Figure 1. Process flow diagram of a typical monoethanolamine carbon dioxide scrubbing unit.

Corrosion Control In CO$_2$ Removal Systems

Where used, "Amine Guard" has completely eliminated corrosion as an operating problem at design and above design conditions in carbon dioxide removal systems.

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In 1967, Union Carbide initiated a study on corrosion and corrosion inhibition for the monoethanolamine, water, carbon dioxide-steel system. The experimental program consisted of weight-loss testing, potentiostatic polarization experiments, electrode potential measurements under self-polarization conditions, and characterization of surface barriers. The results of this program provided the experimenters with a better understanding of the corrosion mechanisms involved and allowed them to discover an effective inhibitor for the system, Union Carbide's "Amine Guard".

To provide a perspective for discussing our experimental program and its results, we will first review the monoethanolamine-water-carbon dioxide removal system that was used before these studies were undertaken, Figure 1. Very briefly, a 20% by weight monoethanolamine solution was circulated at such a rate that the rich solution exiting the absorber contained approximately 0.45- to 0.50 moles of carbon dioxide per mole of monoethanolamine (mol./mol.) with reboiler heat duty set such that the lean solution exiting the regenerator contained 0.10- to 0.15 (mol./mol.). The principal material of construction for this system was 304-316 stainless steel.

Improving the design

This design, although excellent in concept and in operation, showed many areas for improvement, provided corrosion could be eliminated as a design and operating constraint. One of the major areas for improvement lie in the elimination of alloy materials of construction; hence, our choice of carbon steel for the majority of the experimental program. It should be noted

Table 1. Inhibitor performance in accelerated laboratory tests.

Additive to 65% MEA Solution Presaturated with Carbon Dioxide			Range of % Protection
Additive A	Additive B	Additive C	Given to Mild Steel Panels
0.1	0.01	0	0-16
0	0	0.1	42-99
0.05	0.005	0.05	99±1
0.05	0.005	0	0
0	0	0.05	70-99
0.025	0.0025	0.025	99±1

that we also included stainless steel in our program since process gas(synthesis gas) is used as a heat source in certain carbon dioxide removal systems. Acid-gas condensation occurs during heat transfer; hence, the need for 304-316 stainless steel.

The second area of improvement lies in the reduction in the size of the equipment by operating at high monoethanolamine concentrations, higher acid-gas loadings, and lower circulation rates. Needless to say, operating at the new conditions would result in a significant reduction in pumping and reboiler heat duty operating costs.

The third opportunity for improvement involved the removal of the reclaimer to change the unit into a closed operating system.

In brief, our goal was to develop an inhibitor system that would apply not only to existing carbon dioxide removal units, but would also serve as the prime factor in the design and operation of future units.

For simplicity, our experimental program was divided into three phases:

1. A detailed literature search and several comprehensive discussions with experienced acid-gas removal system personnel.

2. A fundamental study of the corrosion mechanisms involved in the aforementioned system.

3. An evaluation of potential corrosion inhibitors.

The literature search, subsequent discussions, and laboratory evaluations suggested the following points:

1. In the absence of acidic components (e.g., carbon dioxide and hydrogen sulfide), aqueous monethanolamine solutions do not cause serious attack of steel in the liquid phase.

2. With mixtures of two common gases, carbon dioxide and hydrogen sulfide, the corrosion behavior may be relatively complex.

Table 2. Corrosometer probe data.

Before Inhibitor Addition

Date	Probe Element	Dial Reading	Corrosion Rate mils/yr.
12-1	Mild Steel	59.5	0
12-2	Mild Steel	170	604.8
12-2	Mild Steel	209.5	532
12-7	Mild Steel	905	536.8
12-8	Mild Steel	1000+	297
1-30	304 Stainless Steel	55	0
1-31	304 Stainless Steel	56	3.65
2-3	304 Stainless Steel	58	2.34
2-4	304 Stainless Steel	59	3.65
2-6	304 Stainless Steel	59.5	0.91
2-7	304 Stainless Steel	60	1.75
2-10	304 Stainless Steel	61	1.23
2-17	304 Stainless Steel	63	1.04
2-19	304 Stainless Steel	63	0
2-25	304 Stainless Steel	65	1.22
3-3	304 Stainless Steel	68	1.83

After Inhibitor Addition

Date	Probe Element	Dial Reading	Corrosion Rate mils/yr.
3-6	304 Stainless Steel	70.5	0
3-10	304 Stainless Steel	70.5	0
3-11	304 Stainless Steel	70.5	0
3-12	304 Stainless Steel	70	0
3-13	304 Stainless Steel	70	0
3-13	Mild Steel	41.5	corrosometer
3-13	Mild Steel	43	had not
3-13	Mild Steel	42.5	stabilized
3-14	Mild Steel	42	0
3-17	Mild Steel	42	0
3-18	Mild Steel	41.5	0
3-20	Mild Steel	41.5	0
3-21	Mild Steel	41.5	0
3-24	Mild Steel	41.5	0
3-26	Mild Steel	41.5	0
3-26	Mild Steel	41.5	0
3-28	Mild Steel	41.5	0
4-3	Mild Steel	41.5	0
4-10	Mild Steel	42	0.26
4-13	Mild Steel	41.5	0
4-21	Mild Steel	41.5	0
4-30	Mild Steel	41.5	0
5-3	Mild Steel	41.5	0
5-16	Mild Steel	41.5	0
5-30	Mild Steel	41.5	0
6-16	Mild Steel	41.5	0

Table 3. Mild steel corrosion coupon[*] data.

Before Inhibitor Addition

Coupon No.	Days in Service	Weight Loss, g.	Corrosion Rate mils/yr.
DU — 368	14	6.0789	429
369	14	4.2665	301
370	5	2.3303	460
371	5	2.1392	423
372	5	2.1911	433
373	5	2.0377	403

After Inhibitor Addition

Coupon No.	Total Days in Service	Service Days Between Cleanings	Weight Loss, g., Between Examinations	Corrosion Rate mils/yr.
DU — 394	9	9	0.0027	0.3
395	9	9	0.0033	0.4
396	9	9	0.0027	0.3
397	9	9	0.0033	0.4
394	16	7	0.0019	0.3
395	16	7	0.0017	0.2
396	16	7	0.0021	0.3
397	16	7	0.0015	0.2
394	24	8	0.0016	0.2
395	24	8	0.0003	0.04
396	24	8	0.0014	0.2
397	24	8	0.0010	0.1
394	34	10	0.0015	0.1
395	34	10	0.0015	0.1
396	34	10	0.0008	0.1
397	34	10	0.0015	0.1
394	48	14	0.0011	0.10
395	48	14	0.0017	0.12
396	48	14	0.0009	0.06
397	48	14	0.0012	0.08
394	66	18	0.0000	0
395	66	18	0.0000	0
396	66	18	0.0001	0
397	66	18	0.0002	0

*The test coupons used had a surface area of 18 sq. cm. and weighed approximately 10.5 g..
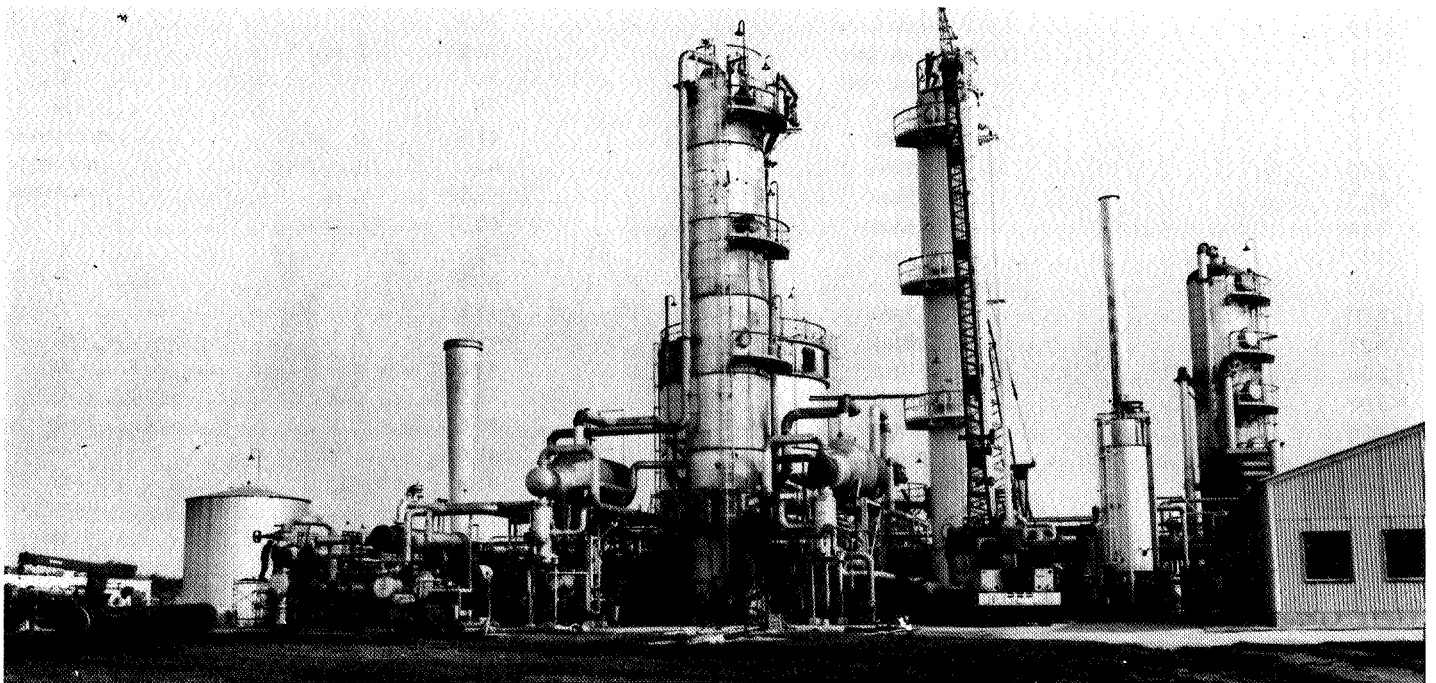
350 ton / day ammonia plant operated by C. F. Industries in Terre Haute, Ind.

Table 4. Mild steel corrosion coupon data.

Rich Stream Before Inhibitor Addition

Coupon No.	Days in Service	Corrosion Rate mils/yr.
1	5	1,260
2	4	1,179
3	7	1,356

Rich Stream After Inhibitor Addition

Coupon No.	Days in Service	Corrosion Rate mils/yr.
1	5	15.8
2	4	18.8
3	14	3.6
4	28	0.2
5	28	0.02
6	28	0.02

Reboiler Overhead Before Inhibitor Addition

Coupon No.	Days in Service	Corrosion Rate mils/yr.
1	5	59.0
2	4	67.5
3	7	76.0

Reboiler Overhead After Inhibitor Addition

Coupon No.	Days in Service	Corrosion Rate mils/yr.
1	5	0.26
2	4	0.20
3	14	0.08
4	28	0.02
5	28	0.02
6	28	0.02

3. Solution temperatures may approach 300°F and high metal surface temperatures are particularly demanding with regard to inhibitor response.

4. Monoethanolamine solutions seem to become more corrosive with use, perhaps for several reasons.

5. Monoethanolamine has good thermal stability in aqueous media; however, the carbonate salt can be converted upon heating to other products, such as, N-(2-hydroxethyl) ethylene diamine (HEED). The greater corrosivity of this conversion product has been verified.

6. Although corrosion is often of a general nature, insidious localized attack does sometimes occur. This suggests that a passive-active condition may occur, which could help explain some of the unpredictability of the corrosion problems.

7. In general, the corrosion of steel by carbon dioxide-containing monoethanolamine solutions is in agreement with its fundamental electrochemical characteristics as indicated by potentiostatic studies.

8. Vapor phase as well as liquid phase corrosion may occur.

It is not within the scope of this article to discuss in detail the corrosion mechanisms involved in this system, however, it must be said that it was found that the system could indeed be passivated even under deaeration conditions as found in the normal acid-gas removal system.

Corrosion inhibitors

Our selection of inhibitors for this system involved evaluation of three fundamental categories of inhibitors, i.e., oxidant-type, precipitant-type, and adsorption-type inhibitors. The results of this evaluation showed a combination of additives for corrosion control to be the optimum, Table 1. Two points should be noted with respect to this table. First, our test program involved several hundred known additives and not one when used alone afforded complete protection to mild steel test panels. Second, additive C, when used alone, gave sporadic protection (42- to 99%) to the test panels; yet, when combined with additives A and B at the proper concentration, resulted in an inhibitor "system" that afforded complete protection to the test panels. This phenomenon is best described by the definition of synergism: the cooperative action of discrete agencies such that the total effect is greater than the sum of the two effects taken independently.

The last and most severe test of the efficacy of our inhibitor "system" was conducted in a Parr Series 4500 reactor with a monoethanolamine solution saturated with carbon dioxide. This experiment was conducted at 300°F with pure carbon dioxide injected into the bomb to maintain a constant pressure. The corrosion rate on mild steel at these conditions was essentially nil.

The first commercial unit to utilize the inhibitor ("Amine Guard") system was a 1000 ton/day ammonia unit that had been in operation for approximately four years. At the time of injection, this unit was experiencing some degree of corrosion as evidenced by corrosometer, coupon, and operating data. Table 2 contains the corrosometer data before and after injection with these data being verified by visual inspection during a scheduled turn-around. Two comments on these data are

appropriate; first, one should note the efficacy of this inhibitor with respect to carbon steel and, second, attention is drawn to the immediate reduction of corrosion after injection of the inhibitor system.

Table 3 contains corrosion rate data for carbon steel coupons located in the rich solution piping on the discharge side of a hydraulic turbine. It is fully understood by the authors that the corrosion rate on the mild steel coupons is not representative of the corrosion rate with respect to the piping. However, a measurement of the coupon corrosion rates before and after injection at this particular location does give one a good indication of the effectiveness of the inhibitor system.

Table 4 also contains corrosion rate data on carbon steel coupons located in the rich solution piping downstream of the heat exchangers and in the reboiler overhead line to the stripper. These data were generated in a 350/ton day ammonia plant. The data obtained at the latter location are noteworthy in that this particular section of piping, plus the stripper overhead piping and condenser, were of prime concern with respect to corrosion inhibition. The vapor pressures of the various components in our inhibitor system are relatively low, therefore, one would not expect the inhibitor system to be in contact with the piping and vessels in these areas. However, it was found through coupon corrosion rate data that these areas were afforded a significant degree of corrosion inhibition. We have attributed this phenomenon to entrainment.

As mentioned earlier, one of our goals was to operate a closed system, i.e., one without a reclaimer. Our first test unit has been on line for approximately three and a half years without the reclaimer in service with no excessive accumulation of N-(2-hydroxyethyl) ethylene diamine (HEED), in organic residues, or heat-stable salts in the circulating monoethanolamine solution. Solution analyses data from all other units employing "Amine Guard" are in agreement with these test data. One additional comment with respect to the operation of a closed system is warranted, though somewhat painful: the usage of monethanolamine in these systems has been reduced by 40- to 60%.

In 1970, an optimization study was begun which incorporated theoretical, laboratory, and operating data. This study was conducted primarily for carbon dioxide removal systems in ammonia production. We are not at liberty at this particular time to discuss in detail the results of our optimization program; however, we may generalize.

Presently, we have several units, including an essentially all carbon steel unit, on an optimization program. This program consists of systematic increases in monoethanolamine concentrations and acid-gas loadings, and decreases in solution circulation rates. These changes have resulted in significant reductions in reboiler heat duties which is our prime goal for existing units. In addition to this, we have not evidenced any significant corrosion problems, foaming problems, or increases in soltuion contaminants at the new operating conditions.

In summary

Carbon dioxide removal systems utilizing inhibited ("Amine Guard") aqueous alkanolamine solutions have completely eliminated corrosion as an operating problem at design and above design conditions. A systematic program to determine the true value of the inhibitor is in progress with favorable results to date. When complete, the data generated from this program, coupled with accurate physical property data, should result in the
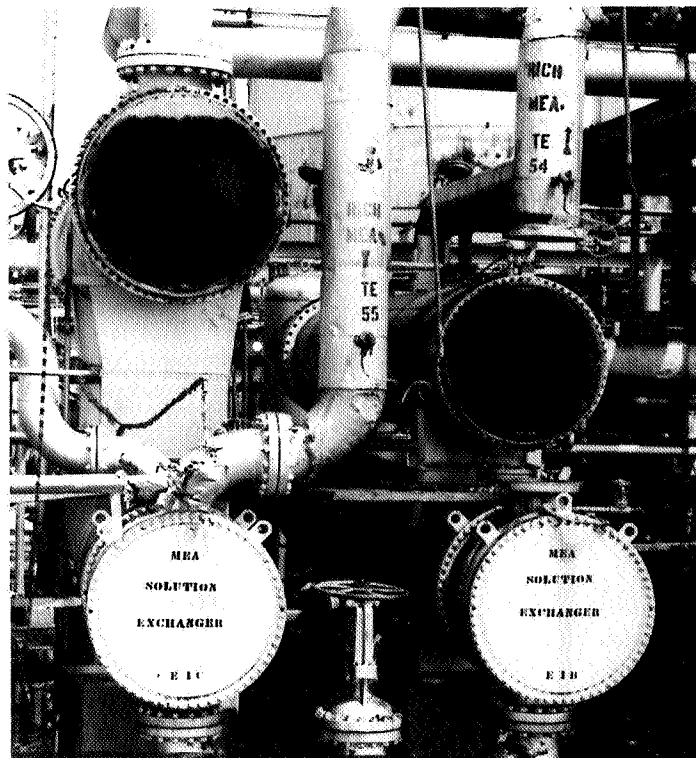
End view of MEA solution exchangers.

design of a monoethanolamine-carbon dioxide removal unit at substantially lower capital and operating costs.

Acknowledgment

We would like to extend special thanks to the Management and Operations personnel of the commercial test plants for their cooperation and support in evaluating this inhibiting system. Also, special thanks are due C.W. West and others for the basic research work that resulted in the discovery of the inhibitors involved.#

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DISCUSSION

BUTWELL: There are three main factors that Union Carbide takes into consideration with respect to the optimization program: Point one, no unit utilizing the inhibitor has experienced a failure due to corrosion at this particular time. Secondly, when you make an operating change, for example, in a 1000 ton/day Ammonia Carbon Dioxide Removal Unit, you must realize that this is not a laboratory test unit but an intergral part of an industrial complex that has a capital cost of perhaps 30 million dollars. Therefore, a conservative approach should always be taken. The third factor, and I think we have finally overcome this, is the precise steam and water balance around these units. During normal operation, the steam condensate is utilized in other areas of the complex. This source of water is essentially eliminated during the optimization study as we have to vent the steam to the atmospehre; therefore, we have only six to eight hours to determine the approximate mechanical and chemical limits of the chemical limits of the carbon dioxide removal system. Once these limits have been established, condensing turbines can be put into service and our optimization program can be continued to completion.

JIM FINNERAN, M.W. Kellogg Co.: This development represents a very efficient way of chemical debottlenecking an ammonia plant. I believe this is the major application for the development at this time. I have two questions I would like to ask.

Would you care to comment on the MEA concentration with which you have experience at this time. You mentioned 20% MEA as the starting point. Can you tell us the MEA concentration actually used with your additive? My second question concenrs whether this inhibitor has other applications. It occurs to me that there may be other application, in other solvents, or other solutions, in which this inhibitor might be highly effective.

BUTWELL: In answer to your second question: at this time, we are actively engaged in five particular applications for the "Amine Guard" inhibitor system:

1) We are currently utilizing the inhibitor system in a few natural gas processing plants where the hydrogen sulfide feed concentration is less 5 ppm by volume.

2) It is in the developmental stage (semi-works) for the removal of hydrogen sulfide and carbon dioxide from a sour naptha cracking operation.

3) We are finalizing our plans for the installation of the inhibitor system in a acid-gas removal unit associated with the Wulfe Process.

4) We are currently studying its application in the acid-gas removal system associated with a coke-oven type installation.

5) We are currently utilizing the inhibitor system in a monoethanolamine-carbon dioxide removal unit that is very similar to the carbon dioxide removal facility associated with an LNG operation. The outlet carbon dioxide specification concentration is maintained at less than 12ppm by volume.

The answer to your first question is somewhat complicated by the fact that our inhibitor system is proprietary in nature. In all fairness to our clients and ourselves, it would be inappropriate at this particular time to discuss in detail the operating data generated at various units during our optimization program. However, I will say that these conditions are well above the design conditions.

W.D. CLARK, ICI Britain. If I understood what you said during your paper, you had a large plant running and corroding fairly badly, and you added the inhibitor to the solution, and it stopped corroding.

BUTWELL: Yes sir.

CLARK: Now this is rather unusual, because in most cases where a plant is corroding, it is heavily coated with corrosion products and an inhibitor has difficulty in getting down to the metal surfaces. Did you, in fact, do any extensive cleaning-out operations so that the inhibitor had its best chance, or was it as simple as perhaps you implied.

BUTWELL: As mentioned earlier, Table 2 contains Corrosometer Probe data as a function of time. A review of this data shows the inhibitor system to be effective almost immediately after injection of the inhibitor system. Presently, this is typical for all systems employing this inhibitor system. However, it does not contain the inhibitor depletion rates as a function of time nor does it contain some of the anxious moments we at Carbide have had during the initial period (six weeks) of inhibition at a few units. Examination of metal surfaces at several units utilizing this inhibitor system shows our system to perform as both a cleansing agent and a passivating agent. In addition to this, examinations of solid residues from these units show a positive test for the inhibitors. With this background information, we prefer, naturally, to inject into a unit that has been thoroughly cleaned. At these conditions we show immediate passivation and a low inhibitor depletion rate as expected. When we inject into a system that is experiencing severe corrosion rates we expect a high inhibitor depletion rate for the simple reason that our inhibitor will not only passivate the equipment metal surfaces but also any iron particles floating around the system. In these particular instances we try to maintain a sufficient quantity of our inhibitor in the solution such that we are able to continually passivate the equipment metal surfaces. Presently, we have not experienced an equipment failure in these units.

RALPH FREEMAN, Cherokee Nitrogen Co.: We're currently using a combination of sodium metavenadate and petromeen 52 in our system. We have corrosion rates of less than one mil per year, and we do not use a side stream filter or a reclaimer. I'm interested in knowing whether this would in any way infringe upon the patents for your current procedure. We have been using this method for corrosion protection for 5 years and as far as we're concerned it is working very well for us. The equipment that we see Union Carbide portraying here seems to be very similar to the system we are using at Pryor, Oklahoma. Can you tell us if there is any chance of a patent conflict between our corrosion inhibitors and the system you are offering?

BUTWELL: The gentleman is utilizing a combination of inhibitors in his moneothanolamine-carbon dioxide removal system which he claims is effective. His question is: Are we infringing on any of Union Carbide's patents?

As a chemical engineer from the Research and Development Department, I am not qualified to answer your particular question. A representative from our Patent Department could supply the answer.