OPTIMIZING CORROSION INHIBITOR BATCH TREATMENT INTERVALS FOR OILWELLS

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ABSTRACT

This paper chronicles efforts to extend batch treatments using hydrocarbon-solvent solutions of corrosion inhibitor. Inhibitors were developed in the laboratory using parameters felt to be important for this endeavor. That is, good high-inhibitor concentration inhibition, good reduced-inhibitor inhibition, and intermediate brine dispersibility. Field-testing proved these inhibitors to be effective during the extended intervals.

INTRODUCTION

Application of corrosion inhibitors to corrosive oil wells is usually accomplished by either continuous or periodic batches.' Batch applications can be by hand lubricate and circulate, or by pump and flush from a treater truck. For both logistic and economic reasons, attempts have been made to reduce frequency requirements for batch treatments.[2,3] While experiencing some success, the previous schemes have been difficult to implement in the real world oilfield. This paper outlines a laboratory and field tested approach to this problem which is simpler to implement.

EXPERIMENTAL

Laboratory

Most of the laboratory testing was conducted in 2000 ml glass resin kettles, stirred at room temperature for 24 hours. Sweet tests received constant sparging with CO, Sour tests were first CO, sparged, then 1 gr. per liter of sodium sulfide added, then the kettle sealed. Corrosion was constantly monitored by linear polarization resistance on mild steel electrodes. This type of testing gives results which relate to performance in many field systems.[4] **A** few tests were conducted using wheel test methodology.

Field

Oil wells were chosen which were already receiving batch corrosion inhibitor treatments from a treating truck. Many of the test wells were rod pumped, a few were lifted with electric submersible pumps. All had enough H_2S in the associated gas to be considered sour. Water cuts varied from about 60% to 95%. Some of the rod pumped wells were produced full-time, some were timed by pump-off controllers. Each field had a cross section of 3 to 6 test wells, see table 1.

Initial corrosion monitoring was by wide scan d.c. polarization on steel electrodes mounted in the flowlines. This type of testing gives information both on corrosion rate and corrosion/inhibitor mechanism.[5] In wells producing steadily, probes remained usable for several days, whether in steadily producing rod pumped or ESP wells. However, because of the slight paraffin content of the oil in these wells, probes in wells using p.o.c.(pump-off-controllers), saw periodic slugs of mostly-oil coming past the probes, precluding use of this technique. Small amounts of paraffin would deposit which were not removed by the subsequent mostly-brine periods of production. Electrochemistry was therefore intermittent.

Since short-term corrosion rate response was needed, coupon exposures would not be satisfactory. Since the wells were sour, corrosion generated iron ions would be precipitated as iron sulfide, so this method could not be used routinely. Since the manganese content of most API steel is 1%, the amount of corrosion generated manganese is indeed low enough that it remains soluble irons. For individual wells, the amount of manganese, water, and corroding steel surface can be manipulated into an average mpy corrosion rate. The equation used for this purpose is:

$$\text{Mpy} = \frac{\text{Mn ppm x bbl/day } H_2O \text{ x } 35}{\text{Factor x Depth in thousands of Feet}}$$

The factor value depends on the tubing size and whether or not the tubing contains a rod string. For example, for 2 7/8 in tubing in a rod or progressive cavity pumped well, the factor is 127; for an e.s.p. or other open tubing well, the factor for

2 *718* tubing is 89

Even though this analysis was performed for individual wells, the data tabulated in this paper are left as manganese concentration in ppm from sets of test wells. Samples were taken just after treatment with the inhibitors, at intermediate times, and just before retreatment. Since we were stretching treatment intervals, the latter points were particularly important.

DISCUSSION

General

One attempt to extend treatment intervals uses a high internal phase ratio emulsion[2]. One limitation of this approach is that proper amounts of post-flush must be applied. Otherwise, the treatment does not last long enough, or the emulsion remains in the annulus too long and insoluble amids form. Another approach utilizes a two-component treatment[3]. Again, the volume of post-flush is critical; too much and the batch is forced into produced fluids at too great a concentration, yielding emulsions. Too little and the batch can harden low in the well; the corrosion inhibitor isn't placed properly on the tubing and rods, and in the worst case, pumps can be stuck. In all cases, the proper amount of flush is suggested by inhibitor solubility/dispersibility and the annular fluid level above the pump. Sometimes the annular fluid level isn't known, sometimes it fluctuates because of flood response or pump-off-controlled pumps. This means that either of these methods can be difficult to implement.

Many people today believe that most oilfield corrosion inhibitors function by incorporation into a thin corrosion product film and that the inhibited film is dynamic and fairly short lived, continuously spalling and regrowing. [1,6,7] Therefore, the longest lasting batches should be those which establish a good film, then provide for small amounts of corrosion inhibitor to feed from the annular area for several days to repair the spalling film. The initial film should be very protective and need only a very small amount for film repair. The above parameters are measurable in the laboratory. **A** corrosion inhibitor should give lower corrosion rates at high concentrations and give lowered corrosion rates even at lesser concentrations.

Another portion of the equation, optimum storage and feed around of inhibitor from the annulus, is more difficult to measure. One major factor is the dispersibility of the corrosion inhibitor in the flush water. The optimum dispersibility should be attainable in a variety of salt concentrations. Flush liquid is usually brine from the formation being treated. Experience may be more important than science in proper choice of this parameter. Limited dispersibility was chosen as the optimum for this property. Inhibitors too dispersible are likely to go through the system quickly; inhibitors with too little dispersibility are not likely to provide enough feed-through for proper film repair.

Finally, for widespread application, the desired chemical should inhibit effectively in sweet (mostly CO_2), sour (significant H_2S) and in systems with oxygen contamination. This latter condition often exists in older wells.[4]

Laboratory

The earlier described kettle test was utilized for most of the laboratory tests. Data from these tests are summarized in Figures 1 and 2. Many of the results in both lab and field are from Inhibitor A. Based on further laboratory tests, Inhibitor B has been identified which gives better laboratory tests results and to date, better field performance. The original field inhibitor, designated Inhibitor **O,** has demonstrated good effectiveness for several years, especially in the sour, corrosive oil wells in the Permian Basin.

Although the results are not tabulated here, Inhibitor **A** gave better results in film persistency wheel tests than Inhibitor **O** under both sweet and sour conditions, especially so in sweet tests.

Inhibitors **A,** B and **O** were run at various concentrations in sweet kettle tests. **As** data in Figure 1 show, Inhibitor B gives lower average rates at all concentrations than Inhibitor A and both are considerably lower than with Inhibitor **O.** For the reasons outlined above, both the higher and lower concentration results are encouraging.

The next series of kettle tests was run under sour conditions. Incidentally, experience has suggested that inhibitors which inhibit effectively in sweet conditions are equally or more effective in sour conditions. The converse, however is not true, effective sour-condition inhibitors may not be nearly as effective in sweet conditions.[8] This is certainly true for Inhibitor **O**. This conclusion is confirmed by examining data in Figure 1.

The results for the three inhibitors in sour tests also show greater effectiveness at low concentrations for Inhibitors A and B. Again, this characteristic is felt to be important to an inhibitor candidate for stretched interval treatments.

At this point, two comments about kettle testing should be made. First, it is a characteristic of oilfield inhibitors to have a critical concentration above which corrosion rates go no lower; lower concentrations give lesser inhibition. No attempt was made in these tests to identify this critical concentration for the following reason. All inhibitors tend to migrate to surfaces, steel covered with a sulfide or carbonate is preferred, but all surfaces, even glass, is involved. The outgrowth of this fact is that a given inhibitor concentration added to a test gives a lower value in the bulk brine after just a short period of time. Careful analytical work could quantify this effect but this was beyond the scope of the study. It is very likely that the 200 ppm added gave concentrations above the critical concentration in the bulk brine for all three inhibitors.

Oxygen tolerance tests results are summarized in Figure 2. These were conducted in kettles set up for sour conditions, then a small port left open to the atmosphere for 2 ½ hours, then the kettle sealed for the balance of the tests.[4] The results of these tests show that Inhibitors A and B were much more oxygen tolerant than Inhibitor **O**. Again, this feature is perceived to be important in selection of widely applicable chemistry for the desired purpose.

Field

General field characteristics are summarized in Table 1. Production rates varied from 50 to 550 bbl total per day. Brine T.D.S. ranged from 30,000 to 230,000 ppm; corrosivity as measured by dissolved H_2S and CO, was in a common range for sour oil wells. Field C wells were responding to C02 flooding so had higher dissolved C02 concentrations then the others. Original treatment frequencies ranged from twice per week to once per month. These wells represented a typical range of conditions.

The sets of field test conditions were:

1. Background with inhibitor **O** at as-found batch size and intervals (1x,1x)
2. Inhibitor A at as-found batch size and intervals (1x, 1x)
3. Inhibitor B at as-found batch size and intervals (1x, 1x).
4. Inhibitor **A** at 1.5 times batch size, double intervals (1.5x, 2x)
5. Inhibitor A at 1 times batch size, double intervals (1x, 2x)
6. Inhibitor B at 1 times batch size, double interval (1x, 2x)

Not all test sets were run at all fields but enough for comparison. Post flush volume were not adjusted from the ones used in the Inhibitor **O** background tests. These volumes were nearly always 2 or 3 barrels of produced brine per treatment.

The first two fields were used for preliminary testing only. In these and in the other fields, Inhibitor A gave considerably lower rates at the same batch size and interval as the original inhibitor. This was a requirement for proceeding to the next step. Inhibitor B gave even lower rates at the same batch size and treatment frequency as used originally.

Inhibitor A has a higher active concentration than Inhibitor **O**. So, to provide about the same inhibitor molecule concentration, the first double-interval tests used 1.5 times the usual batch size. As can be seen in Table 2, this scheme gave the same or better corrosion protection than the original inhibitor program.

Surprisingly, the doubled-interval equal-batch size with Inhibitor A gave even lower manganese averages. To date Inhibitor B is exhibiting lowered manganese averages but was still under test at the time this paper was being written.

Another parameter examined for many of the test wells was the individual manganese content during the period just before re-batching. Table 3 summarizes this set of data. Manganese concentrations during these periods proved to be as low with the same batch size, doubled treatment interval with Inhibitor A as they had been at original intervals with Inhibitor **O**.

According to the test data, the average corrosion rates, as indicated by manganese concentrations, remained under control during the entire stretched interval. Therefore, this program (for now using both Inhibitor A and B) is being expanded to other fields and to entire fields. Eventually, it is likely that program results will dictate continuation with either Inhibitor **A** or Inhibitor B. The two inhibitors have many functional similarities so long-term pursuit of both seems unwarranted.

CONCLUSIONS

1. There is at least qualitative agreement between kettle test results in the laboratory and corrosion results in the field with the three inhibitors studied.
2. The concepts of good optimum corrosion protection, good protection at lower inhibitor concentration, and medium brine dispersiblity appear to be important for stretched-interval corrosion inhibitors.
3. There are logistical and economical advantages to longer batch treatment intervals for both the oil well producer and a specialty chemical company.
4. Even though all test fields to date have been sour, sweet fields will be examined. Extrapolation of the laboratory/field relationships observed to date predicts good performance in sweet wells.

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Table 1

Field Summary

Name	Test Wells	Gross Production	Average TDP, ppm	Batches per Month	Dissolved Gases H_2S	CO_2	Oxygen Influence
EL	3	280-380 bbl.day	230,000 ppm	4-8	50 ppm	225 ppm	No
WL	4	245-350	230,000	4-8	70	250	No
W	6	240-550	30.000	2-4	320	600	Yes
C	6	50-500	90,000	2-4	110	1200	No
D	5	70-300	85,000	1-4	50	210	No

Table 2
Average Manganese Concentration
Inhibitor/Batch Size – Batch Frequency

Field	O/1X-1X	A/1X-1X	B/1X-1X	A/1.5X-2X	A/1X-2X	B/1X-2X
EL	0.27	0.14		0.27		
WL	0.35	0.20				
W	0.20	0.10	0.07			
C	0.41	0.25		0.24	0.20	0.16
D	0.34	0.19		0.26	0.16	0.13
Averages	0.31	0.18	0.07	0.25	0.18	0.15

Table 3
Individual Well Data
Parts per Million Manganese

Well	Treatments/ Month Change	Inhibitor O Mid Point	Inhibitor O Last Day	Inhibitor A (1X-2X) Mid Point	Inhibitor A (1X-2X) Last Day
1	8 to 4	0.08	0.09	0.09	0.10
2	8 to 4	0.12	0.20	0.14	0.15
3	8 to 4	0.13	0.14	0.13	0.11
4	4 to 2	0.08	0.07	0.07	0.10
5	4 to 2	0.14	0.07	0.06	0.10
6	4 to 2	0.12	0.11	0.07	0.12
7	4 to 2	0.18	0.14	0.10	0.11
Average		0.12	0.12	0.09	0.11

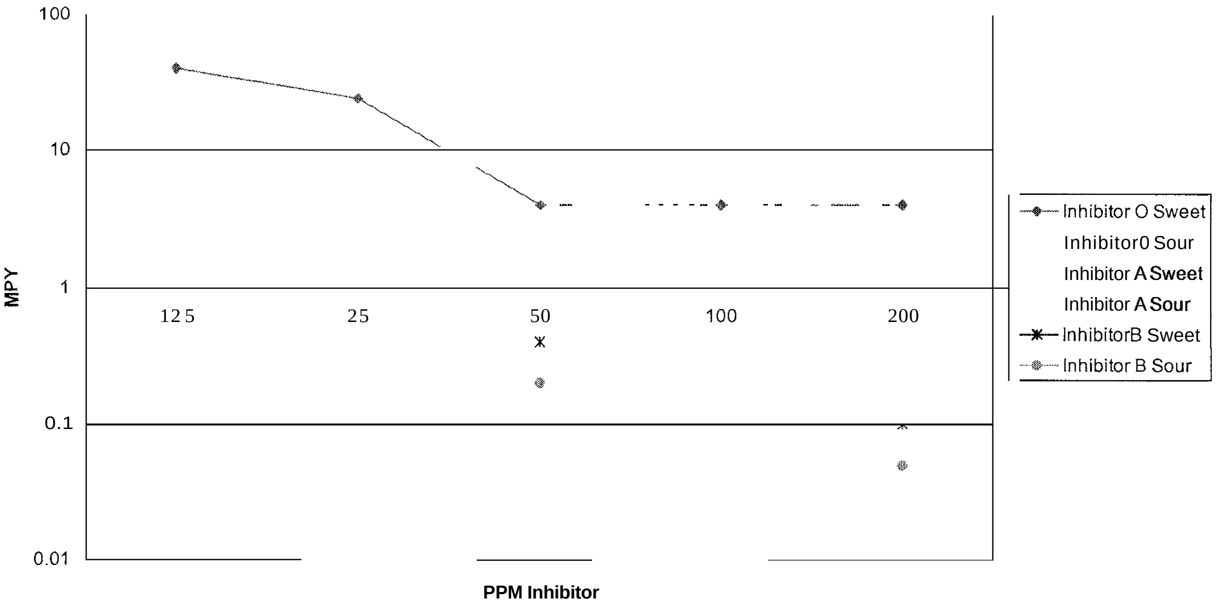

Figure 1 - Concentration Profile Laboratory Kettle Tests

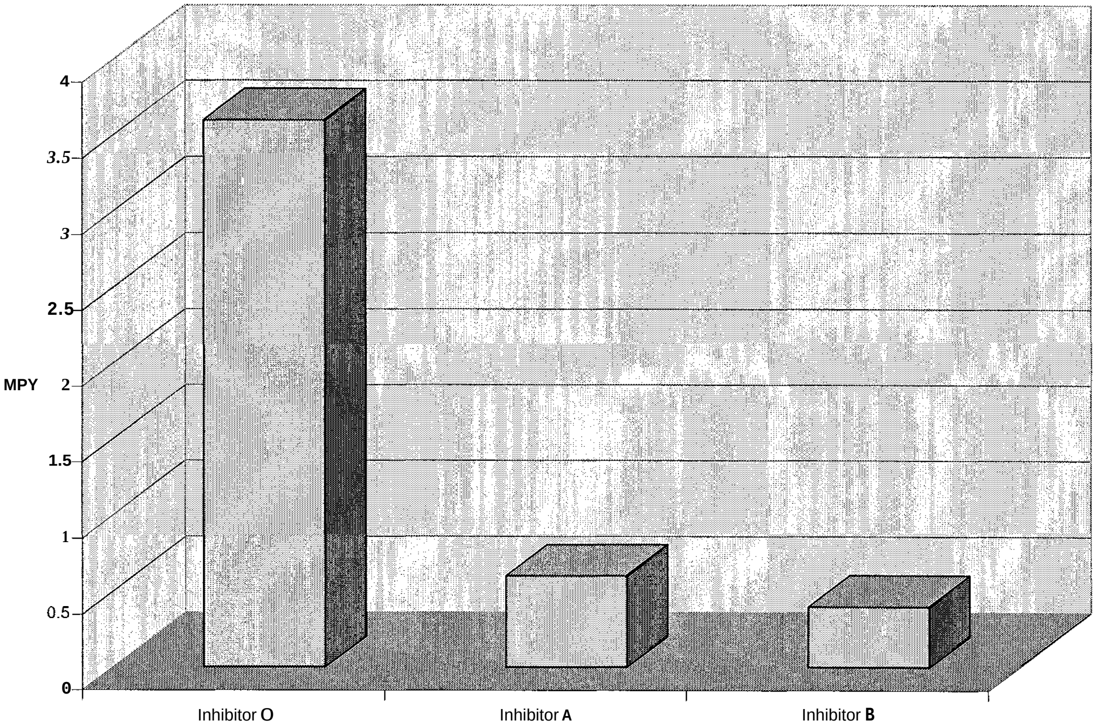

Figure 2 - H_2S/O_2 Corrosion Kettle Tests