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

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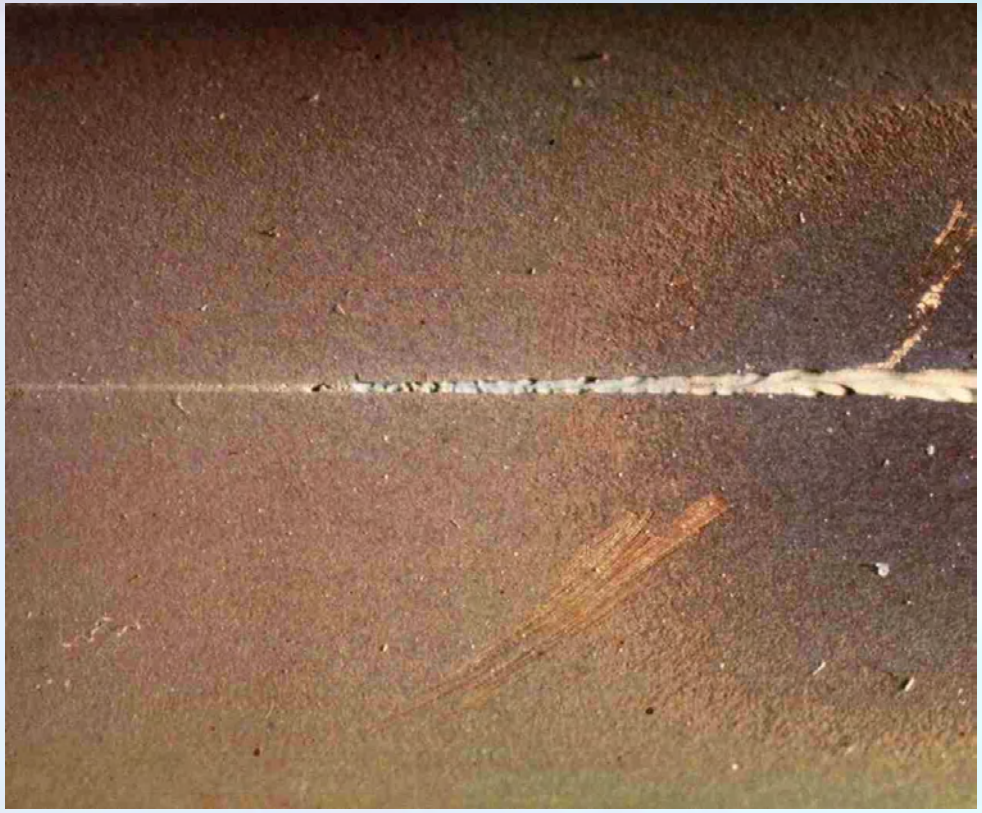
INTRODUCTION

- DURING THE EARLY 1970'S A FLEET OF 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 10 YEARS.



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OBJECTIVES

- **THE INITIAL PROGRAMME WAS CHARGED WITH DETERMINING THE EFFECT 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.**

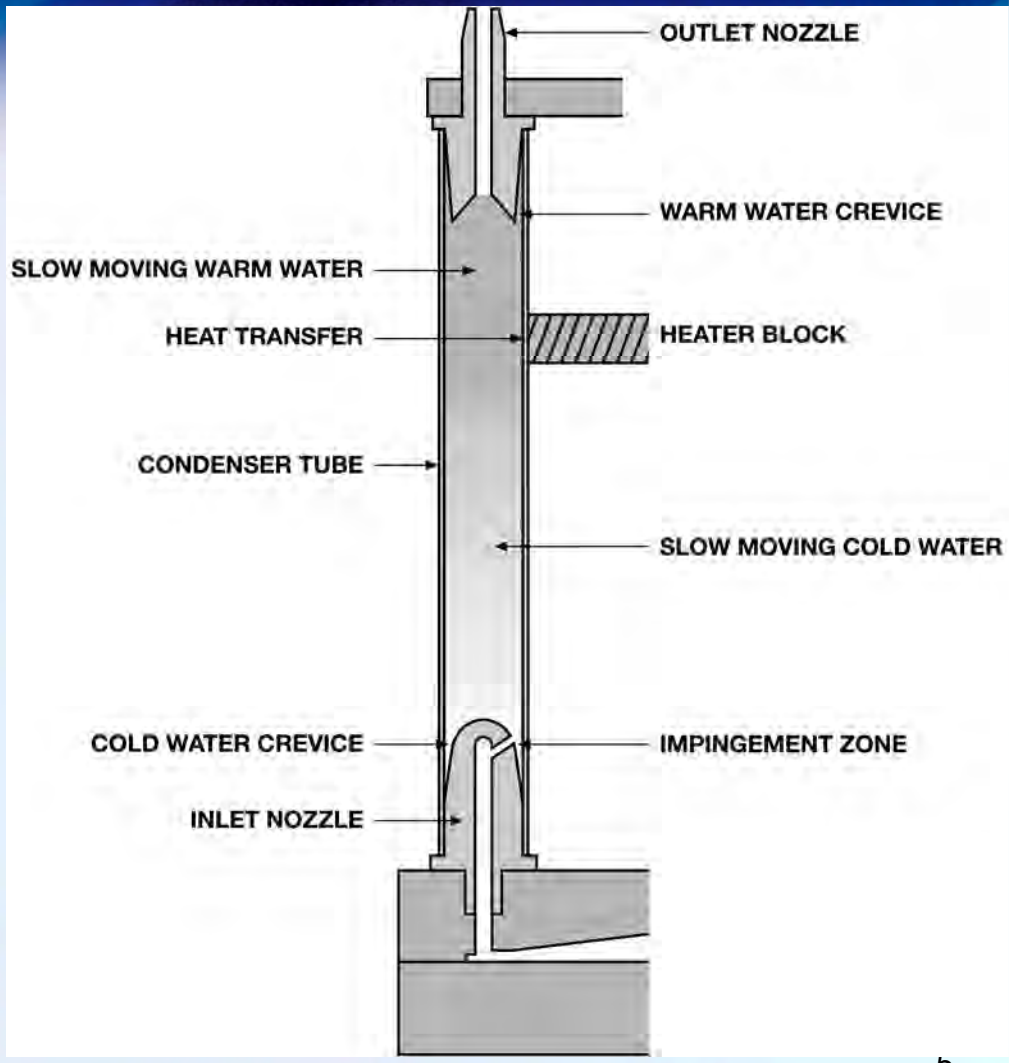
ALLOYS

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

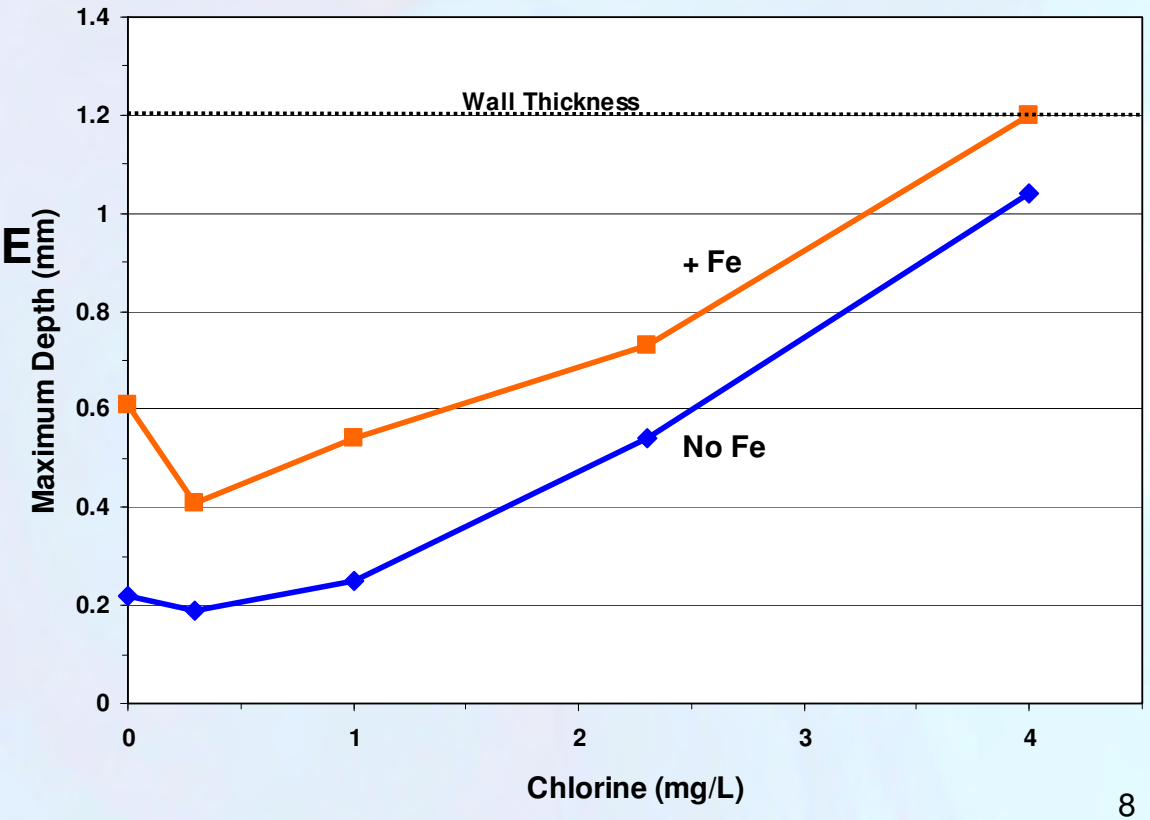
CHLORINE TEST MATRIX

- **FERROUS SULPHATE** This was added as solution to give a concentration of 1mg/L Fe^{++} for one hour per day in the seawater.
- **CHLORINE** This was added as hypochlorite that was generated electrolytically in a bypass loop. Continuous concentrations of 0.3, 1.0, 2.3 and 4 mg/L were used. In addition, intermittent dosing at either 1mg/L for two hours every twelve hours or 2mg/L for two hours every twelve hours was investigated.

RESULTS (Al-Brass)

- IRON ADDITIONS PRODUCED A NARROW ZONE OF ATTACK, THAT WAS ALSO DEEPER.
- THE ATTACK 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.

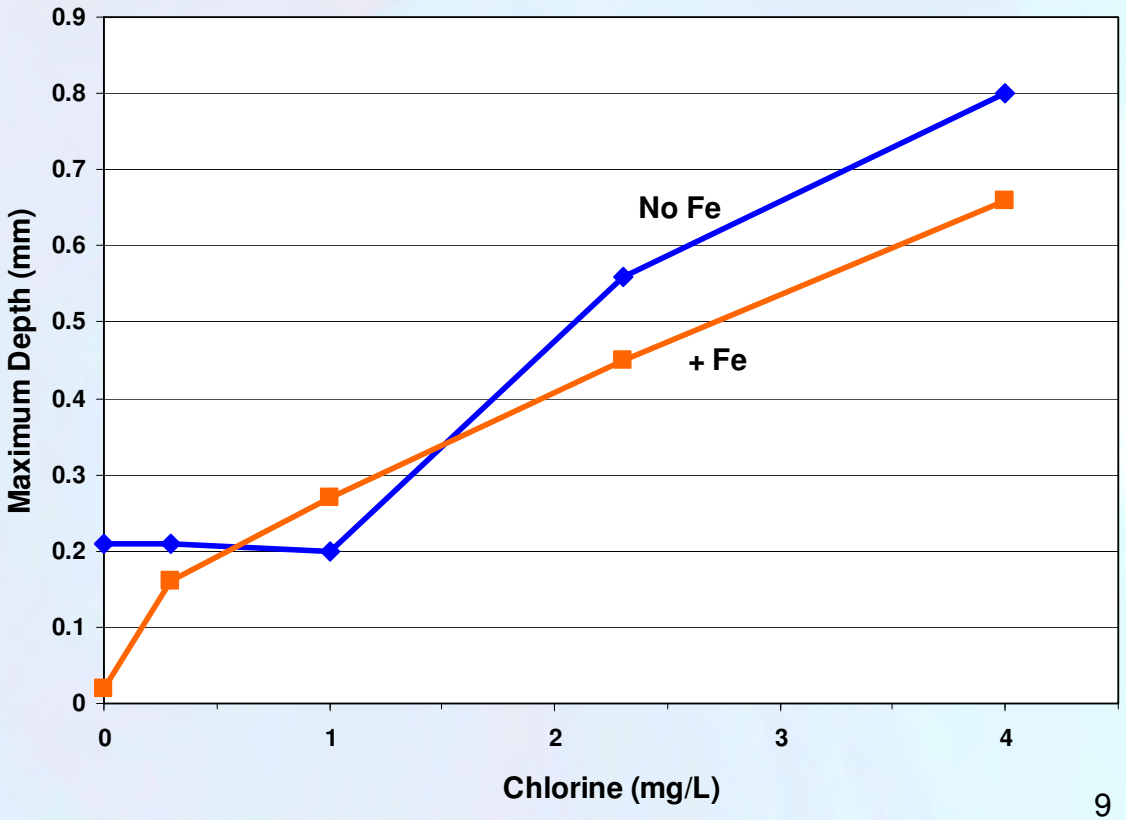
Depth of Impingement Attack versus Chlorine Concentration for Aluminium Brass at 9m/s



RESULTS (90/10 Cu-Ni)

- THE ATTACK DID NOT START TO INCREASE UNTIL THE CHLORINE LEVEL EXCEEDED 1mg/L.
- IRON ADDITIONS LARGELY SUPPRESSED ATTACK, BUT THIS EFFECT WAS SLOWLY LOST AS THE CHLORINE CONCENTRATION INCREASED.

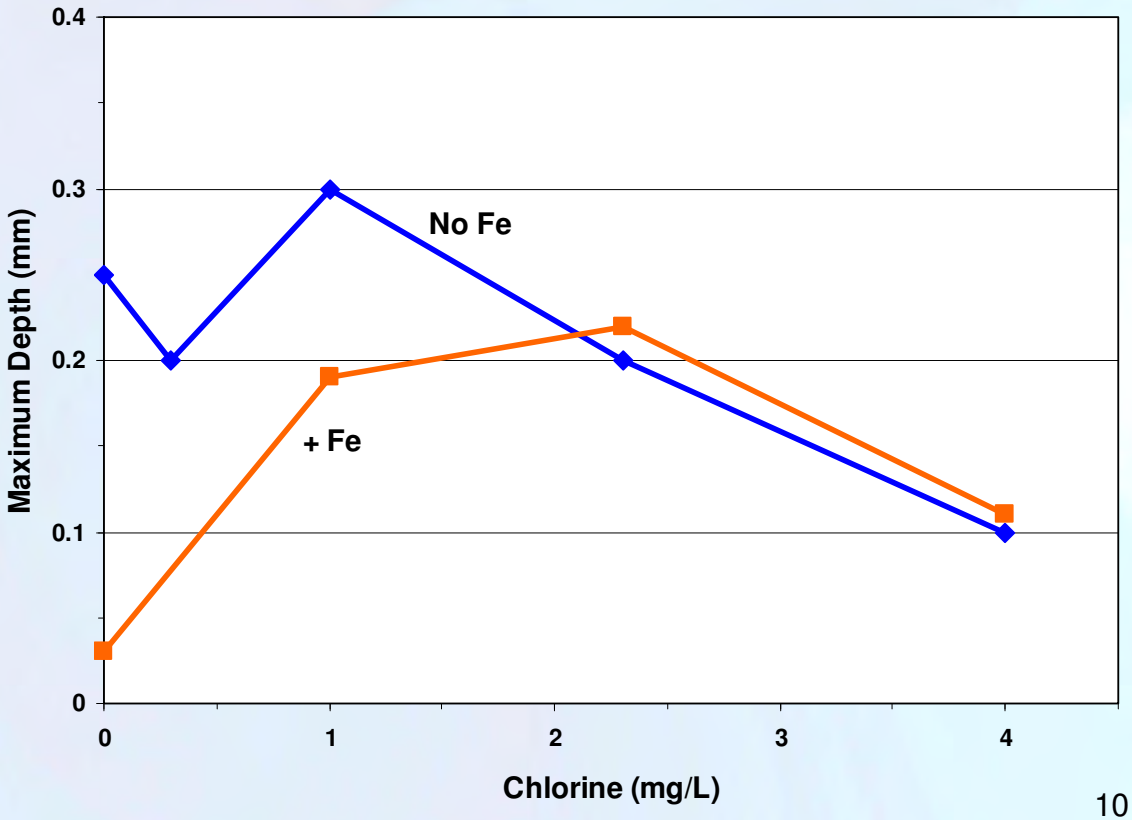
Depth of Impingement Attack versus Chlorine Concentration for 90/10 Cu-Ni at 9m/s



RESULTS (70/30 Cu-Ni)

- **WITH 70/30 COPPER-NICKEL THE ATTACK BECAME BROADER AND SHALLOWER AS THE CHLORINE CONCENTRATION INCREASED.**
- **IRON ADDITIONS SUPPRESSED THIS ATTACK AT LOW CHLORINE CONCENTRATIONS, BUT THIS EFFECT WAS LOST WITH >1mg/L CHLORINE.**

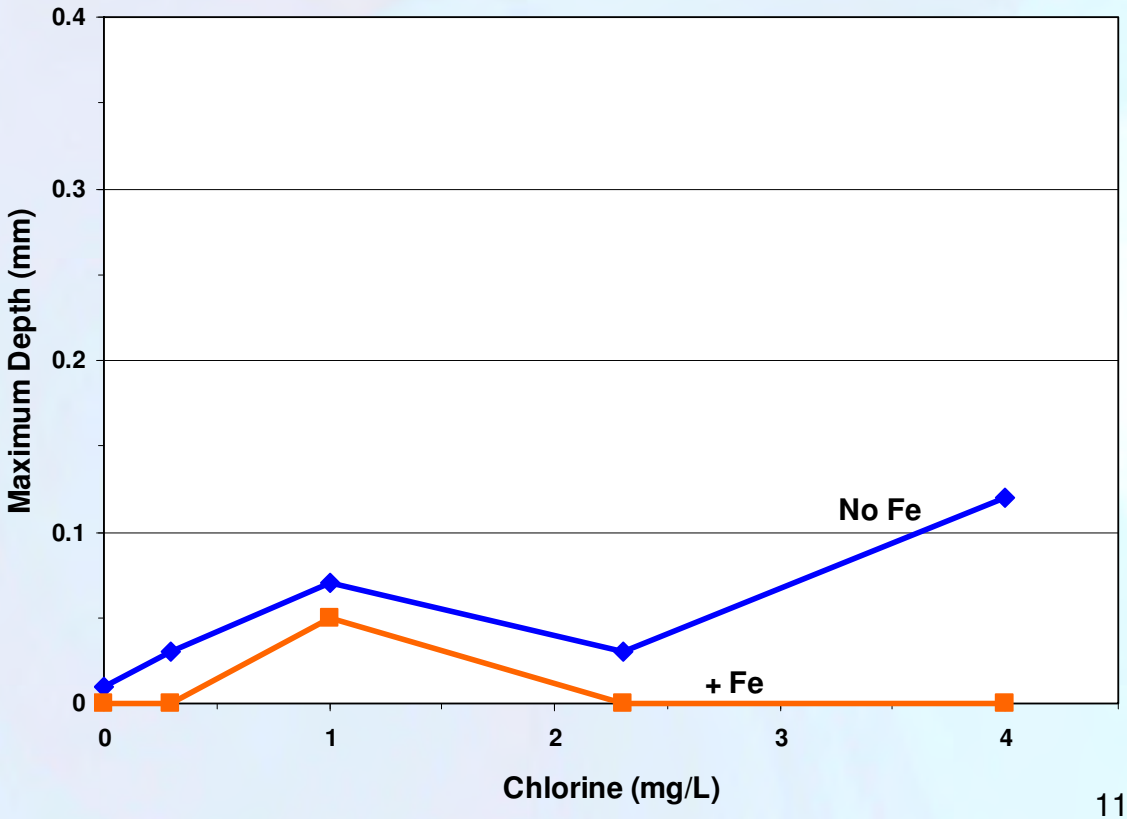
Depth of Impingement Attack versus Chlorine Concentration for 70/30 Cu-Ni at 9m/s



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 COMPLETELY 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 9m/s



RECOMMENDATIONS

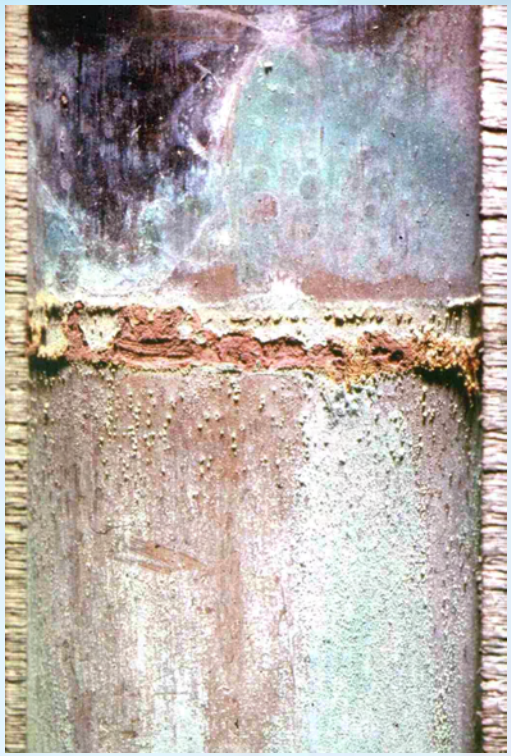
- **ALUMINIUM BRASS** Intermittent dosing at 1mg/L is preferred. Continuous dosing up to 0.5mg/L chlorine is OK provided that ferrous sulphate dosing is carried out and the chlorine dosing is turned off at this time.
- **90/10 COPPER-NICKEL** Continuous chlorine dosing up to 0.5mg/L is OK even under turbulent water conditions. Iron dosing can increase the corrosion resistance under aggressive conditions.
- **70/30 COPPER-NICKEL** Intermittent chlorination up to 2mg/L every 12 hours is preferred, but continuous dosing up to 0.5mg/L is OK once a protective film has formed.
- **66/30/2/2 Cu-Ni-Fe-Mn** Continuous chlorine dosing up to 2mg/L is acceptable. There is no need to dose this alloy with iron.

AMMONIA TEST MATRIX

- **AMMONIA** This was added as ammonium sulphate solution to give a concentration of either 0, 1mg/L or 2mg/L ammonium ions.
- **FERROUS IONS** These were added continuously from driven iron anodes to give a concentration of 0.042mg/L, equivalent to 1mg/L Fe^{++} for one hour per day.
- **CHLORINE** This was added as hypochlorite that was generated electrolytically in a bypass loop. Continuous concentrations of 0 or 0.5mg/L were used.

CREVICE CORROSION 1

ATTACK OCCURRED WITH 2mg/L AMMONIA IN THE WARM CREVICE.



90/10 Cu-Ni

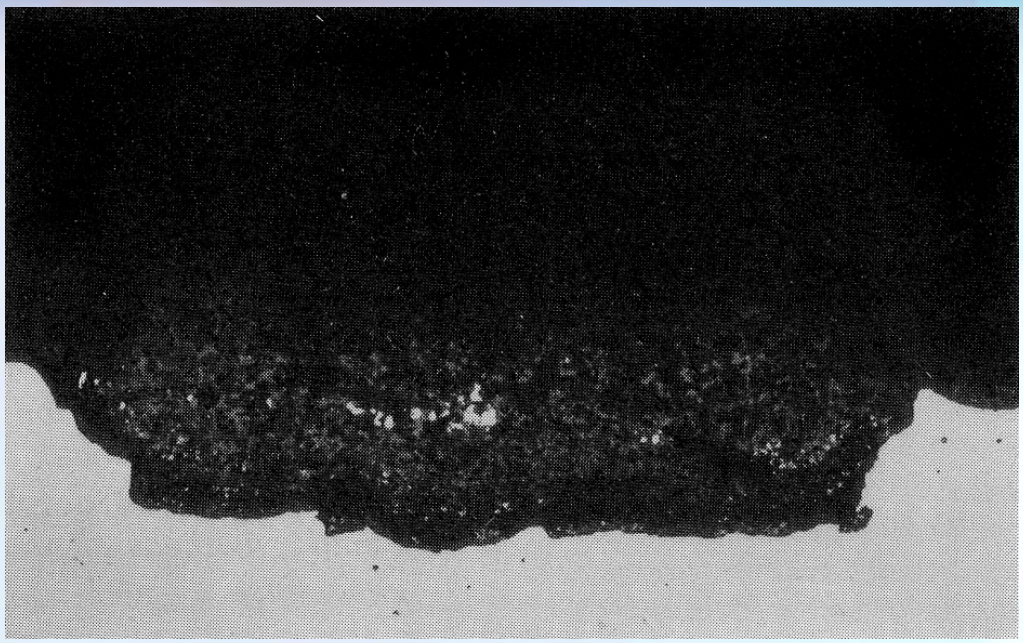
As-received

Acid cleaned

NO ATTACK OCCURRED WITH 1mg/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 ALLOYS.
- THE APPEARANCE OF THIS CORROSION 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<Alloy722

RECOMMENDATIONS

- **IN SOME CASES THE PROBLEM CAN BE ELIMINATED BY INCREASING THE 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 (1mg/L Fe FOR 1hr/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 0.1mg/L sulphide.
- **FERROUS IONS** These were added continuously from driven iron anodes to give a concentration of 0.042mg/L, equivalent to 1mg/L Fe^{++} for one hour per day.
- **CHLORINE** This was added as hypochlorite that was generated electrolytically in a bypass loop. Continuous concentrations of 0, 0.25 or 0.5mg/L were used.

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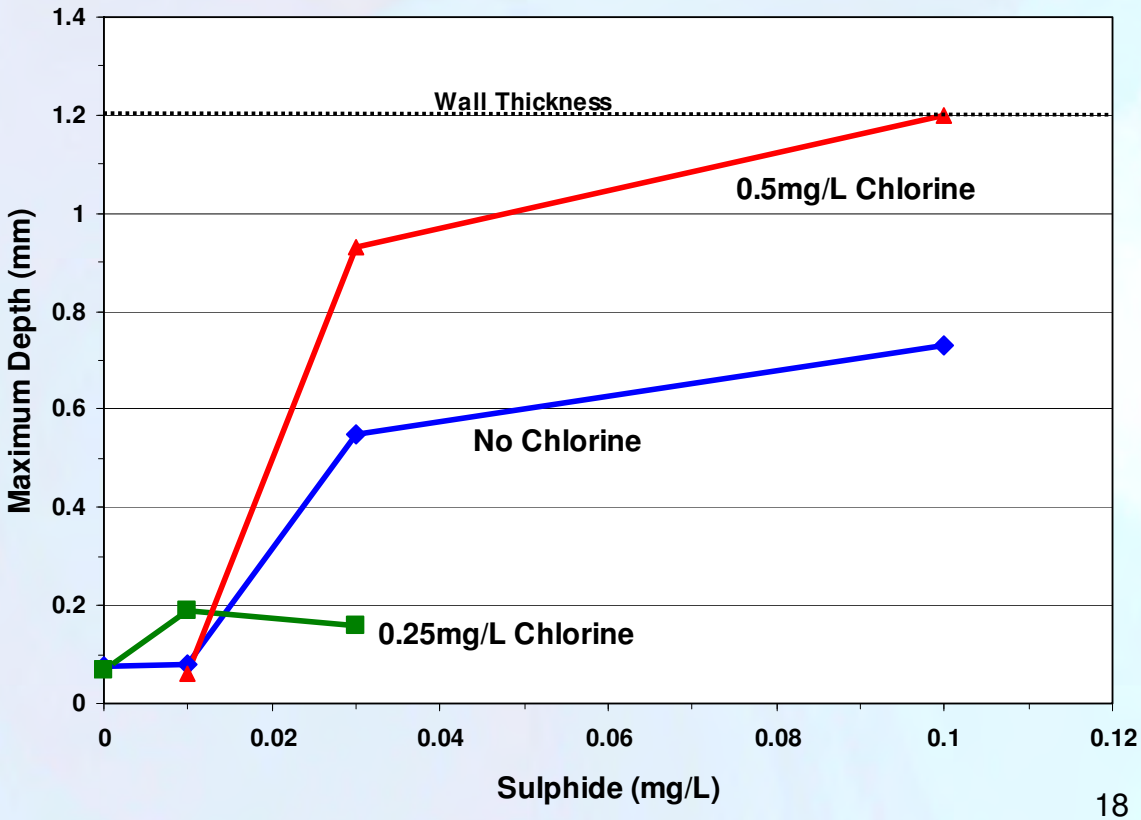
RESULTS (Al-Brass)

- THE MAIN EFFECT OF SULPHIDE WAS TO CHANGE THE SEVERITY OF IMPINGEMENT ATTACK.
- SULPHIDE GREATLY INCREASED THE DEPTH OF IMPINGEMENT ATTACK.
- A LOW LEVEL OF CHLORINE REDUCED THIS ATTACK, BUT 0.5mg/L CAUSED A SUBSTANTIAL INCREASE IN ATTACK.

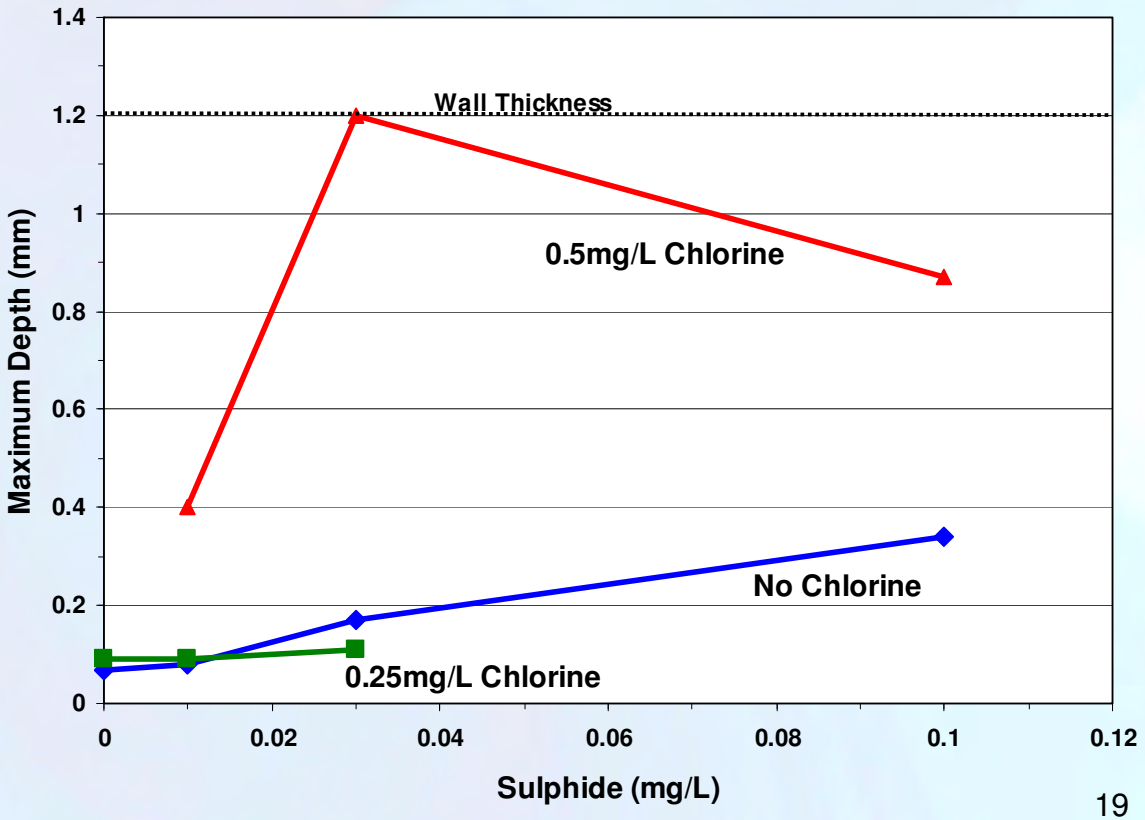
Depth of Impingement Attack versus Sulphide Concentration for Aluminium Brass at 7m/s



RESULTS (90/10 Cu-Ni)

- 90/10 Cu-Ni WAS VERY RESISTANT TO SULPHIDE ATTACK COMPARED WITH OTHER COPPER ALLOYS.
- 0.25mg/L CHLORINE HAD NO SIGNIFICANT EFFECT.
- 0.5mg/L CHLORINE CAUSED A LARGE INCREASE IN ATTACK, LEADING TO PERFORATION.

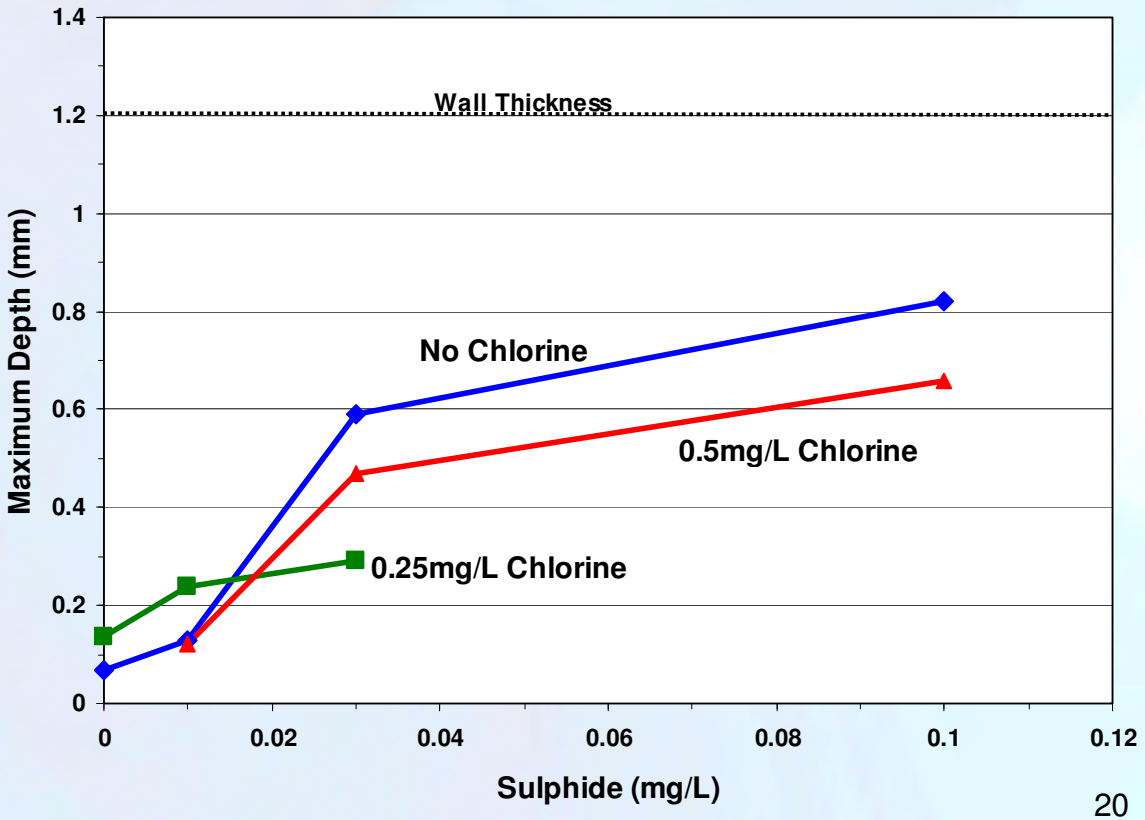
Depth of Impingement Attack versus Sulphide Concentration for 90/10 Cu-Ni at 7m/s



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 IMPINGEMENT ATTACK, BUT THE LEAST ATTACK WAS WITH 0.25mg/L CHLORINE.
- THIS IS THOUGHT TO BE BECAUSE 70/30 Cu-Ni IS MORE RESISTANT TO SULPHUR OXIDATION PRODUCTS THAN OTHER COPPER ALLOYS.

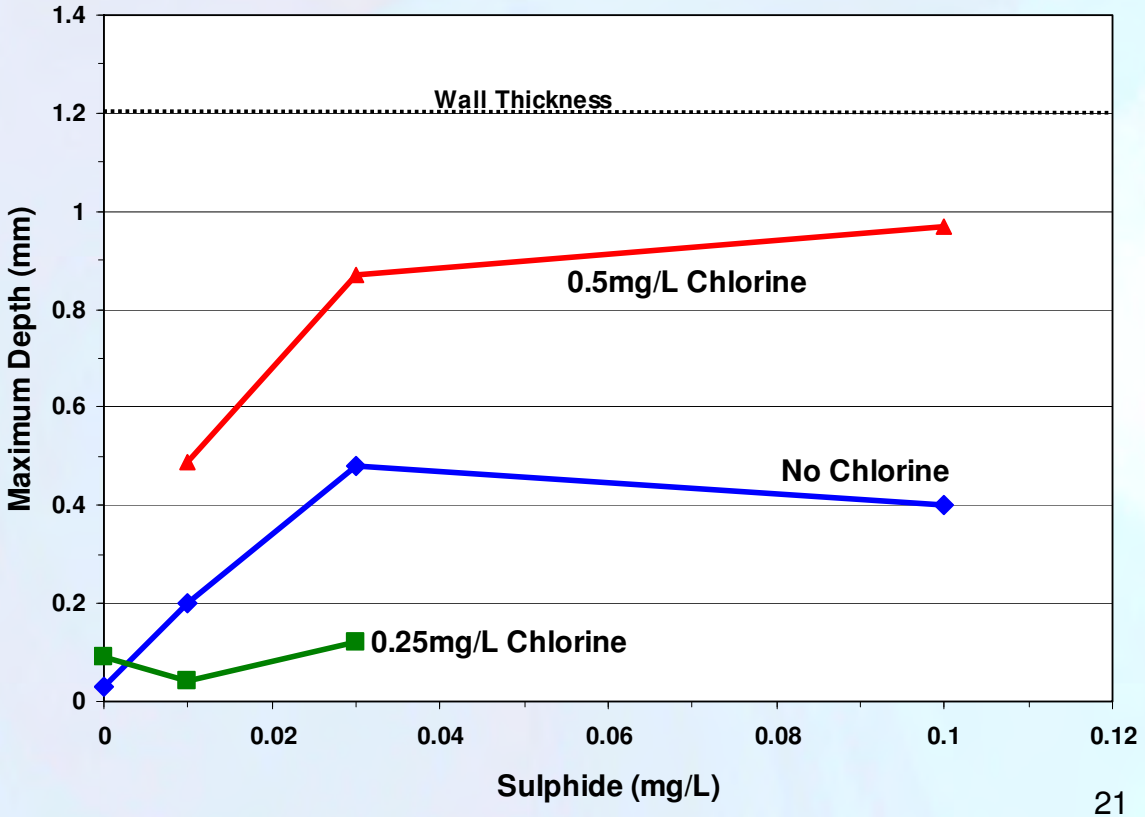
Depth of Impingement Attack versus Sulphide Concentration for 70/30 Cu-Ni at 7m/s



RESULTS (Alloy 722)

- ALLOY 722 SHOWED INCREASING IMPINGEMENT ATTACK WITH INCREASING SULPHIDE CONCENTRATION.
- A LOW LEVEL OF CHLORINE GREATLY REDUCED ATTACK, WHILE 0.5mg/L GREATLY INCREASED IT.
- THE PERFORMANCE WAS SOMEWHERE BETWEEN THAT OF 90/10 Cu-Ni AND 70/30 Cu-Ni.

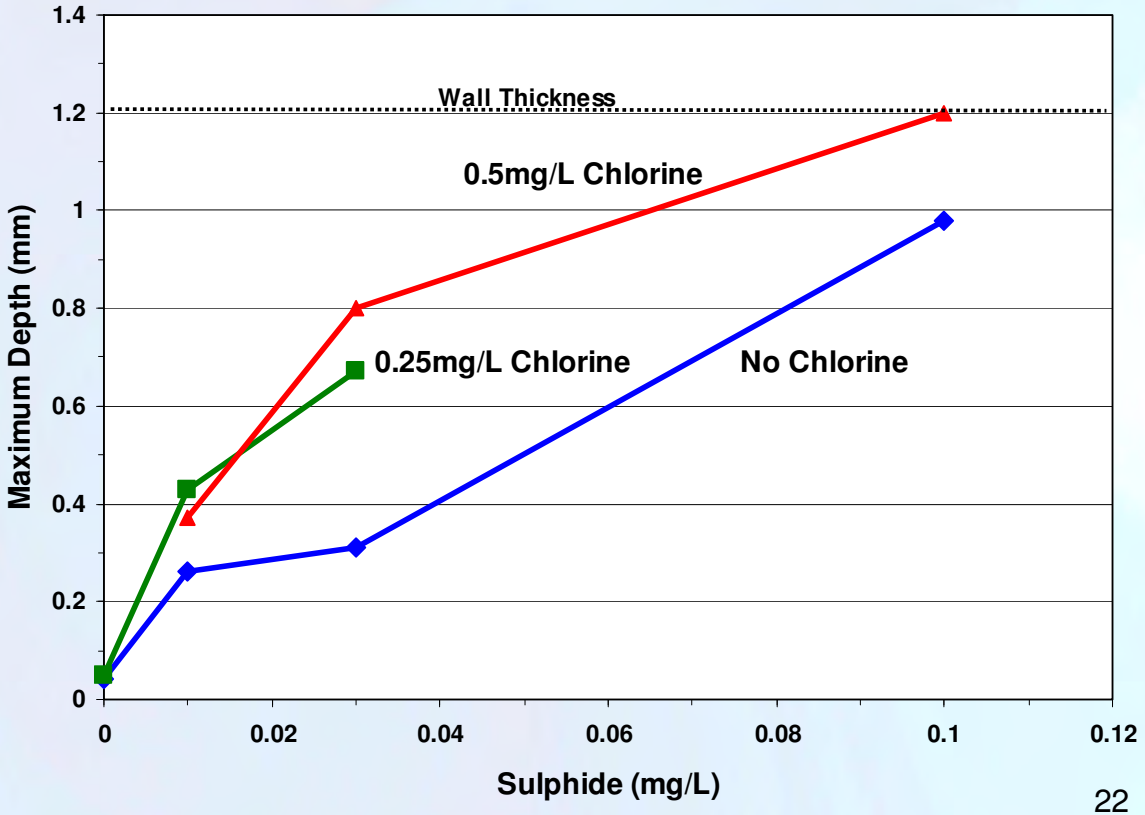
Depth of Impingement Attack versus Sulphide Concentration for Alloy 722 at 7m/s



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 7m/s



CONCLUSIONS

- **THE RANKING ORDER (Worst to Best) WAS 66/30/2/2 Cu-Ni-Fe-Mn<Al-BRASS<ALLOY 722<70/30Cu-Ni<90/10Cu-Ni.**
- **WHEN OXIDIZERS WERE PRESENT, SUCH AS CHLORINE, 70/30 Cu-Ni WAS THE BEST.**
- **IRON ADDITIONS TO THE SEAWATER HAD NO SIGNIFICANT EFFECT ON CORROSION, 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 PRODUCT. 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 DUE TO SULPHIDES WITH CHLORINE WAS EXPLOITED AT A BELGIAN POWER STATION.**
- **WHEN SULPHIDE IS PRESENT, THE REDOX POTENTIAL DECREASES SIGNIFICANTLY.**
- **A REDOX PROBE WAS FITTED IN THE COOLING WATER LINE AND CHLORINE WAS INJECTED TO INCREASE THE REDOX POTENTIAL WHEN IT WAS LOW. DOSING WAS STOPPED WHEN THE POTENTIAL INCREASED TO NORMAL LEVELS TO AVOID OVER- CHLORINATION.**
- **THIS ENABLED THE ALUMINIUM BRASS TUBES TO PERFORM SATISFACTORILY, WHILE A SISTER STATION HAD TO BE RE-TUBED IN 70/30 Cu-Ni.**

CONCLUSIONS

- **THE PRESENCE OF POLLUTANTS SUCH AS AMMONIA AND SULPHIDE AND DELIBERATE ADDITIONS SUCH AS 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 SULPHIDE ATTACK.**
- **IRON ADDITIONS CAN REDUCE OR PREVENT ATTACK IN SOME INSTANCES AND THESE ARE A LOW COST SOLUTION.**

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

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