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Using Hydrochloric Acid to Remove Ilmenite Water-Based Filter Cake in HPHT Applications

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Abstract

The growing demand for well-designed weighting agents to overcome the currently drilling challenges such as ECD management and the settling tendency of the weighting agents led to the development of a new micronized ilmenite ($FeTiO_3$). The acid solubility of ilmenite is of great importance to remediate any damage that might occur during its use in the drilling operation.

Extensive lab work was conducted to: 1) assess the reaction of 10 wt% HCl with ilmenite particles at 300˚F and 300 psi using an aging cell, 2) optimize the concentration of HCl to remove the filter cake using a modified HPHT filter press at 250˚F, 3) determine the removal efficiency of the filter cake, and 4) calculate the retained permeability of Indiana limestone cores.

The reaction of hydrochloric acid with ilmenite showed that HCl (10 wt%) dissolved 75 wt% of the iron from ilmenite particles after 10 hrs of reaction at 300˚F. SEM and XRD results showed that the reaction product was mainly rutile (TiO_2) after 6 hrs of reaction.

Ilmenite-based filter cake was removed completely after reaction with 5 wt% HCl (300 g solution) for 16 hrs soaking time at 250˚F. The retained permeability of the Indiana limestone and Berea sandstone cores was nearly 100% after HCl treatment (5 wt%). Removal of ilmenite water-based filter cake is a simple process as compared with barite water-based filter cake, which cannot be removed using HCl. This study will provide a complete evaluation of the reaction of HCl with ilmenite and will help the drilling and completion engineers to better design the chemical treatments to remove the filter cake for HPHT wells.

Introduction

Ilmenite was introduced as a weighting material in drilling fluids to avoid the shortage and high cost of API barite (Tran 2007 and Blomberg 1984) and also to avoid the pollution that resulted from using barite (Rae et al. 2001). Ilmenite as a hard mineral with Mohs scale hardness of 5-6 is less susceptible to erosion during drilling over the barite, which has a hardness of 3-3.5. Saasen et al. (2001) reported on field operations from a semi-submersible rig offshore northern Norway using ilmenite with an average size (D50) of 10µm (measured by Sedigraph) as weight material. The author showed the benefits of using a 10µm ilmenite grade such as the reduction in abrasion, which was observed with the coarser ilmenite, longer life time of drilling fluids, and the less need for dilution due to the good stability of the fluid.

Al-Bagoury and Steele (2011) reported the use of micronized ilmenite with an average size (D_{50}) of 5 µm as a weighting agent for drilling fluids. It was demonstrated that under similar conditions, micronized ilmenite showed low sag tendency and low plastic viscosity compared to API barite. These features are of great importance and can be employed in challenging drilling operations such as horizontal drilling, low margin pressure drop (ΔP), deep water, and slimehole.

Manganese tetraoxide had some restrictions on the removal operation. Al Moajil and Nasr-El-Din (2011) reported that the solubility of Mn_3O_4 in acetic acid is low. HCl acid can be used to dissolve Mn_3O_4-based filter cake at concentrations less than 5 wt% because chlorine gas will be produced at high HCl concentrations (Al Moajil and Nasr-El-Din 2010).

Reaction of Ilmenite with Acids

The solubility of ilmenite by acids particularly HCl and H_2SO_4 is widely used industrial process to obtain TiO2 for pigment application. The ilmenite leaching reaction can be described by the following chemical reaction (van Dyk et al. 2002):

$$FeTiO_3 + 2HCl \longrightarrow Fe^{2+} + TiO_2 + 2Cl^- + 2OH^-$$

The main parameters that can influence the rate of this reaction are particle size, acid concentration, temperature, stirring, acid-to-ilmenite mole ratio, and additives (van Dyk et al. 2002).

Jackson and Wadsworth (1976) studied the effect of particle size on the rate of ilmenite dissolution. They found that particle size did not influence the rate of ilmenite dissolution. They used three size fractions namely: -150 + 106, -230 + 150 and -328 + 230 µm. The samples were leached in 6 M HCl at 75˚C at an initial acid-to ilmenite mole ratio of 692:1. Iron and titanium went into solution under these conditions and almost 100% extraction of both elements was reached within 250 min for all size fractions. In contrast, Olanipekun (1999) stated that particle size does influence the rate of ilmenite dissolution. Three size fractions were used namely: + 20–37, + 37–53 and + 53–74 µm. The samples were leached in 7.2 M HCl at 70˚C at an initial acid-to-ilmenite mole ratio of 8:1. The rate of iron and titanium extraction increased as the particle size decreased. The maximum amount of iron dissolution achieved was about 62% after 300 min. This was for the + 20–37 µm fraction. At the same time, about 58% of the titanium in this fraction dissolved.

Hussein et al. (1976) found that the rate of ilmenite dissolution is strongly dependent on acid concentration. However, in their experiments, mainly iron was dissolved. They used four different acid concentrations ranging from 2.16 to 6.48 M HCl. The leaching tests were performed at 90˚C at initial acid-to-ilmenite mole ratios that varied between 6:1 and 17:1, depending on the acid strength. The maximum iron extraction was about 35% after 160 min in the 6.48 M solution, while only 7% of the iron was removed in the 2.16 M solution after the same period. Jackson and Wadsworth (1976) used 4, 5 and 6 M HCl solutions. The leaching tests were conducted at 90˚C at initial acid-to-ilmenite mole ratios, which depending on the acid concentration, ranged from 188:1 to 353:1. They found that after 400 min, 100% of the iron and titanium was extracted in the 6 M HCl solution, while about 10% of the iron and titanium were dissolved in the 4 M HCl solution in the same time period.

Temperature has a significant effect on the dissolution of the ilmenite. The rate of ilmenite dissolution increased as the temperature increased (Sinha 1984). He conducted his experiments at temperatures ranging from 80 to 108˚C. A 6 M HCl solution was used at an initial acid-to-ilmenite mole ratio of 1:1. After 4 hrs, almost 95% of the iron was extracted at 108˚C, while less than 50% was extracted at 80˚C. He found that under these conditions, only iron went to solution.

Tsuchida et al. (1982) and Sinha (1984) found no significant increase in the rate of iron or titanium extraction with in an increase in stirring speed in the range of 100–500 min^{-1}. Sinha (1984) reported that higher stirring speeds resulted in the production of excessive quantities of less than 10 µm TiO_2 fines.

Duncan and Metson (1982) found that by adding bisulphate and fluoride to the leach solutions, the dissolution rate of both iron and titanium increased, but when they added phosphoric acid and Ti (IV) to the leach solution, the dissolution rate of iron and titanium decreased dramatically. Girgin (1990) performed a similar experiment using methanol additions. He found that the rate of iron and titanium dissolution increased dramatically when methanol additions were used compared to dissolution in the normal hydrochloric acid solution (3 M HCl).

Van Dyk et al. (2002) studied the leaching mechanism of ilmenite with hydrochloric acid and showed that the dissolution of ilmenite follows initially a chemical reaction controlled mechanism and later a diffusion controlled mechanism as the Ti-(IV) fines produced by hydrolysis reaction (Ti(IV) polymerises in hydrochloric acid solutions) precipitate inside the pores of the unleached particles.

In the sulfate process, ilmenite concentrate is digested in concentrated sulfuric acid in the temperature range of 150–180°C to dissolve titanium and iron. The dissolved Ti is precipitated as hydrous TiO_2, by preferential hydrolysis of the leach solution. However, the kinetics of dissolution of ilmenite in sulfuric acid is slow (10 to 12 hr per batch), costly and the by-product ferrous sulfate is less marketable and poses an environmental hazard (Abdel-Aal et al. 2000).

Studies on leaching behavior of ilmenite with sulfuric acid showed that the chemical reaction at the particle surface was the rate limiting step and a value of 64 kJ/mol was estimated for the activation energy based on the dissolution of iron (Han et al., 1987).

Studies by Sasikumar et al. (2004) on the leaching kinetics of mechanically activated ilmenite of Chatrapur coast, India with H_2SO_4 revealed that the titanium as well as iron in ilmenite dissolves differentially and not according to their stoichiometry. Their maximum dissolution of Ti was restricted to 65% whereas 90% of Fe could be dissolved in 240 min at 120°C for 4 h. They did not observe any hydrolysis of TiO_2 with sulfuric acid leaching (Sasikumar et al. 2004).

Sasikumar et al. (2007) concluded that the dissolution kinetics of ilmenite in hydrochloric acid appears to be marginally favorable compared to that in sulfuric acid. However, the enhanced dissolution of Ti in HCl for the activated sample is affected by the hydrolysis and precipitation reactions that set in at higher temperatures and lower acid concentrations for prolonged periods of leaching. The activation energy for dissolution of Fe and Ti is higher in H_2SO_4 (68 and 70 kJ/mol, respectively) compared to HCl (64 and 68 kJ/mol, respectively). The activation energies for dissolution of Fe and Ti also showed a monotonic increase with time of milling.

Mahmoud et al. (2004) concluded that synthetic rutile was produced from a medium grade Egyptian ilmenite ore by a process that eliminates the high temperature pretreatment and pressure leaching. The addition of iron powder during leaching of ilmenite creates the Ti^{3+} in solution, which was expected to have a main role in accelerating the leaching of ilmenite ore through keeping the dissolved iron in the ferrous state. They found that the optimum leaching conditions were as follows: HCl stoichiometry: 1.2, HCl concentration: 20%, temperature: 110˚C, Fe powder stoichiometry: 1.1 added after 30 min and retention time: 5 hrs. The produced rutile at the optimum conditions contains about 90% TiO_2 and only 0.8% iron as Fe_2O_3 with 0.12% coloring metals and 5.8% SiO_2.

Based on the literature, the chemical reaction of ilmenite with different acids depends on the particle size of ilmenite and the concentration of different acids. As the ilmenite particles decrease to 5 µm, the objectives of this study work are to: 1) study the kinetic reaction of different acids with microsized ilmenite (5 µm) at different temperatures, 180 and 300˚F, 2) perform SEM and XRD analyses of the reaction products, 3) determine the removal efficiency of ilmenite water-based filter cake, and 4) calculate the retained permeability of Indiana limestone cores.

Experimental Studies

Materials

Indiana limestone cores were used to simulate the pay zone. Indiana limestone cores were cut from a block with an average porosity of 23 vol% and a permeability of 80 to 120 md.

HEDTA with pH of 4 and a concentration of 40.8 wt% and EDTA of pH 5.9 and a concentration of 40 wt% were used. Glycolic acid (70 wt%) xanthan gum and starch were obtained from a local service company.

Microsized ilmenite (D_{50} = 5 µm) was obtained from Elkem Company.

Equipment

A batch reactor under magnetic stirring (Fig. 1) was used to perform the kinetic reaction at 180˚F and atmospheric pressure. Aging cell with Teflon rubber was used to conduct the kinetic reaction at 300F and 300 psi under hot rolling in the oven. Inductively coupled plasma (ICP) was used to obtain the concentration of dissolved iron and titanium in the solution. Scanning electronic microscopy (SEM) and X-Ray diffraction analysis (XRD) were used to analyze the remaining solid after the chemical reaction. High Pressure- high temperature (HPHT) filter press was used to do the filtration and removal process at 250˚F and 300 psi.

Procedures and Parameters

The following procedure was conducted for the kinetic reaction;

1. A solution with acid was put in the batch reactor and the temperature was adjusted at 180˚F.
2. The solid was added at 180˚F and samples were collected at different times.
3. ICP analysis was conducted for the collected samples.
4. The remaining solid was filtered and SEM, XRD analysis was performed.
5. Aging cell was used at 300˚F and 300 psi. Ilmenite with the solution was put in the aging cell, then the cell was pressurized at 300 psi. After that the cell was put in the oven at 300˚F. The experiment was stopped at the determine time.
6. The aging cell was cooled down and sample was collected. The remaining solid was filtrated and SEM, XRD analysis was conducted.

HPHT filter press procedure

1. Ilmenite water-based drilling fluid was mixed and prepared as shown in Table 2.
2. Initial permeability was calculated using Darcy's law for the used core.
3. Filtration test was done at 250˚F and 300 psi.
4. The formed filter cake was soaked with acid solution for 16 hrs at 250˚F and 300 psi.
5. Filter cake removal efficiency was calculated.
6. Final permeability was calculated for the used core after the removal process.

Results and Discussion

Kinetic Reaction at 180˚F

The reaction of HCl with ilmenite particles was examined at 180°F under magnetic stirring using the system shown in **Fig. 1.** The weight ratio of HCl solution to ilmenite was 62.5:1 (4 g ilmenite / 250 g HCl solution). During each experiment, samples were collected at different times and filtered immediately through 0.2-micron Whatman syringe filter.

The collected samples were diluted and ICP analyses were performed. **Fig. 2** shows that 10 and 15 wt% HCl had a solubility of iron of 40 and 45%, respectively. The solubility of titanium was 15% when using and 10 wt% HCl and it was 35% when using 20 wt% HCl as shown in **Fig. 3**.

The same procedure was performed using glycolic acid (10 wt%) and HEDT (20 wt% of pH 4) at 180˚F. **Figs. 4 and 5** show that glycolic acid dissolved 5wt% of iron and around 0.5 wt% of titanium after 9.5 hrs at 180˚F. While HEDTA (pH 4) dissolved 4 wt% iron and 2.5 wt% titanium after 9.5 hrs at 180°F, **Figs. 4 and 5**.

Kinetic Reaction at 300°F

A 250 g aqueous solution of 10 wt% HCl was prepared and mixed with 4 g ilmenite in the aging cell. The cell was placed in the oven at 300˚F for different time intervals under hot rolling. **Fig. 6** shows the change of the solution color with time and it changed from green to yellow after 6 hrs, which indicated the increase of iron percentage in the solution with time. **Fig. 6** shows the change of solids color from black to white after 6 hrs of reaction.

SEM and XRD analysis for the remaining solids were performed. **Fig. 7** shows that the iron concentration was small as 4% after the reaction of 10 wt% HCl with ilmenite for 6 hrs. Titanium concentration was almost constant during the reaction for 10 hrs.

XRD analysis indicated that the remaining solids contained iron titanium oxide (Fe_9TiO_{15}) 14.12% and hydrogen titanium oxide hydrate ($H_2Ti_5O_{11}$) 19.06% for the first 4 hrs of the reaction. While after 6 hrs, the remaining solids contained mainly Rutile (TiO_2), **Table 1**.

Fig. 12 shows that 10 wt% HCl dissolved around 50% of the 4 g ilmenite at 300˚F. The change of the color of the remaining solids indicated the change of the ilmenite to rutile (TiO_2).

Chemical reaction of chelating agent such as HEDTA (20 wt% pH 4 and EDTA 20 wt% pH 5.88) with 4 g ilmenite was performed at 300˚F. **Figs. 8** and **9** show the change of solution color of HEDTA and EDTA as it react with ilmenite for 16 hrs at 300˚F.

ICP Analysis

Fig. 10 shows that HCl (10 wt%) dissolved 93 wt% of iron after 10 hrs while HEDTA (20wt% of pH 4) dissolved 31 wt% of iron after 16 hrs and EDTA (20 wt% of pH 5.88) dissolved 39 wt% of iron after 16 hrs.

Fig. 11 shows that HCl was unable to remove titanium from ilmenite and the dissolved concentration was around 10 wt% as the ilmenite particles changed to rutile (TiO_2). HEDTA dissolved around 20 wt% and EDTA dissolve around 25 wt% of titanium after 16 hrs. Therefore, it can be concluded that these types of chelating agent HEDTA and EDTA cannot be used to remove ilmenite water-based filter cake even at 300˚F.

Filtration and Removal Process

Drilling Fluid Properties

Water-based drilling fluid that contained ilmenite (D_{50} = 5μm) as a weight material was prepared and mixed as shown in **Table 2**. The drilling fluid contained xanthan gum for viscosity control, modified starch and PAC-R for filtration control, and calcium carbonate with different sizes (fine and medium of D_{50} = 25 and 50 μm, respectively) as a bridging material.

Table 3 shows that the drilling fluid had a density of 110 pcf, a plastic viscosity of 32 cp, a yield point of 24 lb/100 ft^2, and gel strength of 4 and 6 for 10 sec and 10 min, respectively.

HPHT Filtration

The drilling fluid was placed in the modified cell and the cell was placed in the heating jacket; the system was adjusted at 250˚F and 300 psi differential pressure. **Fig. 12** shows that the spurt volume was 4.4 cm^3 and the filter cake was ideal, which had a lower slop till reached zero permeability after around 25 min of filtration.

Removal Process

The formed filter cake was soaked with 300 g solution, which contains 20 wt% HEDTA (pH of 4) for 16 hrs. **Fig. 13** shows the filter cake remaining on the surface of the core after soaking with HEDTA (pH 4) for 16 hrs.

To calculate the removal efficiency, the weight was measured for the saturated core before the filtration, the core with the filter cake after the filtration, and the core with the remaining cake after the removal process. The removal efficiency was determined from Eq. 1. The removal efficiency was 48%, **Table 4**. It can be concluded that chelating agent cannot be used to remove ilmenite water-based filter cake either by cracking or dissolving the filter cake.

$$Efficiency = \frac{W_{\text{core+cake}} - W_{\text{core+remaining cake}}}{W_{\text{core+cake}} - W_{\text{core}}}, \qquad (1)$$

The filter cake was soaked with a 300 g solution that contained 5 wt% HCl for 16 hrs. **Fig. 14** shows that the core surface was clean after the removal process. The removal efficiency was around 100%, **Table 4**. **Fig. 15** shows the removal efficiency calculation with different acids.

Permeability Calculation

Darcy's law was applied to calculate the initial permeability of each core. The time required to flow 150 cm3 of DI water through the cores at a constant pressure of 60 psi was recorded. The final permeability was obtained by the same procedure after the removal process.

The retained permeability, which is a relation between the initial and final permeability, was calculated using Eq. 2.

$$k_r = \frac{k_f}{k_i} x100, \qquad (2)$$

where

k_f = final permeability, md
k_i = initial permeability, md
k_r = retained permeability

The retained permeability calculations and the leakoff time before the filtration and after the removal process were summarized in **Table 5**.

Fig. 16 shows that the retained permeability was 100%, which indicated that 5 wt% HCl was able to remove the filter cake from the surface of the rock and the invaded solid from the core. The experiment was repeated 4 times and the same results were obtained.

Conclusions

Based on the experimental results, the following conclusion can be made:

1. HCl dissolved 93 wt% of iron and changed the ilmenite particles to rutile after 10 hrs.
2. Chelating agent (HEDTA and EDTA) at lower pH (4 and 5.88) dissolves ilmenite water-based filter cake but at much lower rate compare to HCl solution.
3. Glycolic acid cannot be used to remove ilmenite particles. It dissolved 5 wt% iron and 0.5 wt% titanium.
4. Based on these experimental results HCl is seems to be the best dissolver to be used to remove ilmenite water-based filter cake at high temperature (300˚F).
5. HCl (5 wt%) had a complete removal of the filter cake after 16 hrs soaking time at 250˚F.
6. No formation damage was obtained when using HCl to remove the filter cake, the retained permeability of Indiana limestone cores was 100%.

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TABLE 1: XRD analysis of the remaining solids after reaction with HCl at 300˚F.

Time, hrs.	Mineral	Formula	Weight Percent, %
2	Iron Titanium Oxide	Fe_9TiO_{15}	14.21
	Hydrogen Titanium Oxide Hydrate	$H_2Ti_5O_{11}$	19.06
3	Iron Titanium Oxide	Fe_9TiO_{15}	14.21
	Hydrogen Titanium Oxide Hydrate	$H_2Ti_5O_{11}$	19.06
4	Iron Titanium Oxide	Fe_9TiO_{15}	14.21
	Hydrogen Titanium Oxide Hydrate	$H_2Ti_5O_{11}$	19.06
6	Rutile, syn	TiO_2	28.34
8	Rutile, syn	TiO_2	28.34
10	Rutile, syn	TiO_2	30

TABLE 2: Ilmenite drill-in fluid formula.

Additive	**Function**	**Lab. Unit, g**	**Mixing Time, min**
Water	Base	290	…….
Defoamer	Anti-foam	0.08	1
Xanthan gum	Viscosifier	0.25	20
Modified starch	Fluid loss	5	20
PAC-R	Fluid loss/ Filtration Control	1	20
KCl	Density and shale inhibition	72	20
KOH	pH control	1	1
$CaCO_3$ Fine (25 µm)	Bridging Material	7	20
$CaCO_3$ Medium (50 µm)		3.5	
Ilmenite	Weighting material	300	20

TABLE 3: Properties of the drill-in after hot rolling for 16 hrs.

***Property**	**Temperature, °F**	**Value**	**Units**
Density	77	110	pcf
Plastic viscosity	120	32	cp
Yield point		24	lb/100 ft^2
10 s gel strength		4	lb/100 ft^2
10 min gel strength		6	lb/100 ft^2
pH	77	9	………

*all properties were measured at atmospheric pressure (14.7 psi)

Table 4: Filter cake removal efficiency using HCl and HEDTA.

Code	Condition	W1	W2	W3	Removal Efficiency, %
LM1	20 wt% HEDTA	180	228	205	48
LM2	5 wt% HCl	181.18	231.8	181.2	100
LM3		180.65	229.87	180.9	99
LM4		180.9	230.3	180.9	100
LM5		181.5	231.8	181.6	100

Table 5: Calculation of the retained permeability.

Code	leakoff time before filtration, s	leakoff time after removal, s	Retained permeability, %
LM2	10	9.9	101
LM3	11	11.1	99.1
LM4	9.9	10	99
LM5	10.5	10.6	99.1

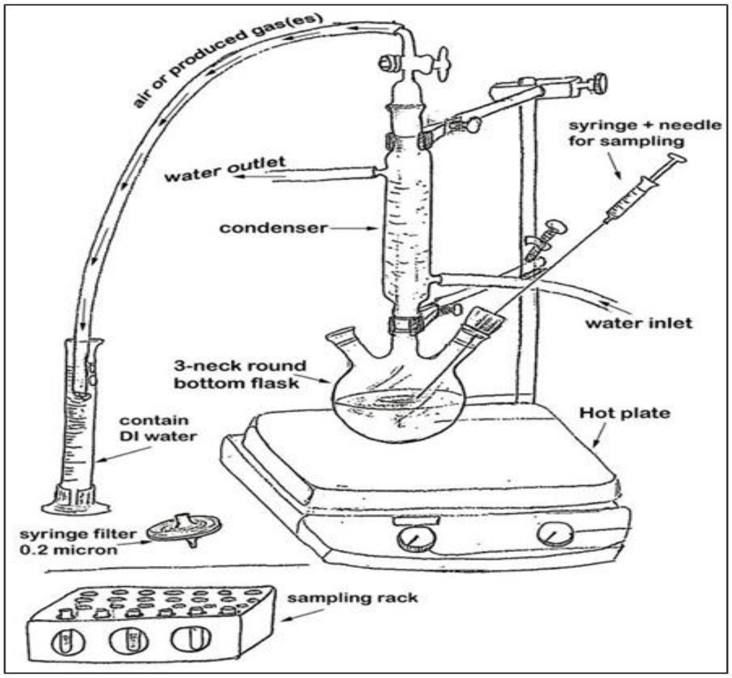

Fig. 1: Setup used to measure solubility of ilmenite (Al Mojil 2010).

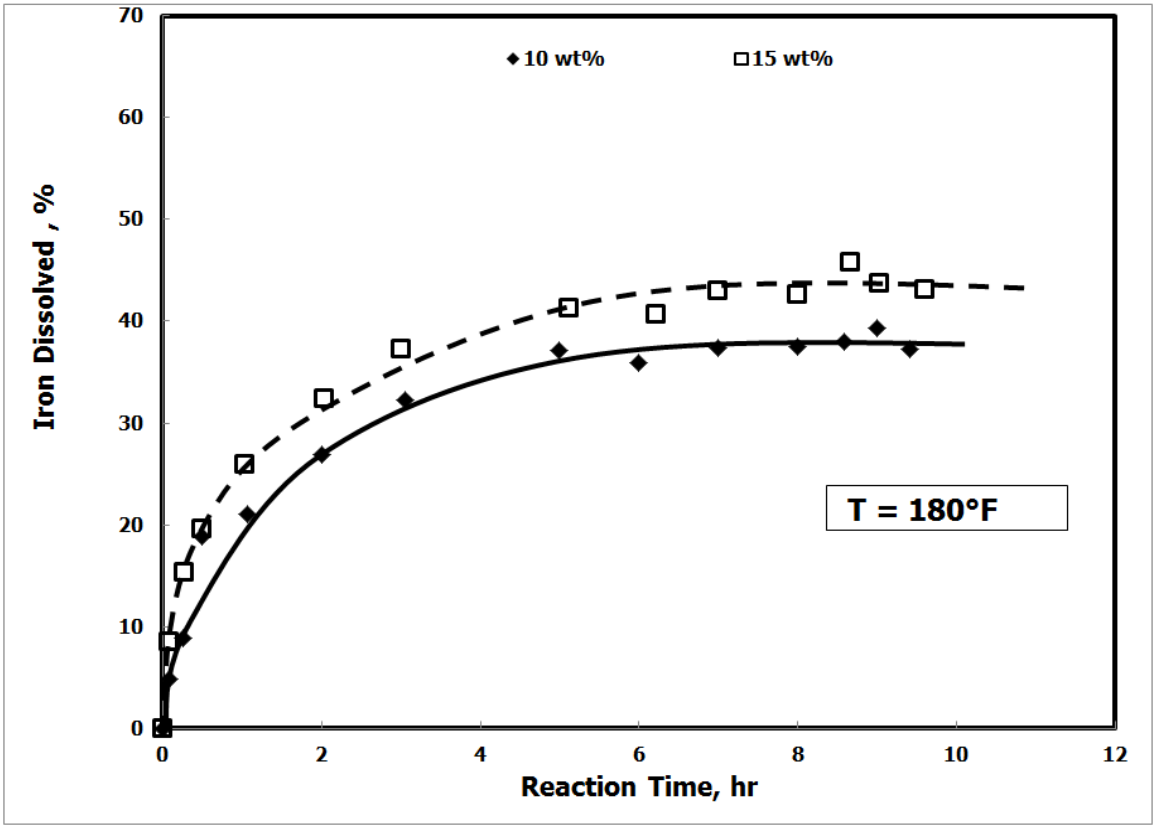

Fig. 2: Dissolution of iron using different concentration of HCl.

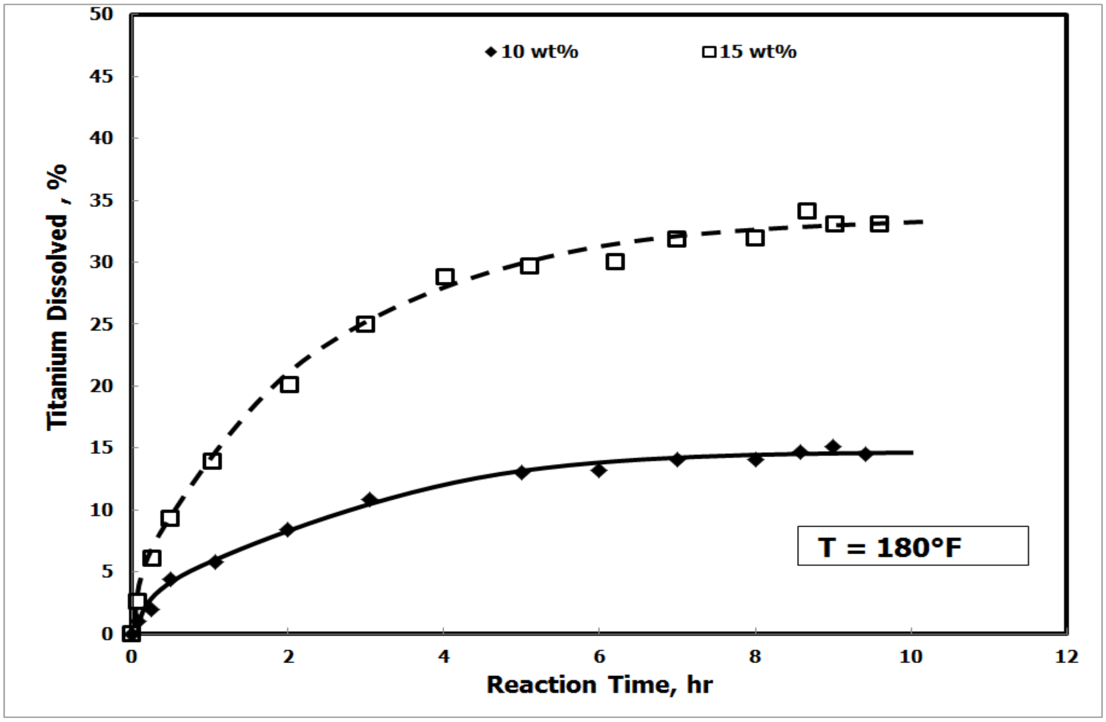

Fig. 3: Dissolution of titanium using different concentration of HCl.

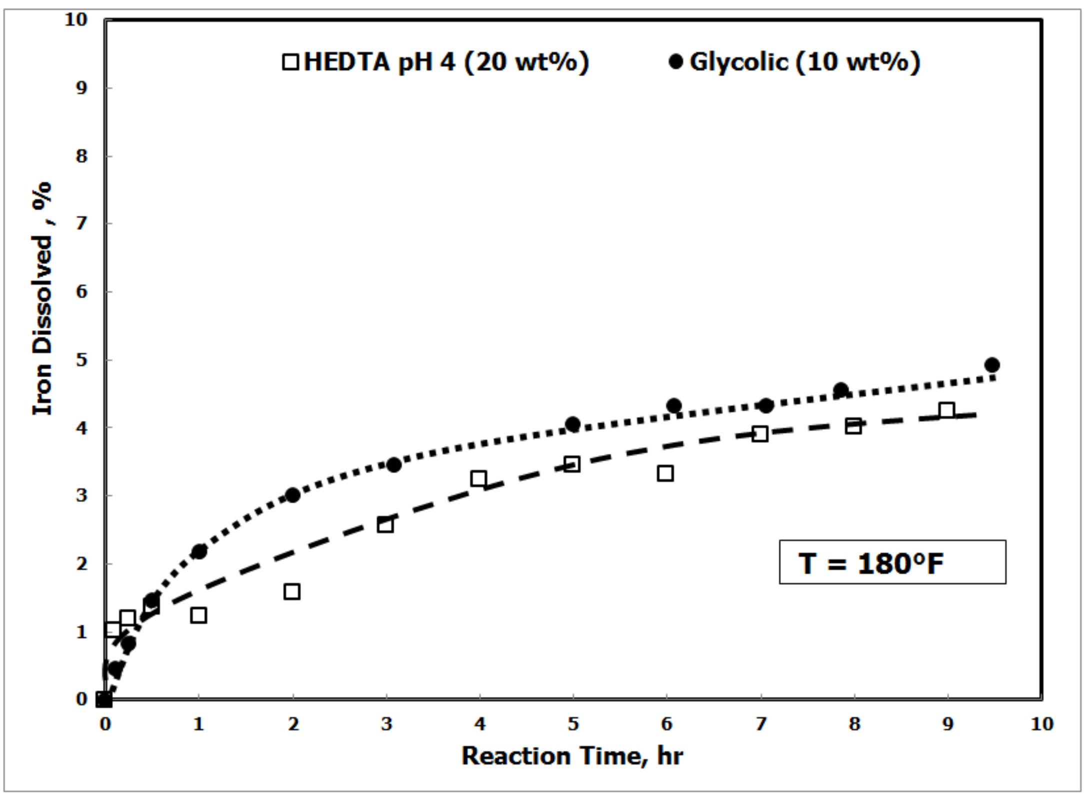

Fig. 4: Iron dissolution by reacting glycolic acid and HEDTA with ilmenite at 180˚F.

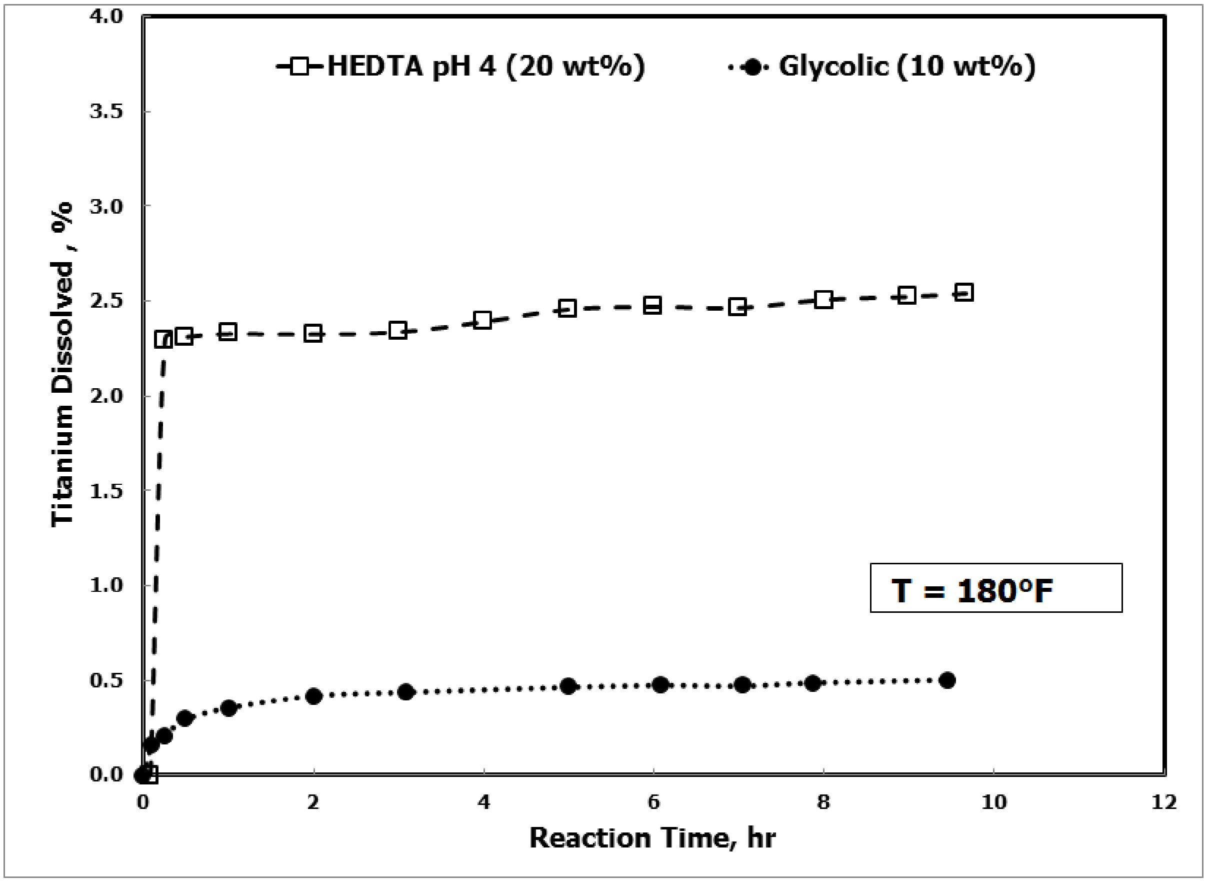

Fig. 5: Titanium dissolution by reacting glycolic acid and HEDTA with ilmenite at 180˚F.

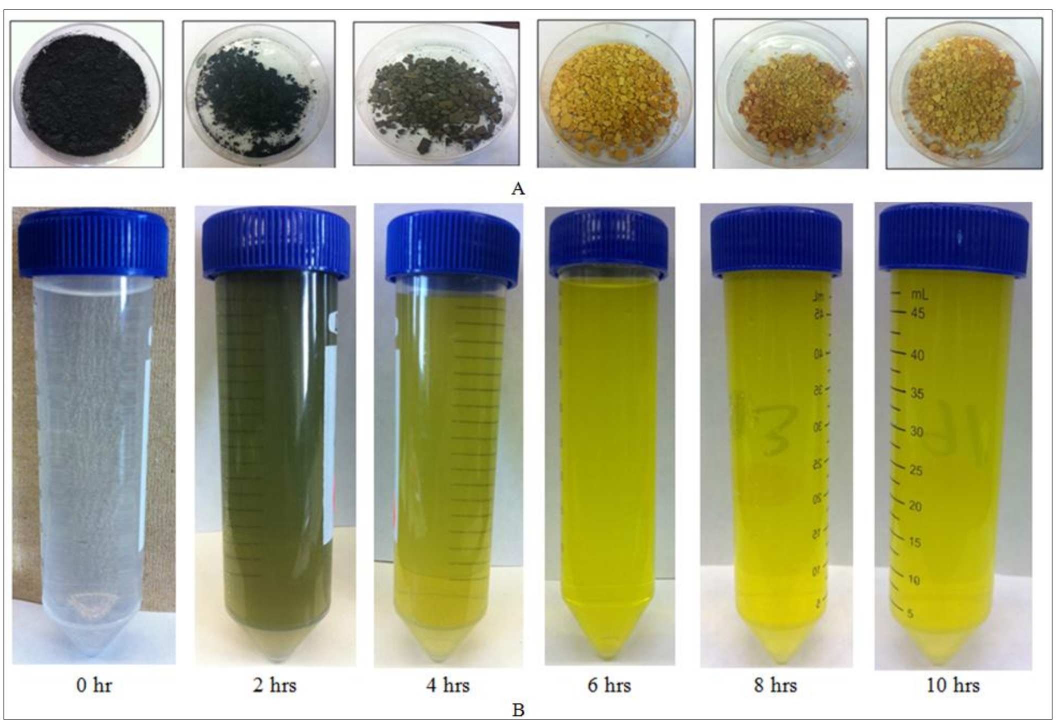

Fig. 6: Chemical reaction of 10 wt% HCl (250 g solution) with 4 g ilmenite at 300˚F, A) change of color of the remaining solid after the reaction, B) change of the solution color with time.

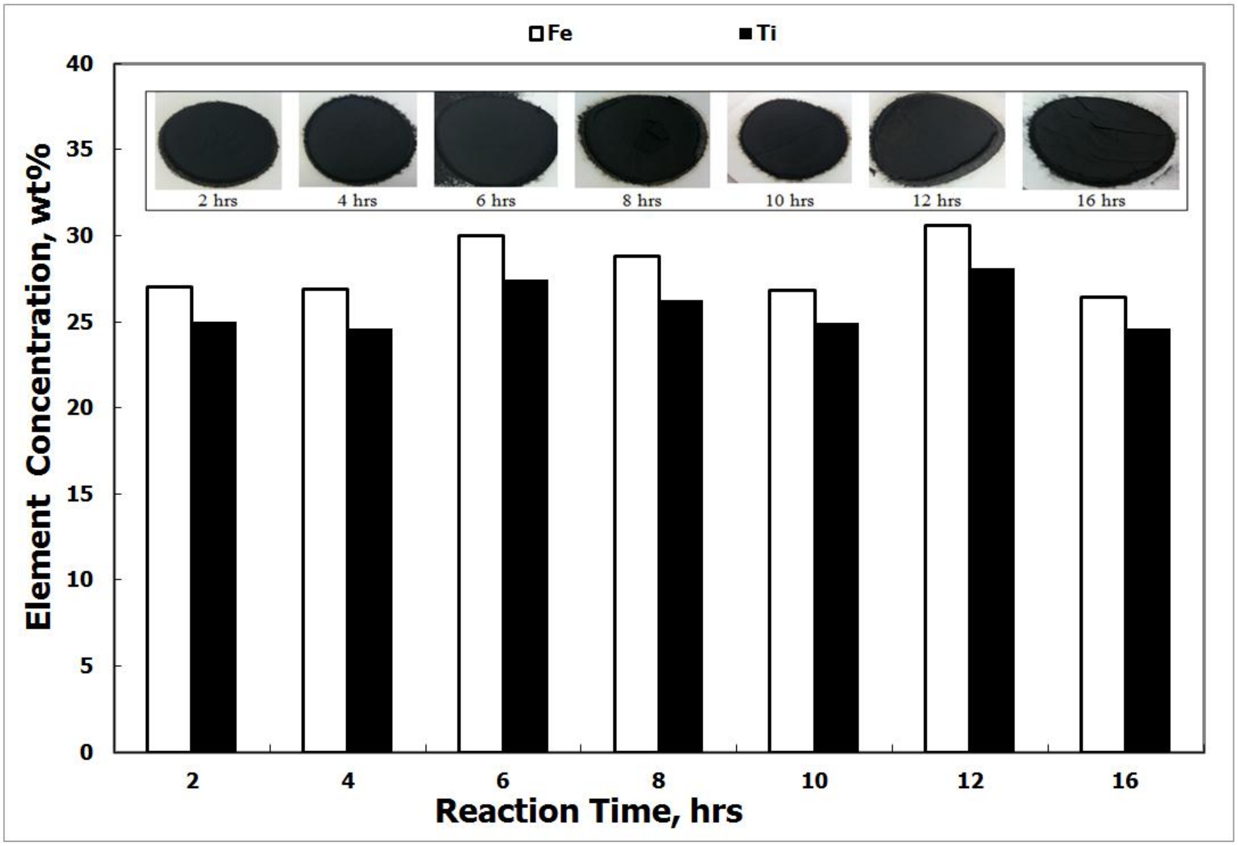

Fig. 7: SEM analysis of the remaining solids after the reaction of HCL with ilmenite.

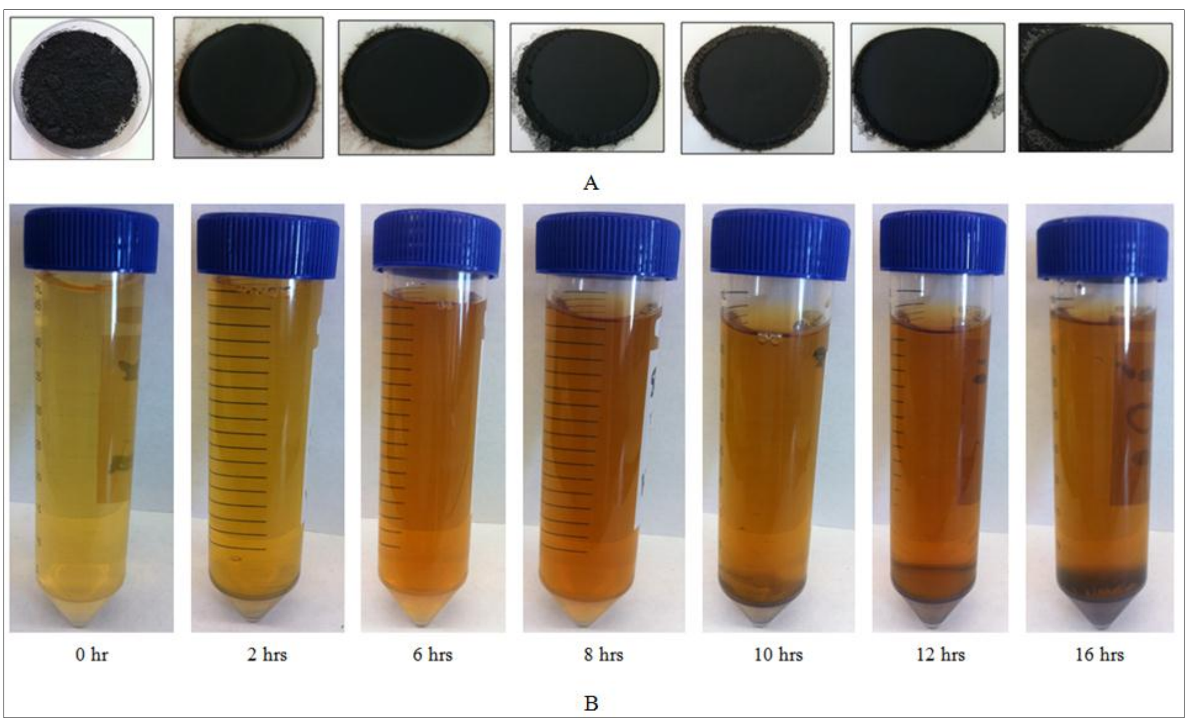

Fig. 8: Chemical Reaction of f 20wt% HEDTA (250 g solution with pH 4) with 4 g ilmenite at 300F, A) Remaining solid after the reaction, B) Filtrated solution after the reaction.

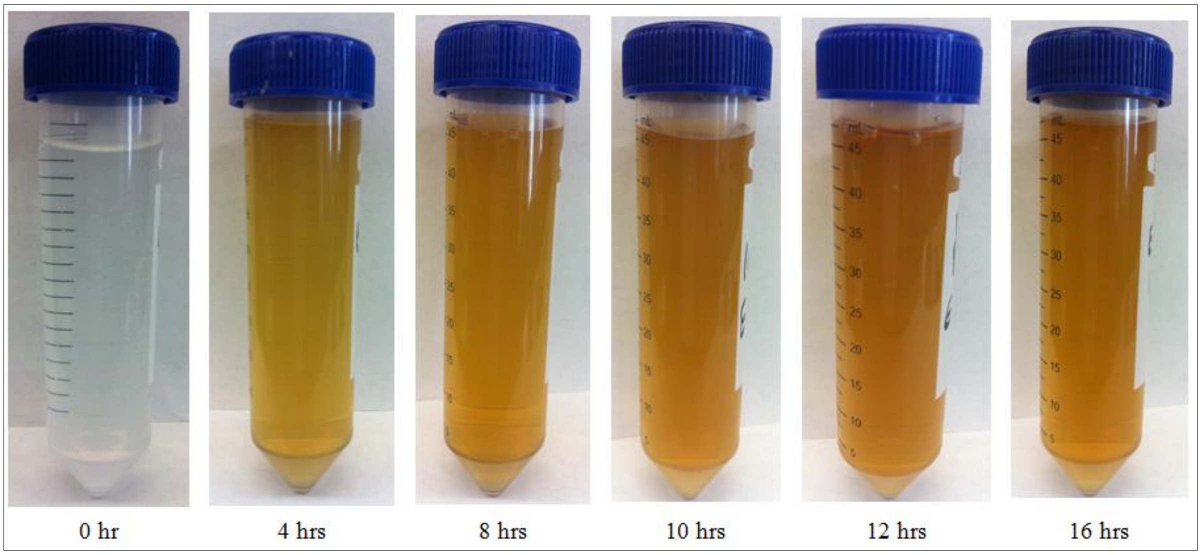

Fig. 9: Chemical Reaction of f 20wt% EDTA (250 g solution with pH 5.88) with 4 g ilmenite at 300˚F.

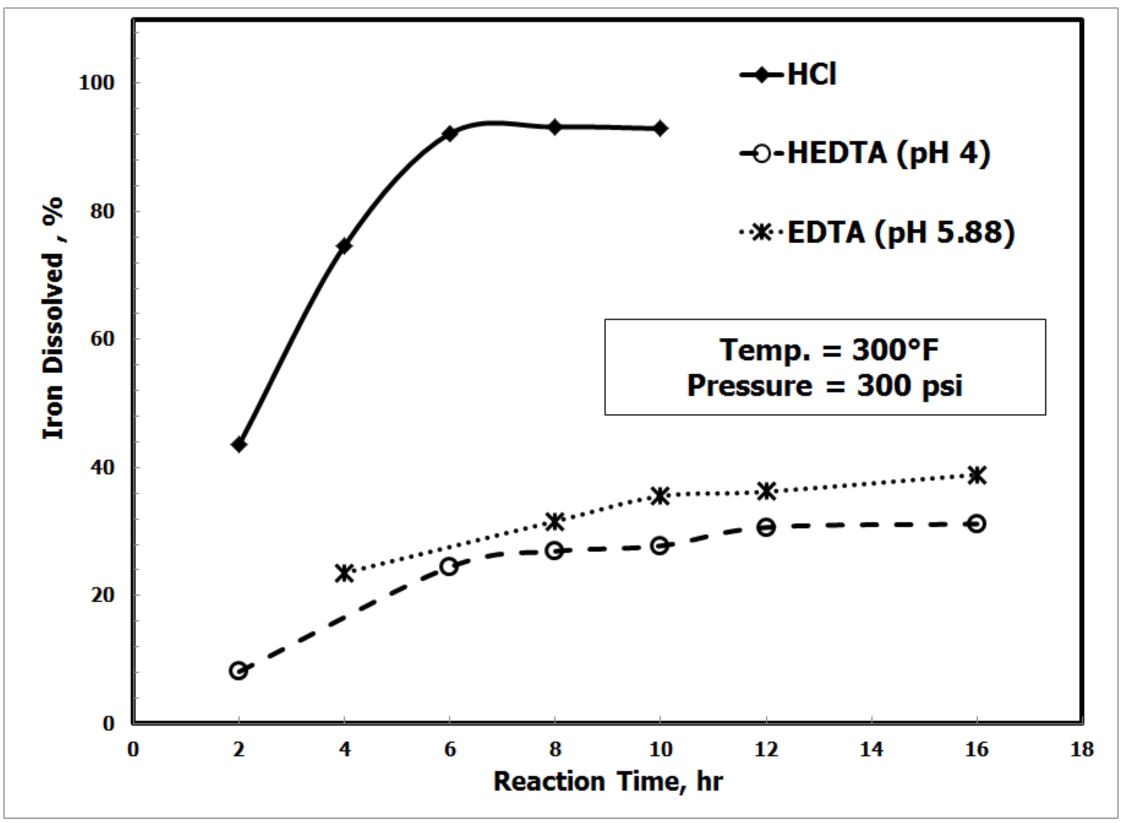

Fig. 10: Iron dissolution after reaction of different acids with ilmenite particles.

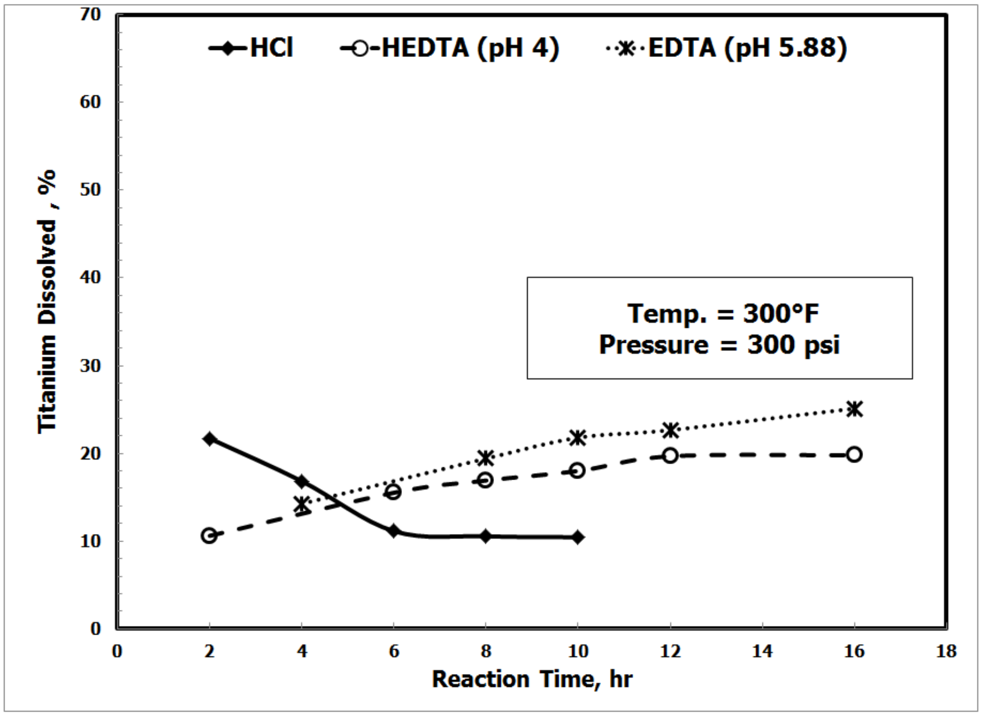

Fig. 11: Titanium dissolution after reaction of different acids with ilmenite particles.

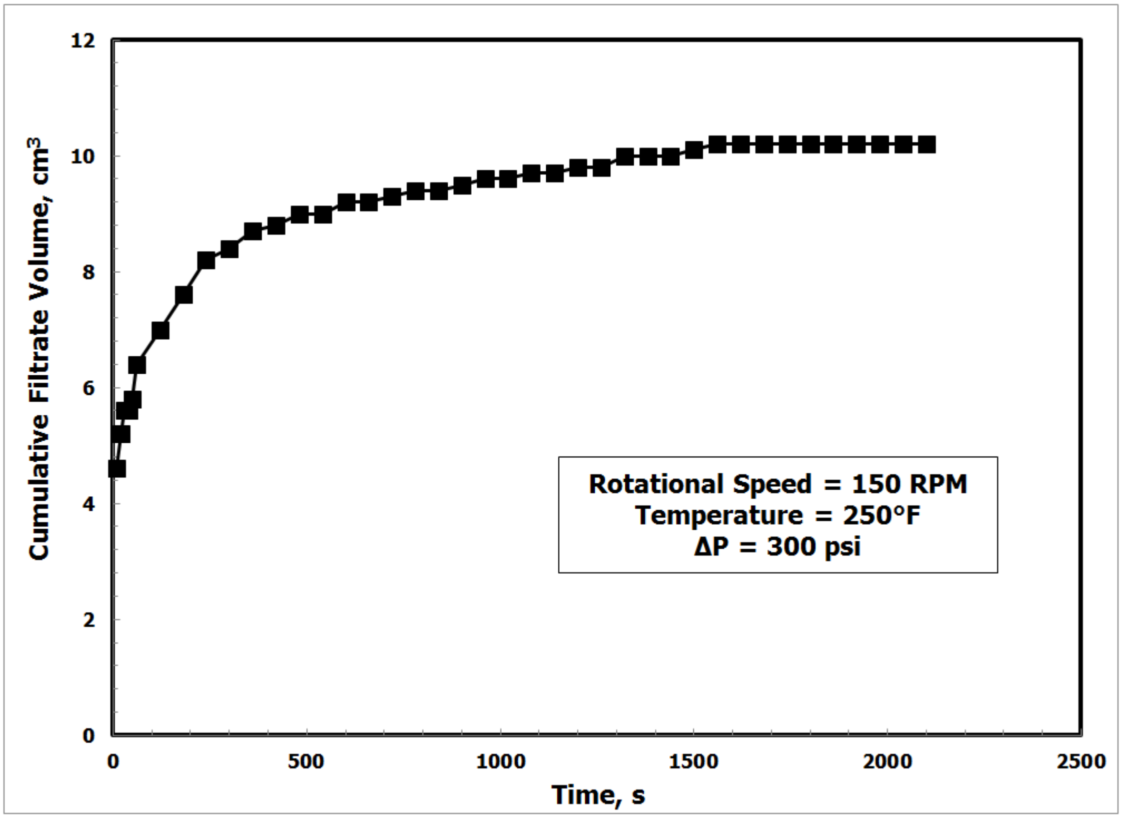

Fig. 12: Cumulative filtrate volume as a function of time under dynamic conditions.

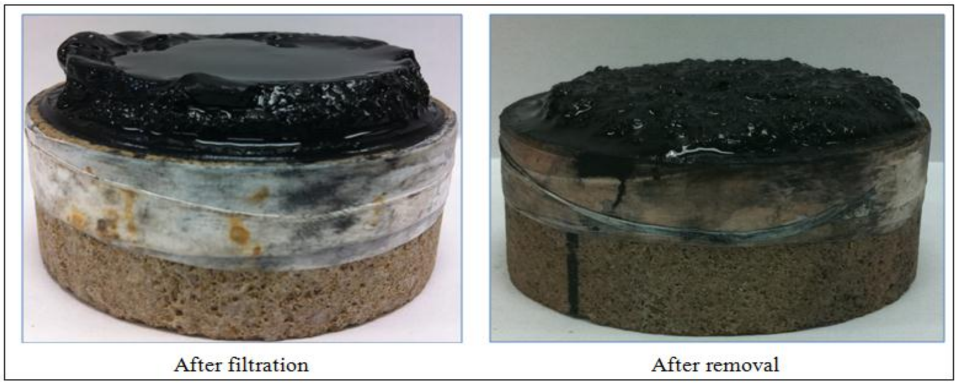

Fig. 13: HEDTA (pH = 4) had a removal efficiency of 48% after soaking 16 hrs at 250˚F.

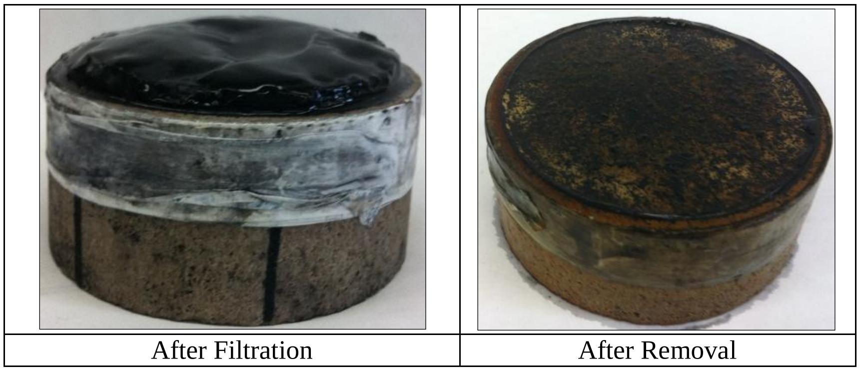

Fig. 14: Complete removal of the filter cake after soaking with 5 wt% HCl for 16 hrs.

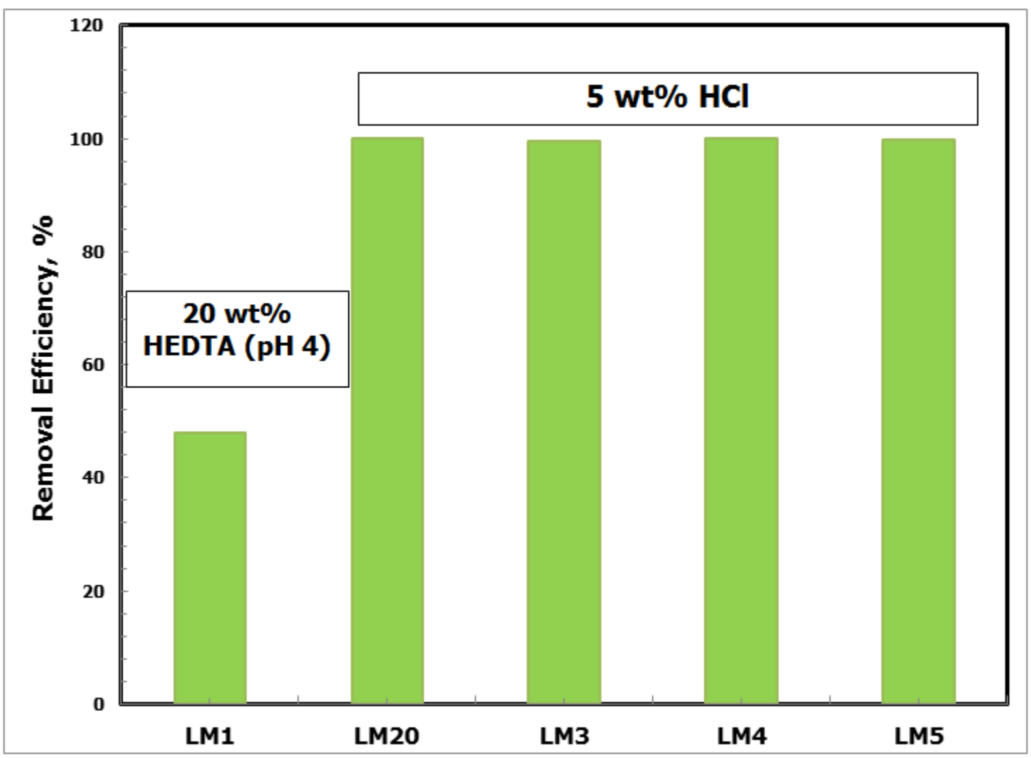

Fig. 15: Complete filter cake removal using 5 wt% HCL after 16 hrs.

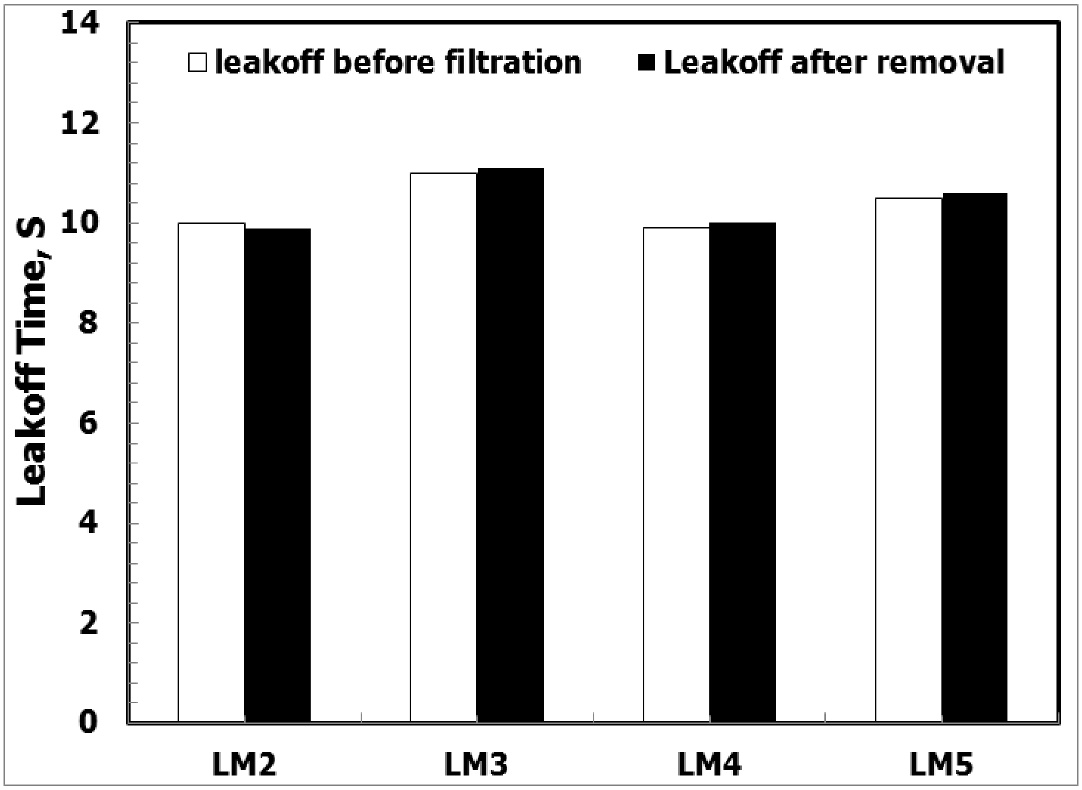

Fig. 16: Retained permeability of 100% using 5 wt% HCl for 16 hrs.