MATERIALS

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

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# INTRODUCTION

- 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.

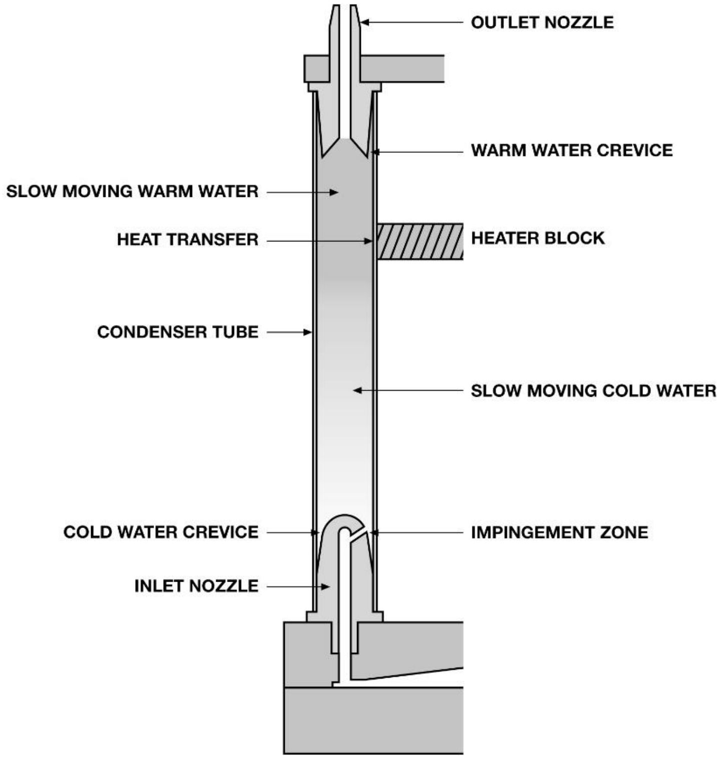
# ALLOYS

| ALLOY | NOMINAL COMPOSITION (wt.%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cu | Zn | Ni | Fe | Mn | Al | Other |
| Al-Brass | 77 | Balance | - | - | - | 2 | 0.04 As |
| 90/10 Cu-Ni | Balance | - | 10 | 1.5 | 0.7 | - | - |
| 70/30 Cu-Ni | Balance | - | 30 | 0.7 | 0.7 | - | - |
| Alloy 722 | Balance | - | 15 | 0.5 | 0.5 | - | 0.4 Cr |
| 66/30/2/2 Cu-Ni-Fe-Mn | Balance | - | 30 | 2 | 2 | - | - |

All of these were tested as 1" od, 18 SWG tubes, usually in duplicate, from several different suppliers.

# CONDENSER TUBE TEST RIG

- 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.



# CONDENSER TUBE TEST RIG

Test rigs at Portland Harbour without the heater blocks.

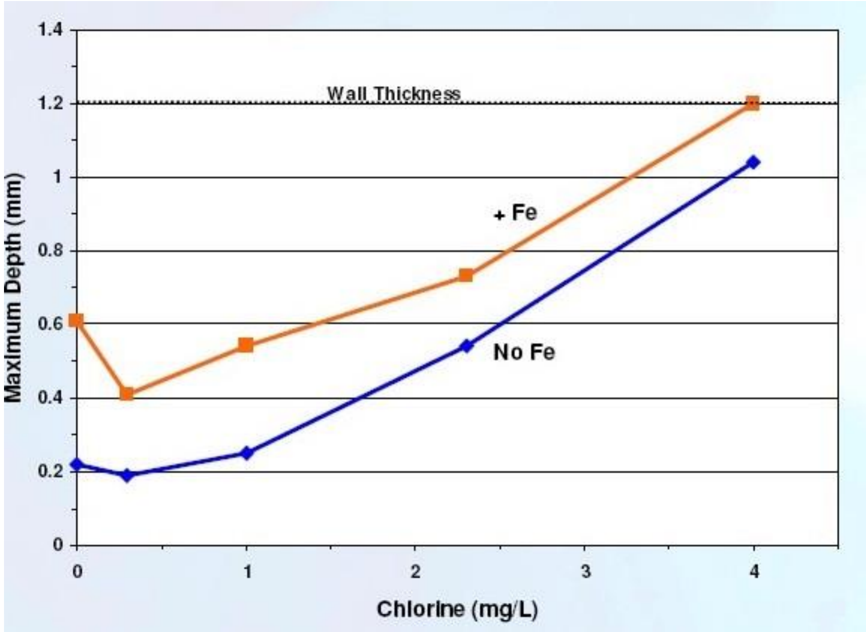
# CHLORINE TEST MATRIX

- 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.

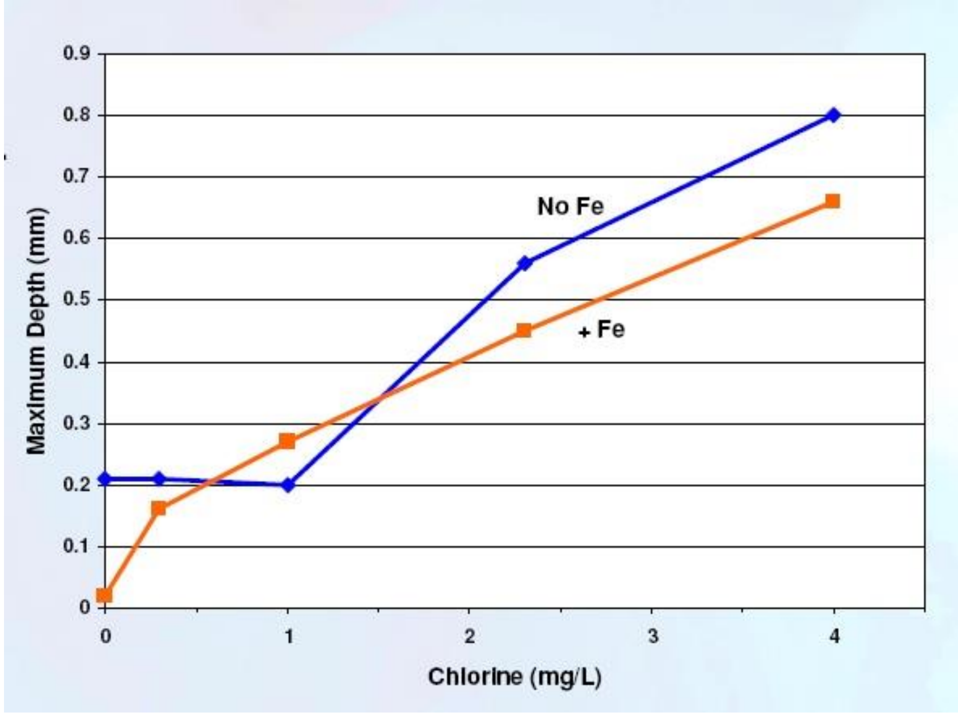
Depth of Impingement Attack versus Chlorine Concentration for Aluminium Brass at 9 m/s



# 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.

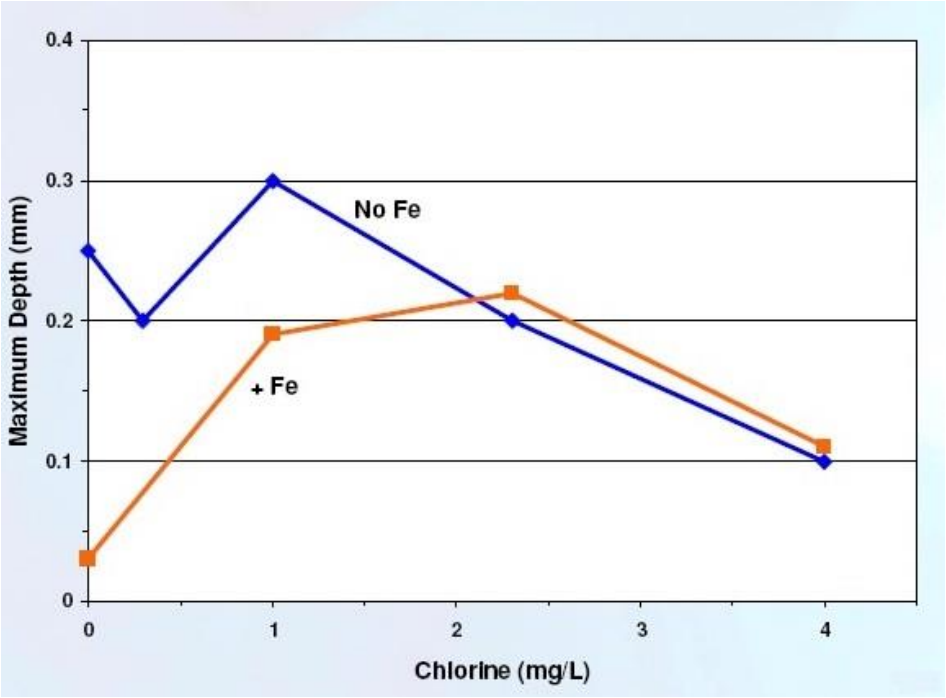
Depth of Impingement Attack versus Chlorine Concentration for 90/10 Cu-Ni at 9 m/s



# 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.

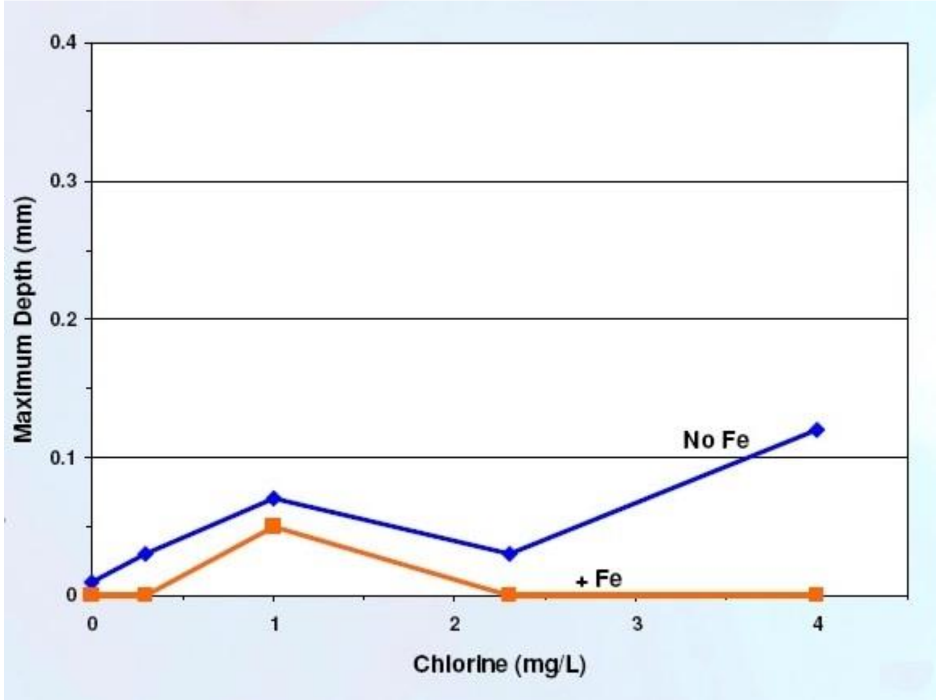
Depth of Impingement Attack versus Chlorine Concentration for 70/30 Cu-Ni at 9 m/s



# 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.

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



# RECOMMENDATIONS

- **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.**

**90/10 Cu-Ni**

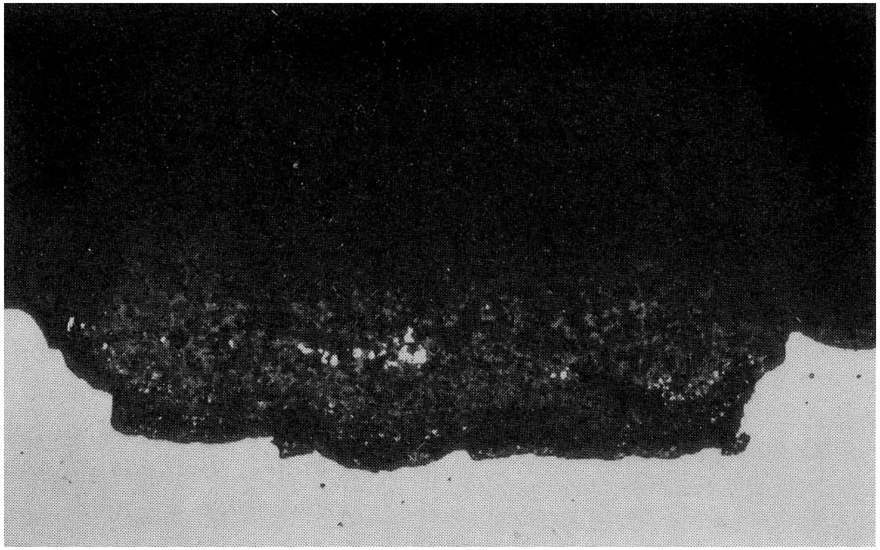
**As-received**

**Acid cleaned**

**No attack occurred with 1 mg/L ammonia and it was suppressed on tubes receiving iron additions.**

# CREVICE CORROSION 2

- 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.

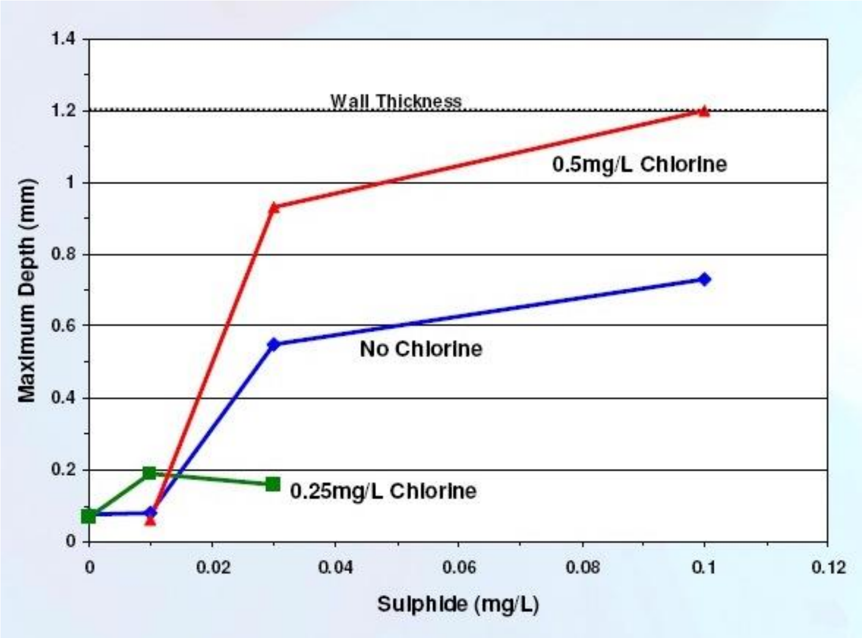
# SULPHIDE TEST MATRIX

- 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.

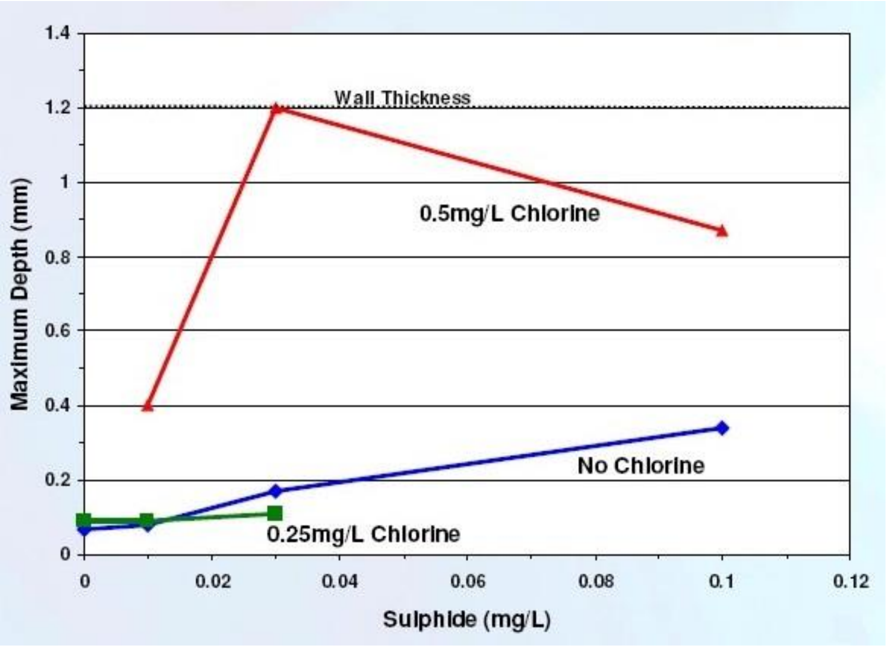
Depth of Impingement Attack versus Sulphide Concentration for Aluminium Brass at 7 m/s



# 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.

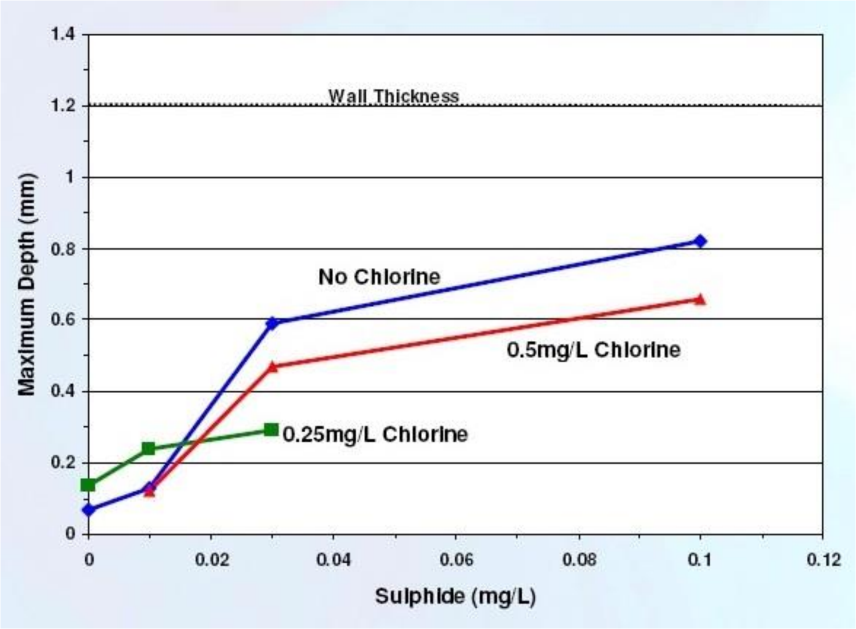
Depth of Impingement Attack versus Sulphide Concentration for 90/10 Cu-Ni at 7 m/s



# 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.

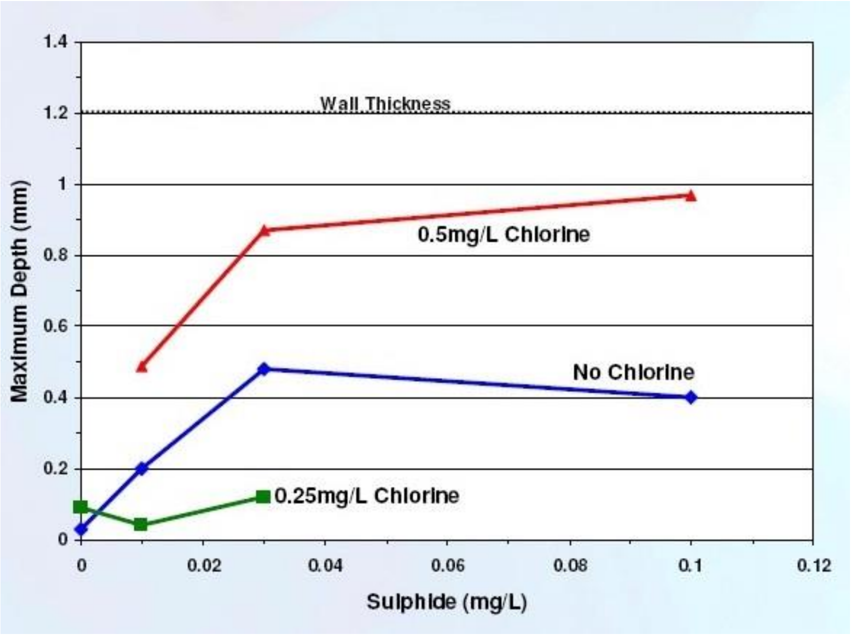
Depth of Impingement Attack versus Sulphide Concentration for 70/30 Cu-Ni at 7 m/s



# 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.

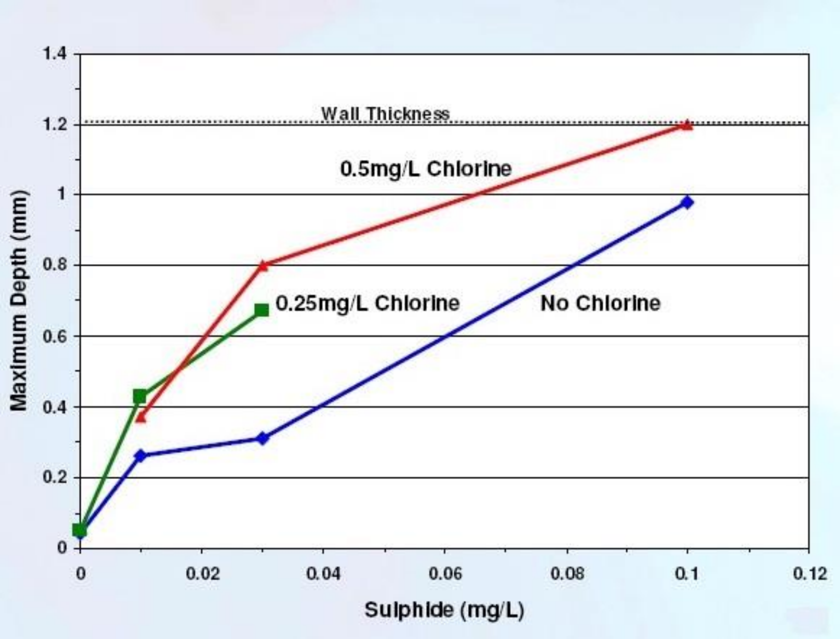
Depth of Impingement Attack versus Sulphide Concentration for alloy 722 at 7 m/s



# 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
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4) R Francis, Brit Corr J **22** (1987) 199
5) R Francis, Corr Sci. **26**, 3 (1986) 205