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GALVANIC CORROSION OF PIPING AND FITTING ALLOYS IN SULFIDE-MODIFIED SEAWATER

By
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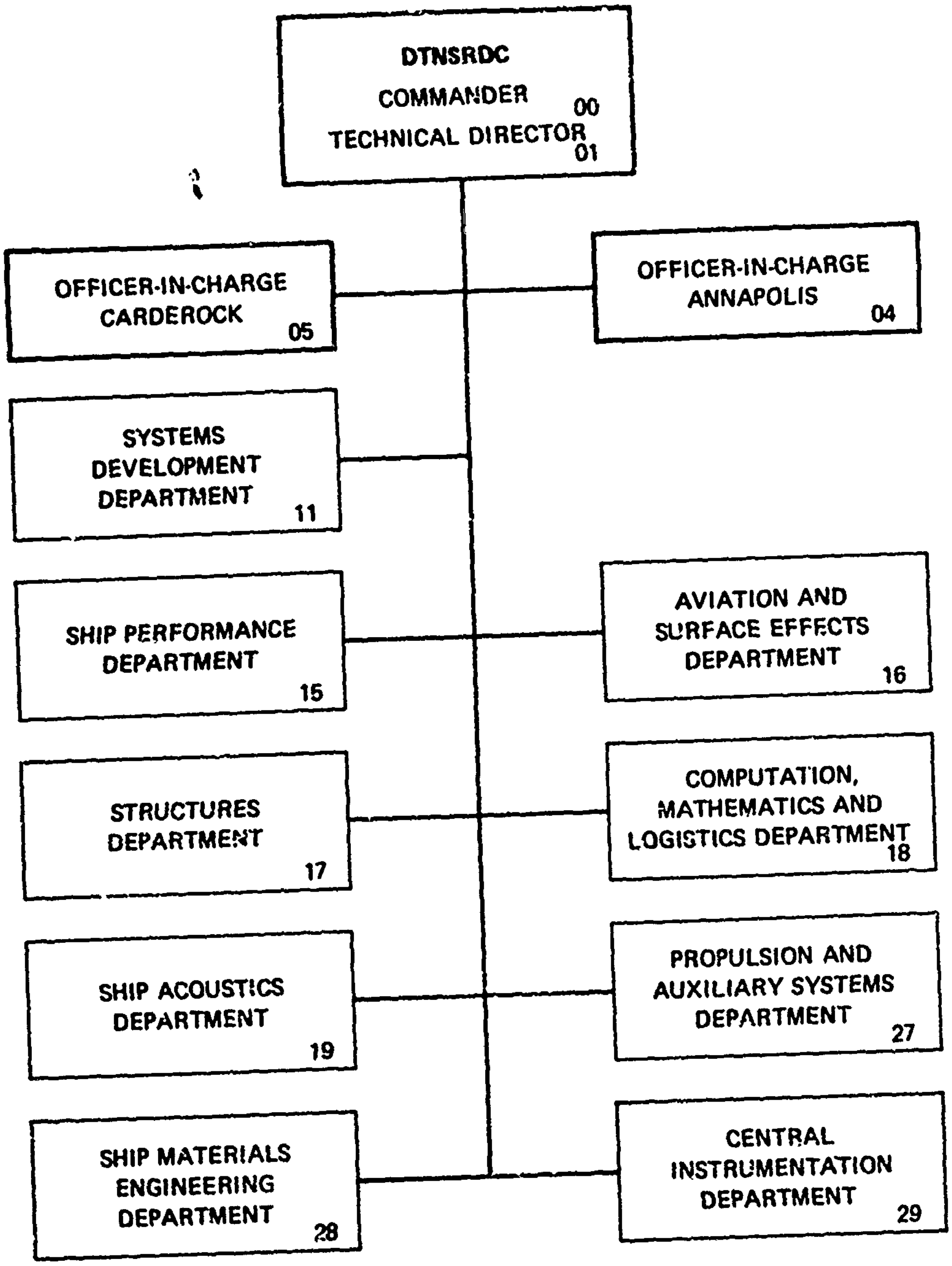

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Two wrought piping alloys, 70-30 and 90-10 copper-nickel, were each galvanically coupled to each of four fitting alloys in sulfide-modified seawater for 30 days. The fitting alloys used were bronze (Composition M), cast Monel, wrought nickel-aluminum bronze, and cast 70-30 copper-nickel. The piping material/fitting material area ratio was 3:1, and the seawater velocity was 2.4 meters per second. Results indicated that the galvanic relationship → over
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(Cont) by sulfide additions in a manner that increases the corrosion of the fitting material, whereas similar couples with 90-10 copper-nickel show little effect of sulfide.

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LIST OF ABBREVIATIONS

mg/l	Milligram per liter
mm	Millimeter
mm/yr	Millimeter per year
m/s	Meter per second
mV	Millivolt
rms	Root mean square

ABSTRACT

Two wrought piping alloys, 70-30 and 90-10 copper-nickel, were each galvanically coupled to each of four fitting alloys in sulfide-modified seawater for 30 days. The fitting alloys used were bronze (composition M), cast Monel, wrought nickel-aluminum bronze, and cast 70-30 copper-nickel. The piping material/fitting material area ratio was 3:1, and the seawater velocity was 2.4 meters per second. Results indicated that the galvanic relationship between M-bronze or Monel and 70-30 copper-nickel is affected by sulfide additions in a manner that increases the corrosion of the fitting material, whereas similar couples with 90-10 copper-nickel show little effect of sulfide.

ADMINISTRATIVE INFORMATION

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INTRODUCTION

The occurrence of accelerated corrosion of copper-nickel alloys exposed to flowing seawater containing sulfide pollutants has been of concern to both the Navy[1,2*] and to industry.[3-5] Many studies of the corrosion of various copper-based materials have been conducted,[1,5-10] and some solutions to the problem have been investigated.[11-20] The corrosion mechanism has been postulated to involve an electropositive shift in the corrosion product film potential in the copper-nickels, and such a potential shift has been documented.[1] It would, therefore, be expected that the galvanic relationships between the copper-nickels and other alloys in seawater may be altered in an environment containing sulfide pollution. This could, in polluted environments, lead to galvanic corrosion of materials which have usually been considered compatible in more normal environments. For example, both 90-10 and 70-30 copper-nickel piping have in the past been coupled with bronze fittings in seawater systems without encountering unacceptable galvanic corrosion of any of the materials involved. The purpose of this study was to determine if sulfide-containing seawater would cause galvanic corrosion in certain piping/fitting combinations which would not be observed in unpolluted seawater.

*A complete listing of references may be found on page 23.

INVESTIGATIONS

MATERIAL

The piping materials chosen for this study were 90-10 and 70-30 copper-nickel. The fitting materials selected were cast bronze (Composition M), cast Monel (Composition E)*, wrought nickel-aluminum-bronze, and cast 70-30 copper-nickel. Compositions of all materials are listed in the following tabulation.

COMPOSITION OF TEST MATERIALS

	90-10 Cu-Ni	70-30 Cu-Ni	M-Bronze	Ni-Al-Bronze	Cast 70-30 Cu-Ni	Monel
Cu	88.09	68.52	87.52	80.41	Bal	29.7
Al				9.23		0.19
Fe	1.50	0.49	0.15	3.94	0.61	2.88
Ni	9.8	30.12	0.55	4.24	30.7	60.4
Mn	0.46	0.74		1.46	1.03	1.32
Sn			5.86			
Pb	<0.02	0.01	1.66	Nil	0.002	
Zn	0.09		Bal			
Si				0.08	0.43	3.48*
P	<0.02	0.001	0.006			
Nb+Ta					0.91	1.86
S	<0.02	0.004				
C						0.12
Others				0.04		

*Analysis suspect. Silicides not detected metallographically.

*Trademark of the International Nickel Company

APPARATUS AND EXPERIMENTAL PROCEDURE

Corrosion exposures were conducted in polarization cells located at the Francis L. LaQue Corrosion Laboratory at Wrightsville Beach, North Carolina. In each cell, one piping and one fitting alloy specimen were mounted with their surfaces parallel to the seawater flow. The piping material/fitting material area ratio was 3:1, and the seawater velocity was 2.4 meters per second. One surface of each specimen was wetted while the other was kept dry with gasketing to allow for electrical contact. Wetted surfaces of the two specimens were mounted parallel and opposing, with a 6-mm* gap between them. Provisions were made for the use of a silver/silver-chloride reference cell for each test unit. The sulfide level in the seawater could be controlled by the addition of sodium sulfide. The seawater was not recirculated but was discharged after one pass through the test cell and subsequent neutralization of excess sulfide. Sulfide concentrations were measured using the p-phenyenediamine colorametric technique. Dissolved oxygen in the untreated water was 5 to 9 mg/l. No detectable pH shift was observed during sulfide injection.

The standard specimen dimensions for these cells are 72.5x30.5x6 millimeter. Reduced size specimens were mounted with nonmetallic spacers to fill the specimen holders. Specimen surface finish was 32 rms.

Galvanic couples of each piping/fitting material combination were exposed to seawater flowing at 2.4 m/s and containing 0, 0.01 or 0.05 mg/l sulfide for 30 days. Couple potential and galvanic current were monitored. At the conclusion of the exposures, the specimens were cleaned and data were recorded on weight loss and pit depth which were converted to corrosion rates and maximum depths of attack, respectively.

RESULTS AND DISCUSSION

CORROSION RATE AND DEPTH OF ATTACK

Corrosion rate and maximum depth of attack data for the fitting alloys as a function of coupling and sulfide concentration are illustrated in Figures 1-4. Figure 1 presents the data for M-bronze. Since uncoupled

*A list of abbreviations appears on page iv.

specimens were run in duplicate, two vertical lines appear in these bars. There is an overall increase in corrosion of uncoupled specimens with increasing sulfide concentration as expected. Also, as predicted from service experience, there is little difference in corrosion between coupled and uncoupled bronze at 0 mg/l sulfide. As sulfide level increases, there is still little difference in behavior between uncoupled bronze and material coupled to 90-10 copper-nickel. However, significant increase in both corrosion rate and maximum depth of attack is evident in bronze coupled to 70-30 copper-nickel in sulfide containing seawater. Thus, although M-bronze and 70-30 copper-nickel are galvanically compatible in unpolluted seawater, addition of sulfide will cause galvanic attack to occur on the M-bronze. This does not take place in couples with 90-10 copper-nickel.

Figure 2 presents corrosion data for Monel. An increase in corrosion rate with increasing sulfide can be observed, although the depth of attack remains relatively unaffected. Galvanic coupling to either copper-nickel has little effect on the corrosion in unpolluted seawater. As sulfide is added, the corrosion of the Monel is decreased, that is, it is cathodically protected upon coupling to 90-10 copper-nickel. Corrosion either remains the same or increases, depending on the sulfide level, when coupled to 70-30 copper-nickel. Thus, here is another example of a material which in unpolluted seawater is not affected by coupling to copper-nickels but is affected differently upon coupling to each alloy in polluted seawater.

Figures 3 and 4 present the corrosion data for nickel-aluminum-bronze and cast 70-30 copper-nickel, respectively. For either material, corrosion increases with increasing sulfide and, with two exceptions, is unaffected by coupling at any sulfide level. The exceptions are the low corrosion rate and depth of attack of cast 70-30 copper-nickel when coupled to 90-10 copper-nickel and the low depth of attack when coupled to 70-30 Cu-Ni at the 0.01 sulfide level. Since these occurrances were not duplicated at either the higher or the lower sulfide level, they are not considered significant.

Figures 5 and 6 illustrate the behavior of the wrought 90-10 and 70-30 copper-nickel piping specimens, respectively, in the couples with all the materials. Four uncoupled control specimens were run at each sulfide level so four lines are shown in these bars. Once again, a general increase in corrosion of both copper-nickels was evident on uncoupled specimens as sulfide concentration increased. Due to the large scatter in the maximum depth of attack data from the uncoupled control specimens of both alloys, no additional conclusions could be drawn from this data. Several trends can be observed in the corrosion rate data, however. Coupling to M-bronze does not signficantly affect the corrosion rate of 90-10 copper-nickel since coupled values are within the control specimen scatter. Even considering scatter, coupling to 70-30 copper-nickel decreases corrosion rate if sulfide is present, however. Thus, the 70-30 copper-nickel is receiving cathodic protection from the increased corrosion of the M-bronze in sulfide-containing seawater. The increase in the corrosion rate of 90-10 copper-nickel when coupled to Monel corresponds with the previously reported decrease in corrosion of the Monel in this couple in sulfide-containing seawater. No conclusions can be drawn about the corrosion of 70-30 copper-nickel when coupled to Monel or about the behavior of either copper-nickel when coupled to either nickel-aluminum bronze or cast 70-30 copper-nickel.

CORROSION POTENTIALS

Figures 7-14 present average corrosion potentials of uncoupled alloys and couples as a function of sulfide concentration. The potentials illustrated are averaged only over the last 20 days of testing. Since there were four piping alloy control specimens for each material at each level, this information is presented as a band. In addition, there were two fitting alloy control specimens for each material at each sulfide level. This information is, therefore, also presented as a band. Couple potential information was derived from individual coupled specimen pairs and is, therefore, illustrated by a solid line on the figures.

Figures 7 and 8 present the data for M-bronze and 90-10 or 70-30 copper-nickel, respectively. In Figure 7 all potentials are within the same range and signficant galvanic interactions would not be expected. As described earlier, none were observed. A small (50 mV) potential difference can be seen between 70-30 Cu-Ni and M-bronze in Figure 8 at 0 mg/l sulfide. When sulfide is added this difference increases to 150 mV, which could explain the observed behavior of these couples.

Figure 9 indicates that Monel tends to be protected by 90-10 Cu-Ni when sulfide is not present but has little galvanic interaction at higher sulfide levels. In Figure 10 a reversal can be seen in the behavior of Monel and 70-30 Cu-Ni. The Monel is protected when sulfide is not present and becomes sacrificial in the presence of sulfides. Both of these observations are verified by the corrosion data.

Nickel-aluminum-bronze tends to be equal in potential or slightly cathodic to 90-10 Cu-Ni, with the potential difference increasing somewhat in sulfide. This can be seen in Figure 11. Figure 12 indicates that the potential of Ni-Al-bronze is similar to, or slightly anodic to, that of 70-30 Cu-Ni throughout the range of sulfide concentrations. Thus, a difference in corrosion behavior of Ni-Al-bronze when coupled to 90-10 or to 70-30 Cu-Ni is expected. The reason this did not occur in these exposures may be due to the polarization characteristics of the Ni-Al-bronze.

In Figure 13 an increased potential difference can be observed in sulfide between cast 70-30 and 90-10 Cu-Ni. Cathodic protection of the cast material and increased corrosion of the 90-10 Cu-Ni should, therefore, be observed in sulfide-containing seawater. Although tendencies in this direction can be observed in the corrosion data in Figures 4 and 5, these tendencies are small compared to the data scatter. Figure 14 illustrates that the potentials of cast and wrought 70-30 Cu-Ni are seen to be similar throughout the range of sulfide concentrations, thus no galvanic interaction is expected and none was observed.

It should be noted that the potentials of all alloys tested except Monel shifted in the electropositive direction upon the addition of sulfide. All of these materials derive their corrosion resistance from the buildup of a copper-oxide corrosion product film. The inclusion of sulfide ions into the film as it is being formed is thought to cause the cathodic shift by increasing film conductance through a semiconductor doping mechanism. The Monel derives its corrosion resistance from the formation of a complex nickel-oxide film which might not behave in the same manner as the copper-oxide. In fact, the potential of the Monel shifted more electronegative when sulfide was present.

CONCLUSIONS

There is a change in the galvanic relationship between normally compatible piping and fitting alloys in sulfide-containing seawater. This change causes an increase of corrosion of M-bronze or Monel when these materials are used with 70-30 Cu-Ni in sulfide-containing seawater. Behavior of these alloys when coupled to 90-10 Cu-Ni is relatively unaffected by the sulfides. All of these couples have been used and are usually considered compatible in environments without sulfide. Therefore, if a polluted environment is to be encountered, galvanic interrelationships of all materials in the systems involved should be reappraised.

ACKNOWLEDGMENT

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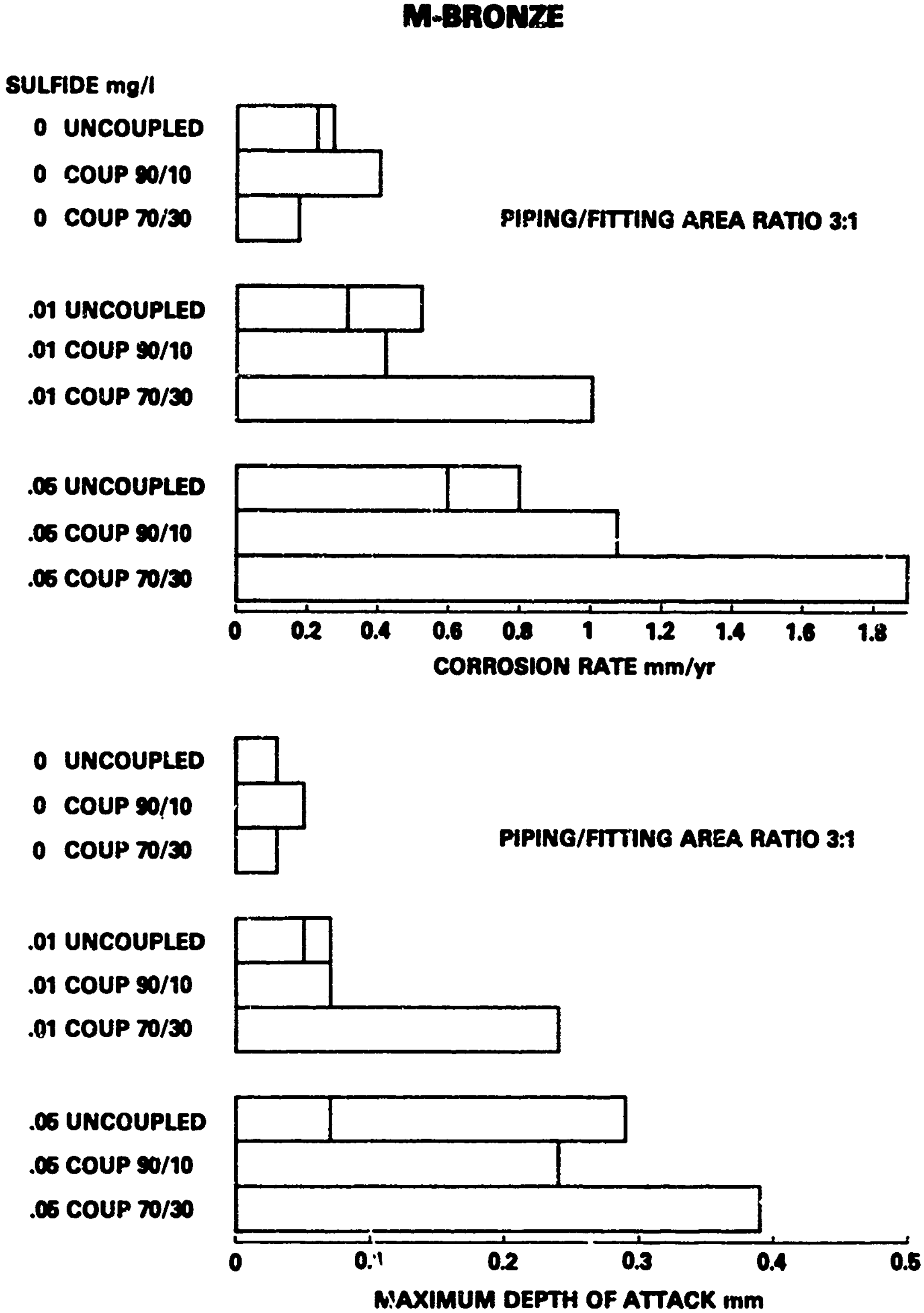


Figure 1 - Corrosion of M-Bronze Coupled to Piping Materials in Sulfide

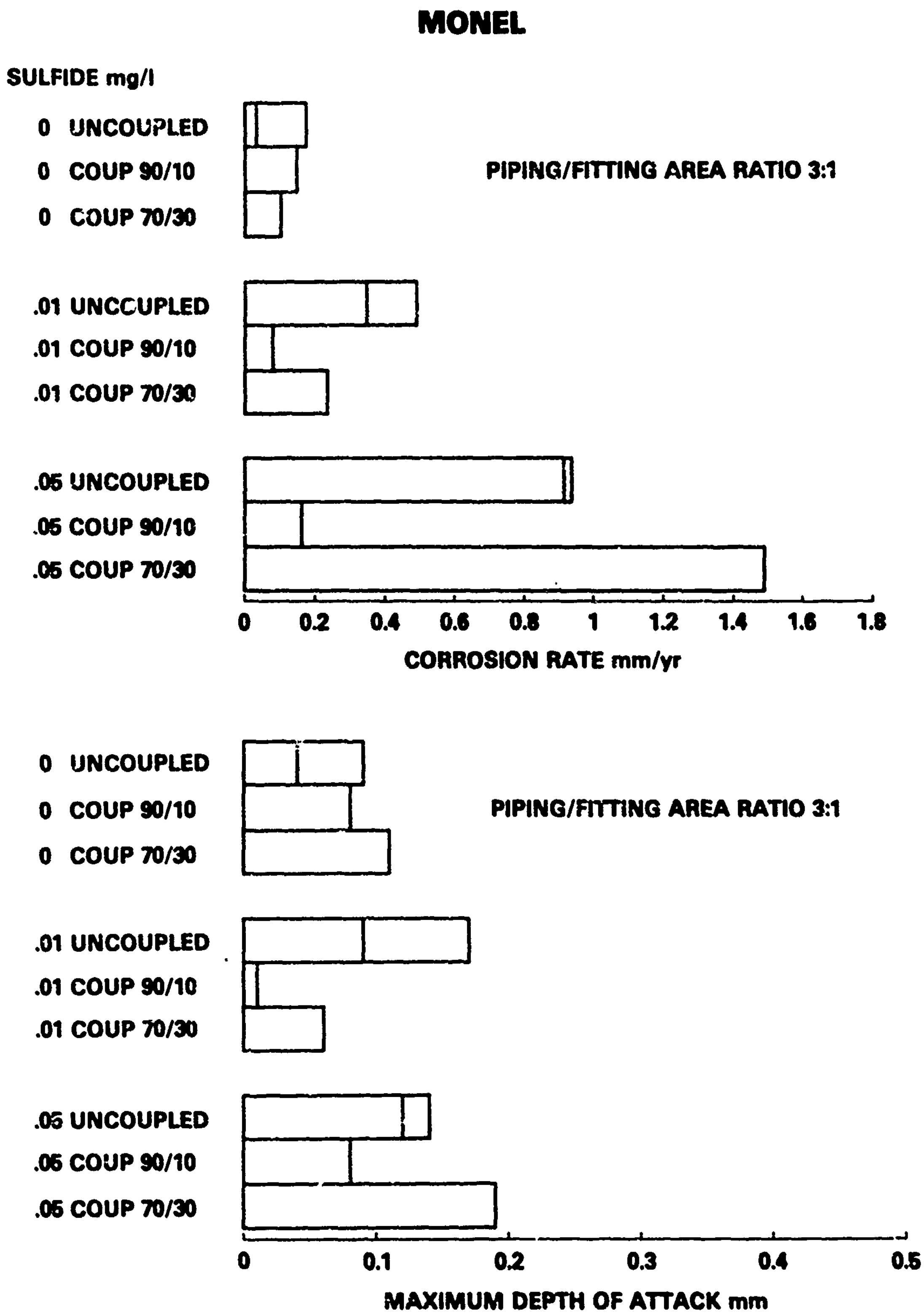


Figure 2 - Corrosion of Monel Coupled to Piping Materials in Sulfide

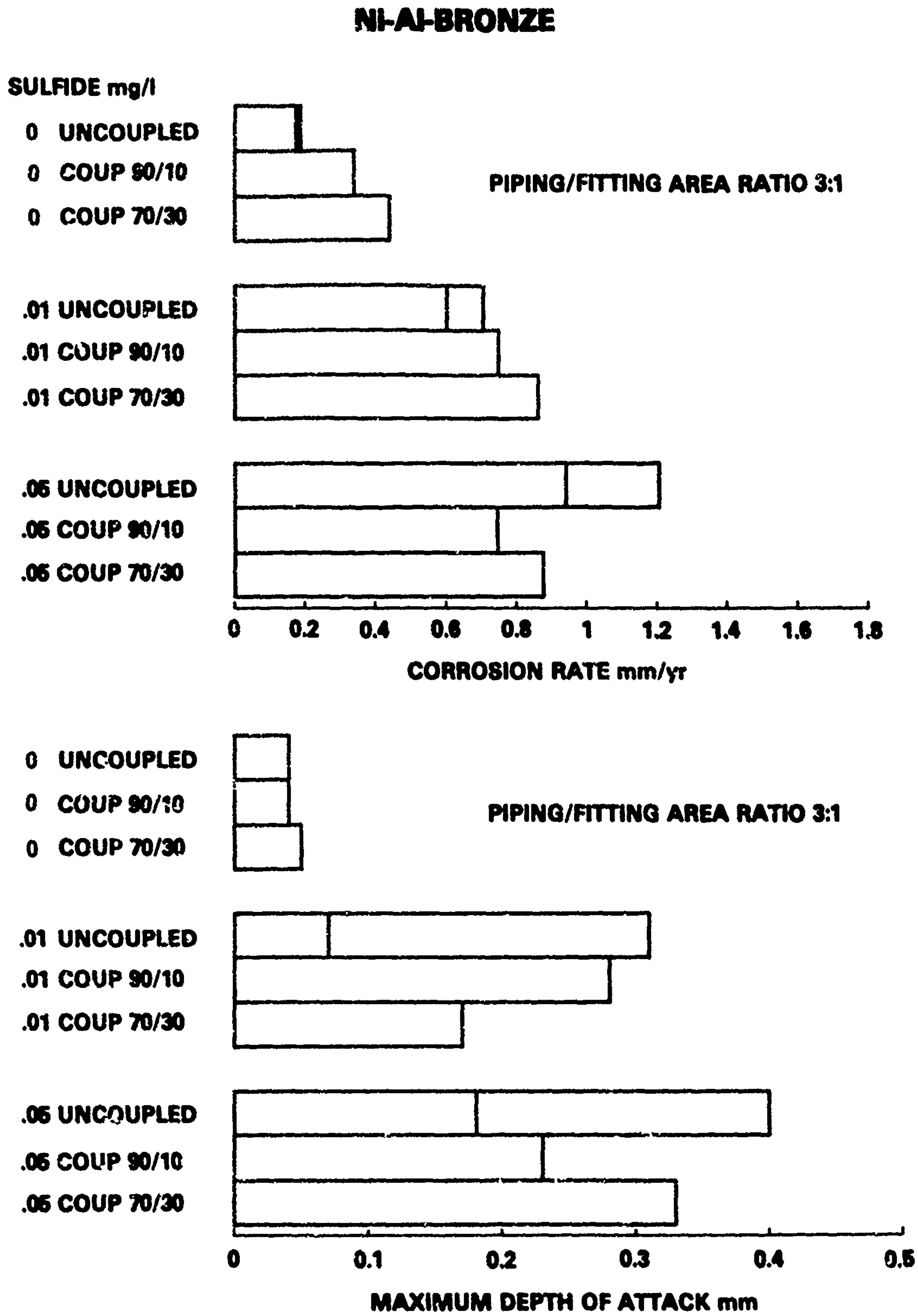


Figure 3 - Corrosion of Ni-Al-Bronze Coupled to Piping Materials in Sulfide

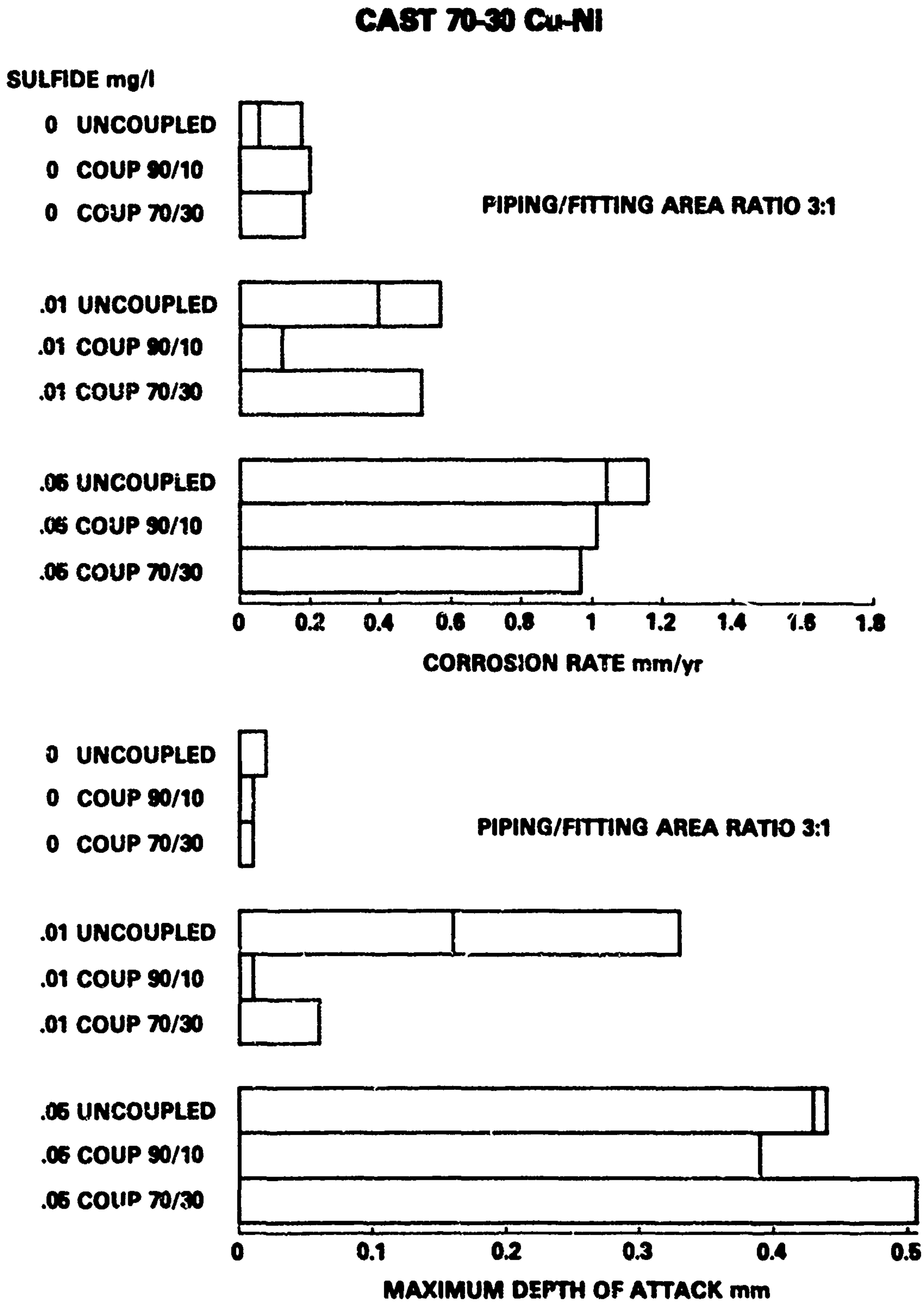
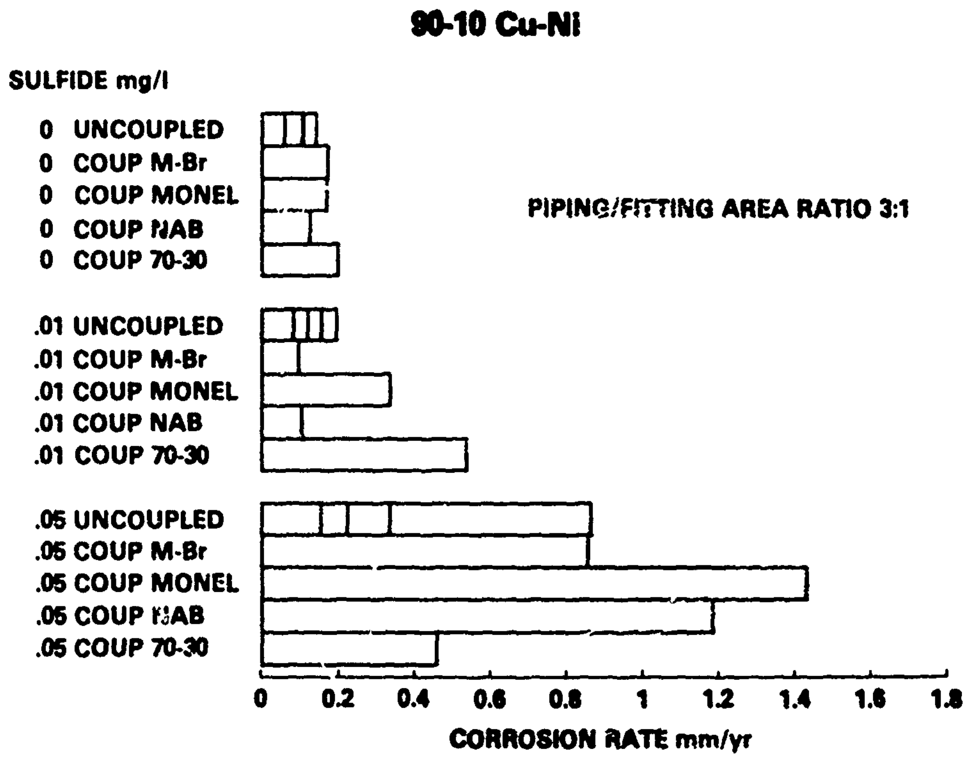


Figure 4 - Corrosion of Cast 70-30 Cu-Ni Coupled to Piping Materials in Sulfide



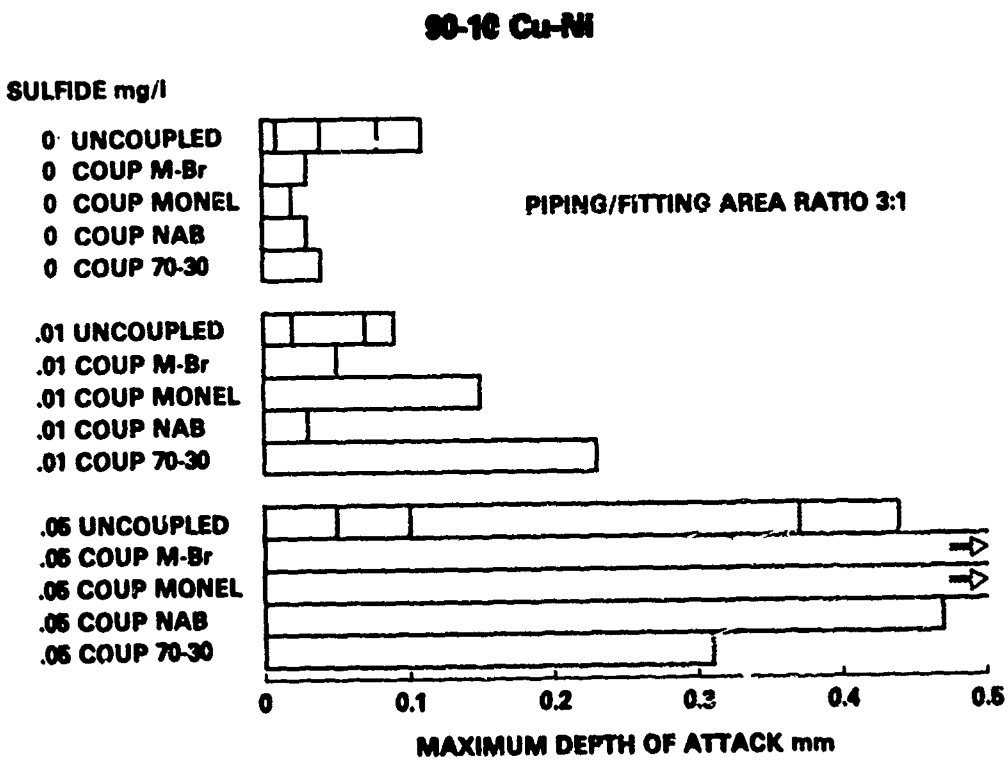
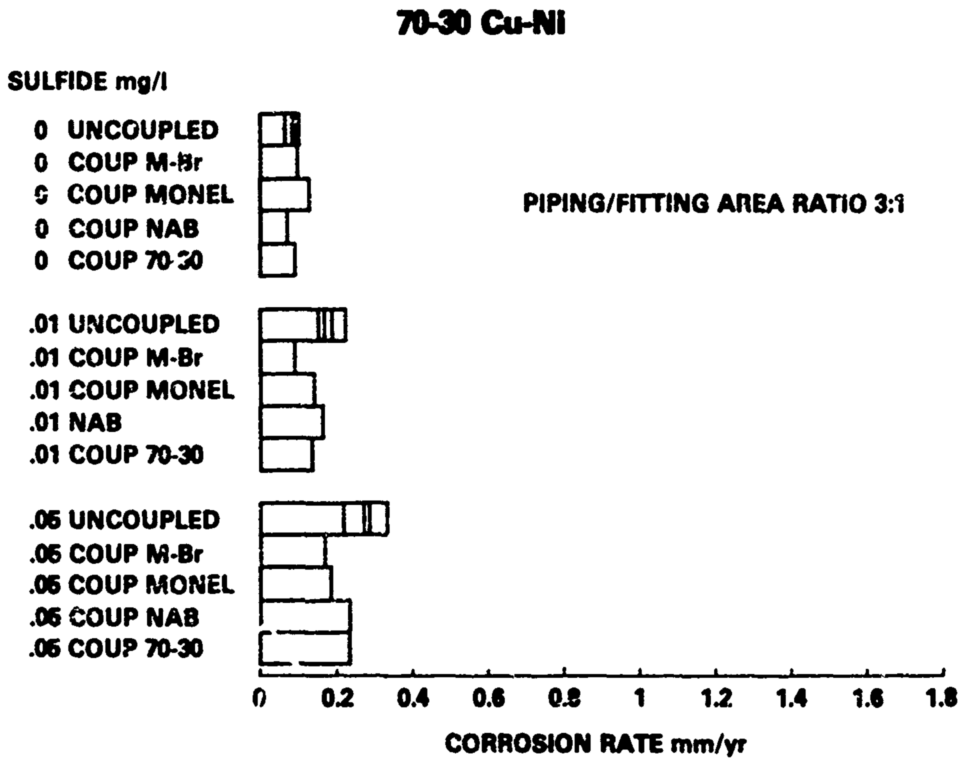


Figure 5 - Corrosion of 90-10 Cu-Ni Coupled to Fitting Materials in Sulfide



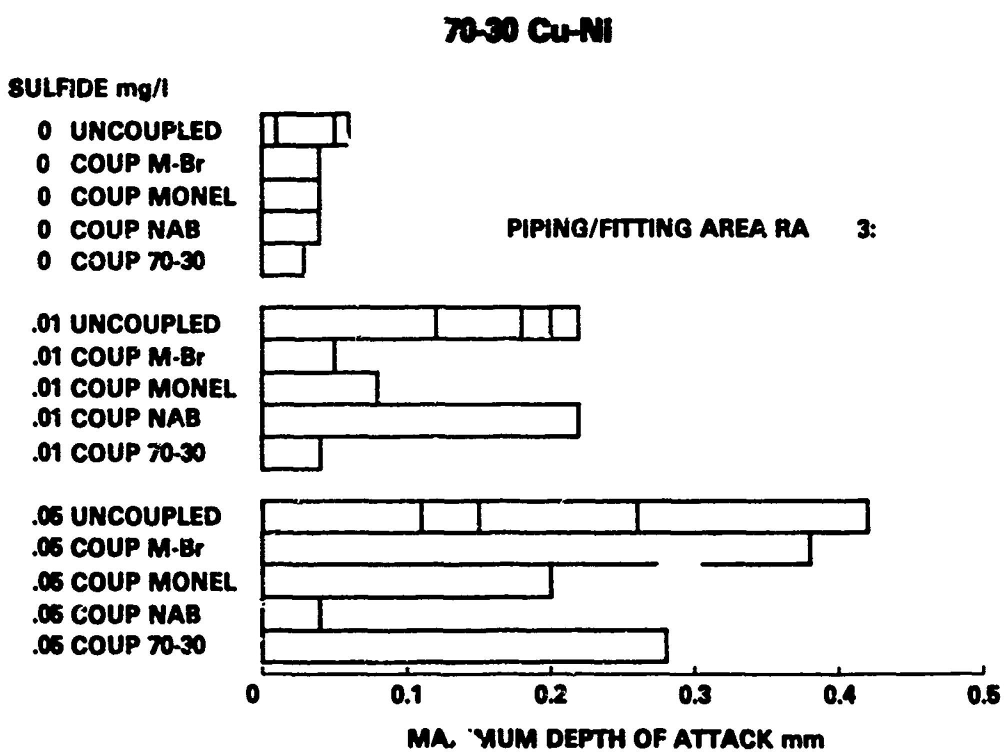


Figure 6 - Corrosion of 70-30 Cu-Ni Coupled to Fitting Materials in Sulfide

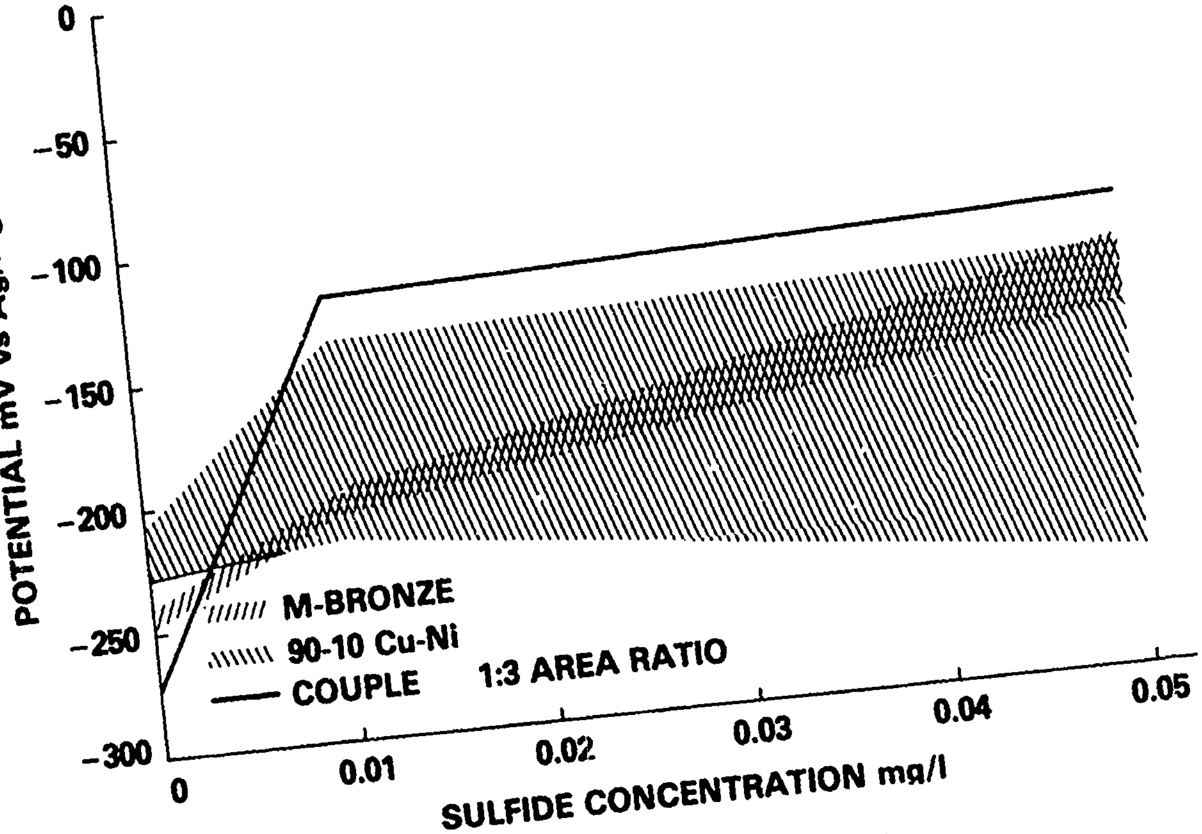


Figure 7 - Potentials of M-Bronze and 90-10 Cu-Ni

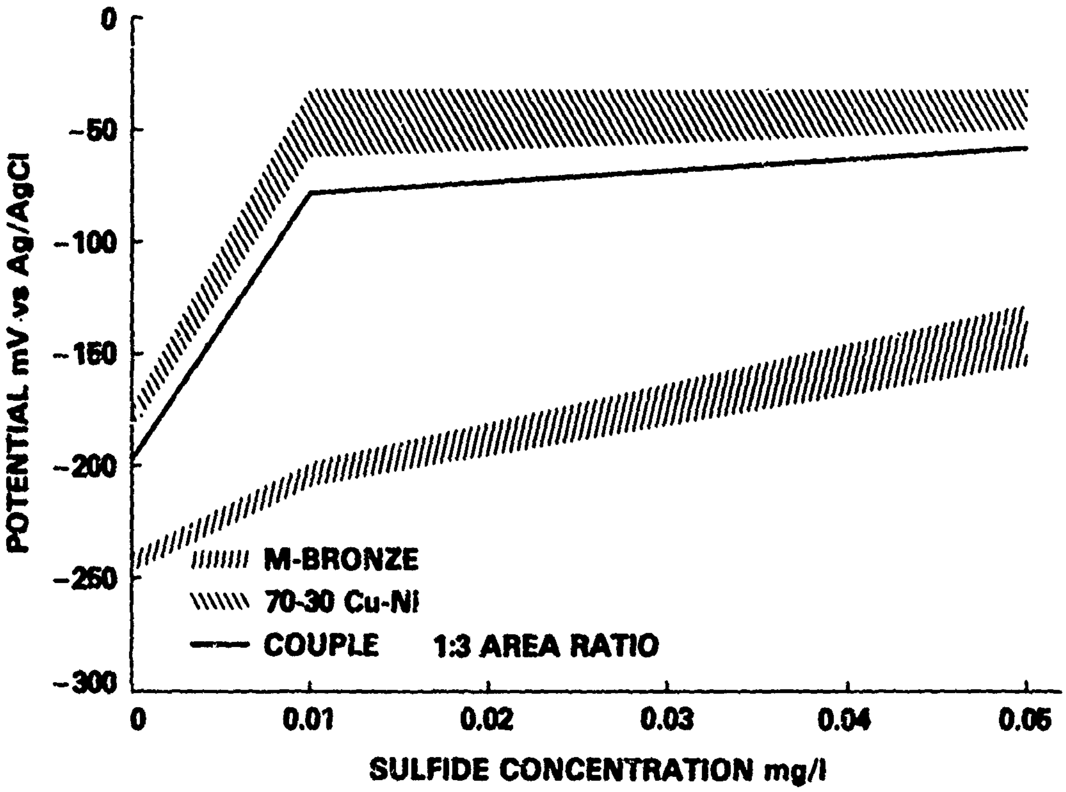


Figure 8 - Potentials of M-Bronze
and 70-30 Cu-Ni

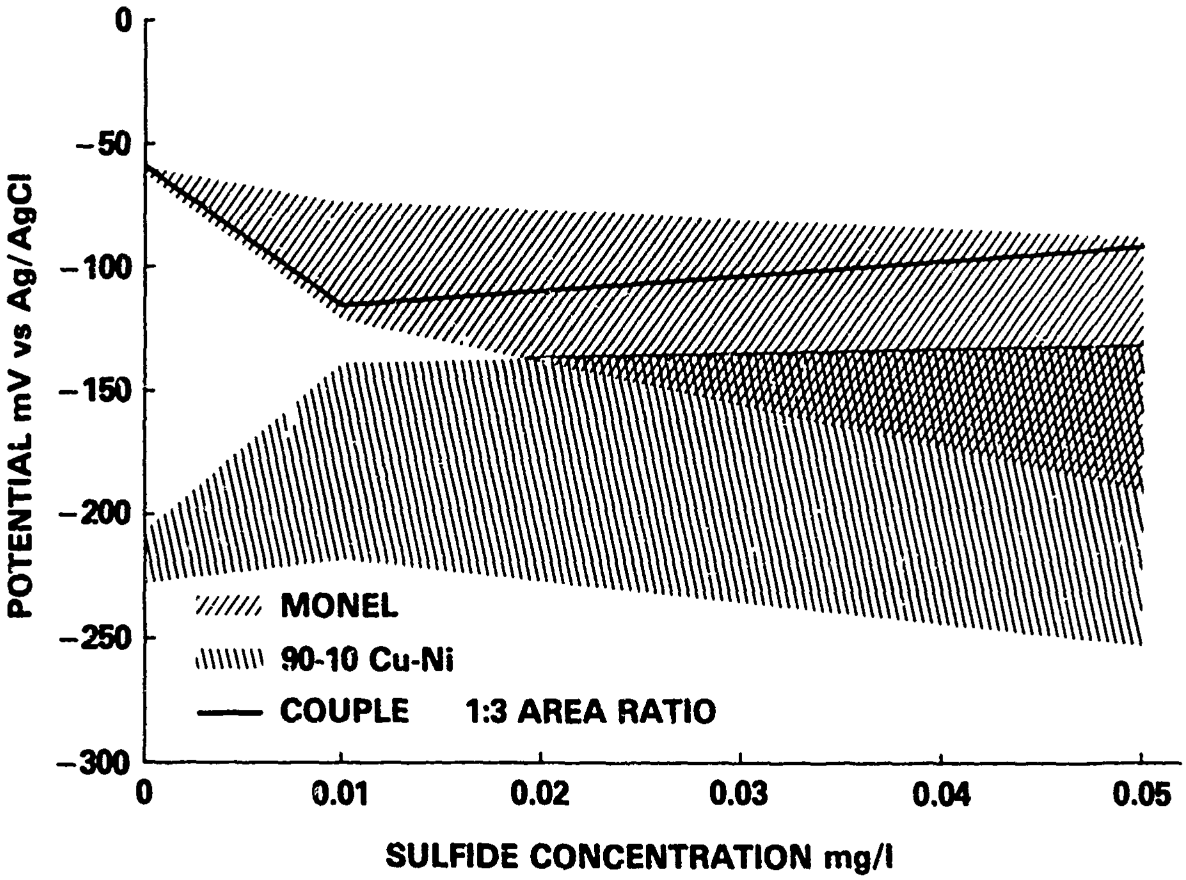


Figure 9 - Potentials of Monel
and 90-10 Cu-Ni

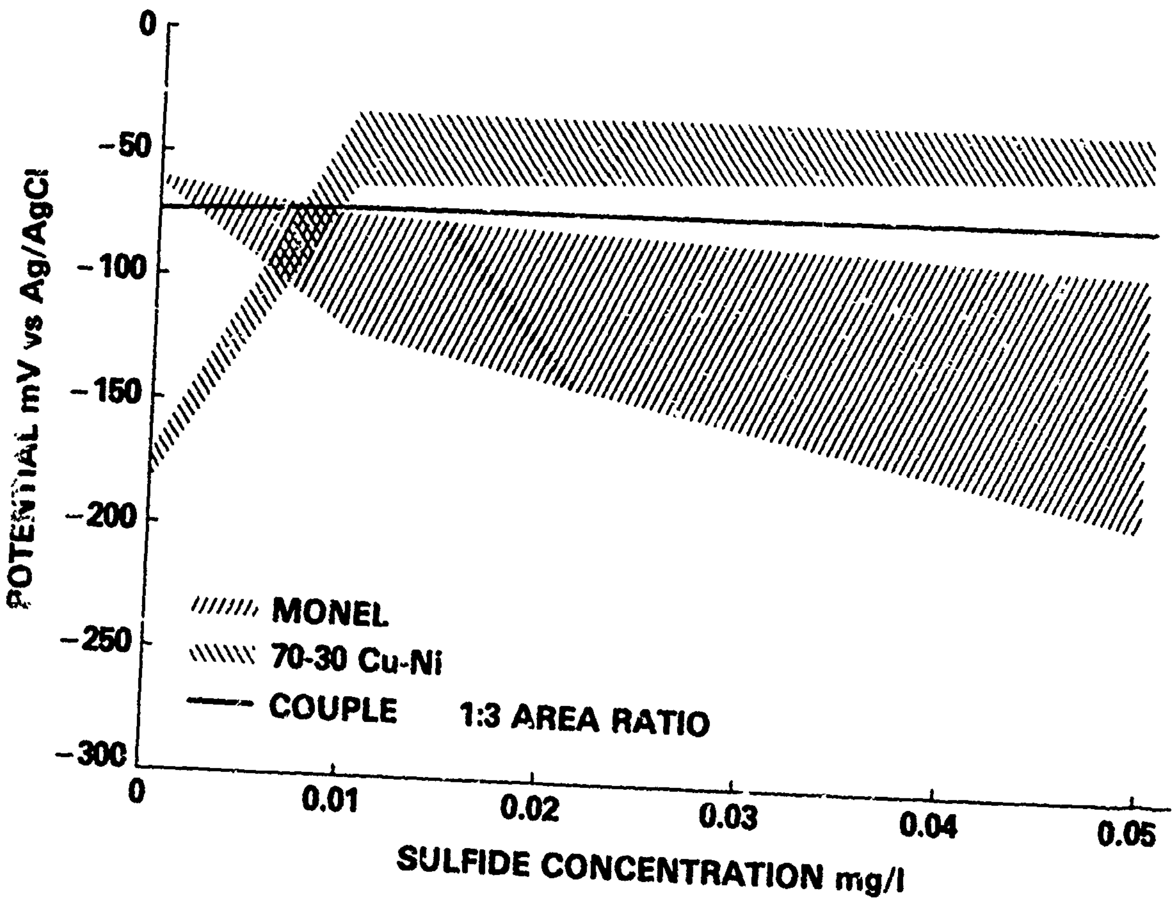


Figure 10 - Potentials of Monel and 70-30 Cu-Ni

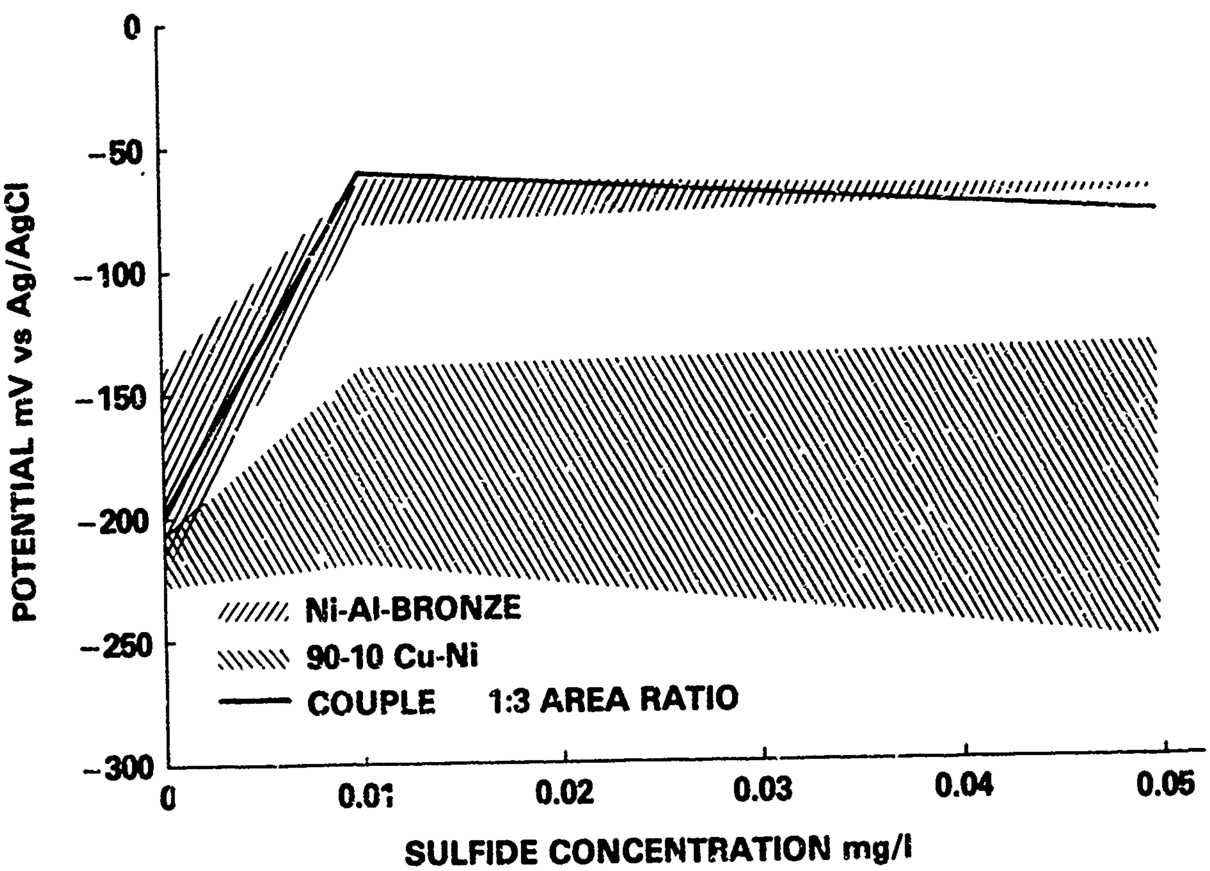


Figure 11 - Potentials of Ni-Al-Bronze
and 90-10 Cu-Ni

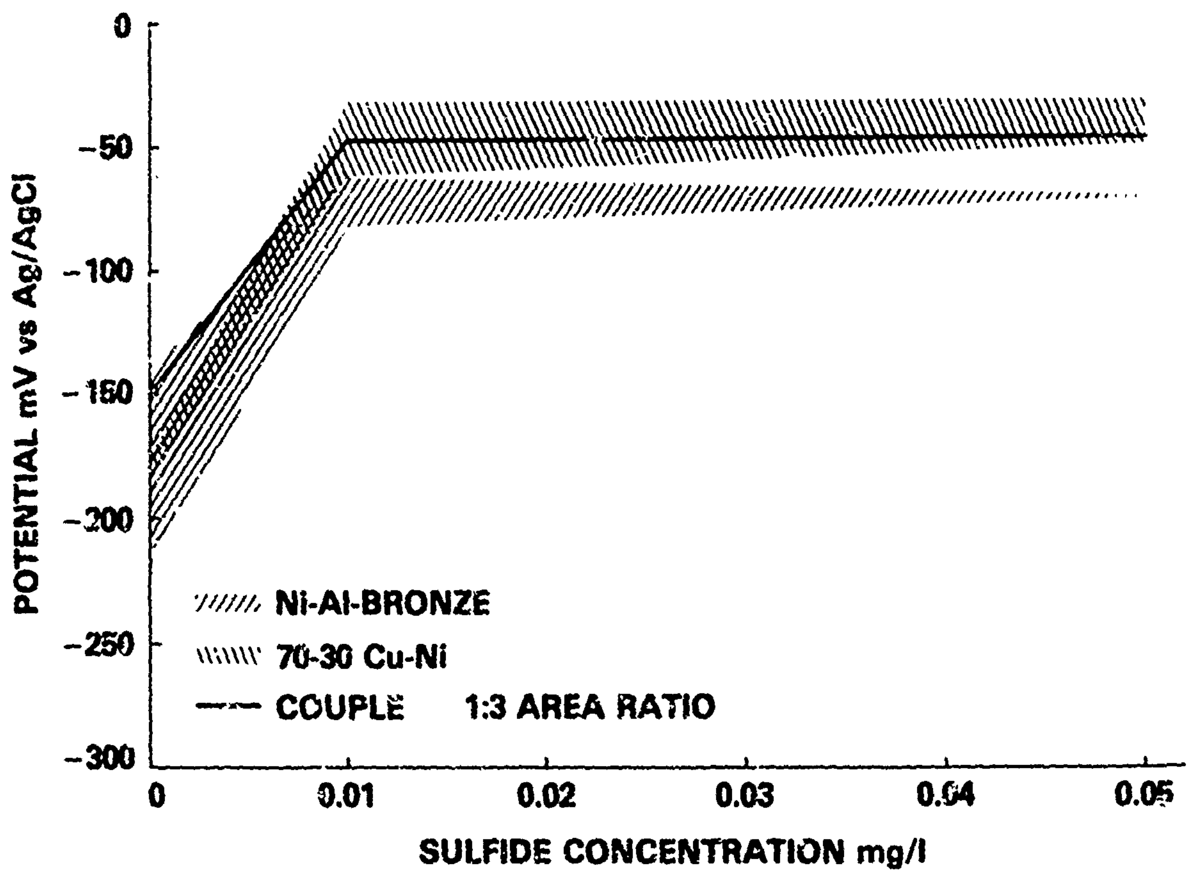


Figure 12 - Potentials of Ni-Al-Bronze and 70-30 Cu-Ni

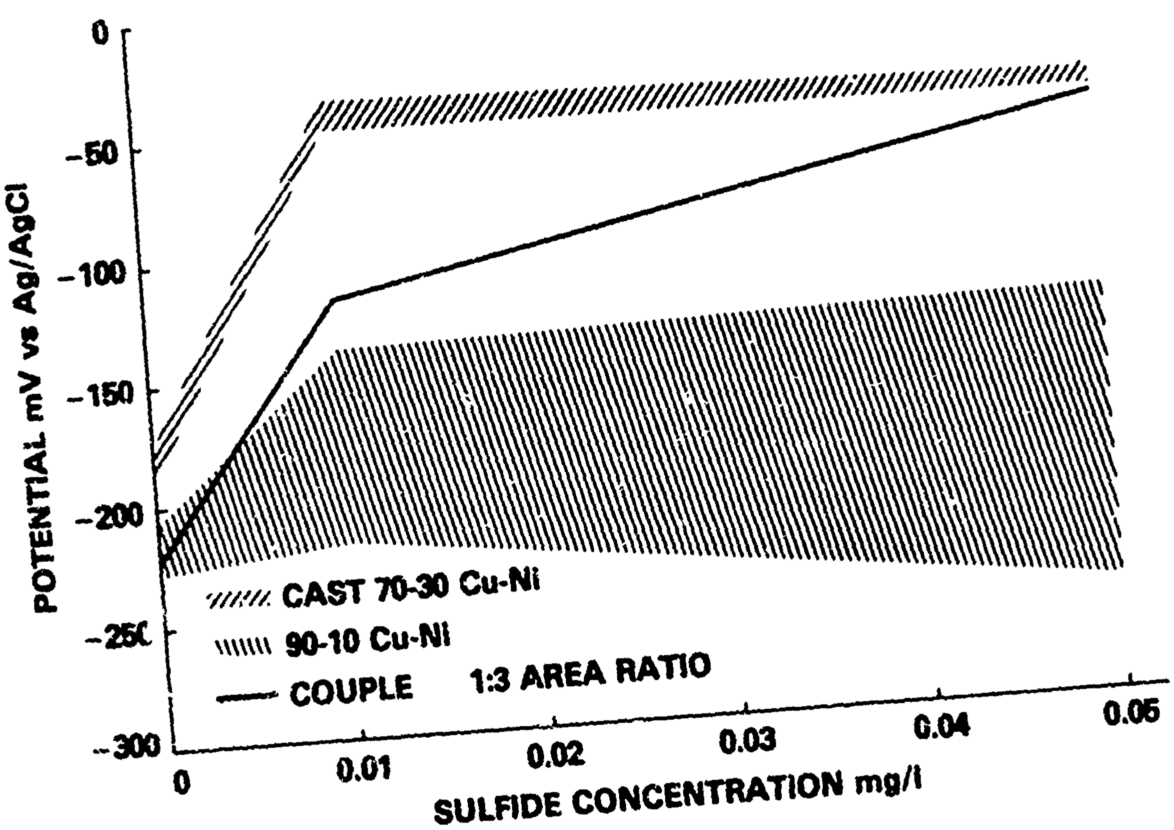


Figure 13 - Potentials of Cast 70-30 Cu-Ni and 90-10 Cu-Ni

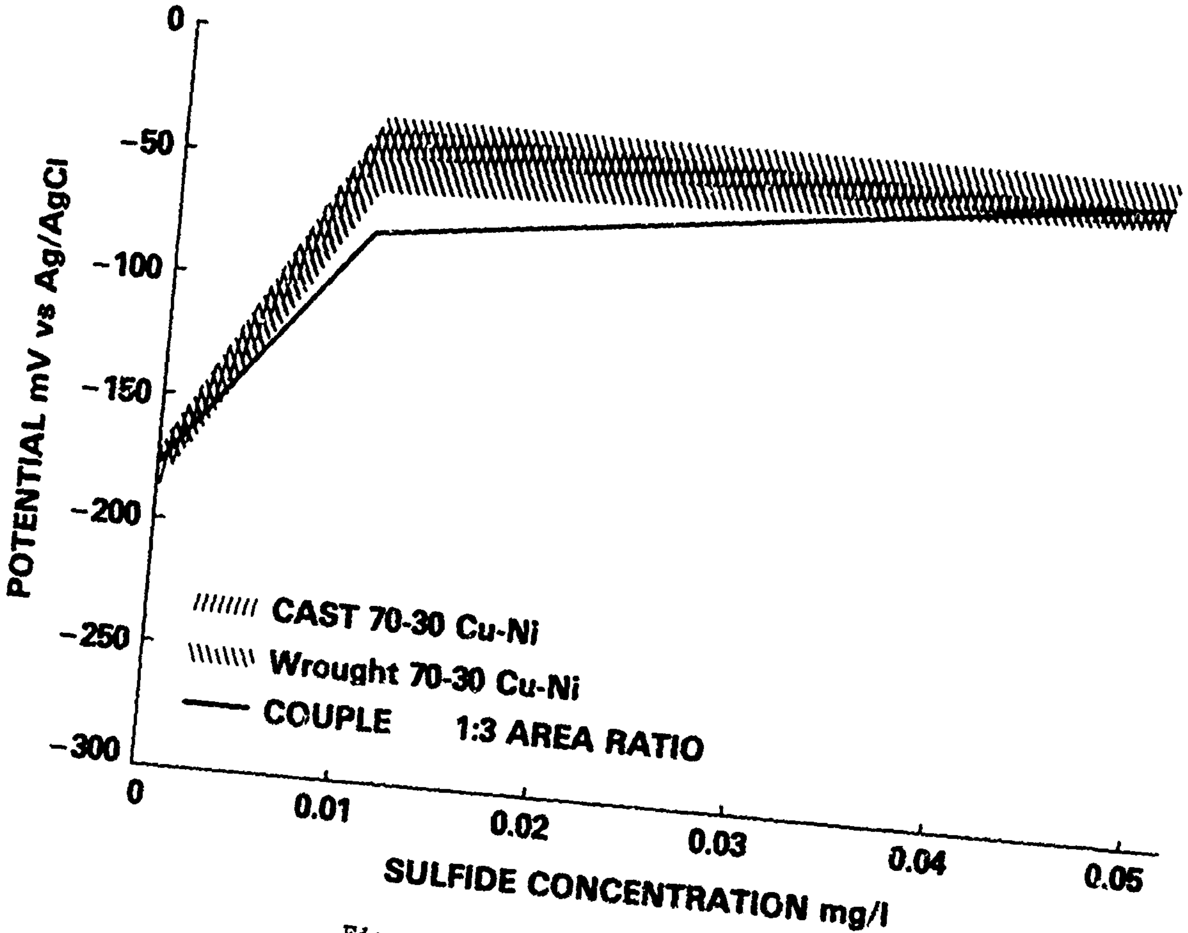


Figure 14 - Potentials of Cast and Wrought 70-30 Cu-Ni

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