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Stress-Corrosion Cracking of Austenitic Stainless Steels in Chemical Plant Equipment

Some case histories of condensers and heat exchangers, cooling coils, and contact with wet thermal insulation may aid in solving stress-corrosion cracking failures

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SINCE the first articles on stress-corrosion cracking of austenitic stainless steels appeared in technical journals in the late 1930's, very little has been learned about the fundamental mechanism of stress-corrosion in the austenitic stainless steels. Several theories have been advanced, but no single theory has been accepted as truly pointing out the mechanism of the phenomenon. The research work now in progress has, however, developed several laboratory tests for producing cracks in stainless steel samples under conditions and in solutions more nearly representative of actual operating conditions than was the boiling 42% magnesium chloride test. In this test, described by M. A. Scheil in the ASTM, AIME Symposium on Stress-Corrosion Cracking of Metals, 1944, stressed austenitic stainless steel samples were immersed in a solution containing 42% magnesium chloride at the boiling point, 309° F. Many of the samples cracked in less than 10 hours.

Probably the most valuable contributions to date, as far as designers and operators of chemical equipment are concerned, are compilations of case histories of failures of equipment due to stress-corrosion cracking. Du Pont's experience has been that close cooperation between materials en-

Figure 1. Cracked area in one of the $3^1/_2$-inch outside diameter pipe sections with a wall thickness of 0.083 inch

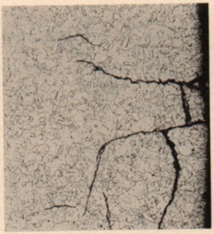

Figure 2. Photomicrograph of typical transgranular cracks in Type 347 stainless steel tubing. Magnification 75×

Figure 3. Cross section of wall of a 4-inch schedule 10 Type 347 stainless steel pipe showing stress-corrosion cracks

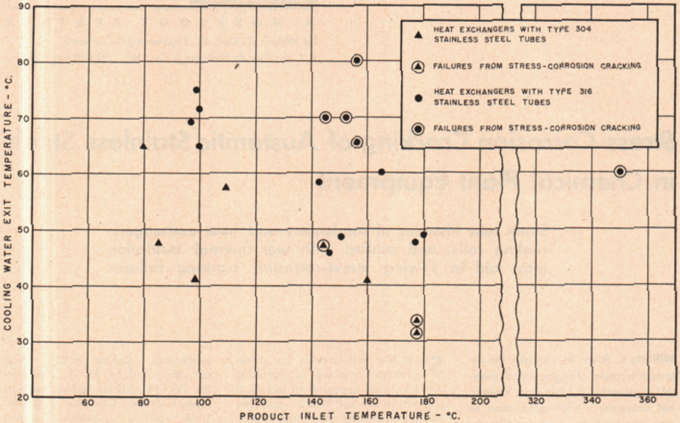

Figure 4. Product inlet temperature *vs.* cooling water exit temperature

gineers and designers or plant people is required for the most effective use of the information derived from the case histories. We are beginning to see the results of such efforts in the form of a sizable reduction in the number of failures from the peak year of 1952. The remedy in many cases was to use more expensve materials of construction and more costly design features, but the result has been a higher degree of reliability in equipment operation.

This article will present some of the case histories from which we obtained valuable information and will summarize our experience in this field.

General Experience

Our experience can be summarized in a general manner as follows:

1. In all failures that were investigated, aqueous media containing chlorides were involved.
2. It was impossible to establish the minimum chloride content at which cracking would occur because there was evidence in all cases that concentration of chlorides had taken place. It is suspected that, in the absence of crevices or heated surfaces on which concentration of chlorides can occur, a high chloride concentration (several per cent) would be necessary to initiate cracking.
3. The lowest metal temperature at which stress-corrosion cracking occurred was 80° C. Usually the metal temperature was 100° C. or higher.
4. Annealing after fabrication was not effective in the prevention of stress-corrosion cracking.
5. Service failures have occurred in piping or equipment items of Types 304, 304L, 316, 316L, 347, and 309 stainless steels.

Case Histories of Stress-Corrosion Cracking Failures

Condensers and Heat Exchangers. At one plant, 11 similar, large, Type 304 stainless steel tubular condensers failed in the range of 100 to 200 days after being placed in operation. Failures occurred in the tubes, in the crevice between tube and lower tube sheet, or just above the lower tube sheet. Water with chloride content varying from 25 to 1000 p.p.m. was used on the shell side for cooling. Operating cycle was approximately 45 minutes and during this time the temperature varied from 80° to 215° C. It is believed that the temperature fluctuation permitted water to enter the crevices between tubes and tube sheets. Vaporization of the water concentrated the chlorides.

The situation was remedied by changing the tubes from Type 304 stainless steel to Type 446 stainless iron and the lower tube sheets from Type 304 to Type 430. The upper tube sheets of Type 304 stainless steel were not changed because of the low temperature at that point. After 2 years, no further trouble has been experienced with these units and no pitting of the Type 446 tubes of the water side has been detected.

At another Du Pont plant, failures in over 50 units have occurred just beneath the upper tube sheets in condensers and vertical heat exchangers. The chloride concentra-

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For further information, circle number 75 A on Readers' Service Card, page 135 A tion in the cooling water varied from 45 to 90 p.p.m. Process inlet temperatures were over 100° C. Due to tube sheet vents not operating properly, a vapor space existed beneath the tube sheets in many of these units. Water splashing on the hot tubes in the vapor space evaporated, leaving behind a salt deposit under which cracking occurred. In some cases, deposits of mud and debris on the hottest portion of the tubes just below the upper tube sheets reduced heat transfer, allowed evaporation of water, and concentration of chlorides. Both Type 304 and Type 316 stainless steel tubes have failed under these conditions. The chart (Figure 4) gives the conditions of cooling water outlet and process inlet temperature at which failures occurred at this plant. Some remedies that show promise are:

1. Eliminate vapor space beneath tube sheets by keeping vents cleaned out or by using four vents instead of two.
2. Keep tubes free from mud and debris in hottest portion.
3. Use bimetallic tubes with copper or a copper alloy on the water side.
4. Change position of heat exchangers from vertical to horizontal.

At another plant, a 250° C. process inlet temperature was encountered in a condenser and Type 316 stainless steel tubes failed in 3 years. Failures occurred just beneath the upper tube sheet under a heavy carbonate scale where highest temperatures were encountered. In this unit, a Probolog was used to detect cracks in the tubes before they penetrated the tube walls and caused shutdowns. Cracks could be detected with this instrument as much as 6 months before actual failure would occur.

The Probolog is an instrument that detects irregularities such as cracks and pits in tubes of nonmagnetic materials. It is sold by the Shell Development Co., Emeryville, Calif. The instrument consists of a probe, a probe puller, and an electronic recorder. In operation, the probe is pulled through the tubes which are to be examined. The energized coils within the probe produced a magnetic field which penetrates the metal of the tube. The metal acts as a

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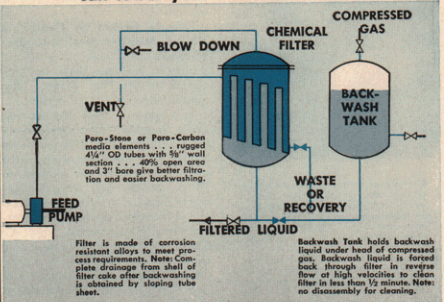

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variable resistance of a balanced bridge. Any variation of resistance caused by a pit or crack unbalances the bridge, causing a pen deflection on the recorder.

Cooling Coil in Reaction Vessel. A cooling coil of Type 347 stainless steel was used to control the temperature of a reaction. Water with 25 to 3000 p.p.m. Cl^- was circulated through the coil. The temperature of the reaction was limited to 80° C. The stainless steel coil failed by stress-corrosion cracking out of the crevices formed at the root of the circumferential welds. This failure was of interest because the metal temperature could not exceed 80° C. The remedy in this case was to use a coil of bimetallic tubing with stainless steel on the outside and Admiralty brass on the inside.

Failures Caused by Contact of Heated Stainless Steel with Wet Thermal Insulation. Over 40 failures from this cause have been reported in Du Pont plants. Two typical failures are listed below:

A column of Type 304 stainless steel, annealed after fabrication, was insulated with 85% magnesia insulation. The temperature ranged from 175° C. at the bottom to 92° C. at the top. Cracking occurred from the outside of the column at a point where the metal temperature was approximately 100° C. Chlorides leached out of the insulation by rain water concentrated on the surface of the stainless steel and caused failure by stress-corrosion cracking.

At another plant, steam was passed through insulated sections of Type 304 stainless steel pipe which were open at the lower end. Steam leaving the tubes flowed upward over the magnesia insulation, keeping it moist and leaching out the soluble chlorides (Figure 1).

One suggested remedy for situations where contact with wet thermal insulation has resulted in the failure of heated stainless steel parts by stress-corrosion cracking is to keep the insulation dry. All of the commonly used types of thermal insulating materials contain water-soluble chlorides. If water passes through the insulation these chlorides can be leached out and will concentrate on the heated stainless steel surface.

Conclusion

The number of equipment failures was reduced considerably by application of information derived from a careful study of previous failures. The range of conditions that caused the failures has been established—thus providing an improved basis for material selection and equipment design. The first attempt is to use materials which are immune to stress-corrosion cracking. When this is not possible, efforts are directed toward obtaining a design that keeps the metal temperature as low as possible and avoids vapor spaces and crevices where concentration of chlorides can occur.

The Du Pont Engineering Research Laboratory is engaged in a research program on stress-corrosion cracking of stainless steels. A test has been developed that simulates the conditions encountered at sites of stress-corrosion cracking failures. This test is described in the article, "Stress-Corrosion Cracking Test," by A. W. Dana and W. B. De Long, [*Corrosion* **12,** 19 (July 1956)]. The information which will be developed in this research program may give additional insight of the fundamental mechanism of stress-corrosion cracking.

It is seldom difficult to distinguish between fractures produced by stress-corrosion cracking and by conventional stress-rupture. In the former, cracks are transgranular and without reduction of cross section, which differentiates them from the latter. The macro and micro patterns exhibited by stress-corrosion cracking vary considerably, but Figures 2 and 3, both of cracks in Type 347 stainless steel, may be considered as typical.

Readers who may wish to learn more about stress-corrosion cracking of austenitic stainless steels are referred to the following article, which should be informative and interesting.

W. Lee Williams and John F. Eckel, "Stress-Corrosion of Austenitic Stainless Steels in High Temperature Waters," *J. Am. Soc. Naval. Engrs.,* **68,** 93 (February 1956).

Acknowledgment

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