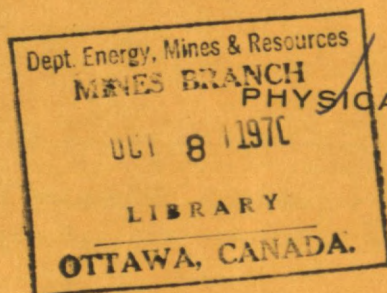


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DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*THE EFFECT OF pH ON
THE FREE-CORROSION CHARACTERISTICS
OF 18% Ni (250) MARAGING STEEL
IN 3.5% NaCl SOLUTIONS*



B. C. SYRETT

PHYSICAL METALLURGY DIVISION

JULY 1970

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THE EFFECT OF pH ON THE FREE-CORROSION CHARACTERISTICS
OF 18% Ni (250) MARAGING STEEL IN 3.5% NaCl SOLUTIONS

by

B. C. Syrett*

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ABSTRACT

The free-corrosion characteristics of 18% Ni (250) maraging steel in 3.5% NaCl solutions have been studied, using tests in which the ratio of specimen area to solution volume was high (about $0.15 \text{ cm}^2/\text{ml}$). Initial pH values lay in the range of about 1 to 12, and both aerated and de-aerated solutions were employed.

The observations were consistent with the established behaviour of many iron alloys in aqueous media.

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EFFET DU pH SUR LES CARACTÉRISTIQUES DE CORROSION
ORDINAIRE DE L'ACIER MARTENSITIQUE À 18 p. 100 DE
Ni (250) DANS DES SOLUTIONS À 3.5 p. 100 DE NaCl

par

B. C. Syrett*

RÉSUMÉ

L'auteur a étudié les caractéristiques de corrosion ordinaire de l'acier martensitique à 18 p. 100 de nickel (250) dans des solutions à 3.5 p. 100 de NaCl, au moyen d'essais dans lesquels le rapport entre la surface de l'échantillon et le volume de la solution était élevé, soit environ 0.15 cm^2 par ml. La valeur initiale du pH se situait entre 1 et 12, et l'auteur a employé des solutions aérées aussi bien que non aérées.

Les observations concordaient avec le comportement classique de nombreux alliages de fer en milieu aqueux.

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INTRODUCTION

As part of a study of the stress-corrosion and hydrogen-embrittlement cracking properties of 18% Ni (250) maraging steel, it was considered appropriate to make a rapid assessment of the free-corrosion characteristics of this steel in 3.5% NaCl solutions of various pH. This report describes the tests performed and how the corrosion processes were influenced by de-aeration of the corrodent.

EXPERIMENTAL PROCEDURES

Material and Specimen Dimensions

The chemical composition of the 18% Ni maraging steel used in this work is shown in Table 1. Two types of specimens were used, one for electrochemical potential measurements and one for weight-loss tests. The latter was simply a rectangular block, approximately 0.375 x 0.5 x 0.5 in., with its surfaces abraded with 120-grade silicon carbide paper. Specimens for potential measurements were twice as large, approximately 0.375 x 0.5 x 1.0 in., and an iron wire was spot-welded to the end of one of the largest faces to provide an electrical contact. Glass tubing protected the wire from corrosion during the test, the joint between tubing and metal being sealed with Lepage's epoxy glue. All exposed surfaces were abraded with 120-grade silicon carbide paper. Both types of specimen were degreased in carbon tetrachloride, using ultrasonic agitation.

TABLE 1

Chemical Composition* of the 18% Ni (250) Maraging Steel

<u>Element</u>	<u>% By Wt</u>
C	0.018
Si	0.04
Mn	0.04
S	0.008
P	0.004
Al	0.06
Ti	0.40
B	0.003
Mo	4.46
Co	7.92
Ni	19.22
Zr	0.01
Ca	0.003

* Analysis at the Department of Energy, Mines and Resources.

Weight-Loss Tests

Each specimen was exposed to 55 ml of 3.5% NaCl solution, the initial pH being adjusted to the desired value, in the range 1.1-11.9, by making small additions of either NaOH or HCl. The corrodent was contained either in a 150-ml glass beaker covered with a watch glass, or in a stoppered 60-ml glass bottle fitted with a gas bubbler and air lock. The latter corrosion-cell was used when the corrodent was to be flushed with high-purity nitrogen to remove the absorbed oxygen. In either case, the specimen, previously degreased and weighed, was allowed to rest on the bottom of the cell during the two-day test period.

De-aerated solutions were prepared in advance of the testing period by bubbling nitrogen through the test solution for at least 0.5 hour. The pH of the corrodent was measured, and after flushing with nitrogen for a further 10 minutes, the steel specimen was introduced into the test cell. It was considered likely that small quantities of oxygen were carried into the cell as an absorbed layer on the specimen surface; also, no special precautions were taken to ensure that the nitrogen, which flushed the corrodent before and during the test period, was completely oxygen-free. However, the so-called de-aerated solutions undoubtedly had a substantially lower oxygen content than those solutions exposed to the laboratory air. All tests were performed at room temperature, i. e., about 25°C (77°F).

The progress of film formation and hydrogen evolution on the specimen surface was noted at appropriate intervals during the two-day test. The specimens were then removed from the corrodent, and loose corrosion products washed off with water, before they were dried. The specimens were then reweighed, and the corrosion rate was calculated. The final pH's of the test solutions were also measured, and qualitative tests were conducted to detect the presence of ferrous or ferric ions in solution*.

Potential Measurements

Electrochemical potential measurements were made only in aerated solutions of various pH. Because the specimens used for these measurements were larger than those used in the weight-loss tests, the volume of corrodent was increased so that ratio of metal surface-area to volume of corrodent remained approximately the same as in weight-loss tests (about 0.15 cm²/ml). Consequently, the specimen was suspended in 120 ml of the test solution, such that the upper surface of the steel specimen was the same distance (0.5 in.) from the waterline as in the weight-loss tests.

* (1) Potassium ferrocyanide solution forms a dark-blue precipitate in the presence of ferric salts, but in the presence of ferrous salts produces a bluish-white precipitate; (2) potassium ferricyanide solution produces a dark-blue precipitate in the presence of ferrous salts, but with ferric salts no precipitate is formed, though the solution is coloured brown or green; (3) potassium thiocyanate gives no reaction with ferrous salts, but with ferric salts a blood-red solution is formed.

All potentials were measured at room temperature with respect to a saturated calomel electrode, by means of a Keithley 601 electrometer; the output from this high-impedance electrometer was fed into a Texas Instruments Servo/Riter II potentiometric chart recorder, so that the potential was recorded continuously over the two-day test period.

The pH of the corrodent was measured before and after testing so that the pH changes in these tests could be compared with those in the weight-loss tests.

RESULTS

Corrosion Rate

The rate of corrosion of the steel in aerated and de-aerated salt solutions is shown in Figure 1 as a function of initial pH. It is apparent that in solutions of pH 3 or less, the corrosion rate is unaffected by the presence of oxygen, but that at higher pH's the aerated solutions are much more corrosive than the de-aerated solutions. In either type of solution, the rate of corrosion increased rapidly as the pH of the test solution was decreased below 3.0; the corrosion rate in a pH 1.0 solution, for instance, would be about thirty times the rate at pH 3.0.

Above pH 4.0, the corrosion rate remained fairly constant in aerated solutions, although the rate did decrease a little at higher pH values. In de-aerated solutions of pH 6.0 or above, there was no measurable corrosion.

Changes in pH of Test Solution

Figure 2 summarizes the pH changes which occurred in the testing period. The acidity of all aerated solutions tended towards a pH of 7.4; those which were initially more acid than pH 7.4 had a higher final pH, but solutions initially more alkaline than pH 7.4, generally decreased in pH during the test. However, the solution initially of pH 12.0 changed little, if at all, during the testing period.

De-aerated solutions also changed acidity, but, whereas aerated solutions tended towards pH 7.4, de-aerated solutions tended towards pH 9.2. Again, the pH of the most alkaline solutions (pH 11.0 and above) changed very little during the tests.

The maximum pH increase occurred in solutions initially about pH 2.0, whereas the maximum pH decrease occurred in solutions initially about pH 10.0.

The pH change during a test is of particular importance when the formation of surface films, the evolution of hydrogen and the production of ferrous and ferric ions are being considered, because all are very dependent on the pH of the solution.

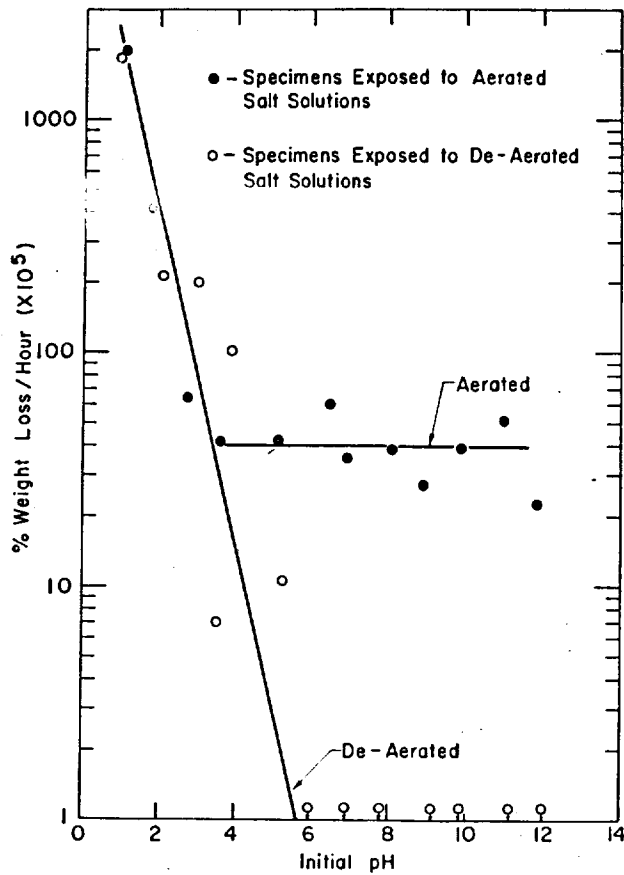


Figure 1. The effect of initial pH on the corrosion rate of 18% Ni (250) maraging steel in aerated and de-aerated 3.5% NaCl solutions.

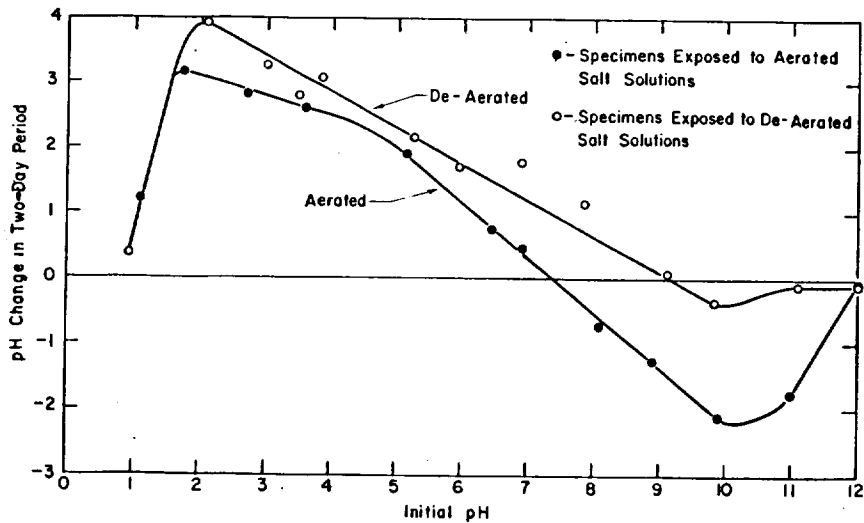


Figure 2. The pH changes which occurred in the two-day testing period in (a) aerated solutions, (b) de-aerated solutions of 3.5% NaCl.

Surface Films (a) Aerated Solutions

Observations made during the first few hours of testing, when the pH's of the aerated solutions were close to their initial values, indicated that the character of the surface corrosion products was dependent on the pH of the test solution: in solutions of pH 2.7 or less, a black film was formed, and in solutions of pH 3.6 to 9.9 there were small areas of black film which were covered by a loosely adherent red rust. In aerated solutions of pH 11.0 to 11.8 specimens were essentially film-free. However, the pH changes which occurred during a test were sometimes responsible for a change in the surface corrosion reactions. Thus, specimens exposed to solutions initially of pH 1.8 or 2.7 quickly formed a thin black film over most of the surface (including the lower surface, in contact with the bottom of the glass beaker), but during the second day the pH had increased sufficiently for rusting to commence. The final pH values of these two solutions were 4.9 and 5.5 respectively, well above the apparent lower pH limit for rusting (about pH 3.5-4.0). The most acid solution used in these tests was initially pH 1.1 and finally pH 2.2, so it was not surprising that only the black surface film was observed, this completely covering all six sides of the specimen after the first day.

The upper pH limit for rusting in aerated solutions appears to be about pH 10.0 and, in line with this, the specimen exposed to the solution, initially of pH 11.0 but finally of pH 9.25, was film-free for the first day, but showed a little rusting during the second day. The pH change in this solution was probably promoted by the crevice corrosion which occurred between the bottom of the specimen and the beaker: after only 1 hour of testing, a green liquid was seen to be diffusing from this crevice, and black film formation and rusting first developed near this region. The pH 11.8 solution showed little or no change in pH during the testing period, and all visible surfaces of the specimen were film-free. However, as for all specimens exposed to aerated salt solutions, part of the surface in contact with the glass beaker developed a black film, but no red rust. Therefore, it would appear that concentration cells of one type or another were being produced within the crevice and were allowing the formation of films which were not typical of those formed in the bulk solution.

When rusting occurred on a specimen, it was always preceded by the formation of black spots. These spots rarely exceeded an area of 0.003 sq in. before rust developed and concealed further growth of the black spots. In a solution initially of pH 5.2, for instance, black spots formed during the first 5 minutes and increased in area thereafter; after 5 hours of exposure, rusting had progressed to the point where the black corrosion product was no longer visible, but when the poorly adherent rust was brushed off the specimen surface after two days, it was apparent that lateral growth of the adherent black areas had been continuing.

The top surface of the specimen, nearest the waterline and the oxygen supply, normally rusted in preference to the vertical sides of the specimen. The sides appeared to be acting as the cathodes in the rusting reaction, and often were completely unattacked during the two-day testing period.

Surface Films (b) De-Aerated Solutions

In the majority of cases, there was no surface film visible on specimens exposed to de-aerated solutions of pH 3.0 or higher. Occasionally, one or two black spots formed early in the test, but they were considered to have formed only because oxygen was introduced into the system as an absorbed layer on the specimen surface. Red rust was never observed in these solutions.

At the lower pH values, a black film formed on the surface, the rate of formation increasing with decreasing pH. At pH 0.9, though no film was observed after a 4-hour exposure, after one day a black film covered the entire specimen. After one day in the pH 2.1 and pH 3.0 solutions, respectively, large and small patches of a black film formed on the steel surface.

Some specimens, exposed to solutions of pH 3.5-6.7, showed signs of a black corrosion product on the surface in contact with the glass beaker, even though the other surfaces were essentially film-free.

Hydrogen Evolution

Bubbles of hydrogen were observed to form on the surface of specimens immersed in aerated and de-aerated solutions more acid than pH 3.8. However, as tests proceeded, the pH values of these acid salt-solutions increased, and, except in solutions initially about pH 1.0, visible hydrogen evolution ceased before the end of the two-day testing period. In all cases, cessation of visible hydrogen evolution was associated with final pH values in excess of 4.9, whereas sustained hydrogen evolution was associated with final pH values of 2.3 or less.

The rate of evolution increased as the pH decreased, but it could not be described as "vigorous" in any of the solutions tested. It was observed that hydrogen was liberated only after a delay time of 5 to 60 minutes; this delay time may reflect the time required to break down air-formed films.

Production of Ferrous and Ferric Ions

Both the potassium ferrocyanide test and the sodium thiocyanate test failed to show the presence of ferric ions in any solution. Ferrous ions were detected with potassium ferricyanide in aerated and de-aerated solutions initially of pH 3.5 or below.

Potential Measurements

Figure 3 shows the electrochemical potential changes occurring during the first 3 hours of testing in aerated solutions of various initial pH. The potential was recorded over the entire two-day testing period, but it became clear that the pH changes, which occurred during the test, acted as a potential "equalizer": in all but the most acid solution and most alkaline solution tested, the potential after 30 hours was $-545 (\pm 25)$ mV, and after 48 hours was $-550 (\pm 25)$ mV. In the solution initially of pH 0.94, the potential after 48 hours was -361 mV, not significantly more active than the values shown in Figure 3. In the alkaline solution of pH 11.10, the potential remained within 10 mV of -490 mV after the first 10 hours of testing. The pH changes occurring during these tests were in close agreement with those shown in Figure 2 for aerated solutions. Reference to Figure 2 indicates that the final pH of all but the most acid solution and most alkaline solution used in the potential measurement tests lay in the range 5.0-8.0. It would appear, therefore, that within this range, at least, the potential is fairly independent of pH. The pH changes occurring during the first 3 hours of testing are probably small, so Figure 3 would also support the suggestion that the free-corrosion potential is relatively insensitive to pH over a fairly wide range. In fact, the curves shown in Figure 3 are similar over the pH range 4.00-9.94.

Maraging steel specimens immersed in solutions of pH 2.93 or pH 11.10 exhibit relatively rapid drops in potential, to more active values, during the first 3 hours (see Figure 3). On the other hand, in solutions of pH 2.02 and pH 0.94, the potential remains almost constant over the same period, this being indicative of steady state corrosion conditions.

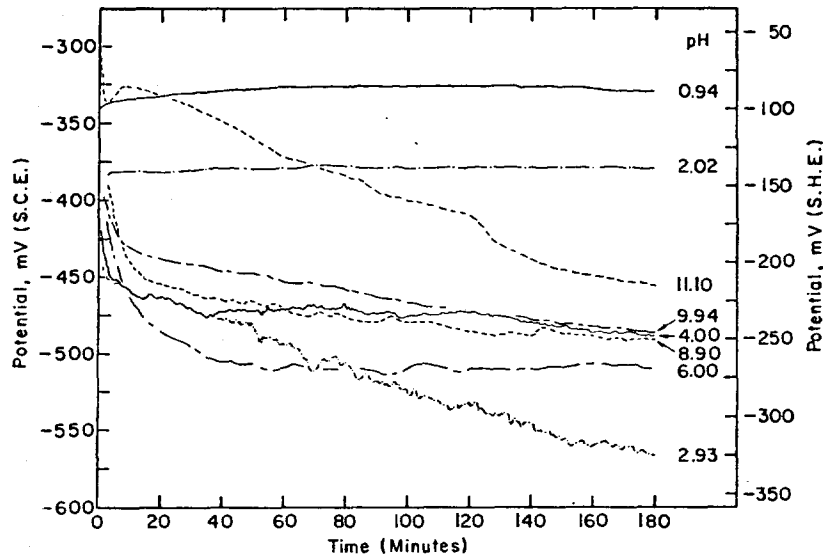
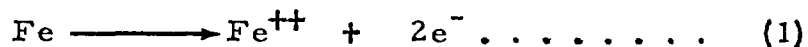


Figure 3. The effect of initial pH on the free-corrosion potential of 18% Ni (250) maraging steel in aerated 3.5% NaCl solution.

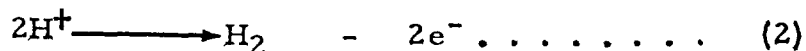
DISCUSSION

Although most of the results have been reported quantitatively, the absolute values are open to criticism: the presence of a crevice between specimen and corrosion cell, for instance, undoubtedly provided conditions which were not typical of those on the visible surfaces of the specimen. However, these tests were designed to give a rapid assessment of the corrosion properties of this steel in salt solutions of various pH, and, within these terms, the results allow valid comparisons.

The results are consistent with the established behaviour of many iron alloys in aqueous media: the important reactions are described below in simplified form. At anodic areas on the metal surface, ferrous ions go into solution:

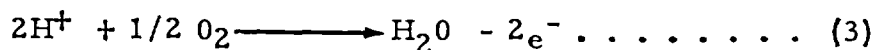


This reaction occurs rapidly in most corrodents, and the rate of corrosion is normally controlled, not by this reaction, but by the concomitant cathodic reaction. In de-aerated solutions, the cathodic reaction



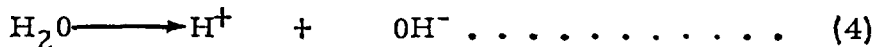
occurs fairly rapidly in acids, but proceeds very slowly (or not at all) in solutions more alkaline than about pH4. This behaviour is reflected in the apparent absence of corrosion in the de-aerated solutions more alkaline than pH6, shown in Figure 1. Reaction (2) is also the dominant cathodic reaction in aerated solutions of pH4 and below; thus, the corrosion rate in these acid solutions is independent of their oxygen content, as is illustrated in Figure 1.

In more alkaline solutions which do not favour reaction (2), the cathodic reaction may be accelerated if the solution has access to a supply of oxygen, e.g. the atmosphere. The cathodic reaction then depends only on how quickly oxygen can diffuse to the metal surface to allow the following reaction to occur:

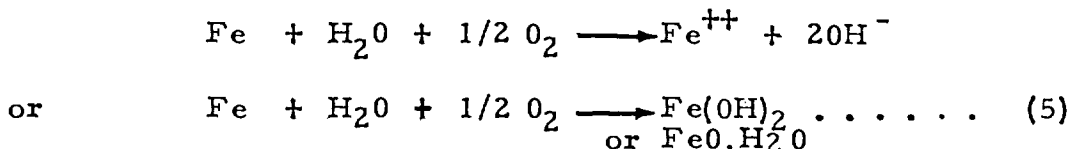


The corrosion rate in nearly neutral and alkaline aerated-solutions is thus independent of pH, as the results in Figure 1 would indicate.

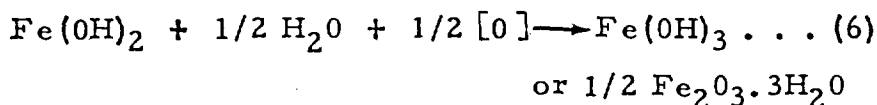
The dissociation of water may be written as



Combining equations (1), (3) and (4) gives



The ferrous hydroxide, $Fe(OH)_2$ (or hydrated ferrous oxide, $FeO.n H_2O$) acts as a barrier layer, next to the steel surface, through which oxygen must diffuse. The corrosion reaction continues to produce ferrous hydroxide, so the surface of the metal is always in contact with a saturated solution of the hydroxide. Regardless of the pH of the bulk solution in the range pH4 - 10, the alkaline solution of ferrous hydroxide at the metal surface has a pH of about 9.5. Solid ferrous oxide soon begins to form on the metal surface; though white when pure, it is normally observed as a green or black film because of incipient oxidation by air. Further oxidation of the oxide may occur at the surface to produce hydrated ferric oxide or ferric hydroxide, according to the reaction:



Hydrated ferric oxide comprises most of the very familiar red "rust". The rust film forming on the surface of steel in aerated solutions will normally

consist of three layers of iron oxides in different states of oxidation: between the inner layer of hydrated ferrous oxide and the outer layer of ferric oxide, described above, there is usually an intermediate layer of black hydrated magnetite, $\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$.

In solutions of pH 4-10, very little ferric hydroxide is required to saturate the solution, so most of it precipitates as rust. The saturated ferric oxide solution has a pH of about 7, so it is not surprising that all aerated test solutions, initially of pH 4-10, tended towards neutral pH values. The corrosion occurring in de-aerated solutions, in this pH range, was minimal, and probably entirely due to the minute volumes of oxygen introduced into the system. The tendency for the pH to change towards a value of about 9 is, no doubt, indicative of the production of a saturated ferrous hydroxide solution. In both aerated and de-aerated solutions more acid than pH4, the pH increase during a test is due, in part, to the loss of hydrogen ions by their reduction to hydrogen gas.

The solubility of ferric ions in aqueous solutions drops rapidly with increasing pH, and negligible quantities are present, in solutions more alkaline than pH10. The solubility of ferrous ions also drops with increasing pH, but in acid solutions of pH4 and below, the solubility is appreciable. These statements are in agreement with the present results, in that the presence of ferric ions was not detected in any of the test solutions, and ferrous ions were detected only in solutions of pH 3.5 and below.

In aerated solutions having initial pH values of about 11 and 12, the steel can passivate and corrosion can be reduced to an almost negligible rate. However, in the present work, the expected low corrosion rate in these alkaline solutions was not observed, and corrosion occurred at about the same rate as in solutions of pH 4-10. Such departure from the expected behaviour could undoubtedly be attributed to accelerated attack in the crevice between the specimen and the glass beaker. The green liquid observed in this area, in the aerated pH 11.0 solution, might have obtained its colour because ferrous ions (Fe^{++}) or dihypoferrite ions (HFeO_2^-) were present in solution, but it is equally likely that nickelous ions (Ni^{++}) were responsible.

Metallographic examination of many of the specimens showed that corrosion attack was always more or less uniform; localized attack, in the form of pitting, intergranular corrosion, etc., was never observed.

CONCLUSION

The corrosion processes occurring in 18% Ni(250) maraging steel, immersed in 3.5% NaCl solution, are essentially similar to those occurring in many iron alloys in aqueous media.

ACKNOWLEDGEMENT

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