

THE COMPLETE DOWNHOLE CORROSION INHIBITOR PROGRAM
FORD GERALDINE UNIT CO₂ FLOOD

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ABSTRACT

A complete program of screening inhibitors, monitoring field results, correlating lab results with the results from the Plate Bending Corrosion Fatigue Machine^{1,2} and defining service availability was initiated in the Ford Geraldine Unit CO₂ Flood. The new downhole inhibition program has resulted in corrosion inhibitor treatment savings up to forty-five percent and a noticeable decline in corrosion related well servicing failures.

INTRODUCTION

In establishing corrosion inhibition programs it is essential to determine the most effective inhibitor for a given environment; however, the complete program deals with more than inhibitor selection. The complete program provides methods of monitoring and maintaining an inhibition program.

This paper presents the results obtained from an eighteen month downhole treatment evaluation program in the Ford Geraldine Unit CO₂ Flood. The program consisted of:

1. dividing the CO₂ Flood area into three treating areas
2. running laboratory persistency tests on corrosion inhibitors
3. monitoring field results
4. running fatigue box tests
5. defining service availability

PROJECT CHARACTERISTICS AND TREATING CONCERNS

The Ford Geraldine Unit is located in northern Reeves and Culberson Counties, Texas. Production is from the Bell Canyon Formation of the Delaware Mountain Group at an average depth of 2680 feet.

The Ford Geraldine Unit CO₂ Project was initiated in early 1981. The continuous CO₂ injection project consists of 154 producing wells. Historically, the Ford Geraldine Unit had not been a problem lease to treat; however, the installation of the CO₂ flood created new and challenging treating conditions. Water analysis (Table 1) show the changing conditions as dissolved CO₂ concentrations increase from a base level of 0 ppm to as much as 950 ppm and the pH shows a gradual lowering to an acidic condition.

The maturity of the waterflood at the time that the CO₂ flood was installed presented another treating problem. Many wells that had been shut-in as they watered out during the prior waterflood had to be returned to production. Forty-five percent of the producing wells made less than one percent oil. The selection of an appropriate inhibitor for these wells would be more difficult.

In order to hold back CO₂ breakthrough and maintain the desired reservoir pressure, the producing rates on most wells were restricted; resulting in high fluid levels. This created another treating problem. In wells producing oil, the fluid in the annulus will be oil. The oil in the annulus can become saturated with an oil soluble inhibitor that will constantly feed around as the well produces; however, several wells did not produce any oil. The annulus of these wells contained either all water or mostly water. The usual practice of batch treating with an oil soluble inhibitor is questionable for these wells. The inhibitor does not reach the pump intake; therefore, it cannot effectively protect the exposed metal surfaces. As CO₂ injection progressed, additional treating concerns developed. Many wells experienced increased gas production with high CO₂ concentrations (Table 2). Some wells even flowed from the increase in gas.

INHIBITORS EVALUATED

The selection of an appropriate inhibitor was our primary concern. With many of the wells being one hundred percent water productive, both oil soluble and water soluble chemicals were evaluated (Table 3).

The entire program served to evaluate twelve corrosion inhibitors through laboratory and field testing. The only chemicals not evaluated in the laboratory were A, B and F. Inhibitors A and B were used in the field prior to the start of our evaluation program. These inhibitors were not laboratory tested because of the poor performance in the field. Inhibitor F was not evaluated by an independent laboratory; however, the chemical company did supply test data on this chemical. This inhibitor was introduced into the program after the initial inhibitor failed to perform satisfactorily. Normally, all inhibitors are tested by an independent laboratory before they are used in the field; however, since this inhibitor was introduced so late in the program it was not.

INHIBITOR SELECTION

In September, 1982 six companies were supplied fluid samples from four wells in the Unit. These wells were considered representative of the field with respect to producing fluids and corrosion history. Table 4 provides the production data for these wells.

The inhibitor selection involved performing laboratory film persistency tests³ and constant concentration tests to determine the most effective inhibitor. The persistency test is used to test oil soluble inhibitors, while the constant concentration test evaluates water soluble inhibitors. The procedure for performing these tests are shown in Tables 5A and 5B. The chemical companies were requested to carry out persistency tests at 5,000, 10,000 and 20,000 ppm concentration for each fluid sample. Constant concentration tests were run at 25, 50 and 100 ppm. Samples from the same wells were submitted to an independent laboratory for tests with the inhibitors recommended by the chemical companies. Test results are presented in Table 6. The results presented are only those from the independent laboratory tests. All results reported by chemical companies compared favorably with the independent results, except for inhibitor I.

Constant concentration test results were extremely poor for the two water soluble inhibitors tested; therefore, a decision was made to go with an oil soluble inhibitor. Generally, an inhibitor is considered acceptable if it shows greater than 80 percent protection in an independent laboratory persistency test at all three concentration levels. As indicated, none of the inhibitors met this criteria for all well fluids tested. Noting the poor persistency results on well nos. 177 and 268, it

is important to examine the well characteristics. As shown in Table 4, both of these wells had less than 1% oil in their test samples. For well nos. 177 and 268 the persistency tests were carried out with 99 and 100% produced water, respectively. It is not unusual to get poor persistency results with an oil soluble inhibitor when all stages of the testing are carried out at low oil concentrations. Well nos. 249 and 194 had 5% and 10% oil volumes, respectively. The persistency results from these wells were notably better than for the low oil volume wells. The results from these two wells were used as a basis for inhibitor selection.

Several companies had comparable, and competitive results; based on these observations; however, only three companies had been invited to participate in the field portion of the test. Initially, inhibitors C, E and G were chosen for the field test. These inhibitors represented the best for each of the three companies. Eventually, inhibitors D and F were also used on the field.

In addition to the persistency tests, emulsion tendency tests⁴, outlined in Table 7, were carried out on each inhibitor to determine if a stable emulsion is formed when mixed with produced fluids. Two inhibitors failed the emulsion tendency test, inhibitors I and J.

The corrosion fatigue machine was not used until later in the program; it can also serve as an inhibitor selection tool. This device permits accelerated corrosion fatigue testing in the actual well environment. The fatigue machine was used on Ford Geraldine Unit No. 194 to help add validity to our inhibitor selections. Test results are presented in Table 8. Only the three inhibitors used in the field test were used in the fatigue machine. The production from well no. 194 was 12 percent oil. No tests were run with wells that produced only water.

FIELD PROGRAM

Unable to obtain a distinctly superior corrosion program, the field was split between three treating companies in October, 1982. The field was split based on an even distribution of high fluid level, high CO₂ concentration, high water cut wells and historically problem wells. The program was initiated with inhibitors C, E and G based on persistency results previously outlined.

Treatment Method

Inhibitor treatment volumes for each well were based on weekly fluid production and a maximum inhibitor concentration of 100 ppm. A 25 ppm concentration was considered a maximum treatment level⁵ for all oil productive wells. With the absence of oil, the inhibitor concentration was increased to 100 ppm by some chemical companies.

Each well was treated by batch treatments. The desired inhibitor treatment volume was dispersed in produced water down the annulus. The inhibitor was then flushed with either three barrels of produced water or three barrels of produced oil down the annulus permitting the oil soluble inhibitor to feed slowly into the produced stream. The oil flush was used only with inhibitor E in wells that produced no oil. The chemical company using inhibitor E felt the oil soluble inhibitor used would perform more favorably if an artificial fluid level of oil were formed in the annulus. The oil flush was used for the first three treatments only. As the field program proceeded, unsatisfactory results on water productive wells resulted in a decision by two of the chemical companies not only to change inhibitors, but ultimately to use circulation as a treatment method. Inhibitor C was changed to inhibitor D which performed somewhat poorer in the persistency tests, while inhibitor G was changed to an untested inhibitor F. Neither of these alternatives proved successful.

Monitoring

Each chemical company was required to prepare a monitoring program. The programs included installing downhole corrosion coupons, flowline corrosion coupons and copper ion displacement coupons. Seven wells were designated for monitoring the effectiveness of the inhibitors. Most of the wells selected were not oil productive; while all of them had high fluid levels and high CO₂ concentrations. The production data for these wells is shown in Table 9.

The copper ion displacement test (CID) procedure was used to determine inhibitor film persistency under actual well conditions. The procedure for the test is defined in Table 10. This test proved quite successful on the Ford Geraldine Unit; however, the use of this monitoring technique has limited success in areas where paraffin or scale buildup interfere. The CID test results of two representative wells are shown in Figures 1 and 2. The results represent the effectiveness of seven different inhibitors. As indicated, the tests results were inconsistent initially with generally poor readings. In March, 1983 both test wells were changed to inhibitor E. Treatment with inhibitor E on both of these wells was initiated with an oil flush. After the first treatment series, film coverage was one hundred percent until the wells were shut-in in early July, 1983.

The corrosion coupon test results are presented in Table 11 for five field tested inhibitors. Although inhibitor G shows the lowest metal loss (MPY), it is not considered representative since it consisted of only one coupon reading. Inhibitor F was also evaluated with only one coupon and is not considered representative. Inhibitor E was evaluated with eleven corrosion coupons over the field test period. It had the best with an average weight loss of 0.27 MPY which is exceptionally good.

One of the most effective monitoring techniques used was visual inspections of downhole equipment. Several wells during the field test were pulled strictly for evaluation of the program, while others were examined following failures. Table 12 shows the history of two wells examined under several different treatment programs. the visual inspection reports compare favorably with the copper ion displacement test results (Figure 1 and 2). In both evaluation techniques, inhibitor E appeared to perform better than any others tested.

EVALUATION RESULTS

In July, 1983 the program was completed and the corrosion treatment program was awarded to the chemical company with inhibitor E. It is important to note that during the eighteen months of the program, approximately sixty wells have been shut-in to facilitate the proper reservoir management of the CO₂ flood.

In the old program many wells were treated with inhibitor volumes in excess of 200 ppm. In addition, on many wells biocides and surfactants were used on a regular basis. The new program not only eliminated all biocide and surfactant treatments, but decreased both inhibitor volumes and the number of truck stops. (Table 13). Chemical inhibition costs have dropped forty-five percent. This table has been corrected for wells shut-in during the evaluation.

The result is a more effective corrosion inhibition program that has brought corrosion related failures (Figure 3) to a virtually stand still. Unfortunately, the figure showing the corrosion related failures could not be corrected for the shut-in wells.

MAINTAINING THE PROGRAM

After carefully designing an effective corrosion inhibition program it is extremely important to maintain it. Maintaining the program requires setting up checks on all aspects of the program. The program should continue to be monitored using the tools previously mentioned. In addition, periodically the corrosion technician should witness the inhibitor treatments. The inhibitor used should be checked, as well as, the flush water quality and volumes. The technician should continue to make careful examinations of downhole equipment failures. Treating volumes should be recalculated as production volumes or fluids change on wells. Maintenance of the program can assist in early detection of problems.

CONCLUSIONS

1. Screening of corrosion inhibitors, using both laboratory and field tests, is the first step in developing an effective corrosion inhibition program.
2. Selection of inhibitors from persistency tests should include an examination of the test well characteristics. The well characteristics can often explain inconsistent test results.
3. Maintaining a successful program involves monitoring and evaluation on a continuous basis. Early detection of problems can eliminate costly equipment failures.

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Table 1
Typical Water Composition

	January 30, 1979	June 21, 1981
	PPM	PPM
Chlorides	45,700	42,966
Sodium	23,300	22,278
Calcium	4,160	3,640
Magnesium	1,240	966
Bicarbonate	290	205
Carbonate	0	0
Sulfates	1,380	845
Specific Gravity	1.056	1.0512
CO ₂	0	950
pH	7.6	6.8
H ₂ S	-	11

Table 2
Typical Gas Composition

	MOLE PERCENT
Carbon Dioxide	65.29
Nitrogen	0.37
Methane	10.44
Ethane	3.84
Propane	6.59
Isobutane	1.58
n-Butane	4.50
Isopentane	1.50
n-Pentane	1.79
Hexanes	4.10
Heptanes	-
H ₂ S	750 ppm

Table 3
Corrosion Inhibitors Evaluated

- A Solution of fatty amine - aryl quarternary thio-phosphates, carboxylic acid salts of carboxylic acid/polyamine reaction products, acylated polyglycols, aromatic hydrocarbons, isopropanol, methanol. Oil soluble, water dispersible.
- B Solution of acylated amines and alkyl aryl sulfonates, aromatic hydrocarbons, methanol.
- C Solution of carboxylic acid salts of a carboxylic acid/polyamine reaction product, alkyl aryl sulfonates, aromatic hydrocarbons and isobutanol.
- D Solution of phosphated alcohols, carboxylic acid salts of carboxylic acid/polyamine reaction products, alkyl aryl sulfonates, aromatic hydrocarbons, isobutanol.
- E Dimer-trimer acid. Highly water and oil dispersible. Activity level is 25%.
- F Alkyl sulphonic acid and fatty acid salts of amide; oil soluble and water dispersible. Activity level 35-40%.
- G Alkyl sulphonic acid and fatty acid salts of amide with oil dispersant. Oil soluble water dispersible. Activity level 35-40%.
- H Salted amide azolene. Water Soluble. Activity Level is 25%.
- I Amido-amine imidazoline. Oil soluble and water dispersible. Activity level 30-40%.
- J Organic, filming amine. Oil soluble and water dispersible. Activity level 30-40%.
- K Imidazoline and dimer-trimer acid. Oil soluble and water dispersible. Activity level 30%.
- L Solution of carboxylic acid salts of carboxylic acid/polyamine reaction products, phosphated alcohols, oxyalkylated alkyl phenol, alkyl aryl sulfonate, isopropanol, methanol and water. Water soluble.

Table 4
Sample Wells Production Data

Well No.	Oil (Bbls)	Water (Bbls)	Gas (MCF)	CO ₂ CONCENTRATION (%)
177*	1	10	1	10
194	7	63	50	40
202	2	39	2	26
268	0	84	NA	62

* test sample had 1% oil

Table 5A
Persistency Test Procedure

- I. SAMPLING
Collect well fluid samples free of corrosion inhibitors. Samples are submitted with inhibitors using blind numbering to a laboratory for testing.
- II. FILMING
Place clean, weighed steel samples in bottles containing produced fluids at the oil-water ratio of the test well. Add corrosion inhibitors at 5,000, 10,000 and 20,000 ppm. Saturate the fluid sample with one corrodent, either CO₂ or H₂S. The fluids in our test were saturated with CO₂. The bottle is then rotated for one hour at 150°F.
- III. RINSING
The excess inhibitor is rinsed off the steel samples. The samples are then placed in sample bottles containing uninhibited produced fluids that are saturated with CO₂. The bottle is then rotated for one hour at 150°F.
- IV. EXPOSURE
The steel samples are placed in fresh bottles containing produced fluids saturated with CO₂. The bottles are rotated for 24 hours at 150°F.

An additional set of uninhibited steel samples are placed in bottles containing produced fluids saturated with CO₂. The bottles are rotated for 24 hours at 150°F. These samples are the blanks.
- V. PROTECTION
The protection obtained from the various inhibitors and inhibitor concentrations is determined by comparing blank weight loss with inhibited weight loss.

Table 5B
Constant Concentration Test Procedure

- I. SAMPLING
Collect well fluid samples free of corrosion inhibitors. Samples are submitted with inhibitors using blind numbering to a laboratory for testing.
- II. EXPOSURE
Add corrosion inhibitors at 25, 50 and 100 opm to bottles containing produced fluid of the test well. Place clean, weighed steel samples in the bottles. Saturate the produced fluids with CO₂ or H₂S. Rotate the bottles for 24 hours at 100° F.

An additional set of uninhibited steel samples are placed in bottles containing produced fluids saturated with CO₂. The bottles are rotated for 24 hours at 100°F. These samples are the blanks.
- III. PROTECTION
The protection obtained from the various inhibitors and inhibitor concentrations is determined by comparing blank weight loss with inhibited weight loss.

Table 6
Independent Laboratory Persistency Test Results
(Average Percent Protection)

CHEMICAL	WELL NUMBERS			
	202	194	268	177
A	---	Not Evaluated		---
B	---	Not Evaluated		---
C	75.6	85.5	52	49
D	75	70.5	63	62.5
E	77	87.5	54	38
F	---	Not Evaluated		---
G	85	94	56	44
H	56	71.6	50	44.5
I	71	78.8	41.6	48.5
J	78.5	74.7	64.8	58.2
K	69.6	74	63	54.8
L	76	83	66.6	49.3

Table 7
Emulsion Tendency Test Procedure

- 1) Collects a fresh sample of the produced fluids from the test well/s prior to batch treatment.
- 2) Place 100cc of total fluid with the desired ratio of produced water and oil in each of two 5 ounce (160cc) graduated prescription bottles.
- 3) Add 1cc of inhibitor to one bottle. The remaining bottle is a blank.
- 4) Shake bottles vigorously. Stop and observe break time.
- 5) Note cleanliness of water and oil. Also note the appearance of the interface.
- 6) Select only those inhibitors that exhibit 90 percent breakout within 5 minutes into clean oil and water phase.

Table 8
Average Fatigue Life

(Uninhibited Versus Inhibited Life)

INHIBITOR	SPECIMEN COUNT	AVERAGE FATIGUE LIFE (CYCLES)	IMPROVEMENT FACTOR	RANK
NONE	4	272,970	1.0	---
C	3	738,720	2.7	3
E	4	845,640	3.1	1
G	3	819,720	3.0	2

Table 9
Monitoring Wells - Production Data

Well No.	Oil (Bbls)	Water (Bbls)	Gas (MCF)	CO ₂ Concentration (%)	Pump Submergence (Ft)
177	1	10	1	10	2310'
301	3	10	34	90	1580'
163	1	21	6	40	1466'
157	4	44	50	65	2274'
121	0	18	4	63	480'
268	0	84	NA	62	1323'
249	0	10	1	48	1759'

Table 10
Copper Ion Displacement Test Procedure

- 1) Place 6 clean steel coupons in the flowline at the wellhead immediately before the well is treated.
- 2) After 24 hrs open bypass, remove a coupon, replace coupon holder, return production to flowline.
- 3) If oil film exists on coupon, rinse briefly with isopropyl alcohol or warm kerosene - Not Gasoline
- 4) Hold coupon in 10% copper sulfate (CuSO₄) bath for 60 seconds.
- 5) Remove coupon from CuSO₄ bath and examine it for presence of orange copper deposits.
- 6) Estimate area of coverage by inhibitor.
- 7) Repeat steps 2-6 daily until the level of film persistency is defined.
- 8) Adjust schedule of examination based on individual well results.

Table 11
Corrosion Coupon Readings (MPY)

INHIBITOR	NUMBER OF SAMPLES	AVERAGE READING
E	11	0.27
C	6	2.16
D	6	2.95
G	1	0.10
F	1	0.50

Table 12
Typical Well History Downhole Corrosion Problems

FORD GERALDINE UNIT NO. 249		
DATE	INHIBITOR	OBSERVATIONS
4-28-82	A	Pump Failure - Severe Corrosion
8-2-82	C	Install Downhole Coupon - No Inhibitor Film
9-24-82	C	Severe Pitting - Light Inhibitor Film
3-29-83	D	Change Out Rods, Some Tubing, Change to Inhibitor E
5-18-83	E	Pulled To Evaluate - Good Film, Clean Rods
7-6-83		Shut In - Pull to Evaluate, Good Film, Clean Rods

FORD GERALDINE UNIT NO. 177		
DATE	INHIBITOR	OBSERVATIONS
2-12-82	A	Tubing Leak
7-30-82	C	Change Out Some Rods. Severe Pitting - Install Downhole Coupon
8-16-82	C	Coupon Pitted, Newly Installed Weight Bars Pitted
11-18-82	G	Severe Corrosion
12-13-82	F	Severe Corrosion - Light Inhibitor Film Change Out Producing Equipment
3-21-83	E	Change To Inhibitor E
5-4-83		Shut In - Pull To Examine Light Film, Clean Rods

Table 13
Monthly Treatment Summary

	Truck Stops	Inhibitor Gallons	Biocide Per Month	Surfactant
January 1982	473	691	157	126
March 1982	494	1153	255	404
September* 1982	364	383	0	0

*Reflects current treating status if no wells had been shut-in.

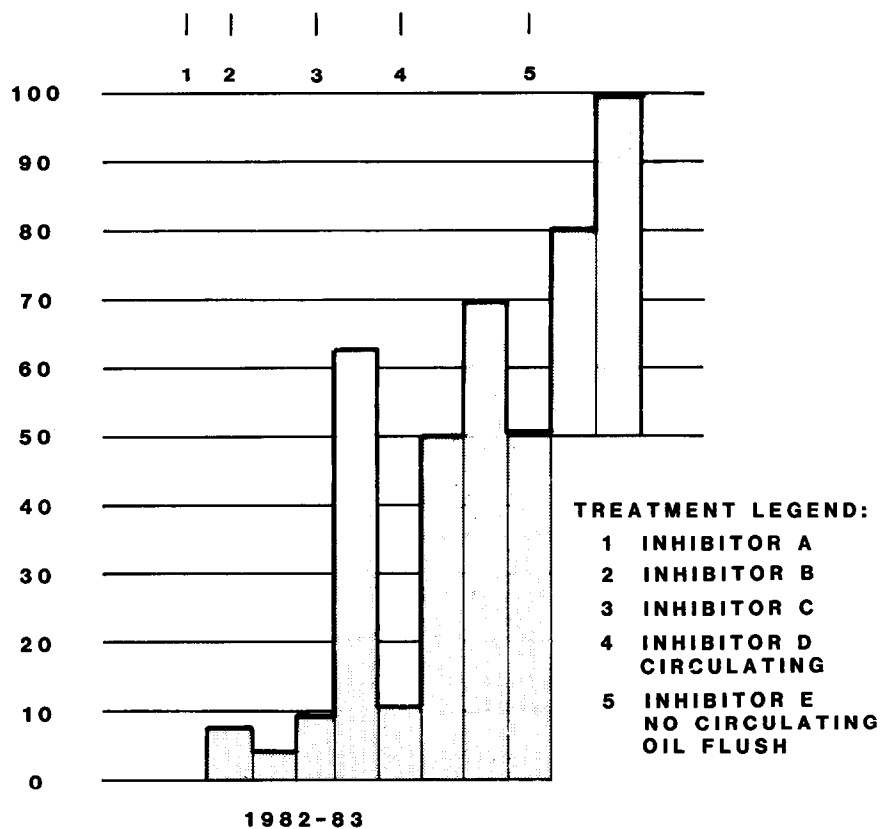


Figure 1 - Copper ion displacement results - FGU No. 249

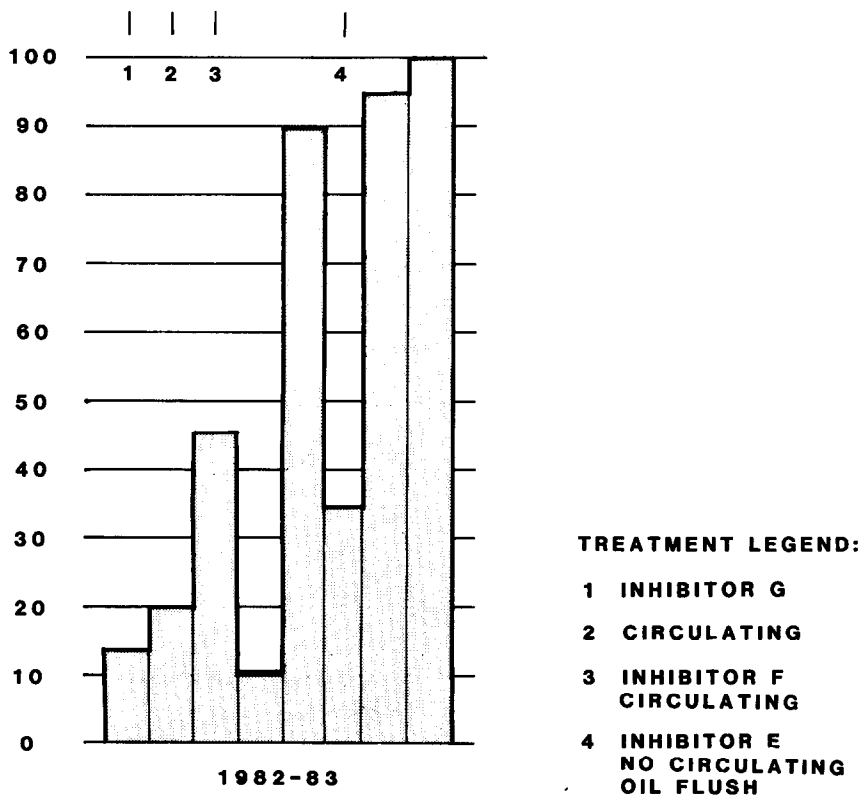


Figure 2 - Copper ion displacement results - FGU No. 177

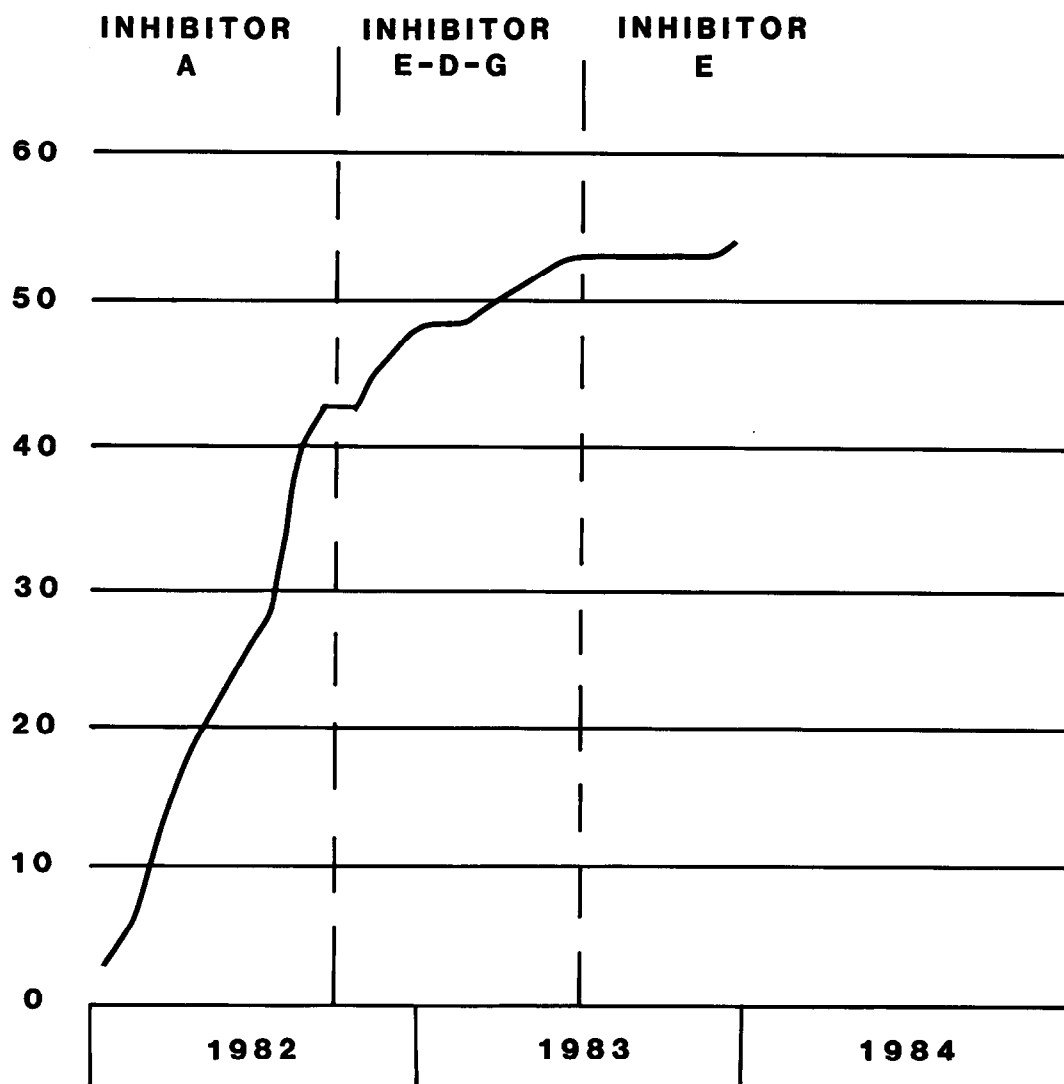


Figure 3 - Cumulative number of corrosion related failures