

Dynamic Kinetic Modeling of Manganese Tetroxide (MicroMax) Filter Cake Dissolution under High-Pressure/High-Temperature (HPHT) Conditions

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ABSTRACT

Filter cake clean-up remains a challenging operation in drilling, largely owing to the chemical inertness and low solubility of traditional barite-weighting agents. To address this challenge, we investigated the solubility of MicroMax as a high-density alternative to the traditional weighting agents. The experiments focused on kinetic solubility and static filter cake removal efficiency under High-Pressure/High-Temperature (HPHT) conditions (85 °C and 3.45 MPa). The MicroMax formulation achieved a similar macroscopic filter cake thickness of 3.18 mm, while providing reliable wellbore pressure control, yielding a mud density of 15.0 ppg (at a 300 g dosage) compared with that achieved by barite (13.54 ppg, at a 250 g dosage). A pure MicroMax solubility test was conducted to establish the maximum thermodynamic solubility limit of MicroMax in 20 wt.% EDTA-K plus citric acid solution at 11 g/100 mL. During static HPHT removal testing, the traditional barite cake treated with a DTPA-K-based solution exhibited severe kinetic resistance, plateauing at 25%–30% mass removal after 16 h of exposure. By contrast, the MicroMax/EDTA-K solution (basified with KOH and adjusted to pH 5 using citric acid) removed 12 g out of the initial 24.9 g (48%) after 16 h of exposure, which is equivalent to 84% of the theoretical maximum removal capacity. Finally, this study demonstrated that replacing barite with MicroMax maintains critical drilling fluid properties while fundamentally resolving filter cake removal challenges through highly efficient chelation. Consequently, this MicroMax/EDTA system offers operators a field-ready solution to reduce non-productive rig time and minimize formation damage.

Keywords: drilling fluid, water-based mud, barite, filter cake, MicroMax, solubility, EDTA

1. INTRODUCTION

Efficient hydrocarbon recovery in deep and complex reservoirs relies heavily on maintaining wellbore stability and minimizing formation damage. In this context, The drilling fluid is a crucial contributor to drilling operations, acting as the primary barrier for well control and forming a filter cake to control filtration into the formation. Ultimately, the filter cake should be removed to avoid interference with production and injectivity. However, mud is formulated according to its formation properties. These mud formulations impose various removal challenges for each formation based on the exposure time and treatment formula. Barite has traditionally been used as a standard weighting agent for deep and high-pressure formations.¹ However, barite forms a filter cake that is removed with difficulty because of its chemical structure and cake layer.¹ Therefore, researchers have sought alternative weighting materials such as MicroMax, which provides sufficient pressure control and is easier to dissolve.²

The physical and chemical properties of the drilling fluid components largely determine the filter cake structure. Drilling fluids weighted by fine particles typically result in a highly compact filter cake. Such compacted cakes dissolve with difficulty because of

limited flow through the matrix.³ Barite-weighted mud forms filter cakes that are difficult to remove using standard acids, owing to their chemical nature and insolubility.⁴ Additionally, barite filter cakes exhibit complex layering owing to the separation of heavier particles and lighter polymers; this stratification results in nonuniform chemical reactions with the removal solution.⁴ One proposed solution is the use of a single-stage formulation that combines a high-pH DTPA solution with converting agents and polymer-degrading enzymes for a soaking time of 24 h.⁵ Studies on coordination chemistry have demonstrated that the chelation process can be reversible; therefore, excessively long soaking periods decrease the overall dissolution of barite owing to complex instability, highlighting the necessity of an optimum removal time.⁶ Another critical factor influencing the removal efficiency is the thermodynamic state of the chelating solution, and studies on the fundamental kinetics of DTPA-promoted barite dissolution have demonstrated significantly cleaner removal at elevated temperatures.⁷

Alongside the persistent removal challenge, barite has operational risks of sag and escalating material costs driven by high global consumption.⁸ To address these problems, an alternative

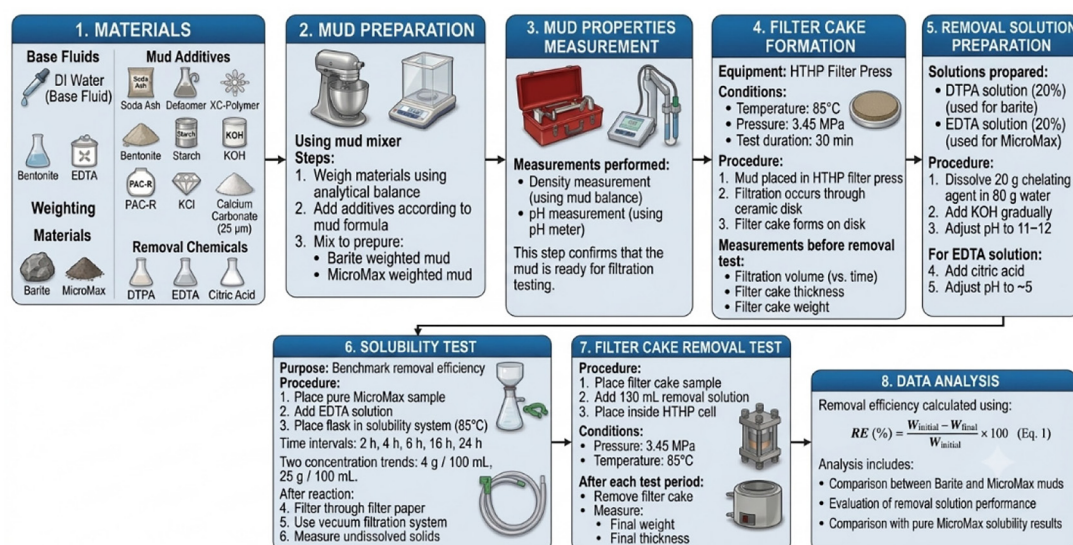


Figure 1. Experimental workflow for filter removal

is MicroMax (manganese tetroxide, Mn_3O_4), which has been introduced in the industry. MicroMax generates thinner and more uniform filter cakes than traditional barite owing to its uniform spherical particle shape and high specific gravity.⁹ Furthermore, conventional chelating agents such as EDTA provide the dual advantage of dissolving solid weighting materials while actively degrading the structural viscosity of the protective polymer networks within the cake matrix. This high solubility makes it an effective candidate for rapid and formation-friendly filter cake removal.^{10,11}

Despite these advantages, previous papers have highlighted the need to optimize the removal efficiency (e.g., pH, concentration, and temperature).^{4,6} However, previous studies have not explicitly evaluated the impact of exposure time as an isolated kinetic parameter for the removal of the MicroMax filter cake. The primary objective of this study was to evaluate filter cake removal efficiency as a strict function of exposure time by analyzing the time-dependent chemical dissolution of MicroMax. To achieve this, static High-Pressure/High-Temperature (HPHT) filtration and solubility tests were conducted to evaluate the dissolution behavior of pure MicroMax and consolidated filter cakes treated with an EDTA-based solution at various time intervals. This study should assist in optimizing exposure time for specific mud formulas and solutions to reduce the nonoperational time with maximum efficiency.

2. METHODOLOGY

Experiments were conducted by beginning with mud preparation and property measurements; thereafter, a filtration test was performed to form a filter cake for placement in the removal system under the specified solution. Additionally, a solubility test was performed on pure MicroMax under similar conditions for comparison with the filter cake. Figure 1 summarizes the workflow of this study.

2.1. Mud Preparation and Filtration. Two distinct water-based muds were prepared using a mud mixer (Fig. 2a),

Table 1 shows the detailed formula for each. The mud density and pH were measured using a mud balance and pH meter (Fig. 2b–c). After the mud property measurements were completed, the mud was subjected to HPHT using a filter press (Fig. 2d). A filter cake was formed on a ceramic disk with a known weight and permeability of 775 mD. The test was performed at 85 °C and 3.45 MPa for 30 min. The test was conducted while measuring the filtration volume at different periods. Final measurements were taken before the removal test; these were the thickness and weight of the filter cake, which are the primary parameters for the removal efficiency calculation.

2.2. Removal Solution Preparation. The removal solutions used were 20% DTPA-K for barite, and 20% EDTA-K plus citric acid for MicroMax. Hereafter, these specific formulations will be denoted as DTPA and EDTA throughout the manuscript, respectively. In a 100 mL solution, 20 g of DTPA/EDTA was dissolved in 80 g of water. Potassium hydroxide was gradually added

Table 1. Formulation for barite and MicroMax weighted water-based mud

Material	Barite	MicroMax
Water(g)	280	245
Soda Ash (g)	1	0.5
Defoamer (g)	0.1	0.1
XC-Polymer (g)	1.25	1.5
Bentonite (g)	-	4
Starch (g)	6	1
Potassium Hydroxide (g)	0.5	0.5
PAC-R (g)	2	1
Potassium Chloride (g)	20	-
Calcium Carbonate (25) (g)	10	5
Calcium Carbonate (50) (g)	10	5
MicroMax (g)	-	300
Barite (g)	250	-

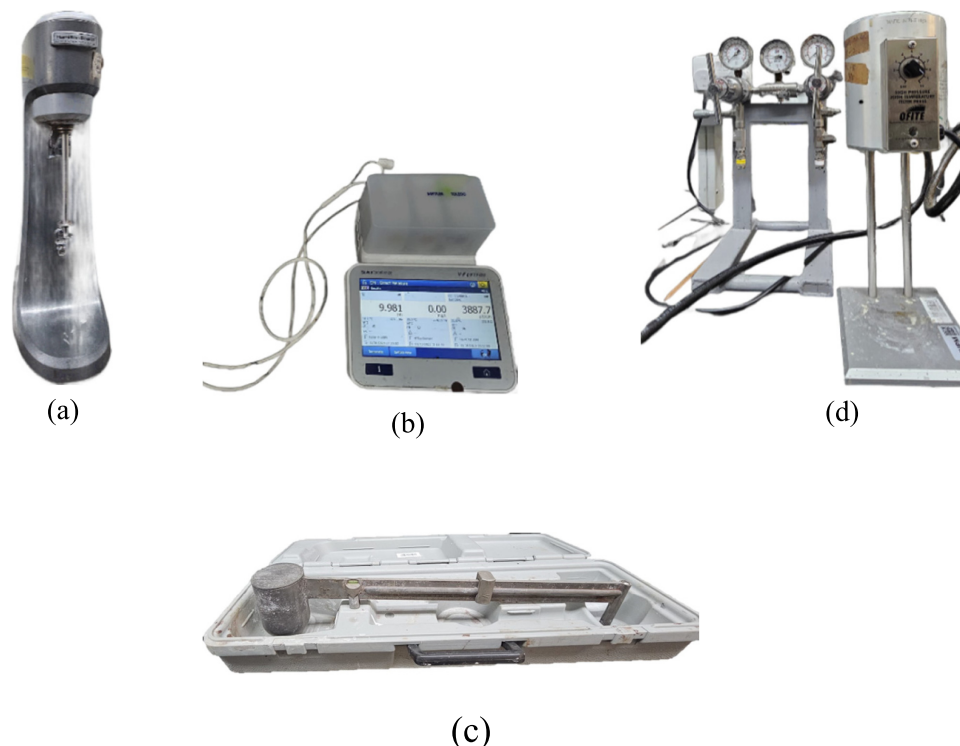


Figure 2. Mud mixer (a), pH meter with an accuracy of ± 0.01 pH units (b), Mud balance (c), HPHT cell with volume of 130 mL (d)

to dissolve the base and increase the pH to 11–12. However, in the EDTA-based solution, an additional step was required after achieving a pH of 12 by adding KOH; citric acid was added until the pH reached 5. This acidic pH and the presence of citric acid were necessary to provide protons (H^+) and a reducing environment to actively break the stable Mn_3O_4 metal-oxide bonds, allowing EDTA to subsequently capture the released manganese ions.¹²

2.3. Solubility. A solubility test was performed on pure MicroMax to act as a benchmark for the removal efficiency. This study utilized two solubility conditions: 4 grams in 100 mL of solution and 25 grams in 100 mL of solution. The pure sample of MicroMax was placed in a flask containing the EDTA solution and subsequently placed in the solubility system (Fig. 3a) at 85 °C for 2, 4, 6, and 16 h for each trend; an extra test of 24 h was used for the second trend. The contents of the flask were then poured onto a filtration paper placed above a vacuum (Fig. 3b) system that removed the solution, leaving behind the nondissolved MicroMax. Finally, Eq. 1 was used to calculate the solubility. The equation is given as

$$RE (\%) = \frac{W_{initial} - W_{final}}{W_{initial}} \times 100. \quad (1)$$

2.4. Filter Cake Removal. Following the preparation of the filter cake and solution, the sample was placed in an HPHT cell (Fig. 2d), and 130 mL of solution was added. The mixture was pressurized to 3.45 MPa and heated to 85 °C. After each period, the filter cake was carefully removed from the HPHT filter press for a final efficiency check. thickness and weight of the removed filter cake were measured a final time and compared

with their values before the removal test; Eq. (1) was used to determine the removal efficiency.

2.5. Experimental Uncertainty and Limitations. To mitigate experimental uncertainty, all the instruments were rigorously cleaned and calibrated before testing. Specifically, a highly calibrated analytical balance with a precision of ± 0.01 g was used, ensuring the removal efficiency calculations remained highly accurate and consistent. Furthermore, HPHT test conditions were thermodynamically stabilized, maintaining parameters within ± 5 °C for temperature and ± 10 psi for differential pressure throughout the extended soaking periods. Owing to the operational constraints of the extended HPHT testing, each kinetic interval was evaluated through a single iteration; consequently, a statistical standard deviation across multiple identical runs could not be derived. Therefore, the main limitation of this kinetic study was the absence of a second or third iteration for each test. Although this reliance on single-iteration data points is a limitation of the study, the results showed a logical and consistent mathematical trend for each test, validating the accuracy of the kinetic study.

3. RESULTS AND DISCUSSION

3.1. Initial Properties of Mud and Filter Cake. Table 2 summarizes the initial properties of each type of mud and the resulting filter cake before chemical treatment. Both muds exhibited a similar alkaline pH. Additionally, based on the specific formulation concentrations outlined in Table 1, the MicroMax mud had a density of 15.0 ppg, while the barite mud had a density of 13.54 ppg. When the two muds were filtered through the ceramic disk during the 30-minute HPHT test (Fig. 4), different fluid loss behaviors were observed; however, filter cakes with

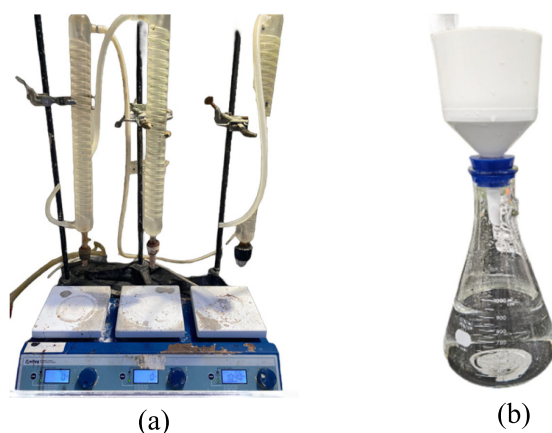


Figure 3. Solubility system (a), filtration system using filtration paper, and vacuum (b)

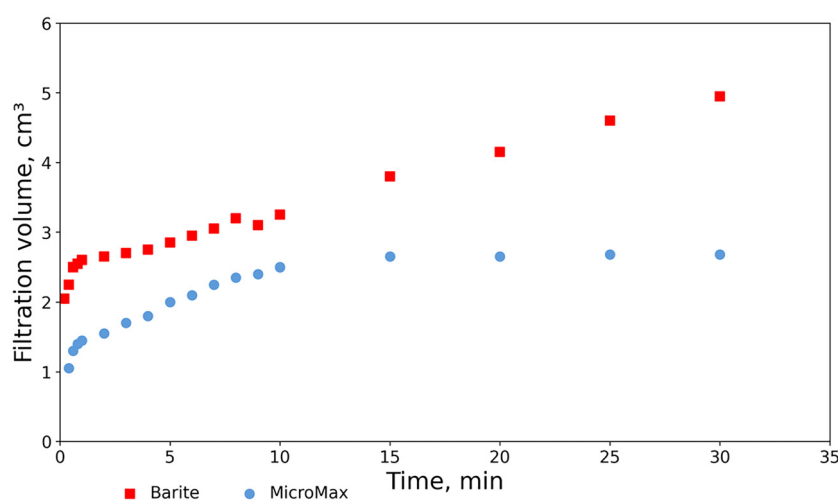


Figure 4. Initial fluid loss behaviors of both mud formulations during the 30-minute HPHT test before chemical treatment

identical final thicknesses (3.18 mm) were deposited. The sample filter cakes for each base are shown in Fig. 5. The MicroMax filter cake exhibited a rougher and less uniform surface morphology than the highly compacted barite cake. This nonuniformity provides a larger initial contact surface area for the treating fluid, which is physically advantageous for initiating rapid early-stage chemical dissolution.

3.2. Solubility of Pure MicroMax. Solubility tests were conducted on pure MicroMax to establish a kinetic baseline in a 20 wt.% EDTA-based solution, independent of the physical matrix effects present in a consolidated filter cake. The test was conducted using two distinct concentration trends at 85 °C to evaluate different dissolution rates: a low-concentration trend (4 g/100 mL) was designed to assess the unhindered reaction kinetics when the chelating agent was in excess, and a high-concentration trend (25 g/100 mL) was designed to oversaturate

the solution to establish its absolute maximum thermodynamic solubility limit.

A low-concentration trend was conducted at 2, 4, 6, and 16 h, demonstrating rapid and highly efficient chelation kinetics. The solution dissolved 93.35% of MicroMax within the first two hours, maintaining a consistent dissolved mass of approximately 3.7–4.0 g/100 mL across all periods. However, the higher concentration trend dissolved only 8.42–8.74 g within the first 4 h at 33.63% dissolution; after the 16-hour test, the solubility range increased markedly to 10.61–11 g/100 at 44% dissolution.

As the low-concentration sample achieved nearly 100% dissolution, the maximum solubility limit could not be determined from this test, suggesting that the solution retained its additional capacity. However, the higher concentration trend achieved only 44% dissolution, thereby enabling the determination of the final solubility. As shown in Figure 6, 44% dissolution is equivalent to 11 g/100 mL, establishing the maximum thermodynamic solubility limit of pure MicroMax in a 20% EDTA-based solution under these specific conditions.

3.3. HPHT Filter Cake Removal Efficiency. Although the pure MicroMax solubility provides a baseline for comparison, the final efficiency is dictated by how the chelating agent interacts

Table 2. Initial properties of mud and filter cake before removal

Property	Density (ppg)	pH	Filter cake thickness (mm)	Filter cake weight (g)
Barite	13.54	11.29	3.18	19.9
MicroMax	15	11.1	3.18	24.9



Figure 5. Sample filter cakes before removal: barite filter cake (a) and MicroMax filter cake (b)

with a dense, consolidated filter cake under reservoir conditions. The final results showed that the MicroMax/EDTA system was easier to clean than the barite/DTPA system (Fig. 7).

The barite filter cake weighed 19.9 g and was immersed in 130 mL of a 20% DTPA-based solution at 85 °C and 3.45 MPa. The barite filter cake exhibited strong kinetic resistance to the DTPA chelating agent during the early stages of exposure, between 1 and 4 h, resulting in a removal of less than 2 g (9%) of the filter cake. This less-than-optimal result at low exposure times highlights the nature of the barium sulfate cake, which exhibits a low-permeability consolidated matrix that prevents solution permeation.⁵ Meaningful removal efficiency from the barite filter cake was observed after 6 h, with approximately 4 g of material dissolved (20%), and it showed a plateau again at 10–16 h with a maximum of 5–6 g (25%–30%) of the material being removed.

The MicroMax filter cake weighed 24.9 g and was subjected to identical physical conditions using a 20% EDTA solution. However, significantly better removal from the filter cake was observed in the first 6 h, with 4.3 g of material removed (17.3%). The largest removal of the material was observed at 16 h (12 g, 48%), significantly exceeding that of barite. Additionally, the pure MicroMax solubility test demonstrated that the maximum solubility of MicroMax in EDTA was 11 g/100 mL. When scaled to the 130 mL fluid volume used in the HPHT cell, this limit translates to a theoretical maximum removal value of 14.3 g. Therefore, achieving a 12 g removal from the filter cake represents 84% of the theoretical maximum predicted under these test conditions.

A possible explanation for the contrast in removal efficiency can be given by the different mass transfer mechanisms. The

severe kinetic resistance of barite is likely due to its highly consolidated matrix, which results in a diffusion-limited process in which the mass-transfer resistance prevents deeper fluid penetration, leading to the observed plateau.¹³ Conversely, the experimental results of this study suggest that the MicroMax dissolution is not restricted by the same diffusion limits. Because the macroscopic cake thickness remained constant (3.18 mm) throughout the HPHT testing, we hypothesized that the continuous chelation of manganese ions by EDTA creates a progressive internal porosity enhancement. This dynamically generated porosity allows the unreacted EDTA to continuously diffuse deeper into the matrix until it reaches the established thermodynamic saturation limit (11 g/100 mL).

Figure 8 shows samples of the two filter cakes after their removal. As a secondary measurement, the thickness was observed to be constant before and after removal at 3.18 mm for all samples. This proves that EDTA uniformly dissolved the internal matrix of the cake and increased its porosity without causing the immediate collapse of the macroscopic structure. This confirms that the MicroMax/EDTA system provides superior clean-up performance at all exposure times and approaches near-perfect theoretical removal after 16 h.

3.4. Kinetic Modeling of MicroMax Dissolution.

Finally, to quantify the removal percentage of the MicroMax system at any given time, the data were fitted to a pseudo-first-order kinetic dissolution model. The reaction kinetics of dissolution can be described by the following expression (Eq. 2):¹⁴

$$RE(t) = RE_{max} \times (1 - e^{-kt}), \quad (2)$$

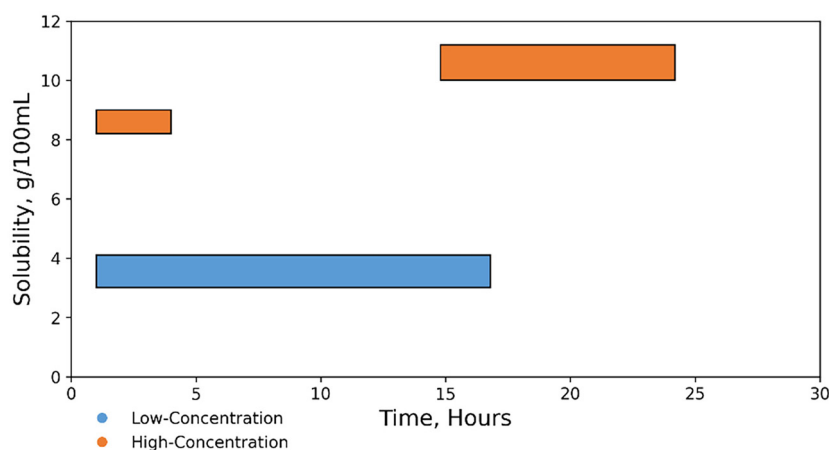


Figure 6. Dissolution trends of pure MicroMax in 20 wt.% EDTA chelating agent: low-concentration trend is 4 g in 100 mL, and high-concentration trend is 25 g in 100 mL

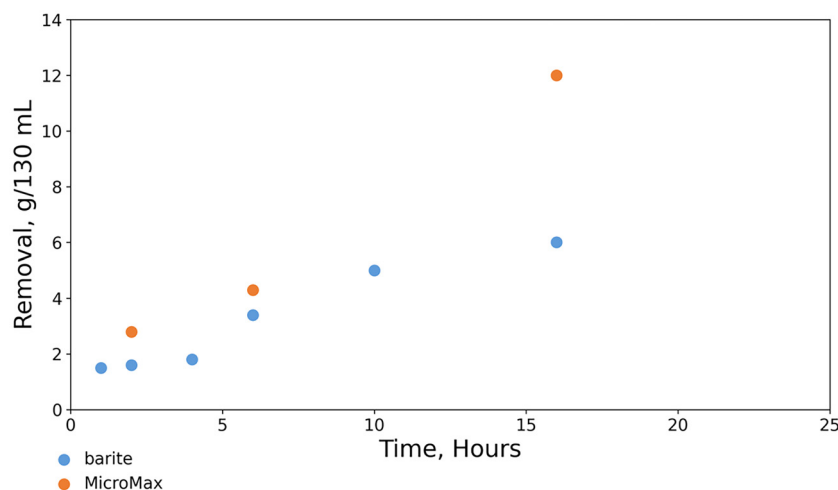


Figure 7. Comparison of mass removal for a 24.9 g MicroMax filter cake in 130 mL of 20 wt.% EDTA chelating agent and 19.9 g barite filter cake in 130 mL of 20 wt.% DTPA chelating agent

where RE is the removal efficiency at any exposure time t , k is the pseudo-first-order reaction rate constant h^{-1} , and $RE_{\max}$ is the absolute theoretical maximum removal efficiency derived from the solubility test. The results of the solubility test supported the prediction that 14.3 g is the maximum solubility in 130 mL of 20 wt.% EDTA. As the initial filter cake weight was 24.9 g, $RE_{\max}$ was calculated as 57.43%. Thus, the final kinetic model was reduced to Equation 3, given as:

$$RE(t) = 57.43\% \times (1 - e^{-0.11t}). \quad (3)$$

Figure 9 illustrates that the application of the kinetic model reveals a strong correlation at the early-stage (2-hour) and late-stage (16-hour) operational marks. However, the experimental data indicate that the intermediate 6-hour interval deviates slightly from the theoretical prediction. Because the model was formulated by combining the pure MicroMax theoretical limit and removal data, the effects of other mud additives were not fully considered. This slight deviation can be attributed to the presence of specific mud additives within the filter cake matrix, namely viscosifying polymers (such as starch, XC-polymer, and



Figure 8. Filter cake after removal, Barite filter cake (a), MicroMax filter cake (b)

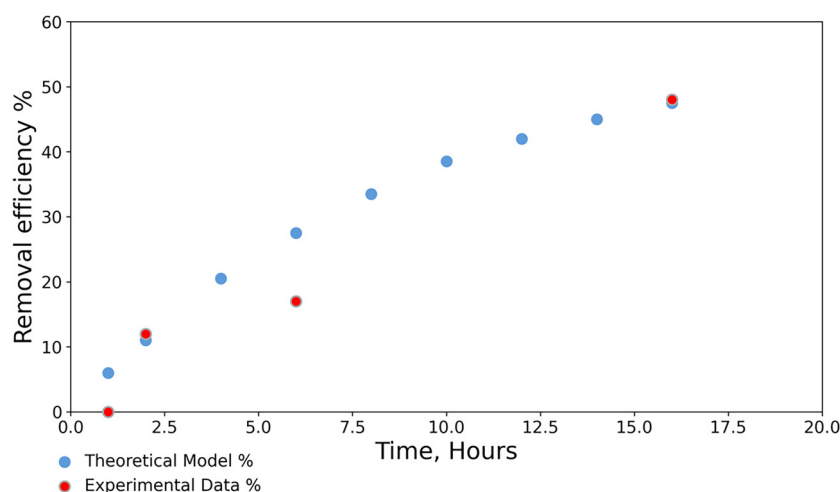


Figure 9. Comparative analysis of the kinetic model and the real experimental results using Pseudo-first-order kinetic modeling of MicroMax dissolution in 20 wt.% EDTA

PAC-R) and fine particulates (such as bentonite and calcium carbonate). A temporary decrease in the reaction rate occurred when the percolating chelating agent encountered the tightly compacted layers of polymers and fine particles, which physically shielded the underlying MicroMax. Once the treatment agent dissolves the polymers and porosity enhancement begins, the experimental observations realign with the theoretical model as EDTA interacts with MicroMax directly.

Although these results confirm the superior solubility of manganese tetroxide in chelating agents compared to barite,¹⁵ this study is limited to static conditions. Future work must utilize dynamic core-flooding to evaluate return permeability under active wellbore shear rates.

4. CONCLUSIONS

In this study, we experimentally evaluated the application of manganese tetroxide (MicroMax) as an alternative weighting agent to traditional barite. The experiments specifically measured the removal efficiencies of both materials under HPHT conditions. The experimental findings are summarized below:

- Both the MicroMax and traditional barite formulations deposited filter cakes with an identical macroscopic thickness of 3.18 mm and exhibited similar alkaline stabilities (pH ~11.1). Based on their specific formulation dosages, the MicroMax mud (300 g) had a density of 15.0 ppg, while the barite mud (250 g) had a density of 13.54 ppg.
- A solubility test on pure MicroMax in 20 wt.% EDTA-based solution at 85 °C gives a theoretical solubility limit of 11 g/100 mL. This baseline provides a predictive metric for the chemical volume calculations.
- The MicroMax filter cake treated with 20 wt.% EDTA achieved up to 48% removal at 16 h.
- The solubility test metric scale was used to calculate the maximum removal of the filter cake in a 130 mL volume cell. The theoretical maximum removal is 14.3 g. This indicates that the MicroMax filter cake successfully reached 84% of the theoretical maximum.
- The MicroMax/EDTA system correlates with a pseudo-first-order kinetic model as it can reach a maximum solubility of 57.43% before reaching the diffusion limit.
- The thickness of the filter cake was constant at 3.18 mm even after 16 h, indicating the potential uniform dissolution of the filter cake matrix.

This study proves that using MicroMax provides similar wellbore control to barite but significantly simplifies clean-up. The results showed reasonable agreement with existing literature on the superior solubility of manganese-based agents. The outcomes of this study contribute to the growing body of research focused on optimizing nondamaging filter cake removal in complex wellbores. Using our kinetic model, engineers can predict optimal soaking times to reduce rig expenditure. Finally, due to our static testing limitations, future work may include evaluating this system under dynamic core-flooding conditions to assess true return permeability.

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