ONE-STEP CALCIUM SULFATE SCALE REMOVAL TECHNIQUE PROVIDES COST-EFFECTIVE REMEDIAL TREATMENT*

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ABSTRACT

Removal of calcium sulfate scale from wells is presently accomplished by several methods including scraping and chemical treatments. The most widely used chemical methods employ either: 1) a time-consuming and moderately expensive two-step conversion/ acid dissolution process or 2) a very slow reacting and expensive, alkaline chelating agent treatment.

In an effort to lower the overall scale removal treatment cost and circumvent the objectionable qualities of the commercially available chemical treatments, a one-step calcium sulfate scale removal technique has been developed and successfully used in over 100 wells. This remedial technique has been employed to increase injectivity in injection wells, increase production in producing wells, and open up perforations to permit more efficient primary stimulation or remedial treatment of producing zones. Treatment costs range from $2000 to $5000, depending on whether or not additional primary stimulation or remedial treatment fluids are to be incorporated with the calcium sulfate scale removal fluid. Posttreatment production increases have ranged from 50% to 10 fold and treatment payout has typically required 30-45 days of post-treatment production.

INTRODUCTION

Calcium sulfate scale deposits occur in producing oil and gas wells normally in one of two forms - anhydrite or gypsum. Gypsum ($CaSO_4 \bullet 2H_2O$) is typically observed at temperatures of 104°F (40°C) or less and low pressures. Anhydrite ($CaSO_4$) is more common at higher temperatures. Above 104°F (40°C), the solubilities of both gypsum and anhydrite decrease with increasing temperature. Hence, calcium sulfate scale deposits can form in injection wells if both the calcium and sulfate ion contents are high in the injected water or if an incompatible water is injected. The solubility of calcium sulfate in water increases with increasing pressure. Consequently, pressure drops can be a major cause of calcium sulfate scale in producing wells. A pressure drop around the wellbore can create scale back in the formation as well as in the perforations and tubing. Typical of many scales, as the salinity of the water increases, the solubility of calcium sulfate increases [A 55,000 mg/l sodium chloride solution will dissolve 3 times as much gypsum at 104°F (40°C) as will fresh water at the same temperature. Above 150,000 mg/l sodium chloride, the solubility of calcium sulfate begins to decrease.].

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Calcium sulfate is considerably more soluble in water than is calcium carbonate, but considerably less soluble than calcium carbonate in typical oilfield acids [The maximum solubility of calcium sulfate in hydrochloric acid is only 1.8 wt. % at 77 °F (25 ° C) and atmospheric pressure.]. Consequently, alternatives to hydrochloric acid have been necessary for the efficient removal of calcium sulfate scales.

Conventional Scale Removal Techniques

Removal of calcium sulfate scale has historically been accomplished using several methods including scraping, early on, and more recently various chemical treatments. One of the earliest chemical treatments involved strong caustic solutions:

$$CaSO_4 \cdot 2H_2O \quad + \quad 2\ NaOH \longrightarrow Ca(OH)_2 \ + \ Na_2SO_4 \quad + \quad 2H_2O$$

These treatments required continuous wellbore circulation in order to flush off the surface layer of water insoluble calcium hydroxide reaction product. Even with continuous circulation, occlusion problems and the inherently slow reaction prevented efficient removal of the wellbore scale buildup. Normally a second stage treatment with hydrochloric acid was required to completely remove the calcium hydroxide. The strong caustic solutions also caused corrosion of the tubulars.

A more rapid reaction was effected when the scale deposit was treated with carbonate or bicarbonate solutions:

$$CaSO_4 \cdot 2H_2O \quad + \quad (NH_4)_2CO_3 \longrightarrow (NH_4)_2SO_4 \quad + \quad CaCO_3 \quad + \ 2H_2O$$

$$CaSO_4 \cdot 2H_2O \quad + \quad 2NH_4HCO_3 \longrightarrow CaCO_3 \quad + \ CO_2\uparrow \ + \quad (NH_4)_2SO_4 \ + \ 3H_2O$$

Even though the reaction was more rapid than with the strong caustic solutions, the surface buildup of water insoluble calcium carbonate reaction product led to occlusion problems and necessitated a second stage treatment with hydrochloric acid. Since carbon dioxide was evolved as a reaction product of the bicarbonate treatments, the reaction was observed to be inhibited by elevated pressures.

In an effort to convert the calcium sulfate scale into an acid soluble reaction product without the corrosion problems inherent in the caustic treatments or the pressure sensitivity inherent in the carbonate/bicarbonate treatments, conversion reactions with salts of weak organic acids such as potassium glycolate became popular:

$$CaSO_4 \cdot 2H_2O \quad + \quad 2KC_2O_3H_3 \longrightarrow Ca(C_2O_3H_3)_2 \quad + \ K_2SO_4 \quad + \quad 2H_2O$$

These conversion reactions were slow and suffered from occlusion problems.

In an attempt to avoid the occlusion problems associated with the "converters" and the subsequent hydrochloric acid stage requirement, treatment with alkaline solutions of polyaminocarboxylic acid chelating agents such as ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were employed:

$$CaSO_4 \bullet 2H_2O \; + \; Na_4EDTA \longrightarrow CaNa_2EDTA \; + \; Na_2SO_4 \; + \; 2H_2O$$

These treatments were expensive, required long reaction times and elevated temperatures, and their high pH's caused corrosion problems.

In order to lower the treatment cost associated with the polyaminocarboxylic acid chelating agents; minimize the corrosion problems caused by the alkaline treatments; reduce the inefficiency of the occlusion-limiting reactions of the "converters"; and avoid the additional treatment cost and potentially prohibitive increase in water production in water-drive reservoirs caused by the subsequent acid treatments; a study was undertaken with the intention of developing an improved calcium sulfate scale removal technique.

DEVELOPMENT OF IMPROVED FORMULATION

The laboratory portion of this study focused on evaluating the calcium sulfate scale dissolving efficiency of the aforementioned conventional scale removal formulations and comparing them individually with blends of same and blends containing synergistic buffering and complexing agents. Initial screening tests revealed that the formulations containing salts of EDTA were the most efficient in dissolving the gypsum material employed.

A second round of tests was undertaken in order to identify the most efficient blend of EDTA salts and potentially synergistic additives. These tests were conducted at atmospheric pressure and temperatures of 80°F (27°C) and 120°F (49°C) in a thermostatically controlled waterbath and at 500 psi (3.45 MPa) and 120°F (49°C) in a pressurized cement curing chamber. The gypsum employed was 97% $CaSO_4 \bullet 2H_2O$ by analysis and was sieved to 6/20 mesh in order to standardize the particle size. All tests involved 24 hour exposure times and each gypsum solvent was diluted 1:1 by volume with deionized water prior to the test. The quantity of gypsum dissolved was determined gravimetrically and normalized to 1.00 with 1.00 representing the smallest quantity dissolved. Table 1 presents the results of the 120°F (49°C)/500 psi (3.45 MPa) tests.

The test results depicted in Table 1, consistent with earlier screening tests, indicate that under these test conditions, the addition of several synergistic additives can enhance the gypsum solvency of EDTA salts, while the addition of a buffer or alkali alone may not. Subsequent tests employing "Formulation 1" both with and without various penetrants and wetting agents identified an additional improvement in gypsum solvency resulting from the addition of an anionic surfactant. "Formulation 1" was thus modified to incorporate this surfactant.

In order to determine the effect of solvent-reacted gypsum upon subsequent contact with hydrochloric acid, an additional series of tests was performed. For this series, another sample of gypsum was employed. This sample was more granular and less flake-like in morphology than the previously used material. This sample also had a slightly higher purity (99+% $CaSO_4 \cdot 2H_2O$ by analysis). In addition to grinding the gypsum to 6/20 mesh, it was also washed with a chlorinated solvent to remove any hydrocarbons. This series of tests was performed at 103°F (40°C) in a pressurized chamber at 200 psi (1.38 MPa). The three most efficient formulations, as identified in the two prior series of tests, were tested in this series using the full strength gypsum solvents and the solvents diluted 1:1 by volume with deionized water. The gypsum samples were first exposed to the gypsum solvents for 24 hours under the aforementioned test conditions and the quantity of gypsum dissolved was determined gravimetrically. The reacted gypsum samples were then returned to the pressurized chamber and exposed to 15% hydrochloric acid for 1 hour at 103°F (40°C) and 200 psi (1.38 MPa). The additional quantity of gypsum dissolved was determined gravimetrically. Again the data were normalized to 1.00 with 1.00 representing the smallest quantity dissolved. Table 2 presents the results of this series of tests.

As observed previously, the test results depicted in Table 2 reveal that under these test conditions the addition of several synergistic additives can enhance the gypsum solvency of EDTA salts. The test results also indicate that subsequent contact of solvent-reacted gypsum with hydrochloric acid will lead to the dissolution of additional gypsum, as expected. The total quantity of gypsum dissolved by both treatments was significantly higher for "Formulation 1" than for the other formulations tested. The hydrochloric acid treatment of the "Formulation 3" reacted gypsum sample dissolved more additional gypsum than any of the other hydrochloric acid treatments, due ostensibly to the formation of more acid-soluble reaction products by "Formulation 3".

In comparing the results of the laboratory portion of this study with the aforementioned goals of same, it was concluded that by employing the surfactant-modified "Formulation 1", a significant amount of calcium sulfate scale could be dissolved at a reasonable cost (approximately $4.00-4.50 per gallon chemical cost to the end user). It was also concluded that this could be accomplished: 1) with a minimum of corrosion problems (pH of treatment fluid = 8-8.7); 2) without the occlusion problems associated with the pure "converters"; and 3) without the additional cost and potential dangers associated with pumping acid into an acid-soluble water-drive reservoir.

TREATMENT PROCEDURE

The key elements in effective downhole scale removal include using the proper chemical agent and employing an effective placement technique. Having developed a chemical formulation that had proven effective in dissolving calcium sulfate scales under typical exposure conditions, the next step was to develop an effective placement technique. Various placement techniques were attempted, all of which were designed to maximize the exposure of the treatment chemical to the calcium sulfate scale deposit for the length of time required under the specific exposure conditions (typically 8-16 hr). Since calcium sulfate scales typically form in the vicinity of maximum pressure drops, the bulk of the deposit is typically observed in close proximity to the perforations. Consequently, the treatment volume must be adequate to cover the perforations, the linear buildup in the tubulars, and several feet out into the formation.

The best placement technique attempted to-date has involved: 1) spotting the chemical treatment across the perforations using lease water or a 9 lb/gal (1078 kg/m^3) sodium chloride brine; 2) squeezing approximately 10-20 gallons (0.038-0.076 m^3) of the treatment through each open perforation, making sure that a suitable volume remains in the tubulars to cover the linear scale buildup in the tubulars; 3) allowing the treatment to soak for 8-16 hours; and then 4) flowing, pumping, or swabbing back the treatment prior to performing any subsequent chemical treatments such as a scale inhibitor treatment. If an acid breakdown of the formation is planned, it is best to do so after the chemical treatment, since this treatment will open up perforations that might not otherwise accept the acid, thus insuring a more complete acid breakdown of the formation. Two typical treatment procedures are outlined more fully in Figures 1 and 2.

FIELD RESULTS

From August of 1986 through August of 1987, over 100 wells were treated with this chemical formulation using the "squeeze and soak" placement technique. Some representative case histories are presented to illustrate the utility of this remedial treatment technique.

A 5000 ft (1524 m) well in Hockley County, Texas had been producing 60 bbl oil/D (9.6 m^3/D) and 490 bbl water/D (78.4 m^3/D) prior to treatment. After treatment with 555 gallons (2.10 m^3) of this chemical formulation followed by a scale inhibitor squeeze, the well sustained production levels of 95 bbl oil/D (15 m^3/D) and 432 bbl water/D (69.1 m^3/D).

A 1700 ft (518.2 m) well in Scurry County, Texas had been producing 20 bbl oil/D (3.2 m^3/D) and 58 bbl water/D (9.3 m^3/D) prior to treatment. After treatment with 500 gallons (1.89 m^3) of this chemical formulation followed by 3000 gallons (11.34 m^3) of 15% HCl, the well sustained production levels of 39 bbl oil/D (6.2 m^3/D) and 39 bbl water/D (6.2 m^3/D). Previous treatments of wells in this lease with 1500-3000 gallons (5.67-11.34 m^3) of 15% HCl alone had proven unsuccessful.

The injectivity of a 1700 ft (518.2 m) water injection well in Scurry County, Texas had declined to the point that the well would no longer accept fluid. After treatment with 500 gallons (1.89 m^3) of this chemical formulation followed by 4000 gallons (15.12 m^3) of 15% HCl, the well's injectivity increased to 125 bbl water/D (20 m^3/D) at 520 psi (3.59 MPa).

The average treatment costs for the wells treated to-date have been approximately $2000 without acid to $5000 with acid. Post-treatment production increases have ranged from 50% to 10 fold and treatment payout has typically required 30-45 days of post-treatment production.

CONCLUSIONS

1. EDTA salts were the most efficient individual compounds tested for dissolving calcium sulfate scale.

2. It is possible to enhance the calcium sulfate solvency of EDTA salt solutions by combining them with synergistic additives.

3. By employing a blend of EDTA salts and synergistic additives, a cost-effective calcium sulfate scale removal formulation was developed which can be used either as a one-step scale removal treatment or in combination with acid to enhance the stimulation of the reservoir.

4. A cost-effective "squeeze and soak" placement technique was developed which makes it possible to maximize the exposure of the treatment chemical to the calcium sulfate scale deposit.

5. Posttreatment production increases have ranged from 50% to 10 fold and treatment payout has typically required 30-45 days of posttreatment production.

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Table 1

120°F (49°C)/500 psi (3.45 MPa) GYPSUM DISSOLUTION TESTS

Formulation	Formulation Composition	Normalized Weight of Gypsum Dissolved
1	EDTA salt + buffer + glycolate salt + complexing agents	1.43
2	EDTA salt + buffer	1.24
3	EDTA salt + alkali	1.23
4	EDTA salt	1.00
5	EDTA salt	1.16
6	EDTA salt + buffer	1.10

Table 2

103°F (40°C)/200 psi (1.38 MPa) GYPSUM DISSOLUTION TESTS

Formulation	Formulation Composition	Dilution	Normalized Weight of Gypsum Dissolved by Gypsum Solvent	Normalized Weight of Gypsum Dissolved by 15% HCl
1	EDTA salt + buffer + glycolate salt + complexing agents	Full Strength	2.31	1.01
1	EDTA salt + buffer + glycolate salt + complexing agents	1:1	1.51	1.04
2	EDTA salt	Full Strength	1.37	1.00
2	EDTA salt	1:1	1.00	1.02
3	EDTA salt + alkali	1:1	1.30	1.76

TYPICAL TREATMENT PROCEDURE WITHOUT ACID BREAKDOWN STAGE

1. Spot the chemical treatment across the perforations using lease water or a 9 lb/gal (1078 kg/m^3) sodium chloride brine.
2. Squeeze approximately 10-20 gallons (0.038-0.076 m^3) of the treatment through each open perforation, making sure that a suitable volume remains in the tubulars to cover the linear scale buildup in the tubulars.
3. Let soak for 8-16 hours.
4. Flow, pump, or swab back the treatment.

Figure 1

TYPICAL TREATMENT PROCEDURE WITH ACID BREAKDOWN STAGE

1. Spot the chemical treatment across the perforations using lease water or a 9 lb/gal (1078 kg/m^3) sodium chloride brine.
2. Squeeze approximately 10-20 gallons (0.038-0.076 m^3) of the treatment through each open perforation, making sure that a suitable volume remains in the tubulars to cover the linear scale buildup in the tubulars.
3. Let soak for 8-16 hours.
4. Flow or swab back the treatment.
5. Perform acid breakdown using approximately 100-150 gallons per foot acid.
6. Flush with lease water or a 9 lb/gal (1078 kg/m^3) sodium chloride brine.
7. Flow or swab back the acid.
8. Return to production slowly.

Figure 2