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GALVANIC CORROSION – EFFECT OF ENVIRONMENTAL AND EXPERIMENTAL VARIABLES

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ABSTRACT

Galvanic corrosion behavior of A 516 steel coupled to alloy C-22 and Ti Gr-12, respectively was evaluated in an acidic brine (pH ≈ 2.75) at 30°C, 60°C and 80°C using zero resistance ammeter method. A limited number of experiments were also performed in a neutral brine involving A 516 steel/alloy C-22 couple. The steady-state galvanic current and galvanic potential were measured as functions of anode-to-cathode (A/C) area ratio and electrode distance. Results indicate that the galvanic current was gradually reduced as the A/C area ratio was increased. No systematic trend on the effect of A/C area ratio on the galvanic potential was observed. Also, no significant effect of electrode distance on the galvanic current and galvanic potential was evident. In general, increased galvanic current was noticed with increasing temperature. The limited data obtained in the neutral brine indicate that the galvanic current was reduced in this environment, compared to that in the acidic brine. Optical microscopic examination was performed on all tested specimens to evaluate the extent of surface damage resulting from galvanic interaction. A 516 steel suffered from general corrosion and crevice corrosion in all environments tested. Very light crevice corrosion mark was observed with alloy C-22 and Ti Gr-12 in the acidic brine at 60°C and 80°C. However, this mark appears to be a surface discoloration and no actual crevice was detected.

Keywords: Galvanic corrosion, carbon steel, nickel-base alloy, titanium alloy, galvanic current, galvanic potential, area ratio, electrode distance, pH, and temperature effect.

INTRODUCTION

The waste package design for nuclear spent fuel and vitrified defense high-level waste that is being considered for viability assessment for the potential underground repository at Yucca Mountain, will consist of two layers of metal barriers. The outer cylindrical barrier, made of corrosion-allowance material, will be thicker than the inner-barrier, which will be fabricated from corrosion-resistant material. The thick corrosion-allowance outer-barrier is being designed to degrade very slowly resulting from the potential repository environment, while providing galvanic protection to the thinner corrosion-resistant inner-barrier.

The precise method of fabricating these waste packages has not yet been finalized. Two alternate approaches are currently being considered. One approach is to fabricate the two barriers separately, and then to shrink-fit the inner-barrier inside the outer-barrier by slipping the inner-container into the outer one, which will be expanded by heating prior to insertion of the inner container. Although this technique may provide sufficient bonding between these two barriers, it is likely that there will be gaps at some locations where breached liquid may be trapped, thus causing galvanic interaction between the two barriers. Under this scenario, the more electronegative outer-container material may undergo increased corrosion attack while protecting the more noble inner-container material. The alternate method is to fabricate these waste packages from clad or weld-overlay materials. In this case, the outer corrosion-allowance metallic barrier will have a thin layer of corrosion-resistant clad material inside, thus eliminating the gap between the two barriers while still providing galvanic protection to the more noble material.

In view of these waste package design considerations, an investigation was pursued to evaluate the corrosion behavior of galvanically coupled candidate inner and outer container materials. A previous study(1) performed at the Lawrence Livermore National Laboratory (LLNL) had evaluated the galvanic corrosion behavior of several candidate container materials. This paper presents the results of more recent galvanic corrosion tests involving only a few key materials in environments relevant to that of the potential repository.

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials tested include nickel-chromium-molybdenum (Ni-Cr-Mo) alloy C-22; a titanium (Ti)-base alloy Ti Gr-12; and a carbon steel (A 516 steel). The chemical compositions of these materials are given in Table 1. Test specimens in the form of a thin square plate (5.08 cm x 5.08 cm x 0.317 cm) were fabricated from heat treated materials by a qualified vendor. No additional thermal treatments were given to these specimens prior to their testing. Tests were performed in deaerated acidic and neutral brines containing 5 weight percent (wt%) NaCl at 30°C, 60°C and 80°C. Acidification was done by adding sulfuric acid to the brine. The pH were in the vicinity of 2.75 and 6.40 for acidic and neutral brines, respectively. The rationale for selecting these environments was provided elsewhere.(2)

Galvanic contact between A 516 steel and a corrosion-resistant alloy was established by short circuiting them through use of a computer controlled EG&G Model 283 potentiostat which acted as a zero resistance ammeter. Cell connections were made using A 516 steel as an anode, and a corrosion-resistant alloy as a cathode. Modified EG&G Pyrex cells were used to contain these two working electrodes and a Ag/AgCl reference electrode. The experimental setup was shown elsewhere.(1) Two different exposed surface areas (1.0 and 2.0 cm^2) of the cathode (alloy C-22 or Ti Gr-12) and anode (A 516 steel) were used to perform experiments at A/C area ratios of 2, 1 and 0.5, respectively. Separating distance of either eight or twelve cm were maintained between the anodic and the cathodic member of each couple to evaluate the effect of electrode distance. A controlled temperature liquid (water/propylene glycol mixture) bath maintained the desired test temperature. Tests were performed for periods generally ranging from five to seven days. Both measured galvanic current and galvanic potential were monitored as a function of time until a steady state or equilibrium value was attained.

The specimens were cleaned with distilled water, acetone and ethanol prior to their being exposed to the test environment. The pH of the test solution was measured at room temperature both before and after each experiment. At the conclusion of each test, the specimen was cleaned with a bristle brush, distilled water and ethanol. The cleaned specimen was then visually examined followed by an optical microscopic examination to evaluate the extent of damage in both electrodes resulting from galvanic interaction.

RESULTS AND DISCUSSION

The results of optical microscopic examination indicate that A 516 steel coupled to either alloy C-22 or Ti Gr-12 suffered from general corrosion and crevice corrosion at all three test temperatures, the extent of damage being more pronounced in the acidic brine, and at the higher temperatures. Formation of shallow pits was also observed on the exposed surface of a few A 516 steel specimens. Some of the A 516 steel specimens tested at higher temperatures were covered with thick brown/black corrosion products which were not analyzed. Appearances of surfaces of A 516 steel galvanically coupled to Ti Gr-12 in the acidic brine at 30°C, 60°C and 80°C are illustrated in Figure 1. As to the surface characteristics of the cathodic members (alloy C-22 or Ti Gr-12) of the couples, only light crevice-like mark was noticed in both alloys at 60°C and 80°C. An interesting observation with these two alloys was that they were covered with black surface films at these temperatures, with the maximum amount of film being formed on Ti Gr-12 (Figure 2).

The excellent corrosion resistance of Ti alloys, which are known to exhibit active-passive transition behavior, is primarily due to the inert, tightly adherent protective oxide films (TiO_2) that cover their surfaces. Although the passive oxide film covering the Ti alloy surface is effective in avoiding or limiting hydrogen uptake, under certain conditions, hydrogen may be evolved on the alloy surface causing hydrogen embrittlement of the alloy.(3,4) Conditions that must be met for hydrogen attack to occur are: the generation of critical concentration of atomic hydrogen on the Ti alloy surface resulting from galvanic coupling, the exposure of the alloy surface at temperatures at which the hydrogen diffusion rate is significant, and the maintenance of solution pH at or below 3. A natural result of galvanic coupling is the evolution of hydrogen gas and the absorption of atomic hydrogen at the surface of the cathodic member while the anodic material (A 516 steel) undergoes dissolution. A temperature of 80°C has been cited(5) to be the critical temperature above which hydrogen diffusion through the TiO_2 film may be significant.

As mentioned earlier, Ti Gr-12 coupled to A 516 steel showed adherent black surface film at 60°C and 80°C even though its surface was shiny at 30°C. It is possible that hydrogen evolution and its absorption at 30°C was quite insignificant, and the hydrogen gases formed at 60°C and 80°C were precipitated on the Ti alloy surface as black hydride films which did not exert any detrimental effect on its corrosion behavior. Efforts will be made in future to analyze the hydrogen content or the thickness of hydride layer formed on the surface of Ti Gr-12. The iron content in the corrosion product resulting from the dissolution of A 516 steel in the acidic brine is most frequently in the form of ferric ions (Fe^{+3}). The thicker black films formed on the surface of Ti Gr-12 at higher temperatures may also be related to the formation of increased concentration of Fe^{+3} with increasing temperature.

Factors such as pH and temperature, which can influence the corrosion of a single metal, can also control galvanic corrosion involving two or more dissimilar conducting materials. Furthermore, factors such as A/C area ratio and distance between coupled materials are unique to galvanic corrosion behavior of many metals and alloys. The effect of A/C area ratio on the steady-state galvanic current for A 516 steel/alloy C-22 couple at different temperatures is illustrated in Figures 3 and 4. The beneficial effect of higher A/C area ratio on the corrosion rate of carbon steel coupled to alloy C-22 in the acidic brine is clearly evident from these data. Under this condition, only slight galvanic effects are produced because of enhanced polarization of the cathodic member. On the other hand, at lower A/C area ratios (<1), the anodic current density on the more active material will be extremely high, thus leading to more pronounced galvanic attack. A similar effect of A/C area ratio on galvanic current was noticed for A 516 steel/Ti Gr-12 couple (Figure 5) confirming observations by other investigators.(6,7)

As to the effect of distance, dissimilar metals galvanically coupled in close proximity usually suffer greater from galvanic corrosion than those that are separated by larger gaps. The distance effect is dependent on the conductivity of the solution since the path of current flow is the primary consideration. The results obtained from the present study suggest that no significant difference in the galvanic current was experienced by A 516 steel when coupled to either alloy C-22 or Ti Gr-12 with separation distance of eight or twelve cm between them.

The effect of temperature on the steady-state galvanic current for A 516 steel coupled to Ti Gr-12 and alloy C-22, respectively in the acidic brine at three different A/C area ratios is shown in Figures 6 and 7. The equilibrium current resulting from the galvanic interaction between the anodic and cathodic members of these couples was increased at higher test temperatures when immersed in the acidic brine. The temperature effect on the corrosion rate of carbon steel is consistent with the results of another study(8) which showed that the amount of atomic hydrogen absorbed in the acidic solution was increased as the temperature was increased from 38°C to 90°C.

Figure 8 shows the effect of pH on the equilibrium galvanic current for A 516 steel/alloy C-22 couple as functions of temperature and A/C area ratio. Results indicate that, as anticipated, the galvanic current was reduced in the neutral brine. The higher galvanic current in the acidic brine may be the result of acceleration of cathodic reaction due to high concentration of hydrogen ions.

Finally, efforts were made to correlate the measured steady-state galvanic potential to different environmental and experimental variables studied in the present investigation. However, no consistent pattern was observed.

SUMMARY AND CONCLUSIONS

A zero resistance ammeter method was used to evaluate the galvanic corrosion susceptibility of candidate nuclear waste package container materials. A 516 steel, a corrosion-allowance material, was coupled to corrosion-resistant materials, such as alloy C-22 and Ti Gr-12 in an acidic salt solution at 30°C, 60°C and 80°C. A few tests were also conducted in a neutral brine. A/C area ratios of 0.5, 1 and 2 were used with a separating distance of either eight or twelve cm between the two electrodes. The steady-state galvanic current and galvanic potential were measured as functions of A/C area ratio, electrode distance, pH, and temperature. The significant conclusions drawn from this study are summarized below.

- A 516 steel suffered from general corrosion and crevice corrosion while galvanically coupled to either alloy C-22 or Ti Gr-12, the extent of attack being more pronounced at higher test temperatures. Shallow pits were also observed in a few test specimens.

- Alloy C-22 and Ti Gr-12 were covered with adherent black surface films in the acidic brine at 60°C and 80°C. Both alloys were immune to corrosion attack.

- The steady-state galvanic current was reduced with increasing A/C area ratio for both couples, confirming observations by other investigators. But no significant effect of electrode separation distance on galvanic current was observed.

- In general, the equilibrium galvanic current in the acidic brine was enhanced at higher test temperatures possibly due to the increased concentration of absorbed atomic hydrogen.

- The galvanic current was reduced at a neutral pH compared to that in the acidic brine. This pH effect may be attributed to the formation of reduced concentration of hydrogen ions in the neutral solution.

- No consistent pattern on the effects of A/C area ratio, electrode separation distance, pH, and temperature on the steady-state galvanic potential were noticed for either of the couples tested.

ACKNOWLEDGMENT

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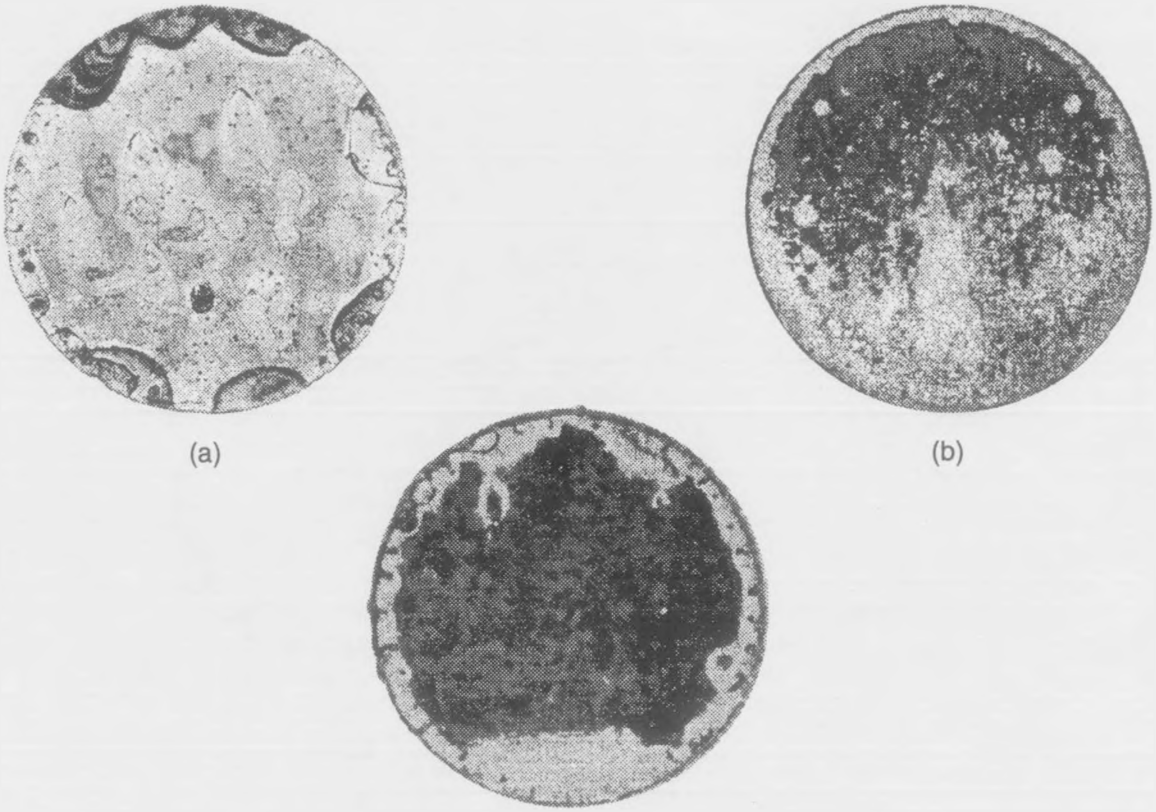
Table 1

Chemical Composition of Materials Tested (wt%)

Material	Lot #	C	Mn	P	S	Si	Ni	Cr	Mo	Fe	Ti	Al	Cu	Others
A 516 Steel	K963	0.14	0.72	0.01	0.021	0.25	0.02	0.04	0.01	Bal	---	0.047	0.04	Nb: 0.001 V: 0.002
Alloy C-22	H157	0.005	0.34	0.02	0.01	0.05	Bal	22.10	13.30	4.50	---	---	---	W: 2.90 Co: 1.30
Ti Gr-12	E133	0.018	---	---	---	---	0.82	---	0.29	0.11	Bal	---	---	---
Ti Gr-12	M273	0.02	---	---	---	---	0.69	---	0.33	0.06	Bal	---	---	O: 0.15; N: <0.01 H: <0.001



(a)

(b)

(c)

Figure 1. Surface Appearance of A 516 Steel Coupled to Ti Gr-12 in an Acidic Brine (pH = 2.74) at an Anode-to-Cathode Area Ratio of 2:1 with an Electrode Distance of 8 cm at (a) 30°C, (b) 60°C, (c) 80°C.

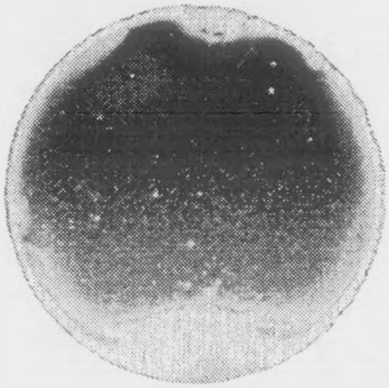


Figure 2. Surface Appearance of Ti Gr-12 Coupled to A 516 Steel in an Acidic Brine (pH = 2.74) at an Anode-to-Cathode Area Ratio of 2:1 with an Electrode Distance of 8 cm at 80°C.

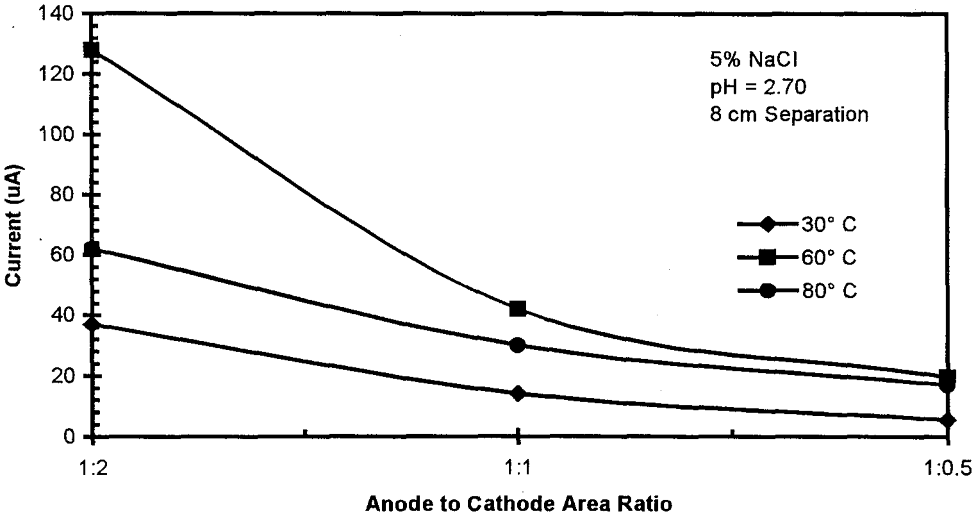


Figure 3. Galvanic Current versus Anode-to-Cathode Area Ratio for A 516 Steel/Alloy C-22 Couples with a Separation Distance of 8 cm

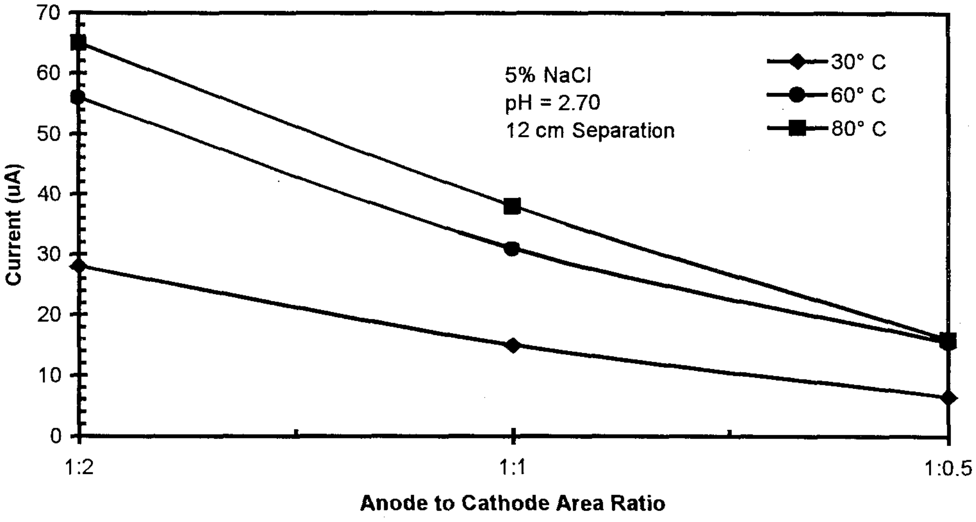


Figure 4. Galvanic Current versus Anode-to-Cathode Area Ratio for A 516 Steel/Alloy C-22 Couples with a Separation Distance of 12 cm

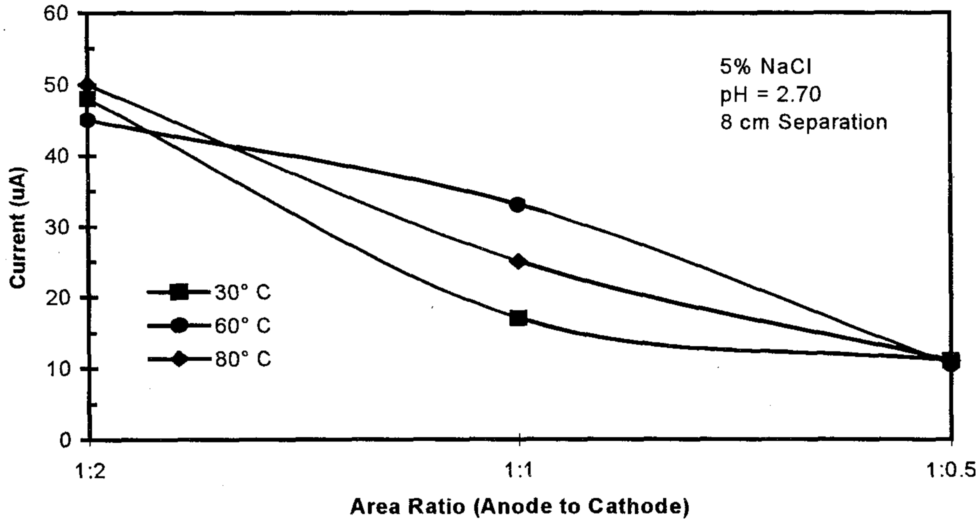


Figure 5. Galvanic Current versus Anode-to-Cathode Area Ratio for A 516 Steel/Ti Gr-12 Couples with a Separation Distance of 8 cm

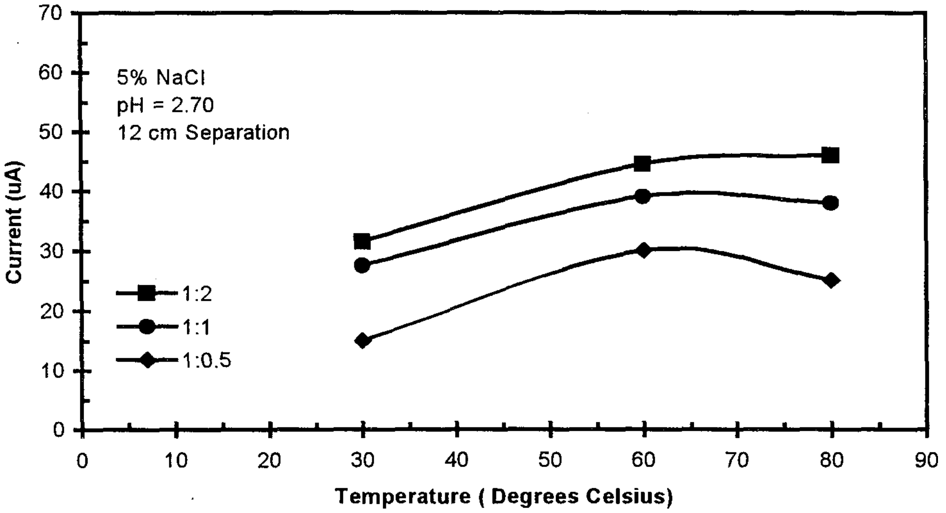


Figure 6. Galvanic Current versus Temperature for A 516 Steel/Ti Gr-12 Couples with a Separation Distance of 12 cm

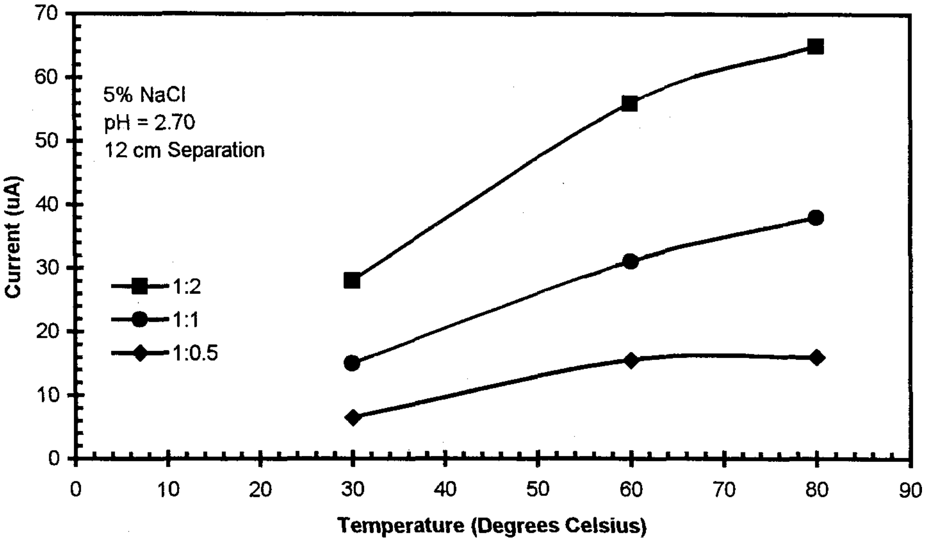


Figure 7. Galvanic Current versus Temperature for A 516 Steel/Alloy C-22 Couples with a Separation Distance of 12 cm

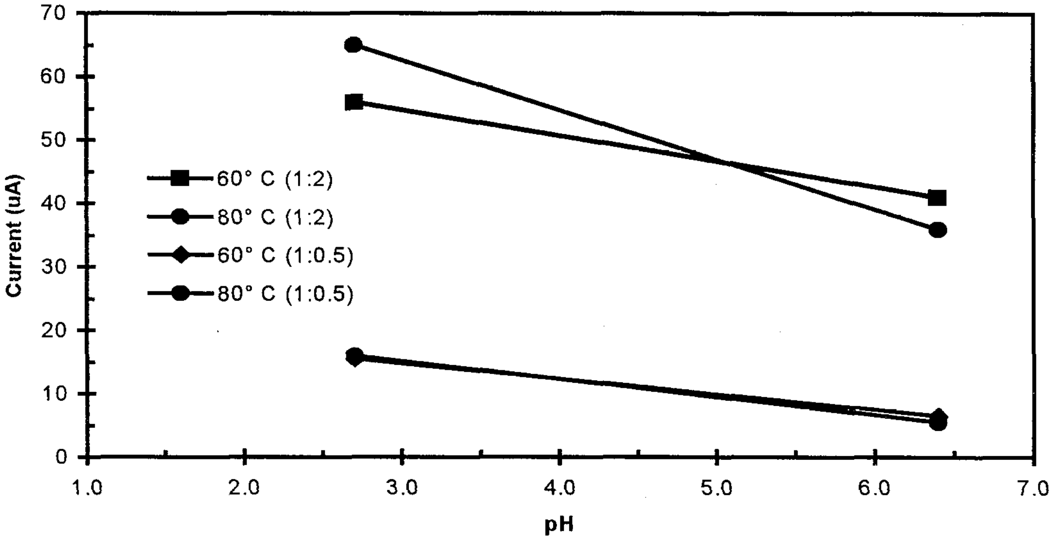


Figure 8. Galvanic Current versus pH for A 516 Steel/Alloy C-22 Couples with a Separation Distance of 12 cm