CHARACTERIZATION AND REMOVAL OF FILTER CAKE GENERATED BY ILMENITE WATER-BASED DRILLING FLUIDS

A Thesis

by

JIANPING SU

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Chair of Committee,	Hisham Nasr-El-Din
Committee Members,	Jerome Schubert
	Mahmoud El-Halwagi
Head of Department,	A. Daniel Hill

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ABSTRACT

With the development of the oil and gas industry, people started to drill deeper wells to get oil and gas. New weighting materials have been developed to help solve the problem caused by the most commonly used barite. Ilmenite is among one of those with higher specific gravity. It can achieve the same density with adding less weighting materials than using barite. Less solids content in drilling fluid is an advantage in rheological properties. Recently, micronized ilmenite has again been tested in labs, after resolving the abrasiveness and magnetic problem that normal ilmenite created. Due to the composition of ilmenite, iron is likely to precipitate in acidic condition and cause formation damage when using acid to remove the filter cake.

The effectiveness of using lower concentration of hydrochloric acid (HCl) as well as using 7.5 wt% HCl and 7.5 wt% hydroxyethyl ethylenediamine triacetic acid (HEDTA) to remove the filter cake generated by ilmenite water-based drilling fluids were investigated. To prepare the ilmenite water-based muds, a high speed mixer was used. After preparing the fluid, the filter cake was generated by high pressure high temperature (HP/HT) filter press at 300 psi and 250°F on a sandstone core with 2.5 in. diameter and 1 in. thickness. Cores with filter cakes were computerized tomography (CT) scanned. Then, the filter cake was soaked with HCl and HCl + HEDTA for several hours. After removal, cores with remaining filter cakes were CT scanned again and compare with the initial. Solutions after reaction were analyzed by inductively coupled plasma (ICP) to determine different cation concentrations. Scanning electron microscopy-energy dispersive

spectroscopy (SEM-EDS) was used to analyze the filter cake, as well as the residual filter cake.

The results showed that lower concentration of HCl cannot completely remove the filter cake generated by ilmenite water-based drilling fluids. With limited volume of the acid, higher concentration of HCl, which can increase the initial acid to ilmenite ratio, will be more efficient to remove the filter cake generated by ilmenite water-based drilling fluids.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 Development of Ilmenite as a Weighting Material

Engineers mostly drill the wells overbalance in order to prevent well kick and even blowout. Weighting materials help to increase the density of the drilling fluid and thus elevate the hydrostatic pressure of the mud over formation pressure. API barite is the most commonly used weighting material (Al-Bagoury and Steele 2012); however, it is not applicable for all conditions. When using high density drilling fluid weighted with barite, rheological properties become a serious issue. In addition, the filter cake generated by barite cannot be removed by HCl. Different iron containing materials have been used in the oil industry since the 1970s.

Menzel (1973) introduced FER-O-BAR (synthetic iron oxide, manufactured from pyrite). It has been tested both in the lab and the field. Conclusions were drawn by comparing FER-O-BAR with barite:

1. Higher specific gravity (4.7 over 4.2),
2. Abrasivity is similar or lower, and lower than natural iron oxide,
3. Good rheology property in heavy oil and water-based mud,
4. Acid removable up to 85% by HCl,
5. Lower sag rate, and
6. Separate by magnetic process from the mud while not influencing the drilling or logging.

The average particle size was approximately 10 μm. The reason that it is not widely used today may be due to its high cost and limited production.

To dissolve all the weighting materials in the drilling fluids, Sloan et al. (1975) introduced iron carbonate (Siderite), $FeCO_3$, which can be removed by both HCl and formic acid. Gravity and hardness of the iron carbonate were similar to barite. It can be used for both water-based and oil-based mud and can increase the density up to 19 lb/gal. Permeability after removal by using iron carbonate was higher than using other weighting materials, such as barite, barite with iron carbonate, or barite with calcium carbonate. In theory, the reaction product of iron carbonate with acid is ferrous iron, which will precipitate at a pH of 6-7 at room temperature. But during the drilling process, there will be fresh fluid coming from the surface which will carry oxygen. Ferrous can then be oxidized to ferric, which will precipitate earlier at a pH of 1-2 at room temperature (Taylor et al. 1999).

Haaland et al. (1976) compared hematite, ilmenite and FER-O-BAR with barite (**Table 1**). The specific gravity of iron oxide is higher than barite, which means to achieve the same density, less weighting materials can be used. The hardness and abrasivity of iron oxide are higher than barite, which may add additional cost to the drilling process.

Table 1 - Mechanical properties between hematite, ilmenite, Fer-O-BAR with barite (Haaland et al. 1976).

Material	Formula	Hardness (Moh)	Specific gravity	Abrasivity in relation to barite
Hematite	Fe_2O_3	5.0-6.0	4.54	131
Ilmenite	$FeTiO_3$	5.0-6.0	4.56	107
Fer-O-Bar	Fe_2O_3	-	4.68	132
Barite	BaSO4	3.0-3.5	4.37	100

Blattel and Rupert (1982) compared the penetration rate among different sizes of ilmenite, barite and hematite, which determined the overall economics of drilling a well. The higher the penetration rate, the lower the rig time and the less cost it would be. This was due to lower solids content (higher specific gravity of ilmenite). At a similar particle size, the penetration rate of fluid with ilmenite was higher than that with barite.

Bloomberg et al. (1984) reported observation of abrasion problems when using ilmenite in the field, and these problems were further confirmed in the lab. They also mentioned supply of barite was geographically limited and thus caused higher transportation costs. Two wells were drilled with ilmenite in the North Sea (1979) with improved rheological properties; however, it caused excessive wear, and even a washout. Additionally, they reported ilmenite was difficult to water-wet and disperse, air entrainment and foaming occurred, and the generation of excessive dust, which caused a cleaning problem. After lab tests, they came up with solutions that can overcome the disadvantages of using ilmenite, such as: (1) decreasing the particle size to reduce abrasion;

and (2) reducing the flotation chemicals during production (either by treating with sodium silica and caustic or gravimetric) to solve the hydrophobic character.

Fjogstad et al. (2000) and Saasen et al. (2001) reported using ilmenite as a weighting material offshore in northern Norway. They further decreased the mean particle size from an average 50 microns to 10 microns and got acceptable erosion rates especially for water-based drilling fluid. They substituted ilmenite for in consideration of less heavy metals and are less harmful to the environment. This ilmenite drilling fluid gave good rheological and fluid-loss properties during drilling, as well as a low tendency to separate or sag (stable density). The black color of ilmenite made the weighting material easier to identify. Abrasion was observed in MWD tools, which was caused by using thinner fluids. Abrasion problem in a dry bulk system was increased due to more homogenous particle size and can be reduced by a reduction of the transfer speed.

Amighi and Shahbazi (2010) recommended rather than using barite, using ilmenite or manganese tetraoxide for HP/HT drilling operations and high-angle wells. They concluded that ilmenite is more suitable than barite on an overall perspective.

Al-Bagoury and Steele (2012) and Al-Bagoury (2014) showed that a new micronized ilmenite can be used with both water-based and oil-based drilling fluids for difficult drilling conditions and fluid requirement. This new ilmenite had an even smaller average particle size 5 µm. Abrasion problem was solved by removing the coarse materials and the magnetic problem was solved by the removal of a very small amount of magnetic component from the ilmenite sample. Results showed with lower plastic

viscosity, medium sag problem, and large fluid loss volume compared with using API barite. The reason is due to the wide size distribution of barite.

Elkatatny et al. (2012) optimized the rheology properties of the ilmenite water-based mud, as well as pH, which gave stable dispersion, thermal stability under hot roll, reduce filtration volume, and got a thin filter cake. The formula of the drilling fluid used in this thesis is based on this paper.

Tehrani et al. (2014) mentioned the unstable supplies and increased need for barite, which made it more expensive and led to alternatives. Ilmenite and hematite were among the candidates. However, the natural magnetic characteristics of these weighting materials could affect downhole tools that were used to measure the earth's magnetic field direction, as well as other magnetic tools. Their work combined abrasiveness with magnetic characteristics, to show their effect on the drilling fluid properties.

1.2 Reaction between Ilmenite and Acid

Ilmenite is mainly composed of $FeTiO_3$ and reacts with HCl (Olanipekun, 1999):

$$FeTiO_3 + 4HCl \rightarrow FeCl_2 + TiOCl_2 + 2H_2O \quad \text{---------- (1)}$$

The problem with the dissolution of ilmenite is iron. Iron can precipitate under acidic condition. Smith et al. (1969) found iron (III) precipitate at a pH of 2. Taylor et al. (1999) did experiments and showed iron hydroxide precipitated at a pH 1 and the reaction was almost complete at 2 at room temperature. Precipitation will occur even earlier at higher temperatures. By adding HCl, the filter cake can be dissolved, but this cause iron precipitation which can induce formation damage.

Olanipekun (1999) investigated different factors that can affect the reaction with ilmenite and HCl. He concluded that stirring had no effect on the reaction, particle size was inversely proportional to the reaction and acid concentration and temperature had significant effect on the reaction. Olanipekun further pointed out that titanium ions formed polynuclear species, $[(TiO)_8(OH)_{12}]^{4+}$ and titanium oxide could be precipitated by hydrolysis of titanium ions in the solution.

After presenting a thorough literature review, Van Dyk et al. (2002) proposed a new mechanism of ilmenite react with HCl. The rate of chemical reaction controlled the first period, in which both iron and titanium could go to solution. Next, titanium species that formed in the solution (polymerization of titanium) determined the reaction. This process depended on the initial acid to ilmenite mole ratio. The last determining factor of the reaction was the reaction product that formed ($TiOCl_2$). It could precipitate in the pores of the ilmenite or as fines in the leach solution. They recommended using higher initial acid to ilmenite mole ratio to delay the polymerization of titanium and form fine particles in the solution.

Borhan and Nee (2015) discussed the reaction of ilmenite with H_2SO_4. The researchers tried to remove iron only and to yield only TiO_2. They found that with the increasing reaction time, polymeric species would be destroyed and thus enhance the formation of multinuclear complexes of titanium $[TiO_2(OH)_3]^+$ and $Ti_4O_6(OH)_3]^+$, which would lead to more titanium dissolution. They also concluded that higher temperature increased the instability of titanium, enhanced its polymerization.

1.3 Application of CT Scan in Removing the Filter Cake

In this thesis, CT scan will help to aid characterize the filter cake generated with ilmenite water-based mud. Wellington and Vinegar (1987) summarized the use of X-Ray Computerized Tomography as it applies to petroleum engineering studies. It was originally used in hospitals to help doctors see inside patients' bodies. The technique first came into being in 1972. The inventor, Godfrey Hounsfield received Noble prize. The petroleum industry first began using CT during the 1980s in petrophysics and reservoir engineering. A CT scan can complete in a few seconds with accuracy. As for drilling fluid area, CT scan can be applied to characterize of the core materials and visualize mud invasion.

In recent years, Elkatatny et al. (2012) used the CT scan method to determine filter cake properties of water-based drilling mud. Bentonite water-based mud was weighted with calcium carbonate. Through CT scan, the filter cake contained two layers. The internal and external parts of the filter cake were different in thickness and porosity and components. The different components of the two layers became a serious issue when dealing with a removal process. The layer closer to the disk contained calcium carbonate, which reacts easily with hydrochloric acid. The layer closer to the drilling mud contained materials which cannot be easily removed by HCl. It is necessary to remove this layer before using HCl to remove layers closer to the disk.

CT scan facilitates the measurement of the thickness of the filter cake. In the past, after HP/HT static filtration, the thickness of the filter cake was measured by Vernier Caliper. This method proved less accurate and the accuracy depended on the skills of the

person who conducted the experiments. Sometimes, a Vernier Caliper also damaged the filter cakes if the person touched the surface of the filter cake with it by mistake. Even though, other methods were developed as summarized in Bageri et al. (2013), they proved time consuming and complicated. With CT scan, the thickness of the filter is only one of the useful pieces of information that can be received in those few seconds, with the most accuracy and no damage to the filter cakes.

1.4 Removal of the Ilmenite Filter Cake

Filter cake is generated during the drilling process. Small particles, usually called bridging materials and most likely calcium carbonate, go into pores in the rock. As a consequence, fluid starts to build a thin layer on the surface of the rock. This thin and strong layer of filter cake can prevent additional fluid from entering the formation. This thin layer of filter cake can also reduce incompatible fluids going deep into the formation, which can cause formation damage. After drilling, it is necessary to remove this thin layer of filter cake to control formation damage. Different drilling fluids with different weighting materials, such as ilmenite have unique advantages in their rheological properties. These fluids are better at drilling (lower solid content, stable density and viscosity), and cause few problem. However, filter cake generated by these fluids is hard to remove.

Limited work has been done to date on the effective removal of the ilmenite filter cake. HCl at lower concentration (5 wt%) was used to remove filter cake generated by ilmenite weighted water-based mud (Elkatatny et al. 2013b). Chelating agent and glycolic

acid have also been tested independently. The conclusions drawn at that time were that either chelating agent or glycolic acid alone was not effective in removing filter cake generated by ilmenite water-based mud.

Xiao et al. (2015) removed ilmenite filter cakes based on oil-based mud. The difference between water-based muds and oil-based muds is the wettability of the filter cake. The difference of removing the filter cake by oil based mud involves first using mutual solvent to change the oil-wet filter cake to water-wet filter cake, and then following the same procedure. The results show that to remove the filter cake, a higher concentration of HCl (10-15 wt%) should be used.

1.5 Research Objective

The objective is to evaluate the effectiveness of HCl at a lower concentration (7.5 wt%) to remove the filter cake generated by ilmenite water-based drilling fluids. In addition, 7.5 wt% HEDTA was also added to stabilize cations, especially iron. HEDTA, as one of the chelating agents, could react with cations that has two or three positive charges and form complexes, which are soluble in water.

In order to achieve these objectives, ilmenite water-based drilling fluid was prepared at room temperature. Rheological properties were measured with a Grace M3600 viscometer. Density was measured by a Baroid mud balance. HP/HT static filtration filter press were used to generate filter cake by ilmenite water-based drilling fluid at 250ºF and 300 psi. CT scan wsd used to characterize the filter cake generated by ilmenite water-

based drilling fluid. SEM-EDS was used to visualize and determine the composition of the filter cake.

Acid was prepared and mixed with corrosion inhibitor. Density and pH were measured. The combination then soaked with the core and the filter cake inside the filter press for four or six hours. Solutions after reaction were collected. pH and density were measured again. Solution were filtered and diluted and analyzed by ICP to determine different amount of cations. The remaining filter cake was analyzed by SEM-EDS to determine the composition.

CHAPTER II

EXPERIMENTAL STUDIES

2.1 Materials

Table 2 gives the formula and chemicals used for preparing the ilmenite water-based drilling fluid. Ilmenite used as a weighting agent is a micronized material with average particle size 5 µm (Al-Bagoury and Steele 2012). Bandera and Berea sandstone cores with 2.5 in. in diameter and 1.0 in. in thickness were used for the HP/HT static filtration. The concentration of HCl was 36.31 wt%. And the concentration of HEDTA-Na_3 was 42.5 wt%, pH 13.5. The chemical structure of HEDTA was shown in **Fig. 1**.

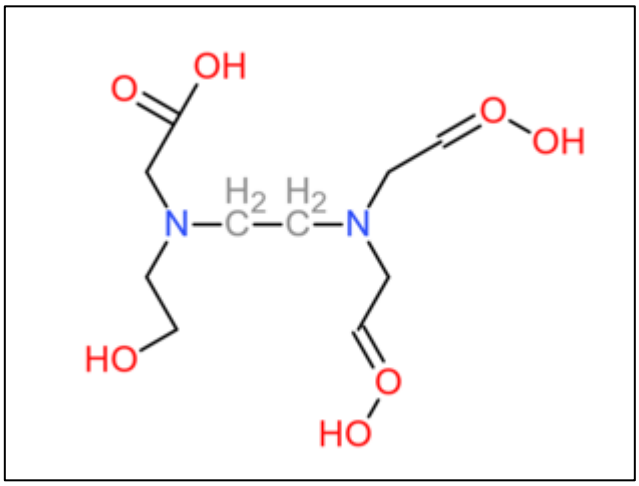

Fig. 1 - Chemical structure of HEDTA.

Table 2 - Ilmenite Water-based Drilling Fluid Formula (Elkatakty et al. 2013a).

Addtive	Function	Amount, g	Mixing time, min
Deionized water	Base	290	-
Defoamer	Anti-foaming	0.08	1
Xanthan gum	Viscosifier	0.25	20
Modified starch	Fluid loss	5	20
PAC-R	Filtration control	1	20
KCl	Density and shale inhibition	72	20
KOH	pH control	1	1
CaCO3 fine (25 μm)	Bridging material	7	20
CaCO3 medium (50 μm)		3.5	
Ilmenite	Weighting material	300	20

2.2 Equipment and Procedures

2.2.1 Drilling Fluid Preparation

Ilmenite water-based drilling fluids were prepared using a multi mix by adding chemicals in the order given in **Table 2**. Polymers were added first to mix for the longest time, and to make sure they were completely dissolved and no aggregation happened. Calcium carbonate fine at 25 μm and medium at 50 μm were added for the bridging material and built the filter cake. Finally, 300g of micronized ilmenite was added to increase the density of the drilling fluid.

2.2.2 Rheological Properties Measurement

Rheological properties were measured with a Grace M3600 viscometer at 120ºF and atmosphere pressure. RPM at 600, 300, 200, 100, 6, 3 were measured after the temperature reached the target. 10 s and 10 min gel strength were measured after mixing the drilling fluid at 600 RPM for 1 minute and then stop and start to count time. Density was measured using a Baroid mud balance.

2.2.3 Characterization of the Filter Cake

Both Bandera and Berea sandstone cores were used to simulate the formation downhole. The core was first dried in an oven at 212ºF for three hours and weighted. Then the core was saturated with 5 wt% KCl to prevented fines migration. After the saturation, the core was weighted again and numbered.

Static filtration was performed using an Ofite HP/HT filter press at 200/250ºF and 300 psi. The core was wrapped with the sealing tape before putting into the filter press. After putting the core and the drilling fluid inside the filter press cell, temperature was added through a heating jacket outside the cell. Then, pressure was added through a valve from the top. After 30 minutes heating time and then the pilot light turned on, then the valve under the cell was opened and filtrates were collected via a measuring cylinder. At the same time of opening the valve, volume at different time was recorded and plotted. Spurt volume can be derived from the intercept of the curve.

After 30 minutes, the core with the filter cake was taken out of the filter press carefully. The core with the filter cake was measured again to determine the weight of the filter cake. The core with the filter cake was CT scanned later.

After static filtration, the core with the filter cake was dried in the oven at 212ºF for three hours. After the drying, the core was separated with the filter cake mechanically. One small piece of filter cake from the top part and another from the bottom part were collected and analyzed by SEM-EDS to visualize the differences as well as compare the elemental compositions.

2.2.4 Removal of the Filter Cake

After generated the filter cake and CT scanned, the filter cake with the core was again put inside the filter press. The acid was prepared and mixed with the corrosion inhibitor. pH and density of the acid were measured before adding acid into the filter press. Then temperature and pressure were added again. The filter cake was soaked with the solution for four or six hours. Remaining filter cake with core was taken out finally and weight measured, CT scanned.

Solution after the reaction was collected. Density and pH were measured again. After being centrifuge for 10 minutes, solutions were diluted 2000, 1000, 500, 400 times to determine different cations concentration using ICP.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Rheological Properties

The rheological properties were shown in **Table 3**. Values were measured immediately after preparing the drilling fluid and left in room temperature for 24 hours. The value does not change significantly, which indicates that biopolymers did not degrade because of bacteria attack in 24 hours. The stability of the drilling fluid increased the flexibility of experiments. Personnel can prepare the drilling fluids on the first day and use it on the second day without rheological properties changing significantly.

Fjostad et al. (2000) found that when using ilmenite in the field, keeping plastic viscosity at 30-35 cp and yield point at 20-24 lb/100ft^2 will prevent the settling of the weighting material. Without significant settling, the density will be stable and the drilling fluid can function normal and ensure the safety of the drilling.

Table 3 - Properties of ilmenite water-based drilling fluid.

Properties	Temperature, ºF	Value	Value overnight	Units
Density	77	109	110	pcf
Plastic Viscosity	120	35	33.35	cp
Yield Point	120	21	20.7	lb/100 ft^2
10 s Gel Strength	120	3	2	lb/100 ft^2
10 min Gel Strength	120	4	4	lb/100 ft^2

3.2 HP/HT Static Filtration

Fig. 2 shows static filtration under HP/HT condition. The y-axis is the cumulative filtrate volume in cm^3 and the x-axis is the square root of time ($s^{0.5}$). The two lines represented static filtration on two different permeability Bandera sandstone cores. The cumulative filtration volumes for high permeability (k= 80 mD) and low permeability Bandera sandstone (k= 6 mD) were 12.7 cm^3 and 11 cm^3 at 300 psi and 200/250ºF. The intercept on the y-axis was the spurt volume of the drilling fluid. The value represented the volume that invaded the formation before the filter cake start to builds.

The filtration volume can be related to temperature, permeability of the core and the particle size of the weighting material in the drilling fluid. With the increasing temperature, more filtration should be expected. Higher permeability cores can cause more filtration. Thus, the filtration volume was higher on the higher permeability Bandera sandstones cores, although with a lower temperature.

For the high permeability Bandera cores, during the filtration process, the cumulative volume was not a parallel line with the x-axis after 30 minutes, which indicated the permeability of the formed filter cake was not low enough the stop the filtration. The drilling fluid formula should be further adjusted when using the mud on a higher permeability core.

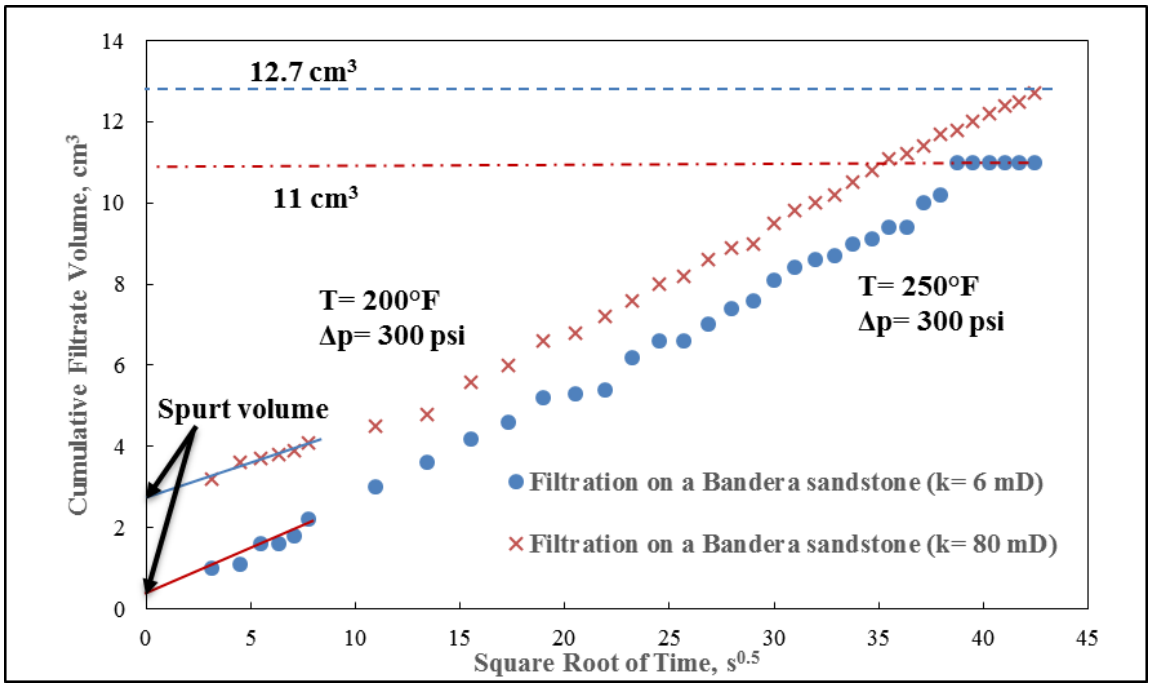

Fig. 2 - HP/HT static filtration curve on Bandera sandstones at 300 psi and 200/250ºF.

3.3 Characterization of the Filter Cake

The thickness of the filter cake was measured using the CT scan, which did not touch and damage the surface of the filter cake. **Fig. 3** shows how CT scan can measure the thickness of the filter cake. To see the homogeneity of the filter cake, four locations were chosen to measure the thickness of the filter cake. **Table 4** compares the thickness of the filter cake by measuring directly using the Vernier Caliper and the CT scan. The real thickness of the filter cake by CT scan was only half of the thickness measured by Vernier Caliper. It is because of the error of eyes. When using Vernier Caliper, researchers attempted to get as close as to the surface of the filter cake, but avoided touching. This caused the error. However, when using CT scan, measurement can be done on the

computer and without damaging the filter cake. And more importantly, the result is accurate. The filter cake was firm and thin with the average thickness 0.266 ± 0.013 in., which could reduce the risk of pipe sticking during the drilling. Bageri et al. (2013) also concluded the CT scan was a more accurate method in measuring the thickness of the filter cake than directly using Vernier Caliper.

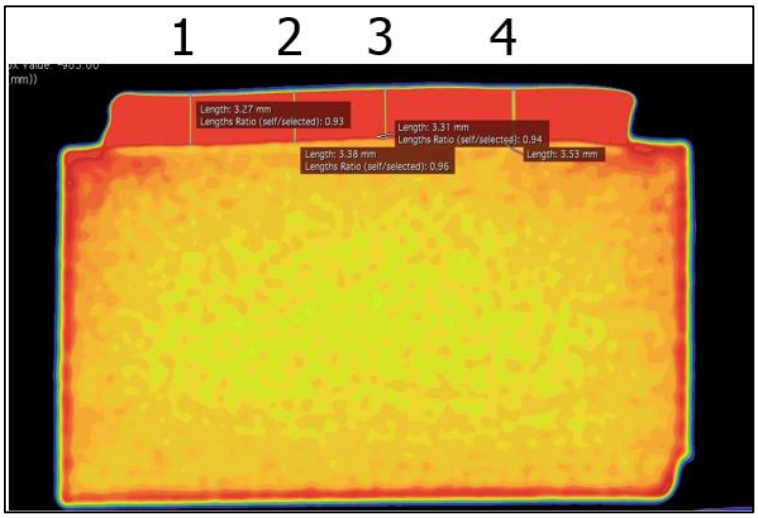

Fig. 3 - Measurement of the thickness of the filter cake using CT scan.

Table 4 - Comparison of thickness of filter cake by CT scan and Vernier Caliper.

Location	Thickness, in. by CT scan	Thickness, in. by Vernier Caliper
1	0.129	0.288
2	0.133	0.251
3	0.133	0.262
4	0.139	0.264
Average	0.13± 0.005	0.266± 0.013

CT scan images showed the filter cake contained two layers with different CT numbers. **Fig. 4** shows a Bandera sandstone core on the left after static filtration with the black filter cake on the top. On the right, the CT image shows the average thickness of the filter cake is 0.337 in. The CTNs stands for the relevant density. With a higher CT number, the density of the material will be higher. The average CTNs for the core was 1776. And the CTNs for upper layer was 2400 and 3500 for the lower layer. **Fig. 5** presents a Berea sandstone core with the filter cake on the top. The two layers were also existed under CT scan with lower CTNs for the upper layer (2411) and high CTNs for the lower layer (3396). The CTNs of the core was 1650 and thickness of the filter cake was 0.203 in.

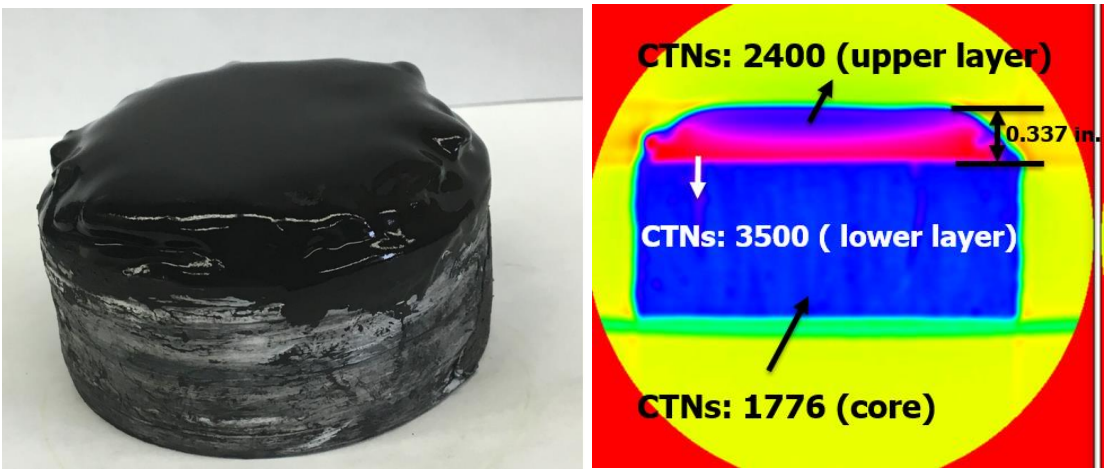

Fig. 4 - Left: Bandera sandstone core with filter cake after static filtration; right: two layers of filter cakes under CT scan.

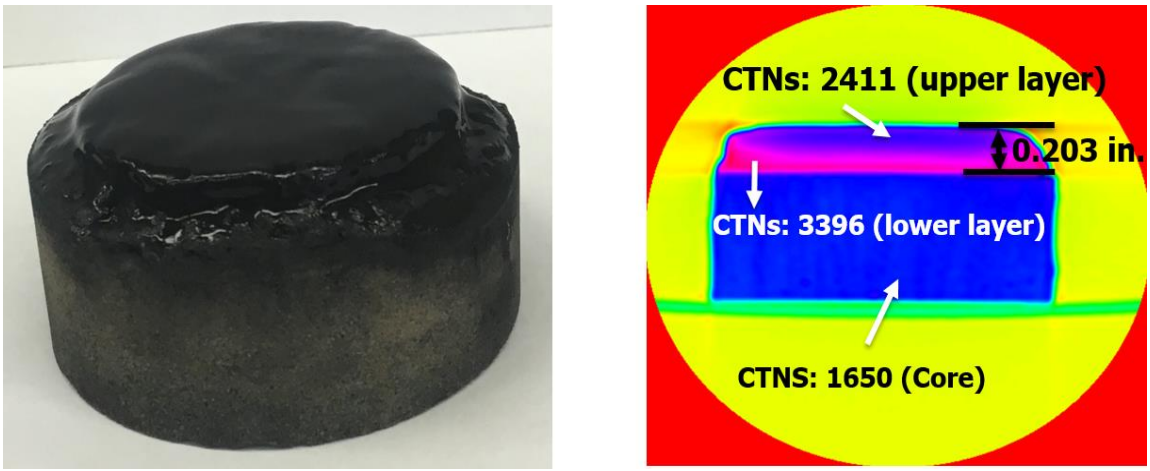

Fig. 5 - Left: Berea sandstone core with filter cake after static filtration; Right: two layers of filter cakes under CT scan.

To better understand the two layers of the filter cakes, SEM-EDS was used to both visualize and determine the elemental composition of the filter cake. **Figs. 6** and **7** show the EDS result as different peaks. The two different peaks for iron were added together to determine the iron concentration. **Table 5** gives the elemental composition of the upper and lower filter cake. Both layers contain more than 50 wt% iron and 30 wt% titanium. The amount of potassium and chloride came from the drilling fluid, in which 72 g KCl was added for shale inhibition and increasing the density of the drilling fluid. Besides, calcium also came from the drilling fluid. Calcium carbonate was added to be the bridging material. In the EDS analysis, other elements also existed. They may come from the impurities of the chemicals that used to prepare the drilling fluid.

The weight concentration shown indicates similar components of the upper and lower filter cakes. **Figs. 8** and **9** compare the upper layer of the filter cake with the lower layer of the filter cake under 300 magnification. From 300 magnification, more pores were

observed in the upper filter cake. And the lower layer of the filter cake was more dense and compact. **Figs. 10** and **11** further confirmed the differences between the two layers under 500 magnification.

The difference comes from the deposition of the filter cake. At first, the high density, heavy weighting materials start to deposit on the surface of the core. Later, smaller and lighter materials deposit on the top part of the filter cake. And the lower filter cake is kept being compacted until the end of the filtration.

Elkatatny et al. (2012) used bentonite based drilling fluid, with at most 50 g weighting material. They found that closer to the core contained mainly the weighting material and the layer closer to the drilling fluid contained other materials.

In this research, the drilling fluid formula contained 300 g weighting material. This amount of the weighting material was far more than other components. Thus, the filter cake was composed mainly the weighting material and with minor other materials from the drilling fluid. And the difference was in the porosity or density.

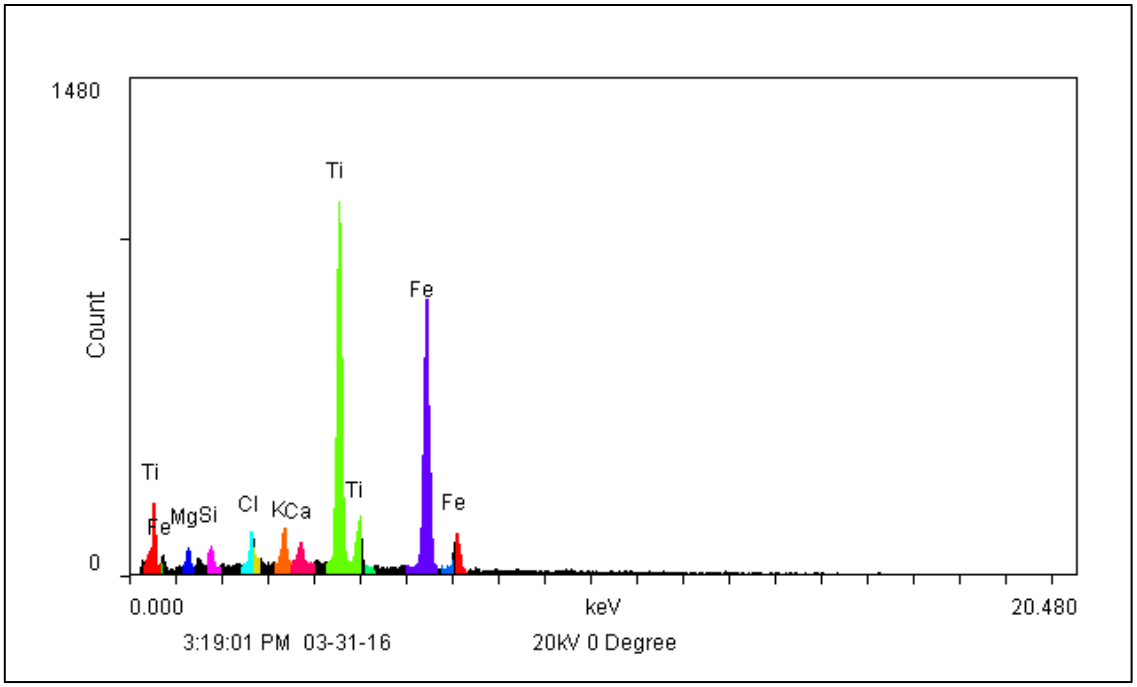

Fig. 6 - EDS analysis of unreacted upper filter cake.

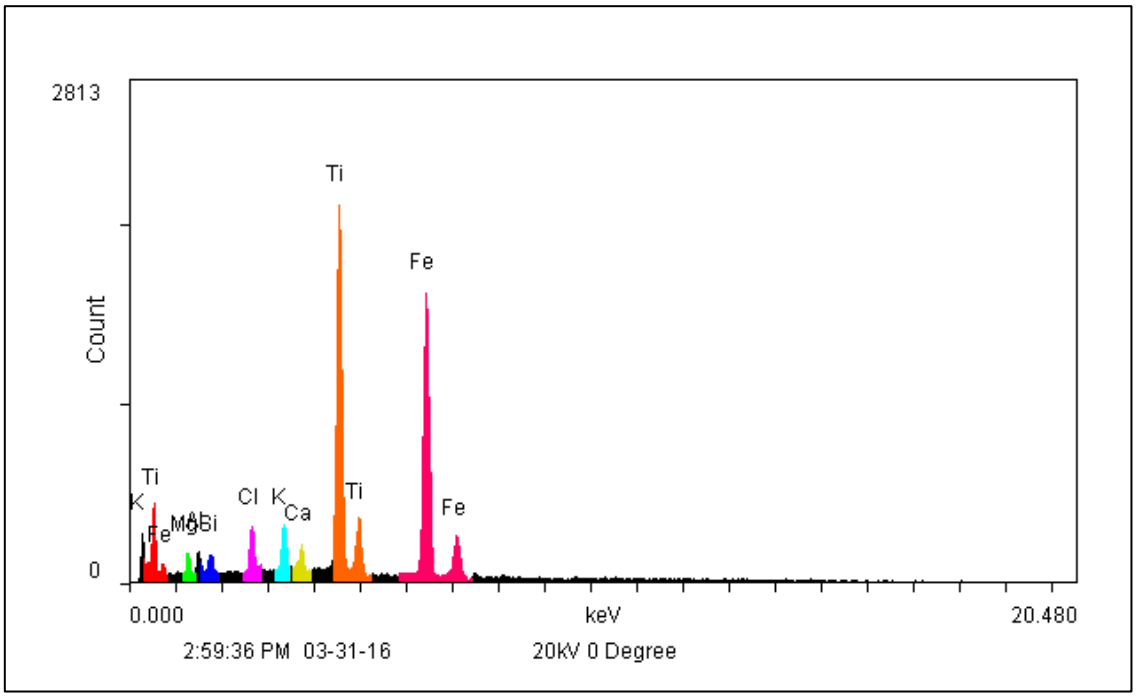

Fig. 7 - EDS analysis of unreacted lower filter cake.

Table 5 - Different elemental compositions and concentrations of the upper and lower filter cake.

Element of the upper filter cake	Concentration, wt%	Element of the lower filter cake	Concentration, wt%
Fe	55.86	Fe	51.73
Ti	29.66	Ti	29.03
Mg	5.1	Mg	4.96
Si	2.54	Si	2.51
Cl	2.79	Cl	3.56
K	2.44	K	3.09
Ca	1.61	Ca	1.61
Sum	100	Al	3.6
		Sum	100

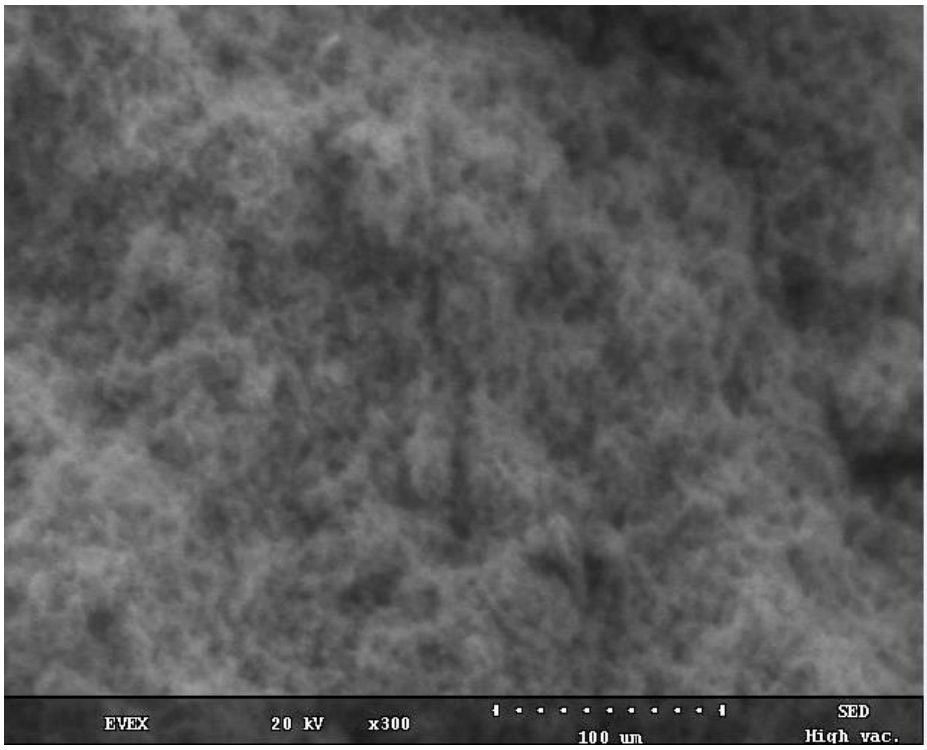

Fig. 8 - SEM of upper filter cake (location one) with X300 magnification.

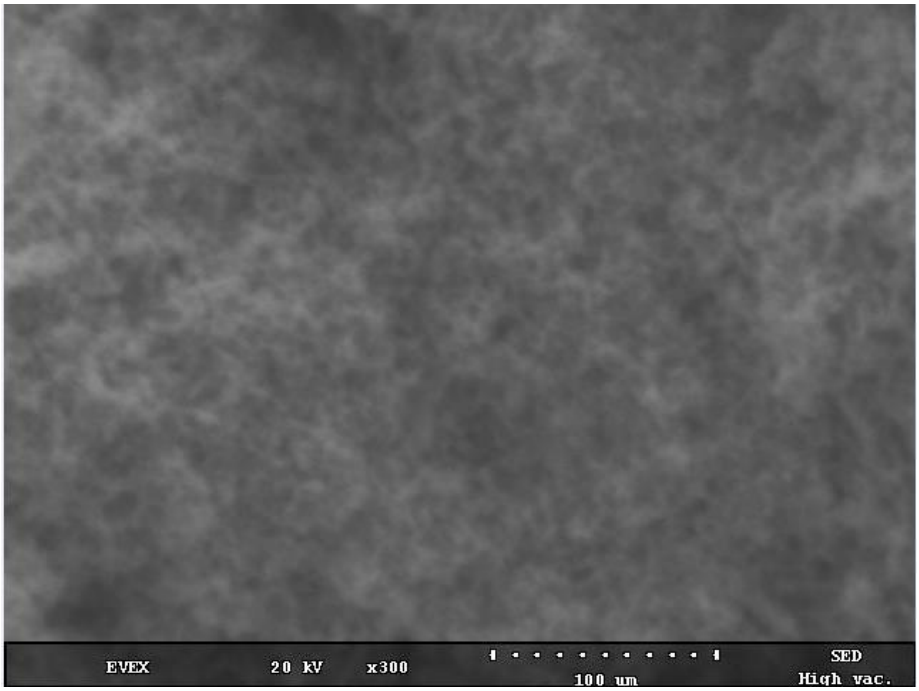

Fig. 9 - SEM of lower filter cake (location one) with X300 magnification.

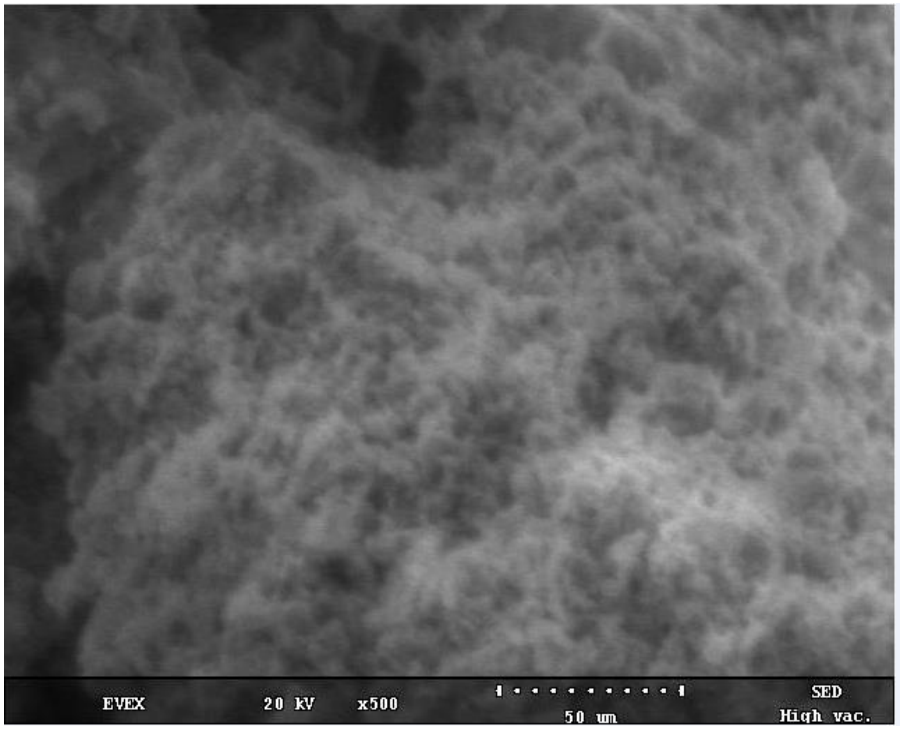

Fig. 10 - SEM of upper filter cake (location two) with X500 magnification.

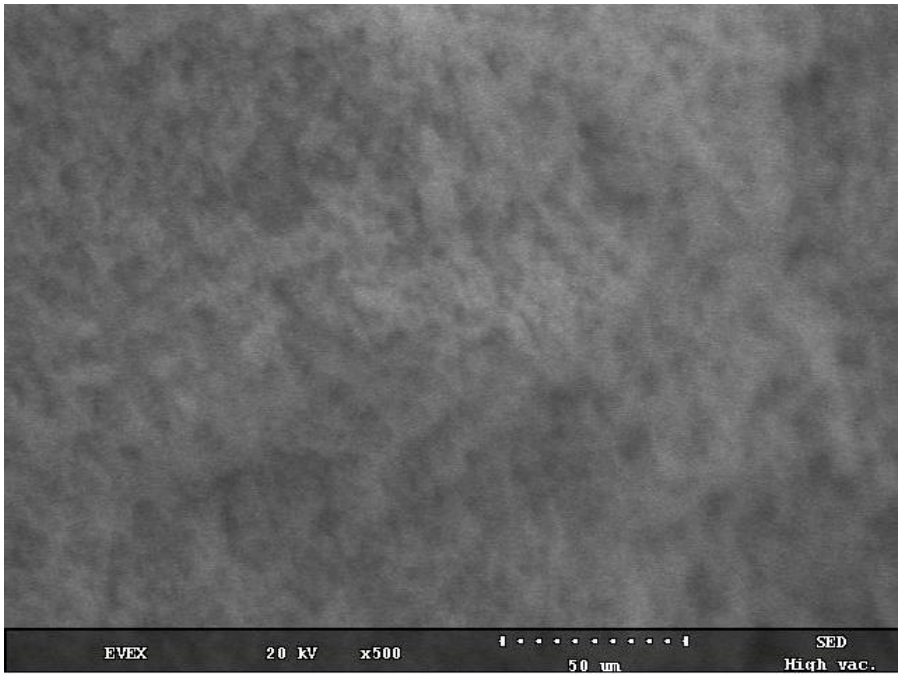

Fig. 11 - SEM of lower filter cake (location two) with X500 magnification.

3.4 Filter Cake Removal

Filter cakes generated by ilmenite water-based muds were removed at 300 psi and 250ºF with:

1. 7.5 wt% HCl + 1 vol% corrosion inhibitor,
2. 7.5 wt% HCl and 7.5 wt% HEDTA + 1 vol% corrosion inhibitor.

The first attempt was using 7.5 wt% HCl with 1 vol% corrosion inhibitor with four hours soaking time. **Fig. 12** shows the filter cake after static filtration, after treatment with 7.5 wt% HCl soaking for four hours, and after drying at 212ºF for three hours. Incomplete removal filter cake remained on the surface of the core. **Fig. 13** shows a 3-D model of the filter cake under CT scan. On the left side, after static filtration, some drilling fluid invasion can be observed which may due to the bridging process. On the right side, after reacting with 7.5 wt% HCl for four hours, more filtration into the core was observed.

Table 6 shows the weight differences of the core. The dry weight of the core was 168.4 g and after saturation with 5 wt% KCl, it was 178.2 g. After static filtration, the core with the filter cake was 219.7 g. Later, after the filter cake removal, the core with remaining filter cake was 191.4 g. Compares to the saturated core 178.2 g, the filter cake removal was incomplete. The remaining filter cake with the core was also dried and compared with the initial and the conclusion was also incomplete filter cake removal.

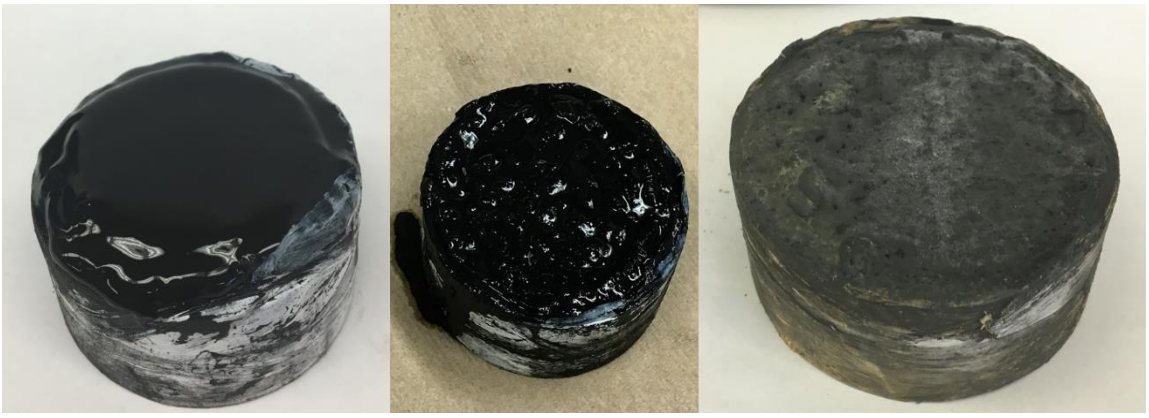

Fig. 12 - Left: Filter cake after static filtration at 300 psi and 250ºF; middle: filter cake after soaking with 7.5 wt% HCl at 300 psi and 250ºF; right: filter cake after drying at 212ºF for three hours.

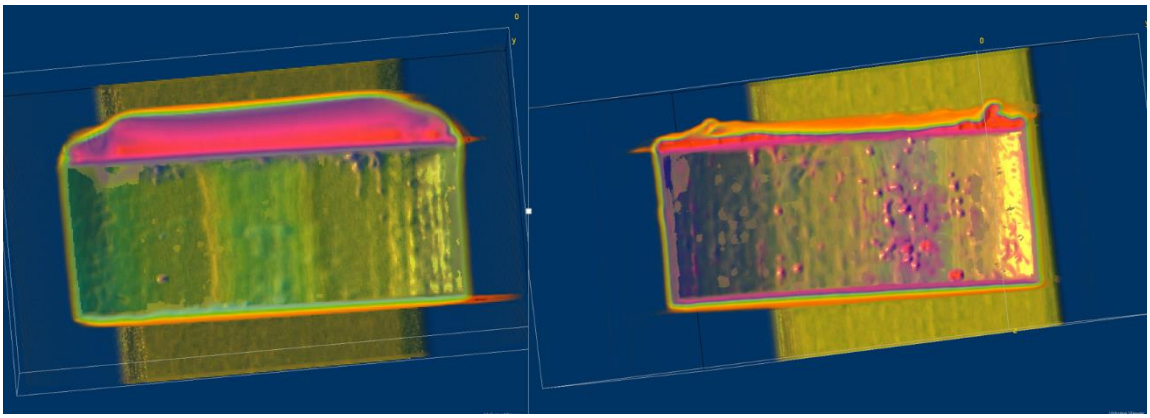

Fig. 13 - Left: 3-D model of the CT image after static filtration; 3-D model of the CT image after treating with 7.5 wt% HCl.

Table 6 - Weight difference of the core when using HCl.

	Dry weight, g	Wet weight, g
Core	168.4	178.2
Core with filter cake	-	219.7
Core with remaining filter cake	179.8	191.4

The second attempt was using 7.5 wt% HCl with 7.5 wt% HEDTA and 1 vol% corrosion inhibitor at 300 psi and 250ºF. **Table 7** shows the pH, density and acid concentration changes before and after the experiment. pH was 0 before and 0.3 after the treatment. Density increased from 1.078 g/cm^3 to 1.124 g/cm^3. The concentration of HCl decreased from 7.5 wt% to 2.13 wt%.

Table 8 compares the weight differences of the core before and after the experiment. The dry weight of the core was 169.4 g. And after saturation, the weight of the core was 182.8 g. After static filtration, the core with the filter cake was 238 g, and after the treatment with acid combination, the weight was 199.7 g. Compared with the wet weight of the core, remaining filter cake still existed on the surface of the core. It was also incomplete filter cake removal.

Fig. 14 shows the filter cake after static filtration and filter cake after soaking with 7.5 wt% HCl and 7.5 wt% HEDTA for six hours. Remaining filter cake was observed. **Fig. 15** shows CT scan image of the core with the filter cake and after the treatment. Before using acid, the thickness of the filter cake was 0.337 in. and after the treatment it became 0.094 in. The average CT number of the filter cake after static filtration was 2400 for the upper layer and 3500 for the lower layer. After the reaction with acid combination, the upper layer had been removed and CT number of the lower layer became 3200.

Incomplete filter cake removal was also achieved using 7.5 wt% HEDTA with 7.5 wt% HCl at 300 psi and 250ºF for six hours. In the past, weight difference was used to calculate the removal efficiency. However, it is not an accurate method because of the

ignorance of the dissolution of the core. The acid will react with the filter cake, as well as the core. Thus, the results obtained by using weight loss is not the true removal efficiency.

Table 7 - Values of pH and density before and after treatment with 7.5 wt% HCl and 7.5 wt% HEDTA.

Value	Before treatment	After treatment
pH	0	0.3
Density, g/cm^3	1.078	1.124
HCl concentration, wt%	7.5	2.13

Table 8 - Wet different of the core when using HCl with HEDTA.

	Dry weight, g	Wet weight, g
Core	169.4	182.8
Core with filter cake	-	238
Core with remaining filter cake	-	199.7

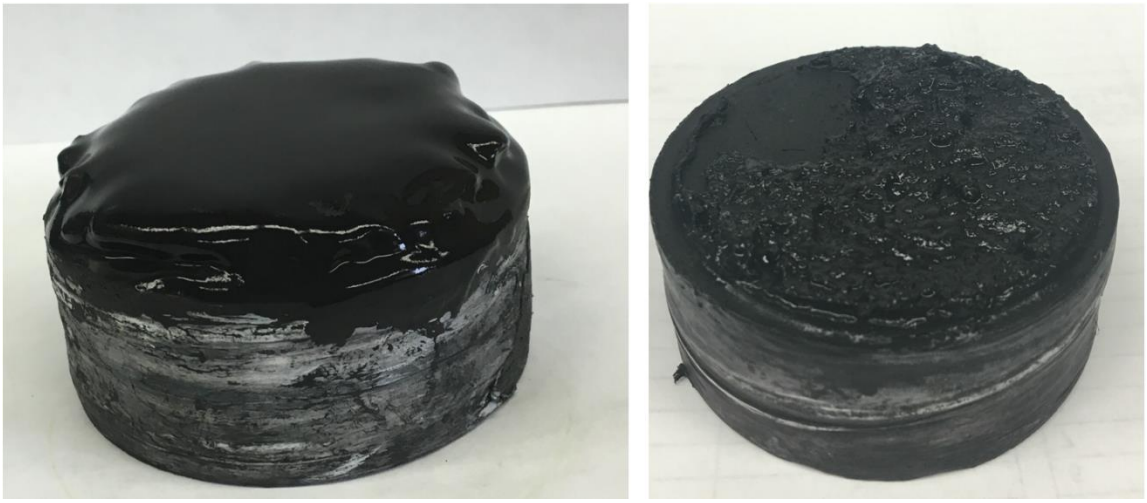

Fig. 14 - Left: filter cake after static filtration; remaining filter cake after soaking with 7.5 wt% HCl and 7.5 wt% HEDTA for 6 hours.

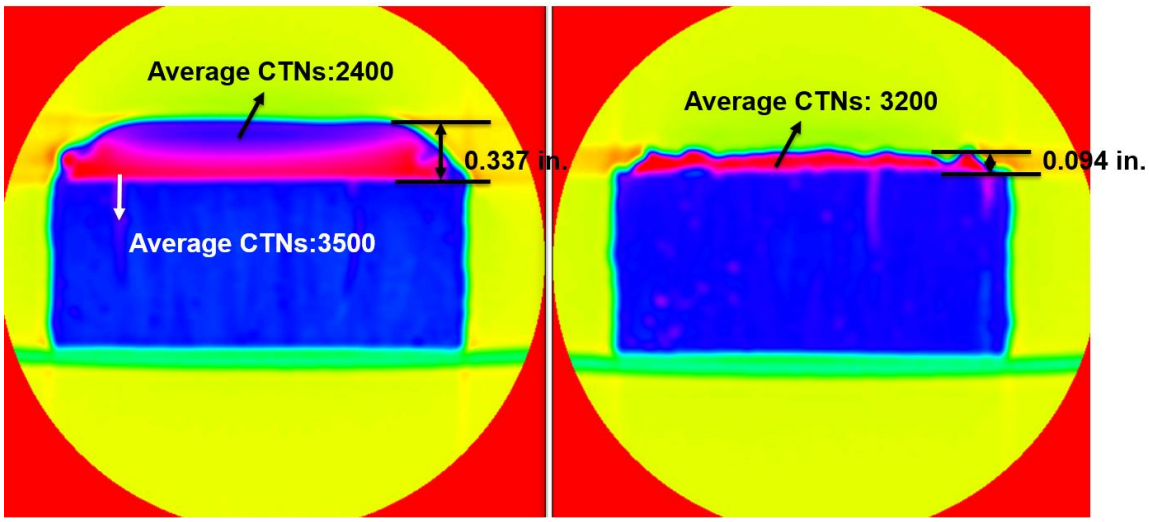

Fig. 15 - Left: CT scan of the filter cake after static filtration; CT scan of the remaining filter cake after soaking with 7.5 wt% HCl and 7.5 wt% HEDTA for 6 hours.

Fig. 16 shows the solution color before and after the treatment. The yellow color came from the corrosion inhibitor. The purple color after reaction was abnormal and rarely seen in the lab. **Table 7** presents the elemental composition of the solution after reaction

determined by ICP. HEDTA with Cr^{3+} changed the color of the solution (De wolf et. al, 2012). **Table 9** showed the solution contained a large amount of iron, which was 23530 ppm, and sharply contrasted with titanium 71 ppm. Calcium, magnesium and aluminum were also detected by ICP in the solution. The Bandera sandstone core has calcium, magnesium and aluminum and the acid reacted with the core. Besides, abnormal high concentrations of Ni and Cr were also observed which a sign of corrosion. **Table 10** shows the element composition of the filter press cell, which is made of stainless steel 316. The high concentration Cr and Ni came from the cell, which confirms the corrosion.

Figs. 17 to **19** show the remaining filter cake under different magnifications under SEM. Three different locations were chosen to be analyzed. Before the removal, the filter cake was smooth, dense and compact for the lower layer. After the removal, more pores were generated which is a sign of filter cake removal. Besides, some of the particles aggregate and formed new structures.

Table 11 summarized the result of the EDS analysis obtained from **Figs. 20** and **21**. The peaks in **Figs. 20** and **21** of different elements were used as the concentration of each elements. For both of the EDS analysis, iron and titanium were presented. And the differences between the two element compositions had decreased. This result agreed with the ICP results that more iron went to the solution.

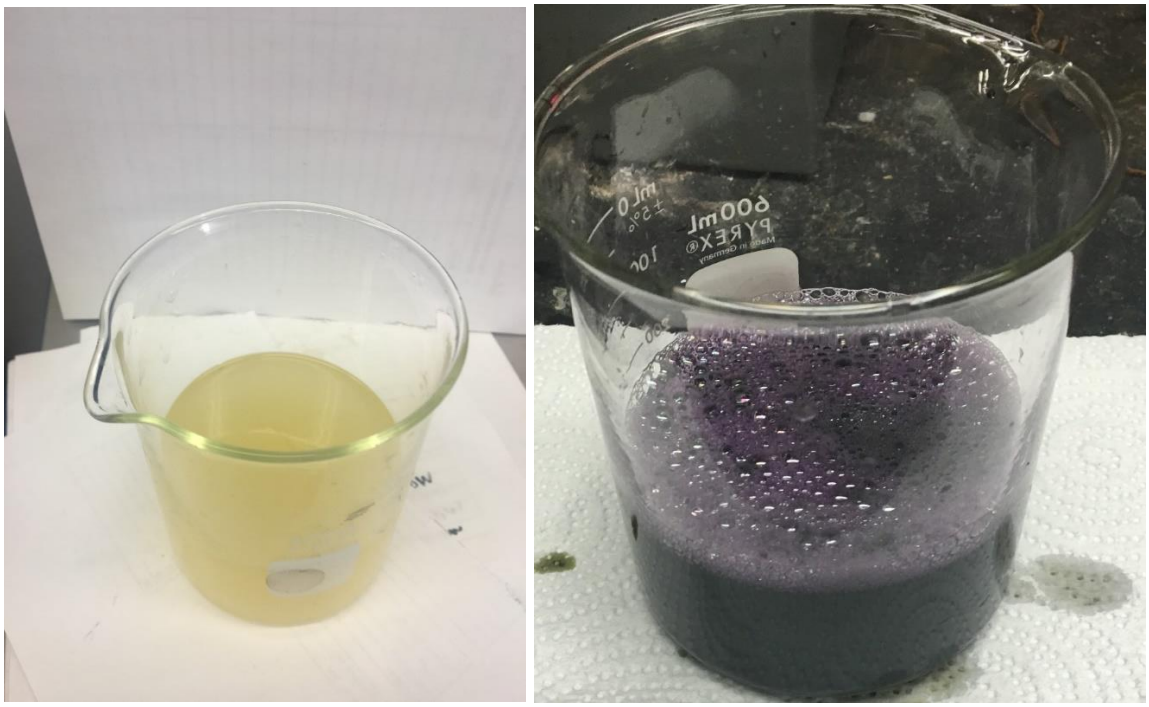

Fig. 16 - Left: solution before reaction with 7.5 wt% HCl and 7.5 wt% HEDTA; right: solution after reaction with 7.5 wt% HCl and 7.5 wt% HEDTA.

Table 9 - Cation concentration in solution after reaction with 7.5 wt% HCl and 7.5 wt% HEDTA.

Element	Concentration, ppm
Fe	23,530
Ti	71
Ca	1,982
Mg	374
Al	252
Ni	2,851
Cr	4,616

Table 10 - Elemental composition of the filter press cell (stainless steel 316).

Element	Concentration, wt%
Cr	16.90
Ni	10.52
Mo	2.02
Mn	1.40
Cu	0.48
Si	0.32
Co	0.26
C	0.01
N	0.043
P	0.035
Fe	67.98

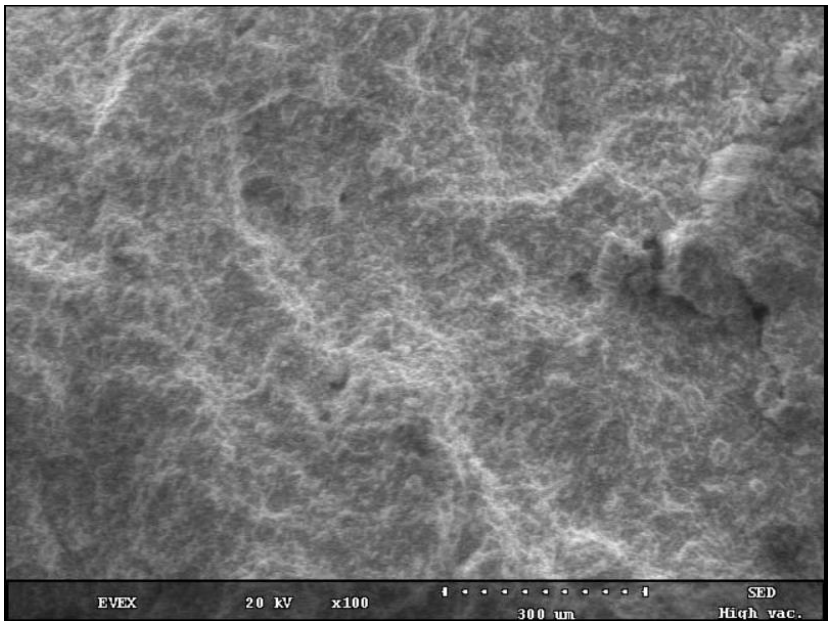

Fig. 17 - SEM of the remaining filter cake (location one) with X100 magnification.

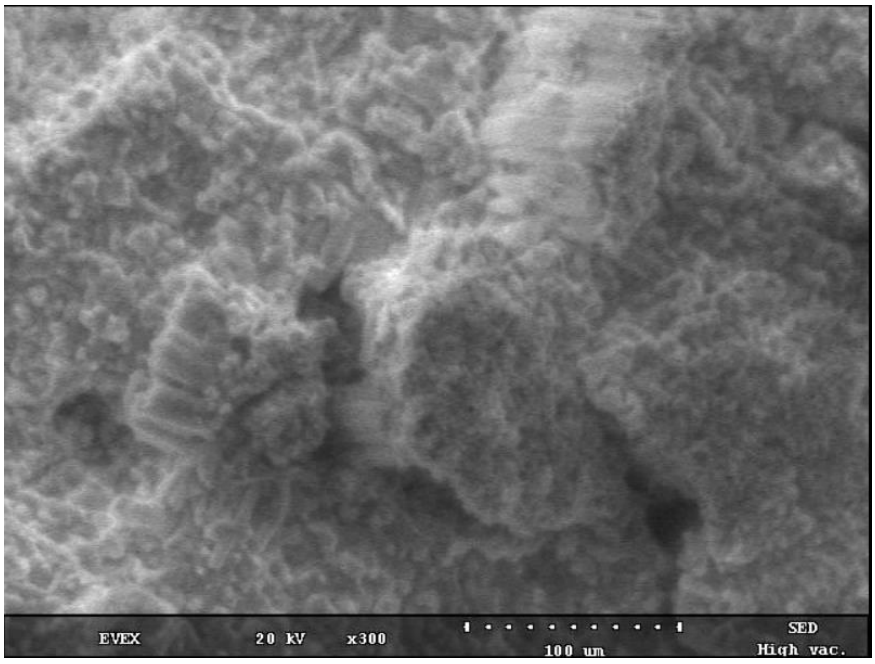

Fig. 18 - SEM of remaining filter cake (location two) with X300 magnification.

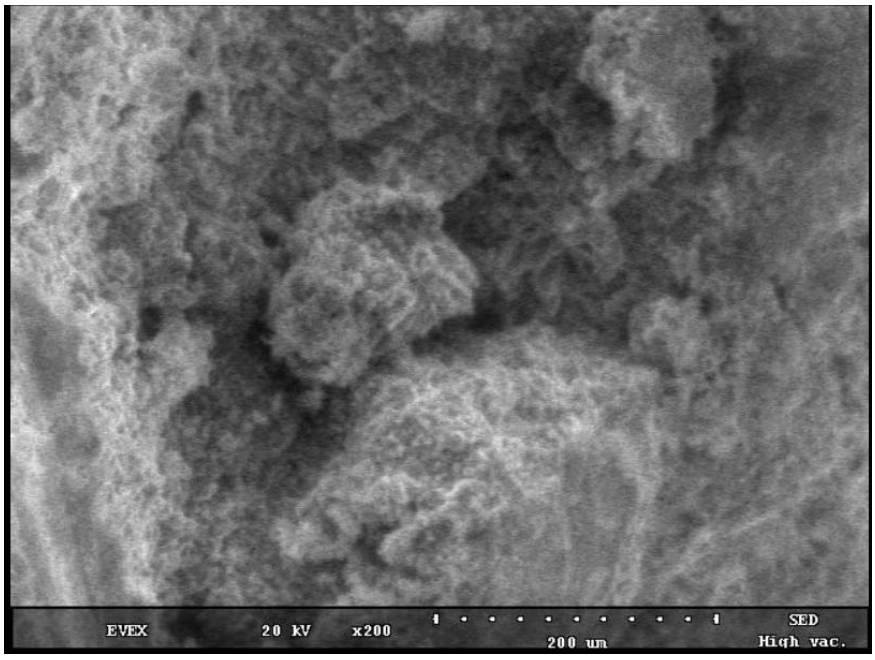

Fig. 19 - SEM of remaining filter cake (location three) with X200 magnification.

Table 11 - Left: elemental composition of location one; right: elemental composition of location two.

Element	Concentration, wt%	Element	Concentration, wt%
Cl	28.7	Mg	4.48
K	29.57	Si	1.97
Ti	17.85	Pd	9.99
Fe	23.88	Ti	34.63
		Fe	48.92

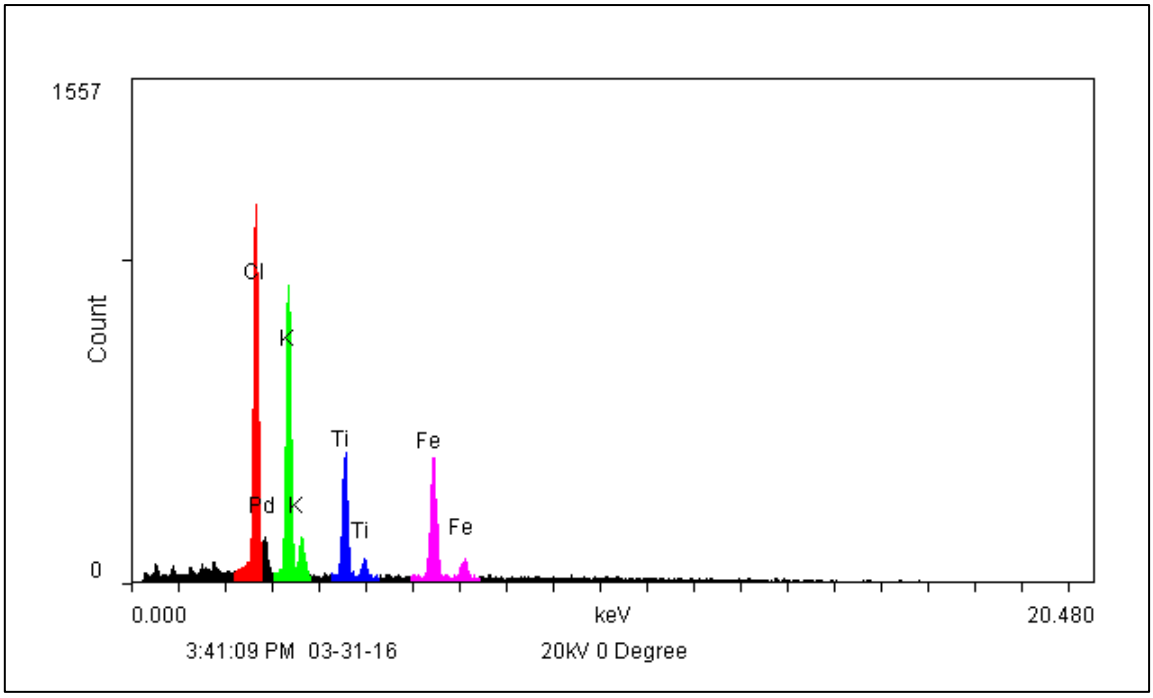

Fig. 20 - EDS analysis of location two.

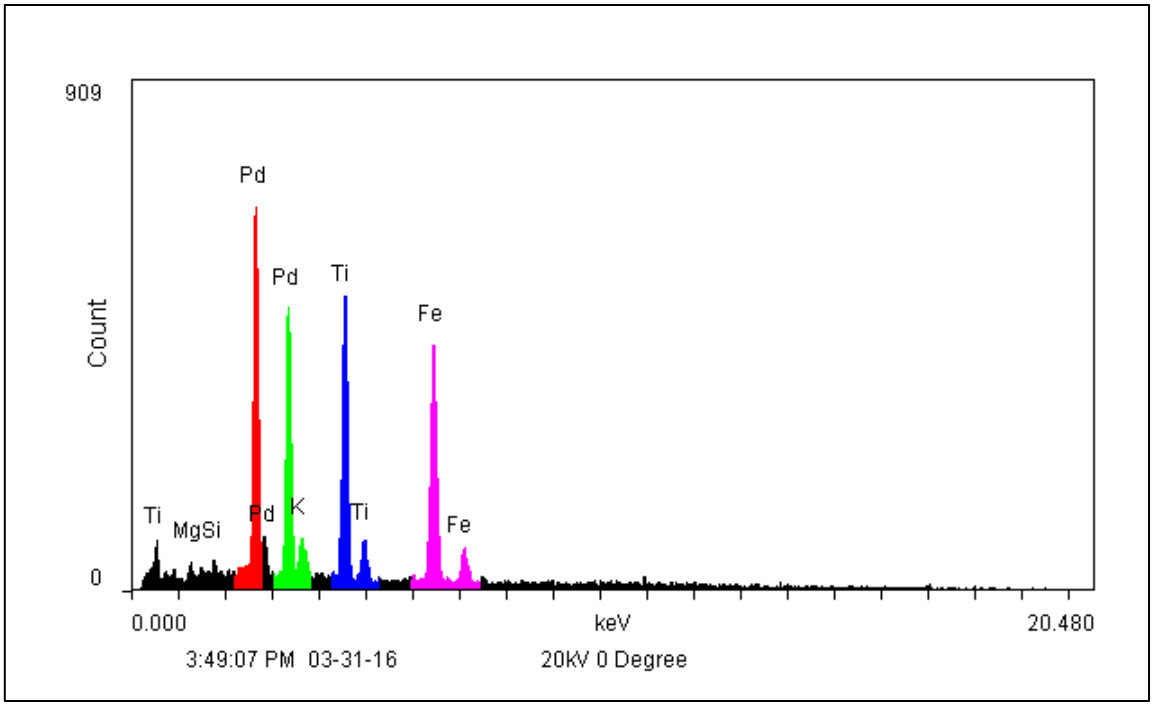

Fig. 21 - EDS analysis of location three.

The filter cake was not removed completely and the acid was not fully spent. The concentration of the acid after the reaction determined by acid titration was 2.13 wt%. Comparing to the initial HCl concentration, 71.6% acid was spent. Van dyk et al. (2002) discussed mechanism of ilmenite leaching and concluded titanium could polymerizes in HCl. Low initial mole ratio of acid to ilmenite will cause titanium polymerization which forms a product layer. After forming this layer, the acid is separated with the remaining filter cake and no more reaction could happen. Precipitation of $TiOCl_2$ would happens in the pore of the particles. Thus, Van dyk et al. (2002) recommended higher initial acid-to ilmenite mole ratio will delay the polymerization of titanium and will allow much more titanium to dissolve from the ilmenite.

The start point of polymerization of titanium as described in Van dyk et al. (2002), when the concentration of titanium is larger than 10^{-3} mol/L. 71 ppm titanium determined by ICP and divided by the molecular weight of titanium, 47.867 is 1.48×10^{-3} mol/L. So it is concluded that titanium polymerize in the solution and mass transfer limited the reaction.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Ilmenite water based drilling fluid was prepared and used to generate the filter cake at HP/HT conditions. CT scan and SEM-EDS were used to characterize the filter cake. Different acids were used to remove the filter cake. The following conclusions were obtained by the results:

1. Ilmenite water-based drilling fluid provides a good rheological properties, with acceptable filtration volume (<15 cm^3). This will decrease the mud invasion into the formation and cause less formation damage.
2. CT scan is a good method to characterize the filter cake generated by ilmenite water-based drilling fluid. Two layers were overserved and confirmed by SEM-EDS. The two layers were different in the density, which led to different CT numbers. SEM showed less pores in the upper layer. The lower layer was more dense and compact. EDS showed similar elemental compositions of the two layers.
3. Removal of filter cake generated by ilmenite water-based mud with lower concentration of HCl (7.5 wt%) was not complete. Remaining filter cake was observed by both weight difference and CT scan.
4. Adding HEDTA is a good method to prevent iron precipitation in the solution. Corrosion issue was noticed when adding HEDTA. The solution color changed from yellow to purple, which is the color of HEDTA with Cr^{3+}.

5. The combination of 7.5 wt% HCl with 7.5 wt% HEDTA also cannot completely remove the filter cake. Unspent acid and remaining filter cake indicates the polymerization of titanium, which could separate ilmenite from the acid and stop the reaction.
6. A filter press cell made of stainless steel is not a good reactor for the acid. Corrosion happened inside the cell. A special cell (Hastelloy) is needed in the future to minimize corrosion.
7. After solving the corrosion issue, future work can be done by using higher acid concentration to remove the filter cake generated by ilmenite water based drilling fluid to achieve high initial acid to ilmenite mole ratio.
8. For the application in the field, more cost and benefit should be calculated before applying acid to remove the filter cake. It may not be economic to remove the filter cake than leave untreated.

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