CORROSION INHIBITORS FOR 13Cr STEEL

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ABSTRACT

Corrosion inhibitors developed for low alloy metals have been found to have limited use on stainless steels such as 13Cr. Stainless steels are being successfully used to combat H_2S and CO_2 corrosion but are proving susceptible to hydrochloric acid (HCl).

This paper presents results of tests made with 13Cr steel subjected to corrosion by HCl. Several inhibitors and inhibitor systems are compared under varying temperatures and acid concentrations. These comparisons reveal (1) 13Cr steel's greater susceptibility to corrosion than that of low alloy N-80 steel, and (2) the effects of different corrosion inhibitors in reducing the attack on the metal tested.

INTRODUCTION

Corrosion damage to high alloy stainless steel such as 13Cr tubing can occur during stimulation and scale removing operations requiring acidic solutions.[1,3,4] Compounding this problem further is the fact that inhibitors developed for low-alloy carbon steel tubing such as N-80 are not as effective in preventing corrosion of high alloy steel; in fact, some of these inhibitors have even been observed to accelerate the corrosive action of hydrochloric acid (HCl).[5,6]

High alloy stainless steels such as 13Cr are being widely used to avoid corrosion caused by hydrogen sulfide (H_2S) and carbon dioxide (CO_2).[2] However, laboratory and field experience has demonstrated that these alloys are susceptible to corrosive attack by acids used in stimulation operations at temperatures above 150°F.[6] Recent publications on the subject of stainless steel tubing have cautioned about HCl corrosion without defining what form this corrosion may take or possible consequences of its occurrence.[5]

Of the high alloy steel tubing being used for the purpose of avoiding CO_2 and H_2S corrosion, 13Cr probably has seen the longest history of usage in the industry and remains the most widely used stainless tubing today.[1] For this reason, this paper will focus on corrosion inhibition tests involving 13Cr steel. Tests involving N-80 steel will also be presented for purposes of comparison with conventional tubing.

EVOLUTION OF 13Cr USAGE

Corrosion caused by CO_2 and H_2S is not new to the oil and gas industry, having been reported in the 1940's in Louisiana and Texas.[4] In those days and even more recently, corrosive effluents may have forced an otherwise promising well to be closed in. Since 1973 however, economic conditions have made this approach an unacceptable means of dealing with corrosion of H_2S and CO_2 in produced fluids. Today of course, CO_2 exposure is frequently intentional; CO_2 is sought as a resource to be used in enhanced oil recovery (EOR) and in stimulation operations.[1,4]

Both CO_2 and H_2S present potentially serious problems to production tubing in the form of sulfide stress cracking (SSC) in the case of H_2S, and severe, localized corrosion in the case of CO_2. Another type of corrosion related to H_2S, occurring under conditions of high temperature and high chloride concentrations, is stress corrosion cracking (SCC).[1] Both SSC and SCC manifest themselves as a sudden failure of tubing in the form of a rupture, split, or crack; whereas CO_2 attacks the metal at specific sites causing rapid, localized corrosion, while leaving adjacent areas unaffected. None of these types of corrosion is acceptable, especially when reasonable solutions are available.

Strategies for fighting and avoiding CO_2 and H_2S corrosion which have been effectively employed include: (1) low alloy carbon steel with chemical inhibitors, (2) coated low alloy steel, (3) non-metallics such as fiberglass or other plastics, and (4) high alloy stainless steel.[1] Each of these has disadvantages and the potential of each must be measured for specific applications, but apparently the most favored approach in the last few years has been the high alloy stainless steels, led by 13Cr in popularity. High alloys such as 13Cr show very good resistance to the corrosive effects of CO_2 and H_2S, and have been used in locations all over the world.[4]

One major consideration in the choice of 13Cr is the favorable economic situation. Tubular prices have become very competitive with low alloys like N-80 when these factors are considered: (1) premium threaded connections are mandatory in most situations where H_2S and CO_2 are encountered, (2) initially, low alloy tubing with premium connections are only slightly cheaper than 13Cr, but when workover or other remedial costs are considered, 13Cr may easily be cheaper in the long run, (3) other types of tubing - internally coated low alloy, grades of low alloy tubing for sour service, for instance - are equal to or more expensive than 13Cr in cost.[1]

Pay-out costs are very favorable as well. For instance, wells with high production rates in the Tuscaloosa Trend have had calculated pay-out times of just a few months; a moderate gas well that produces CO_2 may have a pay-out of possibly a year.[2]

In the Tuscaloosa Trend, some of the harshest conditions encountered by 13Cr tubular goods have been solved with no reported failures after more than 3-1/2 years on 26 wells. These wells were drilled in areas of high concentrations of H_2S, high pressure, CO_2, very high chloride concentrations, water production, and bottom hole temperatures up to 375°F.[3]

BACKGROUND TO ACID CORROSION

High alloy steels are able to withstand the rigors of H_2S and CO_2 but evidence is growing that strong acid solutions encountered during stimulation treatments and scale-removing operations can be extremely corrosive to these alloys.[5,6] Aggravating the situation further is the inability of conventional inhibitors to prevent this corrosion from occurring, especially at elevated temperatures.[6]

Acid corrosion does not appear to be a major problem until temperatures above
150°F are encountered. From this approximate range corrosion becomes increasingly severe, especially above 250°F. For example, a well containing N-80 steel would be adequately protected by a low temperature-low alloy inhibitor (LT-LA) at 200°F, whereas 13Cr steel would likely suffer extensive corrosion damage.

An important aspect of corrosion control is the cost of the corrosion inhibitors used. Inhibitors developed for high temperature applications are usually considered too costly for application at lower temperatures. At these lower temperatures, less expensive inhibitors generally can adequately protect against corrosion from acidic fluids. For this reason, different inhibitors have been developed for different temperature ranges. These inhibitors and their effective temperature ranges are:

1. Low alloy - low temperature (LA-LT) less than 150°F
2. Low alloy - moderate temperature (LA-MT) 150°F to 250°F
3. Low alloy - high temperature (LA-HT) above 250°F
4. High alloy corrosion inhibitor (HA-INH) for high alloys above 150°F.

Test results reported in this paper were gathered with the intent of finding the approximate temperature level at which an inhibitor would cease to effectively protect N-80 low alloy steel and 13Cr high alloy stainless steel. This is accomplished by comparing directly the effects of various corrosion inhibitors and acid solutions on test specimens of N-80 and 13Cr.

The major factor influencing the effectiveness of an inhibitor is temperature. Elevated temperatures increase the aggressiveness of the acidic attack in the downhole environment. There are two methods of combating acidic corrosion when an inhibitor begins to lose effectiveness due to temperature effects.

1. Increase inhibitor concentration. This approach is popular because no other chemicals are required; expenses of stocking extra chemicals are saved.
2. Employ an inhibitor designed to withstand higher temperatures. A lower concentration of inhibitor should provide protection at the higher temperature at a comparable price to the higher volume of low temperature inhibitor.

The choice between the two should be based not only on the economic factors for the short term but should also take into consideration the performance level of the inhibitor.

TEST PROCEDURE

Corrosion values are determined by weight loss methods. Test specimens, called coupons, with a surface area of approximately 4 sq. in. are submerged in 100 ml of acid solution giving a volume to surface area ratio equivalent to 25 ml/sq in. Corrosion losses are reported for the time periods indicated.

Apparatus: For tests at and below 200°F, coupons are cured in a container of an acid solution which is immersed in a water bath at the appropriate temperature. For tests above 200°F, a pressurized autoclave is used to maintain the test temperature. Test coupons are placed in a glass or teflon container holding the acid solution and pressurized to 600 psig. The heat transfer medium used is kerosene which aids in electrically isolating the test solution from the metal body of the autoclave.

Coupon Preparation: Coupons were cut from 2 3/8 in. production tubing, degreased in trichloroethane, rinsed in acetone, dried, sand blasted, and stored in a dessicator until ready for use. Prior to immersion in the acid, the coupons are weighed.

Acid Solutions: Two solutions were used in this investigation: 15 percent hydrochloric acid (HCl), and an acid mixture of 12 percent HCl and 3 percent hydrofluoric acid (HF). The percentages used reflect commonly used concentrations for stimulation treatments.

TEST RESULTS

Test results indicate that when lower temperatures are encountered there is little difficulty in providing protection from acid corrosion on either N-80 or 13Cr steel. Above temperatures of 150°F, conventional inhibitors provide protection for N-80; while in the case of 13Cr, either increasing the concentration of the inhibitor used or going to an LA-HT inhibitor is required. However, above 250°F the conventional inhibitors failed to prevent acid corrosion of 13Cr stainless; even the low alloy-high temperature inhibitor (LA-HT). At this temperature though, an effective inhibitor designed to function on 13Cr was developed and used while conducting tests for this examination.

Test results show that at 150°F there is generally adequate protection provided for N-80 low alloy steel. On 13Cr at the same temperature, excellent protection can be obtained by increasing the concentration of the LA-LT inhibitor or switching to an inhibitor with higher temperature performances, such as LA-MT or LA-HT.

As the temperature is increased to 200°F, the upper limit of the LA-LT is reached. No protection is found even at concentrations two and one half times greater than used previously on either N-80 or 13Cr. The LA-MT temperature does provide excellent protection for N-80, but falls radically short in providing protection for 13Cr. An increase in the concentration of the LA-MT did increase corrosion protection, but in 15% HCl on 13Cr very high corrosion losses were observed. Here going to a LA-HT inhibitor did provide protection on 13Cr steel. The use of an inhibitor designed for 13Cr was tested at this temperature. It was found to provide lower corrosion losses than found for the LA-HT, but the LA-HT inhibitor probably provided sufficient protection for most purposes.

At 250°F, the LA-MT inhibitor was found to reach its thermal limit for the test time indicated. Poorer results were noticed on the 13Cr steel than on N-80. Corrosion protection was achieved on both metals using the LA-HT inhibitor. Lower corrosion losses were obtained on 13Cr using an inhibitor system designed for that metal, HA-INH.

At temperatures above 250°F, the LA-HT inhibitor performed to protect N-80 in conjunction with intensifiers at these more aggressive temperatures. Above 250°F no low alloy inhibitor was found to protect 13Cr. That is, the thermal limit of the LA-HT and associated intensifiers was reached for 13Cr. The inhibitor designed for the high alloys metal was found to protect 13Cr up to 350°F.

The high alloy inhibitor not only provided protection for 13Cr up to 350°F, but was also found to provide a higher degree of corrosion protection over the LA-HT inhibitor systems on N-80. This is advantageous when inhibiting tubing strings containing more than one alloy.

CONCLUSION

It appears that acid corrosion of 13Cr stainless steel at high temperatures can be prevented with a new inhibitor system discovered in the course of this investigation.

REFERENCES

1. Murali, J.: "13Cr Stands Above Low-Alloy Steel OCTG," Oil and Gas Journal (July 9, 1984), 56-58.
2. Murali, J.: "13Cr Tests High Against CO_2 Corrosion," Oil and Gas Journal (July 23, 1984), 66-69.
3. Murali, J.: "13Cr Stainless Proven in Field Use," Oil and Gas Journal (August 6, 1984), 56-58.
4. Crolet, J-L.: "Acid Corrosion in Wells (CO_2, H_2S): Metallurgical Aspects", Journal of Petroleum Technology (August, 1983), 1553-1558.
5. Garber, Dr. J. D.; Kantour, Mohammed: "How High-Alloy Tubulars React in Acidizing Environments", Petroleum Engineer (July, 1984), 60-68.
6. Walker, M. L.: "Sour Gas Operation and Design," SPE Forum Series, 1984, Jackson, Wyoming, August 6-10, 1984.

Table 1
Corrosion Losses Observed on N-80 and 13Cr Tubing Steel at Various Conditions

Temperature (°F)	Inhibitor (Concentration)	Time (Hours)	Corrosion Loss in lb/sq ft: N-80 15%	N-80 HCl-HF 12%-3%	13Cr 15%	13Cr HCl-HF 12%-3%
150	LA-LT (0.15)	16	0.003	0.003	0.060	0.005
150	LA-LT (0.30)	16	-----	-----	0.007	-----
150	LA-MT (0.15)	16	0.001	0.001	0.003	0.003
150	LA-HT (0.15)	16	0.001	0.001	0.003	0.003
200	LA-LT (0.20)	16	0.223	0.259	0.430	0.375
200	LA-LT (0.50)	16	0.106	0.112	0.130	-----
200	LA-MT (0.20)	16	0.104	0.116	0.569	0.200
200	LA-MT (0.50)	16	0.008	0.005	0.664	0.013
200	LA-HT (0.20)	16	0.007	0.005	0.012	0.029
200	HA-INH (0.20)	16	0.009	0.008	0.005	0.009
250	LA-MT (2.0)	16	0.069	0.076	0.121	0.201
250	LA-HT (2.0)	16	0.025	0.033	0.039	0.088
250	HA-INH (2.0)	16	0.013	0.010	0.026	0.011
300	LA-HT (2.0)	6	0.050	0.061	0.299	0.318
300	HA-INH (2.0)	6	0.010	0.012	0.020	0.016
325	LA-HT (2.0)*	6	0.030	0.025	0.225	0.297
325	HA-INH (2.0)	6	0.013	0.015	0.013	0.019
350	LA-HT (2.0)**	4	0.100	0.076	0.412	0.494
350	HA-INH (2.0)	4	0.015	0.009	0.016	0.021

The high alloy inhibitor (HA-INH) is a two-component system. The concentrations of component A are listed above. For component B, at and below 300°F, 1% by volume is used while above 300°F, 2% by volume is used.

*30 lbs/Mgal of corrosion inhibitor intensifier is used in this test.
**55 lbs/Mgal of corrosion inhibitor intensifier is used in this test.