

SPE-204771-MS

A Novel Approach for Near Wellbore Stimulation and Deposits Removal Utilizing Thermochemical Reaction

Abdullah Alharith, Sulaiman Albassam, and Thamer Al-Zahrani, Saudi Aramco

Copyright 2021, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE Middle East Oil & Gas Show and Conference, Manama, Bahrain, 28 November – 1 December, 2021. The event was cancelled. The official proceedings were published online on 15 December, 2021.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

Organic and inorganic deposits play a major issue and concern in the wellbore of oil wells. This paper discusses the utilization of a new and novel approach utilizing a thermochemical recipe that shows a successful impact on both organic and inorganic deposits, as an elimination agent, and functions as stimulation fluid to improve the permeability of the near wellbore formation.

The new recipe consists of mixing nitrite salt with sulfamic acid in the wellbore at the target zone. The product of this reaction includes heat, acidic salt, and nitrogen gas. The heat of the reaction is enough to liquefy the organic deposits, and the acidic salt will tackle the carbonate scale in the tube and will increase the permeability of the near wellbore area. The nitrogen gas is an inert gas; it will not affect the reaction and will help to flow back the well after the treatment.

The experimental work shows an increment in the temperature by 65 °C when mixing the two chemicals. The test was conducted at room conditions and the temperature reached around 90 °C. Adding another 65 °C to the wellbore temperature is enough to melt asphaltene and wax, the acidic salt tackles carbonate scale. As a result, the mixture works on eliminating both the organic and inorganic deposits. The permeability of the limestone sample shows an increment of 65% when treated by the mixture of the reaction recipe.

The uniqueness of the new thermochemical recipe is the potential of performing three objectives at the same time; the heat of the reaction removes the organic deposits in the wellbore, the acidic salt tackles carbonate scale, and improves the permeability of the near wellbore zone.

Introduction

The interaction between different materials including oil, water, rock, drilling material, production chemicals, and many other materials under downhole conditions will create different deposits in the wellbore. Wellbore deposits vary including organic deposits such as wax and asphaltene originated by hydrocarbon or microbial base materials, and inorganic material such as scale, iron sulfide, corrosion products, and formation fines. Well deposits are not easy to classify due to the wide variety and complexity of their compositions. Many scholars describe the well deposits in different ways differ from author to another; however, the most common consensus brought is "Schmoo," "Black Sticky Stuff," or Oily Sticky Deposits" (Eroini et al. 2015).

The typical compositions of the well deposits are classified as 15-20% inorganic materials and 80% organic materials (Bohon et al., 1998). Other publications (Horsup et al., 2007; Jones et al., 2010) suggest similar compositions described by Bohon. Figure 1 illustrates the suggested compositions of wellbore deposits.

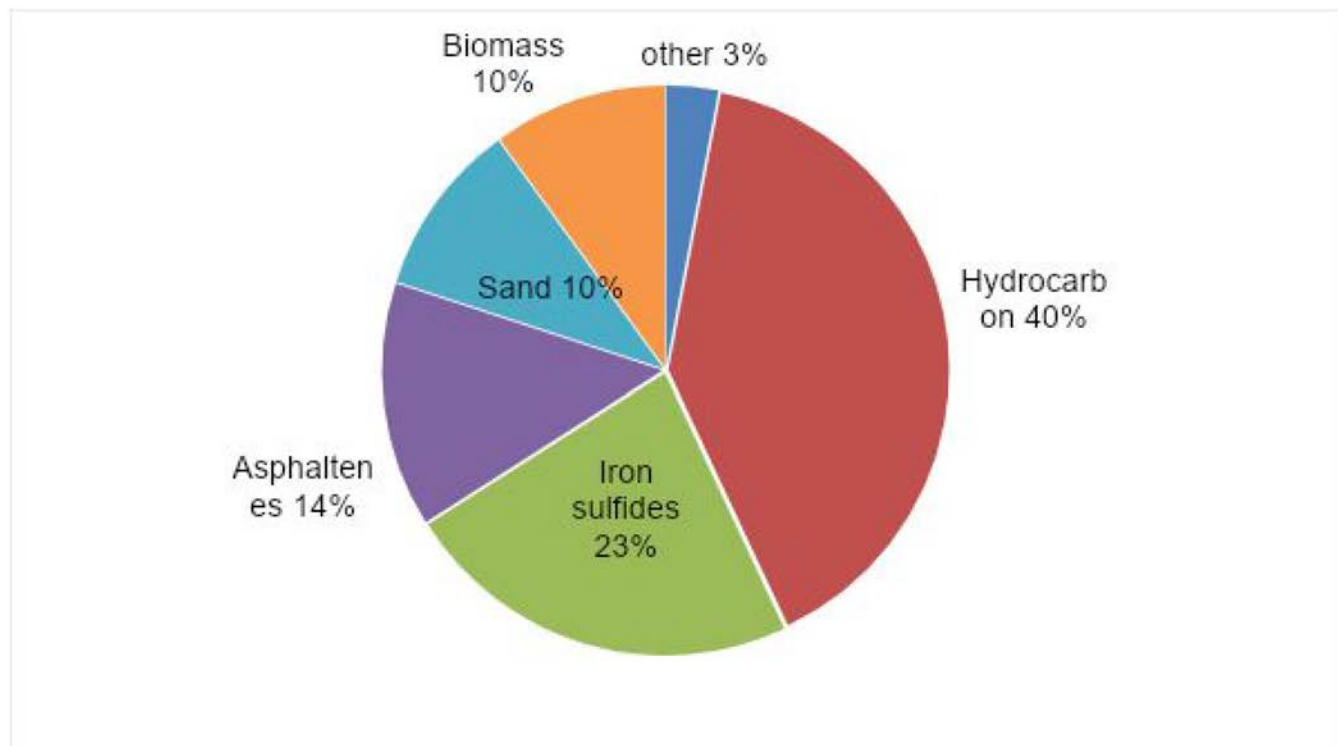


Figure 1—Suggested compositions of wellbore deposits sample (Horsup et al., 2007)

Generally, the organic part is dominated, which contains a significant percentage of oil-base materials, and another percentage of microorganism base materials. The inorganic part has a wide variety include; iron carbonate, iron oxide, iron sulfide, calcium scale, and clays (Eroini et al. 2015). The different well deposits can co-precipitate with each other based on different consequences, and include the change in wellbore temperature and pressure, change in the pH, water/oil percentage, compositions of formation water, and the different operational activities applied to the well that includes pumping of different chemicals in the well. In some regions, the inorganic deposits are minimal and most of the deposits are organic.

Types of organic deposits in oil wells

Paraffins

Paraffins are defined as alkanes that have a high molecular weight (C₂₀+) that can build up in the wellbore, in feed lines, etc., as deposits. The main cause of the accumulation of wax or paraffin is essentially the lack of solubility in crude oil (McClaflin et al.1984; Thomas et al.1988). This lack of solubility is typically attributed to changes in crude oil temperature, pressure, or composition due to the loss of dissolved gases. Paraffins with the highest melting point and molecular weight are typically the first to detach from the solution, paraffin's with a lower molecular weight splitting as the temperature drops. The major cause of loss of solubility of the paraffin in the crude oil is the decline in temperature, which could occur for a variety of reasons such as (Newberry et al. 1988):

- The expansion of hydrocarbons, when entering the wellbore through perforation, lead to temperature change.
- Gas expansion due to lifting fluids operations.
- The different in temperature between the tubular, and the formation.
- The loss of lighter hydrocarbon leaving behind the heavier materials.

There is little or no effect on the solubility of paraffin in crude oil by the pressure itself. It does, however, have a major effect on the crude oil composition. Pressure reductions typically lead to the depletion of volatiles from crude oil, which may cause paraffin precipitation. This is the key reason why, in the more advanced regions of the globe, paraffin issues are more frequent. The risk of paraffin precipitation dramatically increases as the reservoir pressure depletes and the lighter constituents of the crude oil are formed in preference to the heavier constituents (McClafflin et al. 1984).

Removal of paraffin deposits. Paraffin removal techniques can be classified into three categories mechanical, chemical, and thermal techniques (Misra et al. 1995; Fan, Y. and Llave, F.M. 1996; Bailey, J. Claire and Stephan J. Allenson 2009):

Mechanical techniques

Paraffin scrapers and cutters can be used to remove paraffins and hinder wax deposition by using plastic or coated pipe. Replacement of the affected part of the well takes place in case of very hard deposits, which will add more cost for remediation.

Chemical technique

This technique does not only remove paraffin deposition, but also delay the deposition processes, which include:

- Solvents: There are two types of solvents, aliphatic and aromatic solvents. The aliphatic include diesel, kerosene, and condensate, while aromatic include; xylene and toluene.
- Wax crystal modifiers: These types of chemical are work to prevent the growth of deposits by interfering the molecular structure of paraffin. Example of these modifiers are some synthetic polymers, co-polymers and esters.
- Dispersants: Neutralize and break the forces, which holed paraffin particles, and that will breakdown the deposits into finds and remove with production.
- Detergents or surfactants: Increase the solubility of deposits, and alert the wettability to inhibit paraffins deposition.

Thermal treatment technique

Applies hot water or oil to remove paraffin deposition. The remedy requires large quantities of the fluid, which will add extra operational cost. Adding chemicals to the water or oil can improve the performance of thermal treatment technique.

Asphaltenes

Asphaltenes are a high-molecular component of crude oil comprising compounds containing nitrogen, sulfur, and oxygen (N, S, and O). Clearly, this diverse class of compounds is not hydrocarbons since they contain a significant portion of heteroatoms in their composition. NSO compounds with a lower molecular weight are called resins. The separation of crude oil from resins and asphalts and other materials is largely dependent on solubility. Asphalt and resins are commonly known as the pentane-insoluble fraction of crude oil (YEN, 1974).

It consists mostly of concentrated aromatic rings connected with aliphatic tails, which are organic compounds that contain hydrogen and carbon atoms formed in straight or branched chains or non-aromatic

rings. Via their π electron systems, which have an electron that resides in a π bond, the polynuclear aromatic rings link with each other to form clusters of stacked rings. These asphaltene structures are distributed in crude oil and are preserved in suspension through the action of resins. If the crude oil contains ample amounts of resin molecules, the asphaltenes remain scattered in solution. Adding large amounts of alkanes or removing the resin fraction can result in a loss of solubility because the molecules of asphaltene interfere with each other, forming and precipitating large aggregates or micelles. Asphaltene precipitation occurs by the formation of certain aggregates. Asphalt solubility is thus a function of the temperature, the pressure, and the composition of crude oil. Any behavior that affects the crude oil's compositional balance can affect the oil's ability to keep the asphaltenes in solution (YEN, 1974).

A very typical example of a change in crude oil composition is what happens in a reservoir during pressure depletion. The solubility of asphaltene at the bubble point pressure is at a minimum. (Hirschberg et al. 1984) This has important implications for predicting when precipitation of asphaltene in a reservoir would occur. The probability of asphaltene accumulation exists at these sites as the reservoir is exhausted and the bubble point pressure is reached lower in the tubing or also in the formation itself. Indeed, the location of asphaltene deposition is found in studies published in the literature to move from the top of the tube to the bottom and into the reservoir over a period of time as the pressure of the reservoir is depleted and the spot where the pressure of the bubble point is reached shifts farther out into the reservoir.

Changes in the composition of crude oil by the injection of fluids, such as CO₂ or lean gas, may cause asphalt deposition (Monger et al. 1987; Monger et al. 1991). The risk of asphaltene precipitation during lean gas and CO₂ injection has been reported in many studies (Browne et al., 1995; Zain et al. 1999). Significant temperature variations can also cause the deposition of asphaltene (Leontaritis et al. 1989; Kawanaka et al. 1991).

Removal of asphaltene deposits. The treatment of asphalt residues often involves the use of solvents or mechanical equipment. The solvents used to dissolve asphalt are very distinct from those used by paraffin. Since asphaltene is soluble in aromatic solvents, mixtures of aromatic solvents such as xylene have been used to extract asphaltene deposits (Schantz et al. 1991).

In general, the conventional deposits treatments tend to tackle one type of deposit. Solvent treatments work on the organic deposit types, and acidizing treatments are selected for inorganic deposit types, or both one after another to remove different deposit types. The deposits tend to originate from both crude oil and water, and tend to precipitate over each other (Mohamed et al. 2016).

Novelty of New deposits Remedy

Most of the deposit remedies are designed to remove the organic deposits from the wellbore, and in this new method the remedy is designed to tackle both organic and inorganic deposits. The novelty of the new thermochemical method is the multiple objectives that can be achieved when applying this method. Mainly, the method consists of two chemicals mixed in the wellbore at the target zone to achieve the objective. The main reactants of this method are sulfamic acid and sodium nitrite, and the product of the reaction are acidic salt, water, nitrogen gas, heat, Equation 1.



This method will work on both organic and inorganic deposits. In addition, it will stimulate the near wellbore area. Therefore, this method performs three objectives at the same time; the reaction generates heat, which is enough to liquefy the organic deposits, the product of the reaction is an acidic salt, which will tackle the inorganic deposits, and will stimulate the formation at the near wellbore zone. The reaction generates nitrogen gas, which will not affect the process or interfere with the reaction; however, it will help to flowback the well after the treatment.

Lab Experimental Work:

Figure 1 shows the behavior of the reaction when mixing sodium nitrite with sulfamic acid. The reaction produces nitrogen gas that is indicated by the bubbles in the test tube.

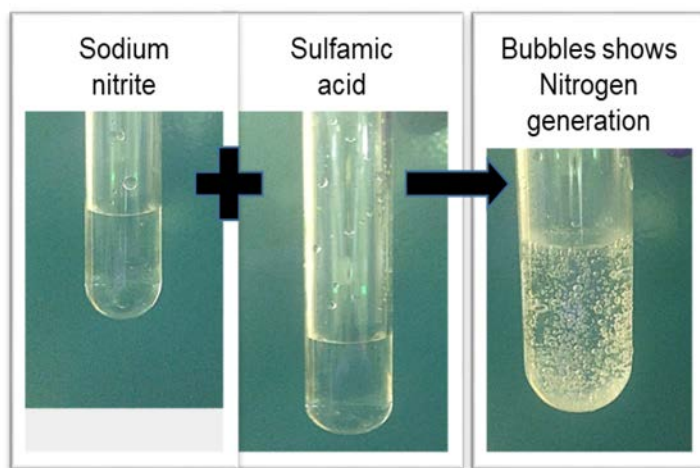


Figure 2—The reaction between sodium nitrite and sulfamic acid.

The amount of nitrogen gas depends on the concentration of the reactants. Another experiment using a closed reactor to conduct the reaction to check and observe the pressure behavior of the reaction. Gradually mixing 800 ml of the reactants into a 1000 ml reactor chamber result in increasing of the pressure from ambient to about 1200 psi; Figure 3.

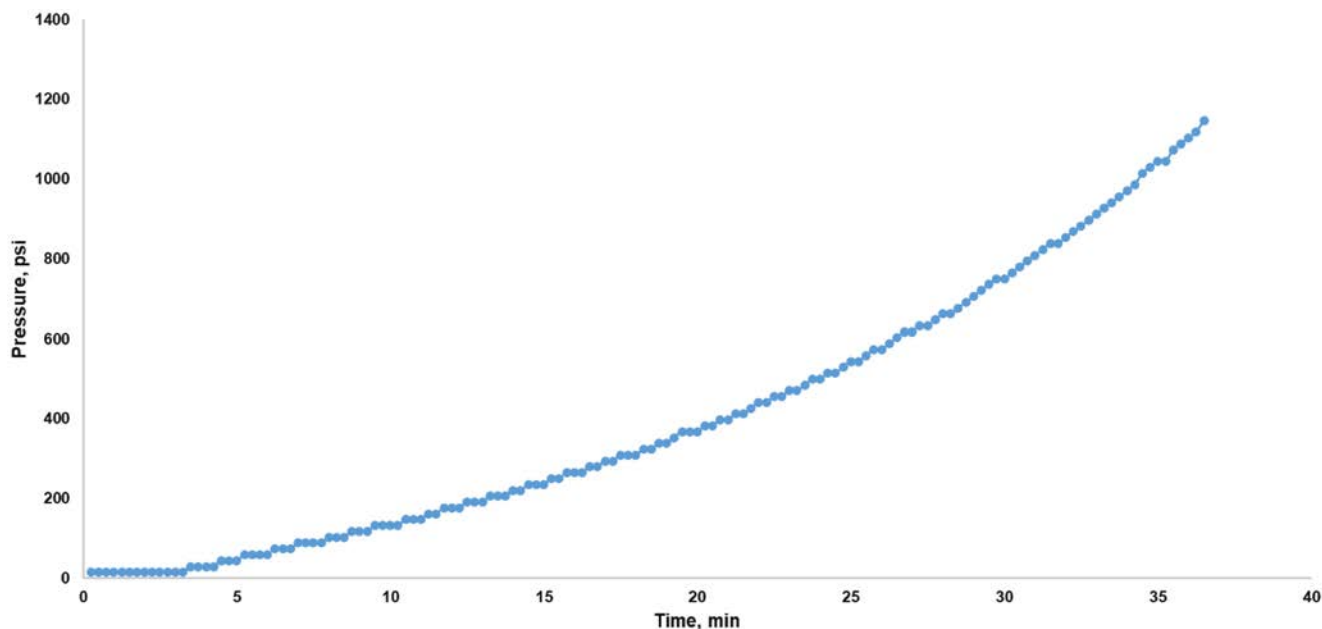


Figure 3—The pressure increase during the reaction between sodium nitrite and sulfamic acid.

The pressure increase constitutes the large amount of gas that is generated as the product of the reaction. In addition, the rapid change in temperature, during the reaction, indicates the amount of heat resulting from the reaction. A thermometer device records the behavior of the temperature during the reaction, which shows a significant change in temperature during the mixing step of the two chemicals; Figure 4.

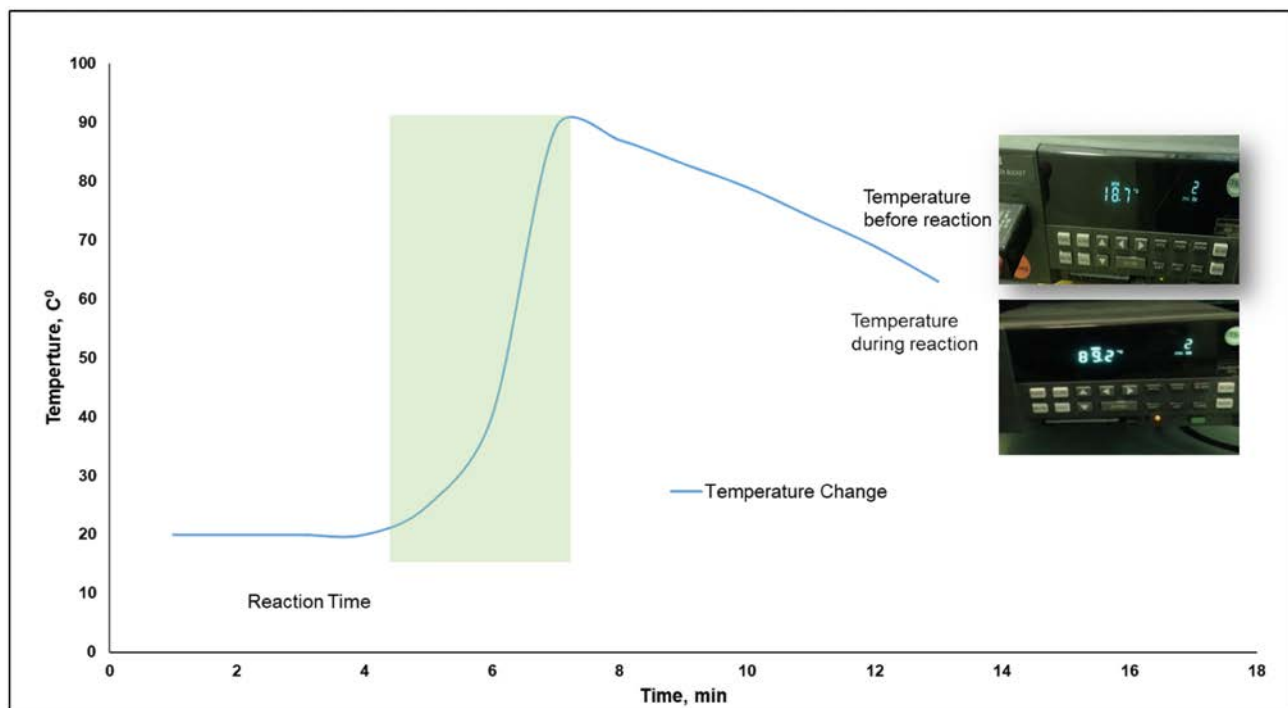


Figure 4—Temperature change during the reaction.

The unique mechanism of the reaction makes it applicable means to remove oil well deposits. The lab experimental work shows an effective result on a field wellbore deposit sample. Figure 5 shows the decomposition of the deposit sample when treated with the thermochemical reaction recipe.

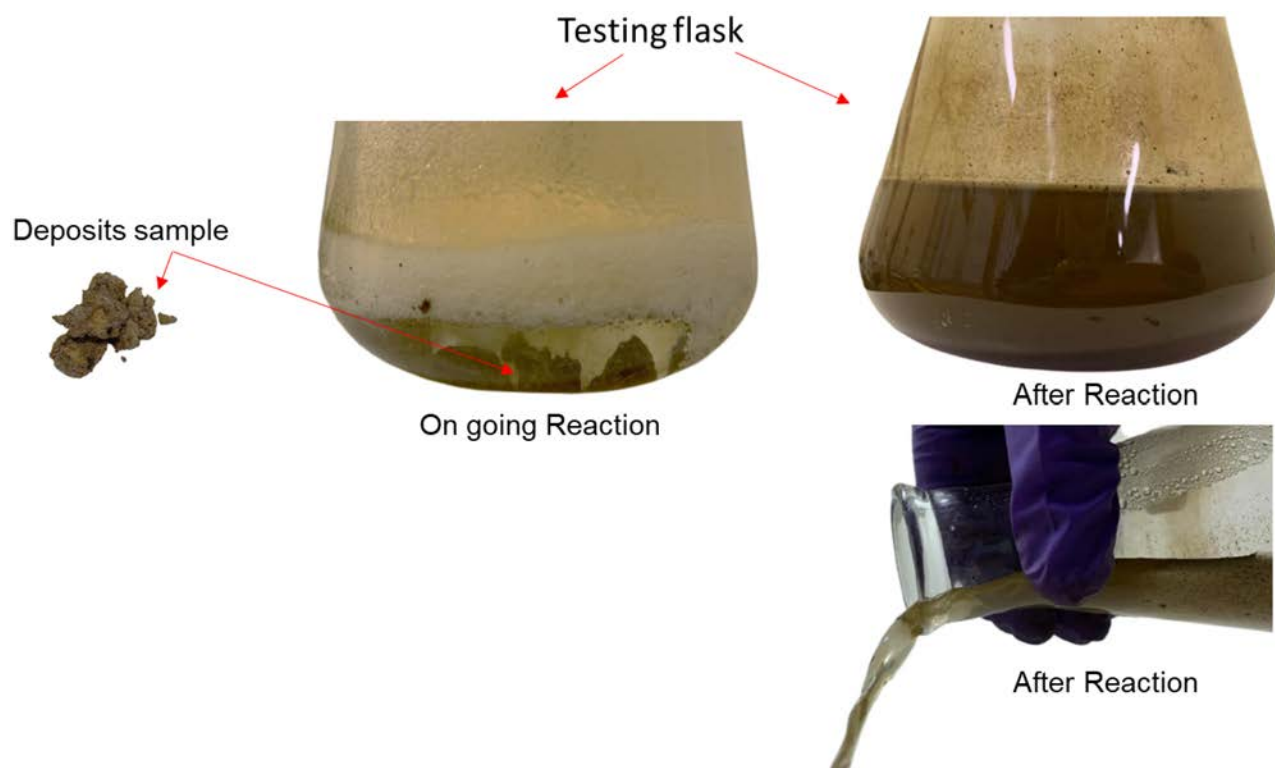


Figure 5—Reaction effect on deposit samples.

The deposits breakdown into small parts when the heat of the reaction mobilizes the rigid organic deposit, and acidic salt, which is one of the reaction products, and tackle the wedged inorganic deposit in the main organic material.

The mixture of the reaction, which produces acidic salt (sodium bisulfate, NaHSO_4), is utilized as a stimulation chemical. A coreflooding experiment is utilized to examine the efficiency of the acidic salt to stimulate the formation. First, brine, 2% KCl, is injected into a carbonate plug sample to establish the base permeability. The acidic salt (product of the reaction) is then, injected after the brine. After that, the brine is injected again to find the final permeability. The test shows 65% increment in permeability (Figure 6).

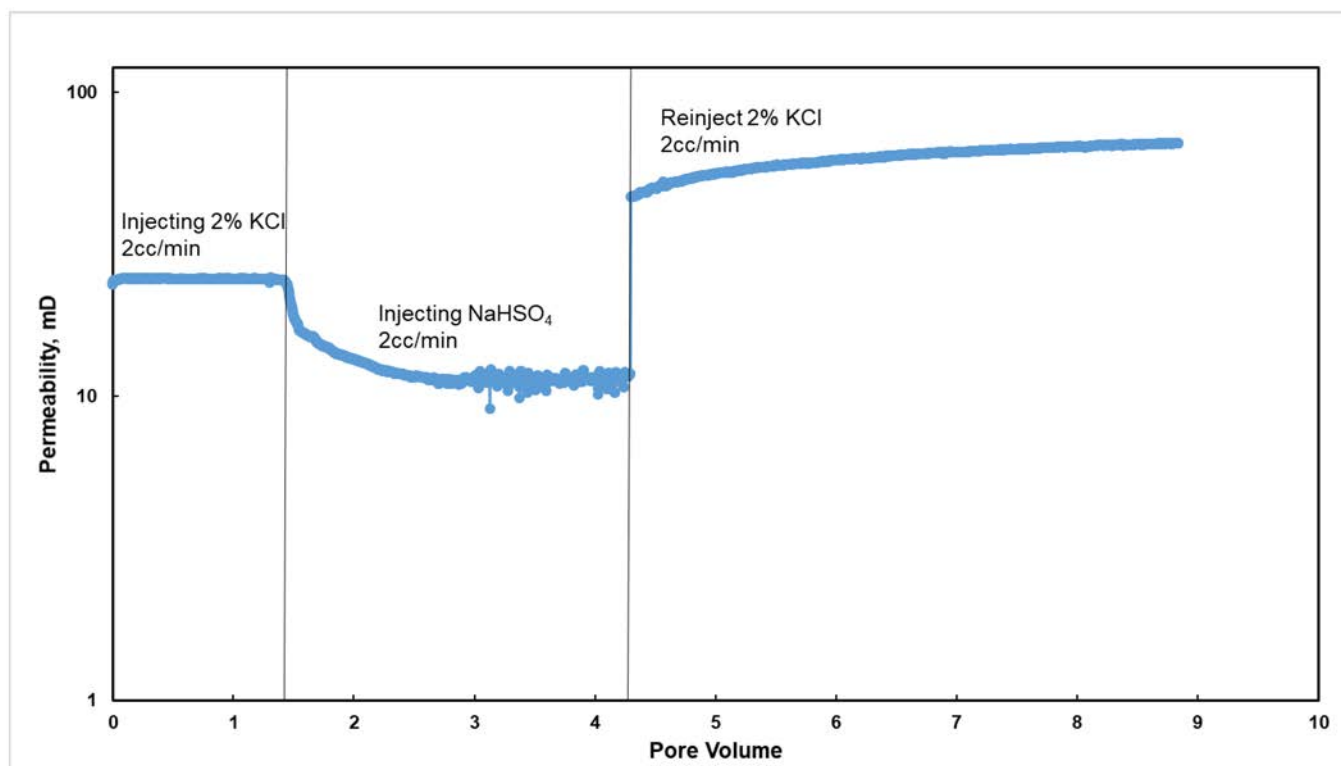


Figure 6—Permeability improve after using the acidic salt in carbonate plug sample.

In addition, the clear wormhole that is created in the plug concretes the ability of the mixture to stimulate the wellbore; Figure 7.

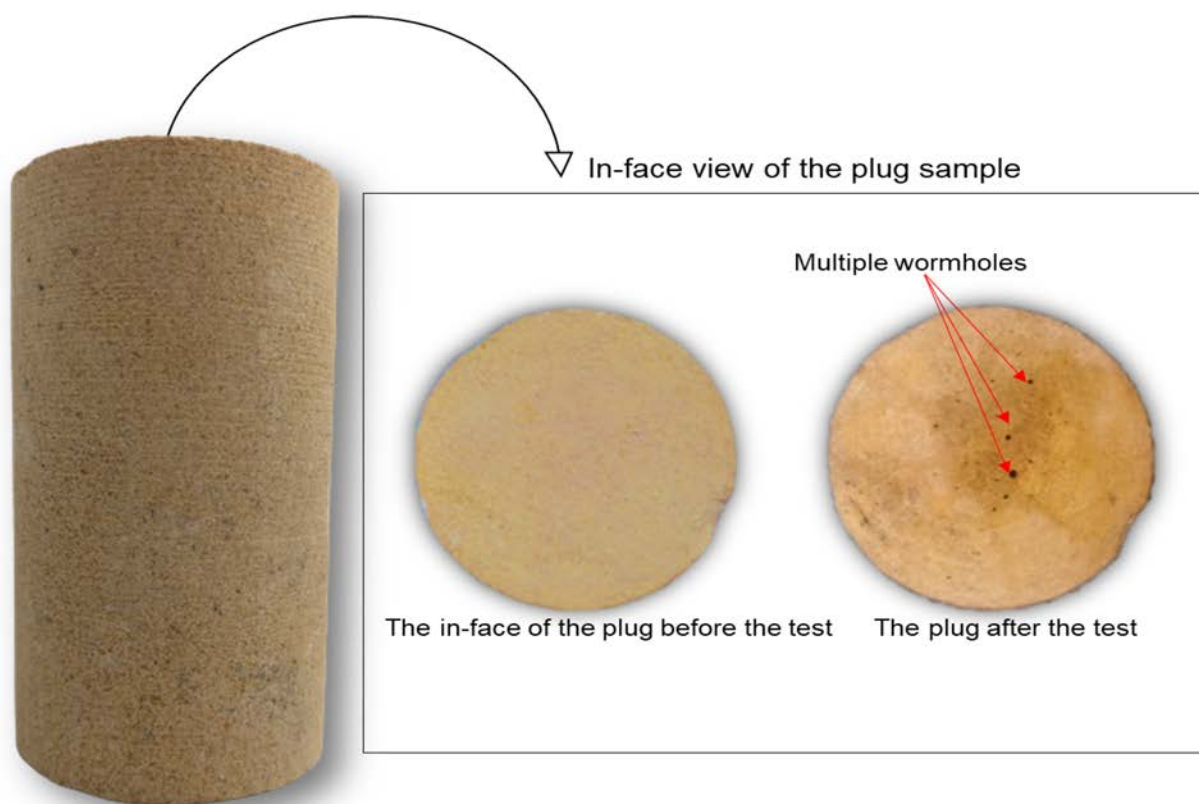


Figure 7—Treated carbonate plug sample using the mixture of the reaction.

For field application, it is important to use a scale inhibitor to prevent the precipitation of sulfate scale. The mixture of the reaction contains sulfate ions, and the dissolution of carbonate, either calcium scale or carbonate rock from the formation, can be a source of calcium ions. The presence of both ions, with abundant amount, at the suitable pH and temperature will lead to calcium sulfate scale. Methylene phosphonic acid is an effective scale inhibitor under various temperatures, and in an acidic environment (He J., Arensman D. and Nasr-El-Din HE, 2013).

Conclusion

Damage from well deposits leads to a reduction in production, and sometimes fully plugs the wellbore, and the porous media of the formation. The deposits mainly consist of different organic material; however, some other inorganic materials stick to the organic materials, making different layers of organic/inorganic deposits impeded with each other or covering each other.

The methodology of this thermochemical reaction can be a useful solution for the removal of well deposits. This methodology can achieve three objectives in one treatment; remove the organic deposits, tackle inorganic deposits, and stimulate the near wellbore area. The physical and chemical properties, including heat, and acidic salt, that is associated with this chemical reaction are suitable to tackle different types of deposits including organic and inorganic deposits. The use of this method can lead to the breakdown of deposits and remove them with the flowback of the well. Importantly, proper scale inhibitor must be considered to prevent sulfate and calcium ion from crystallization, and prevent scale precipitation during the treatment.

References

1. Bailey, J. Claire, and Stephan J. Allenson. "Paraffin Cleanout in a Single Subsea Flowline Using Xylene." *SPE Proj Fac & Const* **4** (2009): 1–7. doi: <https://doi.org/10.2118/125131-PA>
2. Bohon, W.M., Blumer, D.J., Chan, A.F. and Ly, K.T. 1998. Novel chemical Dispersant for removal of organic/inorganic "Schmoo" scale in produced water injections systems. *NACE International, Corrosion* **98**. Paper No. 93
3. Browne, S.V., Ryan, D.F., Chambers, B.D., Gilchrist, J.M., and S.A. Bamforth. "Simple Approach to the Cleanup of Horizontal Wells With Prepacked Screen Completions." *J Pet Technol* **47** (1995): 794–800. doi: <https://doi.org/10.2118/30116-PA>
4. Eroini, Violette, Anfinsen, Hilde, and Anthony F. Mitchell. "Investigation, Classification and Remediation of Amorphous Deposits in Oilfield Systems." *Paper presented at the SPE International Symposium on Oilfield Chemistry*, The Woodlands, Texas, USA, April 2015. doi: <https://doi.org/10.2118/173719-MS>
5. Fan, Y. and Llave, F. M. 1996. Chemical Removal of Formation Damage From Paraffin Deposition Part I - Solubility and Dissolution Rate. *Presented at the SPE Formation Damage Control Symposium*, Lafayette, Louisiana, USA, 14-15 February. SPE-31128-MS. <http://dx.doi.org/10.2118/31128-MS>
6. He J, Arensman D, Nasr-El-Din HE (2013) Effectiveness of Calcium Sulfate Scale Inhibitors in Spent Hydrochloric Acid/Seawater System. *J Pet Environ Biotechnol* **4**: 159. doi:10.4172/2157-7463.1000159
7. Hirschberg, A., deJong, L.N.J., Schipper, B.A., and J.G. Meijer. "Influence of Temperature and Pressure on Asphaltene Flocculation." *SPE J.* **24** (1984): 283–293. doi: <https://doi.org/10.2118/11202-PA>
8. Horsup, D.I., Dunstan, T.S. and Clint, J.H. 2007. A break-through corrosion inhibitor technology for heavily fouled systems. *NACE International, Corrosion* 2007. Paper No. 07690
9. Jones, C.R., Downward, B.L., Hernandez, K., Curtis, T. and Smith, F. 2010. Extending performance boundaries with third generation THPS formulations. *NACE International, Corrosion* 2010. Paper No. 10257
10. Kawanaka, Seido, Park, S.J., and G.A. Mansoori. "Organic Deposition From Reservoir Fluids: A Thermodynamic Predictive Technique." *SPE Res. Eng.* **6** (1991): 185–192. doi: <https://doi.org/10.2118/17376-PA>
11. Leontaritis, K.J. "Asphaltene Deposition: A Comprehensive Description of Problem Manifestations and Modeling Approaches." *Paper presented at the SPE Production Operations Symposium*, Oklahoma City, Oklahoma, March 1989. doi: <https://doi.org/10.2118/18892-MS>
12. McClafflin, G.G., and D.L. Whitfill. "Control of Paraffin Deposition in Production Operations." *J Pet Technol* **36** (1984): 1965–1970. doi: <https://doi.org/10.2118/12204-PA>
13. Misra, S., Baruah, S., and Singh, K. 1995. Paraffin Problems in Crude Oil Production and Transportation: A Review. *SPE Prod & Oper* **10** (1): 50–54. SPE-28181-PA. <http://dx.doi.org/10.2118/28181-PA>
14. Mohamed, Anwarudin Saidu, Alian, Sima Sheykh, Singh, Jasvinder, Singh, Rajindar, Goyal, Arvindkumar, and Gurunathan Munainni. "Remediation of Well Impaired by Complex Organic Deposits Embedded with Naphthenate and Contaminated with Inorganics." *Paper presented at the Offshore Technology Conference Asia*, Kuala Lumpur, Malaysia, March 2016. doi: <https://doi.org/10.4043/26524-MS>
15. Monger, T.G., and D.E. Trujillo. "Organic Deposition During CO₂ and Rich-Gas Flooding." *SPE Res Eng* **6** (1991): 17–24. doi: <https://doi.org/10.2118/18063-PA>

16. Monger, T.G., and J.C. Fu. "The Nature of CO₂-Induced Organic Deposition." *Paper presented at the SPE Annual Technical Conference and Exhibition*, Dallas, Texas, September 1987. doi: <https://doi.org/10.2118/16713-MS>
17. Newberry, M.E., and K.M. Barker. "Formation Damage Prevention Through the Control of Paraffin and Asphaltene Deposition." *Paper presented at the SPE Production Operations Symposium*, Oklahoma City, Oklahoma, March 1985. doi: <https://doi.org/10.2118/13796-MS>
18. Schantz, S.S., and W.K. Stephenson. "Asphaltene Deposition: Development and Application of Polymeric Asphaltene Dispersants." *Paper presented at the SPE Annual Technical Conference and Exhibition*, Dallas, Texas, October 1991. doi: <https://doi.org/10.2118/22783-MS>
19. T. F. YEN (1974) Structure of Petroleum Asphaltene and Its Significance, *Energy Sources*, 1:4, 447–463, DOI: 10.1080/00908317408945937
20. Thomas, D.C. "Selection of Paraffin Control Products and Applications." *Paper presented at the International Meeting on Petroleum Engineering*, Tianjin, China, November 1988. doi: <https://doi.org/10.2118/17626-MS>
21. Wang, Biao, and Lijian Dong. "Paraffin Characteristics of Waxy Crude Oils in China and the Methods of Paraffin Removal and Inhibition." *Paper presented at the International Meeting on Petroleum Engineering*, Beijing, China, November 1995. doi: <https://doi.org/10.2118/29954-MS>
22. Zain, Zulkeffeli M., and Mukul M. Sharma. "Cleanup of Wall-Building Filter Cakes." *Paper presented at the SPE Annual Technical Conference and Exhibition*, Houston, Texas, October 1999. doi: <https://doi.org/10.2118/56635-MS>