REVIEW OF BNF STUDIES OF THE EFFECT OF CHLORINE AND POLLUTANTS ON THE CORROSION OF COPPER ALLOY CONDENSER TUBES

Roger Francis and Hector Campbell
During the early 1970’s a fleet of oil tankers experienced failures of aluminium brass condenser tubes following the fitting of chlorination equipment. The attack took the form of impingement attack at scratches that would normally be expected to heal. BNF Metals Technology Centre undertook a programme of research that lasted nearly ten years.
OBJECTIVES

- The initial programme was charged with determining the effects of chlorine and ferrous sulphate on some commonly used copper alloy heat exchanger tube materials.
- The reason for the service failures was to be determined. (During the research other operators experienced similar failures)
- Recommendations for safe operating conditions were to be made.
- The programme was extended as service failures thought to be due to the interaction of chlorine and pollutants were investigated.
ALLOYS

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>NOMINAL COMPOSITION (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Al-Brass</td>
<td>77</td>
</tr>
<tr>
<td>90/10 Cu-Ni</td>
<td>Balance</td>
</tr>
<tr>
<td>70/30 Cu-Ni</td>
<td>Balance</td>
</tr>
<tr>
<td>Alloy 722</td>
<td>Balance</td>
</tr>
<tr>
<td>66/30/2/2 Cu-Ni-Fe-Mn</td>
<td>Balance</td>
</tr>
</tbody>
</table>

All of these were tested as 1” od, 18 SWG tubes, usually in duplicate, from several different suppliers.
The Campbell condenser tube test rig incorporates a range of corrosion conditions.

This is important because it was not immediately apparent that only one form of attack would be caused by these additions to the seawater.

Six rigs were used in parallel at the RN facility at Portland Harbour, UK, with once-through seawater.

Inlet seawater temperatures varied from 5 to 20°C.
Test rigs at Portland Harbour without the heater blocks.
CHLORINE TEST MATRIX

- **FERROUS SULPHATE** This was added as solution to give a concentration of 1 mg/L Fe$^{2+}$ for one hour per day in the seawater.

- **CHLORINE** This was added as hypochlorite that was generated electrolytically in a by-pass loop. Continuous concentrations of 0.3, 1.0, 2.3 and 4 mg/L were used. In addition intermittent dosing at either 1 mg/L for two hours every twelve hours, or 2 mg/L for two hours every twelve hours was investigated.
RESULTS (Al-Brass)

- Iron additions produced a narrow zone of impingement attack that was also deeper than without iron.
- The attack that was seen at scratches in service was reproduced in the test rigs.
- The results showed that the depth of attack increased as the chlorine concentration increased.
RESULTS (90/10 Cu-Ni)

- The attack did not start to increase until the chlorine concentration exceeded 1 mg/L.
- Iron additions largely suppressed the attack, but this effect was slowly lost as the chlorine concentration increased.
RESULTS (70/30 Cu-Ni)

- With 70/30 copper-nickel the attack became broader and shallower as the chlorine concentration increased.
- Iron additions suppressed the attack at low chlorine concentrations, but the effect was lost with greater than 1 mg/L chlorine.

Depth of Impingement Attack versus Chlorine Concentration for 70/30 Cu-Ni at 9 m/s
RESULTS (66/30/2/2 Cu-Ni-Fe-Mn)

- This alloy was highly resistant to impingement attack, with only a small increase in depth as the chlorine concentration increased.
- Iron additions almost totally suppressed all impingement attack at all chlorine levels.
RECOMMENDATIONS

cação

ALUMINIUM BRASS Intermittent dosing at 1 mg/L is preferred. Continuous dosing up to 0.5 mg/L is OK provided that ferrous sulphate dosing is carried out, and the chlorine is turned off at this time.

90/10 COPPER-NICKEL Continuous chlorine dosing up to 0.5 mg/L is OK even under turbulent water conditions. Iron dosing can increase the corrosion resistance under aggressive conditions.

70/30 COPPER-NICKEL Intermittent chlorination up to 2 mg/L every 12 hours is preferred, but continuous dosing up to 0.5 mg/L is OK once a protective film has formed.

66/30/2/2 Cu-Ni-Fe-Mn Continuous chlorine dosing up to 2 mg/L is acceptable. There is no need to dose this alloy with iron in the seawater.
AMMONIA TEST MATRIX

- **AMMONIA:** This was added continuously as ammonium sulphate solution to give a concentration of either 0, 1 or 2 mg/L ammonium ions.

- **FERROUS IONS:** These were added continuously from driven iron anodes to give a concentration of 0.042 mg/L, equivalent to 1 mg/L Fe$^{2+}$ for one hour per day.

- **CHLORINE:** This was added as hypochlorite that was generated electrolytically in a by-pass loop. Continuous concentrations of 0 or 0.5 mg/L were used.
CREVICE CORROSION 1

Attack occurred with 2 mg/L ammonia in the warm crevice only.

No attack occurred with 1 mg/L ammonia and it was suppressed on tubes receiving iron additions.
The corrosion products contained redeposited copper and ammonia could be detected in the pits.
The pits were about the same depth on all the alloys.
The appearance of this attack was similar to service failures where flows were very low and ammonia was detected.

The Ranking Order (Worst to Best) was:
90/10 Cu-Ni<66/30/2/2 Cu-Ni-Fe-Mn< 70/30 Cu-Ni<Al-Brass<alloy 722
RECOMMENDATIONS

- In some cases the problem can be eliminated by increasing the water flow rate.
- In others a change of alloy, to one more resistant, may be required.
- A MSF plant in the Middle East was tubed with 90/10 Cu-Ni and experienced failures due to ammonia pollution shortly after starting up block 1.
- When block 2 was started, ferrous sulphate dosing was instigated (1 mg/L Fe for 1 hr/day) for the first 60 days.
- Although ammonia was detected in the cooling water, no failures occurred, and the plant is still running without problems after over 12 years.
- The first block was retubed and started in the same way.
- Another plant, tubed in aluminium brass, with known ammonia pollution, was fitted with ferrous sulphate dosing equipment to prevent attack.
SULPHIDE TEST MATRIX

- **SULPHIDE**: This was added as sodium sulphide solution to give a concentration of either 0, 0.01, 0.03 or 0.1 mg/L sulphide.

- **FERROUS IONS**: These were added continuously from driven iron anodes to give a concentration of 0.042 mg/L, equivalent to 1 mg/L Fe$^{2+}$ for one hour per day.

- **CHLORINE**: This was added as hypochlorite that was generated electrolytically in a by-pass loop. Continuous concentrations of 0, 0.25 or 0.5 mg/L were used.
RESULTS (Al-Brass)

- The main effect of sulphide was to change the severity of impingement attack.
- Sulphide greatly increased the depth of impingement attack at low concentrations.
- A low level of chlorine reduced this attack, but 0.5 mg/L chlorine caused a substantial increase in attack.
RESULTS (90/10 Cu-Ni)

- 90/10 Cu-Ni was very resistant to sulphide attack compared with the other copper alloys.
- 0.25 mg/L chlorine had no significant affect on the depth of attack.
- 0.5 mg/L chlorine caused a large increase in the depth of attack, leading to perforation.
RESULTS (70/30 Cu-Ni)

- 70/30 Cu-Ni was a little more susceptible to attack by sulphide compared with 90/10 Cu-Ni.
- Both levels of chlorine reduced the depth of impingement attack, but the least attack was with 0.25 mg/L chlorine.
- This is thought to be because 70/30 Cu-Ni is more resistant to sulphide oxidation products than other copper alloys.
Results Alloy (722)

- Alloy 722 showed increasing impingement attack with increasing sulphide concentration.
- A low level of chlorine greatly reduced attack, while 0.5 mg/L greatly increased the depth of attack.
- The performance was slightly worse than 70/30 Cu-Ni.
RESULTS (66/30/2/2 Cu-Ni-Fe-Mn)

- This alloy was very susceptible to attack by sulphide, even at low levels.
- Similar behaviour has been seen in service.
- All additions of chlorine greatly increased attack, with perforation at the highest sulphide and chlorine levels.

Depth of Impingement Attack versus Sulphide Concentration for 66/30/2/2 Cu-Ni-Fe-Mn at 7 m/s
CONCLUSIONS

- The ranking order (Worst to Best) in sulphide was 66/30/2/2 Cu-Ni-Fe-Mn < Al-Brass < alloy 722 < 70/30 Cu-Ni < 90/10 Cu-Ni.
- When oxidizers were present, such as chlorine, 70/30 Cu-Ni was best.
- Iron additions had no significant effect on corrosion in the presence of sulphide, positive or negative.
- The effect of sulphide is clearly related to velocity, so the lower the water velocity, the less severe is the attack.
- The attack is not really impingement attack as the pits contain corrosion products. It appears to be a form of pitting that increases its rate of propagation dramatically as the water velocity increases.
APPLICATION

- The ability to reduce corrosion by sulphides with chlorine was exploited at a Belgian power station.
- When sulphide is present, the redox potential decreases significantly.
- A redox probe was inserted in the cooling water feed line and chlorine was injected to increase the redox potential when it was low.
- Dosing was stopped when the redox potential increased to normal levels.
- This enabled the aluminium brass tubes to perform satisfactorily, while a sister station had to be re-tubed in 70/30 Cu-Ni.
OVERALL CONCLUSIONS

- The presence of pollutants, such as ammonia and sulphide, and deliberate additions of chlorine can cause accelerated attack and failure of copper condenser tube alloys.
- This research programme defined safe levels of chlorine dosing for each alloy.
- Chlorine at low levels can be used to mitigate against attack by sulphides.
- Ammonia can cause corrosion at crevices or under deposits under heat transfer conditions. This can be prevented by iron additions to the cooling water.
- Iron additions can reduce or prevent attack by chlorine in some instances, and this action can be a low cost solution.
- The copper alloys have been ranked under each type of corrosion condition.
REFERENCES

1) R Francis, Mater. Perf. 21, 8 (1982) 44
2) R Francis, Brit Corr J 20, 4 (1985) 167
3) R Francis, Brit Corr J 20, 4 (1985) 175
4) R Francis, Brit Corr J 22 (1987) 199
5) R Francis, Corr Sci. 26, 3 (1986) 205