Failure Analysis

Rapid Failure of a Copper/Nickel Overhead Condenser Bundle

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Rapid and unexpected failure of a CuNi bundle of a stabilizer overhead condenser occurred where an Al-brass bundle showed chemical resistance for more than 20 years. An investigation revealed that the intergranular attack/cracking of the cupronickel tubes was caused by attack of a wet hydrogen sulfide (H₂S)- containing medium. Literature indicated that cupronickel is much more susceptible to attack by wet H₂S than Al-brass. Cupronickel is unsuitable as tube material in overhead systems containing significant amounts of H₂S and ammonia (NH₃).

This article concerns a stabilizer overhead condenser of a steam cracker unit. The tube material is a CuNi alloy (ASTM B111, grade C706), with cooling water on the tube side (max. temperature 35°C), and stabilizer overhead (max. inlet temperature 120°C) on the shell side.

The stabilizer overhead contains mainly light components, with significant amounts of hydrogen sulfide (H₂S) (1 to 2 wt%) and ammonia (NH₃) (1 to 2 wt%). The pH of the condensed water in the overhead drum is 9 to 9.5.

The tubes of this condenser failed after only a few months of operation, following the scheduled turnaround in April 2004, during which the condenser had been retubed. The retubing had been carried out to replace a mechanically damaged Al-brass (ASTM B111, grade C687) bundle, which had been in service for more than 20 years without any corrosion problems. The CuNi alloy was chosen because of availability and was expected to behave similarly to the Al-brass under the prevailing conditions. Available information from literature indicated that CuNi is more resistant than Al brass in NH₃-containing environments (as is the case here) and is virtually immune to season (NH₃-induced) cracking. The overhead condenser was found to be leaking in August 2004, after only three months of operation.

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Visual Examination

Three failed tube samples showed numerous longitudinal cracks, although some axial cracks were also observed (Figure 1). The longitudinal cracks were relatively straight-lined, whereas the transverse cracks showed a more irregular path. All cracks were very branched and covered the total circumference of the tube samples; some of them were through-wall cracks. Significant wall loss was not observed, and the cracked zones did not show signs of plastic deformation. The tube samples are totally covered with a black adherent scale.

Identification and Testing of Tube Material

Metal identification was done with a portable analyzer. The analysis of the cracked tube samples confirmed the cupronickel alloy to be CuNi10Fe1Mn (EN12451), or grade C706, according to ASTM B111—88.8% Cu, 9.7% Ni, 1.0% Fe, and 0.6% Mn.

The tensile properties of the tube material (blanc sample) do correspond with
those of a cupronickel alloy C706 for the hard-drawn condition (H105), according to EN12451—a tensile strength of 466 MPa and a yield strength (0.2%) of 433 MPa. These data were not in line with the materials certificate for the tube material; the certificate specified the H075 condition. The deviation from the materials certificate as shown by the tensile properties was confirmed by hardness measurements. The hardness of the failed tube sample and the blank sample were measured to be 140 to 145 hardness, Vickers (HV) 5, values corresponding to the hard drawn condition H105 and much higher than the specification for the annealed H075 condition (75 to 105 HV 5).

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**EXAMINATION AND MICROANALYSES OF FAILED SAMPLES**

Metallographic examination showed the presence of numerous inter-granular and very branched cracks that initiated at the outside tube surface (Figure 2). The cracking was associated with a superficial inter-granular attack of the outside tube surface to a depth of ~0.1 mm. The inter-granular attack and cracks were completely filled with a grey-colored product (Figure 3). The microstructure is in accordance with the specified structure for this CuNi alloy.

The corrosion products present at the surface and in the cracks were analyzed and found to be predominantly composed of CuNi sulfide (Figure 4). The semi-quantitative energy-dispersive x-ray analysis (EDXA) indicated the presence of Cu (50 to 80%), Ni (8 to 25%), Fe (1 to 3%), Mn (0.3 to 3%), and S (8 to 20%). The microanalyses also showed a similar and homogeneous alloy composition inside the grains and at the grain boundaries.

No particular element or inter-metallic phase was detected at the grain boundaries that could have been responsible for the inter-granular cracking and attack. A specific EDXA for Hg was negative.

**Discussion**

At first, the rapid failure of the cupronickel bundle of the stabilizer overhead condenser was a complete mystery, especially because an Al-brass bundle exhibited corrosion resistance in these wet NH$_3$/H$_2$S overhead conditions for more than 20 years. Available information from literature indicated that CuNi is more resistant than Al-brass in NH$_3$-containing environments and is virtually immune to season (NH$_3$-induced) cracking. The only medium the investigators could think of to explain the severe cracking/attack of CuNi alloys was mercury salts, but it was confirmed that the salts did not play a role in this particular failure case—a specific EDXA for Hg revealed no trace of this element.

A microanalysis of the corrosion products on the CuNi tubes and in the cracks (Figure 4) revealed the presence of massive quantities of S. From literature, it became clear that cupronickel is very susceptible to attack in H$_2$S-containing environments, where the Al-brass is almost totally resistant.

This is especially true for overhead systems where there are significant quantities of H$_2$S and NH$_3$ available. The cupronickel (90/10) containing small quantities of Fe and Mn (as is the case for the C706) is even more vulnerable to attack. The authors therefore concluded that the attack of the cupronickel overhead condenser bundle was caused by an exposure to wet H$_2$S in the temperature range of 40 to 110°C. In the cited literature, however, uniform corrosion is mentioned and
not inter-granular corrosion/cracking as found in our case.

The same issue of poor performance of CuNi-10 in an H\textsubscript{2}S- and NH\textsubscript{3}-containing overhead system of refinery fluid catalytic cracking unit was the subject of an April 2005 MP Forum Q and A.\textsuperscript{3} There was some experience and feedback, but the exact causes still remained unexplained.

The inter-granular corrosion/attack of the cupronickel tubes could possibly be explained by the hard-drawn condition of the material. The mechanical properties (tensile strength and hardness) of the cracked tubes did not correspond with those indicated in the material certificate and indicate a hard-drawn condition (H105) rather than an annealed or light-drawn condition (H075).

To avoid attack and cracking of the tubes of the overhead condenser, cupronickel should be avoided as construction material. An alternative material could be carbon steel (CS). CS will resist attack from the product side, but, in our experience, will be attacked quite severely from the cooling-water side.

**Conclusions**

From the different investigations and analyses carried out on several failed tube samples from the cupronickel bundle of the stabilizer overhead condenser, the following conclusions/explanations can be drawn:

- The inter-granular attack/cracking of the cupronickel tubes was caused by attack of a sulfur-containing medium (wet H\textsubscript{2}S), condensed in the overhead of the stabilizer column, on the shell side of the condenser.
- From literature, it was found that cupronickel, being more resistant than Al-brass in NH\textsubscript{3}-containing media, is much more susceptible to attack in wet H\textsubscript{2}S-containing media. The conclusion seems to confirm the excellent performance of an Al-brass bundle for more than 20 years under the prevailing conditions, whereas the cupronickel bundle failed after three months of operation.
- The mechanical properties (tensile strength and hardness) of the cupronickel tube material did not correspond with the annealed condition (H075) stated in the material certificate, but was found to represent the hard-drawn (H105) condition.
- It seems probable that this metallurgical condition played a major role in the degradation of the tubes, by promoting inter-granular attack/cracking.
- Cupronickel, used especially because of its excellent resistance to seawater, is not suitable as tube material in overhead systems containing significant amounts of H\textsubscript{2}S and NH\textsubscript{3}, which is the case for most of the refinery units’ overhead systems.

**References**


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