Exchangers Nitriding in Loop

Corrosion in hot MEA systems is caused by the reaction of the carbon dioxide and the carbon steel equipment, which most plants have.

J. W. Rollins
Hill Chemicals, Inc.
Borger, Tex.

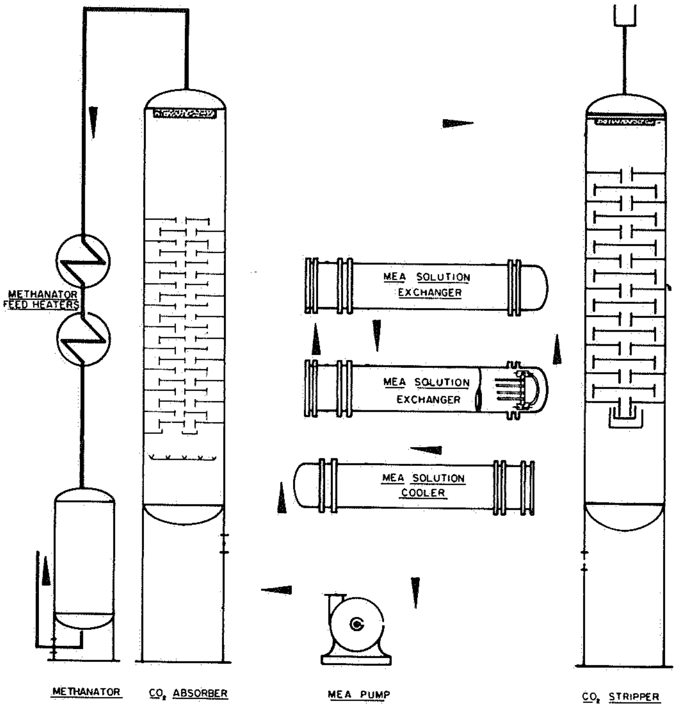


Figure 1. Flow diagram of the synthesis gas purification process.

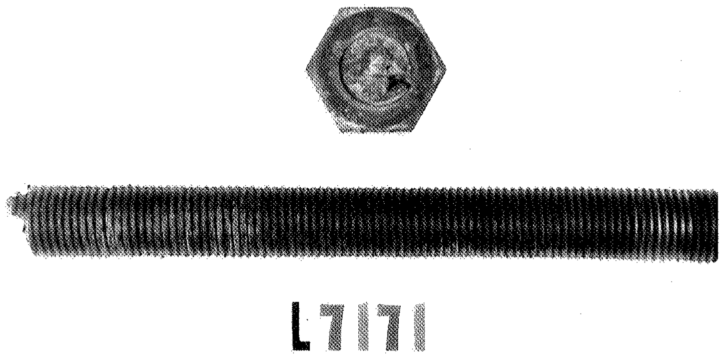


Figure 2. Stud and nut specimen as removed from service.

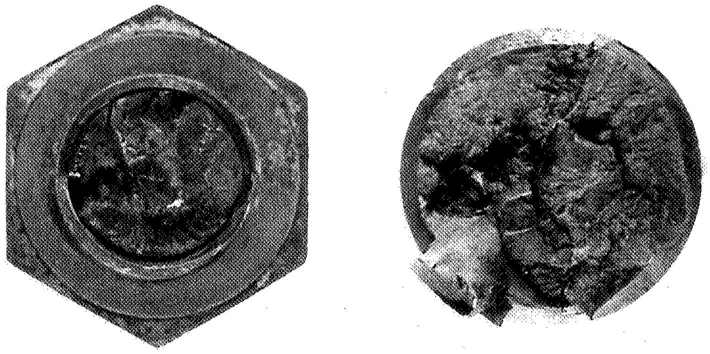


Figure 3. Close-up views of the fracture surfaces.

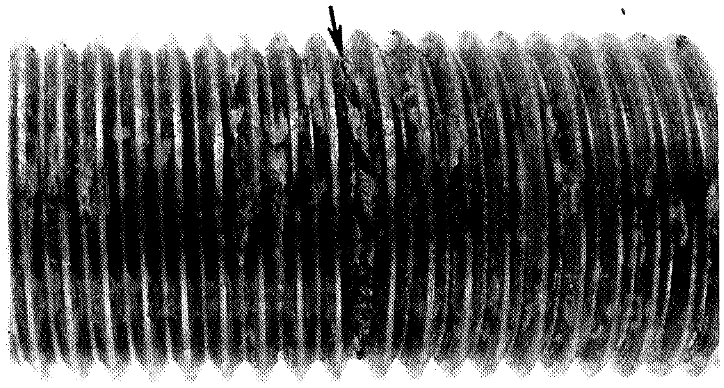


Figure 4. Close-up view of the long bolt illustrating a transverse crack (arrow) located approximately 1 in. from the facture.

Failures have occurred to the floating head bolting in exchangers operating in monoethanolamine (MEA) absorption systems for removing carbon dioxide from a mixture of hydrogen-nitrogen and carbon dioxide. This trinary gas mixture, and an aqueous solution containing approximately 20% by volume MEA are fed counter-currently through an absorber column. The CO_2 is absorbed from the gas by the MEA solution. The rich MEA solution is reactivated in stripper columns and returned to the absorber. The MEA exchangers transfer heat from the lean solution exit the reactivator to the rich solution inlet the reactivator, Figure 1. Further cooling of the lean solution is obtained from coolers using plant cooling water.

The shell side of the MEA heat exchangers in this section are exposed to lean CO_2 aqueous MEA solution at approximately 245°F (118°C), and 11.0 lb./sq. in. gauge.

The tubes are exposed to the rich CO_2 solution at approximately 160°F (71°C), and 390 lb./sq. in. gauge.

Materials testing

The bolting material specification commonly used for this service is a ferritic type, high temperature alloy-steel, conforming to ASTM A-193-66 Grade B7, (AIS1 4140), with a chemical analysis in the following range:

Carbon, %	0.38 to 0.48
Manganese, %	0.75 to 1.00
Phosphorous, max. %	0.04
Sulfur, max. %	0.04
Silicon, %	0.20 to 0.35
Chromium, %	0.80 to 1.10
Molybdenum, %	0.15 to 0.25

Typical physical analysis for this material are:

Tensile strength min. lb./sq. in.	125,000
Yield Point, min. lb./sq. in.	105,000
Elongation, % of 2 in.	16
Reduction of area, %	50

Many different tensile properties may be obtained, depending upon the form or condition of the steel and the heat treatment process.

Failed bolting material from which examinations and tests were performed to determine the cause of the failure, Figures 2, 3 and 4, consisted of the following chemical and physical analysis as originally installed:

ASTM A-193 Gr B-7

Carbon, %	0.41
Manganese, %	0.82
Phosphorus, %	0.011
Sulfur, %	0.018
Silicon, %	0.27
Chromium, %	0.91
Molybdenum, %	0.20
Tensile Strength, lb./sq. in.	138,000
Yield Point, lb./sq. in.	121,500
Elongation, %	20
Hardness, Rc	29.9

Laboratory analysis of scale and deposits removed from the surface of several bolts showed it to consist principally of iron, calcium, and carbonate. Traces of copper, phosphate, sulfate, silica, chlorides and sulfides were present.

Hardness tests have been performed on several failed samples and readings of Rc 29 to 33 were found. Tension tests on the failed bolting were:

Tensile Strength, lb./sq. in.	145,400
Yield Point, lb./sq. in.	127,500
Elongation, %	21.8
Reduction, %	61.7

Metallographic examinations of radial, longitudinal sections showed the cracking to be principally intergranular, with the degree of branching varying from slight to pronounced, Figures 5 and 6. The microstructure consisted essentially of moderately uniform tempered martensite. No defects or deterioration of materials were detected in the specimens. The metal looked fine except it was cracked.


Figure 5. Photomicrograph illustrating branching cracks in the long sample (nital etch; mag: 10X).

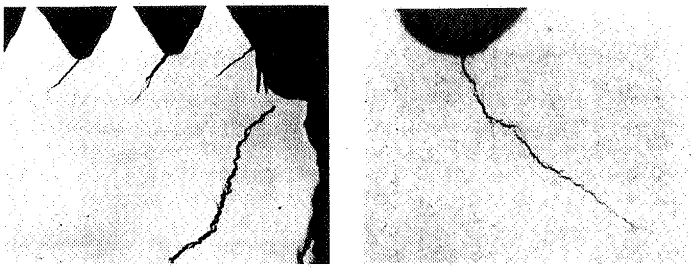
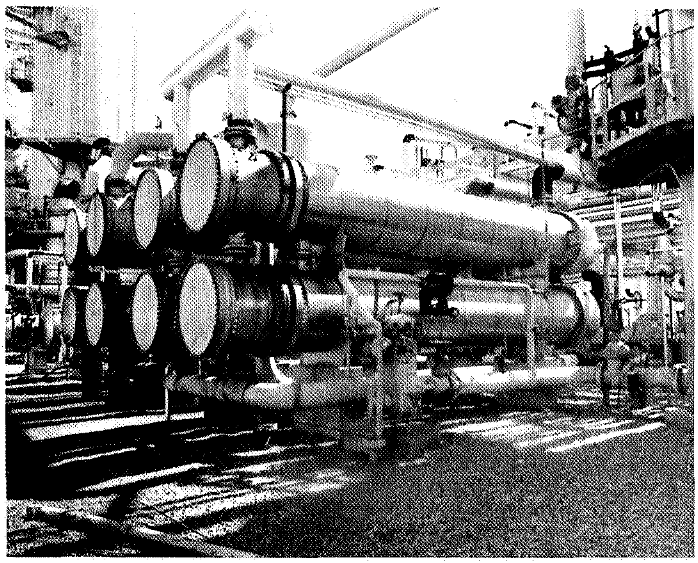


Figure 6. Photomicrographs illustrating transgranular cracks originating at the thread roots of the short sample (nital etch; mag: 10X (left) 50X (right).

Corrosion mechanism

In high temperature reducing atmospheres sulfur will decompose into hydrogen sulfide. As little as 0.010% H_2S can damage equipment and create seriuous heat transfer rates by spalling on cooled surfaces. Increasing the hydrogen sulfide concentration to 1.0%, increases the



corrosion rate by 20 times.

The pH of the solution also determines the corrosion rate. Acidic environments promotes the reaction, and alkaline solutions usually retards, especially above the 8 to 9 pH range.

Corrosion in hot MEA systems is caused from the reaction of the carbon dioxide and the carbon steel process equipment, which most plants have. It is generally accepted that stress corrosion cracking requires two basic requirements:

1. Residual or internal stress. In the case of boltings, the applied load.
2. Corrosion

Corrosion rates can be reduced by material selection, inhibitors, and distillation.

In specific environments where other conditions remain unchanged, laboratory results indicate that stress corrosion cracking of highly stressed A1S1 4140, low alloy steel is directly related to the tensile properties. For most load-environment conditions a Rockwell "C" hardness of 22 should not be exceeded. Lower hardness values may be obtained where allowable stress values will permit.

Failure sequence

The stoppage of the MEA flow, and the emergency shutdown of all downstream systems resulted from the failure of the floating head bolt, Figure 2, A crash shutdown itself creates potential harzards. The tube side MEA pressure was exposed to the low pressure designed shell. It is estimated that it took less than 1 min. for the circulating pumps to loose suction.

Loss of the MEA flow was followed by the sudden depressuring of the absorber and related piping into the bottom and up through the CO_2 strippers. This sudden release of gas caused high differential pressure across the stripper trays. The bottom 12 trays were damaged by the surge of the solution and gas into the bottom of the strippers.

Loss of the synthesis gas purification system allowed high concentrations of CO_2 to enter the methanator, resulting in a rapid temperature increase. Instrumentation recorded temperatures in excess of 1,200°F, and temperatures of over 1,000°F were recorded for a period of at least 24 hr. The maximum allowable stress for the methanator vessel materials (SA-204 Gr. B), is 15,000 lb./sq. in. at 850°F. At 1,000°F, this material is degraded to 6,250 lb./sq.in. and for temperatures of 1,050°F and above, this material is not recommended.

If the vessel steel attained the catalyst temperatures, and had not been depressured, failure might have occurred due to the reduced strength of the material at the elevated temperatures. The potential shell failures would have released a significant quantity of toxic inflammable materials, imperiling both man and machine. #