Developing Innovative Bio-Nano Catalysts Well Clean Up Fluid to Remove Formation Damage by Polymeric Water-Based Drilling Fluids

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Abstract

Drilling and completion fluids may cause significant formation damage in oil and gas reservoirs, directly affecting productivity. For many years, operators have applied different stimulation practices such as acidizing, oxidizers, chelating agents, and enzyme treatment to remove formation damage associated with drilling fluids filter cake. An enzyme-based biological treatment was combined with other chemicals or additives as a selective well clean-up practice to improve removing polymer content in the filter cake. However, the secondary

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formation damage such as deep cleaning of the invaded zone and wettability alteration remained the main concern.

This paper presents the development of an innovative clean-up fluid formulation by immobilizing an enzyme and a selective nanoparticle as Bio-Nano Well Clean Up Fluid (BNWC) in potassium chloride brine to enhance WBM filter cake removal. Several bulk experiments, including; precipitation, iodine test, and viscosity measurement, demonstrate the enzyme's optimization, the nanoparticle concentration, and base fluid brine. BNWC in potassium chloride brine showed the highest HPHT filtration rate at 200 ^{0}F and differential pressure of 100 psi and increased the filtration rate by more than 90 percent compared to the conventional enzyme in the same brine. Contact angle measurements confirmed wettability alteration of the carbonate rock to water wet, and IFT measurements showed higher oil mobility potential. Finally, core flooding tests at reservoir conditions showed a 300 percent enhancement in injection rate and a 50% improvement in core permeability after damage.

The immobilization of the enzyme with the nanoparticle has been developed successfully for other applications in bioremediation, farming, and other industries, but the novelty of this research demonstrates the application of nanobiocatalysts in drilling fluids for the first time. This innovative clean-up fluid enhances the enzymatic activity and removes primary and secondary formation damage associated with drilling fluid filter cake.

Keywords: Well clean-up, Production Enhancement, filter cake breaker, Formation damage, nanobiocatalyst

List of Abbreviations

WBM: Water Based Mud

OBM: Oil Based Mud

HPHT: High Pressure and High Temperature

SEM: Scanning Electron Microscopy

XRD: X-ray diffraction

FTIR: Fourier Transform Infrared Spectroscopy

PSD: Particle Size Distribution

EDTA: Ethylene Diamine Tetraacetic Acid

HEDTA: Hydroxy Ethylene Diamine Tetraacetic Acid

DTPA: Diethylene Triamine Penta Acetate

NTA: Nitrilo Triacetic Acid

PAC: Poly Anionic Cellulose

EOR: Enhanced Oil Recovery

1. Introduction

Filter cakes generated by drilling fluids can impede porous media permeability and reduce well productivity (Hodge et al., 1997). The filter cake is generally heterogeneous and contains two layers. The layer close to the rock has weighting agent materials, and the other side is close to fluid flow with polymers. This layer prevents a proper reaction between acid or solvent with solids (Elkatatny et al., 2012). Uniform dissolution of the filter cake requires a delayed reaction breaker fluid at the laboratory scale by optimizing concentration, determining the appropriate carrying fluid, and addressing environmental and corrosion concerns (Natalia Collins et al., 2011).

1.1. WBM Filter Cake Removal with Conventional Practices

Acidizing and Oxidizing agents such as ammonium persulfate, lithium hypochlorite, sodium chlorite, and hydrogen peroxide are regularly used in the well clean-up process. They are not specific nor controllable and can react with downhole, formation, and reservoir fluid components. They can produce wormholes and divert the reactive solution. Also, acids and oxidizers may react with the tubular, which results in iron precipitation and injection into the reservoir, which can plug the porous media. It does not affect the non-polymeric part of filter cake and solids. Therefore, a two-stage treatment is recommended to inject enzyme-based well clean-up before acidizing (B. Beall et al., 1996). Hodge et al. stated that oxidizers were ineffective in removing polymer damage, especially in horizontal wells (Hodge et al., 1997). Brannon and Tjon concluded that acids and oxidizers attacked any active sites on polymer strands, and they did not react with the polymer backbone. They left partially degraded and untreated polymer strands (Brannon, 1994).

Chelating agents such as EDTA, HEDTA, DTPA, and NTA are common alternatives to acid-based systems, but there are environmental and safety issues regarding this application. EDTA and HEDTA are safe but not biodegradable. NTA is biodegradable, but it has a potential hazard to humans. Metal chelating agents have been used as iron control agents in acidizing treatments with low solubility and high toxicity. The experimental results show loss of solubility of calcium complexes and thermal decomposition of ferrous complexes at low temperatures (Collins et al., 2011).

GLDA and HEDTA were not compatible with alpha-nominated solutions over a wide range of pH and temperature (Elkatatny et al., 2012). By increasing the sulfate and calcium ion concentrations, inorganic scale precipitation rose, and formation damage occurred (Ghasemian et al., 2019). Incompatibility of injected water and reservoir water can cause mineral scale. A particular scale inhibitor was observed to reduce mineral precipitation (Mohammadi et al., 2020). In this research paper, we further investigate the application of nanotechnology to reduce fines migration by decreasing zeta potential, changing the total energy interaction between surfaces, pH, and particle roughness (Madadizadeh et al. 2020).

1.2. WBM Filter Cake Removal with Biological Practices

Water-based drilling or drill-in-fluids typically contains starch, cellulose, and xanthan gam-based polymers with solids such as barite, calcium carbonate, and salts, building a filter cake to minimize invasion into the formation. Burnet et al. mentioned that polymers might coat calcium carbonate particles and act as a barrier that minimizes acid contact with the filter cake (Burnett 1995). Conventionally, clean-up fluids remove filter cake residue by displacing enzyme-based well clean-up fluid in the open hole section (Price-Smith et al., 1996). Enzymes are proteins produced by living organisms' cells, which act as a catalyst to promote specific reactions. They have particular limitations regarding chemical, thermal or mechanical conditions. This method mitigates diversion and corrosion problems but designing specific-enzyme-based well clean-up is not easy compared to other well clean-up practices (Beall et al., 1996). It was observed that wellbore soaking treatment using a particular enzyme improved productivity (Navarrete et al., 2000). Experiments on specific polymer linkage enzymes to break the filter cake showed good efficiency on filter cake clean-up in completion and workover operation (Moore et al., 1996). Without using any acid, biological treatment and oxidizers demonstrated filter cake removal in a clean formation in stand-alone pre-packed screen, slotted-liner completion in the North Sea (Price-Smith et al., 1998). Non-specific enzymes randomly hydrolyze the polymers, producing insoluble crosslink chains and causing permeability damage (Luyster et al., 2000).

1.3. Biological Treatment Performance Enhancement

Different additives improved biological activity specifically for enzyme-based well clean-up fluids. A surfactant-based carrier fluid in a breaker solution containing acid, enzyme, and a chelating agent was used to ensure full contact with filter cake during gravel packing. The results showed that slow reaction and low corrosion rate were advantageous (Parlar et al., 1998). Filter cake removal fluids that contained 5% enzyme, 3% acetic acid, and 1% surfactant showed the highest cleaning performance (Bisweswar Ghosh et al., 2019). A non-damaging fluid for a depleted high-temperature reservoir assessed the productivity by using a chelant/enzyme breaker fluid in an onshore field in Brazil based on potassium chloride brine, calcium carbonate bridging agent, and temperature stabilizer for temperature above 240 ^{0}F. This drill-in-fluid and breaker did not show significant permeability reduction on the Berea sandstone core (Belizário et al., 2019).

Although practical investigations and recent advancements in applying enzymes with other chemicals and solvents to improve breaking water-based drilling fluid filter cake have been reported (Al-Otaibi et al., 2004, Elkatany et al., 2012 and 2017), limited investigations have been done for deep cleaning and removing associated formation damage. It must be mentioned that removing selective polymer in filter cake was discussed in the literature without considering secondary formation damage due to drilling fluid filtration. Also, the authors did not find any reported investigations into the application of nanoparticles in conjunction with an enzyme for the well clean-up practice. Immobilization of enzymes with nanoparticles (nanobiocatalysts) has been introduced in environmental remediation, biosensing, biomedicine, and industrial biocatalysis (Kim, J. et al. 2008). Nanobiocatalysts have shown improved fluid stability, recyclability, and reusability than free enzymes (Jing An et al., 2020). Nanomaterials offer unique advantages such as a large surface area, increased mechanical strength, effective enzyme loading, and high catalytic efficiency (Gahlout, M. et al. 2017). Also, nanostructured supports reduces mass transfer limitation, ease of surface modifications, unique geometry, and size/shape-dependent characteristics (Jing An et al., 2020). The activity enhancement is obtained by immobilization mechanisms usually associated with the alterations in the enzyme structure. Favorable interaction between the enzyme and the nanostructured support is categorized into the following mechanisms; ion activation, morphological, temperature effect, enhanced electron transfer conformational modulation. The morphology of nanoscale supports significantly impacts enzyme activities and bio-nano catalysts' stability (Kunduru, K. R. et al. 2017). Recently, enzyme activity enhancement by enzyme-nanostructured biocatalysts (nanobiocatalysts) was reviewed by An, J. et al. (2020), demonstrating recent advancement in the development of novel nanobiocatalysts with activity enhancement mechanisms, including metal ion activation, electron transfer, morphology effects, mass transfer limitations, and conformation changes (An, J. et al. 2020).

This paper presents an innovative clean-up fluid formulation to enhance enzyme-based treatment by immobilizing an enzyme and a selective nanoparticle in different completion brines. Bulk experiments were carried out to optimize the concentration of the enzyme and nanoparticle to reduce precipitation, foam generation, pH range, and improve temperature stability in different brines. HPHT filtration tests were performed to select proper base fluid for well clean-up fluid. Finally, a Bio-Nano Well Clean-up fluid (BNCW) formulation was formulated by immobilizing a nominated enzyme and a nanoparticle in potassium chloride brine. Contact angle and IFT measurements were performed on carbonate rock, and injection performance was evaluated by core flooding apparatus. The immobilization of the enzyme and the nanoparticle is the novelty of this innovative well clean-up practice in the drilling and production industry developed for the first time.

2. Experiment & Methods

2.1. Material

This experimental material includes Starch, ENZ-A, an industrial enzyme from a local supplier, Polymeric water-based drilling fluids, Colloidal nanoparticle, Sodium, Potassium, and Calcium Chloride brine prepared following the API 13I standard (API 13I, 2009). The IODIN test determined ENZ-A enzyme performance to confirm the enzymatic activity. The FTIR test confirmed the material structure of both drilling starch and enzyme. Additives and polymers were used based on API 13I specifications to mix polymeric WBM in Table 1 using a Hamilton beach mixer model HMD200. Colloidal nanoparticle solution was prepared at the concentration of 15% W/V by dispersing a selective nanoparticle in a surfactant solution by the ultrasonic device. Well clean-up fluids formulations were formulated by mixing ENZ-A 1% V/V (WELL-CLEAN I) in water (Table 2) and immobilizing ENZ-A with colloidal nanoparticle solution (WELL-CELAN II) in Table 3. The polydispersity of the material was evaluated by measuring the particle size distribution test.

Table 1

Polymeric Water-Based Drilling Fluid Formulation

Material Name	Function	Concentration
Water	Based Fluid	78% V/V
NaCl Salt	Weighting Agent	8% W/V
KCl Salt	Weighting Agent	7% W/V
Soda Ash	Hardness Controller < 400 ppm	0.5 ppb
Caustic Soda	pH Controller: Adjust to 9.5	0.25 ppb
Drilling Starch	Fluid Loss Controller	8.0 ppb
Poly Anionic Cellulose Low Viscosity	Fluid Loss Controller	1.5 ppb
Xanthan Gum	Viscosifier	0.5 ppb
Calcium Carbonate 50 mic	Weighting and Bridging Agent	Adjust mud weight to 1.3 SG

Table 2

WELL-CLEAN I: Enzyme Based Well Clean Up Fluid Formulation

Material Name	Function	Concentration (%W/V)
Water	Base Fluid	99
ENZ-A Enzyme	Polymer Degradation	1

Table 3

WELL-CLEAN II: Immobilized Enzyme and Nanoparticle-Based Well Clean Up Fluid Formulation

Material Name	Function	Concentration (%V/V)
Water	Base Fluid	
WELL-CLEAN I (ENZ-A Enzyme Solution 1%W/V)	Polymer Degradation	0.1
Colloidal Nanoparticle Solution (15% W/V)	Enzymatic Catalyst &Wettability alteration	0.1

2.2. Experimental Design and Methods

In this study, experiments consist of four main steps; material analysis and verification, bulk test, rheology studies, and HPHT filtration evaluation.

2.2.1. Material Analysis

FTIR spectra of the amylose starch and the sample structures confirmed the specifications, which have been described in Appendix.

2.2.2. Bulk Test Experiment

Series of bulk tests were carried out, including visual tests (foam generation and precipitation), pH effects, Iodine test, temperature stability, and viscosity measurement. Viscosities were measured by an OFITE dial viscometer 8-speed with +/- 1% measurement uncertainty. This viscometer has an R1 Rotor Sleeve, B1 Bob, F1 Torsion Spring, and a stainless steel sample cup for testing according to API (American Petroleum Institute Recommended Practice for Field Testing Water-Based Drilling Fluids, API RP 13B-1/ISO 10414-1 Specification)". The test fluid is contained in the annular space (shear gap) between an outer cylinder and the bob (inner cylinder) and measured the shear stress caused by a given shear rate. The viscosity in centipoise (or millipascal second) of fluid is indicated on the dial with the standard rotor R1, bob B1, and torsion spring F1 operating 300 rpm. The particle size distribution test confirmed the scale of nanoparticles.

2.2.3. HPHT Filtration

To evaluate the removal performance of formulated well clean-up fluid at downhole condition, the filter cake of WBM sample presented in Table, and OFITE HPHT Filtration cell was utilized based on API 13 procedure. After exiting WBM filtrate in 30 min, the extra mud was removed from the HPHT cell, and the formulated well clean-up fluids were filled in the HPHT cell. The well clean-up fluid was exposed to filter cake at temperatures 120 ^{0}C and 100 Psi differential pressure for 6 hours, and the retained filtration was collected and measured versus time to evaluate the filter cake breaking time.

2.2.4. Filter Cake SEM Evaluation

After performing the HPHT test on the exposed filter cake with the formulation well clean-up fluid, SEM Scan was used to investigate filter cake morphology alteration and the remaining nanoparticles in the filter cake structure.

2.2.5 Contact Angel and IFT Measurement

The pendant drop method measured contact angle and IFT to evaluate the wettability changes and interfacial tension of the formulated well clean-up fluids. The core slices were saturated with reservoir oil samples for four weeks before measurement.

2.2.6 Core Flooding Test

Core flooding experiments were conducted on three carbonate cores from an oil reservoir by utilizing a core flood unit (Fig. 1). Oil and water samples were from the oilfield. The core permeability measured at reservoir temperature, and the differential pressure between 100 and 500 applied to the core sample. The permeability of the core was determined by averaging over three core flood flow tests: K= 36.2 +/- 1.6 (mD)

Fig 1. Customized Core Flood Unit for Drilling Fluid Formation Damage Measurement and Removal

3. Experimental Results and Analysis

Designing different bulk experiments verified the enzyme performance and its compatibility with the nanoparticle.

3.1. Enzyme Solubility and Stability

Visual inspection confirmed that the ENZ-A enzyme was very soluble in tap water at concentrations of 1, 2.5, and 5% W/V without any precipitation and foam during 24 hours. The 1% of ENZ-A enzyme solution (WELL-CLEAN I) showed no phase separation, sedimentation, foam, nor aggregation at different pH levels up to pH 11 from the acidic to the alkaline range. For pH values between 11 and 12, the enzyme solutions have very little precipitation and show some colloidal particles in the solution. Thus, WELL-CLEAN I's pH must be adjusted to 10 to prevent any colloidal particle and sedimentation in the solution.

3.2. Enzymatic Performance Evaluation by Iodine Test

The Iodine test determined starch degradation after reaction with WELL-CLEAN I. The interaction between starch and triiodide is the basis for iodometry, and the combination of starch and iodine is blue-black. Iodine tests confirmed enzymatic activity in the starch solution (10% W/V) treated by WELL-CLEAN I. Fig. 2 presents the starch solution's white-cream color (10% W/V) without triiodide anion (I^{-3}). After performing iodometry by adding triiodide anion (I^{-3}), the starch solution's color was changed to dark blue in 5 minutes up to 24 hours for the test duration. 1% of WELL-CLEAN I was added to the starch solution, and the color of the solution changed to light blue after performing the iodometry test, and it was changed to pick color after 2 hours, which shows the degradation of the starch component by WELL-CLEAN I within two hours. The iodine test continued for a longer time, observing color changes for 6 and 24 hours. The enzymatic reaction was completed when the solution color was changed to white-pink in 24 hours. This test confirmed the enzymatic activity and performance of WELL-CLEAN I on the starch solution.

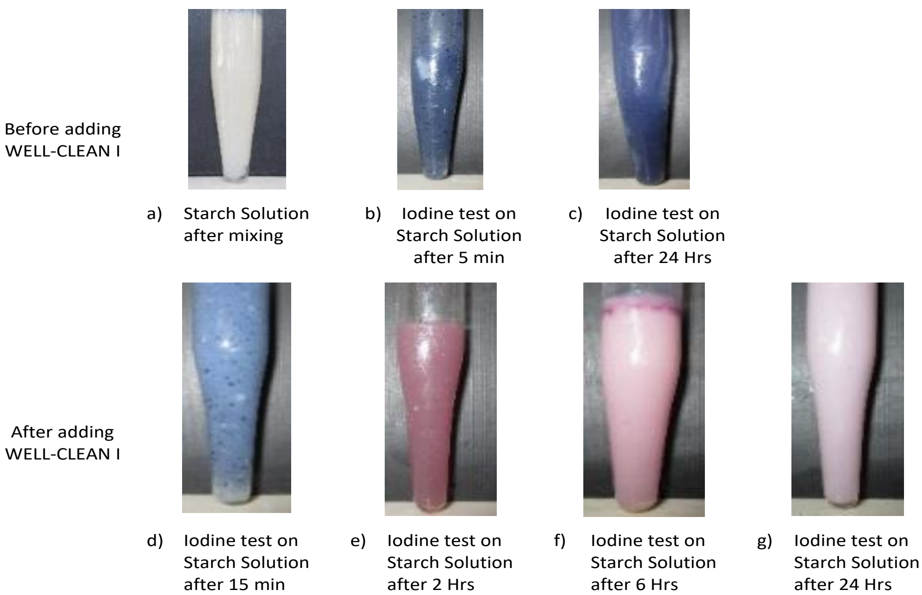

Fig 2. Enzymatic activity observation by Iodine test in starch solution (10% W/V) before (a,b,c) and after (d,e,f,g) adding WELL-CLEAN I

3.3. Temperature Stability

ENZ-A enzyme showed complete stability and no phase separation up to 150 ^{0}C. Above 150 ^{0}C, the solution generated colloidal particles and residues. Table 3 shows colloidal aggregation and sedimentation of WELL-CLEAN I at different temperatures.

Table 4

Temperatures Stability of WELL-CLEAN I

Temperature (^{o}C)	25	50	90	120	150	175
Colloidal aggregation	NO	NO	Trace	Low	Moderate	High
Sedimentation %	NO	NO	Trace	Trace	Low	Low

3.4. Analysis of Nanoparticle

PSD tests confirmed the size distributions of the nanoparticle. SEM was utilized to investigate the crystal structure and morphology of the nanoparticle. The morphologic graph was shown in Fig. 3 indicates that the particles are spherical, and the average particle sizes were approximately 20 - 40 nm, which confirms the Nano range of particles.

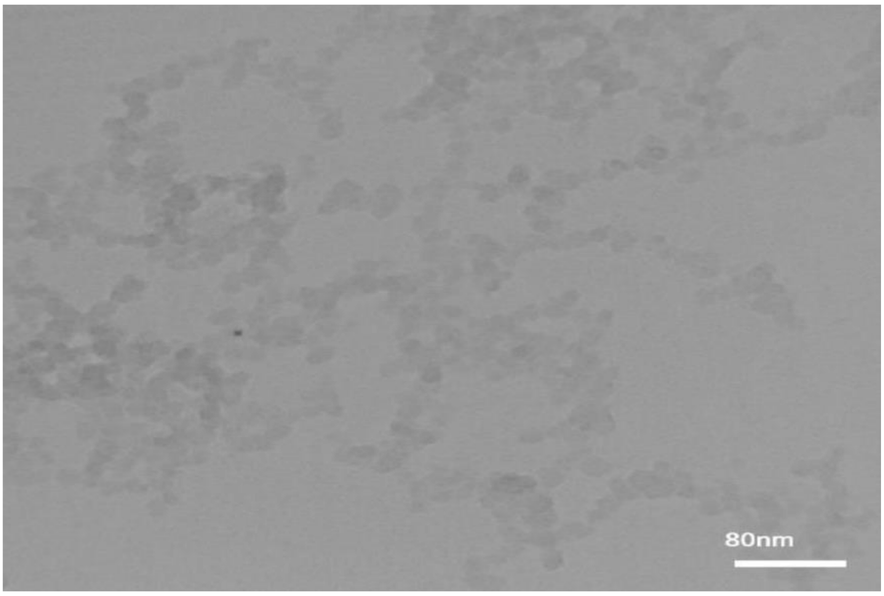

Fig. 3. Structure and morphology of nanoparticles by SEM

3.5. Viscosity Measurement of Enzyme-Based Well Clean-Up Fluid

The 36 ppb (10% W/V) starch solution was mixed using a Hamilton beach mixer model HMD200 as the base fluid of WBM. The solution's viscosity was measured before and after adding various well clean-up fluid formulations with different brine types using an OFITE dial viscometer 8-speed with +/- 1% measurement uncertainty described in section 2.2.2. It should be noted that due to the non-Newtonian behavior of the starch solution before and after WELL-CLEAN I injection, all viscosity measured at the same dial reading at 300 RPM. Three types of brines with different concentrations, including sodium chloride (12.5% and 25% W/V), Calcium Chloride (36% and 20% W/V), and Potassium chloride (7% W/V), were selected as the conventional completion fluids. These types of brines were used as the base of well clean-up fluid mixed with 0.1% V/V of WELL-CLEAN I. Prepared well clean-up fluids were injected into the starch solution to evaluate the enzymatic performance by reducing the viscosity. The viscosities were decreased significantly within 30 to 60 minutes at a temperature of 25 ^{0}C (Fig. 4). This result demonstrates that brines have stimulated the biodegradation of starch and have no adverse effect on enzyme performance in WELL-CLEAN I generally. Also, WELL-CLEAN I has a higher viscosity reduction in Calcium Chloride 36% and 20% W/V than other monovalent brines. Due to the higher activity of Ca^{2+}ions, calcium ions may have a higher reaction with the anionic branches in the polymeric structure of starch and neutralize the ionic charges that can reduce the viscosity of the solution, while monovalent brines such as NaCl and KCl has lower ionic exchange capacity in the solution. All of the brines had the same effect on viscosity reduction after 24 hours, and the viscosity of the starch solution decreased by more than 90%.

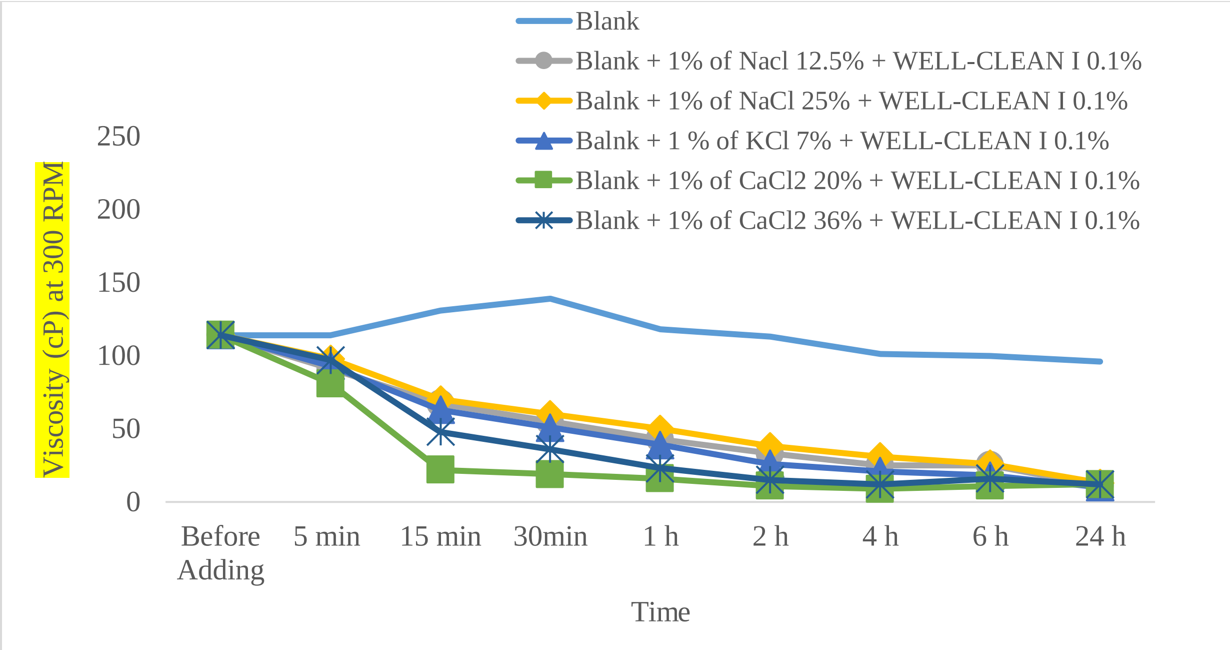

Fig. 4. The Viscosity measurement at 25 °C of Starch solutions 36 ppb (10% W/V) in reaction with WELL-CLEAN I in different brines (Sodium Chloride 12.5% and 25%, Potassium Chloride 7% and Calcium Chloride 20% and 36%. Viscosity measured by Ofite dial viscometer (standard rotor R1, bob B1, and torsion spring F1) at RPM 300 equivalent to centipoise (cP)

3.6 Viscosity Measurement of Bio-Nano Based Well Clean-Up Fluid

WELL-CLEAN II was prepared by mixing 0.1% V/V of WELL-CLEAN I (ENZ-A enzyme solution 1%W/V) and 0.1% V/V of the colloidal nanoparticle solution 15%W/V presented in Table 3. The performance of WELL-CLEAN II in different brines with various concentrations, including sodium chloride (12.5% and 25% W/V), Calcium Chloride (36% and 20% W/V), and Potassium chloride (7% W/V) in 25 ^{0}C is presented in Fig 5. The viscosity of the starch solution 10% W/V decreased after injection of WELL-CLEAN II at temperature 25 ^{0}C temperature gradually. It should be noted that due to the non-Newtonian behavior of the starch solution before and after WELL-CLEAN II injection, all viscosity measured at the same dial reading at 300 RPM. Calcium chloride brine 20% W/V showed the highest performance and reduced the viscosity within 30 minutes compared to other brines. Sodium chloride brine has the lowest performance. Within 24 hours, the viscosities of starch solutions dropped to 90% of the initial value in all types of brines.

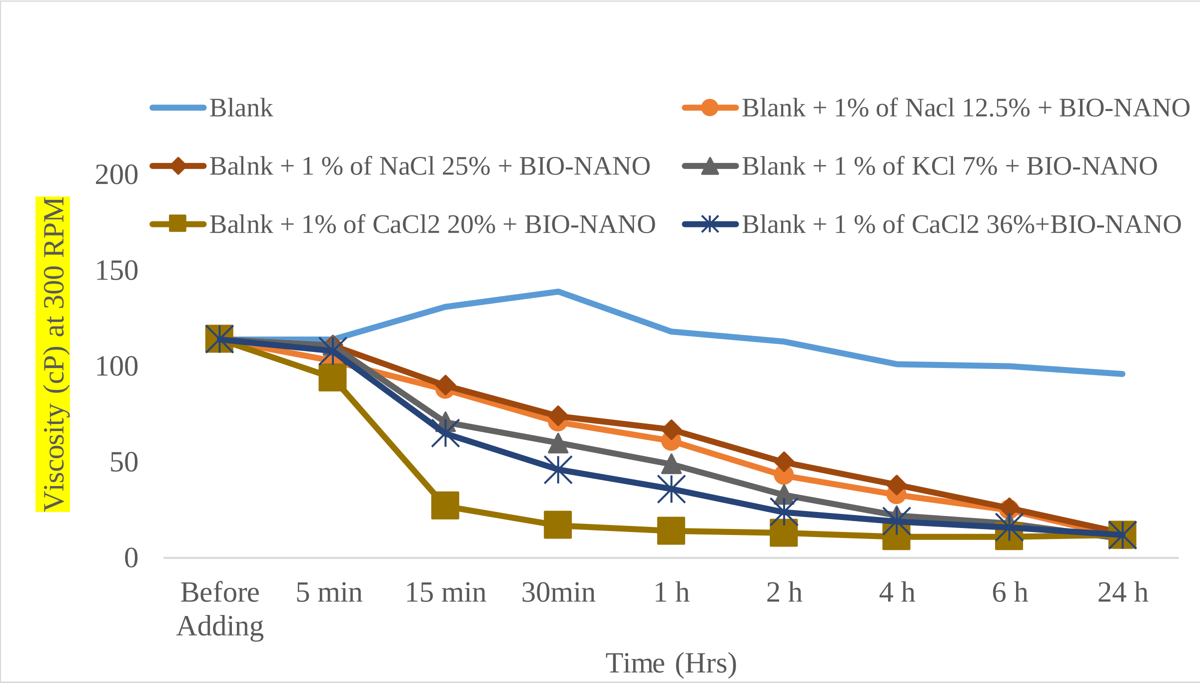

Fig. 5. The Viscosity measurement at 25 ºC of Starch solutions 36 ppb (10% W/V) in reaction with 1% V/V of WELL-CLEAN II (Bio-Nano Well Clean Up Fluid) in different brines (Sodium Chloride 12.5% and 25%, Potassium Chloride 7% and Calcium Chloride 20% and 36%. Viscosity measured by Ofite dial viscometer (standard rotor R1, bob B1, and torsion spring F1) at RPM 300 equivalent to centipoise (cP)

Comparing the viscosity reduction after adding colloidal nanoparticles in WELL-CLEAN II with WELL-CLEAN I showed a smooth reaction in the solution by reducing the direct reaction of ENZ-A enzyme with starch at ambient temperature. Comparing viscosities of WELL-CLEAN I and II showed that both clean-up fluids were efficient in calcium chloride brine 20% and had the same breaking trend within 30 min. Calcium chloride brines at both concentrations showed the highest reduction in viscosity within 30 minutes compared to other brines. After 24 hours, the viscosity of starch solutions reduced by more than 90% in all types of brines. Because the application of well clean-up fluid is at reservoir temperature, biodegradability performance must be evaluated at HPHT condition, discussed in the following section. It is also very important to highlight that viscosity measurement is the initial bulk test for understanding WELL-CLEAN I & II effect on starch solution but it is not key indicator for the final decision on the viscosity changes.

3.7 Performance Evaluation of Designed Well Clean Up Fluids on Filter Cake Removal in HPHT condition

The performance of formulated WELL-CLEAN II in Table 3 at downhole condition was measured by using an Ofite HPHT filtration device describe in section 2.2.3 at temperatures 120 ^{0}C and 100 Psi differential pressure for 6 hours, and the retained filtration was collected and measured versus time to evaluate the filter cake breaking time. In Fig. 6, the HPHT filtration rate of the enzyme-based well clean-up fluid (WELL-CLEAN I) and immobilized enzyme and nanoparticle (WELL-CLEAN II) were collected and benchmarked in different brines. WELL-CLEAN I and II, mixed in sodium chloride brine 12.5% W/V, had the same HPHT filtration rate and volume within the first hours. After the first hour, the HPHT filtration rate and volume of WELL-CLEAN II increased gradually. The effect of immobilization of enzyme and nanoparticle was observed in the semi-saturated sodium chloride brine clearly as the filtration rate and volume are doubled after 6 hours. By increasing the sodium chloride saturation to 25 %W/V, well clean-up fluid performance was reduced significantly (Fig. 6A). This reduction of filtration rate in saturated sodium chloride brine is due to the higher Na^+ ions in the fluid that can reduce the reaction of the enzyme and nanoparticles. It must be mentioned that higher and lower concentrations of WELL-CLEAN II at 0.5 and 3% were tested, but there was no effect on filter cake breaking and filtration performance. Using potassium chloride 7% W/V as the base fluid showed that the filtration volume and rate of WELL-CLEAN II at the concentration of 1% V/V are higher than WELL-CLEAN I. Repeating the test three times shows that the results were satisfactory. WELL-CLEAN II, formulated by enzyme and Nano additives, impacts filtration rate significantly and increases the filtration volume from 41 to

121 cc within six hours (Fig. 6B). Other concentrations at 0.5 and 3 %V/V of WELL-CLEAN II do not show any specific impact on the blank sample. Performance of WELL-CLEAN II in calcium chloride brine 20 and 36 %W/V was low, and filtration rate and volume did not change remarkably compared to the blank sample (Fig. 6C). This result shows that divalent brines can reduce the activity of both enzymes and nanoparticles due to the higher ionic charges. Other WELL-CLEAN II concentrations at 0.5 and 3% V/V did not significantly improve the filtration rate compared with WELL-CLEAN I and blank sample. They demonstrated a direct relationship between the divalent ions and nanoparticles in WELL-CLEAN II as the performance of WELL-CLEAN I is much higher and effective. Despite that the viscosity measurement of different well clean-up fluids in calcium chloride brine confirmed that the nanoparticle could dramatically decrease viscosity, WELL-CLEAN II in potassium chloride enhanced the filtration rate because of the stability of formulated well clean-up fluid in higher temperature. This result is essential for designing completion fluid and selecting well clean up fluid. Based on the achieved results, it is understandable that the brine type in completion fluid plays an important role in well clean-up fluid performance. Immobilized well clean-up fluid must be prepared in low saline brine to remain active for penetrating the filter cake porous media and assisting the ENZ-A enzyme to enter the filter layer of the filter cake by increasing the surface area of the reaction. Saturated brines reduce nanoparticles' activity by adsorption and coagulation of the ENZ-A enzyme and prevent proper reaction with filter cake polymer content. This coagulation can block the porous media of the filter cake and act as a barrier.

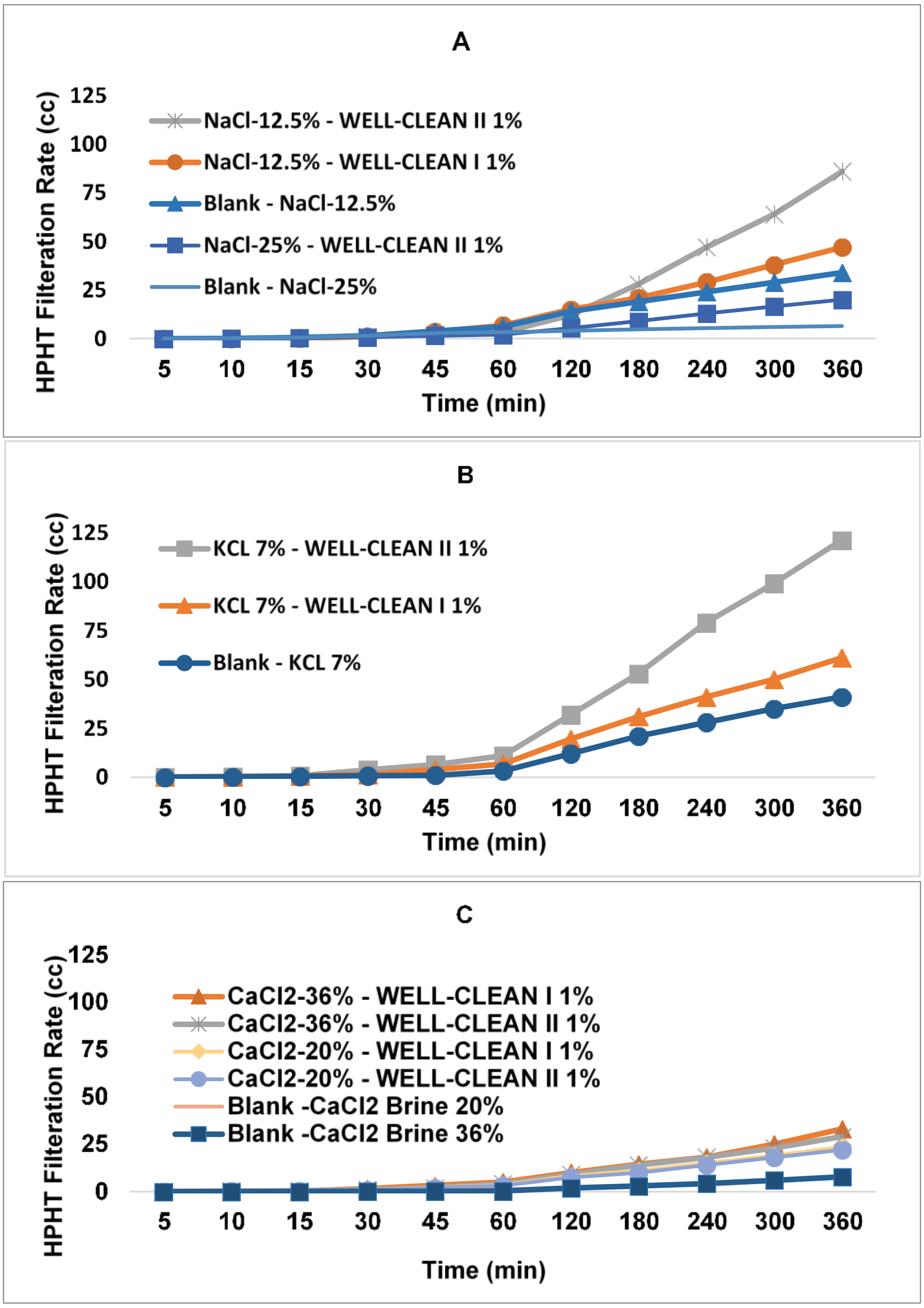

Fig. 6. HPHT Filtration after Injecting WELl-CLEAN I and II with A) Sodium Chloride Brine (12.5 & 25 %W/V), B) Potassium Chloride Brine (7 %W/V), C) Calcium Chloride Brine (20 & 36 % W/V)

3.8. SEM Evaluation of HPHT Filtration and Filter Cake

The immobilized enzyme and colloidal nanoparticle (WELL-CLEAN II) in potassium chloride brine 7% W/V called Bio-Nano Well Clean Up Fluid (BNWC) was screened as a high-performance and optimum well clean up formulation. The exposed filter cake with BNWC was evaluated by the SEM method. SEM analysis showed that the filter cake contained calcium, oxygen, and carbon ions with a coagulated nanoparticle trace (Fig 7). The filter cake surface area is firm and flat with very low porosity before injecting BNWC (Fig. 7A). The filter cake porosity and permeability increased after BNWC injection (Fig. 7B), which indicates a high reaction between the filter cake and the well clean-fluid. The immobilized enzyme with the nanoparticle acted as a catalyst to speed up the reaction.

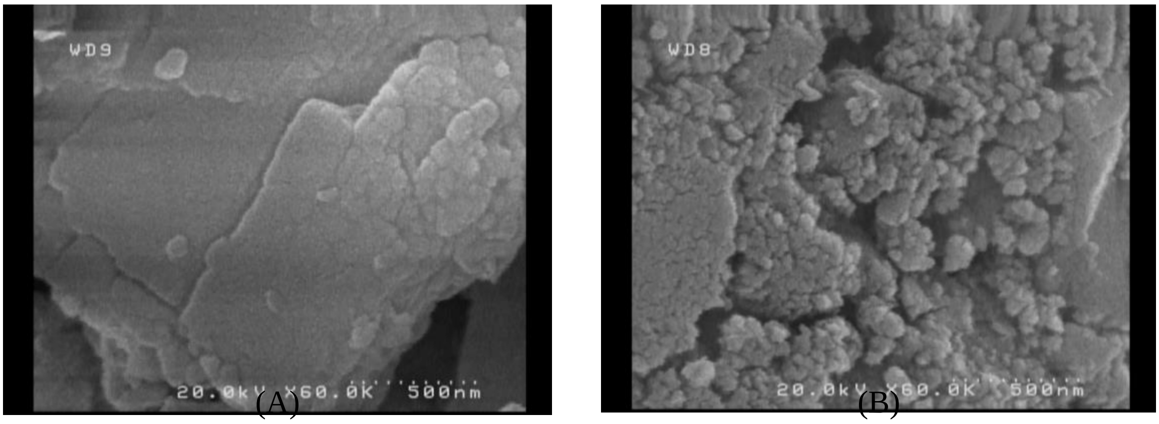

Fig. 7. SEM evaluation of Filter Cake before (A) and after (B) exposing to WELL-CLEAN II with Potassium Chloride Brine (BNWC)

PSD analysis was performed on the filtered brine passed from the filter cake. The PSD analysis presented in Fig. 8 showed that the average size is around 243 nm higher than nanoparticles, which is evidence of nanoparticles' coagulation with filter cake components during the reaction phase.

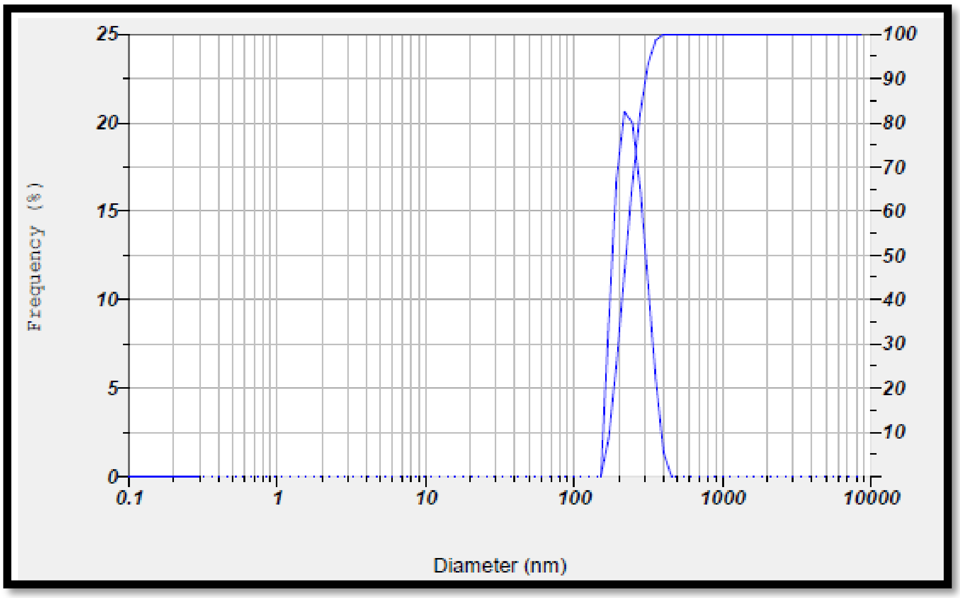

Fig. 8. Particle size distribution of HPHT filtration after injecting WELL-CLEAN II with Potassium Chloride Brine (BNWC)

3.9. Wettability and IFT Measurement

Table 4 shows the contact angle measurement and wettability type, using the classification presented by Iglauer et al. (2015). The contact angles were measured in well clean-up filtrate containing KCl (7% W/V) with saturated carbonate rock in selected oil. The result shows that the carbonate rock is intermediate wet in the presence of KCl brine (7% W/V), and it has more tendency to very weakly oil-wet after exposure to enzyme-based well clean up fluid/filtrate. By increasing the contact angle, there is a possibility of secondary formation. For the immobilized enzyme with nanoparticle well clean up fluid, the carbonate rock's wettability changed to strongly water-wet, which means that the BNWC filtrate can adhere to the rock surface and reduce the rock oil wettability. This wettability alteration is a valuable achievement to reduce the secondary formation damage associated with WELL-CLEAN I as a conventional enzyme-based well clean-up fluid. The main mechanism of wettability alteration is the decoration of nanoparticles on the rock surface, enhancing the water absorption by increasing the area/volume ratio and polar groups' availability in nanoparticles. For comprehensive investigation, IFT measurement was performed to evaluate the fluid trapping potential in reservoirs' pore structures due to the capillary force. Table 5 shows the oil/water interfacial tension in the presence and absence of WELL-CLEAN I and WELL-CLEAN II at 25 ^{0}C. Compared to the blank sample, IFT between the oil and the enzyme-based well clean-up (WELL-CLEAN I) decreased from 7.77 to 3.02 N/m^2 while IFT returned to 6.03 N/m^2 after injecting WELL-CLEAN II. The adsorption of the enzyme at the oil/water interface leads to the reduction of IFT, and it depends on several factors, such as particle wettability and dissolved oil in the water phase. This reduction of IFT is good when flooding the oil with other fluids such as low saline water in EOR application in injection wells, but it can increase the invaded zone, contamination, clean up fluid, and increase the damage zone near the wellbore. IFT of BNWC can decrease slightly compared to the drilling fluid filtrate (Potassium Chloride Brine 7% W/V), increasing the potential of emulsification with the reservoir fluid, leading to dispersion of the oil from rock surfaces and change the rock surface to water-wet. As a result, forming the oil-in-water emulsion can increase the aqueous phase's viscosity and improve the reservoir's mobility control and oil productivity performance. Sometimes, this emulsification leads to the pore throats' blockage, impairs the formation's permeability, especially in low-permeability reservoirs (Feng, X. et al. 2011).

Table 4

The Contact angle measurement in Well Clean-Up Filtrate with KCl 7% W/V / Oil / Carbonate Rock

Sample	Contact Angle		Wettability
	Left Side	Right Side	
Blank (KCl Brine)	97.86	100.75	Intermediate wet (Filtrate & Oil)
Blank + WELL CLEAN I	107.98	107.53	Intermediate to weekly Oil wet
Blank + WELL-CLEAN II	52.13	52.74	Strongly Water Wet (well clean up filtrate wet)

Table 5

Interfacial Tension Measurement for WELL-CLEAN I & II compared to the blank sample.

Sample	IFT (N/m^2)
Blank (KCl Brine)	7.77
Blank + WC I	3.02
Blank + WC I&II	6.03

3.10. Core Flooding Experiment

Core flooding tests were conducted on the nominated core at a temperature adjusted at 200 ^{0}F and a differential pressure range from 0 – 500 psi. The initial permeability of cores was measured by injecting KCl brine 7% (W/V), and it was calculated based on Darcy's law. Then, the cores were damaged by injecting drilling fluid formulation in Table 1, and the rates of drilling fluid filtration were recorded in different pressure and flow rates within 6 hours. The filtration rate increased rapidly after injecting the drilling fluid into the core within the first 30 min and decreased gradually to a constant rate. Equivalent to 3.2 and 2.7 pore volumes were injected into core no. 1 and 2, respectively, to reach a constant rate within 5 hours. Fig. 9 shows the invasion rates of drilling fluid injection during the damage process. The permeabilities were measured based on the invaded filtration of drilling fluid for core no. 1 and 2 calculated 4.8 and 3.58 mD, respectively, which is more than 90% comparing to initial permeability. After injecting 1% of WELL-CLEAN I in KCl 7%W/V and BNWC (WELL-CLEAN II in KCl 7%W/V), the injection rate gradually increased the well clean-up process, as shown in Fig. 10. Both well clean-up fluids had the same injection rate before 2 hours, but BNWC increased the injection rate into the core to 0.3 cc/min significantly compared to the WELL-CLEAN I 's solution with a 0.1 cc/min. The performance of BNWC proved the HPHT filtration performance presented previously. Also, BNWC showed a smooth trend in increasing the injection rate, which is not achievable during WELL-CLEAN I injection.

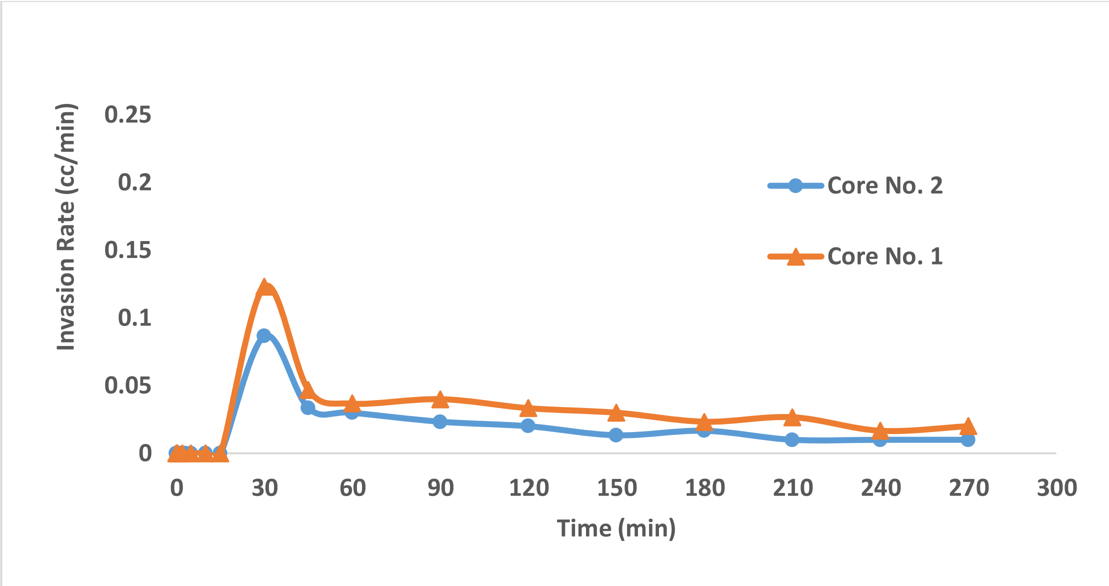

Fig. 9. Core damaging process by WBM injection into the carbonate core

(Confining Pressure : 1000 psi, Pressure : 0 - 350 psi, Temperature : 200 ^{0}F)

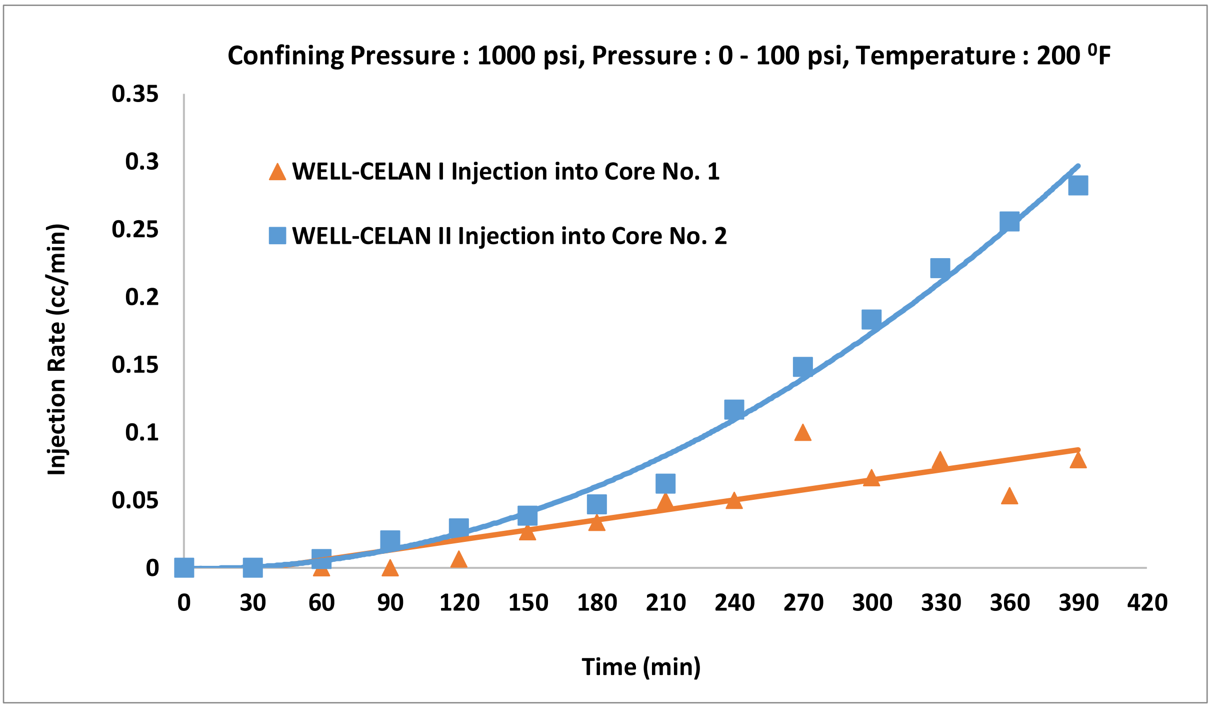

Fig. 10. Well clean up injection into the carbonate core

The last experiment was performed on core no. 3 to measure the initial permeability, damage the core, and clean the core by injecting BNWC. After injecting the drilling fluid into the core, the filtration rate increased rapidly within the first 30 min and decreased gradually to a constant rate around 0.01 cc/min, as shown in Fig. 11. The initial increase in flow rate was related to drilling fluids invasion due to pressure build-up, and the flow rate decreased after 30 min due to filter cake formation on the core face. The core's permeability was reduced to 1.48 mD, which means 96% damage comparing to the initial permeability. BNWC was injected into the core, and injection rates were recorded versus time to remove the filter cake damage. The core flooding test results are summarized in Fig. 11. The core flooding test showed that the injection rate increases significantly, and the permeability increased from 1.48 to 18.33 mD, which removed 50% of the damage from the core. This core flooding experiment proved that the BNWC could remove filter cake on the core face successfully.

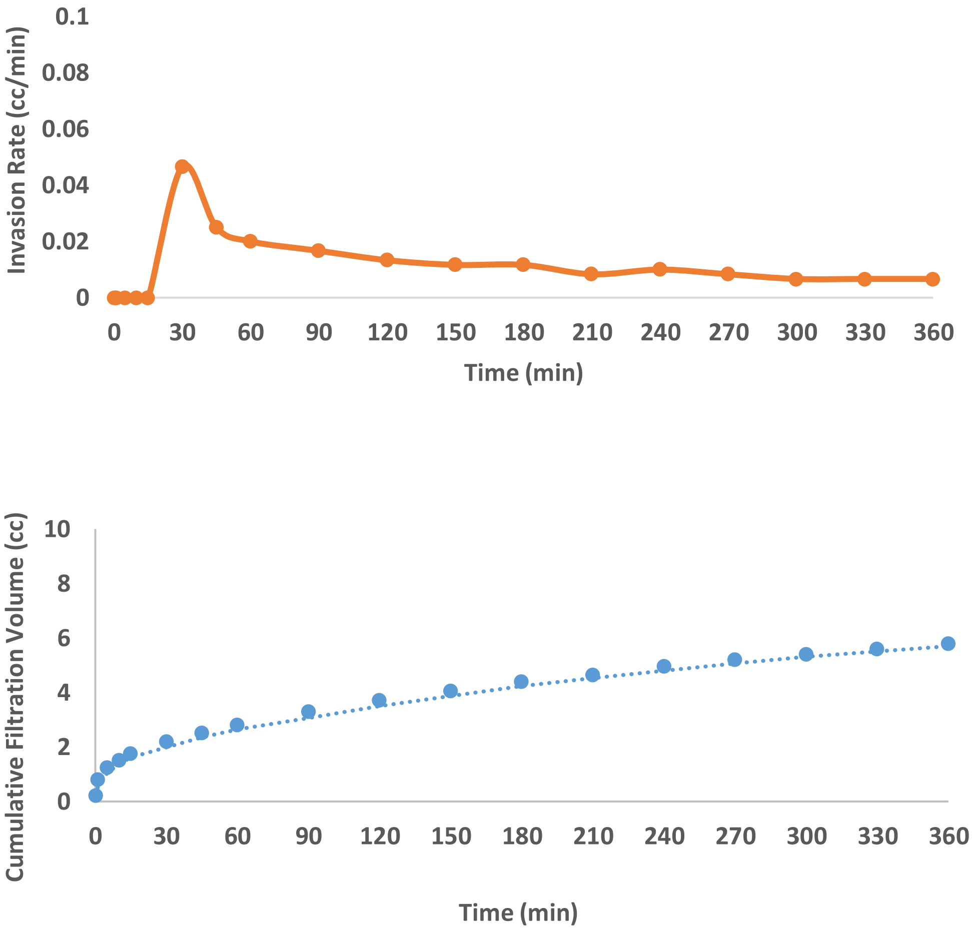

Fig. 11. Core damaging process by the drilling fluid injection into the carbonate core.

A) Drilling Fluids Injection Rate - B) Cumulative Volume of Drilling Fluid Filtration Injection

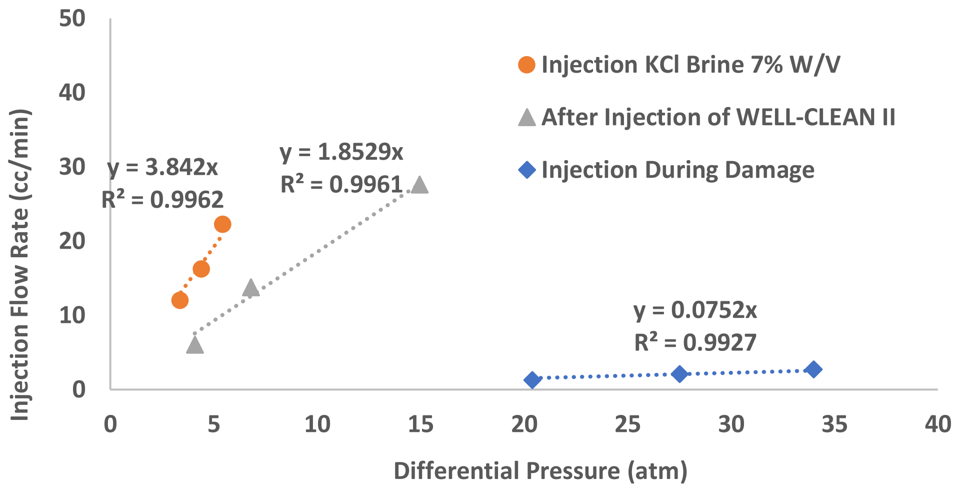

Fig. 12. Core damaging process by the drilling fluid injection into the carbonate core

Based on the core flooding test results, Bio-Nano Well Clean-Up (BNWC), an immobilized enzyme with a nanoparticle in KCl brine 7%W/V, was finalized as a high-performance well clean-up fluid formulation. Although the enzymatic activity already degrades the drilling fluid polymers, specifically starch structure, the immobilization process, which combines enzyme and nanoparticle, further enhanced the ENZ-A enzyme's biological activity. Based on the nanobiocatalysts literature discussed in the introduction section of this paper, enough justification can be provided to interpret the reaction and associated mechanisms behind the enhanced activities of bio-nano catalysts in WELL-CLEAN II formulation. Immobilization of the ENZ-A enzyme with the selected nanoparticle improves the stability and resistance at higher temperatures due to the crosslinking with the enzyme's protein amino surface. Adsorption of nanoparticle particles on the ENZ-A enzyme structure forms molecular complexes that act as a catalyst. The catalytic activity increases, likely due to their higher surface-to-volume ratios and dramatically reduced mass transfer limitations, as enzymes have a greater possibility to react with the enzyme-substrate (An, J. et al. 2020). The high catalytic activity can be obtained via either covalent bonding, adsorption, entrapment, or encapsulation.

The nanoparticle morphology provides a large surface area for increased enzyme loading and reduced diffusion resistance. Immobilization based on metal ion activity does not apply to WELL-CLEAN II as it is not a metal-based nanoparticle.

Higher enzymatic activity of WELL-CLEAN II comparing to WELL-CELAN I in KCl brine can be related to the electron/charge transfer effect (An, J. et al. 2020). This process loses the enzyme's protein structure and helps the enzyme extract electrons from the substrates. The temperature effect seems an important factor affecting enzymatic activity, as observed in the HPHT filtration test. Enhancing the activity of immobilized enzyme as a result of temperature has been reported by Rodrigues, R.C. et al. (2013). Nanostructured can absorb light/electromagnetic waves and convert them into heat for promoting the activities of nanobiocatalysts (An, J. et al. 2020).

The conformational change of immobilized enzyme is another mechanism that can also improve the enzyme's catalytic activity by nanostructure. This mechanism can be seen as an immobilization process of the enzyme with the nanoparticle in calcium chloride brine. Cations can be an effector to bind at an enzyme allosteric site, leading to the enzyme molecules' activation. It must be considered that all conditions which may affect the enzyme activity can also decrease the immobilization process, which reduces the catalytic performance. The pH of the base fluid of well clean up fluid is mixed plays an important role that increases or decreases catalytic activity in different brine types with different pH when mixing with a well clean up fluid such as sodium chloride and calcium chloride brine. The immobilized enzyme at a temperature above the optimal conditions may significantly reduce enzyme activity.

4. Conclusion

In this study, advanced modification of conventional enzyme-based well clean-up was investigated to enhance WBM filter cake removal by immobilizing enzyme with colloidal nanoparticle in potassium chloride brine 7%W/V as Bio-Nano Well Clean Up fluid (BNWC). Based on the experimental results, the following conclusions are achieved:

1- Enzyme-based well clean-up is a proper selective method for removing WBM filter cake, but it requires specific consideration to formulate based on polymer content in the filter cake, downhole temperature, completion fluid type, base fluid type, and alkalinity.
2- Although enzyme-based well clean-up is mixed in the completion fluid, the experiments showed that base fluid is very important for mixing this type of well clean-up while considering both enzymatic activity and secondary formation damage associated with completion fluid.
3- The immobilization of the enzyme with nanoparticles enhanced the viscosity reduction of starch content solution, specifically in calcium chloride brine 20% W/V significantly. However, HPHT and core flooding experiments at reservoir conditions in 200 ^{0}F showed higher enzymatic activity in potassium chloride brine 7% W/V.
4- Bio-Nano Based Well Clean Up Fluid (BNWC) could increase the filtration rate in the HPHT test by 90 percent and enhance the injection rate in core flooding device by three times.
5- Contact angle measurement showed that BNWC changed the carbonate rock's wettability to strongly water-wet and reduce the rock oil wettability. Also, minor IFT changes were observed between BNWC and selected core comparing to WBM based brine.
6- Extending Bio-Nano Science application from other industries into the drilling and completion fluid process has been performed for the first time and developed an innovative catalyst to enhance enzymatic activity in the well clean-up process. It is also required more investigation on the rheological model and behavior of this fluid in order to have proper correlations for scientific investigation.

It is highly recommended to all researchers involved in chemical flooding for stimulation, production enhancement, and EOR/IOR applications to use the advantage of Bio-Nano science for further research and development.

Acknowledgments

The authors would like to acknowledge the Institutes of Petroleum Engineering (IPE), the University of Tehran, and Pars Drilling Fluids Co. to support this research project. We would also like to have special thanks from Dr. Gerald Meeten for reviewing the paper and his valuable feedback.

Appendix

The spectrum of drilling starch in Fig 1 shows identical major reflection peaks that correspond to different functional groups' vibration. The FTIR spectra of starch typically show bands at 3300-3600 cm-1(OH stretching), 2900–3000 cm^{-1} (C H stretching), 1100–1200 cm^{-1} (C O, C C, and C O H stretching), and 1100–900 cm^{-1} (C O H bending) which confirmed the starch structure (Warren et al., 2016). The spectrum of the ENZ-A enzyme in Fig 2 shows bands at 3200-3300 cm^{-1}, 2900–3000 cm^{-1}, 2000–2200 cm^{-1}, and 1000–1200 cm^{-1}, which confirmed alpha-ENZ-A structure (Krieg et al., 1997).

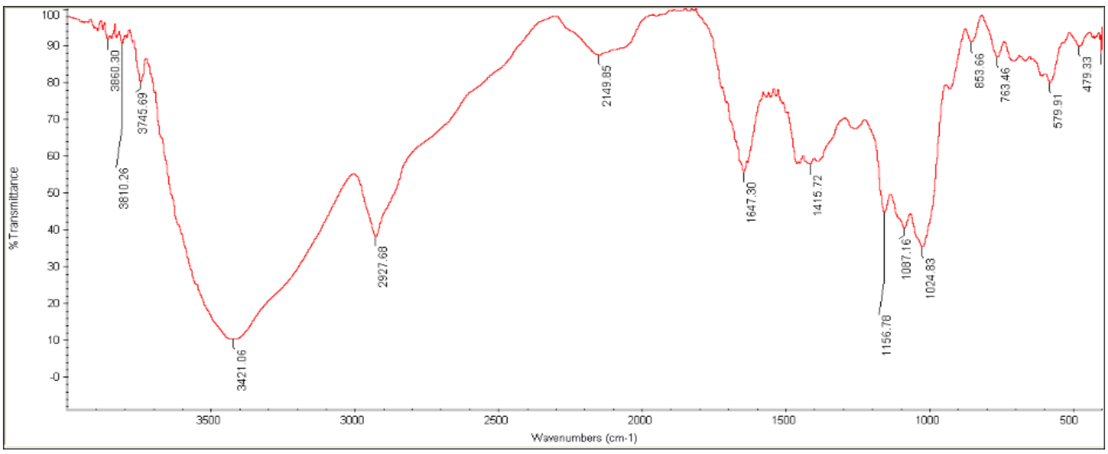

Fig. 1. FTIR spectra of drilling starch

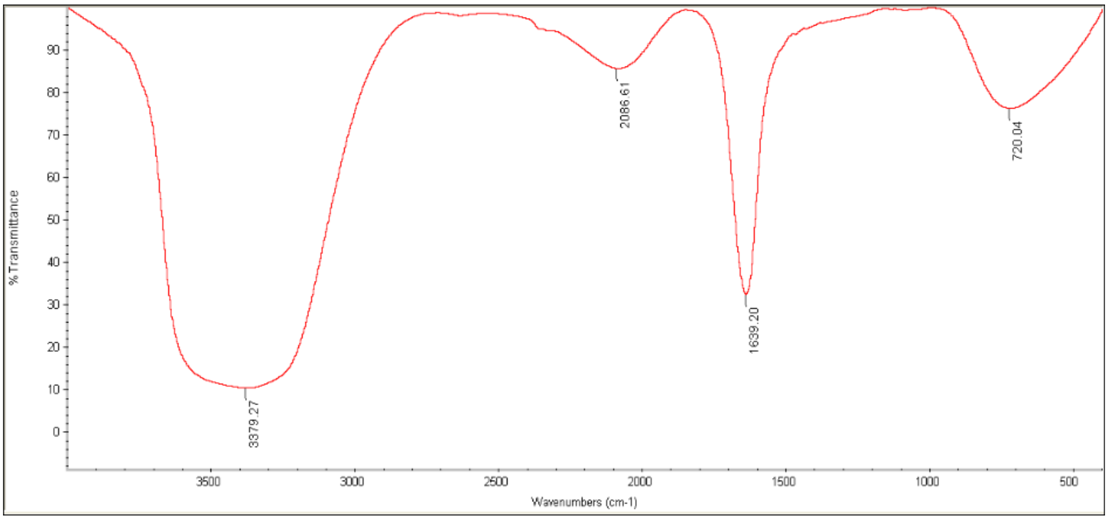

Fig. 2. FTIR spectra of ENZ-A enzyme

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