Failure in Urea Plant Carbamate Condenser

Cause was stress-corrosion cracking on water-side due to freon used for leak tests during maintenance, and result has been adoption of other leak test methods.

G. Cabrini and G. Cusmai,
Snamprogetti,
Milan, Italy

This discussion does not deal with carbamate corrosion problems, or other subjects usually treated in connection with urea plants. It examines instead an unusual case which, however, led to the failure of a vital component of a urea plant, for apparently futile causes.

Urea, as is well known, is produced by chemical reaction of liquid ammonia and gaseous carbon dioxide. In the Snamprogetti process, the reaction products leaving the reactor (urea-carbamate mixture and ammonia solution) are sent to the stripping unit, where the carbamate is decomposed by the stripping action of ammonia and by the heat supplied by steam.

The overhead vapors leaving the stripper, mixed with recycled carbamate solution, are sent to the carbamate condenser, where the ammonia and carbon dioxide are absorbed and condensed, while the condensation heat is utilized to produce steam. The carbamate solution thus obtained is recycled to the reactor.

The material used for the tubes and the lining of the channels of the carbamate condenser is AISI 316L stainless steel, with special prescriptions to withstand carbamate corrosion in the specific process conditions.

In the earlier plants, the carbamate condenser was a vertical single-pass heat exchanger as shown in Figure 1. In new Snamprogetti urea plants the carbamate condenser is of the kettle type.

Heat exchanger failed after three years

About three years after plant start-up, leakage due to tube breakage began to occur in a vertical type carbamate condenser. The trouble was revealed by the presence of NH_3 in the steam, which is periodically analyzed. The ends of the tubes with leaks were plugged and the plant was started up again.

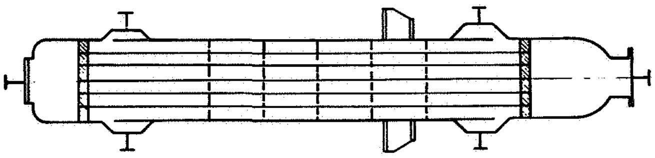

Figure 1. Carbamate condenser (vertical type).

The trouble occurred again several times, and on such a scale that 162 tubes were plugged in three months. In nearly all cases the breakages occurred in non-visible zones of the tubes, far from the welds.

It was decided to remove some of the broken tubes to ascertain the nature of the trouble. On four of these tubes, various longitudinal cracks were found, and some of them appeared to extend through the entire wall thickness. All tube cracks were in a limited area within the upper tubesheet thickness, about 200 mm. away from the weld. Figures 2, 3, and 4 show details.

Chemical analyses and micrographic examinations were carried out to check the quality of the tube material, but

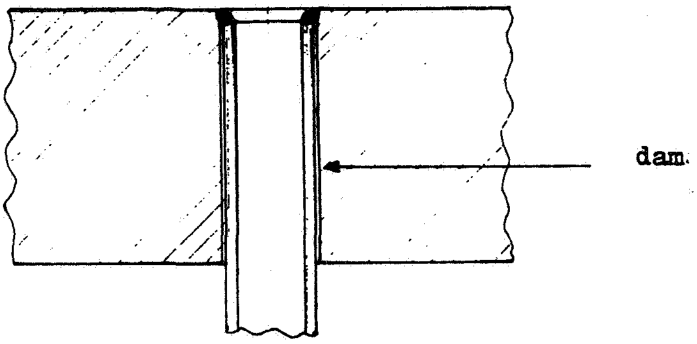

Figure 2. Tube and tubesheet detail.

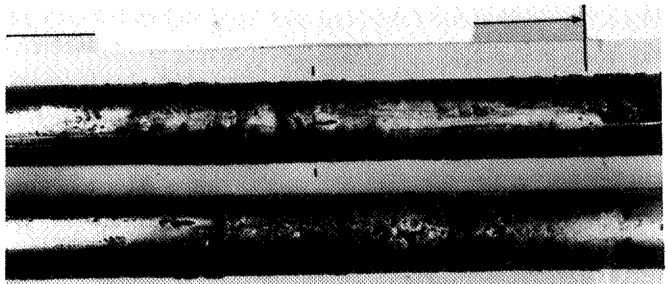

Figure 3. One of the damaged tubes (Breda Institute).

Figure 4. Detail of the defects on the outside surface of a damaged tube (Breda Institute).

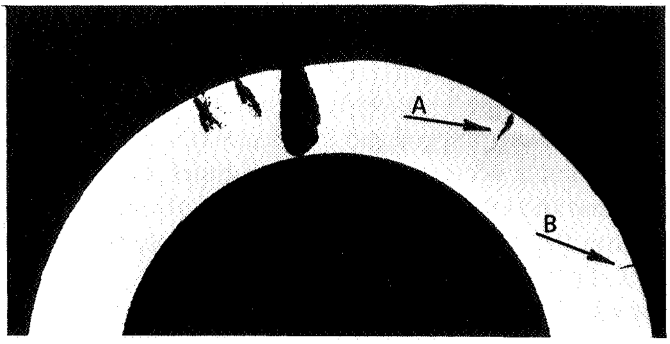

Figure 5. Cross section of defects shown in Figure 4 (Breda Institute).

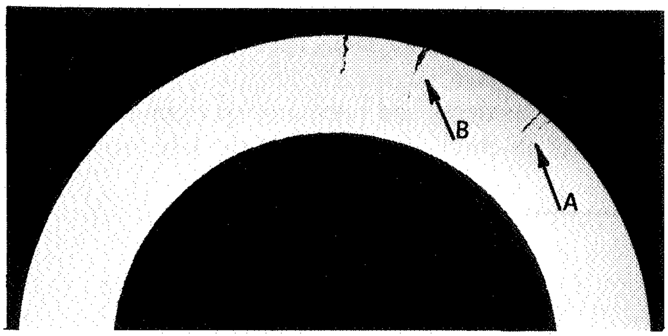

Figure 6. Cross section of another damaged tube (Breda Institute).

everything was found to be according to specification.

Assuming that the material had been damaged by excessive expansion of tubes in the tubesheet, microhardness tests were conducted on transverse sections. However, entirely normal values were detected; also micrographic examinations showed that the tubes had not been subject to any serious work-hardening.

Macrographic examinations of tube sections containing the cracks were most interesting, as they showed that the cracks start from the external surface of the tube, as seen in Figures 5 and 6.

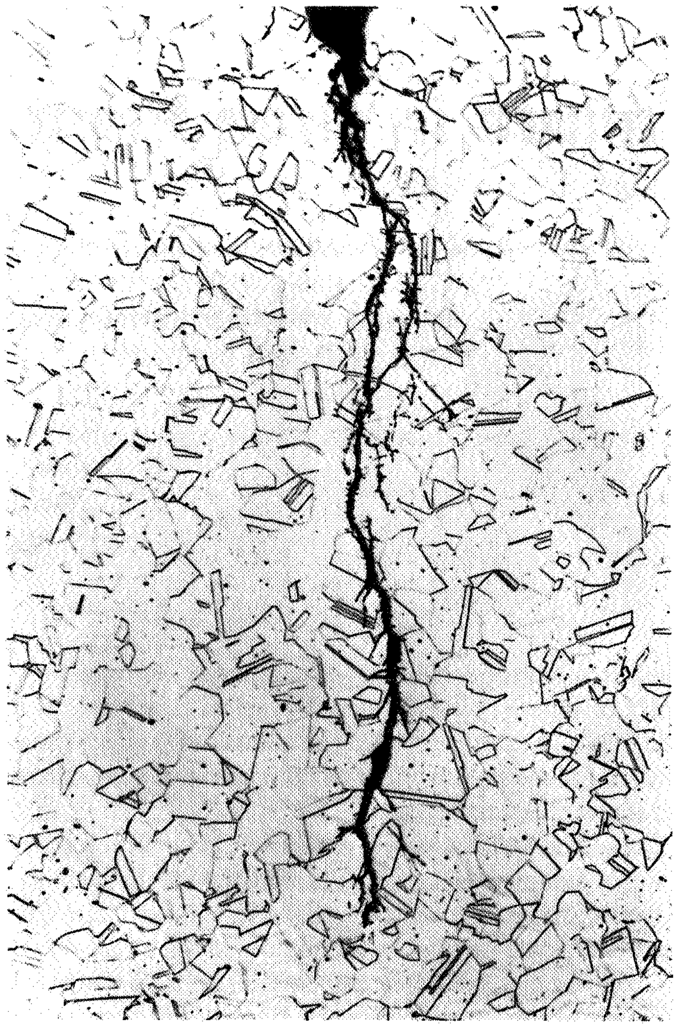

Figure 7. Micrograph of crack B of Figure 5 (Breda Institute).

The micrographs of two of these cracks, in Figures 7 and 8, show a transgranular ramification typical of stress-corrosion cracking on austenitic steels. A microprobe (SEM) examination was then carried out inside some of these cracks and the presence of chlorine was detected in some of them. As is known, chlorine is a specific stress-corrosion cracking agent in austenitic stainless steel. Furthermore, a microprobe examination of the external surface of the tubes was carried out near some of the defects. The presence of chlorine and fluorine was noted. Figures 9 and 10 show the recordings of spectrum FK and CLK on some zones and along a line.

Cracks result of stress corrosion

The laboratory examinations indicated that the cause of pipe breakage was stress-corrosion cracking, which had originated on the outside of the tubes and was associated with the presence of chlorine.

Since vaporizing water circulates on the shell-side, the possibility of chloride pollution in the feed water from a mixed-bed demineralization system was investigated. The periodic water analyses were checked, as was the treatment system. It was found that the water sent to the carbamate condenser could not contain any traces of chloride. On the other hand, the water used for the hydraulic test of the condenser did not appear to be the cause of the phenomenon, as this hydraulic test was conducted with similar criteria as for numerous other equipments still in service which have not given any trouble.

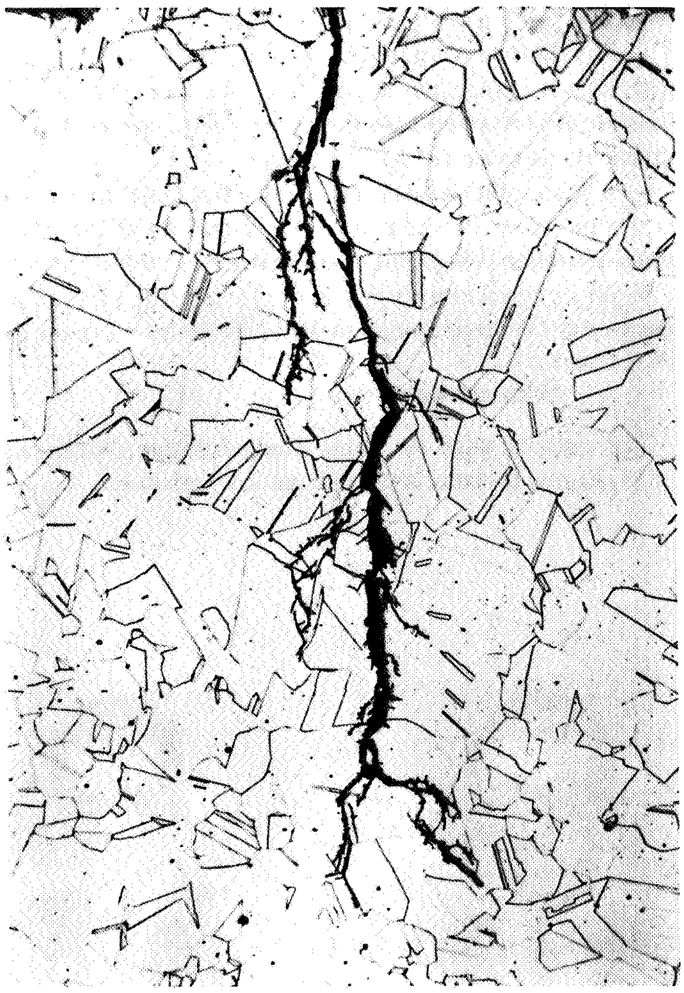

Figure 8. Micrograph of a small crack (Breda Institute).

After a critical review of all the substances which could have come into contact with the external walls of the tubes, attention was focused on the freon used in the leakage test during construction of the equipment and repeated during plant maintenance. In fact, halogen-substituted hydrocarbons, heated in the presence of water, can decompose and release hydrogen chloride.

The conditions in which the leakage tests of the exchanger were carried out, especially those made on the plant, were then examined. It appeared that the freon-22 gas was introduced, shell-side, in the wet exchanger. Immediately after the test the plant was started up again, and the equipment worked at about 200°C.

Since the particular geometry of the exchanger, seen in Figure 1, favors concentration phenomena in the upper part of the shell and in particular in the hollow space between the tubes and the upper tube-sheet, conditions conducive to stress-corrosion of austenitic stainless steels may have been produced.

It is well-known that if the ambient/material combination is highly critical, as in this case, even slight stresses may be sufficient to cause stress-corrosion cracking. A confirmation of the above hypothesis is provided by the fact that the microprobe examinations revealed the presence of fluorine too on the tubes.

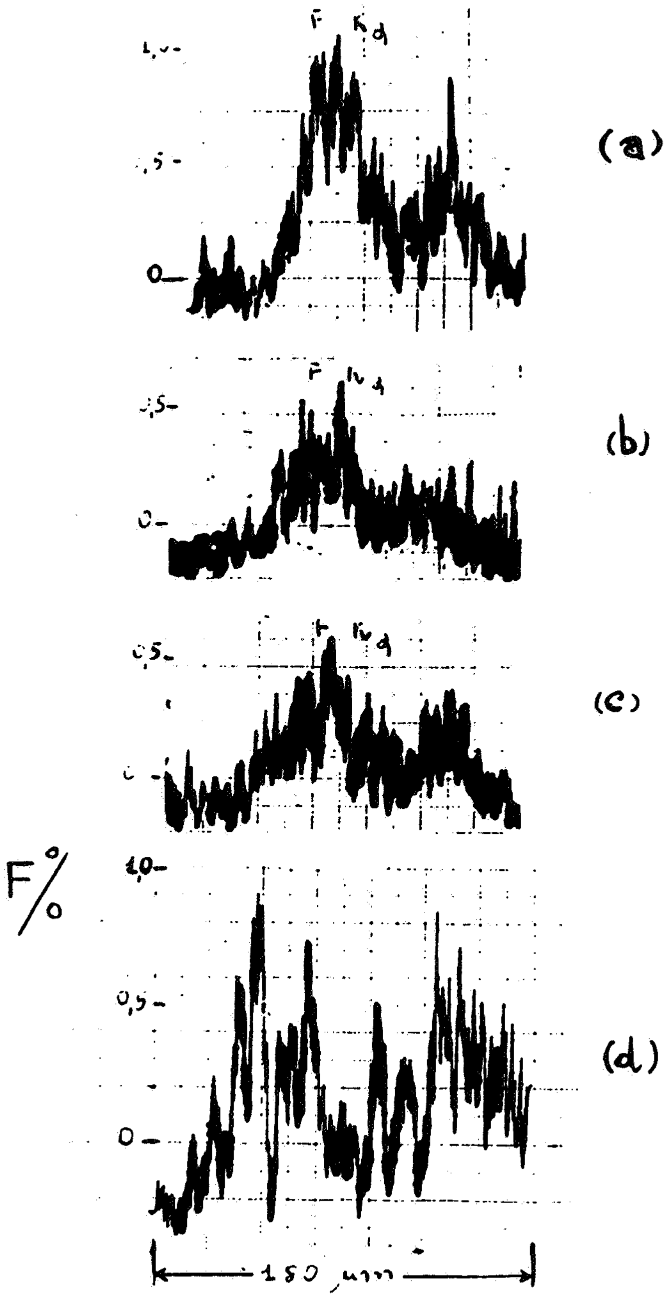

Figure 9. Fluorine spectrum (C.S.M.).

Conclusion

The austenitic stainless steel tubes of a carbamate condenser broke as a result of stress-corrosion cracking. The presence of chloride ions, coming probably from the hydrolysis of the freon-22 used in a leakage test, the vertical arrangement of the apparatus, and its particular geometry, permitted the occurrence of critical conditions which gave rise to the phenomenon.

It can therefore be held that, under particular conditions, tests carried out with freon on stainless steel equipment can cause serious damage, and we consider that in such cases it is advisable to replace this test by others which involve no risks of this kind.

The following are leakage test methods for austenitic stainless steel lined vessels and heat exchangers:

1. The freon test should be avoided.
2. A helium test is not practical on the plant if it is done with vacuum procedure using a mass spectrometer, but it is possible if performed with the same criteria and kind of instruments as those used for the freon test.
3. A soap solution test is practical, particularly to test heat exchanger tubes on the plant. The sensitivity of the test is much less than that of the above-mentioned tests.
4. An ammonia test is possible, provided the precautions required for its toxicity and to avoid explosive mixtures are observed.

Acknowledgements

The authors wish to thank Breda Institute, Milan and CSM, Rome, for laboratory tests and cooperations. #

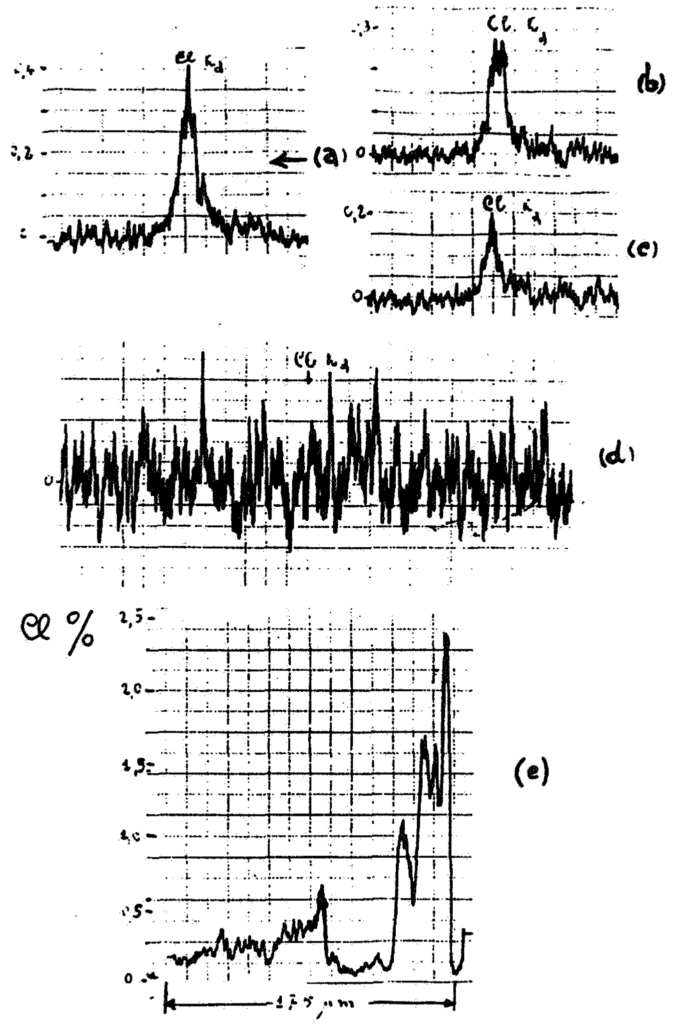

Figure 10. Chlorine spectrum (C.S.M.).

CABRINI, G.

CUSMAI, G.

DISCUSSION

LARRY ZEIS, Pullman Kellogg: Could you tell us the temperatures in and out of both the steam and process sides?

CABRINI: If the process manager in the room wishes to make some comments.

ZARDI, Snamprogetti: That carbamate condenser is producing 4.5 atmosphere steam. The temperature is that corresponding to this saturated steam. The temperature is that corresponding to this saturated steam; on the process sides the temperature of the vapors coming from the stripper ranges from 180 to 200 degrees C. and the outer temperature of the carbamate solution is around 170 degrees C.