

Enhanced Scale Inhibitor Squeeze Treatment with a Newly Developed Chemical Additive

Ping Chen
Multi-Chem, Halliburton
Dhahran Techno Valley
Dhahran 31261, Dammam
Saudi Arabia

Thomas Hagen
Multi-Chem, Halliburton
Citibank Tower , Dubai
UAE

Tawfik Al-Ghamdi
Multi-Chem, Halliburton
Dhahran Techno Valley
Dhahran 31261, Dammam
Saudi Arabia

Mohamed Hamam
Multi-Chem, Halliburton
Dhahran Techno Valley
Dhahran 31261, Dammam
Saudi Arabia

Zhiwei (David) Yue
Multi-Chem, Halliburton,
Houston Global Technology Center
Houston, Texas 77032
United States

Hicham El Hajj
Multi-Chem, Halliburton
Dhahran Techno Valley
Dhahran 31261, Dammam
Saudi Arabia

ABSTRACT

An oilfield in the Middle East experienced both strontium sulphate and calcium carbonate scale depositions. The downhole scale inhibitor squeeze treatment strategy was initiated as one of the most effective methods to control scale depositions. The field's chalk formation reservoir presented these challenges:

- High salinity formation brine with a calcium concentration more than 15000 ppm.
- Low water cut, < 10% in most wells.
- Limestone formation with strong downhole fluid cross flows.
- Relatively low reservoir pressure and gas lift is often utilized.

The reservoir temperature is about 80°C and pressure is less than 3000 psi. Due to concerns on formation damage, the treatment volumes were often limited to the small amounts of main pills and overflush. As a result, the scale inhibitor treatment life was impacted by these challenges.

Since 2019, a research program has been initiated to select a suitable scale inhibitor candidate. In the meantime, the lab test plan was set up to develop an effective squeeze treatment additive to enhance the treatment life. Through the test program, a phosphonate scale inhibitor was identified and a new chemical additive was developed to meet the target of squeeze treatment enhancement.

Field trials were carried out and a comparison between with and without the chemical additive was made. The initial field trial results demonstrated that the newly developed chemical additive can significantly enhance a downhole squeeze treatment lifetime by more than 30%.

In this paper, full laboratory test results are presented. The field trial design methodology for how the chemical additive was applied is outlined. The field data with and without the application of the chemical additive are discussed.

Keywords: Scale inhibitor squeeze treatment, scale inhibitor, minimum effective scale inhibitor concentration, phosphonate, enhanced scale inhibitor retention, squeeze treatment life extension.

INTRODUCTION

Scale inhibitor squeeze treatment technology has often been employed in the industry as one of the best options when a scale control treatment strategy is considered to prevent scale depositions in a reservoir and downhole tubing. It offers a cost effective method without requirements of extra power once the scale inhibitor is placed in a reservoir. The treatment process normally involves several steps as follows:

- **Pre-flush with a specially designed fluid:** The injected pre-flush fluid can push the most formation brine away deeper into the formation to reduce the incompatibility issue between forth coming injected chemical and formation brine. The cooling effect caused by the pre-flush fluid injection can also reduce the rate of the scale inhibitor adsorption and hence more scale inhibitor can be adsorbed on the far distance of the reservoir rocks from well-bore. The surfactant and squeeze enhancing additives are often added in the pre-flush fluids to change the rock wettability in favor of the inhibitor adsorption to extend squeeze treatment life.
- **Scale inhibitor main pill at concentration range typically between 5 and 20%:** Following the pre-flush, the inhibitor pill is injected into a formation. During this stage, the pumping injection pressure is carefully monitored. Any sign of the sudden pressure spiking could be a sign of the incompatibility problem between the injected fluid and reservoir.
- **Well shut-in:** After the main pill injection, the well is shut in between 6 and 24 hours. Phosphonate scale inhibitors have a faster adsorption rate than a polymer scale inhibitor. The shut-in time normally takes over 24 hours for a polymer scale inhibitor.
- **Well production:** Following the shut-in, wells are putted back to normal productions. The brine samples are collected regularly for the ions and residual scale inhibitor analysis. Once the residual scale inhibitor concentration drops below MIC (minimum inhibitor concentration) required to control scale deposition, a new scale inhibitor squeeze treatment is needed.

A successful scale inhibitor squeeze treatment must meet the following criterion:

- The inhibitor must have good retention/release properties to offer a long-term treatment life.
- Inhibitor MIC should offer a low MIC typically between 1 – 20 ppm.
- No formation damage when scale inhibitor is placed in the reservoir.

Obviously, meeting the treatment design life is one of the key challenges. The short squeeze treatment can often result in a high frequency of treatment times and hence results in a high cost of pumping, labor and logistics, etc. In order to meet the design target of the squeeze treatment life, phosphonate scale inhibitors are often selected as good candidate squeeze products due to its excellent property in the inhibitor adsorption on the reservoir rocks. It is believed that squeeze scale inhibitors can be retained in the reservoir by a number of mechanisms including adsorption and

precipitation. For an adsorption squeeze treatment, an inhibitor adsorption level is affected by several factors such as inhibitor type and concentration, brine chemistry, pH, reservoir temperature and rock mineralogy. At lower pH, the weakly acidic scale inhibitor will tend to be more protonated/associated and thus can be retained on the rock surface through hydrogen bonding and Van der Waals forces. At higher pH, the scale inhibitor will tend to be more dissociated and thus can be retained on the rock surface by a number of mechanisms including weak Van der Waals forces and static electric forces due to metal ion bridging.¹

A number of studies have been published in the area of enhancing the scale inhibitor treatment life by the addition of chemical additives in the treatment fluids such as pre-flush, main pill and over-flush fluids. A method using miscible displacement to extend squeeze lifetime was introduced since 1997. The method involves an oil-in-water microemulsion-based scale inhibitor formulation which displayed a significant extension in treatment life compared with an aqueous baseline treatment.²⁻⁵ In 2000, Bache reported that the inhibitor retention could be enhanced by the ester cross-linking of polycarboxylic scale inhibitors, leading to an improved inhibitor return.⁶ Further chemical additives have been identified that could be used to provide an effective method to increase an inhibitor retention on the rock surfaces. It was reported that the chemical additives are positively charged and could be rapidly adsorbed onto negatively charged rock surfaces. These additives were usually applied as a clay stabilizer. As a result, the rock surface charge is modified to the more positively charged surface such as sandstone surfaces, creating a less repulsive surface to the negatively charged scale inhibitors. In other words, the adsorbed additives present a less negatively charged surface than the rock itself, altering the double layer and thereby the interaction forces between chemicals and the mineral surface with which the scale inhibitor compounds can interact. The inhibitor is expected to be adsorbed on the additive coated rock surfaces through static electric forces, hydrogen bonding and Van der Waals force. The pre-treatment of the reservoir zone with the additive or a combination of the squeeze chemical and the additive is therefore expected to enhance the scale inhibitor adsorption through a bridging-type mechanism. These publications have outlined the experimental results, treatment methods and field data for which an enhanced inhibitor treatment lifetime was achieved.⁷⁻¹⁰ A further proposed mechanism and enhanced treatment life was also highlighted by adding the positive charged additives in the over-flush fluids respectively.^{11,12} Both papers showed that the additions of ionic polymer additives could improve squeeze treatment lifetimes as part of the over flush. The field data demonstrated improved chemical retention and scale inhibitor returns compared to treatments without chemical additive in the over flush.

Based on the literature review, it is believed that a wide range of chemical additives should be available for an alternative/cost effective product functioning in the enhanced scale inhibitor squeeze treatment. Under a research program, an extensive study has been carried out to develop a new additive product. In this paper, detailed laboratory test results are presented to demonstrate the effect of newly developed surfactant on the enhanced scale inhibitor retention. The field treatment data are also presented. In addition, the laboratory test results on the selection of scale inhibitor are outlined.

EXPERIMENTAL PROCEDURE

Under the study program, multiple laboratory tests were designed to investigate (i) enhanced scale inhibitor adsorption; (ii) inhibitor compatibility with brine; and (iii) inhibitor efficiency against the scale. Laboratory test procedures are presented in the following sections.

Enhanced scale inhibitor adsorption

The scale inhibitor tested is a phosphonate. The additive used for the enhanced scale inhibitor adsorption is a surfactant, which is often used as a clay stabilizer. Clean, acid washed sand (grain size 0.1-0.3mm), supplied commercially is used as the test substrate.

A 2% KCl solution was prepared by weighing out KCl and making up to the mark in a 1L volumetric flask. 10,000ppm solutions of additive surfactant plus a solution containing 10,000ppm phosphonate was prepared by accurately weighing out 1g of each chemical and making up to the mark in a 100mL volumetric flask using the 2 % KCl solution.

16 grams of clean sand was added to the required number of clean, glass powder jars. Volumes of each of the candidate agent solutions were then added to the jars as follows:

Jars 1-2: 32mls of 10,000ppm additive surfactant in 2% KCl
 Jars 3-4: 32mls of in 2% KCl
 Jars 5-6 32mls of 2% KCl without sand (control samples)

Each jar was stirred with a glass rod to ensure thorough mixing before being placed into a pre-heated oven where the temperature was pre-set at 90°C for 4 hours.

After given time interval, a 20 ml of the supernatant was carefully taken from each jar. Cares were taken to avoid removing any of the sand particles from the jar. 20 mL of 10,000 ppm phosphonate inhibitor in 2% KCl was then added to each jar to replace the volume of the supernatant removed. The solutions were again stirred with a glass rod before being returned to the oven for a further 24 hours. Following the second time period, 10 ml of supernatant samples were removed from each jar. The samples were then analyzed for phosphonate concentration remained in the solutions. The inhibitor adsorption of each sample was then worked out as mg of scale inhibitor vs gram of sand.

Scale inhibitor compatibility with produced brine

Table 1 Water Chemistry

Ion	Concentration	Unit
Sodium (Na ⁺)	58767	(mg/L)
Potassium (K ⁺)	1363	(mg/L)
Magnesium (Mg ²⁺)	4405	(mg/L)
Calcium (Ca ²⁺)	14661	(mg/L)
Strontium (Sr ²⁺)	408	(mg/L)
Iron. (Fe ²⁺)	112	(mg/L)
Chloride (Cl ⁻)	132062	(mg/L)
Sulfate (SO ₄ ²⁻)	692	(mg/L)
Bicarbonate (HCO ₃ ⁻)	113	(mg/L)
pH	6.69	

Brine compatibility tests were performed under the following conditions: