

THE RESISTANCE OF COPPER-NICKEL ALLOYS TO AMMONIA CORROSION IN SIMULATED STEAM CONDENSER ENVIRONMENTS

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INTRODUCTION

The recent trend toward All Volatile Treatment (AVT), using ammonia and ammonia compounds for feedwater chemistry control in power plant circuits, accentuates the need for careful selection of corrosion-resistant condenser-tube alloys, not only in the main body of condensers but also in peripheral areas and the air removal section. Organic amines (such as cyclohexylamine, hydrazine and morpholine) are commonly employed in steam generating power plant systems to scavenge oxygen, adjust pH and reduce the corrosion rate of steel. These chemicals quite readily and conveniently dissolve in boiler feedwater. In contrast to ammonia, they do not tend to concentrate in subcooled condensate in the air cooler section of a steam condenser. These amines can break down or thermally decompose to some extent into ammonia with the resulting ammonia concentration at a somewhat lower level than occurs with straight ammonia injection.

Condensing steam on the outside of tubes in the main body of a condenser does not introduce corrosion problems, as the ammonia concentration is low and oxygen, which is needed for corrosion to proceed, is not present at sufficiently high levels to cause concern.¹ However, oxygenated ammoniacal-rich environments,¹⁻⁶ which can develop in air removal sections of condensers, especially in systems using AVT, can produce significant corrosion of copper alloys.¹⁻⁶ Some condenser designs seem to favor this undesirable situation.⁶

Copper alloys vary widely in their resistance to aerated ammonia corrosion. The copper-nickel alloys, such as CA-706 and CA-715, (*Table I*) are highly resistant, while the high copper alloys, such as those alloyed solely with arsenic or phosphorus, and the copper-zinc alloys, such as Admiralty and aluminum brass, exhibit low resistance.^{1,4,7} Although ammonia stress corrosion cracking is beyond the scope of the

present investigation, commercial implications cannot be ignored.⁸ In general, both the copper-nickels and the high copper alloys, such as those only alloyed with arsenic or phosphorus, are reported to be highly resistant to ammonia stress corrosion cracking⁷⁻⁹ while the brasses are particularly susceptible.⁸

Several investigators have reported that ammonia concentrations found in condensed droplets collected in condenser air removal sections range from 50 to 500 ppm of NH_3 ,^{1,4,6,10-12} although higher concentrations can develop. Relative resistance of copper alloys to ammonia attack has been evaluated in the laboratory but, because of physical limitations, the effects of specific parameters have not been fully isolated. It is difficult to completely simulate the effect of an air removal section in the laboratory and just as difficult, if not more so, to run corrosion tests in the actual component in the field. In laboratory tests, Tice and Venizelos¹ utilized higher than normal ammonia solutions, up to 1000 ppm NH_3 , and simply dripped these through air onto test samples. Effects of CO_2 were also evaluated by including $\text{NH}_3 + (\text{NH}_4)_2 \text{CO}_3$ solutions. These solutions were fully aerated, with resultant corrosion acceleration. In similar tests, Popplewell and Bates⁴ utilized solutions containing up to 1000 ppm NH_3 formed by bubbling NH_3 gas/air mixtures through distilled water. The copper-nickel alloys were found to be superior to the other copper alloys in resistance to attack by ammoniacal solutions in both studies. The present investigation was undertaken independently to further quantify these trends and provide insight for additional parameters.

EXPERIMENTAL PROCEDURE

Test samples were prepared from commercially-produced 16-mm ($\frac{5}{8}$ in.) O.D. condenser tubes of the alloys listed in *Table I*. Two test methods were employed. The first is a Fog Test in which an ammoniacal mist was condensed onto external surfaces of tubes through which cooling water was passed. The second is a Spray Test in which an ammoniacal solution is sprayed and/or impinged on external tube surfaces, but no cooling water is provided.

In the Ammonia Spray Test, all the alloys were 1.2 mm (.049 in.) in wall thickness except stainless steel and Monel* alloy 400, which were 1.5 mm (.060 in.). Samples of arsenical copper, arsenical Admiralty and aluminum brass in the Ammonia Spray Test were 152 mm

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TABLE I
NOMINAL ALLOY COMPOSITION
Percent by Weight

Alloy	Cu	Ni	Zn	Sn	Al	Fe	Mn	Cr	Mo	As	P	Sb
Phosphorized Copper (CA-122)	100										0.03	
Arsenical Copper (CA-142)	100									0.3		
Arsenical Admiralty Brass (CA-443)	71		28	1						0.6		
Antimonial Admiralty Brass (CA-444)	71		28	1								0.06
Phosphorized Admiralty Brass (CA-445)	71		28	1							0.06	
Aluminum Brass (CA-687)	78		20		2					0.06		
Aluminum Bronze (CA-608)	94				6					0.3		
95/5-Copper/Nickel (CA-704)	93	5				1.5	0.5					
90/10-Copper/Nickel (CA-706)	88	10				1.5	0.5					
80/20-Copper/Nickel (CA-710)	78	20				1	0.5					
70/30-Copper/Nickel (CA-715)	69	30				0.5	0.5					
60/40-Copper/Nickel	57	40				2.0	1.2					
MONEL* alloy 400	32	68										
Type 304 Stainless Steel		9				72		19				
Type 316 Stainless Steel		12				69		17	2			

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(6 in.) long with 102 mm (4 in.) of exposed test length, while the remaining alloys were 127 mm (5 in.) long with 76 mm (3 in.) exposed. All the samples in the Ammonia Fog Test were 1.2 mm (.049 in.) in wall thickness, 142 mm (6 in.) long with a 102 mm (4 in.) exposed test length.

Ammonia Fog Test

In the Fog Test, tube samples were arranged so that 12 C (55 F) tap (well) water at pH 7.0 to 7.5 was passed through tubes at 0.2 m/s (0.5 ft/s) to provide cooling.

The outer surfaces of the tubes were exposed to atomized distilled water containing 1000 ppm of ammonia, equivalent to 2000 ppm of ammonium hydroxide (NH₄OH) at 30 C (86 F) for 2400 hours (100 days). Solution pH was 10.9 as measured by titration. Atomization was accomplished with filtered compressed air. All the alloys were connected in series with three samples of each alloy connected in each straight section. In addition, each tube sample passed through a ½-in. thick steel support plate.

Ammonia Spray Test

In the Spray Test, a solution containing 2000 ppm NH₃ at about 21 C (70 F) was sprayed down through air onto sample tubes. The pH of the solution ranged from 10.9 to 11.1. Three samples of each alloy were arranged one above the other so that the spray impinged upon the uppermost sample and washed down to the second sample of the same alloy directly below and finally onto the third sample of the same alloy. No

cooling water was passed through the tubes. Tests were run for 170 days.

Sample Processing

In both tests, the samples were washed in distilled water, scrubbed with a soft brush, dried with alcohol and weighed both before and after testing. In addition, after the test exposures, the samples were descaled in 50 percent HCl to expose clean metal, and again cleaned and dried as described above prior to the final weighing.

RESULTS

Ammonia Fog Test

The Ammonia Fog Test results are shown in *Table II*. Admiralty brass shows the poorest corrosion resistance, followed closely by arsenical copper. Phosphorus deoxidized copper, aluminum bronze and 95-5 copper-nickel are somewhat better, followed by aluminum brass and 90-10 copper-nickel. Of the copper alloys, 80-20, 70-30 and 60-40 copper-nickel are the most corrosion resistant. Monel alloy 400 (%₀ Ni-Cu) has even higher resistance while stainless steel Types 304 and 316 corroded at minimal rates.

In visual examinations the attack qualitatively follows the same trends revealed in the quantitative measurements given in *Table II*. In addition, grooving, caused by the preferential flow of ammonia-rich condensate at the support plates, was observed in phosphorized deoxidized copper, arsenical copper, all three types of Admiralty brass, both aluminum brass and aluminum bronze, and 95-5 copper-nickel.

TABLE II
AMMONIA FOG TEST*
Average Corrosion Rate

Alloy	Average Corrosion Rate	
	mm/yr	m/yr
Phosphorized Copper (CA-122)	0.17	6.8
Arsenical Copper (CA-142)	0.23	8.5
Arsenical Admiralty (CA-443)	0.28	10.8
Antimonial Admiralty (CA-444)	0.28	11.0
Phosphorized Admiralty (CA-445)	0.30	11.6
Aluminum Brass (CA-687)	0.10	3.6
Aluminum Bronze (CA-608)	0.18	6.6
95/5-Copper/Nickel (CA-704)	0.15	5.9
90/10-Copper/Nickel (CA-706)	0.10	3.6
80/20-Copper/Nickel (CA-710)	0.01	0.4
70/30-Copper/Nickel (CA-715)	0.01	0.3
60/40-Copper/Nickel	0.01	0.2
MONEL alloy 400	0.01	0.3
Type 304 Stainless Steel	<0.01	<0.1
Type 316 Stainless Steel	<0.01	<0.1

*100 days' exposure to 30 C atomized water containing 1000 ppm NH₃ with 12 C cooling water passing through the tubes.

TABLE III
AMMONIA SPRAY TEST*
Average Corrosion Rate

Alloy	Average Corrosion Rate	
	mm/yr	m/yr
Arsenical Copper (CA-142)***	14.6	575
Arsenical Admiralty (CA-443)***	13.2	545
Aluminum Brass (CA-687)***	4.3	180
95/5-Copper/Nickel (CA-704)	0.48	19
90/10-Copper/Nickel (CA-706)	0.05	1.8
80/20-Copper/Nickel (CA-710)	<0.01	<0.1
70/30-Copper/Nickel (CA-715)	<0.01	<0.1
70/30-Copper/Nickel DSR** (CA-715)	<0.01	<0.1
60/40-Copper/Nickel	<0.01	<0.1
60/40-Copper/Nickel DSR	<0.01	<0.1
MONEL alloy 400	<0.01	<0.1
Type 316 Stainless Steel	<0.01	<0.1

*170 days of exposure to 21 C water spray containing 2000 ppm NH₃.

**DSR (Drawn and Stress Relieved).

***Testing terminated after only 4 days (96 hours) because of excessive corrosion.

Ammonia Spray Test

The results from the Ammonia Spray Test are shown in *Table III*. Note that three of the alloys: arsenical copper, arsenical Admiralty brass and aluminum brass, showed such high rates of attack that their exposure was discontinued after only 4 days (96 hours). The remainder of the alloys were tested for the full 170-day period. The attack decreased by an order of magnitude upon going from aluminum brass to 95-5 copper-nickel and by an additional order of magnitude in 90-10 copper-nickel. The extent of attack dropped several additional orders of magnitude in 80-20 copper-nickel. There appears to be a threshold nickel content, between 10 and 20 percent, beyond which attack by ammonia is drastically reduced. The difference between 70-30 copper-nickel and 70-30 copper-nickel DSR (Drawn and Stress Relieved) is in temper only. Their corrosion resistance is judged to be equal and within the normal variation experienced in these types of experimental tests, especially when weight losses are so slight. Monel alloy 400 and Type 316 stainless steel also showed high resistance to attack in the Ammonia Spray Test.

Visual observations again confirmed the weight losses, with attack being barely discernible on the 90/10, 80/20 and 70/30 copper-nickel samples or on the Monel alloy 400 or Type 316 stainless steel.

DISCUSSION

It should be noted that both the Fog and Spray Tests are accelerated aggressive tests in which high ammonia concentrations, well beyond those found in the main

body of a steam condenser, were utilized. These ammonia concentrations were also much above those that should develop in the air removal section in a properly designed and operated condenser. Air was used in these tests to greatly accelerate attack and should not be present in a condenser at these concentrations.

The objectives of tests such as these are to establish relative corrosion resistance rather than to develop quantitative design information. It would be incorrect to use these data to establish copper release rates to the steam system, as the attack was purposely accelerated and the protective corrosion films, which account for an alloy's resistance, were removed from the alloys in the process of making measurements.

The 1000 to 2000 ppm NH₃ utilized in these tests corresponds to a pH of 10.9 to 11.1. No steam system supplier suggests that such a high pH is desirable for satisfactory performance of either a fossil or a light water nuclear reactor feedwater circuit.

The relative ranking of the alloys in these two tests was the same. However, the extent of attack varied considerably, as shown in Fig. 1. Here the results for all alloys that were common to the two tests are plotted for comparison. Note that this is a semilogarithmic plot. As shown on the left of Fig. 1, arsenical copper, arsenical Admiralty and aluminum brass were severely attacked in both tests, but the attack is much more extensive in the Spray Test. This higher attack rate in the Spray Test is attributed to the inability of these alloys to develop tenacious, adherent, protective films when a spray of ammonia continuously impinges upon and washes the

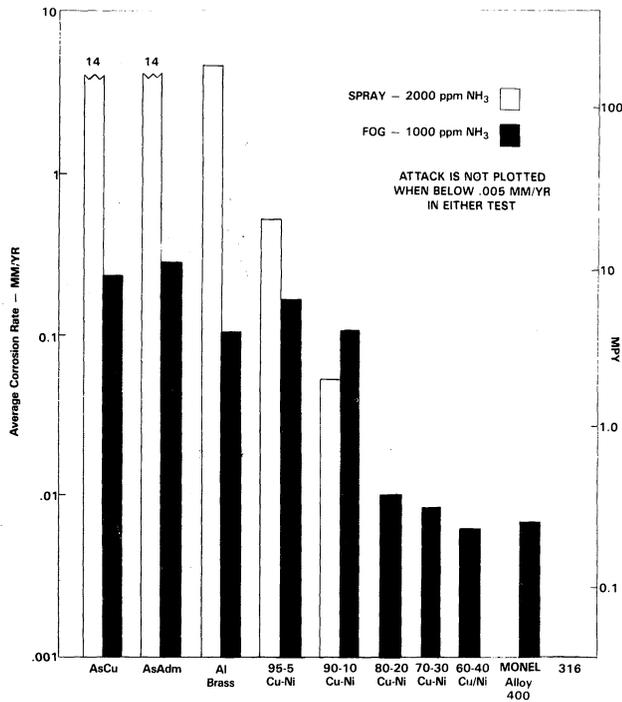


Fig. 1—Comparison of alloy performance in the ammonia fog and spray tests.

tubes. Their loose corrosion films were apparently easily rinsed away, dissolved or eroded by this 2000 ppm ammonia-containing spray. Relative to the brasses, 95-5 copper-nickel shows some improvement in corrosion resistance in the Spray Test but no difference was observed in the Fog Test. In contrast, 90-10 copper-nickel and, to a greater extent, those copper alloys containing more than 10 percent nickel, developed more tenacious corrosion films that protected their copper-containing substrates from attack by ammonia.

In the Fog Test, as a consequence of passing water through the tubes and the low velocity of the fog, ammonia-rich droplets form by condensation. Although 1000 ppm ammonia fog in a pH of 10.9 to 11.1 was measured, even higher pH droplets could probably form by condensation on the tubes. These high pH droplets stay in contact with the tube and are not continuously washed away as in the Spray Test. These droplets also stay in contact for a longer period of time than would occur in the air-removal section of an operating condenser. Protective corrosion films can break down in these high pH environments. In addition, the support plates provide a preferential site for collection of these droplets, allowing them to remain in contact for a greater length of time relative to those portions of the tube not in the vicinity of a support plate. These support plates also provide preferential flow paths for the ammonia droplets. All these factors can lead to ammonia grooving in some alloys. Certain alloys are

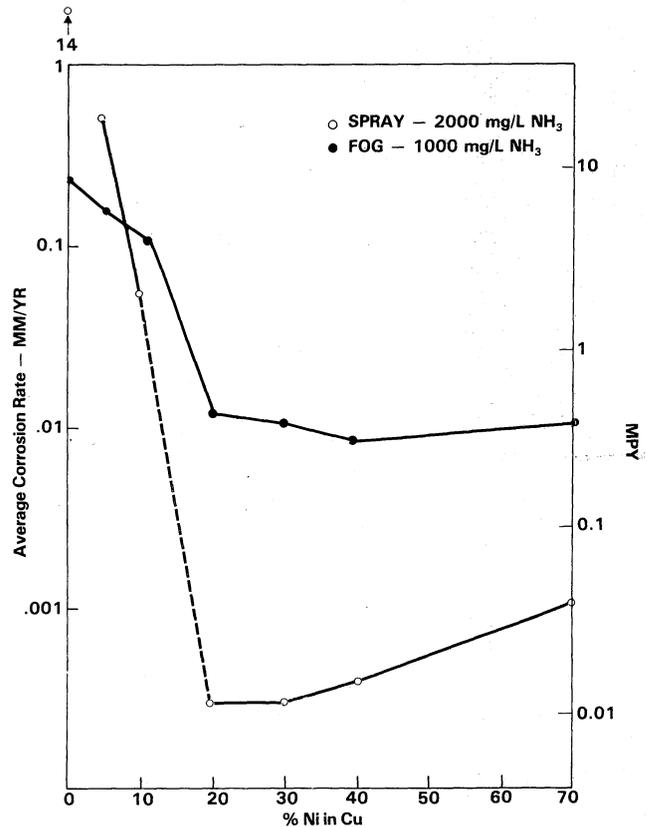


Fig. 2—The effect of nickel on the performance of copper-containing alloys in the ammonia fog and spray tests.

known to be susceptible to ammonia grooving in air-removal sections of condensers.⁶ Ammonia grooving was observed after the Fog Test in arsenical copper, Admiralty, aluminum brass, aluminum bronze, and 95-5 copper-nickel. All the other nickel-containing copper alloys were resistant to ammonia grooving but showed greater rates of general attack in the Fog Test than in the Spray Test, as shown in Fig. 2.

The Fog Test, which utilizes 1000 ppm NH₃ (pH 10.9), is more aggressive to the copper-nickel alloys than the Spray Test, which utilizes 2000 ppm NH₃ (pH 10.9 to 11.1). Apparently even more aggressive ammonia-rich droplets, corresponding to a pH of greater than 11.1, are forming in the Fog Test. It is obvious from the plot in Fig. 2 that 5 percent nickel provides some benefit in the Spray Test relative to arsenical copper (0 percent Ni), but this benefit does not extend to the Fog Test. Raising the nickel content to 10 percent does more good in increasing resistance in the Spray Test but is not sufficient to improve the relative resistance in the Fog Test to any large degree. At 20 percent nickel and beyond, the performance of the copper-containing alloys improves greatly in both the Fog and Spray Tests, as shown in Fig. 2. Thus there appears

to be a threshold, between 10 and 20 percent nickel, at which sufficiently tenacious and protective films can form on copper-containing alloys and optimum resistance is established.

These trends in relative resistance to ammonia attack are reflective in practice as very often the main body of a condenser is tubed with Admiralty brass or arsenical copper while the air removal section utilizes 90-10 copper-nickel. Similarly, where 90-10 copper-nickel is used in the main condenser, 70-30 copper-nickel is commonly installed in peripheral and air-removal sections for added insurance against potential ammonia corrosion problems.

CONCLUSIONS

1. The copper alloys, as a class, vary markedly in their resistance to ammonia attack.
2. Although the addition of nickel, even as little as 5 percent, helps copper-base alloys develop more tenacious and protective corrosion films, raising the nickel content to 10 percent provides a much greater improvement.
3. The addition of between 10 and 20 percent nickel results in the development of tenacious and protective corrosion films that are extremely resistant to general ammonia attack.
4. Increasing the nickel content beyond 30 percent in copper-base alloys does not result in an additional marked improvement in resistance to ammonia attack.

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