A Case History - High Pressure Sour Gas Well Corrosion Control - Brown Bassett Field

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INTRODUCTION

It is probable that more effort has gone into a study of corrosion control in the Brown Bassett Ellenburger Field than in any other single gas field. This is as it should be, since the corrosion problems encountered are more severe than those generally encountered.

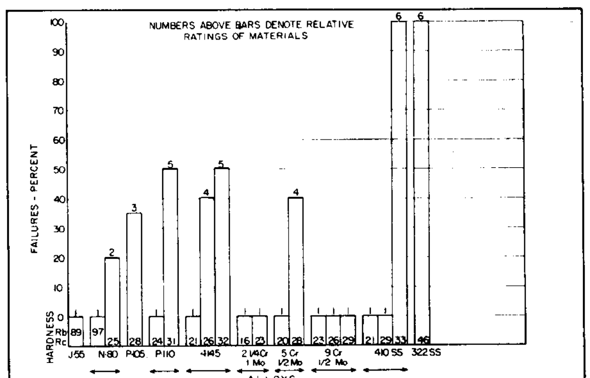
When the field was first discovered, the gas was sampled and the well plugged back to be completed in another formation. The gas was found to contain upward of 50% carbon dioxide, 50 ppm hydrogen sulfide and the rest virtually all methane, with no L.P.G. product. There was no sales pipeline in the area; moreover, such a gas was not marketable because it would not burn under ordinary conditions.

As a result, more than three years passed between discovery and initial sale of gas. During this time several additional wells were completed, using materials which were considered satisfactory but which had not been evaluated in the environment. At the same time, a laboratory program, consisting primarily of a literature search, was initiated. This was followed by a cooperative field study with other operators, duplicating field conditions in a dynamic test. This test included corrosion coupons, stressed beams, tubing subs (in tension and not in tension) and other devices which appeared pertinent. All of these were placed in three different environments: (1) cold (90°F); (2) hot (180° F), and; (3) hot-inhibited. Detailed information covering the tests and the conclusions drawn are presented in a previously published paper[1] and will only be summarized here. This was followed by field studies designed to gain specific information.

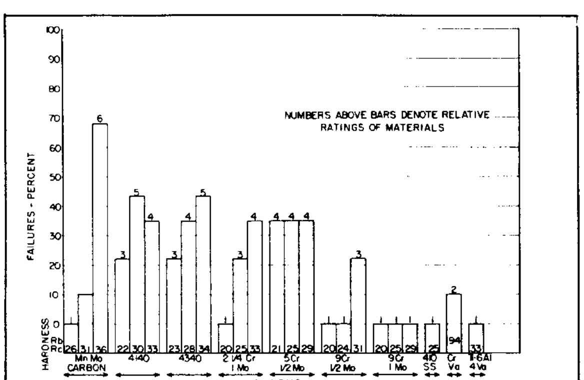
FORMAL STUDY

Some conclusions which were reached as a result of the formal study are as follows:

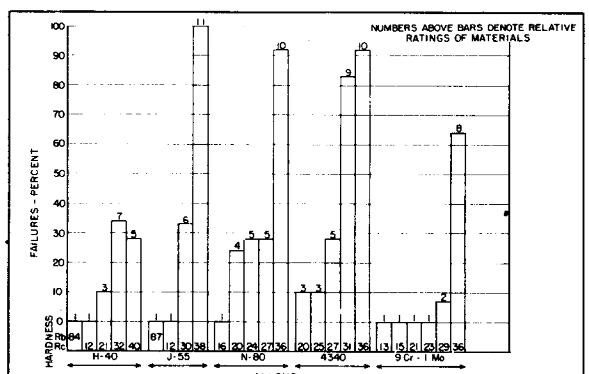
1. Standard materials used in tubing strings are highly susceptible to corrosion in high carbon dioxide, trace hydrogen sulfide systems.
2. Most materials tested indicated cracking susceptibility at hardness levels above Rockwell "C" 25 as shown in Figs. 1, 2 and 3.
3. Cracking susceptibility also was demonstrated to be a function of minimum yield: The higher the minimum yield, the greater the cracking susceptibility of a given metal or alloy.
4. Other things being equal, cracking susceptibility is a function of the applied stress.



ALLOYS AT VARIOUS HARDNESS LEVELS vs TOTAL PERCENTAGE OF FAILURES
GULF STRESSED BEAMS
FIG 2



ALLOYS AT VARIOUS HARDNESS LEVELS vs TOTAL PERCENTAGE OF FAILURES
MOBIL STRESSED BEAMS
FIG 1



ALLOYS AT VARIOUS HARDNESS LEVELS vs TOTAL PERCENTAGE OF FAILURES
CONTINENTAL "C" RINGS
FIG 3

5. The 9 chromium, 1/2 molybdenum (9 Cr, 1 Mo) and 9 chromium, 1 molybdenum alloys were completely resistant to corrosion attack in the high carbon dioxide, trace hydrogen sulfide, condensed water system.
6. Stainless steel of the 410 type was also resistant under the same conditions.
7. Both types of alloys exhibited pinpoint pitting when brine was added to the system.
8. Nine Cr, 1 Mo alloy was easier to work than was 9 Cr 1/2 Mo; moreover it appeared less subject to galling.
9. Plastic coatings, although supplying protection, were not sufficiently rugged to give complete protection.
10. Inhibitors, as applied in the test, gave approximately 80 per cent protection from corrosion attack.
11. Inhibitors did not appear to decrease cracking susceptibility.
12. Integral joints are suitable for this environment.
13. Care in handling is necessary with 9 Cr, 1 Mo tubing because the material is extremely malleable and because threads are more easily galled than those on similar non-alloy tubing.
14. Nine Cr, 1 Mo tubing was concluded to be the most economical for this application.
15. Special precautions were found necessary in running 9 Cr, 1 Mo tubing.
    a. Modified API thread dope must be used to prevent galling.
    b. Tong dies must be kept in excellent condition to prevent scoring.
    c. A stabbing guide should be used to prevent pin end damage.
    d. A torque wrench is essential and overtorquing must be avoided because the pipe is easily flattened.

In addition to those conclusions directly connected with selection of tubing, the following information was established.

1. Polypropylene is a satisfactory blast sleeve material.
2. Neoprene rubber is penetrated by the gas from this formation and on pressure release becomes bloated and distorted.

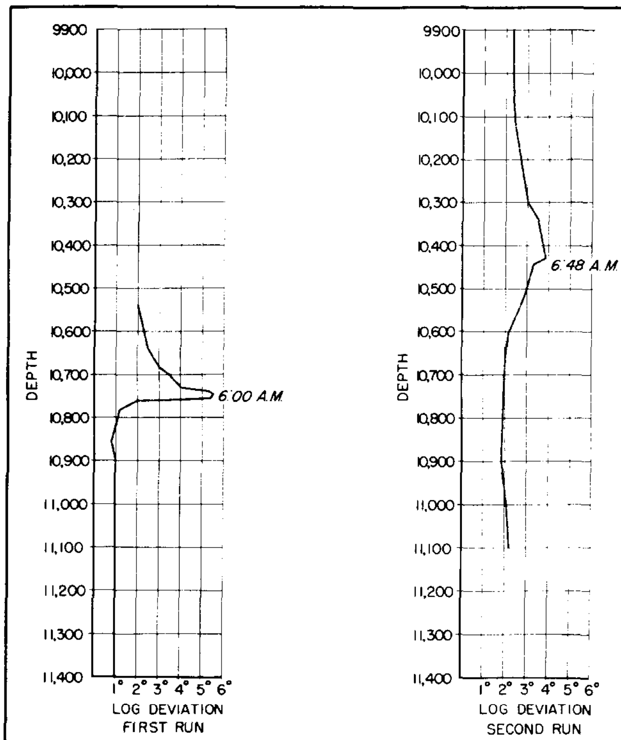
By the time the investigation had progressed to the point at which the above conclusions had been reached, six wells had been completed in the Ellenburger formation. A string of 9 Cr, 1 Mo tubing was plastic coated with a "straight phenolic" and placed in the first well. A string of 4140 tubing, plastic coated with an overlay coating, was placed in the second, and four additional wells were completed with 4140 tubing with a high temperature plastic coating. The flow from these wells ranged from 1.5 MMCFD to 30 MMCFD.

TUBING INHIBITION

Since it was concluded that plastic coatings would not give adequate protection, and since the expected life of bare 4140 tubing is estimated to be approximately two years, it became evident that some other action must be taken. Inhibition appeared to be the least expensive route. Slug treatment was the only approach which seemed logical. Three methods were considered:

1. Conventional squeeze inhibition was rejected because there is no liquid in the formation and there would be nothing to carry the inhibitor back out of the formation. It could, therefore, be expected to form a plugging agent. Handling of reproduced inhibitor would become a problem.
2. Displacement of the tubing with inhibitor is a satisfactory method but is relatively expensive. Also, handling the returning inhibitor would become a problem.
3. Pumping into the tubing the amount of inhibitor and solvent necessary to form a film and allowing it to fall was chosen as the most satisfactory method.

Since no history was available of anyone using this method, some experimental work was done to establish proper procedure. A radioactive tracer tool was lowered to the bottom of a well and a tagged inhibitor in a drum of solvent, followed by six drums of solvent, was pumped into the tubing. This was the proper amount to give a 1/16 in. coating on 13,500 ft. of 3-1/2 in. OD tubing. After waiting eight hr. with no response, the tool was moved up the hole until it encountered radioactivity at 10,700 ft. after 10 hr. total elapsed time. Only a short column of chemical was indicated at that point. Fig. 4 is a profile of the log locating the bottom of the inhibitor.



TRACER LOG EVALUATION CORROSION INHIBITOR PROFILE

FIG. 4

The log further indicated that there was no feathered lead edge of inhibitor. After the inhibitor was located, the tool was again lowered to 11,100 ft. and the same area was logged again. It appears that the tool became coated with inhibitor and that it carried most of the inhibitor down with it. It was noted that an increase in radioactivity was not recorded until the tool was raised above the highest point of its first run. This probably indicates that high temperature had driven off some solvent and thickened the inhibitor at this depth so that it did not flow freely. One, or both, of two things probably prevented the inhibitor from reaching bottom: (1) Eight hours was insufficient time, or (2) seven drums of solvent was insufficient to reach the bottom of the well.

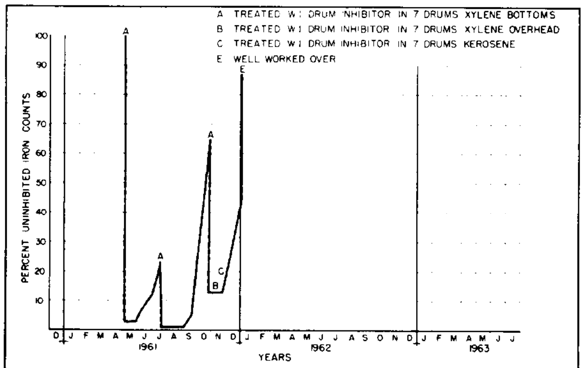
After a few tests on the highest production well and on one of the lowest production wells, a program of treatment was established on all of the wells completed with plastic coated 4140 tubing. Eight drums of fluid containing 10% inhibitor are used in 2-1/2 in. nominal tubing. Iron counts were chosen as the simplest and, at the same time, an effective means of determining corrosion control, although they were initially correlated with corrosion coupons. The accuracy of iron counts in this system is due to the following:

1. Since there is no liquid hydrocarbon phase, no iron is lost to such a phase before analysis.
2. There is no liquid water produced from the formation in most wells, and therefore, any iron found in the water must have resulted from corrosion of the tubing.
3. The pH of the water is estimated as 3.5. This is sufficiently low to hold all iron compounds in solution.

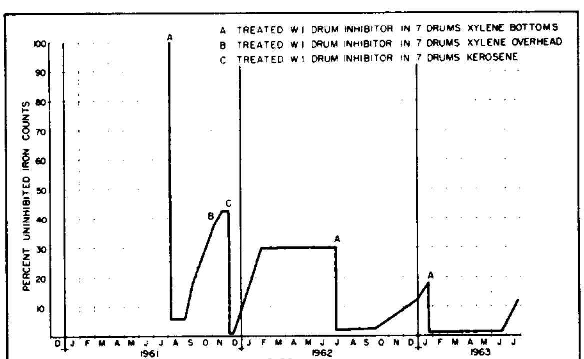
The tests made with various inhibitors showed all of the ones tested to be effective; therefore, no screening of inhibitors was carried out. Instead, the inhibitor was selected on a theoretical basis. The one chosen was as water insoluble as possible. This was done to make the film as persistent as possible, considering that water is the only liquid phase. Since there is no produced hydrocarbon liquid phase, the solvent was also carefully selected. The one chosen was a wide cut solvent containing a high percent of heavy ends. The material used was a bottoms cut from a xylene still. It was believed that such a solvent would help form a tough film and would increase both the life and efficiency of the inhibitor.

Difficulties arose because some of the inhibitor returned to the surface as a heavy, taffy-like material, which not only plugged the Company's separators but carried over into the purchaser's glycol regenerating units. The material which was causing the trouble was analyzed and found to be a combination of inhibitor and heavy ends. It was thought possible that a light solvent might leave the inhibitor in place and return to the surface without fouling equipment. An overhead cut of xylene was tried. Plugging of equipment was decreased, but inhibition was severely limited. Kerosene was then tried as a diluent, since the inhibitor was virtually insoluble in it. Inhibition again was poor. It was eventually decided that the treatment was necessary and that the periodic cleaning of surface equipment could be carried out without prohibitive cost, using the original solvent.

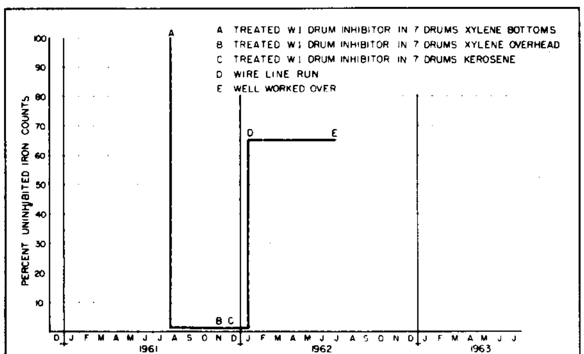
As can be seen from Figs. 5 through 9, excellent inhibition, in excess of 99% in some instances, has been attained. As a result tubing life for the existing coated 4140 tubing is conservatively estimated at 10 years. It was noted, however, that effectiveness of inhibition is a function of production rate. Although six months' inhibition, following treatment, has been the rule, periods of only one month were experienced for Bassett-Goode Well #1. This well produced 30 MMCFD through 3-1/2 in. OD tubing. From this it appears that velocity seriously modifies the effectiveness of inhibitors.



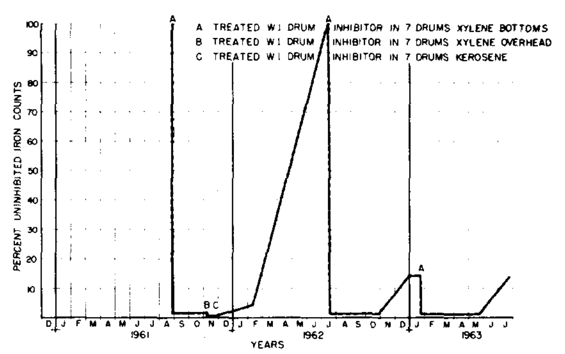
BASSETT GOODE WELL NO 1
PERCENT UNINHIBITED IRON COUNTS vs TIME
FIG 6



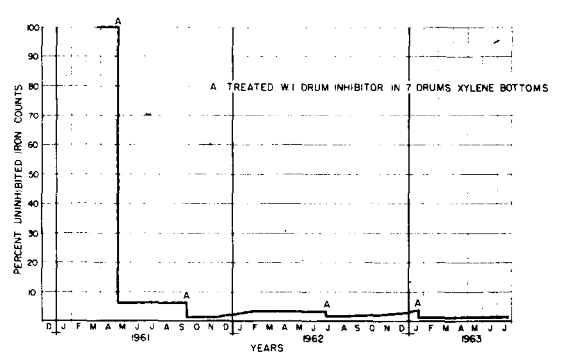
BANNER STATE WELL NO 1
PERCENT UNINHIBITED IRON COUNTS vs TIME
FIG 5



BASSETT GOODE WELL NO 2
PERCENT UNINHIBITED IRON COUNTS vs TIME
FIG 7



GOODE ESTATE WELL NO 2
PERCENT UNINHIBITED IRON COUNTS vs TIME
FIG 8



BANNER ESTATE WELL NO 2
PERCENT UNINHIBITED IRON COUNTS vs TIME
FIG 9

TUBING STRINGS PULLED

Within 6 months after production was initiated, it was decided to run a caliper survey in Bassett-Goode Well #1. In an attempt to clean all inhibitor from the tubing, it was flushed with xylene and flowed back. Nevertheless, the contacts of the caliper tool fouled and it was impossible to obtain any data. This indicated that considerable inhibitor film still remained. Moreover, there was no indication that the caliper tool damaged the remaining coating to any extent. This was borne out by the fact that iron counts never became higher than the initial counts even though inhibition was discontinued for a long period. The effect of velocity on inhibitor film persistancy was confirmed when, in April 1962, the tubing was pulled from this well and the well was dualed in another zone. The tubing was cleaned and examined with an optiscope. It was interesting to note that the worst corrosion occurred within the first 2500 ft. and that none was observed below 5500 ft. This bears out the fact that in the absence of free water, or at least high humidity, corrosion will not occur. Wire line damage was very much in evidence. Not only had the coating been penetrated, but even the steel had been worn to depths up to 0.05 in. Pitting up to 0.105 in. was observed, and failure certainly could have been expected within one year. Upon exposure to the atmosphere the coating popped off and could not have been rerun.

In the summer of 1962, the tubing in Bassett-Goode Well No. 2, which had been treated regularly with inhibitor, was pulled. The coating in this tubing, a high-temperature plastic, was in much better condition than that in Bassett-Goode Well No. 1 and did not show noticeable deterioration upon exposure to air. There were, however, numerous places where the coating had been chipped off or removed by a wire line. This tubing was partially inspected, in that every tenth length was laid down and examined. Eighteen of 49 lengths inspected showed coating chipping, but only one length showed resulting corrosion, and it was minor. Seventeen lengths showed wire line damage, but in most instances the coating was not penetrated. The conclusions drawn were:

1. The high temperature coating in Bassett-Goode Well No. 2 was superior to the overlay in Bassett-Goode Well No. 1.
2. Although installation of the tubing was made with utmost care, the coating was damaged; therefore, installation of a holiday-free coating is considered virtually impossible.
3. As indicated by iron counts, inhibitor treatment of this well was highly effective.

As a result of more than two years of successful inhibitor treatment, completion recommendations have been changed. Now N-80 grade tubing with controlled hardness, not to exceed Rockwell "C" 23, and with minimum yield ranging from 80,000 to 95,000 is specified for new completions. The pipe will be tested at the mill for hardness, yield and end area damage, and any not meeting specifications will be rejected. The joint specified is one of two integral joints which have been tested and found suitable. Plastic coating has not been specified because coatings and inhibitor are not believed to be complementary. It is believed that, as reservoir pressure declines, less pressure drop can be tolerated and that larger tubing may be installed. Such a move would make 9 Cr, 1 Mo tubing less attractive and was one of the considerations recommending a change to N-80 grade tubing.

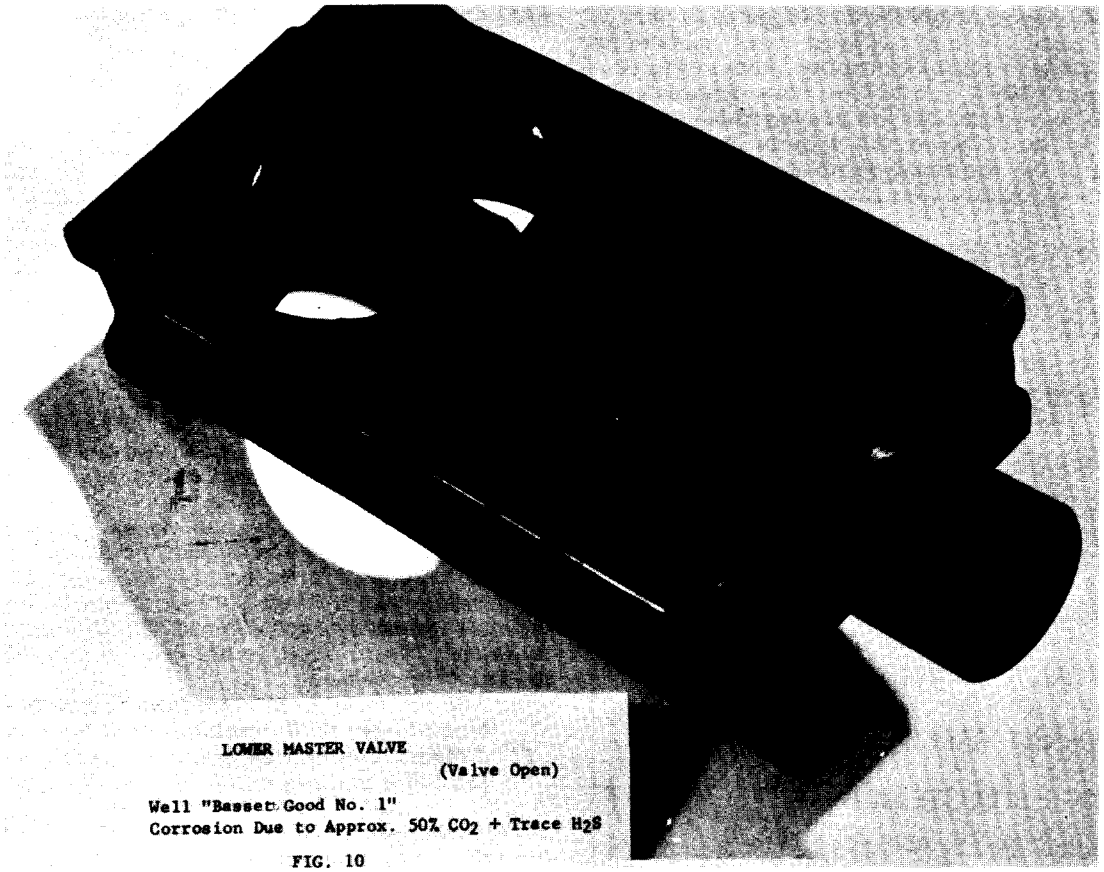
It was considered desirable to determine whether the 9 Cr, 1 Mo tubing was corroding to any extent. This was also attempted by iron counts; however, in this case it could be assumed that corrosion affected all of the area of tubing in contact with free water. Using the data obtained from examination of the tubing string from Bassett-Goode Well No. 1, it was assumed that liquid would condense at -5000 ft. A typical well is taken as one which produces 20 BPD of condensed water, containing 100 ppm of iron. The quantity of iron which would be dissolved each year would be:

$$\frac{100 \text{ PPM} \times 20 \text{ BPD} \times 350 \text{ LB/BBL} \times 365 \text{ DA/YR}}{1 \times 10^6 \text{ PPM}} = 256 \text{ LB/YR}$$

5000 ft. of tubing weigh 5000 ft. x 6.5 Lb/Ft = 32,500 lb. It is assumed that failure will occur when 1/3 of the metal has been lost, then the life of the tubing would be 42 yr. To allow for irregular attack, a life of 20 yr. was given to the tubing.

DESIGN OF TREES

Within a few months after full scale production was started, the tree on Bassett-Goode Well No. 1 developed leaks. Upon examination critical corrosion of the tree was noted and the tree was scrapped. This



LOWER MASTER VALVE
(Valve Open)

Well "Basset Good No. 1"
Corrosion Due to Approx. 50% CO_2 + Trace H_2S

FIG. 10

UPPER MASTER VALVE
(Valve Open)

Well "Basset Good No. 1"
Corrosion Due to Approx. 50% CO_2 + Trace H_2S

FIG. 11

tree was constructed of standard materials. (A picture of the gate from the lower master valve is shown in Fig. 10 and parts of the upper master valve in Fig. 11.) It was replaced with a 410 SS tree, since this material had appeared to be excellent for this environment. (The composition of the replacement tree is found in Fig. 12.) In spite of the corrosion resistance of the metals,

TREE 410 SS SOLID BLOCK

BODY & BONNET: 410 SS

GATE: 410 SS W. COLMONOY NO.5
OVERLAY ON SEATING SURFACES
& THROUGH GATE PORT

RINGS: STELLITE NO 3

SEAL RINGS: TEFLON

STEM: K MONEL

BONNET GASKET: 304 SS

DOGS: STELLITE NO 6

GUIDE PLATES: 410 SS

MATERIALS OF CONSTRUCTION WELL HEAD EQUIPMENT

BROWN BASSETT ELLENBURGER

FIG. 12

within several months considerable corrosion had again occurred. As a result, periodic inspection of trees has been initiated. The first inspection revealed that all of the non-alloy trees had been attacked to some degree. The extent of the attack appeared to be a function of velocity and turbulence. Wells producing less than 5 MMCFD of gas displayed little attack except where the area was sharply restricted, as in the 1-7/8 in. wing valves on most of the trees. The trees on new wells, all of which are now 410 stainless steel, have not displayed such deterioration with one exception. This is, in all probability, due to relatively low gas velocities. One well, which is producing a large amount of salt water, shows serious corrosion in the top of the tree where static conditions exist. No explanation for this has been found. The remainder of the tree is unattacked. It has been decided that, should serious corrosion start to develop at the entrance to the wing or in the wing valve, the wing will be blanked off, and an expansion loop of full tree diameter will be placed on top of the tree, to minimize velocity and turbulence. To date, this has not proved necessary.

SURFACE PIPING

Because surface equipment failure would be extremely hazardous, yearly inspection of lines and separators has been set up using an Audogage. No serious corrosion has been observed.

OTHER CORROSION PROBLEMS

It has been discovered that tubing packers used to isolate the annuli of wells in this field have all leaked. This permits the entry of carbon dioxide, hydrogen sulfide and moisture into the annuli. For this reason, an inhibitor is essential. Because of the high pressure of the formation in some wells, either fresh water or brine is used. Care is taken that the inhibitor used is completely soluble. It has been found that most so-called water-soluble inhibitors are only water or brine dispersible and will eventually stratify; therefore, inhibition is completely lost.

In some of the initial wells, Ellenburger oil was used in the annuli. A small quantity of the same type of inhibitor was used to inhibit any water which would accumulate in the bottom of an annulus.

Studies have also been made on proper inhibition of acid used in the Brown Bassett Ellenburger field. Special problems are induced as a result of high temperature and hydrogen sulfide content. The type of inhibitor generally recommended for high temperatures is arsenic base. This is not deemed satisfactory for the following reasons:

I. Arsenic, under the conditions involved, has been found to promote cracking in some instances.
II. Arsenic reacts with hydrogen sulfide to produce insoluble sulfides which may cause some plugging.

For these reasons other suitable inhibitors were investigated. One of the commonly used organic inhibitors, in a ratio of 1%, was found to be satisfactory, although pitting was not eliminated. Further investigation proved that addition of 0.5% potassium iodide provided virtually 100% protection.

After a well has been acidized, the spent acid is slowly produced over a period of months. Since the spent acid is relatively high in chlorides, it becomes corrosive even against 9 Cr, 1 Mo tubing. For this reason it has become Company practice to inhibit any acidized well in the same manner employed with those wells completed with 4140 tubing.

SUMMARY

The corrosion problems encountered in this field have been varied and difficult. A satisfactory solution has been found for most of them, however. Only time and further study will tell whether the best solutions have been found.

REFERENCE

(1) F. E. Blount, B. C. Arnwine and R. J. Chandler "A Field Study Designed to Select a Tubing Program for Ellenburger Gas - Brown Bassett Field, Terrell County, Texas" presented at Spring Meeting of the Southwestern District, Division of Production API, March 22-24, 1961.

ACKNOWLEDGEMENTS

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