NOVEL MULTI-FUNCTIONAL CHEMISTRY TO MAXIMIZE PERFORMANCE IN PARAFFIN COATED ACID SOLUBLE SCALE CLEANUPS

Rosanel Morales, Revive Energy Solutions

Fadi El Ahmadieh, and Max Reynolds. ConocoPhillips

Abstract

Gradual diminution of the flow path of hydrocarbon in the near-wellbore area is heavily linked to formation damage accumulation and a reduction in well productivity. Organic deposition in the formation and wellbore area can result from the use of hydrochloric acid (HCl) during acidizing, especially in the presence of free iron and organic liquids such as diesel, kerosene, or gasoline and the use of CO2 injection for EOR projects. Laboratory evaluation of the nature of the crude oil and stimulation fluids indicates the potential severity of the problem.

Utilizing of organic and inorganic acids for inorganic deposits removal, like calcium carbonate and iron sulfide, has become one of the most common methods for well clean-up and stimulation. Unfortunately, due to the nature of the produced fluids, organic deposits like paraffin coat the inorganic scale, minimizing the performance of the acid job. Typical aromatic solvents utilized to address the organic deposits are not highly effective, as they are not fully miscible in the volume of the acid, and only dissolve a specific weight of paraffin before the solvent's power is exhausted.

A multipackage formulation has been developed, fully miscible in acid, maximizing the performance of the scale dissolution, by effectively de-oiling and penetrating the organic coating layer build-up on calcium carbonate and iron sulfide scales in shorter soaking periods. This novel formulation cleans spontaneously by diffusion, breaking and solubilizing the organic deposits and providing the following additional benefits:

- Water-wets the surfaces (near-wellbore area, downhole equipment, tubing, and flowlines), including paraffin particles, preventing the re-agglomeration further down in the system.
- Improves formation oil mobility by reducing the capillary pressure in the formation.
- Prevents emulsion creation and acid sludge formation during acid jobs.

The work in this paper studies the effect of this novel chemistry when it is used in acid jobs, and presents case history information on testing, chemical application, and subsequent field results across the Permian Basin in conventional and unconventional production.

Introduction

Organic and inorganic deposition in the near-wellbore area, perforations, downhole equipment, and production tubing begins when the operating conditions (temperature, pression, pH, fluid incompatibility, etc.) fall outside the equilibrium for solubility in the produced fluids. This depositional build-up can severely impact the performance of the well, affecting its deliverability.

As organic deposits, specifically paraffin, and inorganic scale like iron sulfide (FeS) and calcium carbonate (CaCO3) come out of solution, crystals start looking for a nucleation site (suspended solids, pre-existing scale layer, pipe and equipment surfaces, sand, etc) Once nucleation happens, a combination between paraffin crystals and FeS and/or CaCO3 grow beyond the initial barrier, deposition creates more surface area, causing more growth. Once the initial precipitation occurs, the additional surface area creates more depositional opportunities and the cycle rapidly perpetuates, causing a layered deposit of organic and inorganic material, impacting the flow potential of the reservoir into the wellbore and affects the performance of downhole equipment.

The current methods used in the industry to address and remove these organic and inorganic deposits vary from thermal, mechanical, and chemical treatments. Chemical treatments involve solvents, mutual solvents, surfactants, acids, and combinations of the preceding approaches (Bernadine 1993).

For chemical treatments, the selection of the chemical or chemicals depends on the nature of the deposits. Paraffin deposits require solvents, mutual solvents, and surfactants for removal. In the case of inorganic deposits like FeS and CaCO3, inorganic acids like hydrochloric acid (HCl) and chelators are used to solubilize the scale deposits.

Once deposits are precipitated and well performance declines, operators look for a quick approach to remediate the solid build-up to avoid non-economic production or the costly intervention work. This approach needs to involve a minimum sequence and volume of fluids, to deliver high effectiveness. The traditional chemical approach used in the oil and gas industry is to design a pre-flush to de-oil and remove the paraffin followed by an acid job with a 15% HCl system. The pre-flush consists of a volume of a liquid hydrocarbon like condensate, diesel, aromatic solvent like xylene, or combination of them. After pumping the pre-flush volume, a desired volume of acid is pumped to solubilize the scale deposits.

This two-stage job design is required due to the incompatibility between the required fluid to address the different type of deposits (paraffin and scale) present in the well in each stage of the treatment. Additionally, the alteration of rock wettability that results from the adsorption of organic deposits on the rock and surfaces, as well as the derivative of the usage of solvents during the clean-ups, is detrimental to production (Quintero et al. 2017).

Acid treatment is one of the most common techniques used to stimulate wells around the world. The effect of acid stimulation on oil wells has been studied extensively for years (Morales et al. 2017) due to the negative impact on well production and surface treating facilities following the acid jobs. Additionally, operators report that normally well performance after these jobs might result in a small, positive increase in production (which is not sustained) and sometimes detrimental to the well's productivity.

This work discusses an alternative to the traditional chemical treatments to effectively penetrate, break, and solubilize the layers of solid build-up between paraffin and scale deposits while restoring the wettability of the near-wellbore region to a water wet state. A multi-functional formulation is described, together with a discussion of some of the laboratory data related to the multi-functional formulation properties. In this study, a one-stage treatment is designed combining the multi-functional formulation and a 7.5% or 15% HCl package, evaluating the performance of effectively addressing organic and inorganic deposits, and reverting the wettability of the near-wellbore region and surfaces from oil-wet to water-wet. This one-stage treatment is achieved due to the full miscibility and compatibility of the multifunctional formulation and acid.

Description of the Multi-functional Formulation

A multifunctional formulation was developed for removing multi-skin damages present in the near-wellbore area. This formulation includes a combination of highly effective surfactants and a very robust solvent package. The synergy between the components allows it to act instantaneously, penetrating, breaking, reacting, and solubilizing solid build-up in producing and injection wells. Product affinity to both the hydrocarbon and water phase allows it to be combined with acid to perform a one-step job to remove deposits of different natures. The formulation is thermally stable up to 350F allowing application under different system conditions.

Multi-functional Formulation Performance

Evaluation of organic deposit solubility, interfacial tension, contact angle measurement, acid compatibility, and an acid sludge test was conducted with this formulation and demonstrated the effectiveness in the removal of paraffin and scale deposits, and impact in well productivity.

To recreate the performance of formulation for soaking treatments, pumper's test was performed. This test consists of using produced water, crude oil, and solid paraffin. This test screens the products' ability to dissolve solid paraffin in the presence of water and oil to simulate a soak job. During this test, the multi-functional formulation was tested in comparison to a traditional solvent system used for paraffin removal (see Fig 1)

(a) (b) (c) (d) (e)

Fig 1. Pumper's Test Performance Beginning of the Test (Time= 0hrs) with dosage of 100ppm

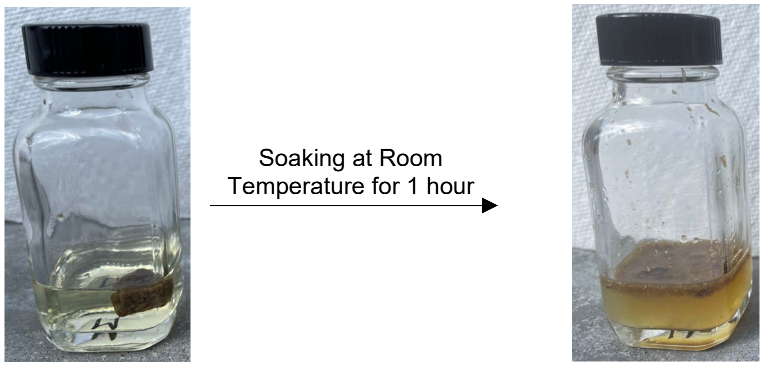
(a) (b) (c) (d) (e)

Fig 2. Pumper's Test Performance Results End of the Test (Time= 3 hrs) with dosage of 100ppm

Testing results showed that the formulation was the best performing traditional solvents systems used in the oil and gas industry for paraffin removal treatments. The formulation removed around 35% of the attached paraffin at 100ppm treatment rate.

Traditional solvent systems used in soaking jobs like xylene and combination products quickly achieve critical saturation, leading to solid particle re-aggregation, dropping out of solution, and re-depositing on the rock surface (Kelland, 2009). Re-deposition of organic deposits can also reverse the formation wettability from water- wet to oil- wet and affect the formation relative permeability (Leontaritis, 1994).

Dissolution and dispersancy evaluation were performed utilizing solid paraffin sample. Dispersancy results demonstrate the removal of organic deposits and restrictions to flow in the wellbore. As observed in Fig 3b, novel formulation effectively dissolves and disperses paraffin deposits (Fig 3a) utilizing neat formulation at room temperature in a 1-hour soaking period.



(a) (b)

Fig 3. Performance Evaluation of Multi-functional Formulation on Paraffin Deposits

Additional testing was performed to measure the formulation's ability prevent the agglomeration of paraffin wax after it has been put in solution. It was shown that the multi-functional formulation successfully broke the paraffin into fine particles, with a distinct clean water phase. An unsuccessful product will allow for paraffin to ball-up and stick to the glass. Testing temperature was 210°F utilizing paraffin and produced water field samples. It is shown in Fig 4 the performance of the formulation at a dosage of 500ppm.

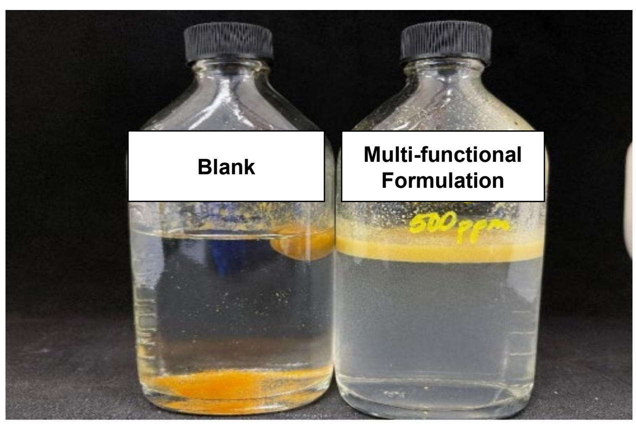


Fig 4. Paraffin Dispersancy Testing Performance with Multi-functional Formulation on Paraffin Deposits

Interfacial tension (IFT) between Permian Basin crude oils and formulation was measured using a manual syringe and a 22-gauge hooked needle. Drop size was dispensed to a maximum sustainable volume before breaking free from needle. The end time (t = end) for all measurements was determined as the time where the drop broke free from the needle. It has been documented in the literature (Miller et al. 1993, Miller 2006) that IFT has a great impact on the cleaning performance and hydrocarbon removal from solid surfaces, allowing to solubilize crude oil and break and solubilize organic deposits like paraffin. The time varied between samples. It was recorded that the novel formulation showed an IFT in the range of 10^{-2} mN/m at the end of the measurement. To achieve this level of solubilization there must be synergy between the key components built-in to the robust multi-functional formulation. This formulation delivers an ultra-low IFT in the system guaranteeing maximum solubilization benefit.

Measurement of contact angle between solid surface and a liquid interface (between xylene and formulation) was conducted on a surface cleaned with an aromatic solvent and the multi-functional formulation. Contact angle is a quantitative measure of wetting of a solid by a liquid where a lower contact angle (<90 degrees) is associated with a water wet surface, and a higher contact angle (>90 degrees) is associated with an oil-wet surface. This study was conducted on surfaces oil-wetted and coated with paraffin. Measurements were completed utilizing Theta flow optical tensiometer with sessile drop and pendant drop methods, using manual syringe with a 30 ga. needle and hooked needle. Results are presented in Fig 5.

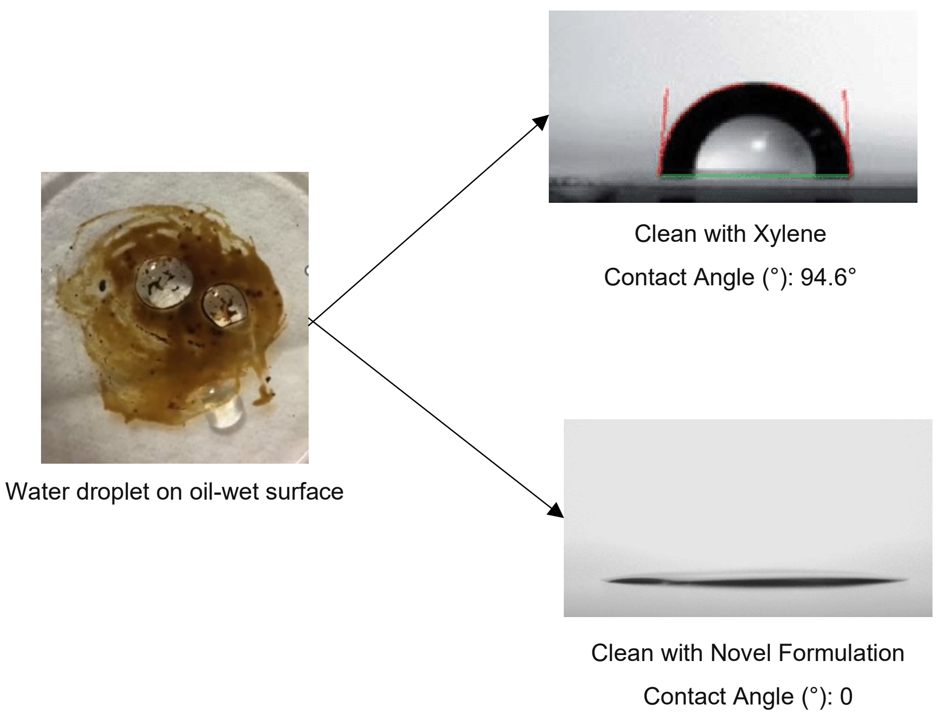


Fig 5. Contact Angle Measurements between water droplet on a cleaned oil-wet surface with xylene and Multi-functional Formulation on Paraffin Deposits

Critical micelle concentration (CMC) is a parameter that is used to determine the minimum amount of surfactant required to reduce the maximum surface tension of water (Ramesh et al, 2021). To determine the critical micelle concentration, we prepared a 2.00% stock solution of the novel formulation and used it as a dosing solution to incrementally augment the concentration of initially pure distilled water while measuring surface tension after each concentration increase. The critical micelle concentration was determined to be the point in concentration at which the surface tension no longer decreased due to increasing concentration, see Fig 6.

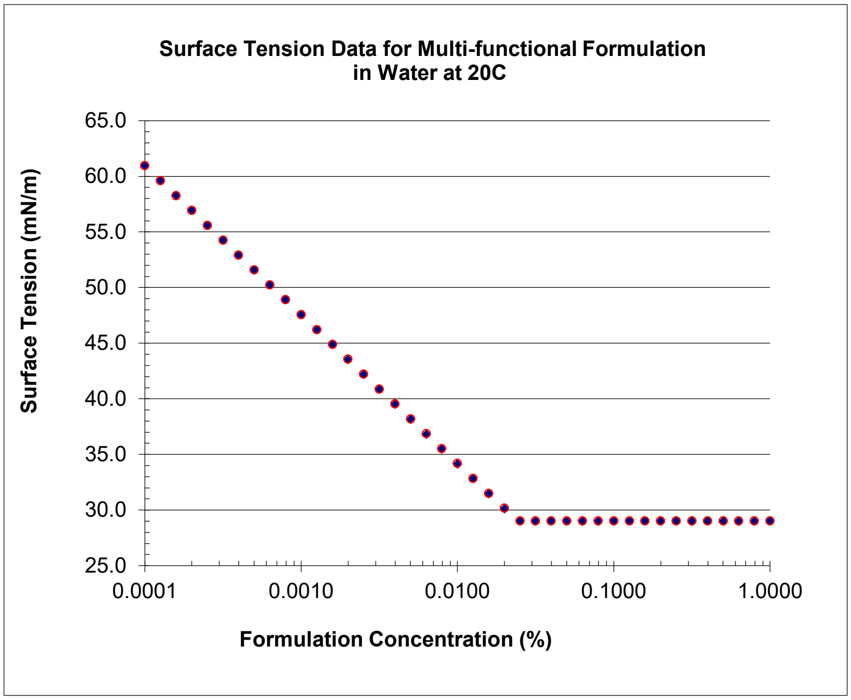


Fig 6. Critical Micelle Concentration of Multi-functional Formulation in Pure Water

Field Applications

The multi-functional formulation was selected to be used in combination with 7.5% HCl NEFE to address paraffin and FeS deposition and evaluate the effectiveness of the multi-functional formulation. The field is a mature field in the Midland Basin.

Selected wells had the following characteristics:

- Vertical wells.
- Rod pumps.
- Formations:
    - Clearfork 1
    - Dean
    - Spraberry 1, 2, and 3
    - Wolfcamp 1,2, and 3
    - Cline 1

  - Strawn 1 and 2

- Producing zone interval ranges from ~7,600’ to 11,300’.
- Low production.
- History of paraffin and iron sulfide deposition.

For the treatment designs, the following criteria were considered for selected wells:

- Multi-functional formulation added to the volume of the acid in a 10% ratio based on a 15% HCl job to ensure the full acid volume is fully treated.
- 10 gallons/ perforated feet was assumed to be the acid volume gradient.
- 7.5% HCl was selected instead of 15% HCl to minimize corrosion issues with old downhole equipment.
- 50% of the perforations are not open.

The following were established KPIs:

- Production uplift.
- Reduction in basic sediment and water (BS&W).
- Run time improvement.

The remediation treatments were designed to fully break and penetrate the paraffin build-up and allow the acid to react effectively with the FeS, preventing the sludge formation while water wetting the near-wellbore region, improving oil mobility. Treatment volume was sized to cover the perforated zone and 1ft inside the formation. The full protocol involved to pump a pre-flush of 2%KCl, followed by the designed volume of 7.5 %HCl mixed with 10% of the muti-functional formulation. Treatment was displaced with 2% KCl and allowed to soak for 12hrs. After the soaking period, wells were brought online straight to facility without special handling.

Pre- and post-treatment data are presented in the Fig 7 and 8:

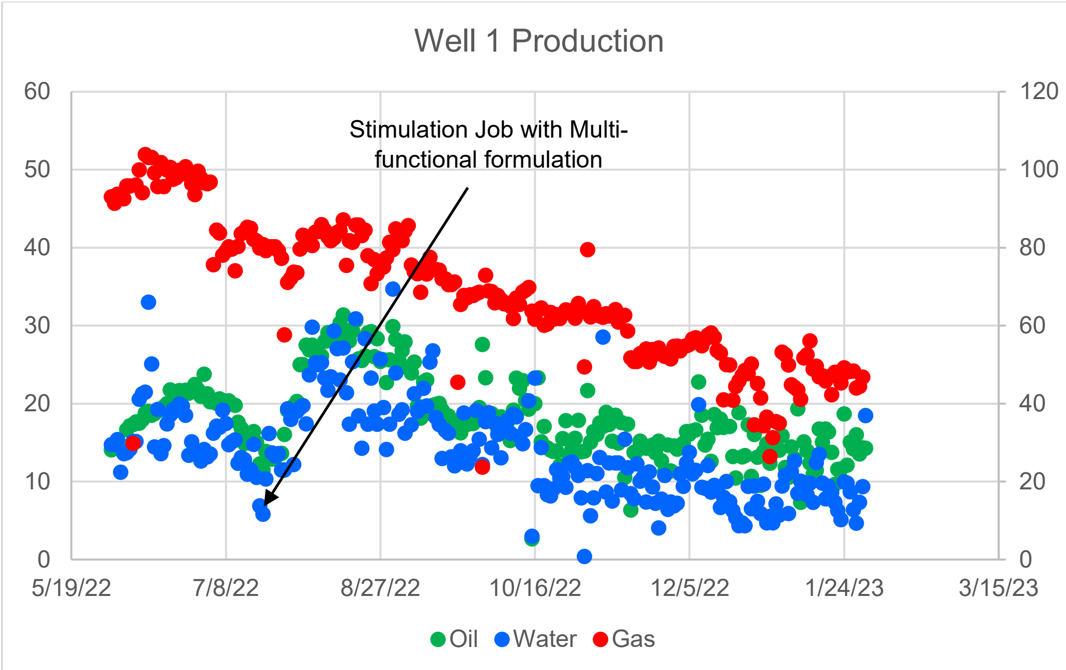


Fig 7. Well 1 Production Trend

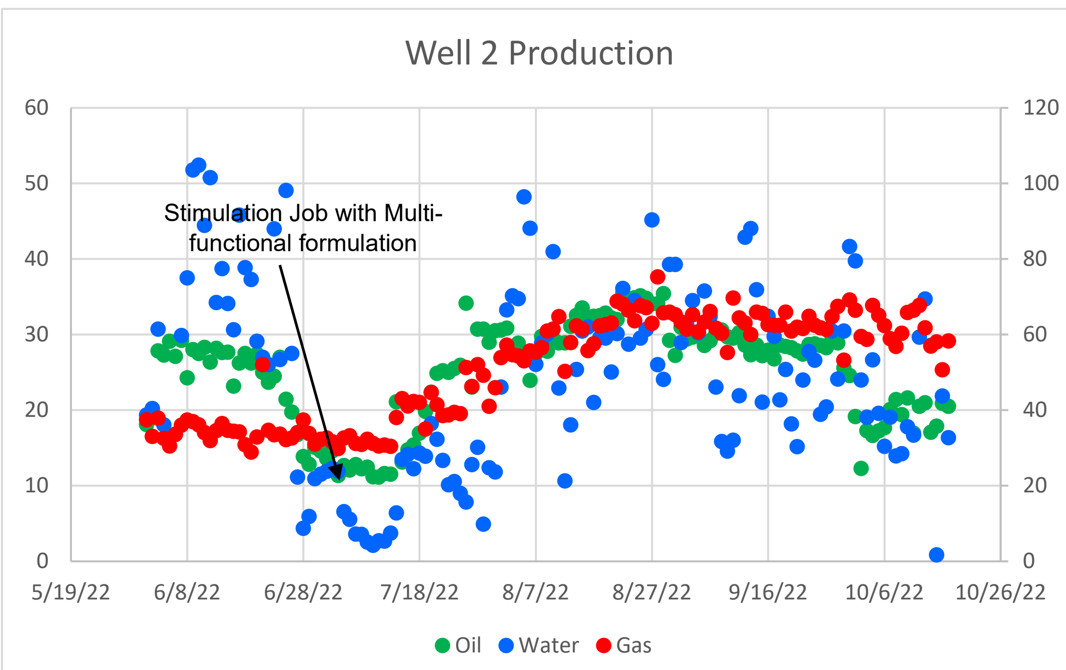


Fig 8. Well 2 Production Trend

As shown, the wells experienced a production uplift post treatment.

Figs. 9 and 10 demonstrate an increase in runtime (in hours per day) and decrease in cycling, reducing cyclical loading and decreasing stress to the equipment caused by startup and shut down.

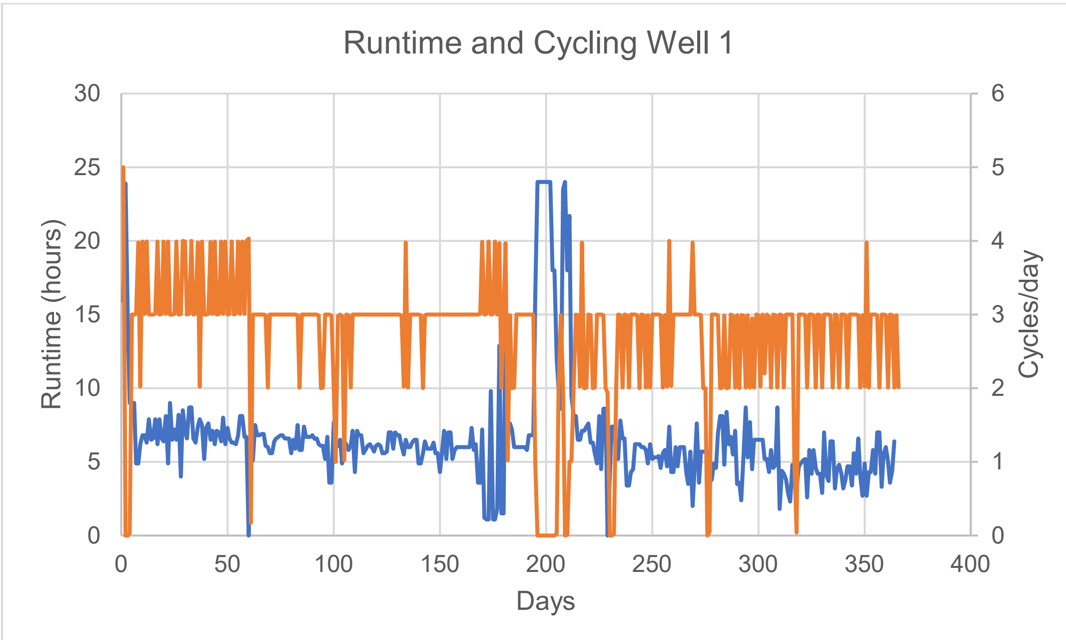


Fig. 9 Runtime and Cycling Well 1

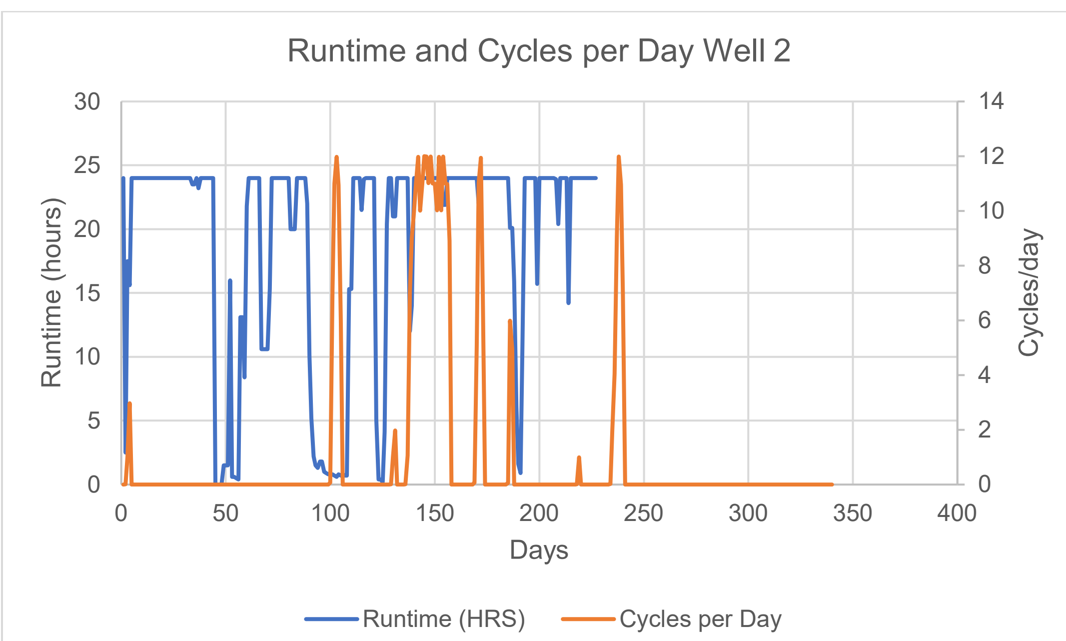


Fig. 10 Runtime and Cycling Well 2

Previous post work-over results done in February 2022 on well 2 shown iron sulfide presented in the produced fluids, even after acid soap, for testing. See Fig 11a, 11b, and 11c.

(a) Post-Workover-Iron Sulfide deposits

(b) Post-Workover- Iron Sulfide-magnetic

(c) Post acid soap for testing

Fig 11. Post-Workover Fluid Quality with Iron Sulfide Deposits

Samples were collected after stimulation clean-up was conducted with multi-functional formulation and results are presented in Fig 12.

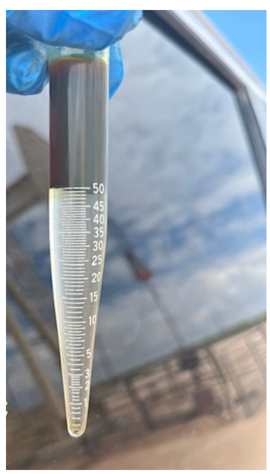


Fig 12. Fluid Quality sample after Stimulation Treatment Conducted with Multi-Functional Formulation and 7.5% HCl

As it can be observed, there are no FeS deposits left in the system as the paraffin layer was removed and FeS solids were de-oiled, and water wet. This process allowed the 7.5%HCl to effectively solubilize the FeS deposits for removal from the wellbore. Full treatment efficiently addressed the solid build-up in the well and stimulated the formation restoring the near-wellbore region wettability to a water wet condition.

Conclusions

A multipackage formulation has been developed to maximize the performance of paraffin-coated acid-soluble scale cleanups. This novel chemistry is fully miscible in acid and effectively de-oils and penetrates the organic coating layer buildup on calcium carbonate and iron sulfide scales in shorter soaking periods.

This new approach provides several benefits, including improved oil mobility, water-wetting surfaces to prevent re-agglomeration further down in the system and effective de-oiling of depositions to allow for more efficient acid treatments.

The paper presents a study on the effect of this novel chemistry when used in acid jobs and provides case history information on testing, chemical application, and subsequent field results across the Permian Basin in conventional and unconventional production. By utilizing this new approach, operators can achieve faster and more efficient cleanups, reducing the time and cost of interventions, and increase overall well productivity.

Acknowledgment

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