MICROENCAPSULATION - A NEW APPROACH TO DOWN HOLE INHIBITOR TREATMENTS

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Abstract

Conventional downhole treatments for scale and corrosion typically rely upon either "squeeze" or batch type treatments for control of corrosion and/or scale. These treatments introduce large amounts of inhibitor into the wellbore area and may adversely affect the production characteristics of the well, require excessive amounts of chemical, and require repeated treatments over short periods of time.

The use of encapsulated materials for scale and corrosion inhibition has recently been shown to be a reliable and economic alternative to the conventional squeeze or truck batch treatment. Encapsulated materials provide a reliable, long term, controlled release of inhibitor at concentration levels high enough to provide the required protection without introducing potentially damaging chemicals into the formation.

This paper details field experiences with the encapsulated materials in a variety of wells and the results that have been obtained with these treatments.

Introduction

To achieve long term protection from scale formation due to calcium carbonate, calcium sulfate, and barium sulfate, one of the industry accepted methods of treatment is the "scale inhibitor squeeze" technique.

The squeeze technique was essentially started after the publication of an article by Kerver *et al.* [1,2] Later this technique was applied to the deposition of scale inhibitor by Smith *et al.* [3] and Kerver and Heilbecker [4,5]

Later modifications such as those described by Miles[6] where the inhibitor is "precipitated " in the matrix of the rock has been practiced with considerable success.

Each of these methods, if designed and properly applied will result in and extended treatment life for the inhibitor. Due to the large amounts of fluids injected, if improperly applied, the productivity of the well may be impaired and in severe cases production may be curtailed completely.

The introduction of an encapsulated scale inhibitor is designed to offset the problems normally associated with conventional treatments by providing long term, controlled release of the inhibitor .

Release rates are designed to provide a concentration high enough to inhibit the scale formation without introducing potentially damaging chemicals into the producing formation.

Utilizing a patented micro-encapsulation technology the desired inhibitor, which in this study was a commercial phosphonate, is incorporated in to a slowly dissolving ,weighted aggregate particle which averages 1 - 3 mm in diameter. The encapsulated inhibitor is a complex matrix of polymer, the active inhibitor, a weighting agent, a brine carrier and various other agents that allow the capsule to form.

Microencapuslation

Microencapsulation may be defined as the formation of a protective wall around a particle or a droplet of a material in order to control the delivery of, or the interaction with, a particular environment.

Microencapsulation is used in numerous industries with diverse applications. Some examples are:

- Pharmaceuticals
- Agricultural processes
- Paints
- Adhesives

There are several methods for encapsulation of various materials and some of the more common methods for preparing encapsulated materials are:

- Fluidized Beds
- Phase separation
- Coaservation (Both simple and complex)
- Interfacial Polymerization
- Meltable Dispersion
- Diffusional Exchange

A detailed discussion of each of these methods is beyond the scope of this paper however the literature does indicate a number of articles have been published on them.

The system with which we are concerned in this presentation is the "Simple Coaservation" technique. Simply put this technique provides a material which is composed of three components:

- Core (The active and Inert materials)
- Capsule Membrane (the Polymer)
- A carrier (Brine)

The rate of release of the active material which in this case is a phosphonate, occurs predominately by *diffusion*, as opposed to *dissolution*.

There are three basic mechanisms occurring simultaneously with regard to the release and transport of the active material . These are:

1. The release of the active material from the cap's polymeric matrix.
2. Transport of the active material from the surface of the encapsulated material to the point where it contacts the incoming produced fluid thus forming a concentration gradient and;
3. Transport of the active material from the well bore up the production string.

Once the active material releases into the fluid above the cap surface, an equilibrium will exist between the cap matrix and the fluid. This equilibrium will set up a concentration gradient with the highest concentration at the cap/liquid interface and the lowest concentration at the point where the incoming produced fluids contact the inhibitor solution in the upper portion of the rathole.

Although thermal effects, such as convection currents help to distribute the active material throughout the column of fluid in the wellbore, transport of the active material throughout the rathole is mainly due to uptake of active material at the point where mixing occurs between the in-coming produced fluids and the concentrated inhibitor solution. This mixing will remove $\underline{x}$ amount of the inhibitor which is dissolved in the fluids in the rathole and this in turn alters the equilibrium of the concentration gradient. This shift in the concentration gradient promotes further release of the active material; from the caps in order to maintain the equilibrium of the concentration gradient.

The amount of active inhibitor carried to the surface by the incoming produced fluids is a function of the production volume and the amount of turbulence as the fluids enter the wellbore.

Laboratory Investigations

Investigations of the behavior of the caps under laboratory conditions, i.e. simulating conditions in the rathole or other non-turbulent areas suggest the following factors influence the release of the active material from the capsule:

Release Rate

Generally speaking, the higher the temperature, the greater the release rate of the active inhibitor from the material. This is particularly true at temperatures above 150° F.

At temperatures below 150° F an increase in the pH of the system will result in a *decrease* in the release rate of the inhibitor.

Also at temperatures below 150° F the higher the chloride level of the water the level of release will be *decreased.*

At temperatures above 150° F the higher the chloride level of the water, the ***higher*** the release rate of the active inhibitor from the material.

Also at temperatures above 150° F the higher the pH value of the water the *higher* the release rate of the active inhibitor.

Application of the encapsulated Materials

Although the encapsulated materials offer distinct advantages over conventional treatments, there are some conditions that must be met before the treatment is successful. These are (1) the scaling problem must exist in the wellbore or the tubing and surface equipment (2) the caps must be placed upstream of the problem (3) the caps must be placed in an area which is large enough to contain the required initial charge and (4) the caps must be placed in an area where they will be undisturbed by the forces of the incoming produced fluids. Generally a "rat hole" of sufficient depth and diameter provides the desired condition.

Treatment consists of the introduction of the caps into wells using a positive displacement type pump, a rotary type gear pump, or a triplex pump. In general the positive displacement type pumps minimize the mechanical shearing of the particles versus centrifugal type pumps. Also it is advisable to minimize other shearing such as pumping through chokes or partially closed valves. A pump rate of 1/4 to 1/2 barrel per minute is recommended.

For those wells which do not have sufficient rat hole volume a "basket" attached to the bottom of the production string . The basket is so designed as to protect the caps from fluid currents while providing sufficient contact between the active material in the in the concentration gradient and the produced fluids.

The wells which are referenced in this paper all had sufficient rathole and the inhibitor was placed in that area. (The rat-hole varies from 50' to 300' of 5" hole thus the total volume is approximately 50 to 300 gallons.)

Representative water analyses will be found in the attached exhibit. In general, the chlorides values of the produced waters were relatively low ranging from 70,000 milligrams per liter (mg/l) to 100,000 mg/l. Barium values ranged from a low of 0.0 mg/l to a high of 200 mg/l. Strontium was also present in many of the waters in a concentration of 80 to 250 mg/l Stability index calculations indicated the range was from + 0.40 at 30 °C to + 2.7 at 80 °C for calcium carbonate.

Depth of the wells treated are from 1400' to 1700' in depth . Production is generally from two zones, one at 1400 to 1600' and the second at 1500 to 1700'.

Water production ranges from 5 to 300 barrels per day.

Gas production is relatively light at 300 mcf to 1.0 mmcf/day.

Generally little or no oil is being produced.

Calcium sulfate has not been detected as being a problem in this area.

While the majority of the wells in this study were treated for calcium carbonate a significant barium sulfate problem exists in this geographic region and has been reported in the literature. [7]

Case Histories

Well # 1

The first wells to be treated in with the encapsulated scale inhibitor were located in the Antrium gas field in Michigan.[8]

A producing gas and water well in northern Michigan experienced calcium carbonate deposition at the rod pump causing pump failure. This well has aged 20 BWPD with gas production of 550 mcf/d.

Bottom hole temperature of the well was 70° F.

This well was treated with 15 gallons of scale caps by pumping the material down the annulus and flushing with three (3) barrels of water. The well was then shut-in for four (4) hours to allow the material to fall into the rat hole.

After five (5) months of operation after treatment a mechanical failure caused the well to be pulled. There was no evidence of scale build up on any of the downhole equipment at that time.

After nine (9) months of operation the well was retreated and has shown no sign of scale formation.

Well # 2

This was a progressive cavity pump on a gas well which produced approximately 100 barrels of water per day. Bottom hole temperature was 70° F.

Calcium carbonate deposition had been noted on the rotor and stator assembly necessitating chemical scale inhibitor treatment.

The well was treated with fifteen (15) gallons of encapsulated scale inhibitor by pumping the material down the annulus followed with approximately three (3) barrels of water. The well was then shut in for four (4) hours to allow the material to fall into the thirty (30) foot rathole.

The well has been operating for over 1 1/2 years, has been treated twice and has shown no evidence of scale formation. The well has been pulled once for mechanical problems and close inspection revealed no sign of scale formation.

Well # 3

This particular well is a gas well which produces approximately 75 barrels of water per day.

Over an 18 week period of time the well was pulled because of barium sulfate deposition on the down hole pump.

A total of fifteen (15) gallons of inhibitor was pumped down the annulus followed with three (3) barrels of flush water and then shut in for a period of four hours to allow the material to fall into the 50 foot rathole.

The well was retreated after a period of 24 weeks during which time no down time was encountered. The well has been producing for over 48 weeks without failure due to scale formation on the down hole equipment.

Estimation of Life Expectancy

The length of the treatment will be dependent upon several factors such as:

- The amount of encapsulated material added to the well
- The bottom hole temperature, salinity, and pH
- The dimensions of the rat-hole
- Volume of production
- The degree of dilution between the concentration gradient and the incoming production fluids.

Monitoring

Because the active material is a phosphonate, the return can easily be monitored by standard test methods such as the digestion method for phosphonates.[9]

Results from approximately 50 well treated with the encapsulated material indicates a ***phosphonate*** residual of 0.2 milligrams per liter is sufficient for scale prevention.

Conclusions

There are several advantages with the use of encapsulated materials, some of which are:

- In the Michigan area most well sites are in remote areas and have no electricity for chemical pumps.
- In the winter months few of the wells have a plowed access road to the well for chemical pump maintenance.
- There is no chemical on the well site that can be vandalized or spilled.
- There is no routine maintenance for the pumper or foreman.
- No containment box is required for the chemical container.

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[1] Kerver, J. K. and Morgan, F. A.: "Corrosion Inhibitor Squeeze Technique: Laboratory Adsorption-Desorption Studies", *Materials Protection* (1965) **4**, No. 7, 69-78
[2] Kever, J. K. and Hanson, H. R. : "Corrosion Inhibitor Squeeze Technique: Field Evaluation of Engineered Squeezed". *J. Pet. Tech.* (Jan. 1965) 50-59
[3] Smith, C. F. , Nolan, T. J. and Crenshaw, P. L. : "Removal and Inhibition of Calcium Sulfate Scale in Waterflood Projects". *J. Pet. Tech* (Nov. 1968) 1249-1256
[4] Kerver, J. K. and Keilhecker, J.K. : "Scale Inhibition by the Squeeze Technique". *J. Cdn. Pet.Tech.* (1969), **8**, No. 1, 15-23
[5] Kerver, J. K. *et al.* : "Treatment of Solids Plugged Wells With Reversibly Absorbable Inhibitor". U.S. Patent 3,481,400 (Dec. 2, 1969)
[6] Miles, L.: "New Well Treatment Inhibits Scale". *Oil & Gas J.* (June 1970) 96-99
[7] Oddo, J. E., *et al.*: "The Chemistry Prediction and Treatment of Scale Containing Naturally Occurring Radioactive Materials (NORM) in Antrium Gas Fields, Michigan". Society of Petroleum Engineers Paper SPE 25485.
[8] Private correspondence, Gary Gallup, Unichem a division of BJ Services
[9] API 45 Method 3.9 (Phosphate-photometric)

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