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**CORROSION DUE TO USE OF CARBON DIOXIDE
FOR ENHANCED OIL RECOVERY**

Final Report

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Work Performed for the Department of Energy
Under Contract DE-AC21-78MC08442

SumX Corporation
Austin, Texas



**National Petroleum Technology Office
U.S. DEPARTMENT OF ENERGY
Tulsa, Oklahoma**

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**Final Report
SumX No. 78-003**

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U.S. DEPARTMENT OF ENERGY

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Section 1

INTRODUCTION

This report was prepared for the Department of Energy, Morgantown Energy Technology Center, by SumX Corporation under Contract No. DE-AC-21-78 MC08442.

Injection of carbon dioxide (CO_2) is a promising method for recovering large amounts of oil that cannot be recovered by conventional (primary and secondary) technology. As with any relatively new technology, there are aspects of CO_2 injection that, without adequate assessment, could discourage its use. One of these aspects is the potential for increased corrosion of oil field equipment that could result from CO_2 injection. The purpose of this study is to document the specific effects of CO_2 on corrosion and to identify promising methods for controlling corrosion in fields using CO_2 injection.

As a result of this study, information has been assembled on the following items:

- 1) CO_2 corrosion problems in general,
- 2) surface and downhole corrosion problems specifically associated with CO_2 enhanced oil recovery, and
- 3) methods to reduce corrosion problems in CO_2 environments.

The information was gathered from the open literature and discussions with personnel active in the subject area. The basic phenomena associated with corrosion in CO_2 environments must be understood before one can forecast

potential problems and outline control procedures. Such understanding is derived from rigid laboratory testing as well as practical field testing and experience. Therefore one of the goals of this study was to assemble and evaluate data on corrosion in CO₂ environments and the effects of other chemical species. Corrosion mechanisms, kinetic behavior, and the effects of various parameters on corrosion by CO₂ are presented in this study. Surface and downhole corrosion problems are examples of actual phenomena with which users of enhanced recovery methods must become familiar if they are to conduct successful programs. This report presents some of the problems that may be faced in the field. The information is not exhaustive because there is still limited experience in the application of CO₂ injection on a large scale long-term basis. Also, different types of fields must be explored before all potential problems can be identified. The ultimate goal once there is an understanding of the occurrence of the corrosion problems and why they occur is to control or alleviate these problems. This report also discusses a number of potential control procedures and their application.

The applied corrosion literature is extensive and somewhat chaotic, particularly when many sites are involved and corrosion phenomena are dependent at least to some extent on the characteristics of the individual sites. The best guide is experience, preferably long-term experience, in field use closely approximating the normal case. This can be supplemented by experience in less directly related environments and by laboratory or pilot scale measurements under controlled conditions. This information provides guidelines for generalization or extrapolation.

The latter type of information is given in Section 2 which is a literature review of the corrosive effects of CO₂. Engineering metals are not attacked by CO₂ under oil field environments unless liquid water is also present. Plain and low alloy steels are attacked by mixtures of CO₂ and liquid water. Attack on these bare metals may become serious at a CO₂ partial pressure as low as 4 psi and it increases with CO₂ partial pressure although not in direct proportion. Fluid flow rate is an important factor in CO₂/water corrosion. Practically all stainless steels and similar

resistant alloys are not particularly subject to corrosion by CO₂/water mixtures alone, even at high CO₂ pressures. Elevated levels of CO₂ can aggravate the corrosive effects of other species such as hydrogen sulfide, oxygen, and chloride. Mixtures of CO₂, carbon monoxide (CO), and water can cause stress corrosion cracking of plain steels.

Corrosion problems in CO₂ systems should be circumvented when possible by avoiding combination of the corrosive components. Although water cannot be excluded throughout the CO₂ injection-oil production-CO₂ and water reinjection chain, air in-leakage can be minimized and oxygen scavengers used to remove any residual. Exclusion of oxygen is important to the successful use of other corrosion control measures.

Section 3 is a discussion of the main control methods including metal selection, protective coatings and nonmetallic materials, and chemical inhibition. The strengths and weaknesses of each method are discussed. While all of the methods have been successfully used, no one method can be totally relied on or used without adequate precautions. This is emphasized in Section 4 which shows how the corrosion control methods are integrated to protect individual blocks of CO₂ injection-oil production equipment. Information for this section was derived mainly from relatively long-term experience at CO₂ injection fields.

Section 2

CORROSIVE EFFECTS OF CO₂

Section 2.1 describes uniform corrosion rates in aqueous CO₂ solutions. The literature results can be roughly divided into two groups: those for bare steel surfaces and those for which a reaction product layer is formed. The bare steel results are mainly applicable to high fluid flow rate locations. There is a relatively large amount of quantitative information on effects of CO₂ concentration, temperature, and other chemical species for this situation. When reaction product layers are formed, uniform corrosion decreases but localized corrosion can become a problem as noted in Section 2.2. Most results and trends are of a more qualitative nature for this case. The presence of other chemical species, especially H₂S, can have a more profound influence on localized corrosion than on uniform corrosion.

The effects of CO₂ on several types of cracking failures are given in Section 2.3. Stress cracking in the CO-CO₂-H₂O system can be important if the injection gas contains CO as an impurity. Acidification by CO₂ could worsen sulfide stress cracking problems in some oil fields. Effects of CO₂ on corrosion fatigue of steel are also given. Corrosion in nearly pure CO₂ is discussed in Section 2.4, and some effects of impurities on corrosion in CO₂ streams are presented. Certain nonmetallic materials are degraded in high pressure CO₂.

2.1 UNIFORM CORROSION RATE IN CO₂ SOLUTIONS

The uniform corrosion rate of steel increases with increasing CO₂ concentration. Much of the early literature attributes this to lowering of solution pH by CO₂ addition. While this is a significant factor, it has been shown that CO₂ has a more direct role in corrosion and that corrosion rates

are generally higher in CO₂ solutions than in solutions of completely disassociated ("strong") acids of the same concentration.

The uniform corrosion of iron proceeds by coupled electrochemical reactions. When no solid reaction products are formed, the overall anodic dissolution reaction can be written as in Equation 1.



This reaction appears to proceed through intermediates involving hydroxyl ions (OH⁻) in such a way that its individual rate decreases with decreasing pH from about pH 5 to pH 1 (1). This effect is seldom noted in corrosion practice due to control by the cathodic reaction. In deaerated media, the usual cathodic reaction is hydrogen evolution as in Equation 2.



The increase in rate of this reaction with decreasing pH more than offsets the pH dependence of the reaction in Equation 1 (1) and the net effect is that corrosion rates increase with decreasing pH. In solutions of highly dissociated acids, the relationship given by Equation 3 is often found (2).

$$\log i_{\text{corr}} = -0.5 \text{ pH} + B \quad (3)$$

The open circuit corrosion current density, i_{corr} , is directly related to the uniform corrosion rate, and B depends on temperature, surface preparation, etc.

Carbon dioxide appears to primarily affect the cathodic reaction rate. In order to explain their results, deWaard and Milliams proposed that hydrogen evolution could occur directly from carbonic acid as in Equations 4a and 4b, with the rate determined by the first reaction (reference 3).



Hydrogen atom combination to H_2 can then occur via conventional routes, and the overall reaction is the same as Equation 2. In this sense, carbonic acid "catalyzes" the hydrogen evolution reaction.

Schwenk proposes that the effect of CO_2 is to augment mass transfer of hydrogen ions to the metal surface (4). Thus, hydrogen is generated from hydrogen ions produced by dissociation of H_2CO_3 near the surface rather than from H_2CO_3 directly. The high concentration of H_2CO_3 or its precursor CO_2 relative to H^+ in the bulk solution increases overall mass transfer rates and depolarizes the cathodic reaction. The distinction between this point of view and that of deWaard may seem rather small, but it could affect the dependence of corrosion rate on CO_2 concentration under certain conditions and thus affect extrapolation accuracy.

In either case, it is noteworthy that the ability of carbonic acid to sustain a high cathodic reduction rate at relatively high pH indirectly also aids the anodic reaction (Equation 1) (1) which is faster at higher pH values.

At high CO_2 partial pressures, the uniform corrosion rates presented in much of the literature are extremely high. It is likely that in most cases such rates do not persist long in practical equipment due to formation of more or less protective films. The rates are important, however, since

- they place an upper limit on the uniform thinning that could occur,
- some of the films are prone to dislodge in large patches exposing metal surfaces to periodic high corrosion rates, and
- high rates may persist in high local flow rate regions.

Experimental procedures used for obtaining the more extensive corrosion data are given first followed by a summary of the results.

DeWaard and Milliams measured the corrosion rate of X-52 carbon steel in oxygen-free solutions of 0.1% NaCl saturated with CO₂ at partial pressures from 0.7 to 15 psi (3). Both polished and grit-blasted steel specimens were used. The solution was stirred to achieve a velocity of about 1 m/sec around the steel specimens. Runs were made at temperatures from 5°C to 80°C. Corrosion rates were monitored by the linear polarization technique calibrated by also measuring weight loss during each run. Potentiodynamic polarization curves were measured in 1% NaCl.

Ovodov measured the corrosion rates of steel 45 and steel 3 at CO₂ partial pressures from 140 to 710 psi in solutions containing 0 to 300 g/l NaCl and in "tap water" containing about 1 g/l of salts (5). Tests were done at room temperature with stirring at 400 rpm in an autoclave. Corrosion rates were determined by weight loss. Corrosion potentials were also measured. Some runs were also made with solutions preacidified with hydrochloric acid or sulfuric acid.

Abramyan measured the corrosion rates of mark 45 steel in a solution containing 0.5 g/l NaCl and 0 to 8 cm³/g of CO₂ (corresponding to CO₂ partial pressure of about 0 to 150 psi at 25°C) (6). Studies were performed at a flow rate of 1 cm/sec, temperatures from 25 to 150°C, and total pressures of 260 to 1420 psi. Test duration was 12 hours. Corrosion rates were determined by weight loss. Open circuit voltages were measured as a function of time and experimental conditions. Polarization curves were measured at various CO₂ concentrations.

Rhodes and Clark measured the corrosion rate of 0.2% carbon steel under static flow conditions at CO₂ pressures from 80 to 450 psig and 22.5°C (7). The liquid medium did not contain any added salts. Rates were determined by weight loss and test duration was apparently several days. Corrosion

rates of various stainless steels and nonferrous metals were measured at 450 psig CO₂.

Greco and Wright measured the corrosion rate of a low carbon steel under static flow conditions at CO₂ pressures from 0.3 to 4.5 atm (8). Conditions for this particular set of tests are unclear, but the solution probably contained 400 ppm NaCl. Weight loss rates were obtained after 48 hours immersion.

A substantial part of the uniform corrosion data for steel in aqueous CO₂ solutions at 25°C is summarized in Figure 1 as a logarithmic plot of corrosion rate* vs. CO₂ partial pressure. All of the data shown in this figure were obtained in solutions of CO₂ in distilled water or water containing 0.5 g/l or 1.0 g/l NaCl. Therefore salting out effects are minimal and the aqueous concentration of CO₂ is directly related to the partial pressure of CO₂. The results from different workers are consistent if they are divided into the two segments shown. The slope of the upper curve up to the highest CO₂ partial pressure is approximately the same as that obtained by deWaard at low pressure and expressed by Equation 5.

$$\log r = 0.67 \log P_{\text{CO}_2} + C \quad (5)$$

where r is the corrosion rate, P_{CO_2} is CO₂ partial pressure and C is a constant. Additional low pressure results and effects of surface preparation and temperature are shown in Figure 2.

The main difference between experimental conditions for the two sets of results appears to be that solution flow near the specimens was present during the upper curve tests while stationary solutions were used for the lower curve tests. However, this is probably not due to mass transfer control since the deWaard's and Abramyan's results merge even though the former tests were done at about 1 m/sec while the latter were at 1 cm/sec.

*Corrosion rates in this report are given in mil (0.001 inch) penetration per year (mpy).

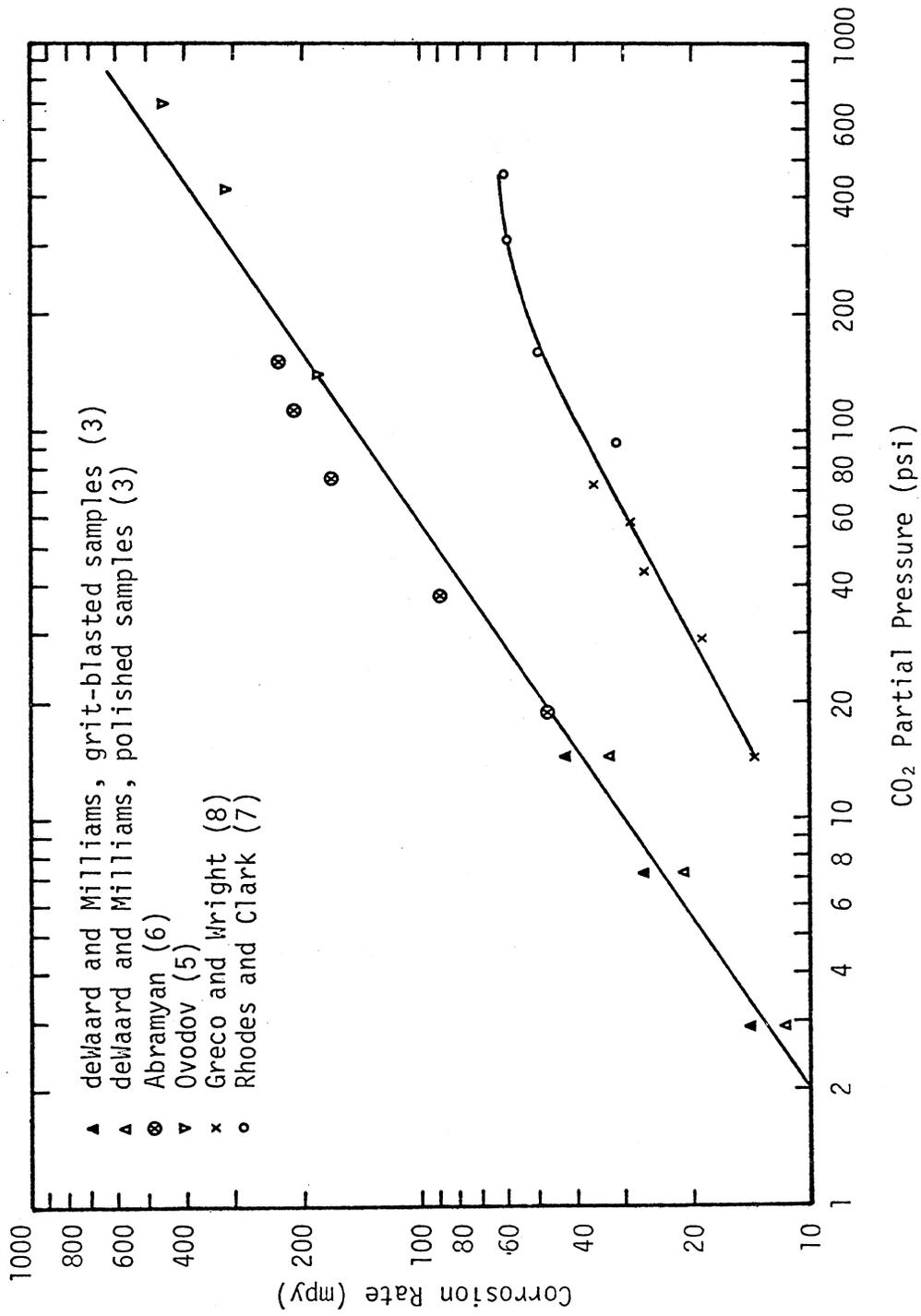


Figure 1. Uniform Corrosion Rate of Steel as a Function of CO₂ Partial Pressure.

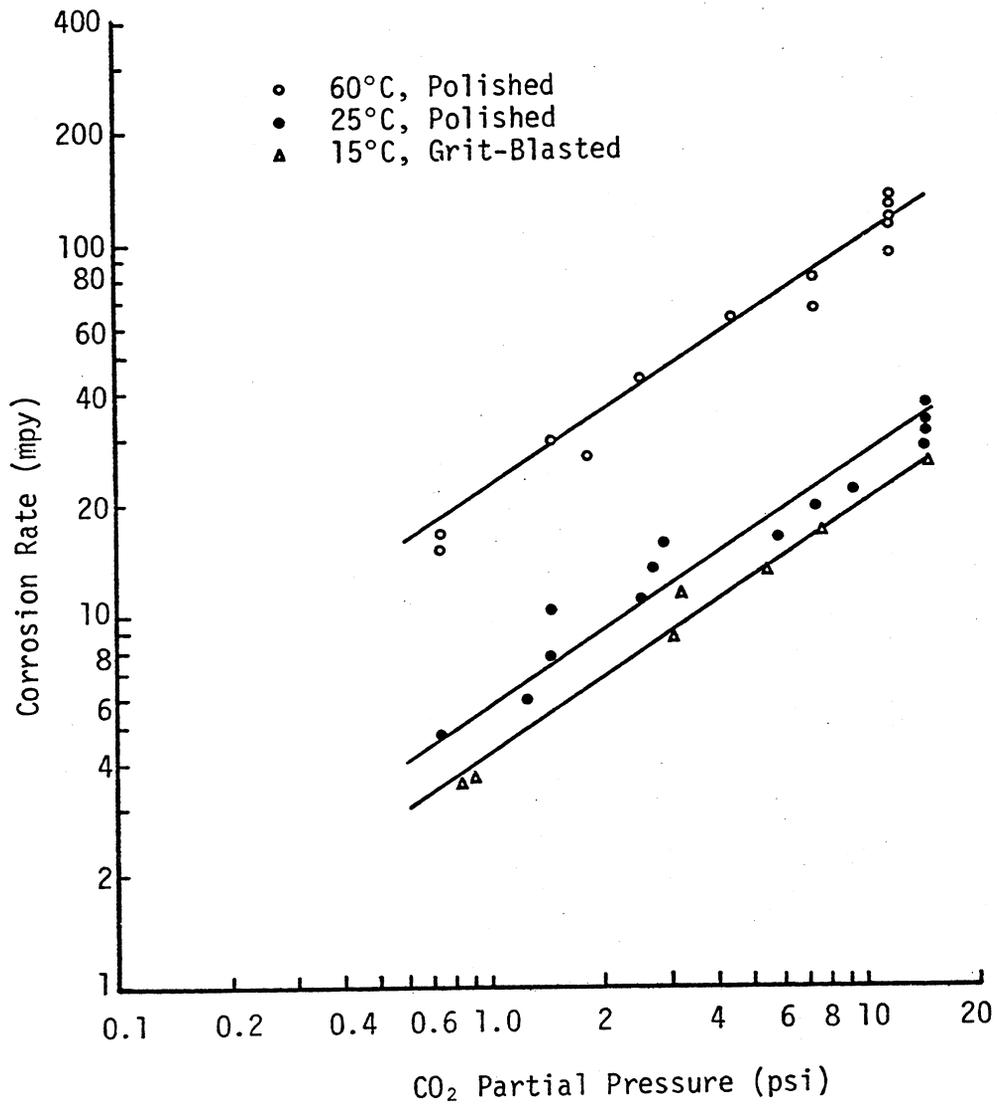


Figure 2. Influence of CO₂ Partial Pressure and Temperature Upon the Corrosion Rates of Steel (Reference 3).

It is more likely that a semi-protective reaction product layer is formed under quiescent conditions which either cannot be formed or is rapidly destroyed by solution movement. When mass transfer is limited, the solution pH near the metal surface can be substantially higher than that in the bulk solution due to consumption of hydrogen ions by the hydrogen evolution reaction. This locally high pH and high ferrous ion concentration can allow the formation of solid products such as FeCO_3 which might not be stable in the bulk solution.

Rhodes mentions that a loose black coating was present on the steel samples after his high CO_2 pressure static experiments (7). This coating could be easily removed by wiping with a cloth. Corrosion films formed in the moderate pressure (1 to 5 atm) static runs were "extremely slight and gray" (8).

Film formation was also occasionally observed in stirred solutions, especially at temperatures above 60°C (3). A drop in corrosion rate accompanied the formation of a black layer, and it was noted that the effect occurred more often in stagnant solutions at even lower temperatures. At 80°C all specimens became "passive" within several hours (3). At 5°C , polished steel specimens often failed to become active on immersion, under conditions where grit-blasted specimens maintained ten times higher corrosion rates. All of these observations can be rationalized by assuming precipitation due to high local pH and ferrous ion concentration near the surface. At high temperatures such conditions can occur due to high initial corrosion rates. Also, rapid precipitation may produce a finer, more closely packed and thus less permeable precipitate on the surface. At low temperatures solution viscosity is increased, thus decreasing mass transport to the surface. But this is overcome at rough (grit-blasted) surfaces due to surface turbulence.

Additional insight into the role of surface films is provided by a study of the corrosion of steel by a spray of dilute acetic acid in a CO_2

atmosphere (9). The corrosion rate varied inversely with acid concentration for less than 500 ppm acetic acid at constant CO₂ partial pressure. For 500 to 1000 ppm acetic acid, initial corrosion rate was high, but continuing corrosion rate was low. Below 1 atm CO₂, the corrosion rate was independent of acetic acid concentration except for the lowest concentration used. A substantial rate increase occurred for 1.5 atm CO₂ at all acetic acid concentrations. The corrosion product film was primarily FeCO₃ which offered some protection to the metal until it became thick enough to part due to internal stresses. It was postulated that the films formed at higher acid concentrations were more protective since the initial rapid attack caused them to precipitate as fine grain particles. Films formed at lower acetic acid concentrations were coarser and more porous, thus exposing more metal area to continuing attack.

2.1.1 Additional Results for Oil Well Steels and Other Metals in Aqueous CO₂

A number of metals were tested in aqueous solutions at a CO₂ partial pressure of 200 psi and 130°F (10). Coupon samples were contained in pressure vessels rotated at 9 rpm and were exposed for periods of 7, 28, and 70 days. This research was prompted by gas condensate well corrosion and metals were chosen accordingly. Uniform corrosion results are shown in Table 1. Pitting and edge attack results are given in a later section.

Comparison of the carbon steel corrosion rates with those presented earlier suggests that these samples were film-covered during most of the test duration. The rates after 7 days exposure were intended to be a more realistic measure of the natural corrosion in wells under conditions such that corrosion products are eroded or otherwise removed soon after formation (10). The corrosion rates after 28 and 70 days exposure are much lower than the 7 day rates and those presented earlier in this report.

The differences between the uniform corrosion rates of the tubular goods carbon steels are relatively small. The corrosion rates of the Cr and

TABLE 1. COMPARISON OF THE RESULTS OF LABORATORY TESTS OF RATES OF CORROSION OF METALS SELECTED BY NACE COMMITTEE

Material	Average rate of corrosion during indicated period of continuous exposure, mpy					
	Propionic acid			Carbonic acid		
	Days,7	Days,28	Days,70	Days,7	Days,28	Days,70
Carbon steels						
J-55	1.8	4.7	4.6	62	13	5.8
H-40	1.1	4.2	3.1	60	15	9.1
N-80	1.5	4.9	4.7	77	17	5.5
Cast HE-3604 L-A	.66	1.4	1.5	14	4.4	2.2
Chromium steels						
Croloy 2½	3.1	3.8	3.3	59	6.2	3.0
Croloy 5	4.2	2.3	3.3	46	.86	4.2
Croloy 9	.46	.19	.55	1.4	.59	.19
Croloy 12	.070	.11	.037	.82	.29	.11
Cast AW-2023 L-12	.064	.13	.037	.070	.048	.015
Cor-ten	1.3	4.4	4.8	83	17	7.5
Grade 8 (Bulletin 26)	2.0	3.8	3.7	54	18	5.1
Nickel steels						
Nickel 3½	1.5	1.0	1.5	28	6.2	3.1
Nickel 5	1.3	3.1	1.6	26	13	2.1
Nickel 9	.96	1.8	1.7	27	4.9	1.2
Nickel metal	.23	.12	.12	.11	.068	.039
Chromium-nickel steels						
Type 304 (18-8)	.00	.018	.00	.00	.00	.00
Type 347 (18-8-Cb)	.00	.00	.00	.00	.00	.00
Type 316 (18-8-Mo)	.00	.00	.007	.00	.00	.00
Copper steels						
Yoloy	.99	1.0	1.8	32	13	7.3
Copper steel	1.5	4.6	3.8	7.3	17	18
Copper alloys						
Copper-Nickel 70/30	1.1	.19	.32	.15	.039	.030
K-Monel (aged)	.26	.036	.16	.065	.013	.0081
Ampco Grade 8	.91	.85	.66	.20	.44	.18
Ampcoloy A-3	.78	.81	.52	.27	.25	.19
Everdur, Alloy 1010	2.0	1.1	.99	.23	.14	.11
Red brass, Alloy 24	.99	.51	1.1	.19	.13	.11
Copper metal	1.4	.37	.48	.27	.069	.047
Admiralty metal	1.6	.27	.49	.37	.022	.076
Aluminum alloys						
Alclad 3S-H14	2.5	1.4	1.0	1.3	.87	.94
61S-T6	1.6	.85	.30	.57	.72	.92
52S-H34	1.5	.96	.28	.67	.81	.81
Plated steels						
Zinc plate	4.6	--	--	9.7	--	--
Copper plate	1.8	--	--	.23	--	--
Nickel plate	.46	.37	.53	.40	.093	.40

Ni low alloy steels are also comparable to carbon steel up to about 9% Cr. The 9% Cr steel has a significantly lower corrosion rate under these conditions.

Parallel tests were done under similar conditions except using 200 ppm propionic acid in place of CO₂. Corrosion rates of ferrous alloys were generally about an order of magnitude lower in this solution than in the carbonic acid solution (10).

Corrosion rates were reported for a series of stainless steels and nonferrous metals at a CO₂ partial pressure of 470 psi in stationary solutions at 72°F (7). Results are shown in Tables 2 and 3. The only metal that was reported to show any pitting was zinc. Test duration is uncertain but was probably on the order of several days.

TABLE 2. CORROSION RATES OF STAINLESS STEELS AT 470 psia CO₂, 72°F (from Reference 7)

Sample	Cr (%)	Ni (%)	Si (%)	Penetration Rate (mpy)
1	13.1	0.1	--	0.5
2	15.0	0.4	--	0.06
3	19.4	0.2	--	0.02
4	16.8	7.9	--	0.1
5	18.2	8.6	2.2	0.07
6	17.0	23.7	2.9	0.06

TABLE 3. CORROSION RATES OF NONFERROUS METALS AT 470 psia CO₂, 72°F
(from Reference 7)

	Meta1	Penetration Rate (mpy)
Brass	(Cu 61, Zn 39%)	0.32
Monel	(Ni 68.7, Cu 28.6, Fe 0.1, Mn 1.0%)	0.17
Nickel	(Ni 99.5, Cu 0.1, Fe 0.1, Mn 0.1%)	0.17
Copper	(electrolytic)	0.24
Duralumin	(Cu 4.0, Mn 0.5, Mg 0.5%)	1.8
Aluminum	(99+%)	3.0
Lead	(chemical)	1.7
Zinc		6.2

High corrosion rates have been noted in high flow rate areas of compressor plant piping and some wellhead piping associated with inert gas injection at a Ventura, California oil field (11). A gas lift gas containing about 1.0 mole % CO₂ was used for years with no appreciable corrosion. Inert gas breakthrough increased the CO₂ content to 2.5% (partial pressure of 4.5 psia) and corrosion started in areas where gas velocities were about 9 to 46 fps. The measured corrosion rates of 150 to 200 mpy correlate well with those predicted from deWaard's nomogram (see below) for bare steel surfaces (150 mpy at 30°C, 68 psi CO₂ partial pressure). Scale samples from low velocity areas contained ferrous carbonate and ferric oxide.

Prange reports results of field tests of N-80 and low alloy steel 4340 in the lead line of a condensate well producing gas with a CO₂ pressure of 1120 psi and daily water production of 4 barrels per MMCF at a wellhead pressure of 4400 psi (12). In this lead line, the corrosion rate of 4340 was 60 mpy while that of N-80 was 30 mpy. There was no measurable corrosion

of 9% chromium steel. Tubing of 4340 steel in other wells in this field showed significantly more corrosion than N-80 as indicated by caliper surveys.

Experience in gas condensate wells has shown that corrosion rates of mild steel may reach 300 mpy in high turbulence areas such as choke bodies, ells, and tees (13).

Shock and Sudbury note that corrosion rates measured at the surface of gas lift wells are not representative of down-hole rates due to the decreased partial pressure of CO₂ (14, 15). They report coupon tests at various depths in wells with CO₂ contents of 2 to 4%, wellhead pressures of 100 to 200 psi and bottom-hole pressure of 3000 psi. The results shown in Table 4 show that bottom-hole rates are about 10 times larger than those at the wellhead.

TABLE 4. CORROSION RATES (MPY) AT VARIOUS DEPTHS IN A GAS LIFT WELL
(from Reference 14)

Depth (ft.)	Run 1	Run 2	Run 3
0	5.6	3.9	7.6
2216	8.4	5.8	---
3076	---	---	33
4164	61	49	---
5373	---	---	66
7618	80	38	65

2.1.2 Effect of Temperature on Uniform Corrosion

Changes in temperature affect pH, equilibria associated with CO₂ solubility in water and dissociation constants of carbonic acid as well as electrochemical rates of both anodic and cathodic reactions.

At CO₂ partial pressures of about 1 atm, deWaard found that the corrosion rate followed an Arrhenius type temperature dependence from 5°C to 80°C. He converted all corrosion rates to rates which would have been obtained at a pH of 4 and produced the curve shown in Figure 3. The activation energy from this plot is 10.7 kcal/mole which indicates that the corrosion rate is controlled by electrochemical reaction rates (activation) under the conditions of his measurements. For grit-blasted steel samples, the results can be expressed by Equation 6 with r in mpy.

$$\log r (\text{pH} = 4) = 9.18 - \frac{10,700}{4.58T} \quad (T \text{ in } ^\circ\text{K}) \quad (6)$$

DeWaard presented an overall rate expression for prediction of "worst case" corrosion rates of grit-blasted X-52 samples. This is given in Equation 7 with t representing temperature in °C, r in mpy, and P_{CO₂} in psi (16).

$$\log r = 8.78 - \frac{2.32 \times 10^3}{t + 273} - 5.55 \times 10^{-3}t + 0.67 \log P_{\text{CO}_2} \quad (7)$$

The results are shown in the form of a nomogram in Figure 4.

At higher CO₂ partial pressures and temperatures, the corrosion rate does not increase as rapidly with temperature as found by deWaard. This is apparently due to mass transfer control or partial product layer formation. A plot of Abramyan's data is given in Figure 5. The curves are nonlinear and the apparent activation energy is only about 2.3 kcal/mole.

2.1.3 Effect of Chemical Species on Corrosivity of Carbonic Acid

Chloride - Chloride ion is known to strongly promote pitting and other forms of localized corrosion in the presence of oxygen or other oxidizing agent. However, in completely oxygen-free carbonic acid solutions, chloride may reduce uniform corrosion by either "salting out" the CO₂ or by surface inhibition. Neither effect is very noticeable at low chloride concentrations (below ~1000 ppm).

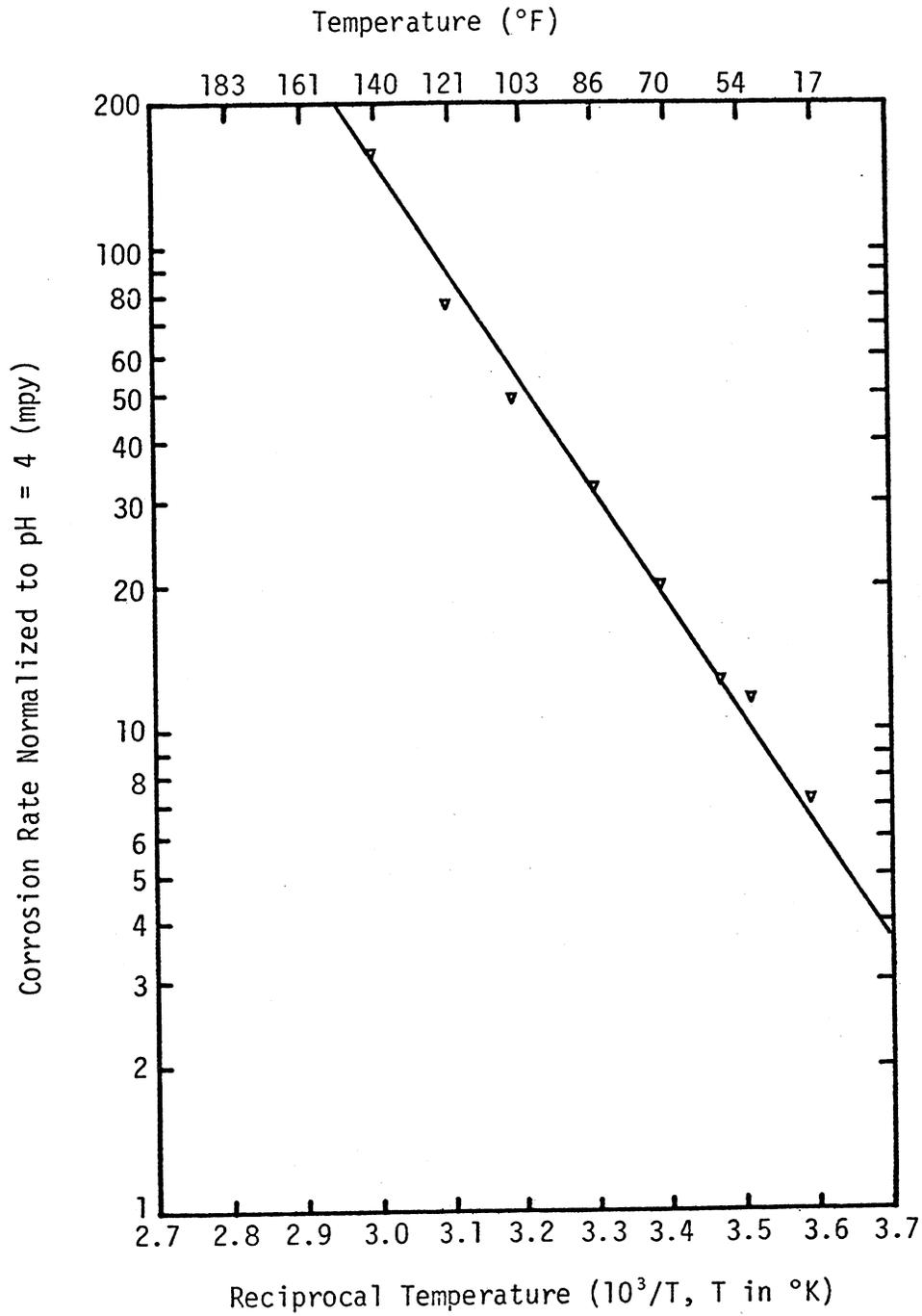


Figure 3. Arrhenius Plot of Corrosion Rates for Grit-Blasted Steel Normalized to pH = 4 (Reference 16).

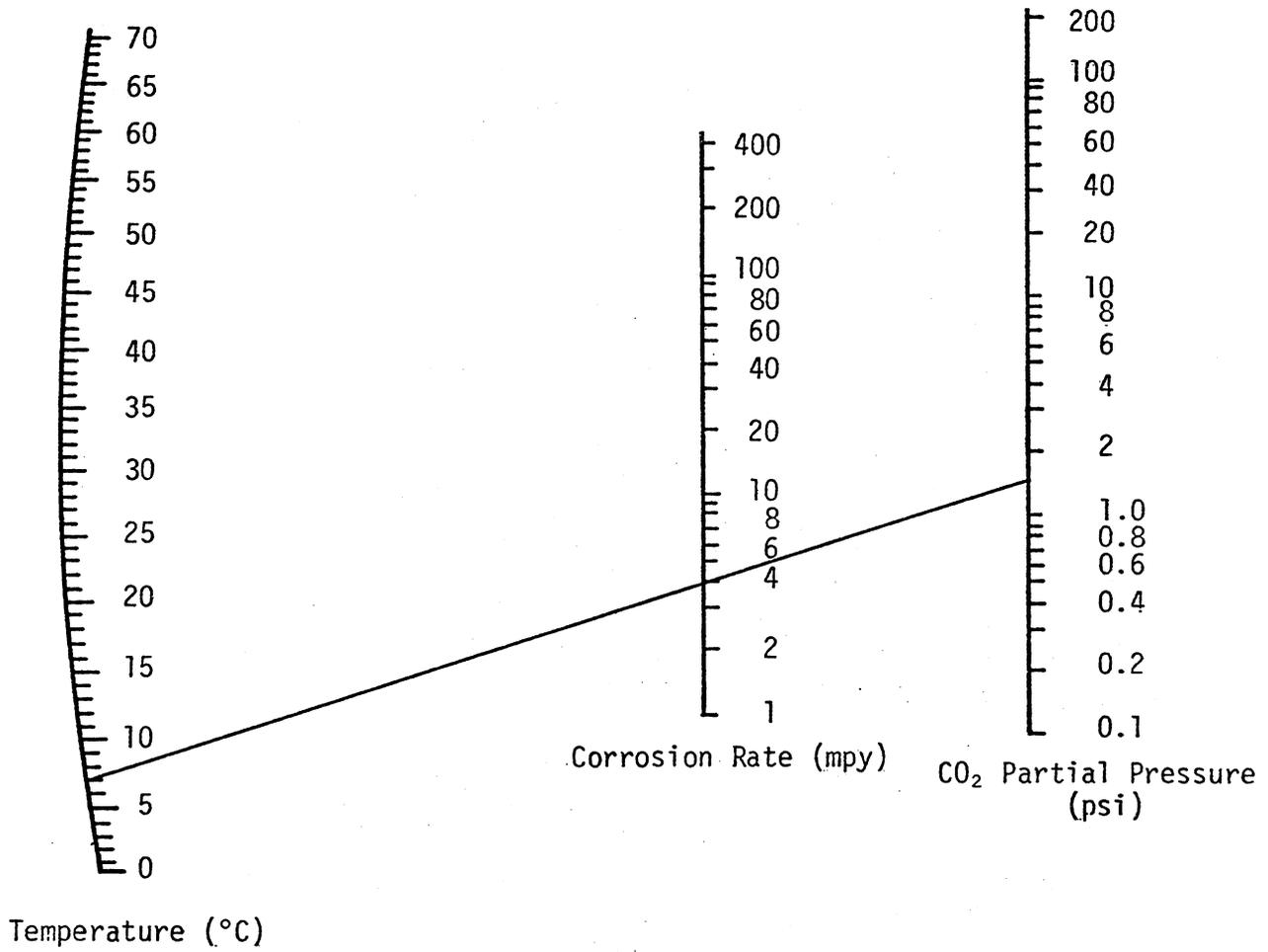


Figure 4. Nomograph for Calculation of Corrosion Rates as a Function of CO₂ Partial Pressure and Temperature. (Example shown: at 1.5 psi CO₂ and 7°C, corrosion rate is 4 mpy.) (Reference 16)

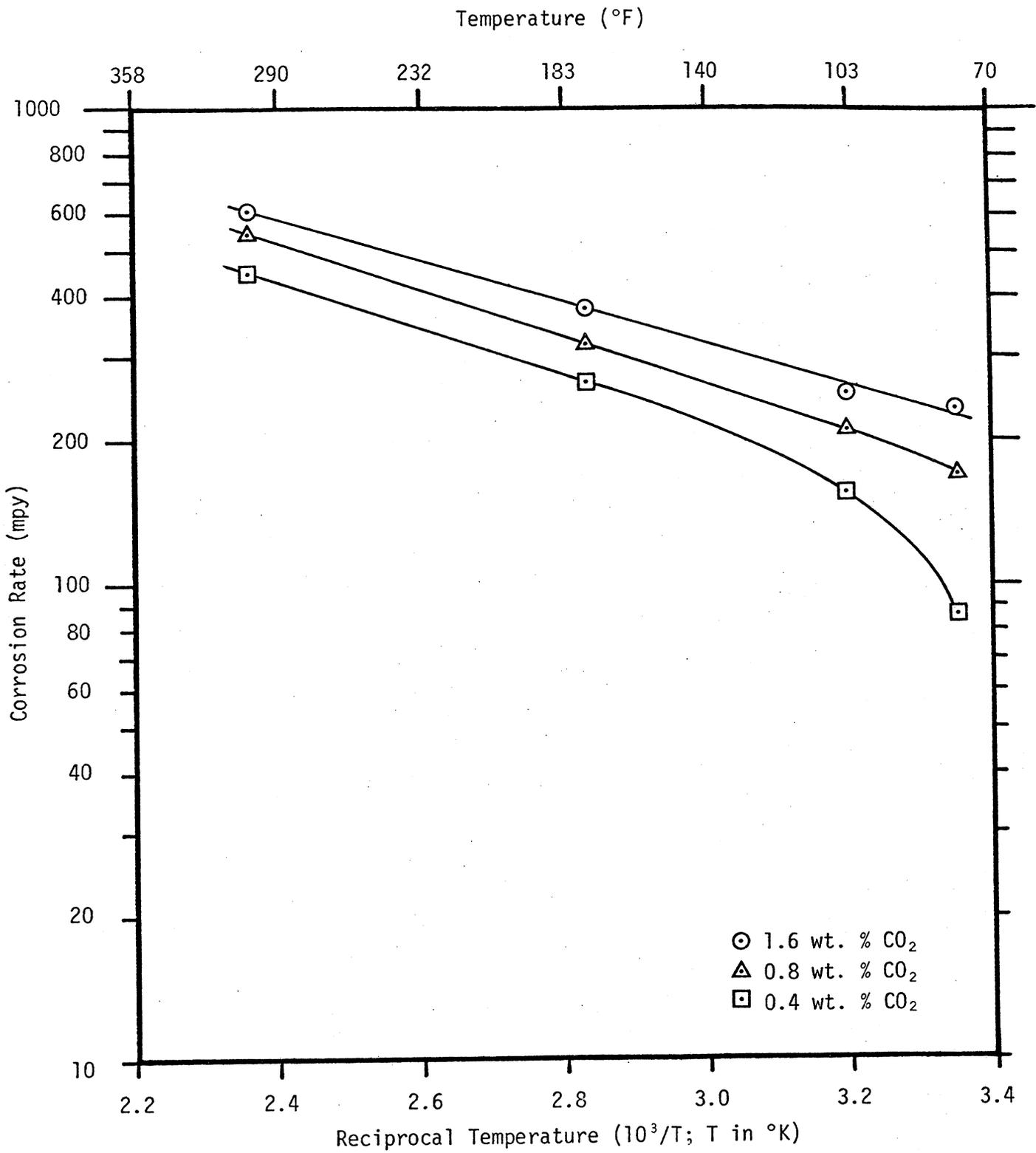


Figure 5. Arrhenius Plot of Data by Abramyan (6) at Constant CO₂ Concentrations.

Both effects are illustrated in Figure 6 which was obtained at room temperature and high CO₂ partial pressure (5). Curve 1 shows the corrosion rate as a function of CO₂ concentration in tap water with the numbers along the curve indicating the CO₂ partial pressure in psia. Curve 2 was obtained at a constant CO₂ partial pressure of 710 psi and the additional numbers indicate the concentration (in g/l) of NaCl added. Curve 3 is like curve 2 except steel 3 was used instead of the steel 45 used in curves 1 and 2.

Although these results indicate a significant decrease in uniform corrosion rate in the presence of chloride, it must be kept in mind that such solutions could cause serious corrosion if accidentally or intentionally aerated.

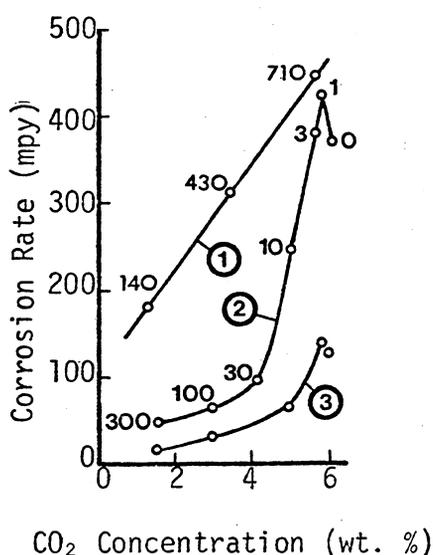


Figure 6. Corrosion Rate of Steels as a Function of Several Variables--see text.

pH - The corrosive species in carbonated solutions are primarily CO₂ and H₂CO₃. Any alkalinity which increases the pH of a solution to favor formation of bicarbonate (HCO₃⁻) and carbonate will decrease the corrosivity of the solution. The concentrations of H₂CO₃ plus CO₂ and HCO₃⁻ are equal

at a pH of about 6.3 at ambient temperatures. At higher pH's bicarbonate will start to dominate, becoming about 10 times higher than the sum of CO_2 and H_2CO_3 concentrations at pH 7.3.

Ovodov found that decreasing the pH of solutions under a high, partial pressure of CO_2 by addition of hydrochloric acid had little or no effect on corrosion rates of steel (5).

Organic Acids - Organic acids are often found along with CO_2 in gas condensate and oil wells. Relative corrosivity will depend to a large extent on relative concentrations of organic acid and CO_2 . Figure 7 shows the effect of addition of CO_2 to liquid from a gas condensate well that had been freed of CO_2 and compares that to distilled water (17). This was done at 20°C , total pressure 1.0 atmosphere using steel 45. Corrosion rates in formic and acetic acid solutions alone are shown in Figure 8 (17). Most natural wells contain only a few hundred ppm organic acids and the authors conclude that CO_2 is the main corrosive agent.

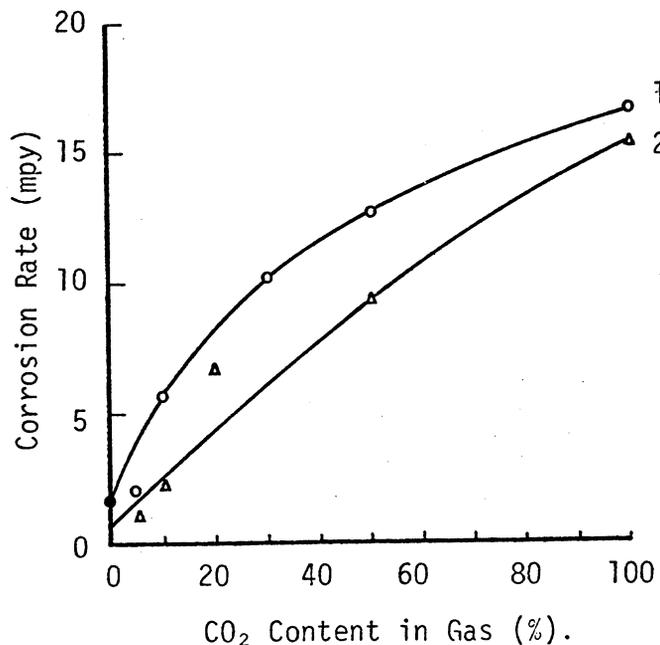


Figure 7. The effect of Carbon Dioxide on the Corrosion Rate. (1--water condensate of well 38 [Maikopskii deposit]; 2--distilled water)

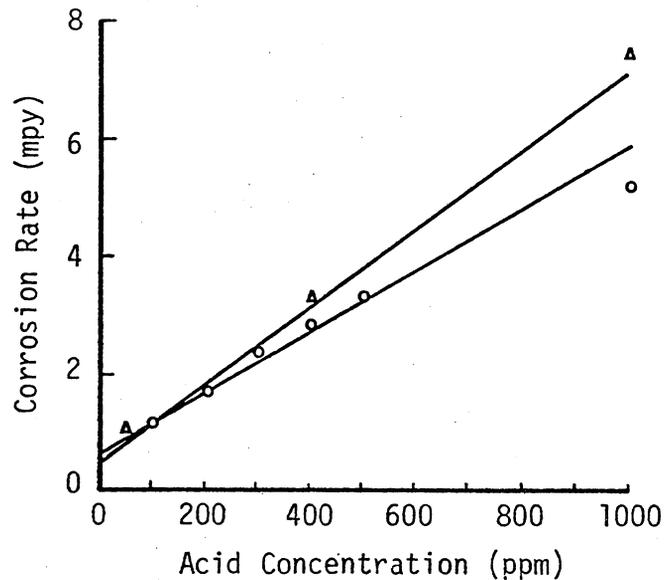


Figure 8. The Effect of Organic Acids on the Corrosion Rate (1--formic acid; 2--acetic acid).

2.2 LOCALIZED CORROSION IN AQUEOUS CO₂

Considerably less basic research has been done on pitting or localized corrosion in CO₂ systems than on uniform corrosion. However, in sweet oil well or gas-condensate well practice, localized corrosion is usually deemed to be a much more serious problem than uniform corrosion. Occurrence of localized corrosion requires the existence of an imperfect reaction product layer on the metal surface. As noted in previous sections, such films are often formed in an erratic manner, especially under low flow or elevated temperature conditions. The metastable, tenuous film probably contributes to the onset of localized corrosion. Unlike most "true", very thin passive oxide films, the structure and protective properties of these films are very dependent on the conditions under which they are formed.

Early field observations and experimental work showed that pitting of carbon steel becomes marked when the partial pressure of CO₂ reaches about 1 atm (18). This has been translated to the rule-of-thumb for sweet oil and gas-condensate wells that a CO₂ partial pressure of 30 psi usually indicates corrosion, between 7 and 30 psi may indicate corrosion, and below 7 psi is considered non-corrosive (15).

Most of the uniform corrosion studies discussed above do not mention the occurrence of localized corrosion even at CO₂ pressures above 15 psi. This is understandable for the cases where high uniform corrosion rates on bare metal surfaces are observed. Lack of localized corrosion in the other studies may be due to short test durations or conditions favoring formation of a relatively protective surface film. Initiation of localized corrosion often requires an induction time which may be as long as several months. Hackerman and Shock postulated that there are at least three types of surface layers formed in gas condensate wells in which the main corrosive agent is CO₂ (19). The first type is a porous, relatively adherent layer which gives rise to serious, more or less localized, attack. The second type involves the formation of a porous but only loosely adherent surface layer which may be removed rather easily in large patches by the flowing stream. This type of attack would be almost uniform and relatively less dangerous than the first type. The third type is a nonporous adherent layer which may act to efficiently protect the basic metal. All three types are primarily composed of ferrous carbonate. The third type may be associated with the presence of an organic natural inhibitor such as naphthenic acid.

A detailed description of localized corrosion in 200 psi CO₂ at 130°F has been reported (10). Coupon samples were submitted to 14 consecutive 7-day duration exposures to this environment and were cleaned between each exposure. Table 5 shows the results obtained from measuring the number and depth of pits in the most severely attacked square centimeter of selected coupons. The depths of smooth hollows in the coupon surface (relief) and edge attack are also given. Numerous pits less than 0.0006 inch were usually

found and the actual number was not measured in most cases. The results should be viewed primarily as qualitative and useful for comparison of resistance of the various metals. The effect of cleaning the specimens after each 7-day exposure is unknown. The most likely result would be a decrease in maximum pit depth and increase in number of pits per unit area.

Pit formation has been noted in carbonic solutions at CO_2 partial pressures less than 15 psi (20). This work was done at 27°C with a flow rate of 0.05 cm/sec and exposure time of 72 hours. Dissolved oxygen was present at an average concentration of 0.4 ppm. A hard, black scale was formed on the mild steel specimens and pits were said to be sharper and deeper but less numerous than in oxygen corrosion tests under similar conditions. Pit depths and frequencies were not reported. Although seemingly low, the oxygen content may have been high enough to instigate pitting which was then made more severe by the presence of CO_2 .

2.2.1 Water-Dependent Corrosion in Low Pressure Sweet Oil Wells

The water content of produced oil well fluids often determines the possible corrosivity of the fluid. Often when the well bore and surface equipment are in an oil-wet condition, the producing system will be protected as long as oil remains the external phase. The phase relationship between the oil and water generally will invert between a cut of 25% to 35% water (21). At this point, the system will eventually become water-wet and corrosion will depend on the corrosivity of the aqueous stream.

The CO_2 content of these wells is thought to be the primary causative agent of corrosion once the system becomes water-wet. This is said to be due to the pitting attack which CO_2 produces and which is usually observed (22). Organic acids are also present but they probably are a contributing rather than a primary factor. In numerous instances, corrosion becomes more pronounced as the gas-oil ratio increases, which might be regarded as further evidence that CO_2 plays a major role.

2.2.2 Pitting in High Pressure Sweet Oil Wells

Severe pitting corrosion has been found in some high pressure sweet oil wells producing very little water (23, 24, 15). Most of the corrosive wells are located on the Louisiana Gulf Coast. Corrosion starts soon after start of production and has been observed with wells producing as little as 0.1% water. Severity of corrosion does not appear to be correlated with water content up to about 5% water. Reported CO₂ concentrations range from 0.5 to 1.2 vol. %. Corrosivity increases with CO₂ content and bottom-hole temperature and pressure (23). Organic acids were also present at relatively high concentrations.

This type of deposition of a porous scale contains both chlorides and sulfates (15). Removal of the scale exposed much deeper pits and ten-fold increase in pitting frequency than that observed with scale intact (23). Thus, the attack appears to be a form of under-deposit corrosion that is aggravated by the CO₂ and organic acid content of the fluid.

2.2.3 Effect of H₂S

The main corrosive actions of H₂S occur in acidic solutions. By providing an acidic environment, CO₂ can often augment corrosion by H₂S and produce more severe attack than would occur for either component by itself. Corrosion by H₂S can take considerable time to develop and thus may go unnoticed in short-term laboratory tests. Additions of small amounts of H₂S to carbonic acid solutions (P_{CO₂} = 15 psi) can actually reduce the uniform corrosion rate as shown by Greco and Wright (8). This is caused by the formation of iron sulfide corrosion products. The properties of these films, composed mainly of FeS and FeS₂, depend on the H₂S partial pressure. At low P_{SO₂}, the black films can be wiped off while at high P_{H₂S}, the films are hard and almost impossible to remove completely. However, the more adherent films allow higher corrosion rates.

According to Rogers and Rowe, the iron sulfide films are cathodic to steel and difficult to polarize (25). Thus, they provide a galvanic driving force for localized attack at exposed patches of steel or pores in the film. Corrosion rates are initially low while the films are being formed and then accelerate rapidly. In one field test, corrosion rates were fairly low for 120 days, but after 180 days serious corrosion loss set in with formation of massive soft black iron sulfides (25).

Further investigation of the composition and properties of sulfide films formed on steel in the $H_2S-CO_2-H_2O$ system are reported in a series of papers by Sardisco, et al (26, 27, 28). Film composition depends on H_2S partial pressure. At higher H_2S partial pressures (0.1 to 4.0 psia), the surface area of the film and corrosion rate increase rapidly indicating formation of a nonprotective, porous film. Blistering can occur at lower H_2S partial pressures. Annand and Martin emphasize the role of the semiconductor nature of the iron sulfides in controlling the corrosivity and the adverse effects of allowing oxygen to enter the system (29). They propose the use of an organic sulfo-phosphate inhibitor when air contamination of sour fluids can occur.

2.2.4 Metallurgical Factors

Ringworm corrosion can become a factor in oil well tubing if the well fluid is made sufficiently corrosive by CO_2 (12). This type of corrosion damage is associated with the spheroidized carbides near the ends of the upsets. It is localized and the corrosion rate can be several times that of the remainder of the tube. It can be eliminated by use of tubing that has been normalized over the entire length after the upsetting procedure. Much of the tubing in older wells is not normalized due to the noncorrosiveness of the fluids. This could present a problem if the fluid becomes corrosive due to CO_2 injection.

2.3 STRESS CRACKING AND CORROSION FATIGUE IN CO₂ SOLUTIONS

Cracking of metals due to a corrosive environment is a sudden and sometimes catastrophic form of corrosion. Carbonic acid or CO₂ alone are not usually considered cracking agents. However, cracking may occur in wet CO₂ under extreme conditions. The probability of cracking may be greatly increased when CO₂ is combined with certain other aspects in aqueous media.

2.3.1 CO₂ - H₂O System

Cracking of highly stressed, high strength carbon steel can sometimes occur in solutions under a high pressure CO₂ atmosphere (30). Table 6 shows this along with other data for comparison. At 15 psi CO₂, no cracking was noted in 695 days even at a hardness of 38 (R_C) and 130% deformation. At 300 psi CO₂, cracking occurred at relatively long exposure times under extreme conditions. One reason for this "non-sulfide" cracking may be leaching of sulfur from the steel itself which eventually causes sulfide stress cracking (see below).

2.3.2 CO-CO₂-H₂O

The observation of cracking of mild and low alloy steels in CO-CO₂-H₂O environments is fairly recent (31, 32). These authors relate several cracking failures due to CO-CO₂-H₂O in chemical plants. Stress cracking of well tubing and line pipe by CO-CO₂-H₂O has been reported when combustion gases containing CO and CO₂ were used for inert gas miscible flooding for petroleum recovery (11).

Following an experimental study, Kawaka and Nagata presented the following conclusions (32).

- no stress cracking of mild and low alloy steels occurred in solutions containing only CO or CO₂,
- cracking was transgranular,

TABLE 6. STRESS CORROSION CRACKING TESTS IN CO₂ SOLUTIONS
AND COMPARISON WITH OTHER "NON-SULFIDE" MEDIA
(Reference 30)

Environment	Material	Hardness	% Deformation	Failure Time
15 psia air ¹	N-80-2	35	105,90,70,60,40,20	NF 211 days ³
15 psia CO ₂ ¹	N-80-1	38	130,100,80,60,40,20	NF 695 days ³
300 psia CO ₂ ¹	N-80-2	18	130	NF 520 days ³
300 psia CO ₂ ¹	N-80-2	25	130	NF 520 days ³
300 psia CO ₂ ¹	N-80-2	34	110	326 hours
300 psia CO ₂ ¹	N-80-2	33	115	22 hours
300 psia CO ₂ ¹	N-80-2	33	115	NF 84 days ³
300 psia CO ₂ ¹	N-80-2	33	100,80	NF 112 days ³
0.013 N HCl	N-80-2	34	110	5.8 hours
1.07 N HCl	N-80-2	34	110	0.35 hour
11.6 N HCl	N-80-1	36	100	.03 hour ²
11.6 N HCl	N-80-1	36	80	.25 hour
9.4 N H ₂ SO ₄	N-80-1	39	100	.18 hour

¹Gases bubbled through 5 percent NaCl

²Triplicates

³No failure

- liquid water must be present for cracking to occur,
- stress cracking occurred over a wide range of CO/CO₂ ratios (see Figure 9),
- susceptibility to cracking decreased with increasing temperature,
- no cracking was observed for several medium alloy and stainless steels, and
- the cracking appeared to be stress corrosion cracking rather than hydrogen embrittlement.

The last conclusion is still open to some question. It is based on the observation that cathodically polarized specimens did not crack while anodic polarization caused severe cracking. Cracking behavior on polarization is often used as a diagnostic since cathodic polarization should favor hydrogen entry into steel and inhibit stress corrosion cracking. While anodic polarization should accelerate stress corrosion cracking and inhibit hydrogen evolution. However, such polarization can also produce local pH changes at the electrodes (more alkaline at the cathode and more acidic at the anode) which could cause opposite results to be obtained, as noted below. Cracking in CO-CO₂-H₂O resembles sulfide stress cracking (SSC), a hydrogen embrittlement phenomena, in several ways.

Like SSC, susceptibility decreases with increasing temperature; the opposite is normally found for stress corrosion cracking.

CO, like H₂S is an inhibitor of the hydrogen evolution reaction, which is a partial cause of SSC.

SSC is favored by acidic conditions; CO₂ may aid cracking by acidification.

Stress corrosion cracking is normally associated with the presence of chloride and an oxidizing agent. These are not present in the CO-CO₂-H₂O systems studied.

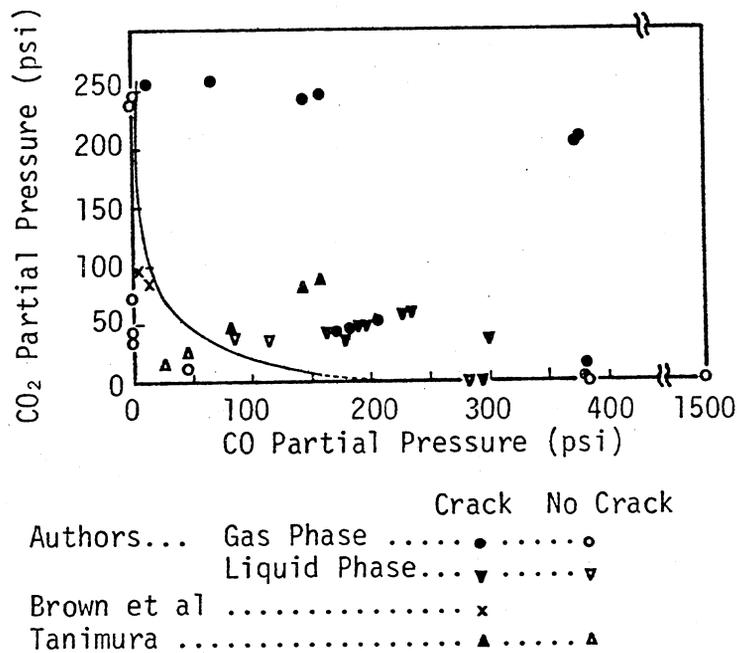


Figure 9. Effect of Partial Pressure of CO and CO₂ on Stress Corrosion Cracking of Carbon and Mn-steels Between 18 and 70°C for 168-1000 Hours (Reference 32).

The mechanism of cracking in CO-CO₂-H₂O systems is of more than academic interest since it influences the type of protection that might be effective. If the mechanism is really hydrogen embrittlement similar to SSC, cathodic protection could increase the chance of cracking in any locally acidic region. Inhibitor selection is also influenced by the operative mechanism.

Oil field failures associated with CO-CO₂-H₂O occurred soon after the start of inert gas-miscible flooding at a Ventura, California site (11). The gas is catalyst-processed exhaust gas from engines used to compress the gas to 5200 psi. Water is attenuated with injected gas once a month for an 8-day period. The produced inert gas is mixed with other produced gas and used for gas lift operation and fuel.

Exterior-initiated cracking of J-55 and N-80 injection well tubing occurred due to leakage of injection gas through tubing joints into the annular packer fluid brine (8000 ppm TDS). Conditions at the points of failure ranged from 43 to 65°C and partial pressures of CO from 10 to 40 psi and CO₂ from 125 to 250 psi. A polycyclic amidine compound added to the packer fluid was found to be an effective inhibitor. Complex interactions occur between the packer fluid, biocides, and various inhibitors tested.

A number of cracking failures occurred in X-52 and A-105, Sch. 160, Grade B surface injection line pipes handling inert gas and water alternately. It was found that one line having successive failures never dried out completely while one without failures dried out in about ten days. The injection system was modified to provide separate water and gas lines to the wellhead.

2.3.3 Effect of CO₂ on Sulfide Stress Cracking

The sudden brittle failure of hard, high strength alloys in sour oil environments due to sulfide stress cracking is well known in the petroleum industry. This type of cracking often occurs well below conservative design stresses. For normal well tubing and casing, cracking can be caused by as little as 1 to 3 ppm of H₂S in aqueous solution at ambient temperature. Sulfide stress cracking is a complex function of H₂S concentration, stress, material yield strength, temperature, and pH. Much of the earlier data has been summarized and discussed by Hudgins, et al (30). Results of a recent and extensive test program have been given by Troiano and Hehemann (33).

Sulfide stress cracking can occur over a wide range of pH, but cracking is more likely and severe in acidic solutions. Although no real critical pH has been established, the threshold stress for failure and time to failure decreases with decreasing pH, particularly for pH values less than 4 to 5 (30, 33). Below a pH of about 4 there is little effect of decreasing pH on time-to-failure (30).

No systematic studies of effects of CO₂ partial pressure or concentration on sulfide stress cracking were found in the literature. Addition of enough CO₂ to lower the pH of a near neutral solution to values of 4 to 5 or less should increase susceptibility to sulfide stress cracking. As in uniform corrosion, carbonic acid could be more effective than a completely dissociated acid at the same pH. The total acidity is higher for carbonic acid solutions at pH ~3 to 5 and the solution near the metal surface will be less likely to become alkaline and inhibit cracking.

2.3.4 Corrosion Fatigue in CO₂ Solutions

Corrosion fatigue is cracking of a metal due to combined action of a corrosive environment and repeated or alternate stress. Under corrosive conditions there is no endurance or fatigue limit below which the metal can be cyclically stressed indefinitely without failure. The corrosion fatigue limit is normally defined as the maximum value of stress at which no failure occurs after a large number of ($\sim 10^7$) cycles. The life of oil well sucker rods is often limited by corrosion fatigue.

Results of corrosion fatigue tests of a carbon steel in brines containing CO₂, H₂S, O₂, and combinations of these have been presented (34). AISI 1035 steel sheets with a 20,000 psi air endurance limit at a cycling frequency of 600 cycles per minute were tested in 5% NaCl for 10⁷ cycles. The chloride had no significant effect on the endurance limit.

Tests were done at about 15 psi CO₂ partial pressure giving 700-800 ppm free CO₂ and 250-300 ppm bicarbonate in solution at a pH of 5.5. The endurance limit decreased 41% to 17,000 psi in this solution. This appeared to be due to the ease with which surface cracks were initiated in the CO₂ environment (34). The authors concluded that a form of stress cracking occurred under cyclical stress conditions which did not occur under static or zero stress conditions in CO₂ solutions.

The endurance limit decreased 20% in chloride solution containing 3000 ppm H₂S at pH 4.5; cracking and blistering occurred. Combined H₂S (60-70 ppm) and CO₂ (700-800 ppm) reduced the endurance limit by 62%. Both pitting and surface cracking occurred in the latter system.

Addition of 3 ppm O₂ to the CO₂ system had little or no effect on the endurance limit. The same amount of oxygen in the H₂S system resulted in a total endurance limit decrease of 48%.

2.4 CORROSION IN NEARLY PURE CO₂ FLUIDS

At near-ambient temperatures, corrosion in CO₂ gas streams depends mainly on the presence of water and other impurities. Pure, dry CO₂ is essentially noncorrosive to engineering metals except at elevated temperatures. High temperature (above 400°C) attack and oxidation of ferrous metals by CO₂ is of concern in some areas of the nuclear industry, but resulting literature does not appear to be pertinent to enhanced oil recovery systems.

Laboratory corrosion tests of pipeline steel under very high CO₂ pressure conditions have been reported (35). Welded X-60 steel specimens were stressed to 120% of yield deflection and nonwelded AISI 4140 specimens were stressed to 110% of yield. Both types of specimens were notched. They were exposed to 2000 psig CO₂ containing 800-1000 ppm water vapor and 600-800 ppm H₂S at 72°F for six weeks and at 38°F for four weeks. A set of tests were also carried out under similar conditions except with less than 5 ppm water. The water saturation point was approximately 2500 ppm.

None of the specimens showed any signs of pitting or general corrosive attack and corrosion rates were less than 0.02 mpy. None of the test specimens failed by cracking. The stressed 4140 specimens were included since it is known to be highly susceptible to environmental failure. Specimens were subsequently exposed to a severe sulfide stress cracking environment (0.5% acetic acid in 6% sodium chloride saturated with H₂S at 15 psi

and 72°F). All of the AISI 4140 stressed beam specimens failed during the first 24 hours of the test. None of the X-60 circumferential butt field welds or longitudinal double submerged arc welds failed during the 30-day test. Two-thirds of the electric resistance welded X-60 specimens failed within 2 to 5 days.

Some nonmetallic materials such as certain elastomers for valve seals were found to be subject to degradation in the high pressure CO₂ (35). Failures generally took the form of swelling on prolonged exposure to high pressure CO₂, blistering or tearing on rapid decompression, and retention of set or deformation due to gas retention. A set of tests indicated that Teflon, nylon, EPR (ethylene-propylene copolymers) polyimide and semi-rigid polyurethane were least subject to these failures. Seals made from Viton, Hypalon and a number of buna-N rubbers were subject to one or more of these failure modes. Some buna-N's and possible other varieties of the latter group might be satisfactory as captive (enclosed) seals but would probably require replacement each time they are decompressed. Stability of EPR seals depended on the actual type of material.

Some effects of impurities and flow rate in a CO₂ gas stream on steel corrosion are illustrated in Figure 10 (36). The weight gain measurements are for carbon steel shavings in flowing gas streams described in the figure caption. Oxygen inhibits corrosion in this system when added in small quantities but above about 3% acidic oxidation products of H₂S are formed which are dangerous corrosive agents (36). Water content is one of the dominant factors. No corrosion was observed when the CO₂ stream was dried to a -70°C dew point using molecular sieves. The authors state that the carbon content of the steel is also a factor; above about 0.7% C the corrosion rate increases significantly.

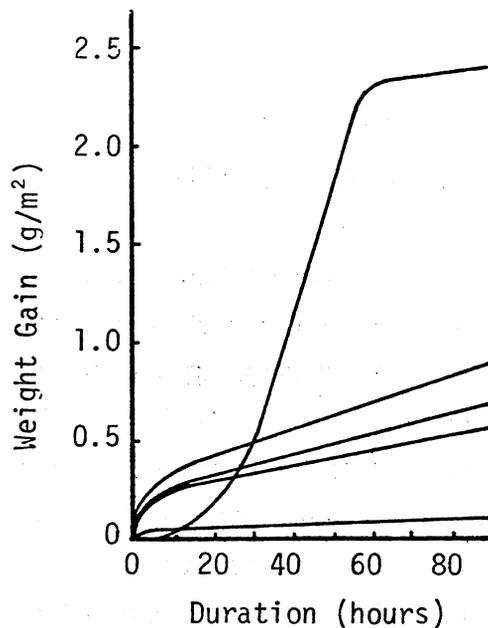


Figure 10. Weight Gain of Steel in Flowing Gas at 70°F Under the Following Conditions.

Curve 1: Gas Content:

CO₂ : 95.0% (vol)
 H₂ : 3.0%
 N₂ : 1.6%
 O₂ : 0.3%
 H₂S : 5.3 ppm
 H₂O : saturated at 21°C
 Flow Rate : 0.5 l/min

Curve 2: Same as 1 except dried to -20°C dew point.

Curve 3: Same as 1 except O₂ raised to 1.7%.

Curve 4: Same as 1 except gas flow increased to 5 l/min; reduced to 0.5 l/min at 60 hr.

Curve 5: Gas Content:

CO₂ : 96.6% (vol)
 N₂ : 0.22%
 O₂ : 0.22%
 methane + butane = 1.58%

Section 3

CORROSION CONTROL METHODS

This section describes the main methods to be used for corrosion control in the CO₂ injection-enhanced oil recovery process. It is intended to complement the process-oriented discussion given in Section 4 while providing additional detail in some areas and a different classification for ease of reference. Choice of materials is included as a control measure. Most of the discussion in this section assumes that corrosion cannot be prevented by removal of one or more corrosive agents from the process stream. The integration of corrosion control methods is touched on but not emphasized in this section.

As often noted in this section, selection of a good corrosion control method does not guarantee good results. Proper detailed specifications, construction and operation is also necessary. Without this attention the most expensive alloy component can be ruined or the "low bid" coating may ultimately cost much more than a quality job.

3.1 METALS

Constructing all equipment from resistant metals could "solve" practically all corrosion problems caused by CO₂. This would be far too expensive, however, due to the scale of equipment involved. The more resistant metals are very useful for limited areas where temperatures or flow rates are too high for coatings to be reliable or where the CO₂ partial pressure is high and the presence of liquid water may be unavoidable. Some such areas might be treatable with inhibitors. If inhibitor effectiveness is marginal, equipment reliability is critical, or it is mechanically difficult

to ensure inhibitor access to the area, the use of resistant metals is probably indicated. Due to the extra initial expense involved in using a resistant metal, the specification should be done carefully and the need for any precautions in applying the material should be recognized. These factors are discussed below for the more likely choices of constructional or special purpose metals.

Fluids containing liquid water and H₂S (sour environments) frequently require more detailed metallurgical specification to guard against sulfide stress cracking than given here. The reader is referred to NACE Standard MR-01-75 (1978 Revision) for guidelines as to what constitutes a sour environment and recommendations on specification and use of metallic materials (37).

3.1.1 Stainless Steels

Stainless steels, those containing more than 12% chromium, appear to be resistant to corrosion by wet CO₂ alone even at high CO₂ partial pressures under laboratory conditions. Dependence of general corrosion resistance on stainless steel compositions follows the usual pattern, with resistance increasing with increasing chromium content and with the addition of nickel. Overall, the selection of a stainless steel for use in aqueous CO₂ depends largely on other environmental factors such as other chemical species present, presence of solids or crevices in the system, and mechanical or strength requirements.

As a class, the stainless steels are very resistant to uniform corrosion in environments such as those considered here. Large quantities of wet, hot CO₂ under pressure are handled in the ammonia industry, for example, and extensive use of stainless steel is made in this case. Type 304 is normally the lowest grade used in this industry. In solutions containing chloride, however, they can become susceptible to pitting and crevice corrosion. Crevice corrosion does not necessarily require a mechanical crevice,

it can occur under solid, scale, or sludge deposits on the metal. Fluid-wet gaskets are often a starting point for crevice corrosion. The likelihood of pitting or crevice corrosion increases drastically when small quantities of oxygen (~ 50 ppb) are present in solution. Susceptibility also increases with increasing temperature and chloride ion concentration. Resistance to localized corrosion increases with increasing amounts of alloying agent, especially chromium and molybdenum, in the steel. Thus Type 304, which contains no molybdenum, has considerably less resistance to chloride induced attack than Type 316. Type 317 with 3-4% Mo generally has the best corrosion resistance in this series.

Certain stainless steels, including the common austenitics Type 304 and Type 316, can undergo stress corrosion cracking (SCC) under certain combinations of chloride ion concentration, oxygen, temperature and stress. The likelihood of SCC increases as each of the above four parameters increases. The amount of stress needed to cause cracking is difficult to quantify in practical situations and it is usually best to assume that SCC is possible if the other three parameters are satisfied, no matter what the applied stress. SCC can occur under zero applied stress. Even so, austenitic stainless steel components should be specified in the fully annealed condition when possible.

Stress corrosion cracking susceptibility is much lower for alloys with less than 1% or more than 40% nickel. However, the normal 400 series metals (with no nickel) are not as resistant to pitting and crevice corrosion as Type 304 or 316, and the high nickel alloys are expensive. Several higher chromium plus molybdenum alloys with no nickel (high purity ferritics) have been introduced, but to our knowledge they have not been extensively used in oil field equipment and so tend to be more expensive and less available than the austenitics. Combining high SCC and fair localized corrosion resistance, they may have some applications. Examples are 26 Cr - 1 Mo and 29 Cr - 4 Mo.

It is noteworthy that small amounts of oxygen are often responsible in large part for corrosion of stainless steels. The removal of oxygen by stripping and addition of oxygen scavengers can eliminate many of these problems. Inhibitors may improve the performance of marginal grades but in view of the expense and complexity of most components relying on the corrosion resistance of stainless steel, it would seem best to either specify a better grade or thoroughly test the steel/inhibitor combination. As in other inhibitor applications, insufficient inhibitor concentration may induce or accelerate localized corrosion.

Welded austenitic stainless steels may be subject to intergranular corrosion near the weld or "weld decay". This is a localized form of corrosion which can cause serious failures. For field-welded equipment, this form of corrosion can be combated by using low-carbon forms of the specified stainless steels such as 304L and 316L. The joint to be welded should be free of oil, grease or other carbon contamination and recommended welding techniques for the low-carbon grades should be followed.

Manufacturer-welded equipment can be protected by quench-annealing or solution-quenching heat treatments. Carbon pickup and decreased corrosion resistance can also occur if austenitic stainlesses are cast into molds containing carbonaceous materials such as organic binders and washes or baked oil sand. Cast alloy equipment specifications should prohibit this.

Austenitic stainless steels are often considered to be immune to sulfide stress cracking. They may become susceptible, however, when cold worked. NACE standards limit austenitic, ferritic, and martensitic stainless steels to a maximum hardness of HRC 22 when used in sour service. Precipitation hardening stainless steels such as 17 Cr - 4 Ni (17-4 PH) may be used up to HRC 33 with special heat treatment (37).

3.1.2 Carbon and Low Alloy Steels

These materials are not considered "resistant" except at low CO₂ pressures or when effectively coated or inhibited. As noted at several places in this report, corrosion of ordinary bare steels can become significant when exposed to uninhibited solutions of CO₂ at a partial pressure above about 4 psia. At CO₂ pressures higher than about 20 psia, serious attack is likely under such conditions.

When operating in a corrosive atmosphere, the grade of steel can be a factor. Normally, J-55 tubular goods are slightly more resistant than N-80 (12) and tubing and couplings in a CO₂ unit field are normally J-55 grade. An example of the importance of this is that in an actual field situation an inadvertent one-time substitution of N-80 couplings, due to supplier error, resulted in severe attack on the couplings (38). Low alloy steels such as 4340 and 4145 do not appear to have any advantage over the normal types from a corrosion standpoint and may suffer more attack than the normal grades (see Section 2).

An exception to this last statement is when higher strength levels are needed in sulfide stress cracking environments than can be safely obtained using the normal grades. In such cases, a high hardenability, modified version of AISI 4130 is said to be the best commercially available constructional steel for downhole service (33). An example is AISI 4135 Modified containing 0.8% molybdenum and 0.05% niobium.

Severe localized corrosion near the upsets of tubing is often noted when a well is made sufficiently corrosive by CO₂. This "ringworm" corrosion can be eliminated by specifying tubing that is fully normalized over the entire length after the upsetting procedure.

Welding procedures can also be critical, especially in sour environments. Detailed precautions and procedures are given in NACE MR-01-75 (1978 Revision), NACE RP-04-72 (1976 Revision) and reference (39).

3.1.3 Nonferrous Metals

A number of nonferrous metals may be used for their mechanical properties or specific corrosion resistance. Often these requirements are linked as when higher hardness or yield strength than safely obtainable with most ferritic materials is needed in a sulfide stress cracking environment. The following alloys should be resistant to wet CO₂ and are usable in sour environments up to HRC 35 when properly heat treated (37).

- Nickel-copper alloys (Monel 400, Monel K-500)
- Nickel-iron-chromium alloys (Incolloys)
- Nickel-chromium alloys (Inconels)
- Nickel-chromium-molybdenum alloys (Hastelloys, Inconel 625)
- Cobalt-nickel-chromium-molybdenum alloys (MP35N, Elgiloy, Havar, Nimonic 105).

Even materials which are highly resistant to sulfide stress cracking can become susceptible under certain conditions. Monel K-500 can become susceptible if it is plastically deformed in service (39). MP35N has cracked when galvanically coupled to iron (33).

Other materials may be desirable from the standpoint of availability or special mechanical properties. Guidelines for use of metallic materials for oil field water handling are given in NACE Standard RP-04-75. It contains material lists for specific equipment in either aerated or nonaerated and H₂S containing or H₂S-free environments (40).

3.1.4 Medium Alloy Steels

Medium alloy steels are classified here as those having more than 3% but less than 11% alloying agents such as chromium or nickel. Early corrosion problems in gas condensate and certain oil wells spurred interest in these materials for downhole tubing. In laboratory tests, the 9% Cr and 9% Ni materials showed significantly lower corrosion rates than the ordinary

steels in corrosive, high CO₂ partial pressure environments (10). In field use, the general corrosion resistance was good but a number of corrosion cracking failures and pitting of the 9% Ni equipment were reported (12). Most of the failures appeared to occur for tubing that was harder than RC-22; a maximum yield strength of 105,000 psi was suggested for use of this material.

The 9% Cr or 8-9% Cr, 1% Mo alloy has been used more extensively in sweet gas condensate wells with generally good results. Some cracking has occurred, however, and this may be due to the high strength of the material combined with traces of H₂S in the fluid. NACE Standard MR-01-75 (1978) lists this material with maximum hardness of HRC22 as acceptable for sour downhole service. Pitting resistance of this material is often poor compared to ordinary steels such as J-55.

In view of the coatings and inhibitors available for carbon steels and the much greater resistance of stainless steels, the usefulness of the medium alloy steels appears to be limited.

3.2 PROTECTIVE COATINGS AND NONMETALLIC MATERIALS

A large number of coatings are available for corrosion protection purposes. Their basic purpose is to isolate the structural metal from the corrosive environment. In many cases the coating itself is not subject to attack, but its effectiveness depends on freedom from holidays, pinholes, and disbonding which expose the bare metal. Coatings are often not applicable in situations where severe erosion, mechanical rubbing, high temperature or large cyclical temperature changes can occur. The use of coatings in very corrosive environments should be evaluated carefully, especially if the protected equipment is critical. The use of chemical inhibitors as back-up protection for large-scale coated equipment is worthy of consideration.

This subsection is primarily concerned with plastic, metallic and inorganic coatings and nonmetallic equipment. Paints and coatings used for exterior atmospheric protection are not included.

3.2.1 Plastic Coatings

While subject to many of the restrictions noted in the introduction, plastic coated steel can display a much longer life than bare steel in moderately corrosive environments. Proper selection, application and use of these coatings must be done to utilize their protectiveness.

The first stage of selection depends on whether the equipment will be under gas pressure, such as injection or production well tubing or will be used in fluids near atmospheric pressure. Thin coatings must be used in high pressure regions since gases such as CO₂ can permeate the coating. When the pressure is released, the gases cannot escape fast enough from thick film coatings and this results in blistering and disbonding. However, thin film coatings allow rapid gas relief and have been successfully used in high pressure CO₂ injection well tubing (38). Thick coatings may be desirable where this is not a problem since they may have fewer holidays and more resistance to erosion and abrasion.

A number of thin film coatings are available from manufacturers and applicators and the quality of application may be as important as the coating composition. The more successful general types are phenolic and epoxy-phenolic in the thickness range of approximately 5-8 mils. Good surface preparation is extremely important in obtaining a satisfactory coating for corrosive environments. Specification of Steel Structures Painting Council (SPPC)-SP5 "White Metal Blast Cleaning" is recommended as a minimum standard. The user should choose an experienced applicator with good quality control standards. The finished coating should be inspected for holidays by continuity conductivity-type test equipment. Some manufacturers may allow specification of holiday-free thin film coating at a relatively small additional cost and this is recommended for critical applications.

Coated surface equipment may not be subject to pressure release disbonding but they are often exposed to fluids that contain oxygen through

air inleakage and to high liquid flow rates. If properly applied, dense, thick films should have greater resistance to oxygen permeation and erosion. As with thin coatings, good surface preparation and application may be as important as actual coating composition. However, experience in handling produced fluids from CO₂ injection has indicated that thick film epoxy coatings have wider application than coal tar epoxy (41).

As with the thin film materials, surface preparation and quality control are very important. Film thickness should be carefully monitored during application. Sharp edges or projections should be avoided in equipment design or specification. Crevices, pits and especially welds should be filled or ground smooth and flush. Thicker coatings (>1/16 inch) should be inspected using a commercial high voltage spark tester. Coatings should be periodically inspected during use since small defects may spread and cause rapid general failure.

3.2.2 Nonmetallic Materials

Equipment based mainly on nonmetallic materials can be considered when the fabricated material can withstand the pressure and temperature requirements of both its normal duty and any transient or upset conditions that may occur. Materials such as fiber reinforced plastic (FRP) can give good, economical corrosion service if carefully specified and designed to operate well below the recommended maximum pressure for any given temperature of use. When properly used, FRP materials can withstand corrosive environments that would rapidly attack steel vessels and piping.

Detailed specifications are needed to ensure satisfactory construction and operation of FRP equipment. A number of "do's and don'ts" are given in the "Desalination Materials Manual" (42). Applications and some corrosion test results are also given. The user should follow such guidelines and work closely with established manufacturers and fabricators during design and construction.

3.2.3 Inorganic and Metallic Coatings

The main inorganic coating to be considered for oil field service is cement. Cement linings in flow lines can offer good protection when the fluid is not too corrosive to cement and fluid flows are not too high to cause erosion which may be a problem if sand is present. Fluids used should be restricted to near neutral pH. An experienced applicator should be chosen for production of cement lined pipe. The condition and finish of pipe ends is of prime concern. Care must also be taken in handling the finish to avoid dropping, banging, excessive flexure, or insertion of hooks or other devices in the ends. A recommended practice for cement lining of tubular goods is given by NACE 1G163 (43).

Sacrificial metal coatings such as zinc will probably dissolve or pit too quickly in carbonic acid solutions to be of any use. Sprayed metal coatings using resistant metals may be useful for prolonging the fatigue life or wear resistance of steels for rods or pumps. Since the sprayed metal coating is porous, a plastic coating is often applied over it.

3.3 INHIBITORS

Inhibitors are chemical substances which can retard the corrosion of metals when added in small concentrations to the fluids contacting the metal. Most of the inhibitors used in the oil industry are organic chemicals which adsorb strongly on the surface of the metal and promote the formation of a mechanically protective oil film on the metal. The organic inhibitor normally has at least one highly polar chemical group which attaches to the metal and a nonpolar, oil soluble "tail" which encourages formation of an oil film over the inhibitor layer.

There is considerable evidence that conventional organic film-forming inhibitors can be effective against corrosion caused by CO₂ in a number of environments. Substances such as the filming amines have been used for a

number of years for treatment of those oil wells which produce acid gases as well as for several years at at least two units during production of injected CO₂ and relatively corrosive water. Such inhibitors are also used in condensate lines that carry wet CO₂ (44, 45). Although the high molecular weight amines usually have a low solubility in near neutral pH water, if dispersed they can dissolve in acidic solution areas and thus protect those parts of a system that are likely to corrode.

The effectiveness of an inhibitor depends on many factors, but in order for it to have a chance to be effective, it must reach the metal surface which is to be protected. Generally, this might be hampered for either chemical or mechanical reasons. The chemical reasons include whether the equipment is oil- or water-wet which in turn depends on the water cut and other properties of the fluids. Inhibitors for production wells are usually available as either oil-soluble, water-dispersible, or water soluble and their relative effectiveness will depend to a large extent on which type can best dissolve in the metal-wetting phase and be adsorbed on the metal to promote formation of a protective film. Inhibition may also be difficult for areas where fluid circulation is low or stagnant. Plans should be made in the design stage to provide optimum inhibitor injection points. It is also desirable to plan an inhibition program for start-up so that the inhibitor can be applied before a corrosion product layer is formed.

When planning an inhibitor treatment program, it should be recognized that too low a concentration of inhibitor can often accelerate rather than inhibit corrosion. Therefore the amount of dilution that can occur from the point of injection through the process stream should be determined and used to calculate the size of a batch or flow rate of continuous inhibitor addition. The lower concentration limit should be established by testing or manufacturer's recommendation.

Most commercially available inhibitors are proprietary formulations which may contain surfactants or other additives in addition to the inhibiting

compound or mixture of inhibiting compounds. The additives are often used to aid the inhibitor in reaching and/or adsorbing on the metal by varying its relative solubility in the oil or water phase or increasing dispersability. Published data on inhibitors usually gives either 1) only the generic classification or a coded reference ("inhibitor A, B, etc."), or 2) is done with a single inhibitor compound and thus may not be representative of a commercial formulation.

Selection of inhibitors and well treatment methods for production wells can be complicated since it depends on the corrosivity and composition of field fluids, type of well completion, wellbore fluid levels, and variable water and CO₂ cuts. A large number of inhibitors are available but their effectiveness will depend on the above factors. Due to the time required and equipment damage that can be sustained during field tests and expense of a large field inventory of different inhibitors, it is desirable to select a fairly small group of inhibitors by lab testing. Some variety is needed since lab tests cannot totally simulate field conditions. Such tests can, however, determine compatibility of the inhibitor with well fluids and also allow variation of CO₂ and water levels to simulate conditions that may occur during the life of the injection program. Detailed procedures for preliminary inhibitor screening tests using synthetic fluids are given in NACE publications 1K55 and 1K60. More detailed tests using field fluids are desirable. Procedures for simulated field usage testing including film persistency are given by Nestle (46).

Selecting the treatment method that assures filming of the equipment is often as important as the inhibitor used for controlling corrosion in production wells. Types of treatment that may be suitable for conventional flowing or sucker rod type wells are shown in Figure 11 (21) with the tubing set at or above the producing interval and some open hole below the bottom of the producing zone. Special considerations may be required for dual and gravel-packed completions, fluid and centrifugally pumped, and gas lift wells. Details on the application of the types of treatment shown are given by

Endean (21) and in reference (15). Effectiveness of inhibition should be regularly monitored using coupons, iron concentration analyses and corrosion probes along with any variations in pH and CO₂ partial pressure.

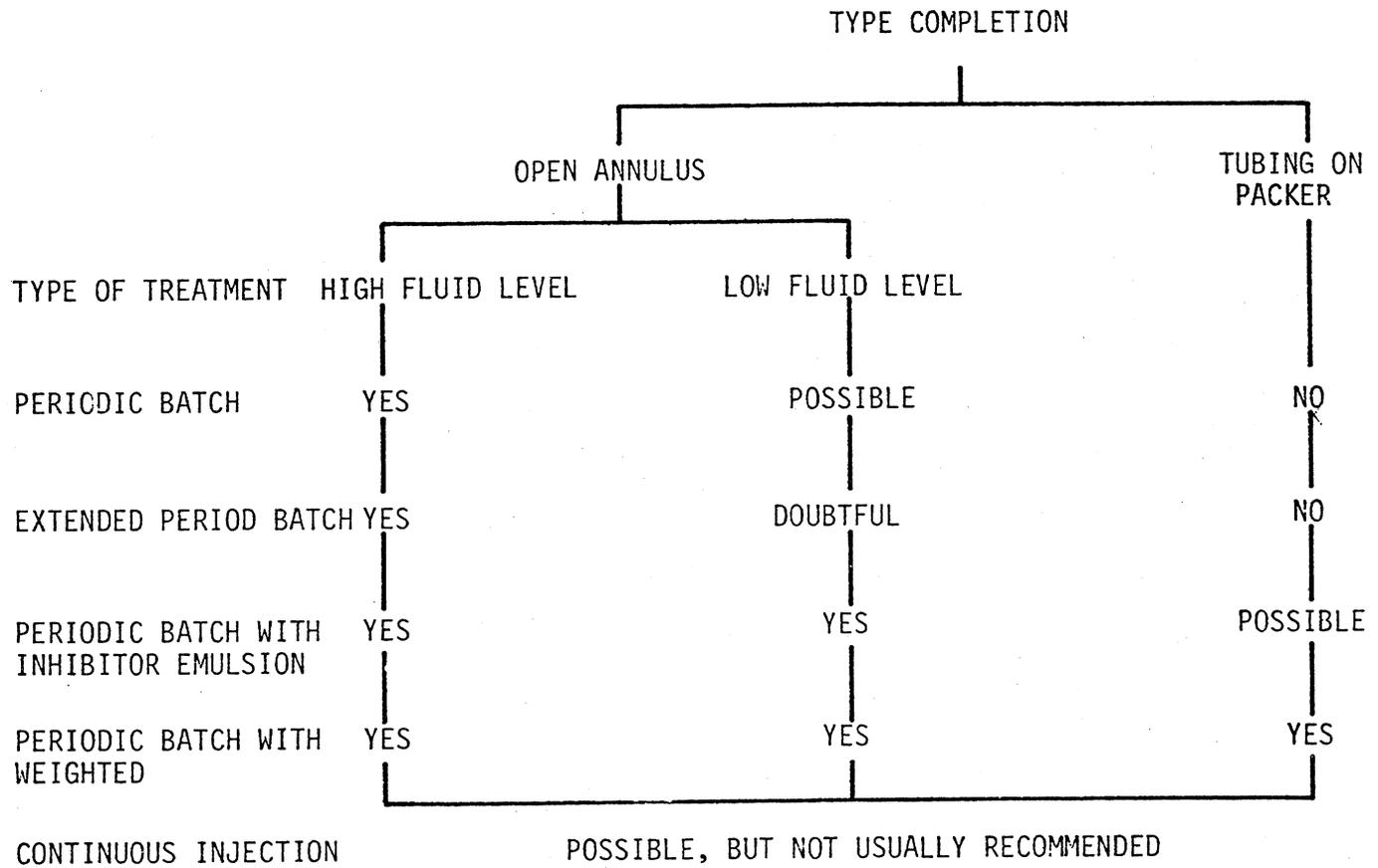


Figure 11. Treating Procedures for Typical Oil Well Completions

While inhibition of corrosion in production wells is most widely known, inhibitors also have application in other parts of the overall process. These applications include the following:

- CO₂ removal processes,
- CO₂ drying processes,

- compressors operating on CO₂ rich gases,
- injection waters, and
- produced waters,

Inhibitors must be selected or tailored to the specific application. Use of inhibitors in the above systems is discussed in Section 4.

Although not a direct inhibitor, chemicals which react with and remove oxygen from a liquid stream are useful for some streams. Low concentrations of oxygen can be very corrosive to both carbon and stainless steels, especially in the presence of chloride, H₂S and CO₂. Streams that may need to be treated include water injected during the water cycle of the WAG process and produced water that may become aerated. Oxygen concentrations as low as 10 ppb can influence corrosion and these can easily arise from inadvertant air inleakage into low pressure lines. Sulfite in the form of sodium sulfite or SO₂ is a commonly used oxygen scavenger. In most cases a catalyst, such as low concentrations of divalent cobalt ion, is needed to increase the reaction rate between sulfite and oxygen. Commercial formulations of oxygen scavengers are available. Highly oxygenated streams may require stripping with inert gas prior to treatment.

Sulfate formed by the reaction of sulfite and oxygen may cause scaling problems in some systems. In these a scale inhibitor may be added along with the oxygen scavenger. Hydrazine is used as a scavenger in other industries but reacts very slowly with oxygen under most oil field conditions. Ammonia formed can be harmful for copper alloys in a hydrazine scavenged system.

Section 4

CORROSION OF CO₂-ENHANCED OIL RECOVERY EQUIPMENT

This section describes methods used to control CO₂-induced corrosion for the major components of a field using CO₂ injection for enhanced oil recovery. The two areas with the highest potential for rapid corrosion are also the ones which are least well known to the industry: the high pressure CO₂ pipeline and the CO₂ injection wells. Although potential hazards exist, corrosion can be minimized in these areas with proper design and operation. Production of CO₂ will increase corrosion of any production well and surface equipment that has been designed to handle only moderately or non-corrosive fluids. The incremental increase in corrosivity is not overwhelming, however, and combinations of standard techniques used to control normally corrosive oil well fluids should be effective.

Overall, it is important for the producer to be aware of and prepare for an increase in corrosion problems ahead of time. Economic considerations will vary from field to field and even from well to well. But since CO₂ injection can produce corrosive conditions for a number of years of operation, the higher initial costs for good corrosion prevention measures will most likely be justified by increased production time and reduced maintenance.

Actual field experience is the most valuable aid in predicting corrosion problems and selecting control processes. There are a number of full-scale CO₂ injection programs underway as well as pilot studies. Length of exposure is, of course, important in establishing the validity of corrosion experience. The information in this section has mainly been derived from active CO₂ injection programs and pilot studies. Two important CO₂ injection programs that have yielded considerable useful operation information are the SACROC and the Houston Natural Gas Twofreds Field. The former has been

operating longer and on a larger scale than any other facilities. This experience may be somewhat atypical in some cases since the field is known to have "corrosive waters" and effects due to increased water production and start of CO₂ injection are difficult to separate. The latter field receives clean, dry CO₂ and no problems have been experienced during the five years of operation of the 15-mile CO₂ pipeline.

4.1 PIPELINES FOR CO₂ TRANSPORT

Pipelines transporting CO₂ will operate under very high CO₂ partial pressures. The pipeline must be constructed from low alloy steel for economic reasons. Coatings or inhibitors should be considered unreliable under such high CO₂ pressures if any liquid water is present. On the other hand, if the CO₂ is effectively dehydrated, it is not corrosive to pipeline steels. Therefore the main means for prevention of interior pipeline corrosion is prior dehydration of the CO₂ at the source. This also eases the corrosion burden on any intermediate booster station equipment, the injection compressors, and to a certain extent on injection well equipment. The injection well presents more of a problem since water is often introduced during part of its operation.

The gas should be dehydrated well below the saturation point to ensure that no condensation will occur in the pipeline under unusual or upset conditions. Water content of supercritical CO₂ at one field is specified as 50 ppm (by weight) maximum even though saturation is 2500 ppm and lab tests showed no attack on pipeline steel at 1000 ppm water and 800 ppm H₂S levels. Such conservatism is probably called for in view of the very rapid corrosion that could occur if any liquid water collects and many historical cases of corrosion in pipelines carrying lower CO₂ pressures but water levels close to saturation. Continuous monitoring of the water content of gas input to the pipeline is highly recommended.

The pipeline should be thoroughly cleaned and dried prior to charging with CO₂. The following procedure has been used (41).

- 1) hydrotesting
- 2) cleaning with multiple mechanical scrapers
- 3) drying with methanol
- 4) displacement with dry air
- 5) packing with CO₂

Difficulties have been experienced with plugging by solid corrosion products from the pipeline soon after start-up using the above procedure. This may be blamed on inadequate drying by methanol and presence of displacement air which caused the large internal area of the system to act as an "iron sponge or dry box treater" during the prolonged packing period. The plugging material disappeared rapidly with continued operation. One leak developed in a distribution system lateral line due to failure to completely displace hydrotest water.

After the initial start-up difficulties, corrosion in the dry CO₂ system has been minimal. The highest measured corrosion rate was 1.2 mpy and the average over five years has been 0.13 mpy. No buildup in hydrogen pressure as measured by H₂ probes has been noted (41).

As noted in Section 2.4, certain elastomers undergo degradation in high pressure CO₂ service. Seals for valves and other applications should be chosen based on these results.

4.2 INJECTION WELL EQUIPMENT

Equipment associated with the injection well is subject to severe corrosion especially during the period when CO₂ injection follows water injection. Considerable time is needed to evaporate the water. During this time, any chloride or other impurities may be concentrated on the equipment and droplets will exist in the presence of high pressure CO₂. These conditions are often favorable for rapid localized corrosion. Pockets of CO₂ temporarily trapped when switching from gas to water injection might also cause problems.

One of the main ways to minimize this attack is to use separate gas and water flow lines to each injection well. This minimizes the amount of material that will be subjected to the alternating CO₂/water environment and which must be made resistant to these conditions. Due to the corrosive conditions and high pressures involved, the use of corrosion resistant metals should be the primary means for protecting surface injection well equipment.

Corrosion experience at one CO₂ injection field has led to the use of 316 stainless steel for injection well meter runs, valves, and wellheads. Plastic coated steel was originally used for meter runs and valve bodies but severe corrosion occurred at any point of coating damage, especially at flange faces. Both gate and check valves using electroless nickel coatings were subject to catastrophic corrosion where the nickel coating was damaged. Coating damage by check valve disc action against the bodies caused failure of almost all such valves. Experience with meter runs using Type 316 pipe and fittings, Type 316 gate valves with Type 316 or ceramic gates and Type 316 check valves has been good. Several aluminum bronze gate valves with ceramic gates have also been used successfully.

Conversion to all 316 stainless steel wellhead assemblies is being done at one field and performance has been good. Original injection wellheads were made from 410 stainless steel with 410 stainless steel valves. This material gave generally good performance but was subject to intense pitting under scale or other debris from the injection water. This is a type of crevice corrosion and stainlesses containing molybdenum and additional chromium such as 316 are much less susceptible to it than the relatively low chromium 400 series materials.

Even the higher grades of stainless steels are subject to localized corrosion in the presence of oxygen and chloride. Stress corrosion cracking of austenitic stainlesses is also of concern if such conditions are encountered along with somewhat elevated temperatures (~120°F). An effective way of protecting stainless steel equipment is by ensuring that aqueous oxygen

concentrations are kept very low. Oxygen scavengers can be added to the brackish and fresh water make-up streams to the injection wells. A water soluble inhibitor can also be used in the injection water. These measures may be partially responsible for the success of Type 316 equipment now in use.

Crevice corrosion is sometimes a problem at stainless steel flanges using water absorbing asbestos gaskets. This can be minimized by using a non-water absorbing gasket, preferably without graphite. Other recommendations for specifying and using stainless steels are given in Section 3.1.

Difficulty in obtaining an entirely leak-free valve seal between the CO₂ and water injection systems can cause rapid corrosion near block-off valves. Present practice at one field is to install a blind flange on either the CO₂ or water side during WAG operation.

Water injection pumps at the above site are made primarily from 316 stainless steel. Associated valves are aluminum bronze. Water piping to the injection wells is by cement-lined pipe. The main cause of leaks in this system is eccentric lining and failure to install asbestos gaskets at joints.

Tubing coated with thin film epoxy-modified phenolic plastic seems to give acceptable downhole performance in injection wells. As noted in Section 3.2, thick film coatings tend to be disbonded by escaping CO₂ when pressure is released. The basic tube material at a major field is J-55. The main problem with downhole injection equipment has been the tube couplings. Teflon seal rings were originally used to prevent access of fluid to the engaged threads, but many failures still occurred, primarily due to mechanical damage and incorrect assembly or handling. Seal rings have been replaced by the use of a baked on polyphenylene sulfide (Ryton) coating material for the couplings. This is a tough, resilient coating which has performed well. Packers coated with either the thin film material or fiber reinforced polyester have performed well. Emphasis should be placed on proper handling of all the plastic coated materials.

The success of coated equipment may depend on use of inhibitors and oxygen scavengers in the injection water. These additives should at least slow corrosive attack at holidays or damaged portions of the coating and prolong equipment life.

4.3 PRODUCTION WELL EQUIPMENT

Production of injected CO₂ will increase the corrosivity of most produced fluids. Severity of corrosion will also depend on the fraction and composition of water produced, H₂S concentration and type of pumping system employed. The partial pressure of produced CO₂ is much lower than in injection wells so any corrosion due to CO₂ itself that occurs is not generally as rapid or catastrophic. Moderate additions of CO₂ may accentuate the corrosion modes of H₂S, however, and mildly corrosive sour wells could become more corrosive for this reason. Industry practice has dealt with corrosion caused by H₂S, CO₂ and water for some time. The user should be prepared to utilize such measures as inhibitor addition, protective coatings and alternate material selection in fields and wells that are not corrosive or only mildly corrosive in the absence of CO₂ injection.

Corrosion in the producing wells at one field due to CO₂ injection has ranged from minimal to severe. Downhole corrosion problems caused by CO₂ are not general throughout the field, but they do occur. Assessment of CO₂ effects is not clear-cut since production of larger quantities of corrosive water started at about the same time as CO₂. This experience does indicate that corrosion under these relatively severe conditions can be controlled using known inhibitors, coatings, and some resistant metals (41).

Before CO₂ and water production started, the typical field installation was a flowing well with uncoated packer, tubing, and surface flow lines. Little water was produced and corrosion was limited. Now most wells use either rod pumps or submersible pumps. Now the usual water cut is fairly high and gas produced up the annulus of a typical well is about 30% (Vol.)

CO₂ at about 150 to 200 psi. Typical produced water contains about 70,000 ppm chloride and 120 ppm or less CO₂ with a pH of about 6.3 to 6.4 (38).

Filming amine inhibitors are used to reduce corrosion in rod pump wells. Usual treatment is a weekly batch pumped down the annulus. Originally, treatment with oil soluble formulations had limited success since high well-bore fluid levels would not allow complete circulation of the inhibitor. Water soluble compounds were more successful under these conditions. Reduced fluid levels has not allowed many wells to be effectively treated with oil soluble inhibitors and has reduced corrosion due to CO₂. Rod pump barrels are Monel 400 with sprayed metal (316 SS) plungers. A very limited number of rod strings are sprayed metal (316 SS) coated when repeated rod parts justify the additional cost.

Equipment in wells using submersible pumps has been found to be subject to corrosion by CO₂ on external pump and motor parts and on the internal areas of the J-55 production tubing. The tubing has been coated with the same thin film epoxy-modified phenolic resin used on the injection tubing. Attack is similar to, but considerably less than, that occurring on injection well tubing. Pump and motor parts were coated with thick, glass-filled epoxy which offered protection but tended to cause the motors to run hot. Electroless nickel coatings were not acceptable due to extreme corrosion at holidays. A sprayed metal (316 SS or Monel) coating with baked epoxy overlay is used at present. Pump internals (NiResist nickel cast iron) have not been subject to appreciable corrosion. Corrosion of submersible pump electric cable, casing, and exterior of tubing due to a continuously injected scale inhibitor was controlled by adding a corrosion inhibitor to the process water used to flush the scale inhibitor.

Inhibitors are also used to control corrosion in the rod-pumped production wells at the Houston Natural Gas Twofreds Field near Pecos, Texas (47). The CO₂ injection program was started five years ago. The typical water cut is 50%. Some wells now produce gas containing 40-60% CO₂. Produced

water pH was originally 6.5 to 7.5 and is now 5.5 to 6.0. Corrosion problems, primarily involving tubes and sucker rods, have increased with the quantity of CO₂ injected. Corrosion rates are higher in wells with higher gas volumes. Most of the tubing is uncoated. Inhibitor treatment was started at an early stage and is now done by weekly batch additions. The main problem has been in getting complete inhibitor circulation through the wells, and the water flush has been increased to deal with this. Another problem is downhole frothing of the inhibitor and different formulations and techniques are being tried. Overall, corrosion has not been severe. Precipitation of calcium carbonate has been a problem since start of CO₂ injection.

4.4 PRODUCTION FLUID HANDLING

Surface equipment servicing wells producing CO₂ will also be subject to corrosion. The course of action to be taken will depend on the materials used prior to start of CO₂ injection. Good quality nonmetallic piping (epoxy-fiberglass or equivalent, see Section 3.2) should be usable for wet CO₂ using conservative pressure ratings. Bare steel separators and similar equipment should be coated with a high quality, abrasion resistant plastic coating (thick film epoxy or equivalent). Water saturated CO₂ gas following separation can be very damaging to bare steel. Protection of existing steel gas lines is possible by treatment with volatile/non-volatile amine inhibitors. Points where water can condense and collect should be eliminated and ample drain points installed in suspect areas. Air in-leakage should be avoided wherever possible. Use of oxygen scavengers and corrosion inhibitors should prolong the life of coated fluid handling equipment.

The main corrosion problem at one large field involving surface production equipment has been the sand filter shells. Erosion/corrosion occurring during backwash of the sand filters resulted in holes in the coal tar epoxy coated shells. No leaks have occurred in filters with a thick film epoxy coating (41).

Removal of CO₂ from produced gases for reinjection will be desirable in most cases. Corrosive conditions can exist in both of the general processes in use, the hot potassium carbonate process and the monoethanolamine (MEA) process. These are primarily due to the presence of wet CO₂ at temperatures ranging from 105° to 300°F, high solution flow rates and hot spots in certain areas, and presence of sorbent degradation products. Corrosion inhibitors are used to protect carbon steel components. Inhibitors based on vanadium pentoxide are used in the hot potassium carbonate processes while amines, including several proprietary compounds, are used in MEA processes (48, 49).

Stainless steels are often used in high flow rate areas (pumps, pressure letdown valves, piping tees and ells), hot areas, traps and ring packing, and critical equipment such as sensors and instrumentation. Type 304 is frequently used in these areas and is usually the lowest grade specified. Type 316 may give somewhat better service in extremely corrosive areas. Equipment handling the hot, wet CO₂ stripped from solutions such as stripper overhead piping, condenser, and accumulator are frequently made from Type 304. Type 304 clad on carbon steel may be used for components such as the upper shell of strippers (48).

Intergranular corrosion and stress corrosion cracking of the austenitic stainless steels do not appear to be a problem in this equipment probably due to the absence of or low levels of chloride. Inadvertent addition of chloride impurities should be avoided. Inhibitors used in the MEA processes also serve to protect Type 304 stainless steel. Air in-leakage which could occur during start-up or shutdown should be guarded against. Products of MEA decomposition can be quite corrosive to carbon steel, and a reclaimer unit for regenerating a side stream of the sorbent is often used.

Corrosion considerations for the lines leading to CO₂ compression and dehydration equipment and components of the units where liquid water can

exist are similar to those for the removal equipment. Stainless steels are preferable for critical pressurized areas. A dual phase amine-type inhibitor has been used to protect carbon steel piping ahead of dehydrators and in interstage piping when stainless steel trimmed equipment was not available (41).

Section 5

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