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Jianping Su
*The University of British Columbia, Canada*

Omar Mahmoud
*Future University in Egypt*, Omar.saad@fue.edu.eg

Hisham A. Nasr-El-Din
*Texas A&M University*

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# Removing ilmenite-based filter cakes using hydrochloric acid and chelating agent – experimental study

*Jianping Su*[a], *Omar Mahmoud*[b,*], *Hisham A. Nasr-El-Din*[c]

[a] *Department of Biotechnology, The University of British Columbia, Canada*
[b] *Department of Petroleum Engineering, Future University in Egypt (FUE), Egypt*
[c] *Harold Vance Department of Petroleum Engineering, Texas A&M University, USA*

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ABSTRACT

Ilmenite is often used as a weighting agent in drilling fluids to increase the fluid density, but the formation of a filter cake on the borehole wall can impact cementing operations and reduce well productivity. To remove the filter cake, various techniques can be employed such as chemical treatments, mechanical methods, or a combination of both. The goal of this study is to evaluate the effectiveness of chemical removal of ilmenite-based filter cake using 7.5 wt.% hydrochloric acid (HCl) and hydroxyethyl ethylene diamine triacetic acid (HEDTA) – chelating agent. The filter cakes were generated using API filter press under harsh conditions of 300 psi pressure and 250°F temperature. Sandstone cores (2.5-in. diameter and 1-in. thickness) were utilized to replicate the formation during filtration experiments. The filtrate fluid was collected and the sandstone cores with filter cakes were scanned using computerized tomography (CT) technology. Immediately after that, the cores and filter cakes were soaked with HCl–HEDTA solution for 6 hours, followed by CT-scanning the cores and remaining filter cakes again. After acidizing, the effluent solution was analyzed using inductively coupled plasma (ICP). Scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS) was used to analyze the dried filter cakes and remaining residue. The results showed that, the use of 7.5 wt.% HCl was effective in partially removing the ilmenite-based filter cake. Additionally, the use of HEDTA showed limited effect on the efficiency of filter cake removal, but it effectively prevented corrosion problems during the treatment. This study presents useful findings on removing ilmenite-based filter cake with a low acid concentration and reducing the risk of corrosion issues.


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## 1. Introduction

The oil and gas industry are facing various challenges in keeping up with the growing global energy demand (Sandera, 2006). Drilling engineers use overbalanced drilling to prevent well kicks and blowouts. Weighting materials are used to increase the density of the drilling fluid and to elevate the hydrostatic pressure in the well over that inside the formation. The most commonly used weighting material is API-barite (Al-Bagoury & Steele, 2012), but it has its limitations such as challenging rheological properties, filter cake removal issues, and potential sources of pollution due to heavy components like lead, cadmium, mercury, and arsenic. In addition, the supply of barite is geographically limited, which increases its transportation costs (Blomberg, Melberg, Bøe, Jacobsen, & Aarrestad, 1984; Rae, Lullo, & Ahmad, 2001).

* *Corresponding author.* Tel.: +2-010-1887-5619. E-mail address: omar.saad@fue.edu.eg
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**Nomenclature**

| | |
|---|---|
| API | American petroleum institute |
| $CaCO_3$ | calcium carbonate |
| CT | computerized tomography |
| CTN | CT number |
| ECD | equivalent circulation density |
| GS | gel strength |
| HCl | hydrochloric acid |
| HEDTA | hydroxyethyl ethylene diamine triacetic acid |
| HP/HT | high pressure/high temperature |
| HU | Hounsfield units |
| ICP | inductively coupled plasma |
| KCl | potassium chloride |
| KOH | potassium hydroxide |
| OBM | oil-based mud |
| PAC-R | polyanionic cellulose |
| PV | plastic viscosity |
| SEM-EDS | scanning electron microscopy–energy dispersive spectroscopy |
| WBM | water-based mud |
| XRD | X-ray diffraction |
| YP | yield point |

Different iron-bearing weighting materials have been used in the oil and gas industry since the 1970s, such as iron oxide (Menzel, 1973; Tuntland, Herfjord, Lehne, & Haaland, 1982) and iron carbonate (Sloan, Brooks, & Dear III, 1975), but they have not been widely adopted. Ilmenite ($FeTiO_3$) is a promising alternative to barite. Ilmenite has fewer heavy metals than barite, making onshore treatment easier (Blomberg, Melberg, Bøe, Jacobsen, & Aarrestad, 1984; Saasen, Hoset, Rostad, Fjogstad, Aunan, Westgard, & Norkyn, 2001). Researchers have found that reducing the particle size of ilmenite can decrease erosion rates, especially for water-based mud (WBM) (Al-Bagoury & Steele, 2012; Amighi & Shahbazi, 2010). Using ilmenite can alleviate many of the challenges in the field such as horizontal drilling, low margin pressure drops, deep water, and slimehole. A new grade of micronized ilmenite, which has an even smaller average particle size of 5 microns, has been introduced which shows low plastic viscosity (PV) and low sag tendency compared to API-barite (Al-Bagoury & Steele, 2012). This new grade of micronized ilmenite also showed excellent dynamic sag, stable rheology and high acid solubility for both water- and oil-based applications (Elkatatny, Nasr-El-Din, & Al-Bagoury, 2012; Elkatatny, Nasr-El-Din, & Al-Bagoury, 2013; Elkatatny, Xiao, Nasr-El-Din, & Al-Bagoury, 2013; Xiao, Nasr-El-Din, & Al-Bagoury, 2013; Al-Bagoury, 2014; Xiao, Nasr-El-Din, & Al-Bagoury, 2015).

Recent studies that have shown successful field applications of ilmenite-WBM. Micronized ilmenite, has been found to provide significantly lower drilling fluid rheology to control equivalent circulation density (ECD), significantly reduced sag potential, and lowered formation damage (Al-Bagoury & Revil, 2018). It was also found that using micronized, acid-soluble ilmenite lowered ECD as compared to sized calcium carbonate. Additionally, the evolution of breaker formulations has allowed for longer breakthrough time, which allows for better coverage of the lateral, better removal of the filter cake, and ultimately, enhanced production through improved inflow profiles (Ivan, Al Katheeri, Reichle, et al., 2018; Feder, 2019).

Micronized-ilmenite has been used in synthetic-based oils, non-damaging non-aqueous fluids, synthetic-based mud, and oil-based mud (OBM) systems (Razak & Ezani, 2020; Ibrahim, Al-Mujalhem, Nasr-El-Din, & Al-Bagoury, 2020). These systems have shown lower PV, higher drilling rate, lower friction factor which reduced torque and drag. Ilmenite has been found to be a more efficient weighting material for ultra-high-density OBM systems than ultra-pure barite or other materials (Li, Li, Li, Teng, Ren, Liu, et al., 2019; Li & Li, 2020). Another study (Moreira, Jeughale, Takahiro, Motohiro, Andrews, et al., 2021) has also concluded that synthetic organophilic clay-free invert emulsion fluid system is the best option for drilling fluid in re-entry drilling techniques associated with Maximum Reservoir Contact and Extended Reach Drilling designs. This system has a low mud weight range of 8.5 to 12.8 ppg and uses micronized ilmenite as a secondary weighting agent to reduce formation damage and maintain low rheology while also reducing sag risk and abrasiveness compared to barite and acid-soluble systems. Bajeri et al. (Bajeri, Aljaberi, Siddiq, Adebayo, & Elkatatny, 2022) improved the filter cake sealing properties of high-density ilmenite drilling fluid.

Weighting materials like ilmenite and manganese tetra-oxide in drilling fluids offer advantages over traditional materials like barite, and cause fewer operational issues during drilling. However, these materials create filter cakes that are more difficult to remove. Filter cake is a thin, strong layer of material that forms on the surface of the wellbore during the drilling process. It is created by the accumulation of small particles, such as bridging materials, on the pores of the rock and helps to control fluid invasion into the formation. After drilling, it is important to remove the filter cake to prevent further formation damage.

Ilmenite reacts with hydrochloric acid (HCl), as shown in Eq. 1 (Van Dyk, Vegter, & Pistorius, 2002);

$$FeTiO_3 + 2HCl \rightarrow Fe^{2+} + TiO^{2+} + 2Cl^- + 2OH^- \quad (1)$$

The challenge with dissolving ilmenite is the presence of iron which can precipitate in acidic environments, leading to formation damage. According to studies by (Smith, Crowe, & Nolan III, 1969) and (Talyor, Nasr-El-Din, & Al-Alawi,1999), iron precipitation occurs at a pH of 2 or lower and can result in the formation of iron hydroxide. Precipitation can occur even sooner at higher temperatures, which makes it important to consider the conditions during dissolution of ilmenite. Different studies have been conducted on the removal of the ilmenite filter cake, one of which used HCl at a low concentration (5 wt%) to remove the filter cake generated by ilmenite-WBM (Elkatatny, Xiao, Nasr-El-Din, & Al-Bagoury, 2013). Chelating agent and glycolic acid have also been tested individually, but the conclusion was that neither chelate nor glycolic acid alone are effective in removing the filter cake. another study has used a mutual solvent to change oil-wet filter cake to a water-wet one, followed by similar acid treatment procedures (Xiao, Nasr-El-Din, & Al-Bagoury, 2015). These studies reported that a higher concentration of HCl (10-15 wt%) should be used to remove the filter cake generated by ilmenite-weighted drilling fluid.

The objective of this study is to assess the effectiveness of using 7.5 wt.% HCl (low concentration) to remove the filter cake generated by ilmenite-WBM and reducing the risk of corrosion. The study aims to examine the effectiveness of 7.5 wt.% hydroxyethyl ethylenediamine triacetic acid (HEDTA) as a chelating agent to stabilize metal ions, particularly iron (El-Kady, Chai, & Nasr-El-Din, H. A., 2021), and prevent their precipitation. The study results showed that the HCl-HEDTA solution has a higher ability to remove ilmenite filter cakes in water. The characteristics of the filter cakes were studied using various methods to gain a better understanding and reach conclusions.

## 2. Materials and Methods

### *2.1. Materials*

WBM was formulated and used in this study. The formulation includes defoamer, potassium hydroxide (KOH), and potassium chloride (KCl) that were used as anti-foamer, alkalinity controler, and shale inhibitor, respectively. Xanthan gum was used to provide primary viscosity, and modified starch to adjust the final rheology and filtrate invasion. Polyanionic cellulose (PAC-R) was used as an API fluid loss agent. Medium (50 µm) and fine (25 µm) calcium carbonate ($CaCO_3$) was used as a bridging material and mirconized ilmenite (5 µm) was used as a weighting material. All of the additives were provided by service companies and used as received. Ilmenite is a mineral that contains iron and titanium ($FeTiO_3$). It has a hydroxyl group on its surface, which gives it unique surface properties compared to barite. Table 1 shows the particle size distribution of miconized ilmenite (Ibrahim, Al-Mujalhem, Nasr-El-Din, & Al-Bagoury, 2020).

**Table 1–** Particle size distribution of micronized ilmenite (Ibrahim, Al-Mujalhem, Nasr-El-Din, & Al-Bagoury, 2020).

| **Parameter** | $d_{10}$ | $d_{50}$ | $d_{90}$ | Density | Bet |
|---|---|---|---|---|---|
| **Value** | 2 µm | 5.5 µm | 12.2 µm | 4.6 g/cm$^3$ | 1.5 m$^2$/g |

The HCl used in this study had a concentration of 36.31 wt%, and the chelate HEDTA has a pH of 4 and a concentration of 42.5 wt%. The chemical structure of HEDTA is shown in Fig. 1. Berea and Bandera core disks were cut to 2.5-in. diameter and 1.0-in. thickness. Table 2 shows the porosity and permeability of the cores and their mineral composition as revealed from X-ray diffraction (XRD) are shown in Table 3.

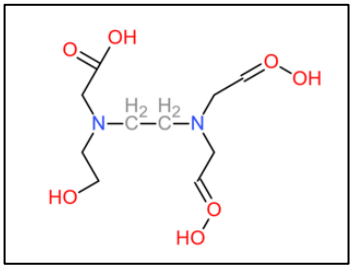


**Fig. 1 – Chemical structure of HEDTA.**

**Table 2 –** Porosity and permeability for different sandstone cores.

| **Sandstone Core** | **Porosity (vol%)** | **Permeability (mD)** |
|---|---|---|
| Low-permeability Bandera sandstone | 10 | 6 |
| High-permeability Bandera sandstone | 20 | 80 |
| High-permeability Berea sandstone | 18 | 60 |

**Table 3 –** Mineral composition for different sandstone cores.

| Berea Sandstone | | Bandera Sandstone | |
|---|---|---|---|
| **Mineral** | **Concentration (wt%)** | **Mineral** | **Concentration (wt%)** |
| Quartz | 91 | Quartz | 59 |
| Kaolinite | 3 | Kaolinite | 3 |
| Microline | 4 | Albite | 12 |
| Muscovite | 1 | Chlorite | 1 |
| Smectite | 1 | Illite | 10 |
| | | Dolomite | 15 |

### *2.2. Ilmenite-WBM formulation*

Table 4 shows the formulation and the equivalent amounts of materials used in the lab and in the field. The preparation of the mud starts by adding the defoamer and xanthan gum to deionized water while mixing it using a Hamilton beach mixer for 20 minutes at a speed of 1. Then the other chemicals were added carefully to the fluid to avoid producing 'fish eyes' in the mud. An adequate stirring time was given for each additive as shown in Table 4.

**Table 4 –** Formulation to prepare the equivalent of 1 barrel of ilmenite-WBM.

| **Additive** | **Function** | **Amount added** | | | | **Mixing time (minutes)** |
|---|---|---|---|---|---|---|
| | | **Laboratory unit (per 350 $cm^3$)** | | **Field unit (per bbl)** | | |
| | | **Quantity** | **Unit** | **Quantity** | **Unit** | |
| Deionized Water | Base | 290 | $cm^3$ | 0.829 | bbl | – |
| Defoamer | Anti-Foaming | 0.08 | g | 0.08 | $lb_m$ | 1 |
| Xanthan Gum | Viscosifier | 0.25 | g | 0.25 | $lb_m$ | 20 |
| Modified Starch | Fluid Loss Control | 5 | g | 5 | $lb_m$ | 20 |
| PAC-R | API Filtration control | 1 | g | 1 | $lb_m$ | 20 |
| KCl | Salt/Shale Inhibition | 72 | g | 72 | $lb_m$ | 20 |
| KOH | Alkalinity Agent | 1 | g | 1 | $lb_m$ | 1 |
| $CaCO_3$ Fine (25 µm) | Bridging Material | 7 | g | 7 | $lb_m$ | 20 |
| $CaCO_3$ Medium (50 µm) | | 3.5 | g | 3.5 | $lb_m$ | |
| Ilmenite (5 µm) | Weighting Material | 300 | g | 300 | $lb_m$ | 20 |

### *2.3. Equipment and Procedures*

The Grace M3600 rotational viscometer was used to measure the rheological properties at atmospheric pressure and 120°F. Six different readings were determined at six different fixed speeds (600, 300, 200, 100, 6, and 3 rpm). The yield point (YP), PV, and gel strength (GS) at both 10 seconds (10-sec) and 10 minutes (10-min) were determined according to the standard protocol (API Recommended Practice 13B-1, 2003). Density and pH of the mud were measured using a regular mud balance and pH meter, respectively.

An HP/HT API filter press was used to conduct the filtration tests and generate filter cake (API Recommended Practice 13B-1, 2003) at 300 psi-differential pressure and 250°F-temperature. The API filter press consists of a 500-$cm^3$ cell that can accomodate the core disk (2.5-in. diameter and 1-in. thickness), cell caps, valve stems, heating element, and a nitrogen gas line. The mud was placed in the cell and then put in a heating jacket. Then, the aforementioned differential pressure and temperature were adjusted for 20 minutes. The lower valve of the cell was opened and the filtrate was collected and recorded as a function of time for 30 minutes. The lower valve was closed and the cell cooled down for 20 minutes. After the filtration process, the disk with the filter cake was taken out from the cell and computerized tomography (CT) scanned while it was still wet to determine the filter cake thickness and characteristics. Additionally, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) was used to analyze the filter cake's surface and chemical composition.

After the CT scanning and SEM-EDS analysis of the filter cake, the acid-chelate solution was prepared and mixed with a corrosion inhibitor. Two solutions were tested: 7.5 wt% HCl + 1 vol% corrosion inhibitor and 7.5 wt% HCl + 7.5 wt% HEDTA + 1 vol% corrosion inhibitor. The density and pH of

the solutions were measured. The core with the filter cake was then soaked in the solution inside the filter press for 6 hours. After the soaking, the effluent solution was collected and the pH and density were measured again. The effluent solution was then filtered and diluted at 2000, 1000, 500, and 400 times with deionized water (DI-water) and analyzed by inductively coupled plasma (ICP) to determine cations concentrations. The remaining filter cake was then analyzed by SEM-EDS.

## 3. Results and discussion

### *3.1. Rheological properties*

Table 5 shows the rheological properties (measured at 120ºF and atmospheric pressure) and the density of the ilmenite-WBM, which are consistent with (Elkatatny, Nasr-El-Din, & Al-Bagoury, 2012; Elkatatny, Nasr-El-Din, & Al-Bagoury, 2013; Elkatatny, Xiao, Nasr-El-Din, & Al-Bagoury, 2013).

**Table 5 –** Properties of ilmenite-WBM.

| Property | Temperature (ºF) | Value | Unit |
|---|---|---|---|
| Density | 77 | 109.5 | pcf |
| PV | 120 | 34.2 | cp |
| YP | 120 | 20.9 | $lb_f/100ft^2$ |
| 10-sec GS | 120 | 2.5 | $lb_f/100ft^2$ |
| 10-min GS | 120 | 4 | $lb_f/100ft^2$ |

The density, PV, YP, and GS (10 sec and 10 min) were all found to be within the desired range for efficient drilling operations. These properties are important for maintaining proper suspension of rock cuttings and weighting materials, reducing frictional losses, and controlling equivalent circulation density (Bourgoyne, Millheim, Chenevert, et al., 1991). The results indicate that the drilling fluid is well-designed for drilling applications.

### *3.2. API filtration*

The filtration loss volume is shown in Fig. 2. The filter cake thickness was measured by CT scan, and the results are shown in Fig. 3. The cumulative fluid loss (30 min) was 12.7 and 11 $cm^3$ for the high- and low-permeability Bandera sandstone disks, respectively, which are acceptable (<15 $cm^3$). The filter cake thickness was measured to be around 0.203 ± 0.003 in.

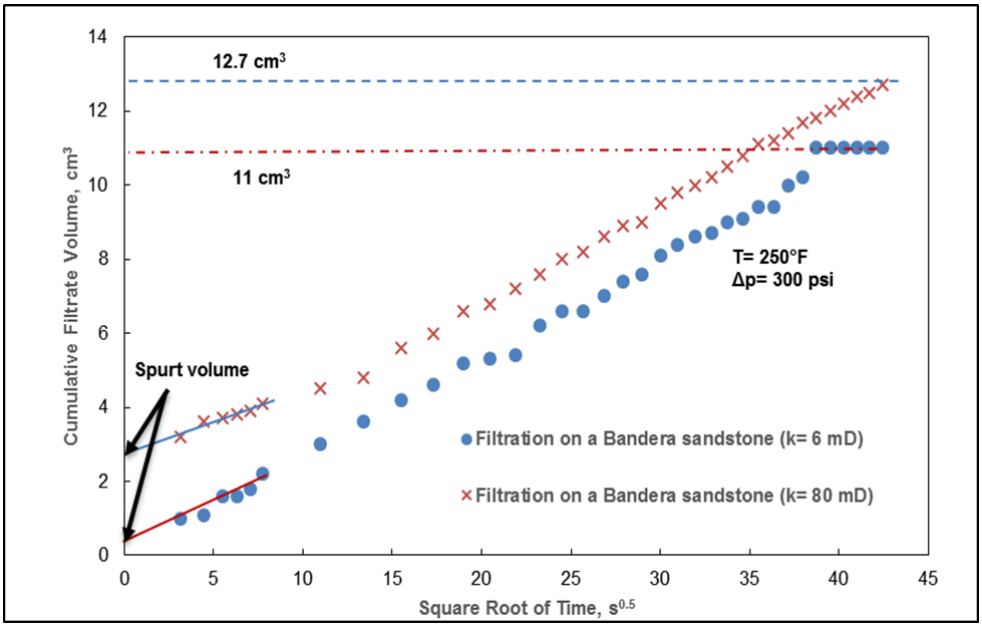


**Fig. 2 – Fluid loss curve of the ilmenite-WBM through Bandera sandstone.**

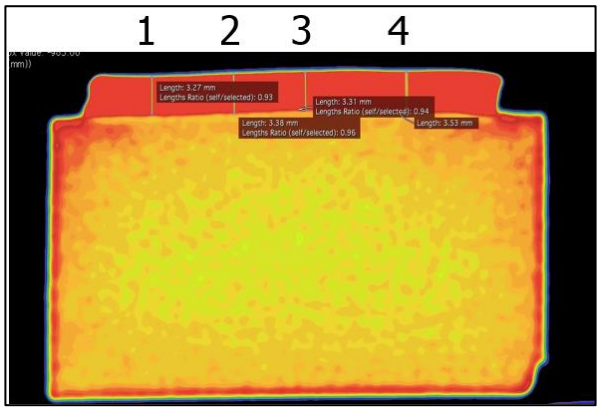


**Fig. 3 – CT scan image of the core disk and filter cake of the ilmenite-WBM through Bandera sandstone.**

Cross-sectional-CT images provide a detailed look into the internal structure of the filter cake and used disk (Vryzas, Mahmoud, Nasr-El-Din, & Kelessidis, 2015; Mahmoud, Nasr-El-Din, Vryzas, & Kelessidis, 2018a,b; Mahmoud & Nasr-El-Din, 2021). The CT images were analyzed using a commercial software. The analysis determined the thickness of the filter cake and the CT numbers (CTNs), which are numerical values obtained from the CT scan – in an internationally standardized scale in Hounsfield units (HU) – that represent the density and composition of the material being scanned. The CT numbers for air and water are typically set to -1000 and 0 HU, respectively, and serve as the reference points for normalizing the CT scale. Each HU represents a 0.1% change in density relative to the calibration density scale, which is based on the CT numbers of air and water (Wellington & Vinegar, 1987; Akin & Kovscek, 2003). This information is used to differentiate different structures and materials in a CT scan and helps in the diagnosis and analysis (Hanafy, Najem, & Nasr-El-Din, 2021; Hanafy, Nasr-El-Din, & Heidari, 2022). The filter cake from an ilmenite-WBM flowing through Bandera sandstone disk at 300 psi and 250ºF is shown in Fig. 4 (a), and Fig. 4 (b) shows CT image. The average thickness of the filter cake was 0.337 in. The average CTN for the core disk was 1776 HU. The filter cake has 2 layers, the CTNs for the upper and lower (close to the disk) layers were 2400 and 3500 HU, respectively. Fig. 5 presents the same for the filter cake from flowing through Berea sandstone disk. Average CTNs of 2411 and 3396 HU were obtained for the upper and lower layers of the filter cake, respectively. The CTN of the core disk was 1650 HU and the thickness of the filter cake was 0.203 in.

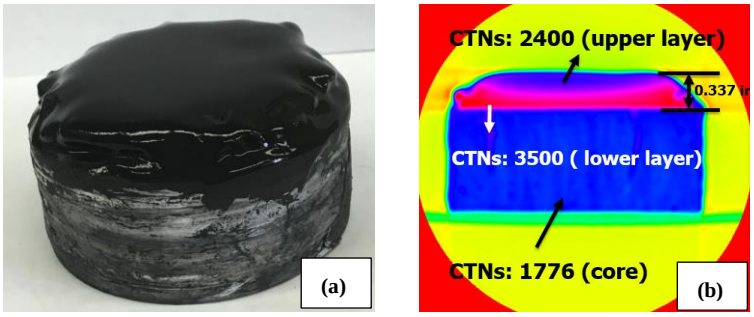


**Fig. 4 – (a) Bandera sandstone core with filter cake after static filtration at 300 psi and 250ºF; (b) Two layers of the filter cake using CT scan.**

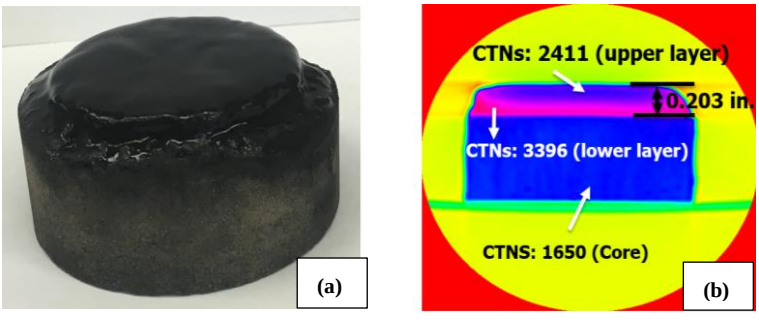


**Fig. 5 – (a) Berea sandstone core disk with filter cake after static filtration at 300 psi and 250ºF; (b) Two layers of the filter cake using CT scan.**

Table 6 shows the elemental composition, using SEM-EDS, of the upper and lower layers of the filter cake of the ilmenite-WBM flowing through Berea sandstone disk at 300 psi and 250ºF. Both layers consist of more than 50 wt% iron and 30 wt% titanium (mainly ilmenite). The other elements represent the chemicals used in the mud. For example, the K and Cl came from the KCl, Ca came from $CaCO_3$... etc.

**Table 6 –** Elemental composition of the upper and lower filter cake layers of the ilmenite-WBM through Berea sandstone disk at 300 psi and 250ºF.

| Upper layer | | Lower layer | |
|---|---|---|---|
| **Element** | **Concentration (wt%)** | **Element** | **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 |
| Al | 0 | Al | 3.51 |
| Sum | 100 | Sum | 100 |

The SEM images (Fig. 6) show a difference in pore structure between the upper and lower filter cake layers. The upper layer had more pores and was less dense, while the lower layer was denser and more compact. This difference is due to the deposition process, where heavier weighting materials deposit first and later lighter materials build upon the upper layer, causing the lower layer to continue compacting until filtration is complete (Civan, 1994, 1996).

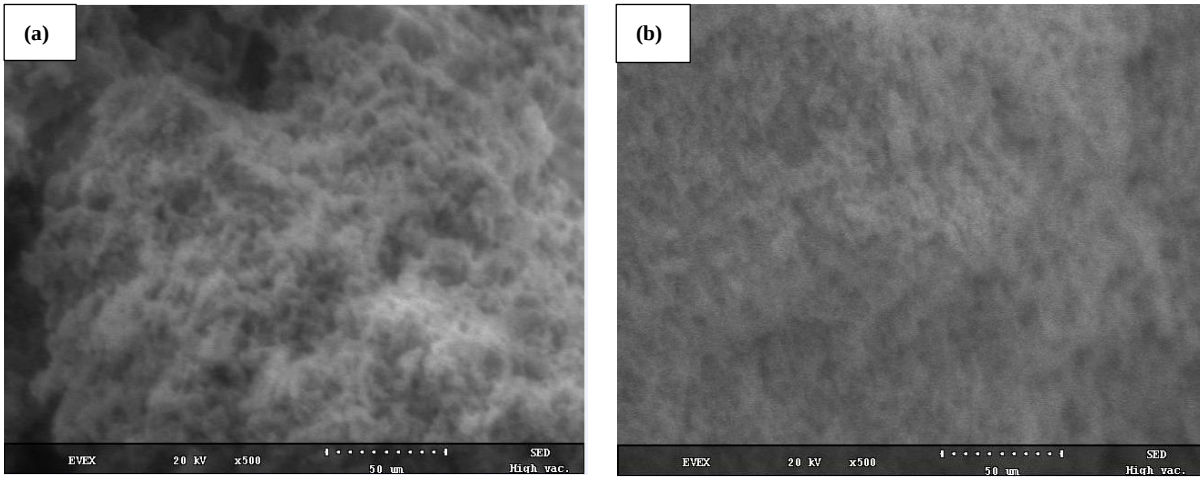


**Fig. 6 – SEM images (500X magnification) of the surface of the upper (a); and lower (b) filter cake layers of the ilmenite-WBM through Berea sandstone disk at 300 psi and 250ºF.**

The results from the CT scan and SEM-EDS analysis indicate that the filter cake generated by the ilmenite-WBM is composed mainly of weighting material (iron and titanium) and minor amounts of other materials from the drilling fluid formulation. The filter cake has two layers, with the upper layer being more porous and the lower layer being denser and more compact. The next step of the study is to investigate the effectiveness of using HCl and HEDTA to remove the filter cake.

### *3.3. Chemical filter cake removal*

Acids solubility of ilmenite is globally used to obtain $TiO_2$ for pigment application. A summary of ilmenite/acids reactions was reported by (Elkatatny, Xiao, Nasr-El-Din, & Al-Bagoury, 2013). In our study, acid solutions were prepared and mixed with a corrosion inhibitor and soaked with the core disk/filter cake inside the filter press for 6 hours at 250°F and 300 psi. The first attempt used 7.5 wt% HCl with 1 vol% corrosion inhibitor. The results, as shown in Fig. 7, indicate that an incomplete removal occurred. Fig. 8 shows a 3D model of the filter cake using CT scan which confirms that after reacting with 7.5 wt% HCl for 6 hours, more filtration into the core was observed.

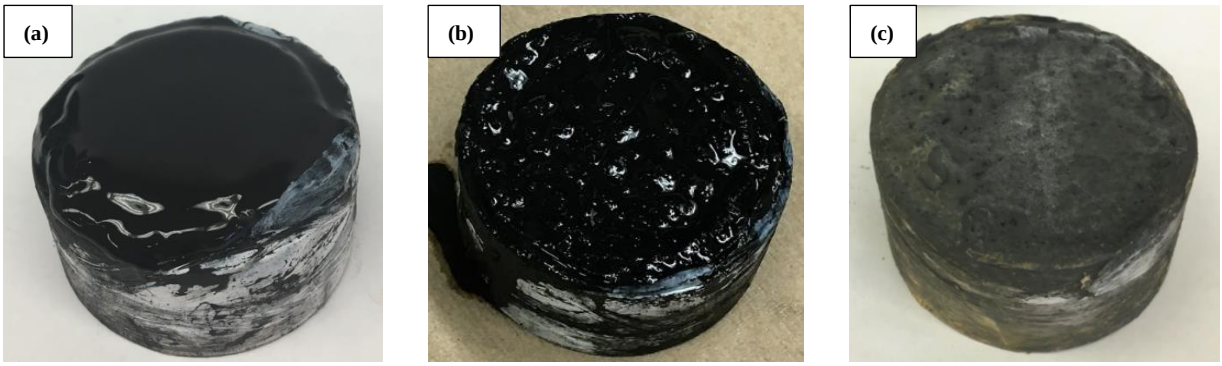


**Fig. 7 – (a) Filter cake after static filtration at 300 psi and 250ºF; (b) Filter cake after soaking for 6 hours with 7.5 wt% HCl at 300 psi and 250ºF; (c) Remaining filter cake after drying at 212ºF for 3 hours.**

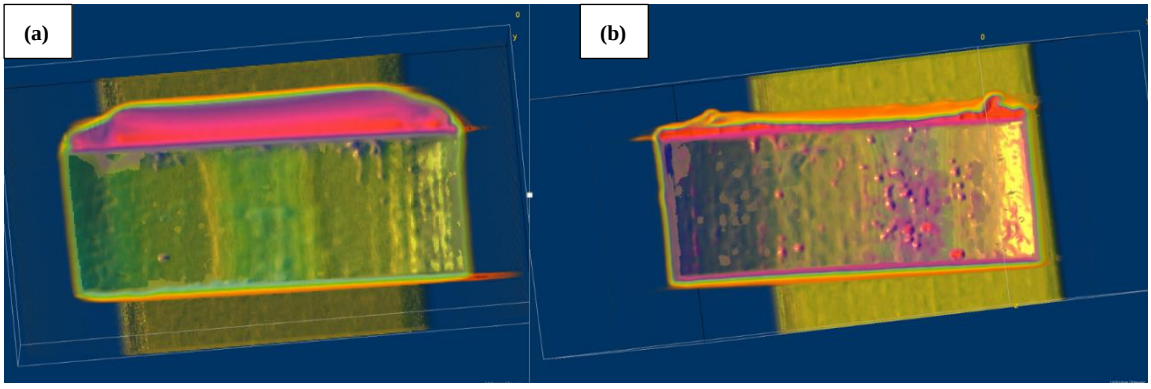


**Fig. 8 – (a) 3D model of the CT image of the filter cake and disk after static filtration at 300 psi and 250ºF; (b) 3D model of the CT image of the filter cake and disk after treating with 7.5 wt% HCl for 6 hours at 300 psi and 250ºF.**

The different weights of the core disk used in the 7.5 wt% HCl acid treatment are shown in Table 7. The dry and wet weights of the core disk was 168.4 and178.2 g, respectively. After filtration, the core with the filter cake weighed 219.7 g. After the filter cake removal, the core with filter cake residue weighed 191.4 g. This comparison shows that the filter cake removal was incomplete, the weight of the core disk with filter cake residue is higher than the saturated core disk (178.2 g).

**Table 7 –** Different weights of the core disk and filter used in the acid treatment for 6 hours with 7.5 wt% HCl.

| | **Dry weight (g)** | **Wet weight (g)** |
|---|---|---|
| Core disk | 168.4 | 178.2 |
| Core disk with filter cake | – | 219.7 |
| Core disk the with remaining filter cake | 179.8 | 191.4 |

The second acidizing attempt uses acid solution of 7.5 wt% HCl + 7.5 wt% HEDTA + 1 vol% corrosion inhibitor at 300 psi and 250ºF. The acid concentration, pH, density before and after the treatment are shown in Table 8. The different weights of the core disk before and after the reaction are shown in Table 9. After the acid treatment, the core with the filter cake weighed 199.7g, which also represents incomplete filter cake removal if compared with the wet weight of the core (182.8 g).

**Table 8 –** pH, density, HCl concentration before and after the acid treatment for 6 hours 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 9 –** Different weights of the core disk and filter used in the acid treatment for 6 hours with 7.5 wt% HCl and 7.5 wt% HEDTA.

| | Dry weight (g) | Wet weight (g) |
|---|---|---|
| Core disk | 169.4 | 182.8 |
| Core disk with filter cake | – | 238 |
| Core disk the with remaining filter cake | – | 199.7 |

Remaining filter cake was observed after soaking with 7.5 wt% HCl and 7.5 wt% HEDTA for 6 hours at 300 psi and 250ºF as shown in Fig. 9. Before acidizing, the thickness of the filter cake was 0.337 in., and after the treatment it became 0.094 in (Fig. 10). The average CTNs of the filter cake were 2400 and 3500 HU for the upper and lower layers, respectively. After the reaction with the HCl-HEDTA solution, the upper layer was removed and the CTNs of the lower layer became 3200 HU. This shows that the filter cake was partially removed.

Weight difference was used to calculate the removal efficiency of acid-treatment. It is not an accurate method because it does not take into account the dissolution of the core. To account for this, researchers have proposed using other methods. In this research where the goal is to compare results with past literature, it may be necessary to use the weight loss formula as shown in Eq. 2;

$$Removal\ Efficiency = \frac{Wt_{core+cake} - Wt_{core+remaining\ cake}}{Wt_{core+cake} - Wt_{core}}\ \% \quad (2)$$

where; $Wt_{core+cake}$ is the wet weight of the core disk and filter cake, $Wt_{core+remaining\ cake}$ is the wet weight of the core disk and the remaining filter cake, ad $Wt_{core}$ = the wet weight of the core before the filtration.

By using Eq. 2, it appears that the removal efficiency when conducting the acidizing with 7.5 wt% HCl is 68.2%. While, the removal efficiency when conducting the acid treatment using 7.5 wt% HCl + 7.5 wt% HEDTA is 69.2%. These results suggest that HCl is the dominant acid in the removal process, with minimal removal effect of HEDTA. It's worth noting that even though HEDTA is not having a significant effect on the removal efficiency, it could be playing an important role in other aspects of the treatment process, such as corrosion inhibition or stabilization of the acid solution, which will be further discussed in coming sections. Previous studies have shown that HCl and chelating agents can be effective in removing ilmenite filter cake, with higher removal efficiencies being reported (Elkatatny, Xiao, Nasr-El-Din, & Al-Bagoury, 2013; Xiao, Nasr-El-Din, & Al-Bagoury, 2015). However, these studies used longer soaking times and did not address the issue of corrosion. For example, Elkatatny et al. found that a soaking time of 16 hours and a concentration of 5 wt% HCl resulted in almost 100% removal efficiency, while 20 wt% HEDTA as a stand-alone acid resulted in almost 48% removal efficiency.

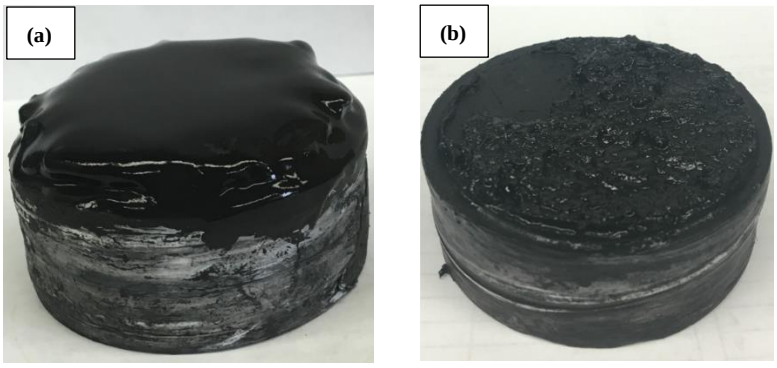


**Fig. 9 – (a) Filter cake after static filtration at 300 psi and 250ºF; (b) Remaining filter cake after soaking with 7.5 wt% HCl and 7.5 wt% HEDTA for 6 hours at 300 psi and 250ºF.**

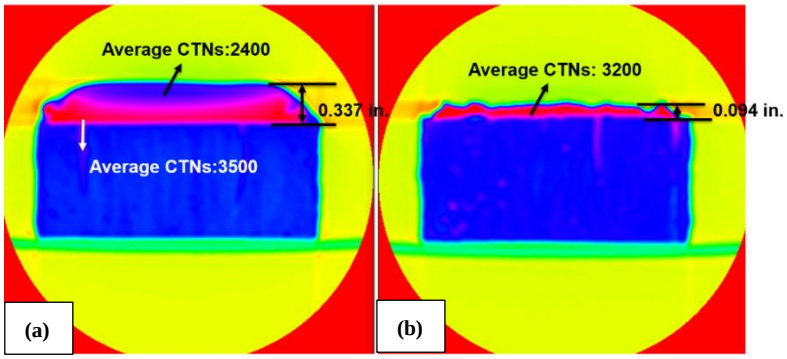


**Fig. 10 – (a) CT scan image of the filter cake after static filtration at 300 psi and 250ºF; (b) CT scan image of the remaining filter cake after soaking with 7.5 wt% HCl and 7.5 wt% HEDTA for 6 hours at 300 psi and 250ºF.**

Fig. 11 illustrates the change in color of the solution before and after treatment. The yellow color is from the corrosion inhibitor, while the purple color after the reaction is unusual and not commonly seen in the lab. Table 10 presents the elemental composition of the effluent solution after the reaction as revealed by ICP elemental analysis. The effluent solution contains a large amount of iron (23,530 ppm) and a relatively small amount of titanium (71 ppm). Calcium, magnesium, and aluminum were also detected by ICP, which confirms the acid reaction with the core. It is also noted that HEDTA complexes with $Cr^{3+}$ and changes the color of the solution (De Wolf, Nasr-El-Din, Bouwman, Bang, & Naylor, 2012). Abnormally high concentrations of Ni and Cr were also observed, which are a sign of corrosion. Fig. 12 shows the SEM of the remaining filter cake after the treatment. Before removal, the lower layer of the filter cake was smooth, dense, and compact, but after the treatment, more pores were generated, indicating partial filter cake removal. Some of the particles aggregated and formed new structures.

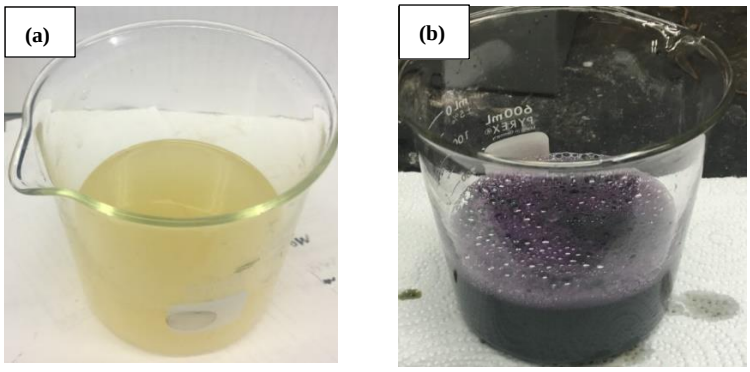


**Fig. 11 – (a) 7.5 wt% HCl and 7.5 wt% HEDTA acid-solution before the reaction; (b) Effluent solution after reaction.**

**Table 10 –** Cation concentration in the effluent solution after reaction with 7.5 wt% HCl + 7.5 wt% HEDTA.

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

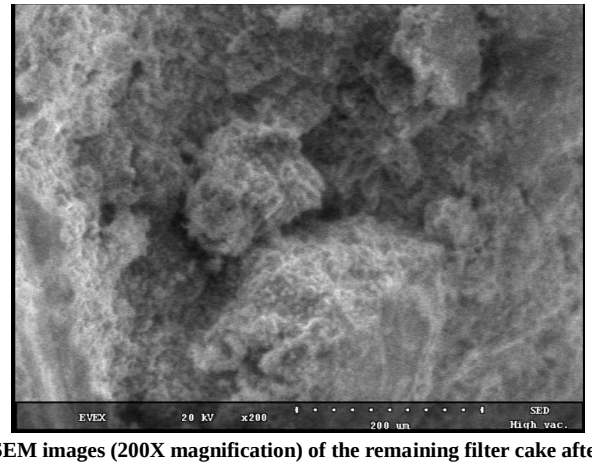


**Fig. 12 – SEM images (200X magnification) of the remaining filter cake after soaking with 7.5 wt% HCl + 7.5 wt% HEDTA for 6 hours at 300 psi and 250ºF.**

The filter cake was not removed completely, and the acid was not fully spent. The concentration of the acid after the reaction, as determined by acid titration, was 2.13 wt%. Compared to the initial HCl concentration, almost 71.6% of the acid was spent. Van Dyk et al. discussed the mechanism of ilmenite leaching and concluded titanium could polymerize in HCl. Low initial mole ratio of the acid-to-ilmenite will cause titanium polymerization, which forms a product layer (Van Dyk, Vegter, & Pistorius, 2002). After forming this layer, the acid is separated from the remaining filter cake, and no more reaction can take place. Precipitation of $TiOCl_2$ would occur in the pores of the particles. The start point of polymerization of titanium occurs when the concentration of titanium is larger than 10-3 mol/cm$^3$. Almost 71 ppm of titanium, as determined by ICP, if divided by the molecular weight of titanium (47.867) is 1.48×10-3 mol/cm$^3$. Therefore, titanium polymerizes in the solution and mass-transfer limits the reaction. Van Dyk et al. recommended higher initial acid-to-ilmenite mole ratio to delay the polymerization of titanium and allow much more titanium to dissolve from ilmenite.

## 4. Summary and conclusion

Different experimental studies were conducted to investigate the removal efficiency of the ilmenite-based filter cake using HCl-HEDTA solution. Based on the results, it can be concluded that HCl-HEDTA solution was found to be effective in removing ilmenite filter cake, with higher removal efficiencies being reported (69.2%). The effluent solution after the reaction was found to contain high concentrations of iron, while titanium was present in relatively small amounts. Calcium, magnesium, and aluminum were also detected in the effluent solution, confirming the acid reaction with the core. The presence of Ni and Cr in the effluent solution were signs of corrosion. A special cell (Hastelloy) is recommended instead of stainless steel to minimize corrosion issues. The SEM of the remaining filter cake after treatment showed the formation of more pores, indicating partial filter cake removal. The filter cake was not completely removed and the acid was not fully spent, indicating that titanium polymerizes in the solution and mass-transfer limits the reaction. To avoid polymerization of titanium and dissolve more titanium from ilmenite, higher initial acid-to-ilmenite mole ratio is recommended. The results also suggest that longer soaking times and higher acid concentrations can lead to better removal efficiencies, but also increase the risk of corrosion.

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