Scale Inhibitor Squeeze Techniques

WAYNE ROBERTS
United Chemical Corporation

INTRODUCTION

Downhole scales commonly encountered in producing operations are often calcium carbonate and calcium sulfate, less frequently barium sulfate and strontium sulfate. The problems vary in severity, the deposits sometimes being sufficient to cause pump failures and to plug up the producing formation itself. The only effective method to inhibit scale formation downhole is squeeze treatment with a scale inhibitor.

CAUSES OF SCALE DEPOSITION

The general causes of calcium carbonate deposits are a pressure drop, increase in temperature, or mixing of incompatible waters. A pressure drop in combination with a release of dissolved gases can occur downhole. The release of dissolved gases or an increase in temperature will cause the following reaction:

$$Ca(HCO_3)_2 \rightarrow H_2O + CO_2 + CaCO_3$$

Calcium sulfate deposits are a very serious problem. This is particularly true where water flooding is in operation. The most frequent cause of calcium sulfate deposits is pressure drop. When the incoming fluids reach the well bore or fractures leading to the well bore, a pressure drop takes place. Some other causes for calcium sulfate deposits are mixing of incompatible waters, temperature change, evaporation and changing the chloride concentrations. The deposits can be the result of a combination of the above reasons.

Barium sulfate is also found but, fortunately, only in a few areas in the Permian Basin. Barium sulfate is almost insoluble under any conditions, and is caused by the commingling of waters containing barium and sulfate ions.

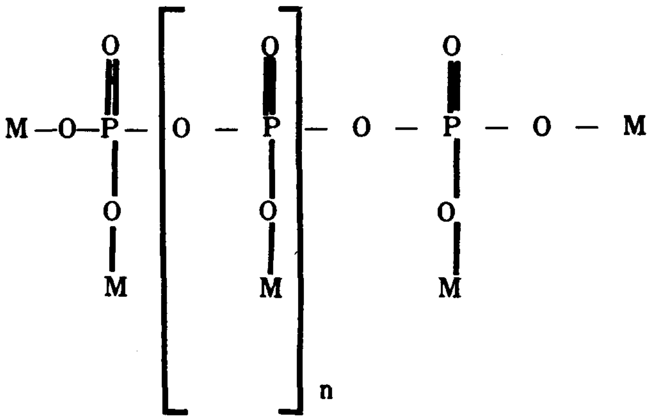
PREDICTING SCALING TENDENCY

It is helpful to predict where and what type of scale should be expected. A method for predicting the formation of scale is the use of water analysis and solubility data in oilfield brines. There are many publications on the solubility of calcium sulfate at one atmosphere and calcium carbonate at different temperatures. Most of the data in these publications are in good agreement. These data, together with the information from the water analysis, are used to predict potential scale deposition. Diagrams, empirical equations, or thermodynamic relations, are used to find the "maximum" solubility in oilfield brines.

The most successful method for inhibiting scale formation in and around the well bore is squeeze treatment with scale inhibitors. Choosing the correct squeeze chemical and squeeze techniques will be discussed below.

TYPICAL SCALE INHIBITOR STRUCTURES

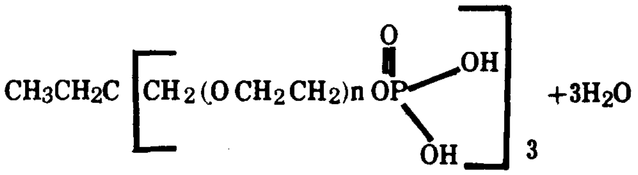
1. POLYPHOSPHATE



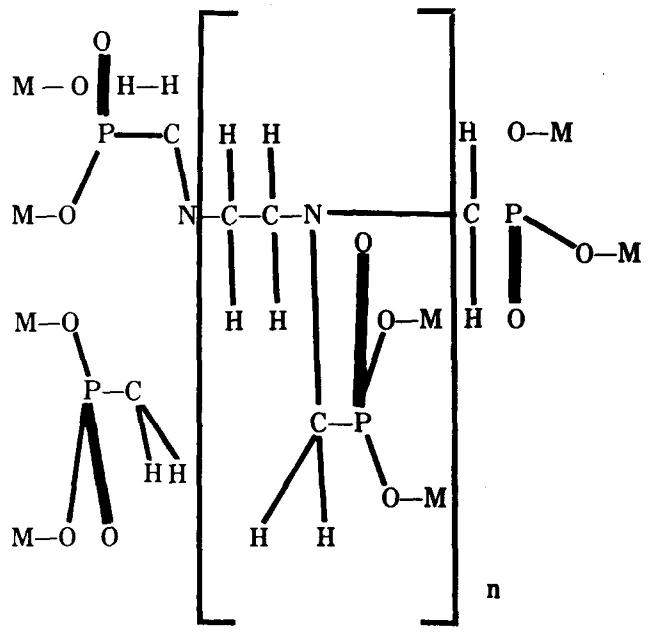
$$M-O-\overset{\overset{O}{\|}}{\underset{\underset{M}{|}}{\underset{O}{\underset{|}{P}}}}-\left[O-\overset{\overset{O}{\|}}{\underset{\underset{M}{|}}{\underset{O}{\underset{|}{P}}}}\right]_n-O-\overset{\overset{O}{\|}}{\underset{\underset{M}{|}}{\underset{O}{\underset{|}{P}}}}-O-M$$

In the diagram, (M) represents hydrogen or ammonium or alkaline metal ion content or combinations of these cations.

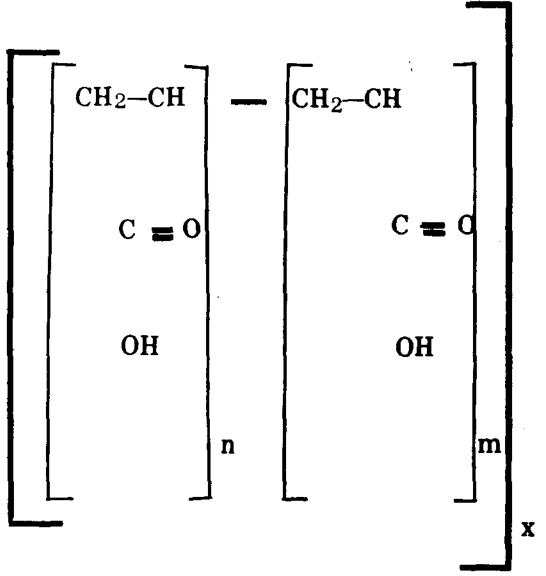
2. ETHOXYLATED PHOSPHATE ESTER



3. AMINO METHYLENE PHOSPHONATE



4. LONG CHAIN ORGANIC POLYACRYLATE POLYMER



The long chain polymer can be properly termed a polycarboxy-ethylene-polycarbamethylene long chain polymer in acid form. This type of polyacrylate polymer is especially useful for the prevention of calcium sulfate scale.

LABORATORY EVALUATION OF SCALE INHIBITORS

The laboratory evaluation of scale inhibitors recognizes that scale deposition is an equilibrium reaction. Thus, it is dependent on a number of factors—concentration of scale-forming ions, common and uncommon ion effect, temperature, pressure, equilibrium time, pH, seeding, flow rate, etc. The test procedures used to evaluate the inhibitors place particular emphasis on the property of scale inhibition. Surface characteristics, or the degree of scale adherence, is not normally investigated.

A typical laboratory scale test procedure is as follows:

Synthetic water of the following chemical composition is used to produce the $CaSO_4$ and $CaCO_3$ super saturation (relative to 1 atmosphere).

ION	Mg/l
Na++	2500
Ca++	2600
Mg++	800
Cl—	40,000
HCO_3—	1050
CO_3——	0
OH—	0
SO_4——	5000

The HCO_3—and SO_4—— ions are mixed into one container while the Ca++, Mg++, and Cl— ions are mixed in another container. All the ions are mixed at twice the required concentrations to allow for dilution when equal volumes from each bottle are finally mixed. A 1000 ml capacity stainless steel aging cell equipped with a moveable piston having a vented screw on top is used. Use a total volume of 600 ml of brine in your tests.

Take 300 ml of the water containing the Ca++ ion and place into the cell containing a stirring bar. With the solution stirring, add the scale inhibitor with a microliter syringe. Leave the solution stirring until after the addition of the oxygen scavenger. Add 300 ml of the SO_4—— water. After about 10 seconds of stirring, add several drops of a concentrated solution of $Na_2 SO_3$ containing trace amounts of $CoCl_2 .6H_2O$ to make about 100 ppm $Na_2 SO_3$ in the 600 ml solution. After about 10 seconds, mixing quickly, add about

0.2 gm of pure $CaSO_4 2H_2O$ in the form of a pellet or crystal. Insert the free piston into the cell making sure all air is displaced from below the piston, then tighten the relief screw. Assemble remainder of the cell and pressure to 180-220 psig with N_2 gas. Submerge this cell in water to check for leaks. Place cell in 110°F environment equipped with provisions to continually stir the fluids in the cells. Leave in this environment for two days or longer. Include a blank run containing zero inhibitor. At the end of the test, place the cells in a water bath for cooling to room temperature. Check N_2 pressure again. Quickly filter the reacted solution by gravity. Take aliquots and measure for Ca^{++}, HCO_3^-, and SO_4^{--}. Calculate from the blank sample the percent inhibition. The criterion is 100 percent inhibition for two days' duration or longer.

ADSORPTION—DESORPTION CHARACTERISTICS

Laboratory test methods can be used to compare the adsorption-desorption characteristics of different chemicals. One method used for laboratory comparison is described below:

1. A column is packed with a known volume of ground dolomite and another with sand. The same technique is used for both sand and dolomite.
2. Artificial brine water is passed through the column until the ground rock is covered. The volume of water used to cover the ground rock is recorded.
3. A 5 percent solution of the inhibitor in synthetic brine is passed through the column. The volume used is the same as the volume used above.
4. The column is shut in overnight.
5. The next morning a synthetic brine solution is passed through the column. Ten ml samples are collected and labeled. The flow of water is continuous until test results indicate a negative residual on two consecutive samples.

The above test is for comparison only. The same procedure should be followed on every test, or the results will be of little or no value.

SQUEEZE TECHNIQUE

Scale inhibitor squeeze techniques have been decided arbitrarily, or have been established by trial-and-error. The amount of inhibitor to be used, the amount of overflush and any diverting agent requirement will depend upon well completion data, amount and flow rate of produced fluids and field experience. Some typical squeeze procedures are described below.

Example 1

Completion and production data: Fifty feet of open hole producing 20 BWPD. The well is to be treated without a packer.

1. Pressure up on the tubing.
2. Mix 110 gal. of inhibitor in 50 bbl of fresh water and pump down annulus.
3. Overflush with 100 bbl of fluid plus the annular volume.
4. Shut in well for 24 hr and put back on production.
5. Regular samples should be collected to determine when the well should be resqueezed.

The 110 gal. of inhibitor used would protect the well for 220 mo if all of the inhibitor were desorbed at a regular rate of 20 ppm. Unfortunately, part of the chemical inhibitor will not desorb, part of it will never be in contact with incoming water and part of it will not be adsorbed, but will collect in small fractures and bleed back into the produced fluid.

The squeeze job should last from 12 to 24 months. Some jobs have lasted for more than two years.

Example 2

Completion and production data: 220 ft of open hole producing 200 BWPD. The well is to be treated without a packer.

1. Pressure up on the tubing.
2. Mix 165 gal. of inhibitor in 75 bbl of fresh water and pump one-half of this mixture down the annulus.
3. Pump 50 bbl of fluid behind the above mixture.
4. Pump 10 to 20 bbl of diverting agent and water down annulus. The amount of diverting agent mixture will have to be determined by field or well experience. The diverting agent should increase the injec-

tion pressure by approximately 150 psi. As an example, if a well is treated with a 10-bbl mixture of diverting agent in water and only a 50 psi increase is achieved, the next time the well is treated, the amount of diverting agent should be increased.

5. Pump the other half of the inhibitor water mixture down the annulus.
6. Overflush with 75 bbl of fluid plus the annular volume.
7. Shut the well in for 24 hr and put back on production.

The best time to squeeze a well with scale inhibitor is immediately after a scale cleanout job. The well can be squeezed while the packer is still in place. The only change in the above procedure would be that all of the fluids would be pumped down the tubing.

The above procedures both call for an overflush with fluids. These fluids can be fresh water, clean produced water, or oil. The fluids used will be discussed separately below:

1. ***Fresh Water***
   Fresh water should not be used in formations containing an appreciable amount of clay sensitive to fresh water. Chemicals should always be used in a fresh water overflush to prevent emulsion blocks. Some scale inhibitor squeeze chemicals contain additives that will prevent emulsion blocks. In this case, the same chemical used for squeeze treatment can be used in the overflush. In any case, an emulsion tendency test should be run before the well is squeezed to make reasonably sure there will not be an emulsion block.
2. ***Clean Produced Water***
   Chemicals should be used in the produced water overflush for insurance against an emulsion block.
3. ***Clean Produced Oil***
   Oil is the preferred overflush. A demulsifier can be used in the oil overflush to break any emulsion that might be around the well bore. Another advantage of using an oil overflush is that the oil containing a demulsifier will tend to oil wet the formation around the well bore.

The effectiveness and life of any scale inhibitor squeeze depends upon the chemical used, maximum amount of inhibitor adsorbed, placement of the inhibitor in the correct zone, volume of formation treated, the desorption characteristics of the formation, and the squeeze technique used.

Scale inhibitor squeeze treatments are profitable. Maximum production is maintained, and maintenance costs are reduced.

Scale inhibitors will inhibit the growth rate of scale-forming crystals and prevent their precipitation from solution for a period of time, but not indefinitely.