external stress corrosion cracking

ESCC of Stainless Steel

FAILURE of stainless steel process equipment caused by external stress corrosion cracking (to be abbreviated for convenience as ESCC in this article) has been a troublesome and costly problem in the Gulf Coast plants of the Chemicals Division of Union Carbide Corporation. Major equipment repairs and replacements, and loss of production caused by ESCC, have occurred at the Texas City and Seadrift plants, as well as the Brownsville plant when operated by its previous owners. The nature and occurrence of ESCC has been reported in the literature and has been found in many areas of the United States, as well as in Europe.[1,2] The frequency of ESCC as reported appears to be highest in coastal locations.

A recent series of ESCC failures at Union Carbide's Seadrift plant was investigated. The cause was cracking resulting from an anti-abrasive coating applied to the inside surface of a non-wicking insulation material (Figures 1 and 2). In efforts to solve this problem, a laboratory test was developed to determine if the insulation material in question would cause stress corrosion cracking of stainless steel. Once perfected, the test was extended to all the common insulation materials which are used in the company's Chemicals Division to determine if any others also were dangerous from an ESCC standpoint. Tests were run to evaluate protective coatings for the metal as well.

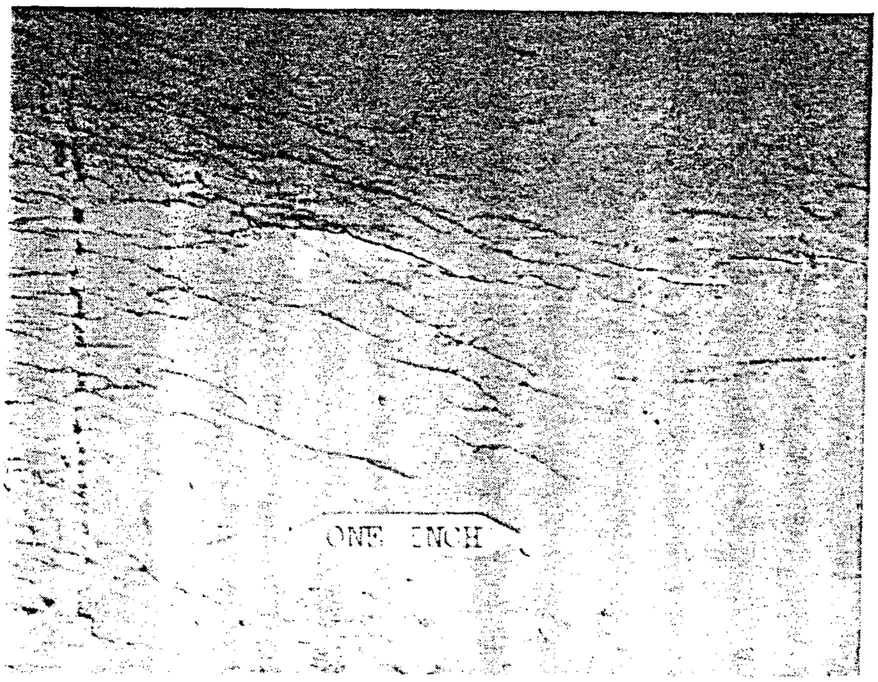
Testing Procedure

To evaluate the ESCC potential of many insulating materials, a multiple test apparatus was designed which would duplicate and accelerate the ESCC mechanism. Although a great deal of literature has been published on testing of stainless steel in stress cracking environments, only one significant work, however, has been attempted on the ESCC of stainless by insulation.[3,4] These tests were limited to 85% magnesia, calcium silicate, and glass fiber materials. All three materials were found to cause stress cracking. These materials are water permeable and suitable for evaluation by a wicking type test. The chloride ion is so soluble in water that it is unlikely that any commercial insulation material, where water is used in its manufacture, would be entirely free of chlorides. Thus, an efficient extraction of chlorides from the insulation and a sufficiently long test interval would inevitably result in stress cracking.

This procedure, however, cannot be used for the testing of cellular or other non-wicking insulation materials nor for coatings, mastics, or cements. Therefore a new test apparatus was designed and is shown in Figures 3 and 4. This apparatus is intended to duplicate as closely as possible the actual field situation where water, steam vapors, or leaking chemicals penetrate the insulation through cracks, joints, or other openings in the waterproof covering or insulation. Only in rare cases in the plant is the insulation material completely saturated with water.

The test apparatus consists of a bronze mandrel which is heated by a 500-watt soldering iron. Over this, a strip of stainless steel is bent and held in tension by bolts fixed to either side of the mandrel. A block of insulation material is cut to fit the horseshoe

Figure 1—External stress corrosion cracking of Type 316 stainless steel on a distillation column. This cracking was caused by an anti-abrasive coating applied to the underside of a non-wicking insulation material. The cracking occurred in less than six months.



SUMMARY

Some 35 different insulation materials were tested in a laboratory device to determine if they would cause stress corrosion cracking of Type 316 stainless steel. Only three of the materials tested caused cracking under the closely simulated plant exposure. Stress cracking occurred only in the temperature range between 50 and 200 C (122 and 392 F). Evaluation of many plant external stress corrosion cracking (ESCC) failures confirmed these test results. ESCC in most cases is not caused by chlorides contained in insulation material. Main chloride source is from industrial or marine atmospheres which induce chloride contamination of the metallic surface under the insulation. Role of insulation is primarily that of trapping the chlorides, thus allowing them to concentrate to a level where ESCC takes place. Painting of the stainless before insulation is recommended as the best protection presently available.

W. G. Ashbaugh

Union Carbide Corporation

Texas City, Texas

under Thermal Insulation★

specimen and clamped to the top of the apparatus. A small hole drilled through the insulation at the center allows distilled water or other liquids to be fed to the surface of the stainless specimen. Two pairs of the testers were set in operation with the temperature automatically controlled. Temperature was measured by a 1/16-inch diameter stainless steel, sheathed thermocouple inserted in the bronze mandrel just below the stainless specimens. Distilled water was fed dropwise at about 3 cc per hour to the surface of the stainless to induce a small amount of moisture to extract chlorides which might be available on the insulation's inner surface. The desired level of temperature was set and the test run for a given time, the conditions depending on the experiment being conducted.

After test exposures were completed, the stainless specimens were removed and cleaned with cleanser and a soft brush, and examined under a low power binocular microscope for evidence of cracking. To make the examination more thorough, ends of the horseshoe specimen were brought together to overstress the test surface, thus opening up any cracks which might be present. Figure 5 shows some of the cracks which developed.

Metallographic examinations of several cracked specimens confirmed that the defects noted were typical transgranular stress corrosion cracks. All the stressed specimens were cut from a single sheet of 16 gauge, Type 316 stainless steel (0.05% carbon, 17 chromium, 12 nickel, 2.5 molybdenum, 1 manganese, and 0.5 silicon). The test strips were sheared to six inches by one inch, with the sheared edges retained to increase the severity of the stresses on the specimen.

Figure 2—These transgranular, branched cracks are metallographic evidence that the cracking seen in Figure 1 is chloride stress corrosion cracking. (Electrolytic oxalic acid etch, 75X)

All tests on the coatings, mastics, or cements were made by applying a generous layer of the material inside a block of expanded Perlite insulation which had been drilled and pre-cut to fit the mandrel. The expanded Perlite insulation was selected as representing a "safe" material which would not cause ESCC in itself. The coated insulation material was then tested in the same manner as the other insulation materials.

The tests were run in two major series. The first was to test the ESCC potential of the anti-abrasive coating believed to have caused the trouble at the Seadrift unit and to evaluate the test procedure. The second set of tests was run on the various insulation materials which are in common plant usage.

Table 1 lists the first series of screening tests. The first test demonstrates how the anti-abrasive coating would cause cracking in as short a time as 120 hours at temperatures of 125 C (256 F). Another check on the testing technique was conducted using magnesium chloride, which is a well known severe stress cracking salt. A 10% by weight solution of this compound produced cracking (see Figure 5) in less than 40 hours at 125 C (256 F). Several other tests were run with both the anti-abrasive coating and the 10% mag-

★ Revision of paper titled "Stress Corrosion Cracking of Stainless Steel Under Thermal Insulation" presented at 20th Annual Conference, National Association of Corrosion Engineers, March 9-13, 1964, Chicago, Ill.

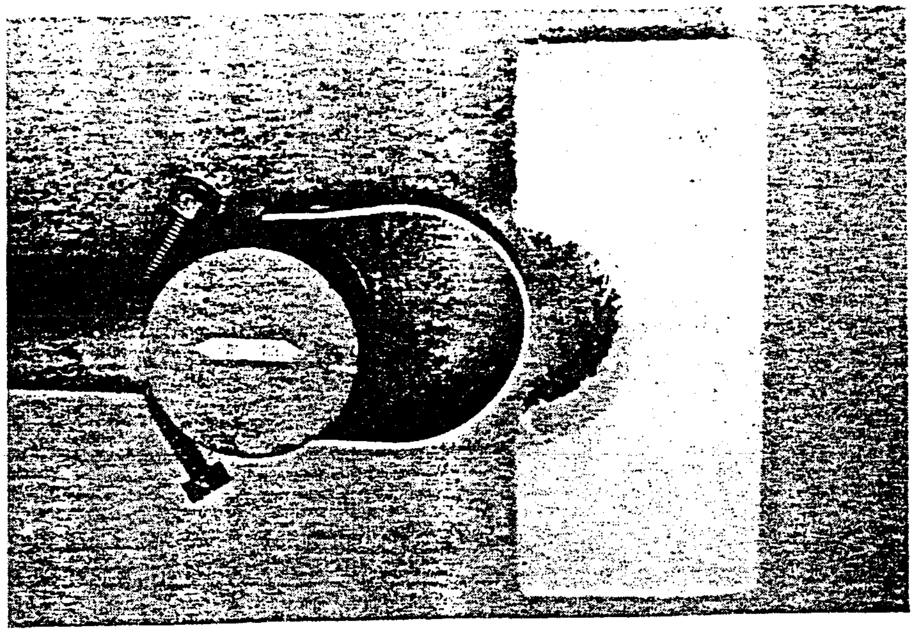


Figure 3—Basic test apparatus consisting of a bronze heating mandrel around which a test strip of Type 316 stainless is bent and secured under stress. The cut out block of insulation then covers the stressed portion of the stainless strip.

nesium chloride at different temperatures. Another experiment in this series was the use of a distilled water solution of 0.10% by weight sodium chloride, plus 0.01% by weight acetic acid fed through expanded Perlite insulation. This chemical mixture caused severe cracking after a 336-hour test at 125 C (256 F). This last test was intended to duplicate a situation of extreme atmospheric contamination which might occur around process equipment.

Another test was run to determine if one of the "inhibited" brands of insulation would prevent ESCC in the presence of externally introduced chlorides. A distilled water solution of 0.10% by weight NaCl plus 0.01% by weight acetic acid was fed through the "inhibited" insulation for 336 hours at a metal temperature of 125 C (256 F). The test specimen cracked. A comparison run was made with the same insulation and distilled water feed; no cracking resulted.

These screening tests, compared with the known time to cause cracking in various plant situations, indicated that the tests did accelerate the ESCC rate considerably. Accelerated tests were considered necessary to complete the testing program within a reasonable time. Many materials were to be tested, and the results needed to be obtained as quickly as possible so they could be applied to plant practice.

Two Coatings Evaluated

Two protective coatings for the stainless were evaluated by painting the stressed stainless strip after it had been placed on the mandrel. The coated coupons then were exposed to both the anti-abrasive coating and distilled water and to 10% magnesium chloride to see if they would be protected from cracking. The only cracking resulted from a holiday in one of the silicone coatings which allowed the magnesium chloride to contact the metal surface.

Of the 35 types of insulation materials, coatings, and cements, which were tested, only three cracked (See Table 2). These were two anti-abrasive coatings and one cement.

Because results were surprising and had not been predicted at the start of the testing program, a review was made of plant experiences which had occurred as a result of ESCC.

Review of Plant Experiences

A re-examination of plant experiences showed that there were confirmed metallurgical diagnosis of ESCC equipment failure as far back as 1947. This phenomenon has been fairly widespread throughout the plant, occurring under several types of insulation materials and in many cases in the absence of insulation. The incidence of ESCC was highest in plant areas where chloride-bearing process materials were being handled: such materials, for example, as chlorine, ethylene dichloride, vinyl chloride resins, salt by-products, etc.

Many plant records described cases of ESCC failure in metal-to-metal contact, such as under steel slip-on flanges or metal pipe support clamps where no thermal insulation was present.

Figure 6 shows a Type 304 stainless pipe nipple which was badly stress cracked under a cellular type insulation (a non-wicking material). The chlorides are believed to have been accumulated from the marine atmosphere because there are no particular chloride-containing chemicals used in the area.

Figure 7 shows a section of a stainless steel condenser head which stress cracked under a steel slip-on ring flange. Chlorides in this particular case were believed to have come from the cooling water cycle. Water is piped up around this condenser head and may have leaked on the bare stainless and collected under the steel flange.

Another case of ESCC which is quite common and occurs without the benefit of insulation is the failure of Type 302 stainless bolts (Figure 8). Here again, chlorides collect on the hot flanges and bolts and are trapped in the bolt hole crevice, resulting in stress cracking.

Finally, there are a good many thousands of square feet of insulated stainless steel which have never failed from ESCC mechanism; therefore, ESCC is not necessarily caused by insulation. A good waterproof insulation job can actually prevent ESCC. However, it is difficult, if not impossible, to keep any insulation system perfectly waterproof.

Mechanism of ESCC

Extensive research and field work have shown that transgranular stress

TABLE 1—ESCC Screening Tests

Insulation Material	Feed	Hours	Temp °C	Cracked
Cellular glass + PVA coating	Distilled Water	120 161 354	125 175 50	Yes Yes No
Cellular Glass	10% $MgCl_2$	336 40 162	125 125 200	Yes Yes No
Expanded Perlite	0.1% NaCl +0.01% HOAC	336	125	Yes
Cellular glass + PVA coating with silicone coating on stainless	Distilled Water	336	125	No
Cellular glass + PVA coating with silicone coating on stainless	10% $MgCl_2$	336	125	Yes*
Cellular glass + PVA coating with epoxy-phenolic coating on stainless	Distilled Water	336	125	No
Cellular glass + PVA coating with epoxy-phenolic coating on stainless	10% $MgCl_2$	336	125	No
Calcium Silicate (Inhibited) Calcium Silicate (Inhibited)	0.1% NaCl +0.01% HOAC Distilled Water	336 336	125 125	Yes No

* Small stress crack found at holiday in coating.

corrosion cracking of stainless steel results from the presence of chloride ions on the surface of a tensile stressed austenitic stainless alloy.[5-8] The detailed mechanism is still obscure by which the chloride ion influences or initiates the cracking and how the cracking proceeds.

Chloride Ion Sources

The chloride ion gets to the surface of the insulated stainless equipment by one of several ways:

1. Salt air and high humidity are prevalent along the Gulf Coast. This moisture can penetrate breaks or voids in the insulation and reach the stainless steel.
2. Chemical spills or fumes present the most potent source of ESCC. Both organic and inorganic chlorides, when blown into the air, can cause serious contamination of adjacent stainless equipment.
3. Water which is used to wash down equipment, in fire lines, spray systems, steam and cooling water all contain chlorides. Any of these waters can easily saturate insulation with far more chlorides than were introduced in the manufacture of the insulation.
4. Chloride-containing compounds may be included in certain of the insulation materials or components. These

TABLE 2—Evaluation of Insulation Materials

Insulation Material	Cracked
Asbestos Perlite Mixture	No
Calcium Silicate (A)	No
Calcium Silicate (Inhibited)	No
Calcium Silicate (B)	No
Calcium Silicate (C)	No
Cellular Glass	No
Expanded Perlite	No
Magnesia, 85%	No
Mineral Wool	No
Molded Asbestos (A)	No
Molded Asbestos (B)	No
Phenolic Foam	No
Polystyrene Foam	No
Polyurethane Foam (A)	No
Polyurethane Foam (B)	No
White Glass Wool	No
Insulating Coating, Inc.	Yes
Asbestos Cement	No
Asbestos Fiber Cement	No
Asbestos Mine Cement	Yes
Asphalt with Gilsonite	No
Cutback Asphalt Coating	No
Graphite Filled Cement	No
Gypsum Cement	No
Hydraulic Setting Cement (A)	No
Hydraulic Setting Cement (B)	No
PVA Coating (A)	No
PVA Coating (B)	No
PVA Coating (C)	No
PVA Coating (low temperature)	Yes
Resinous Coating	Yes
Resinous Joint Sealer	No
Resinous Mastic	No
Sodium Silicate Adhesive (A)	No
Sodium Silicate Adhesive (B)	No
Utility Sealer	No

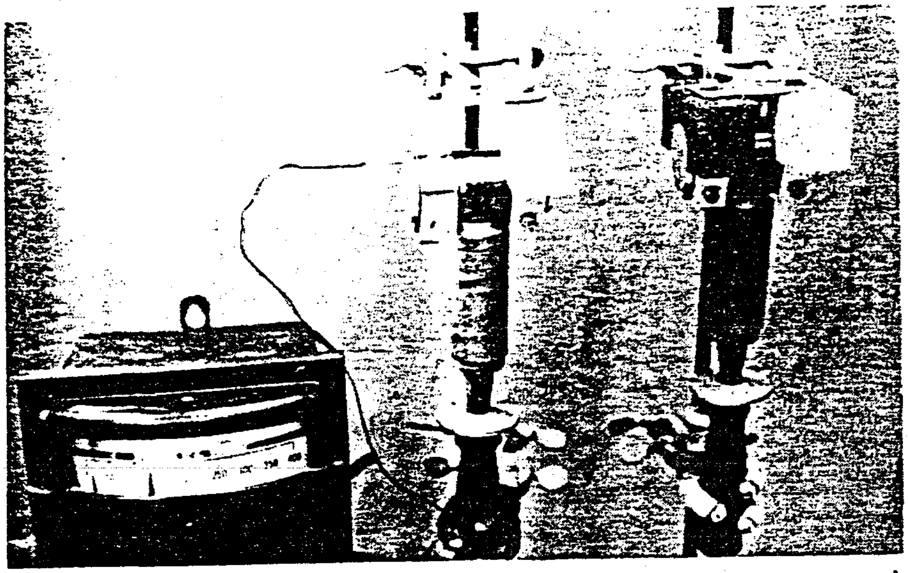


Figure 4—This four station tester is shown with three insulation samples in place, ready for distilled water feed. The dropper tube delivers the distilled water directly to the surface of the stainless stress specimen.

Figure 5—This stainless specimen developed cracks after 40 hours exposure to 10% by weight magnesium chloride with a specimen temperature of 125 C (256 F).

Figure 6—These Type 304 stainless pipe nipples cracked after several years exposure under cellular glass insulation. The insulation did not cause the cracking but helped to trap moisture and chlorides on the surface of the stainless steel.

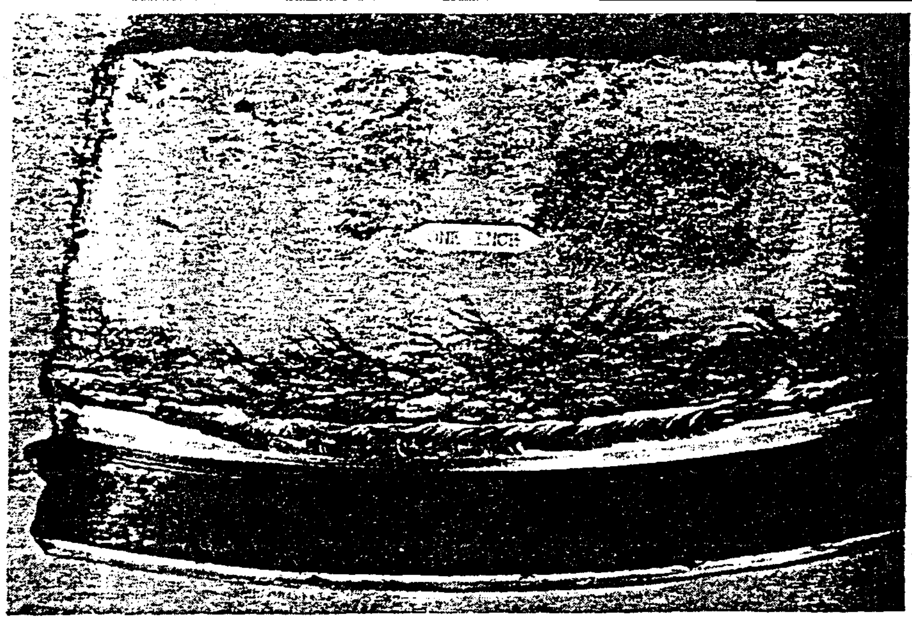


Figure 7—Severe ESCC was found on this Type 304 stainless condenser head under the steel Van Stone flange. The rust-filled crevice proved an ideal pocket for the collection of atmospheric chlorides.

may be water soluble or hydrolyzable and yield sizeable amounts of chlorides. For example, the anti-abrasive coating discussed earlier contains polyvinyl chloride.

5. Chloride contamination of insulation materials can occur easily during its fabrication and installation on the equipment. Significant amounts of chlorides can be introduced when the insulation is handled by the workmen, left open and standing, or when cements and coatings are mixed with water.

Effect of Temperature

The mere presence of the chloride ion on the surface of the stainless equipment is not enough to initiate ESCC. A certain concentration of chlorides must be obtained. The exact theshold value of the chlorides necessary to initiate stress cracking is not known. To obtain such a concentrating effect, several conditions must occur simultaneously. The stainless must be held at a temperature above ambient and must be in physical contact with some other material which will hold moisture and chlorides in place long enough for the concentration mechanism to take place.

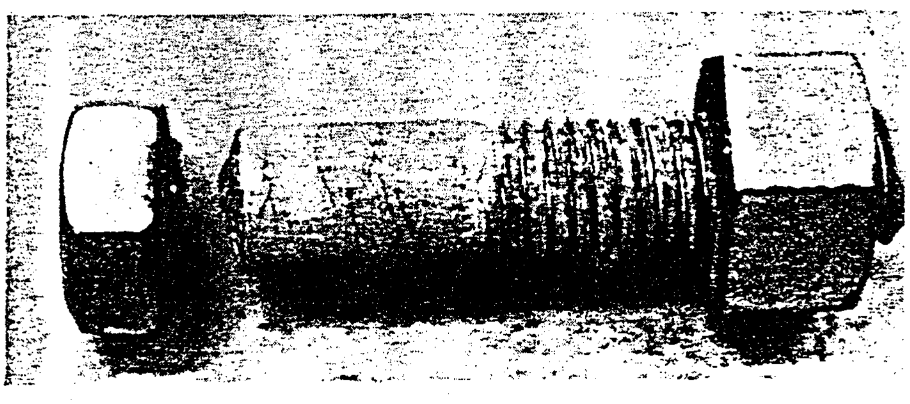
Several exploratory tests were run to determine the effect of temperature on the ESCC mechanism. A test was run with a cellular glass insulation which was known not to cause stress cracking, using a 10% magnesium chloride solution. This system developed cracking of the stainless in 40 hours at 125 C (256 F). The same test at 200 C (392 F) produced no cracking in 161 hours. This confirmed field observations that ESCC failures of equipment operating at high temperatures are rare and, when encountered, are usually traced to periods of down-time. This upper temperature limit apparently is related to the moisture availability which is a necessary part of the chloride concentrating mechanism. If the temperature is high enough, water vapors are either absent or present only for such a short time that an aqueous chloride situation cannot exist, and therefore cracking cannot occur.

On the other side of the temperature scale, a comparision test was run using a non-cracking insulation material coated with the anti-abrasive coating which was known to cause stress cracking. Distilled water was fed, and a test temperature of 125 C (256 F) was maintained. Cracking developed in 120 hours. A similar test run at 50 C (122 F) produced no cracking in 354 hours. Once again, this confirmed field experiences wherein no ESCC had been experienced on the ambient or cold temperature stainless equipment.

A specific example of this is the performance of two Type 347 stainless distillation columns in Union Carbide's Texas City plant. One column operates with a base temperature of approximately 85 C (185 F). This column has a long history of ESCC failures under the steel ring flanges. An adjacent sister column, dismantled in 1962 after some 15 years service, had no ESCC under the flanges. This column has a base temperature of less than 50 C (122 F).

Though the 200 C (392 F) upper limit may be reasonable and valid, it is dangerous to ignore the possibilities of ESCC in equipment operating at temperatures above 200 C (392 F). Obviously, this equipment must pass through the lower temperature range during start-ups and shutdowns, especially if the equipment is in batch operation. The periods when the equipment passes through the temperature range of 50 to 200 C (122 to 392 F) may be sufficient for ESCC to occur.

Figure 8—Chloride stress cracking of this ⅝-inch Type 303 stainless bolt occurred in less than four years. Atmospheric chlorides accumulated in the flange bolt holes, resulting in widespread cracking.



Recommendations

The concept of the ESCC problem as one based on externally introduced chlorides requires that some means of protection be used other than selection of insulation with regard to chloride content. At the present time, recommendations are that all major items of stainless steel equipment be painted before they are insulated if the equipment is to operate in the temperature range of 50 to 200 C (122 to 392 F). In special cases where the equipment operates above 200 C (392 F), the materials engineer should discuss the individual problem with engineering and operating department personnel to determine the risks and value of the use of a protective coating.

Two protective coatings were evaluated in the laboratory tests, both of which proved to be entirely satisfactory. The main criteria for the coatings are ease of application, good coverage in one coat, good adhesion to clean stainless steel without necessity of sandblasting, and sufficient temperature resistance for the particular application desired.

Two coatings are being used by Union Carbide on stainless steel—one a zinc-free silicone high temperature paint and the other is a heavy duty, epoxy-phenolic coating with a rapid catalyst cure. In addition, on ... steel equipment operating in the stress cracking temperature range, it is recommended that the slip-on flanges be embedded in a cut-back asphalt mastic to seal the crevice between the steel flange and the stainless ring.

Painting of lesser items of stainless construction, such as piping and other minor pieces of equipment, is not recommended due to the time and cost involved. However, if the smaller pieces are to be put in service in a particular area where ESCC is known to be a severe problem, it may pay to paint these items before they are insulated.

Insulation specifications of Union Carbide's Chemical Division presently are adequate as to quality of materials and required workmanship to install the insulation and waterproof it. However, the importance of maintaining this high quality insulation system has been emphasized to minimize the chloride contamination which can occur.

Conclusions

Most ESCC failures are caused by chlorides introduced from the atmosphere or from chemical fumes and not from the insulation materials themselves. The insulation acts merely as a trap to hold these externally introduced chlorides on the metallic surface, allowing time for water to evaporate and the salts to concentrate to a dangerous level. ESCC will develop only in areas where the operating temperature of the stainless steel is 50 to 200 C (122 to 392 F).

The inhibition of, or chloride removal from, insulation materials is inadequate protection against ESCC, as demonstrated by the tests in which "inhibited" insulation material did not prevent cracking by an acidified salt solution. The inhibition of insulation by the addition of neutralizers or other agents to the insulation is insufficient protection against externally introduced chlorides which are the major source of ESCC. Although the inhibitor may prevent ESCC from water which passes through the insulation, it cannot be expected to control the chlorides from sources other than the insulation.

The author does not claim that insulation materials cannot or will never cause ESCC, but plant experience and laboratory screening tests indicate that most insulation materials which remain relatively dry play only a secondary role in the ESCC mechanism. The real problem in chemical plants exists as a result of the combination of corrosive atmosphere and the many types of crevices, joints, and areas where atmospheric chloride contamination and concentration can occur.

Acknowledgment

The author acknowledges the work and assistance of H. O. Travis in performing the laboratory tests and metallography; also the contributions of L. M. Rogers in the evaluation of data and preparation of the report. In addition, the author thanks O. T. Carlisle for his helpful suggestions.

WILLIAM G. ASHBAUGH has been active in process corrosion work for 15 years. After graduation from Albion College in 1948 with a BS in chemistry, he started work at the Texas City plant of Union Carbide's Chemicals Division. He is presently a Process Development Department group leader responsible for materials selection, specification, corrosion, and metallurgical investigations for the three Texas plants of the Chemicals Division. Ashbaugh is active in NACE, ASM, and ASTM. He has authored several papers on corrosion and holds membership in several corrosion committees of the various technical societies.

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DISCUSSIONS

Question by G. Lee Erickson, Boeing Company, Wichita, Kansas:

What general types of coatings were applied to the stainless steel prior to insulation application?

Reply by author:

Two general types of coatings were tested and have been used in the field. A zinc-free silicone and an epoxy-phenolic blend both are satisfactory.

Questions by E. H. Phelps, Applied Research Laboratory, U. S. Steel Corporation, Monroeville, Pennsylvania:

1. Have you conducted any analyses of insulation from areas where cracking occurred to establish whether there is, in fact, a measurable quantity of chloride from the atmosphere?

2. Do you have any evidence that the coatings you use prevent cracking?

Replies by author:

1. Spot tests of the cracked metal always reveals the presence of the chloride ion. We have no way of distinguishing one source as opposed to another.

2. In more than two years of plant use, we have had no instance of ESCC of a painted vessel. It would seem that, as long as the coating remains intact, chlorides cannot reach the surface of the stainless and ESCC will not occur.