

Naval Surface Warfare Center

Carderock Division

West Bethesda, MD 20817-5700

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Survivability, Structures, and Materials Department

Technical Report

Mechanism of Corrosion Product Growth on Nickel Aluminum Bronze/Ammonia or Seawater Interface: Modeling Based on Chemical Reaction Kinetics: Part-2

by

A. Srinivasa Rao



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Contents

	<u>page</u>
Contents	iii
Figures.....	iv
Tables.....	ix
Administrative Information	x
Acknowledgements.....	x
Executive Summary	1
Introduction.....	2
Experimental Procedure.....	2
Materials and Testing	2
Theory	3
Results and Discussion	9
Conclusion	15
References.....	17
Distribution	1

Figures

	<u>page</u>
Figure 1. Schematic representation of the electrochemical reaction versus reaction time plots.	18
Figure 2. Normalized change in the (%) weight of the sample versus reaction time profiles for nickel aluminum bronze samples treated with 10% ammonia solution.	19
Figure 3. Normalized change in the (%) weight of the sample versus reaction time profile for nickel aluminum bronze samples treated with 20% ammonia solution.	19
Figure 4. Normalized change in the (%) weight of the sample versus reaction time profile for nickel aluminum bronze samples treated with 50% ammonia solution.	20
Figure 5. Normalized change in the (%) weight of the sample versus reaction time profile for nickel aluminum bronze samples treated with seawater.	20
Figure 6. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with 10% ammonia solution.	21
Figure 7. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with 20% ammonia solution.	21
Figure 8. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with 50% ammonia solution.	22
Figure 9. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with seawater.	22
Figure 10. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH ₄ OH for 1 day.	23
Figure 11. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH ₄ OH for 2 days.	23
Figure 12. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH ₄ OH for 4 days.	24
Figure 13. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH ₄ OH for 7 days.	24
Figure 14. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH ₄ OH for 11 days.	25

Figure 15.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 14 days.....	25
Figure 16.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 17 days.....	26
Figure 17.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 21 days.....	26
Figure 18.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 24 days.....	27
Figure 19.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 28 days.....	27
Figure 20.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 35 days.....	28
Figure 21.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 42 days.....	28
Figure 22.	(%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.	29
Figure 23.	(%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.	29
Figure 24.	(%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.	30
Figure 25.	(%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.	30
Figure 26.	(%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.	31
Figure 27.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 1 day.	31
Figure 28.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 2 days.....	32
Figure 29.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 3 days.....	32
Figure 30.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 7 days.....	33
Figure 31.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 11 days.....	33

Figure 32.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH ₄ OH for 14 days.....	34
Figure 33.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH ₄ OH for 17 days.....	34
Figure 34.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH ₄ OH for 21 days.....	35
Figure 35.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH ₄ OH for 24 days.....	35
Figure 36.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH ₄ OH for 28 days.....	36
Figure 37.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH ₄ OH for 35 days.....	36
Figure 38.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH ₄ OH for 42 days.....	37
Figure 39.	(%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH ₄ OH solution.	37
Figure 40.	(%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH ₄ OH solution.	38
Figure 41.	(%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH ₄ OH solution.	38
Figure 42.	(%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH ₄ OH solution.	39
Figure 43.	(%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH ₄ OH solution.	39
Figure 44.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 1 day.	40
Figure 45.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 2 days.....	40
Figure 46.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 4 days.....	41
Figure 47.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 7 days.....	41
Figure 48.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 11 days.....	42

Figure 49.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 14 days.....	42
Figure 50.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 17 days.....	43
Figure 51.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 21 days.....	43
Figure 52.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 24 days.....	44
Figure 53.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 28 days.....	44
Figure 54.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 35 days.....	45
Figure 55.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH ₄ OH for 42 days.....	45
Figure 56.	(%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH ₄ OH solution.	46
Figure 57.	(%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH ₄ OH solution.	46
Figure 58.	(%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH ₄ OH solution.	47
Figure 59.	(%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH ₄ OH solution.	47
Figure 60.	(%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH ₄ OH solution.	48
Figure 61.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 1 day.....	48
Figure 62.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 2 days.	49
Figure 63.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 4 days.	49
Figure 64.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 7 days.	50
Figure 65.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 11 days.	50

Figure 66.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 14 days.	51
Figure 67.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 17 days.	51
Figure 68.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 21 days.	52
Figure 69.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 24 days.	52
Figure 70.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 28 days.	53
Figure 71.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 35 days.	53
Figure 72.	x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 42 days.	54
Figure 73.	(%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.	54
Figure 74.	(%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.	55
Figure 75.	(%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.	55
Figure 76.	(%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.	56
Figure 77.	(%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% seawater.	56
Figure 78.	Scanning electron micrographs obtained from nickel aluminum bronze samples after reaction with (A) 10%, (B) 20%, (C) 50% NH ₄ OH solution and (D) seawater. Oxide characteristics (A) significant and tenacious corrosion, (B) severe corrosion, (C) dark brown corrosion product with severe “mud cracking” and (D) mild corrosion.	57
Figure 79.	Schematic diagram of oxide growth on nickel aluminum bronze in seawater and or ammonia solution. Different colors represent different oxides such as copper oxide, nickel oxide and aluminum oxide.	58
Figure 80.	Schematic diagram depicting how the iron aluminate particles(kappa phase) are being exposed with time due to the corrosion of NAB sample surface in NH ₄ OH or seawater.	59
Figure 81.	Schematic diagram of how the iron aluminate particles(kappa phase) are being weakened due to the corrosion of NAB matrix in NH ₄ OH or seawater and under applied stress.	60

Tables

	<i><u>page</u></i>
Table 1. The rate of oxide formation and the order of the reaction estimated from the weight change measurement for nickel aluminum bronze in 10%, 20%, and 50% ammonia solution, and sea water.	61
Table 2. The rate of oxide formation and the order of the reaction estimated from the open circuit potential (OCP) values for nickel aluminum bronze in 10%, 20%, and 50% ammonia solution, and sea water.....	61
Table 3. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in 10% ammonia solution.	62
Table 4. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in 20% ammonia solution.	62
Table 5. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in 50% ammonia solution.	63
Table 6. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in seawater.	63

Administrative Information

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Executive Summary

In order to develop a model of the corrosion process based on the chemical reaction kinetics in materials, this investigation was undertaken. A mathematical model relating the process parameter (viz. the weight change, the measured open circuit potentials (versus SCE) and the change in the structure of the material) and the reaction time was developed. This model was tested with nickel aluminum bronze samples in NH_4OH solution and seawater, and the kinetics parameters such as, the rate constant and the order of reaction, were determined.

The nickel aluminum bronze (NAB) samples were exposed to seawater and 10%, 20% and 50% NH_4OH solutions for up to 46 days. The weight change, the open circuit potentials (versus SCE) were measured, and the x ray diffraction patterns were obtained from all the corroded samples. The weight change data and the open circuit potentials were fed into the reaction kinetics based model and the oxide characteristics were determined. The results suggest that the kinetic parameter such as the order of reaction for the corrosion process that was predicted by feeding all three sets of data conclude that the corrosion of NAB in NH_4OH solution or seawater is a diffusion controlled process. The kinetics of the fast reaction stage is controlled by the availability of NAB sample surface for corrosion. The slow chemical reaction stage is very complex. The complexity is perhaps due to the nucleation and growth of complex and mixed oxides/hydroxides. During the corrosion process the rate of corrosion of iron is the highest and the corrosion of the nickel is the slowest.

Introduction

Process modeling is an efficient method to understand a specific process and optimize the process variables. Modeling requires first training a sequence of logical realities and then deriving proper conclusions as dependable mathematical relationships. For example, during simple corrosion of a metal, although one observes the formation of an oxide layer on the metal surface, several other properties such the potential, structure and mechanical strength also changes. Since these properties are related to the chemistry and physics of the metal, it is possible to correlate all the inter-related properties. In order to ascertain some fundamental relationships between the rate of corrosion and the order of the chemical reaction and the nature of the oxide film, the experimental database was obtained from systematic corrosion studies.

The aim of the present investigation is to study the corrosion kinetics of nickel aluminum bronze in ammonia solution and or seawater and model the process. This purpose of the present investigation is to test whether the developed kinetics process model can predict the growth and morphology of corrosion products.

Experimental Procedure

Materials and Testing

During the present investigation three different sets of experiments were conducted and the results were used to model the corrosion process. The experimental measurements were the determination of weight change, the change in the open circuit potential (OCP) and the change in the structure of the material during corrosion of nickel aluminum bronze (NAB) in ammonia or seawater.

The weight change measurements were made by measuring the weight of NAB samples both before and after the corrosion. The samples were weighed and were inserted into the beaker containing either ammonia solution or seawater. The NAB samples were removed from the solution and quickly dried in a vacuum desiccator. The samples were weighed and the change in the weight of the NAB sample due to corrosion was determined. From the weight change, the normalized weight change was calculated.

The open circuit potential (OCP) of NAB samples in ammonia solution or seawater was determined by measuring the potential of NAB against standard silver calomel electrode. Roughly, 1.5 cm X 1 cm X 0.5 cm blocks of samples were cut from as received nickel aluminum bronze plate. The NAB samples were fused with a long insulated copper wire. In addition, all the sample surfaces were coated with a non conducting epoxy resin except one surface (1.5 cm X 1 cm). This ensures that only this NAB face will be corroding. The sample was introduced into a beaker containing ammonia or seawater solution. A graphite rod was used as a counter electrode and the potential was measured against standard silver calomel electrode. The observed potential was recorded as a function of corrosion time.

The change in the structure of the nickel aluminum bronze was measured using x-ray diffraction method. A Sintag XDS-2000 x-ray diffractometer with a $\text{CuK}_{\alpha 1}$ source at 8048 eV, - 2.5 FWHM was used during this investigation. The x-ray energy and the current were 35 KV, and 30 mA respectively. The NAB samples were subjected to corrosion in ammonia solution or seawater. The samples were removed and quickly dried in a vacuum desiccator. The samples were mounted on the x-ray diffraction unit and the structure was recorded as a function of the angle of incidence (2θ).

During the present analysis 10%, 20%, and 50% ammonia solution and simulated seawater was used as the corrosion medium. The simulated seawater was prepared using ASTM standard procedure. For convenience, all the studies in simulated seawater were labeled as in seawater. All the experiments were conducted for about 45 days.

Theory

In general, it can be hypothesized that as the electrochemical reaction progresses, the reaction products continue to grow (Figure 1). While the change in the metal surface concentration that is actively taking part in the electrochemical process has a finite functionality (i.e. the concentration changes with time), the concentration of the corroding media remains constant (the solution concentration remains unchanged or the change in the concentration ratio between the metal and solution is negligible). Under these conditions, the kinetics of the electrochemical process can be represented as follows [1]:

$$\begin{aligned} (dw/dt) &\propto - \{(dw_{\text{oxide}}/dt) \text{ or} \\ (dw/dt) &= A \{ (dw_{\text{oxide}}/dt) \end{aligned} \quad [1]$$

Where A is a constant.

The overall oxide formation depends upon the reaction kinetics and it will be fast at the beginning and very slow at the end. Generally the slow reaction stage is preceded with an intermediate reaction zone. The overall oxide formation during any one of the stages could depend upon several parameters such as direct chemical reaction with the metal surface, a reaction process that involves the diffusion of reacting liquid to reach the new metal surface, a reverse kinetics due to the reduction of formed metal oxide to the metal etc. All the above chemical processes influence the chemical reaction at any given time. Figure 1 shows a schematic diagram of an oxide buildup versus time plots that can be noted during a typical electrochemical reaction.

From Figure 1, it can be understood that the electrochemical process initially occurs at a faster rate (i.e. Stage I). Next the kinetics proceeds at a slower rate (Stage II), and eventually the reaction proceed at a much slower pace (Stage III) or sometimes, the reaction shows a trend that the reverse process is taking place.

During Stage I, the corrosion / electrochemical reaction proceeds at a faster rate as a result of unimpeded chemical reaction between metal and the corroding medium. Therefore, it can be assumed that during Stage I,

The overall chemical reaction rate at

$$\text{Stage I (Fast oxide growth stage)} \quad ((dw/dt)_{\text{Stage I}}) = A(w_1 / t_1) \quad [2]$$

The Stage II reaction represents a transitional zone between the fast and slow chemical reaction (i.e. a chemical zone in which a fast reaction process (i.e. first stage) begins to slow down and the oxide build up begins at a slower pace). In many reactions, the transitional zone may be small, so that this region can be ignored. However, for the process in which diffusion is important, the overall rate of reaction in Stage II is given as

$$\text{Stage II (Intermediate stage)} \quad (dw/dt)_{\text{Stage II}} = A (w_2 - w_1) / (t_2 - t_1) \quad [3]$$

During Stage III, a slow and steady chemical reaction continues with time and a continuous build up of a third oxide at a slower reaction rate can be seen. Therefore, the overall rate of reaction in Stage III is given as

$$\text{Stage III (Slow oxide buildup stage)} \quad (dw/dt)_{\text{Stage III}} = A (w_3 - w_2) / (t_3 - t_2) \quad [4]$$

In metallurgical processes such as the oxidation and reduction of metal alloys, the oxide growth imparts a steady effect on the electrical, mechanical, and or structural properties of the host metal. If the growth of oxide is uniform, the information (viz. electrical, mechanical and structural properties) obtained on the oxidized metal can be assumed to follow the kinetics of the oxidation process. For example, the rate of oxidation can be treated in terms of the normalized change in the structure or change in the mechanical properties or the electrical properties. Thus, the above relationships obtained for different stages can be rewritten as follows:

The overall rate of chemical reaction $\approx$ rate of change in the structure of material at Stage I

$$\text{Stage I (Fast oxide growth stage)} \quad (dS/dt)_{\text{Stage I}} = B (S_1 / t_1) \quad [5]$$

where B is a constant, and 'S' represents the normalized volume fraction and /or the area fraction of a newly formed structure as result of chemical reaction at time 't'.

The Stage II reaction represents a transition zone between the fast and slow chemical reaction (i.e. a chemical zone in which a fast reaction process (i.e. first stage) begins to slow down and the oxide buildup begins at a slower pace). It has to be emphasized that in many reactions, the transitional zone may be small, so that this region can be ignored.

The overall rate of reaction in Stage II is given as

$$\text{Stage II (Intermediate stage)} \quad (dS/dt)_{\text{Stage II}} = B (S_2 - S_1) / (t_2 - t_1) \quad [6]$$

During the third stage, a slow and steady chemical reaction continues with time and a continuous change in the structure of the host occurring at a slower reaction rate can be seen.

Therefore, the overall rate of reaction in Stage III is given as

$$\text{Stage III (Slow oxide buildup stage)} \quad (dS/dt)_{\text{Stage III}} = B (S_3 - S_2) / (t_3 - t_2) \quad [7]$$

A similar transformation based on the measured electrical properties (such as the measured change in the potential) can be equated to the kinetic parameters as follows: As the electrochemical reaction is progressing at the solid liquid interface (corrosion at the metal - solution interface), and if one assumes that an oxide layer forms and grows uniformly covering the entire surface of the metal surface, a constant change in the potential corresponding to the oxide buildup also occurs. Thus the normalized change in the potential (potential measure with

oxide film / the potential of the metal surface at the start of the electrochemical reaction) with time can be represented as:

$$(dV/dt) \propto - \{ (dV_{\text{oxide}}/dt) \} \text{ or } (dV/dt) = C \{ (dV_{\text{oxide}}/dt) \} \quad [8]$$

where C is a constant and 'V' represents the normalized volume fraction and /or the area fraction of a newly formed structure as result of chemical reaction at time 't'.

Therefore, the overall chemical reaction rate at Stage I, Stage II, and Stage III can be given as:

$$\text{Stage I (Fast oxide growth stage)} \quad (dV/dt)_{\text{Stage I}} = C (V_1 / t_1) \quad [9]$$

$$\text{Stage II (Intermediate stage)} \quad (dV/dt)_{\text{Stage II}} = C(V_2 - V_1) / (t_2 - t_1) \quad [10]$$

$$\text{Stage III (Slow oxide buildup stage)} \quad (dV/dt)_{\text{Stage III}} = C(V_3 - V_2) / (t_3 - t_2) \quad [11]$$

The above equations provide solutions for the rate of the oxide film growth and the magnitude of the film growth represents the severity of the corrosion. However, the rate parameter will not provide a detailed analysis of the type of the chemical reaction (viz. the number of components that are participating in the corrosion process, the nature of chemical reaction etc.).

For the oxide formation, an electrochemical reaction between the metal surface and the corroding medium (i.e. ammonia or seawater) must occur. Initially, the corroding liquid will not have any problem reacting with the metal. As the reaction continues, the oxide film may act as a barrier between the corroding medium and the un-reacted metal surface. This requires the diffusion of liquid through the oxide layer to reach the metal surface. If it is assumed that the volume of the corroding solution is very high and the concentration remains independent of the electrochemical reaction time, the kinetic parameters that control the corrosion process are the concentration of the metal species, the diffusion coefficient for the liquid flow through the oxide layers and the time. At the beginning, more metal is exposed to the solution, hence, the oxide forms very fast and the rate of oxide growth is represented as $(dw_{\text{fast oxide growth}}/dt)$. Once the metal surface is covered with oxide film, for the electrochemical reaction to continue, the corroding solution has to diffuse through the oxide layers and the rate of diffusion of this process is represented as $(dw_{\text{diffusion}}/dt)$. Once considerable oxide is formed, the reaction kinetics slows

down. This is because, the solution has to diffuse further into the oxide film to find new metal surface. Therefore, the oxide formation takes a longer time and the rate is very low. The slow rate of corrosion is represented as

$$(dw_{\text{slow oxide growth}}/dt).$$

The general characteristics of oxide that is formed at a faster rate will have oxide that is irregular, coarse, non-uniform, and loose and have a porous morphology. The oxide that is dominated by the diffusion process will have a porous morphology while the oxide that forms slowly will have a dense and uniform microstructure. The oxide formed as a result of fast reaction kinetics and the diffusion will have severe oxide cracking similar to that of mud cracking while the oxide that formed slowly with a slow diffusion of liquid will have uniform oxide with fine pores.

In order to understand the chemistry of the process, the original reaction kinetics equation, Equation 1 can be rewritten in terms of fast oxide growth, diffusion controlled oxide growth, and slow oxide growth as follows:

$$(dw_{\text{oxide}}/dt) = (dw_{\text{fast oxide growth}}/dt) + (dw_{\text{diffusion}}/dt) + (dw_{\text{slow oxide growth}}/dt) \quad [12]$$

During the chemical reaction, if the oxide is assumed to form primarily due to fast chemical reaction between the metal and the corroding liquid, and the time required for the diffusion of the liquid to find new metal surface is small, then the rate of oxide build due to diffusion and the rate of other processes can be ignored. Therefore the overall corrosion process can be rewritten as:

$$(dw_{\text{oxide}}/dt) = (dw_{\text{fast oxide growth}}/dt) \quad [13]$$

Similarly, if the oxide formation requires the diffusion of solution (through the pores of oxide formed) to find new metal surface, then the rates of other processes can be ignored. Therefore the overall corrosion process can be represented as:

$$(dw_{\text{oxide}}/dt) = (dw_{\text{diffusion}}/dt) \quad [14]$$

If the oxide formation requires long chemical reaction time and the rate determining step is only the slow chemical reaction, the other faster chemical processes (viz. diffusion etc.) can be ignored. Therefore during this process, the overall corrosion process is given as:

$$(dw_{\text{oxide}}/dt) = (dw_{\text{slow oxide growth}}/dt) \quad [15]$$

If it is assumed that the corroding liquid concentration remains constant and only the concentration of the metal species change with time, the integrated form of the corrosion process kinetic rate equations are given in terms of concentration (c) of the reacting species as:

$$\ln\{(dc_1/dt_1) / (dc_2/dt_2)\} = -n \{ \ln(c_1) - \ln(c_2) \} \quad [16]$$

$$\text{or } n = - [\ln\{(dc_1/dt_1) / (dc_2/dt_2)\} / \{ \ln(c_1) - \ln(c_2) \}] \quad [17]$$

where 'n' is the order of reaction, and 'c₁' and 'c₂' are the concentration of the reactants at time 't₁' and 't₂' and (dc₁/dt₁) and (dc₂/dt₂) are the slopes measured by drawing a tangent to the concentration versus time curves at ((t₁, c₁) and (t₂, c₂)) respectively. The value of n equals to 'one' means that the concentration of 'one species' is continuously changing with time while the value of n equals to *two* means that the concentration of two species are changing continuously. The value of 0.5 and 0 represents the chemical reaction that is controlled by the diffusion process and time dependent process respectively. A mixed value of 1.5 represents a chemical reaction in which the concentration of one species is changing continuously with the reaction time. In addition, the diffusion process also influences the chemical reaction.

Results and Discussion

Figures 2-5 show the normalized weight change versus corrosion time for nickel aluminum bronze (NAB) in 10%, 20%, and 50% NH_4OH solution, and seawater respectively. The results suggest that the chemical reaction between NAB and (10%, 20%, and 50%) NH_4OH solution and/ or seawater has two distinctive chemical reaction zones or stages [ie. (i). fast oxide growth stage and (ii). slow oxide buildup stage). From the above figures, qualitatively, it can be suggested that the (%) weight change for NAB in 50% NH_4OH is the maximum, while in sea water NAB lost the minimum amount of material due to corrosion. Using the chemical reaction kinetic equations (13-17), the normalized weight loss data was analyzed. The rate of the reaction and the order of reaction for the overall process were determined by drawing tangents for the normalized weight change versus reaction time plots at two concentrations and determining the slopes at those two concentrations. Similarly, the order of reaction for a given stage was determined by taking the slope at two concentrations within the limits of that stage.

The overall rate of the reaction, the rate of fast (first stage) reaction and the slow (second stage) reaction process and their corresponding order of the reactions are given Table 1. The results shown in Table 1 show that NAB sample lost 0.32% of material a day when treated with 50% NH_4OH solution and in 10% NH_4OH solution the corresponding rate of material lost is about 0.11% per day. The degradation of NAB in seawater is the slowest (rate $\sim 0.0077\%$ per day). The results also suggest that the overall chemical corrosion of NAB in NH_4OH or seawater is primarily a diffusion controlled process and the NAB concentration determines the chemical reaction during first stage. The slow oxide build up stage is a process that involves complex chemical reaction in which several reactants are actively participating.

In addition, the results in Table 1 suggest that the corrosion of NAB in 50% NH_4OH also involves a continuous change in the concentration of one component with time. Since the total solution concentration is very large compared to the solid sample surface that is exposed to the corrosion medium, it is possible that the rate of change of the concentration of metal (NAB) changes continuously during the chemical reaction in 50% NH_4OH solution.

Figures 6-9 show the normalized open circuit potential (OCP) change versus corrosion time for nickel aluminum bronze (NAB) in 10%, 20% and 50% NH_4OH solution, and seawater respectively. From the above figures, qualitatively, it can be suggested that the (%) potential

change for NAB appears to be independent of the corrosion medium (i.e. 10%, 20%, and 50% NH_4OH or seawater). Using the chemical reaction kinetic equations derived using the open circuit potentials as the time dependent variables [equations (9-11 and 16-17)], the normalized potential change data was analyzed; and the rate of reaction and the order of the reaction at each stage were determined. The overall rate of the reaction, the rate of fast (first stage) reaction and the slow (second stage) reaction process and their corresponding order of the reactions are given Table 2. The results shown in Table 2 show that the overall open circuit potential change of NAB samples in NH_4OH solution or seawater is $\sim 5\%$ per day. The results also suggest that the change in the open circuit potential of NAB due to chemical corrosion in NH_4OH or seawater is primarily due to a diffusion controlled corrosion process. In addition, the OCP results also suggest corrosion in 50% NH_4OH also changes the concentration of one component continuously with time. This conclusion is similar to that of the result that was arrived based on the weight change data analysis.

The Figures 10 - 21; 27-38; 44-55, and 61-72 represent the x-ray diffraction data obtained from nickel aluminum bronze (NAB) samples reacted with 10%, 20%, and 50% NH_4OH solution, and seawater respectively. The NAB samples with few exceptions were reacted with NH_4OH solution or seawater for 1, 2, 4, 7, 11, 14, 17, 21, 24, 28, 35, and 42 days. The results shown in the Figures (Figures 10 - 21; 27-38; 44-55 and 61-72) suggest that the peaks for NAB in NH_4OH solution or seawater are distinct and the peaks are very sharp and well defined. In order to quantify the ratio between the reactants and products the x ray data was reanalyzed.

The x ray diffraction patterns were analyzed as follows: First the information on the standard peaks for all elements in the NAB and their corresponding oxides and hydroxides was collected. By carefully analyzing the information, a specific “2 theta” angle was selected for each element / compound. A standard chart was prepared. The standard peaks then noted in all the x ray diffraction patterns. The area under those peaks was noted. The oxide/hydroxide formed during the corrosion process was obtained by adding the total areas of all metal oxides and the metal hydroxides. The fraction of oxides/hydroxides formed at a given time is determined by dividing the total oxides/hydroxides formed by the sum of the areas of both oxides/hydroxides and the metal species. Similarly, the amount of a specific oxide/hydroxide (viz. copper oxide/hydroxide) formed during corrosion was determined by dividing the total value of the copper oxides/hydroxides by the sum of the total oxides/hydroxides plus the total

area under the copper peak. The estimated oxides/hydroxides based on the x ray structural determination were plotted as a function of corrosion time.

Figure 22-26, 39-43, 56-60, and 73-77 show the total oxides/hydroxides, copper oxides/hydroxides, nickel oxides/hydroxides, aluminum oxides/hydroxides and iron oxides/hydroxides formed on the surface of NAB due to chemical reaction with 10%, 20%, 50% NH_4OH solution and seawater respectively. The results suggest that the oxides/hydroxide buildup on the surface constitutes two distinctive phases. That is the fast oxide growth followed by a slow oxide buildup.

Using the chemical reaction kinetic equations (5-7), the oxides/hydroxides formed on the surface data was analyzed. The rate of the reaction and the order of reaction for the overall process, fast reaction phase and slow reaction phase were determined and the results are given in Tables 3-6 respectively. The results suggest that the overall reaction process is close to that of the corrosion process of copper. That is, the formation of copper oxides/hydroxides determines the overall corrosion process of NAB. The results also suggest that while corrosion kinetics of nickel in NAB is the slowest, the degradation of iron is the highest. An increase in the concentration of NH_4OH accelerates the corrosion process. However, the overall process kinetics is independent of the corrosion medium. The overall oxide buildup and the oxide buildup during the fast reaction stage on NAB in seawater is the slowest and the slow kinetic process is very complex.

From the structural analysis data, it is clear that the corrosion rate of nickel aluminum bronze in NH_4OH solution and seawater is different for different metallic species. This is due to the difference in the rate of corrosion of the metallic components of the alloy.

The present generalized model that was proposed for a chemical reaction at the solid-liquid interface suggests that any interrelated / interdependent functionalities can be used to predict the order of the overall chemical reaction, and make some suggestions on the type of oxide morphology. The present results obtained from weight change measurements (Table 1), open circuit potential measurements (Table 2) and structure determination using x ray diffraction (Tables 3-6) suggest that within the experimental limitation, the overall chemical reaction between NAB/ NH_4OH solution and NAB/seawater is diffusion controlled. Similarly the process during fast chemical reaction is first order. The results also predict that the morphology of the oxide formed will be porous. While the oxide build up in 10%, 20% NH_4OH solution is

uniform, the oxide buildup in 50% NH_4OH will be very porous with severe mud cracking. Similarly the results also suggest that the oxide that formed on NAB due to corrosion in seawater will be very uniform, dense and porous. The examination of the oxide layer formed on NAB also concluded the same. Figure shows micrographs depicting typical oxide films on NAB that was reacted with 10%, 20% and 50% NH_4OH and seawater [2].

By comparing the results obtained from the structural analysis, the oxide/hydroxide formation on nickel aluminum bronze alloy, the overall process can be suggested schematically as follows: Consider a sample of NAB is in contact with seawater or ammonia solution and at the start of the chemical reaction ($t = 0$), only the air oxide is present and no corrosion products were formed on the sample surface (Figure 34 (A)). As the exposure time is increased, different metallic species form their oxides and deposit on the metal surface. The deposition is uneven and the surface is heterogeneous (Figure 34(B)). The surface potential will vary and tend to change significantly. As the reaction is continued, some of the deposited oxide may dislodge and fall off from the oxide layer, or re-dissolve into solution. Eventually the whole surface will be covered with an oxide layer (Figure 34(C) and (D)). The potential at this time will have a specified value. Furthermore, continued exposure of the oxide-coated alloy to the solution will exhibit a complex electrochemical process. That is, the rate of the depletion of different metallic species of the alloy will be different. This is because while one metal (viz. aluminum) may form a passive oxide layer, the other (viz. copper) may continue to deplete at much faster rate. Such a process will lead to higher copper based oxides/hydroxide/ oxy-hydrate formation than that of aluminum oxides/hydroxide formation. The result is that the measured surface oxide potential will correspond to more of copper based hydroxide than the aluminum based oxides. Such a selective metal dissolution process of the alloy will increase the scatter in the measured potentials. However, prolonged electrochemical reaction will establish a steady state condition and the scatter in the measured potentials will decrease. The final result will be a smooth measured potential versus reaction time plot that shows a clear and a systematic kinetics based chemical reaction trend.

The important result that is discernible from the structure based analysis is the higher rate of removal of iron from the NAB sample followed by aluminum, copper and nickel. While copper is the major constituent of the NAB, it is surprising to notice that at any given time, most of the oxide/hydroxide formation comes from iron. Iron is present in NAB sample as a fine

precipitate with aluminum. The iron aluminide forms a kappa phase and it is distributed throughout the NAB matrix. In addition aluminum also forms an inter-metallic nickel aluminide and it is also equally distributed throughout the NAB sample. Since the rate of removal of nickel is the lowest, it is reasonable to suggest that the aluminum oxide/hydroxide formed during corrosion process comes from the aluminum that is held with iron or aluminum in solution in the copper matrix.

If one assumes that the total aluminum depleted from NAB is from iron aluminide, the weight loss due to corrosion can be hypothesized in two ways. (1) The iron and aluminum in NAB continuously reacts with the corrosion medium (i.e. NH_4OH or seawater) and form their corresponding oxides/hydroxides on the sample surface; or (2) the matrix that surround the kappa phase is continuously is being reacted by the corroding liquid. As a result the adhesion and bonding of embedded kappa phase (FeAl) with the matrix (NAB) is lost. The net result is the removal of kappa phase particles. Figure shows a schematic diagram of how an embedded kappa phase particle can be removed as a result of the dissolution of the surrounding matrix phase.

If it is assumed that the formation and growth of iron aluminum oxides/hydroxides is only due to the chemical reaction between kappa phase and the corroding solution, the total sample surface must be covered with iron and aluminum oxides/hydroxides. However, the structural analysis indicates that the surface is also covered with significant amounts of copper and some nickel oxides/hydroxides. If one attributes the removal of kappa phase via the second mechanism, one would not expect to see the presence of large amounts of iron or aluminum oxides/hydroxides on the sample surface. It is possible that the removal of kappa phase constitutes both the dissolution of some iron aluminide to form iron and aluminum oxides/hydroxides (mechanism 1) and the removal due to the removal of matrix phase around the kappa particles (mechanism 2). If such complex processes are occurring in NAB/ NH_4OH or seawater systems, the degradation of the NAB should accelerate with the concurrent and continuous application of stress. Figure shows the schematic diagram of such process in which stress is applied during the corrosion of NAB.

It will be interesting to see whether, better information on the structure of different oxides can be obtained from oxidized sample surfaces exposed for longer periods and under stress. If such information can be generated from a systematic study, it will not only provide

electrochemical kinetic parameter data, but also validates the present conclusion that the depletion of aluminum is due to the removal of iron aluminide.

Conclusion

From the present analysis the following conclusions can be made:

1. The kinetic parameters of the corrosion process of nickel aluminum bronze (NAB) in NH_4OH or seawater can be determined from (i) weight change measurements, (ii) open circuit potential (OCP) measurements and structure that was determined using x ray diffraction.
2. The structure data not only provides the kinetic parameters not only for the overall corrosion process, but also provides an insight into how each metallic species corrodes with time.
3. The order of the reaction process predicted from all three measurements concluded that the corrosion of NAB in NH_4OH solution or seawater is a diffusion controlled chemical process.
4. In addition to the diffusion controlled reaction mode, the corrosion process of NAB in 50% NH_4OH solution is also a concentration dependent. (ie. The reaction depends upon the NAB sample surface available for corrosion).
5. Based on the order of reaction and rate of the reaction data, it can be suggested that the oxide/hydroxide formed on NAB during corrosion will be porous. The oxide from seawater corrosion will be more uniform and denser. The oxide formed in 10% NH_4OH solution will be porous and denser than the oxide formed in 20% NH_4OH solution. The oxide formed in 50% NH_4OH solution will be very loose and the oxide suffers from “severe mud cracking”.
6. From the weight gain measurements and the measurements based on the structure, it can be suggested that the rate of corrosion increases with an increase in the concentration of NH_4OH solution and the rate of corrosion is slowest in seawater.
7. However, the OCP measurements suggest that the overall reaction rate is independent of corrosion medium (NH_4OH solution or seawater). It is possible that the oxide layer being porous, the electrical potential was measured across the NAB but not NAB/NAB(oxides/hydroxides).
8. The results conclude that the slow chemical reaction process is controlled by the involvement of complex chemical processes. The complex chemical processes may be due to the formation and growth of complex oxides/hydroxides of all metallic species in the NAB.

9. The structure-based analysis concludes that the overall corrosion process is close to the overall corrosion process of copper.
10. The structure based analysis concludes that the amount of the oxide/hydroxide formation on NAB surface during corrosion in NH_4OH solution or seawater is as follows:

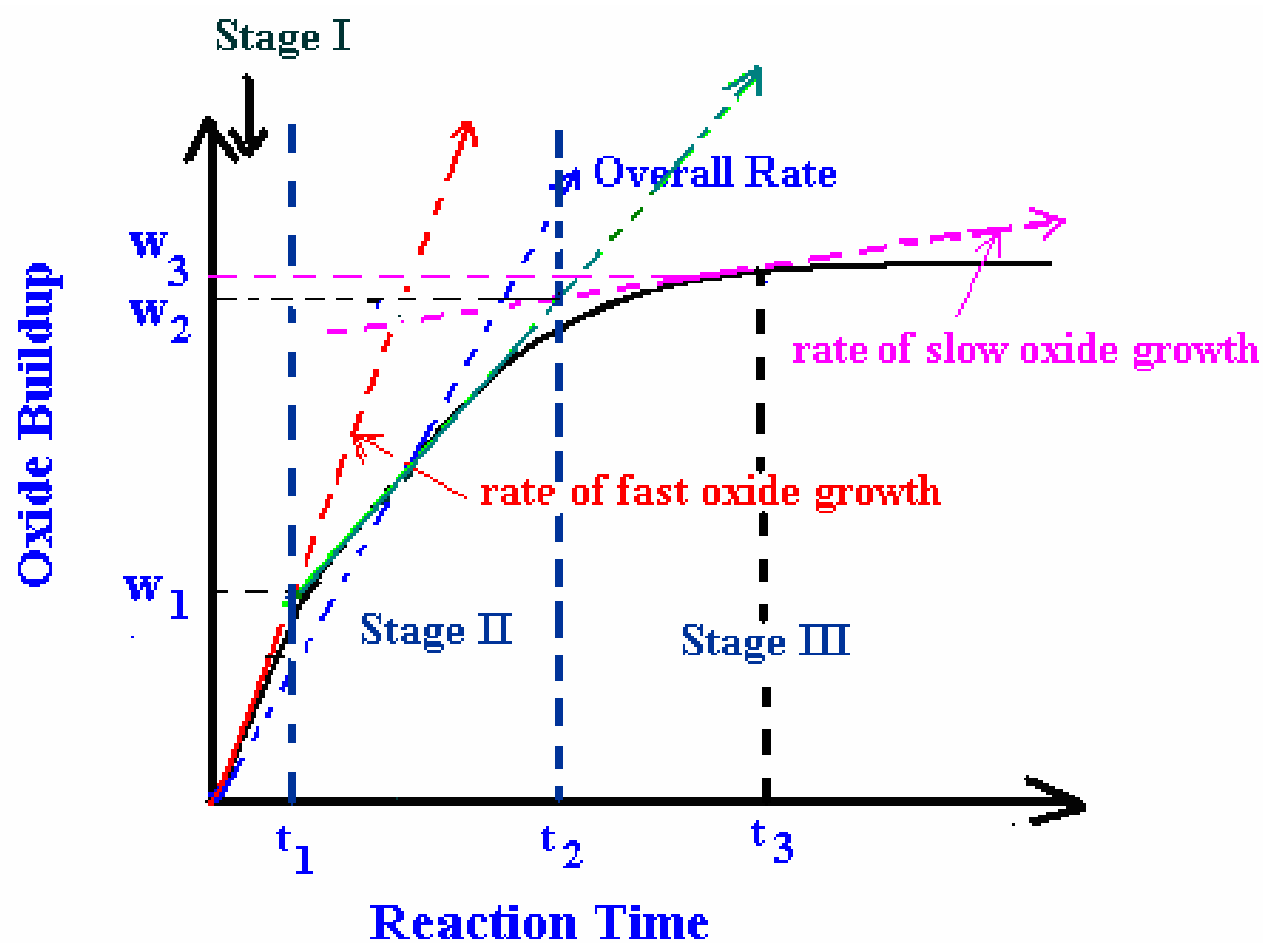
Iron > Aluminum > Copper > Nickel.

The results conclude that while iron is lost from NAB at a much faster rate, nickel corrodes at a much slower rate.

11. Although the aluminum can form a passive oxide film, the higher rate of removal of aluminum that was predicted from structural analysis may be due to the removal of iron aluminide particles. The possible mechanism for such a process is due to the loss of adhesion and bonding of iron aluminide with the NAB matrix. This loss may arise from the selective removal of copper from and near the kappa phase.

References

1. A. Srinivasa Rao, *Mechanism on the Corrosion Product Growth on Nickel Aluminum Bronze/Ammonia or Seawater Interface: Modeling Based on Chemical Reaction Kinetics*, NSWCCD-61-TR-2006/7, Naval Surface Warfare Center, West Bethesda, MD, April 2006.
2. C. Wong and K. L. Vasanth, "Initiation of Stress Corrosion Cracking Initiation in Nickel Aluminum Bronze", ONR FY 2004 End of Year Report, Arlington VA.



w_1 = weight change at the end of Stage 1 at t_1

w_2 = weight change at the end of stage 2 at t_2

w_3 = weight change at the end of stage 3 at t_3

Figure 1. Schematic representation of the electrochemical reaction versus reaction time plots.

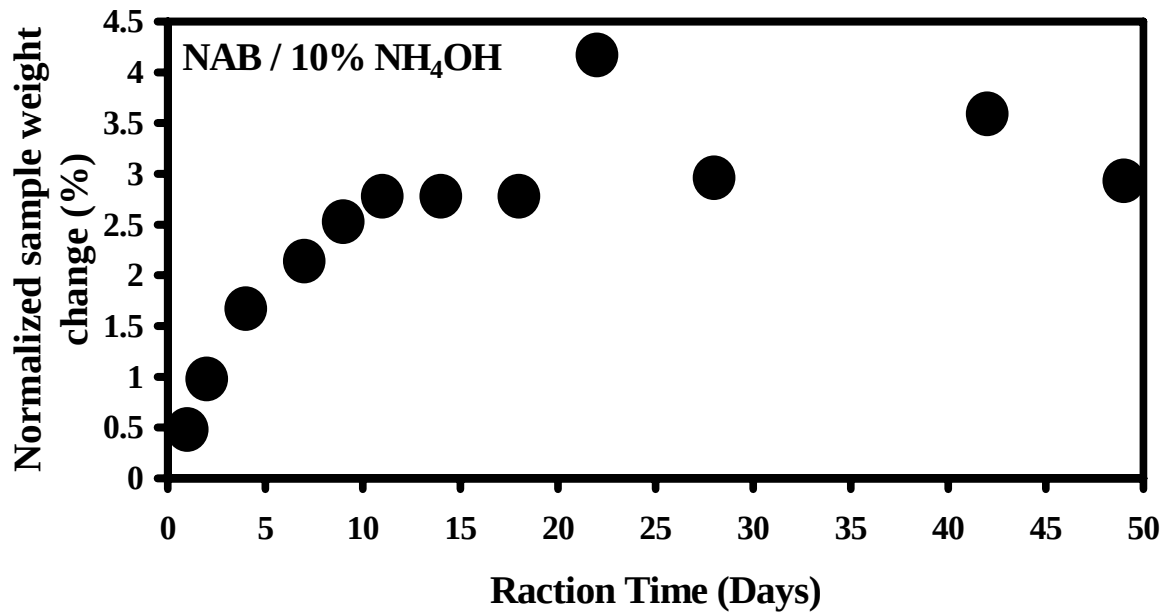


Figure 2. Normalized change in the (%) weight of the sample versus reaction time profiles for nickel aluminum bronze samples treated with 10% ammonia solution.

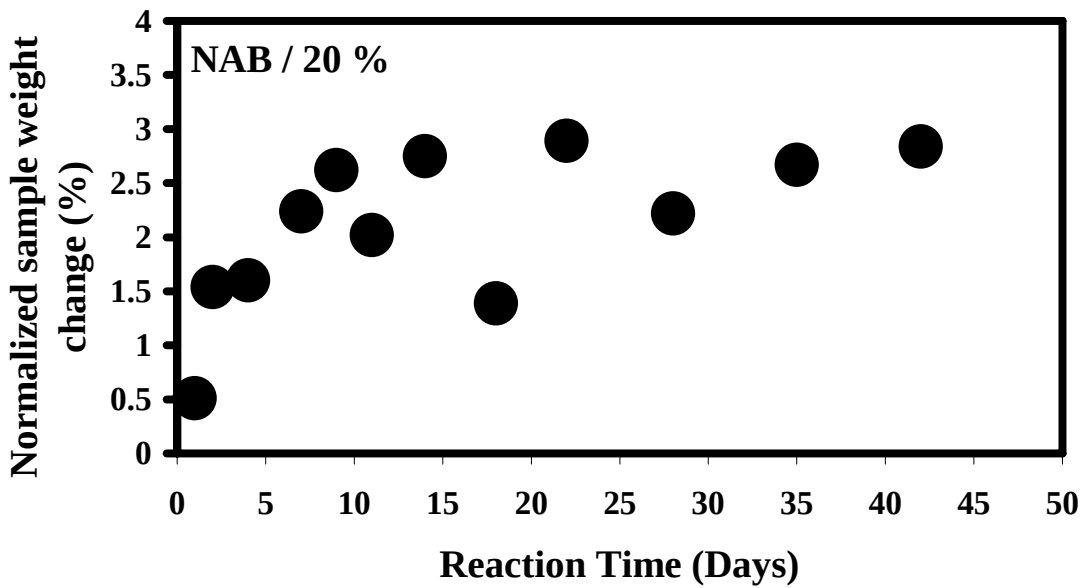


Figure 3. Normalized change in the (%) weight of the sample versus reaction time profile for nickel aluminum bronze samples treated with 20% ammonia solution.

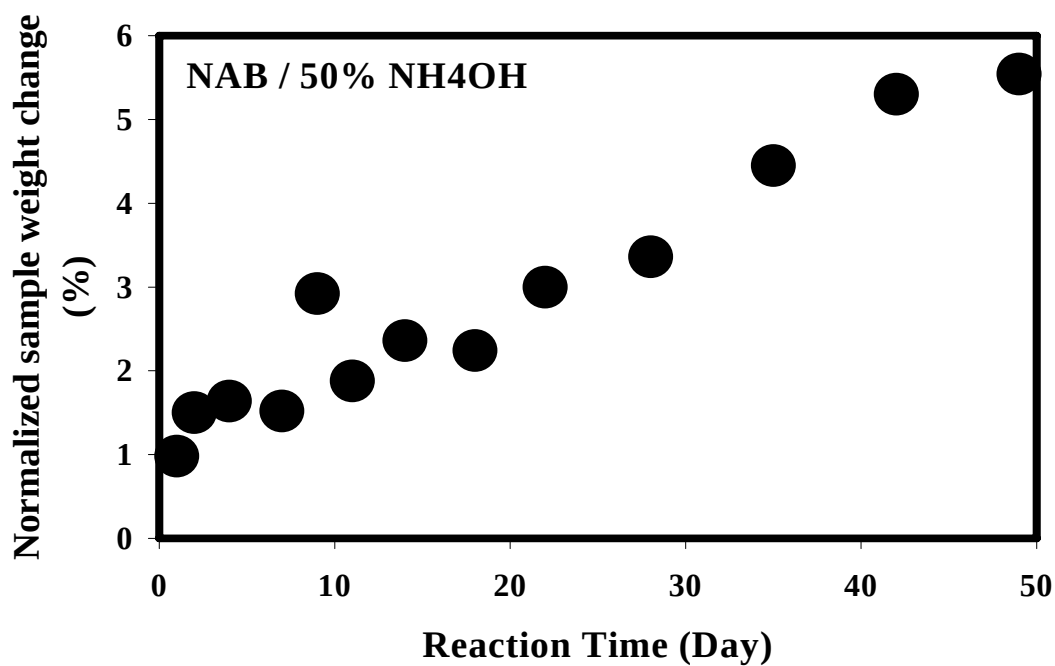


Figure 4. Normalized change in the (%) weight of the sample versus reaction time profile for nickel aluminum bronze samples treated with 50% ammonia solution.

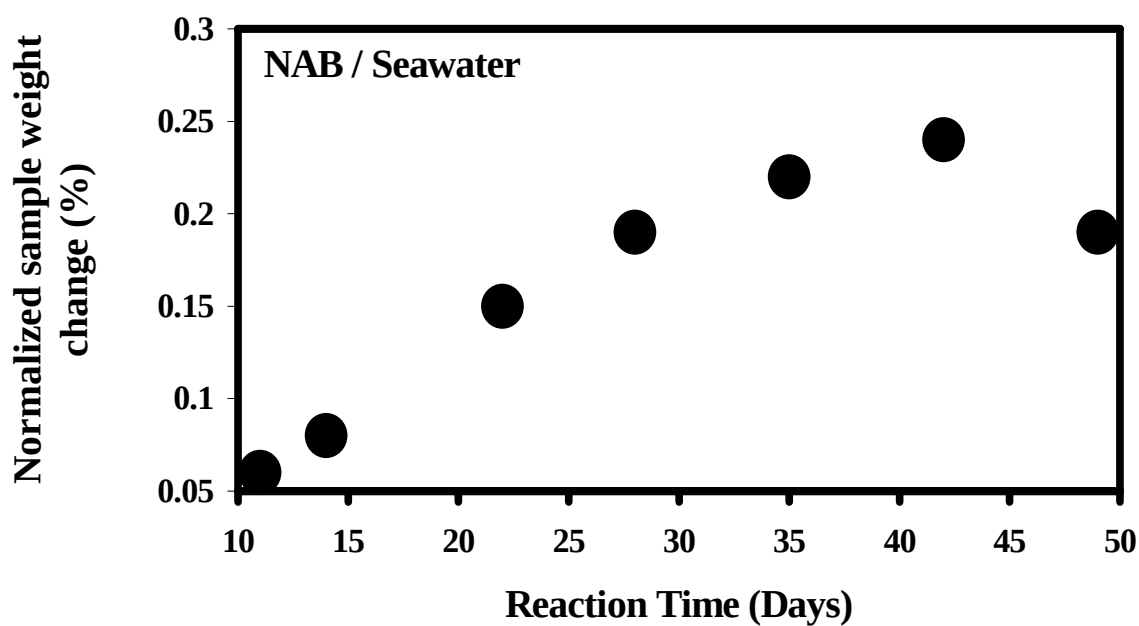


Figure 5. Normalized change in the (%) weight of the sample versus reaction time profile for nickel aluminum bronze samples treated with seawater.

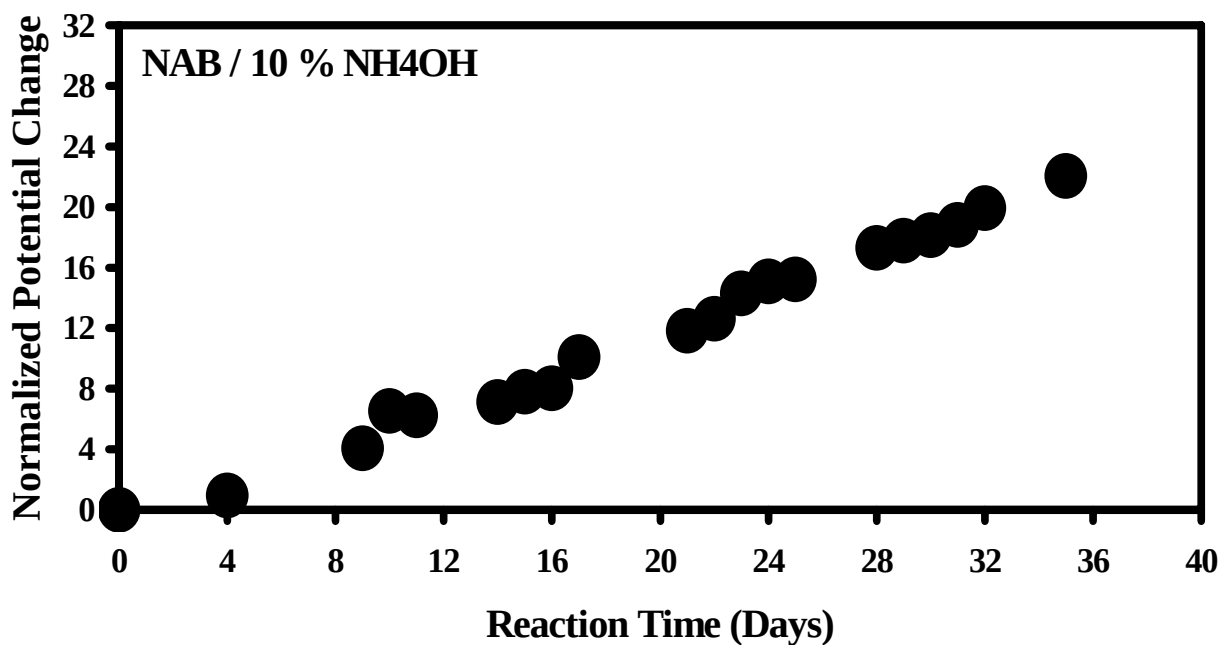


Figure 6. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with 10% ammonia solution.

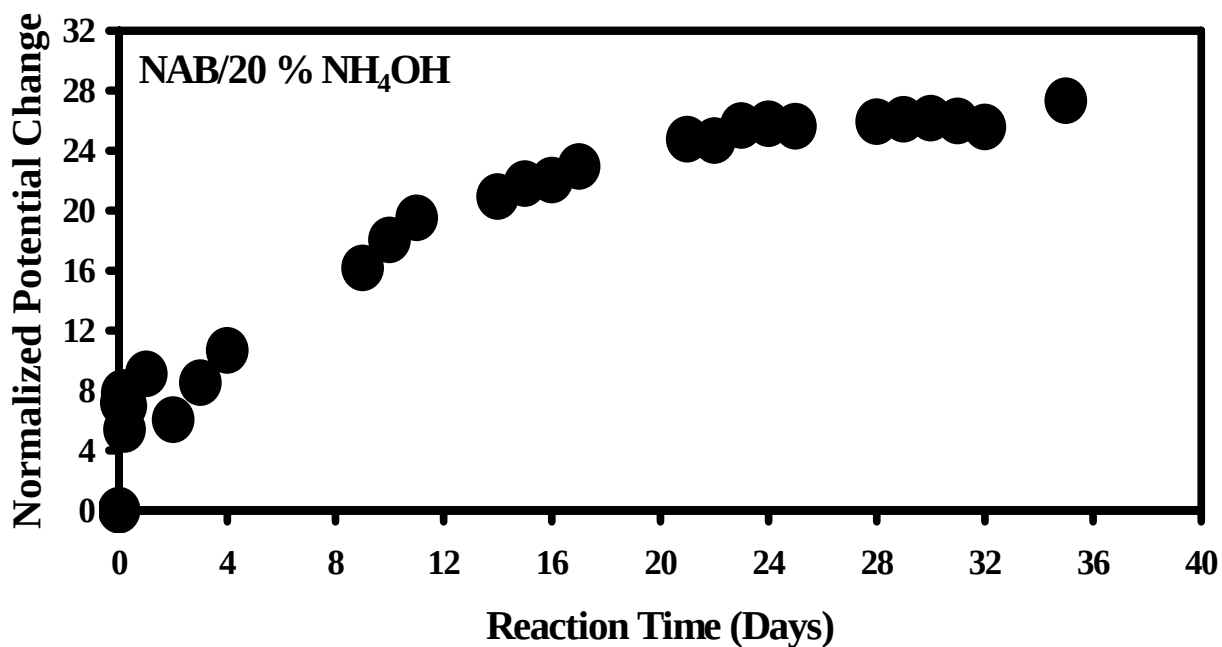


Figure 7. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with 20% ammonia solution.

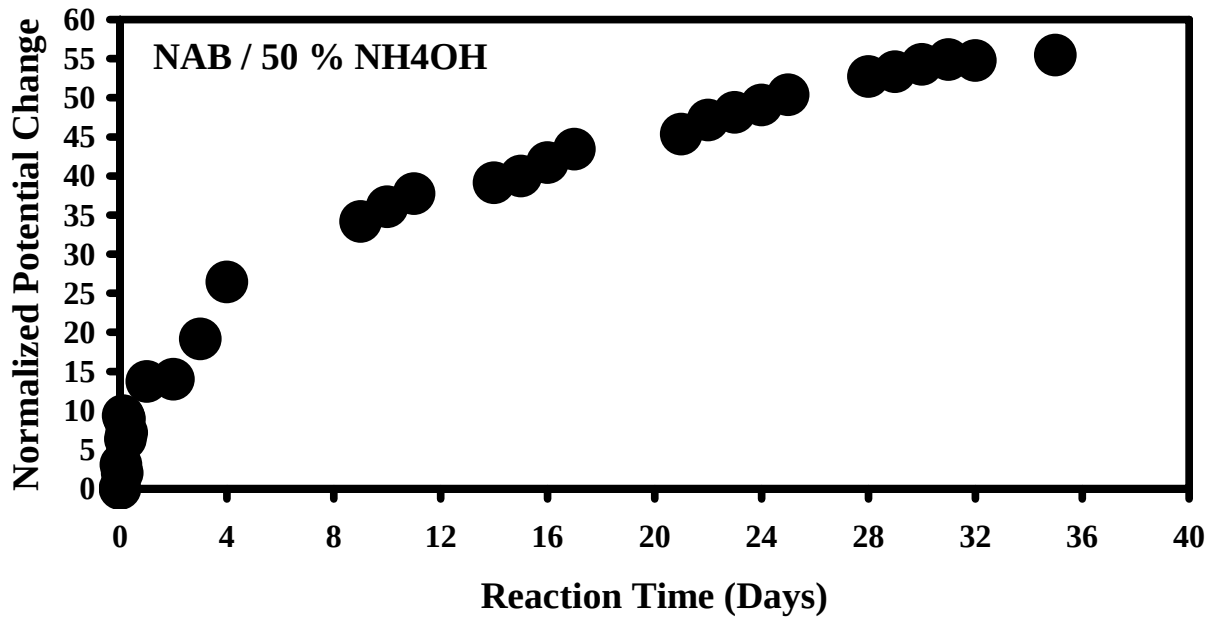


Figure 8. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with 50% ammonia solution.

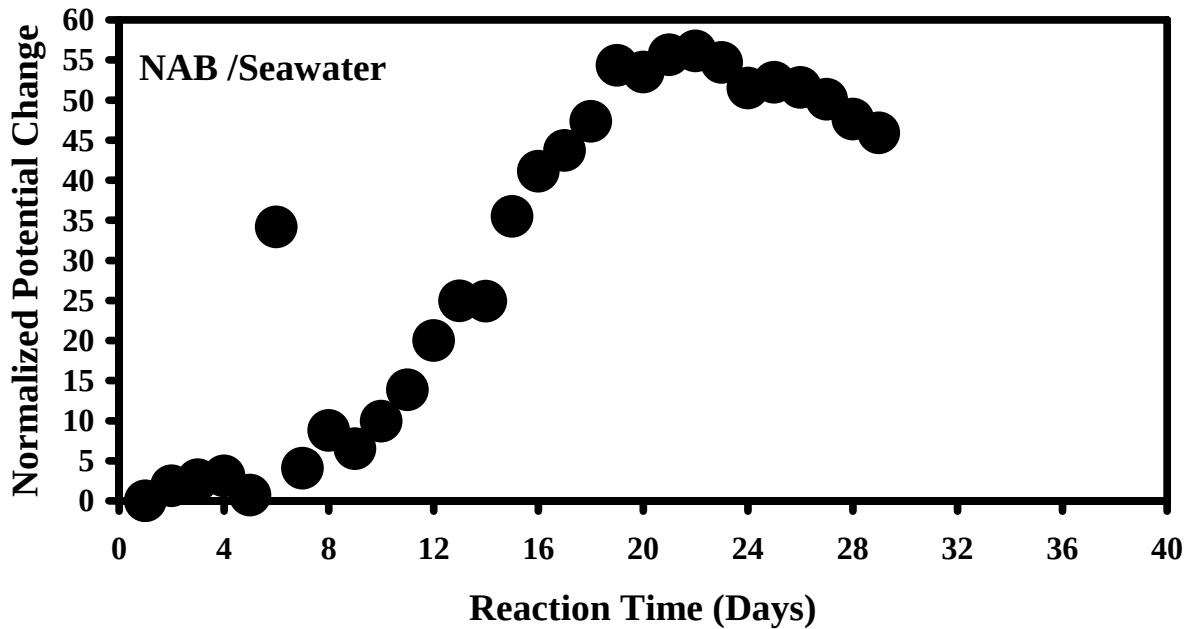


Figure 9. Normalized change in the potential (%) (versus SCE) versus reaction time profile for nickel aluminum bronze samples treated with seawater.

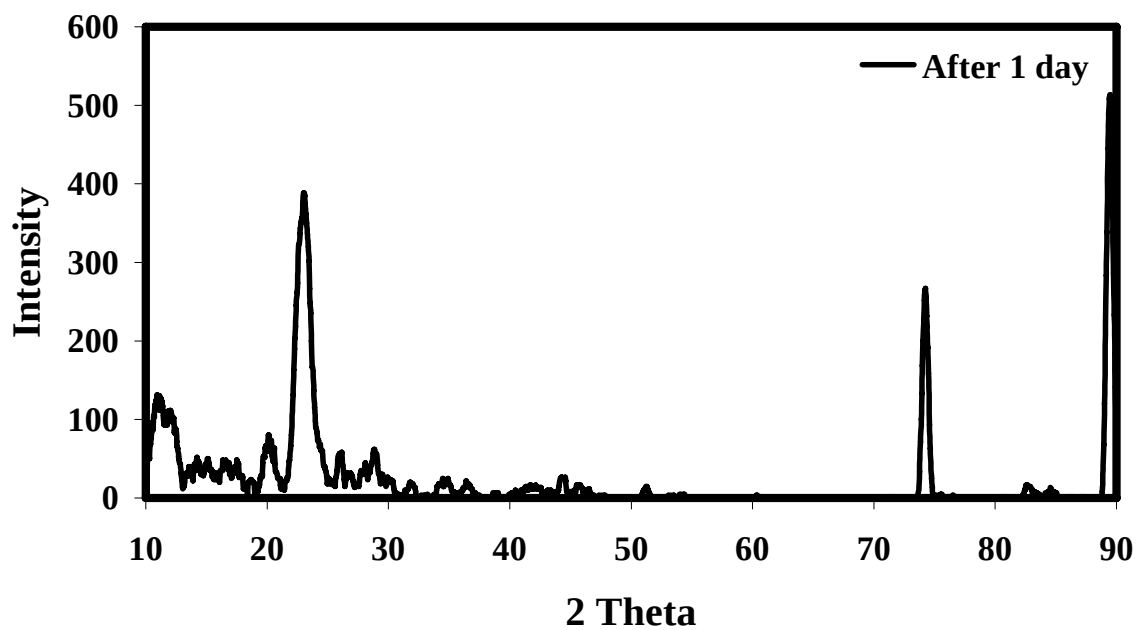


Figure 10. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 1 day.

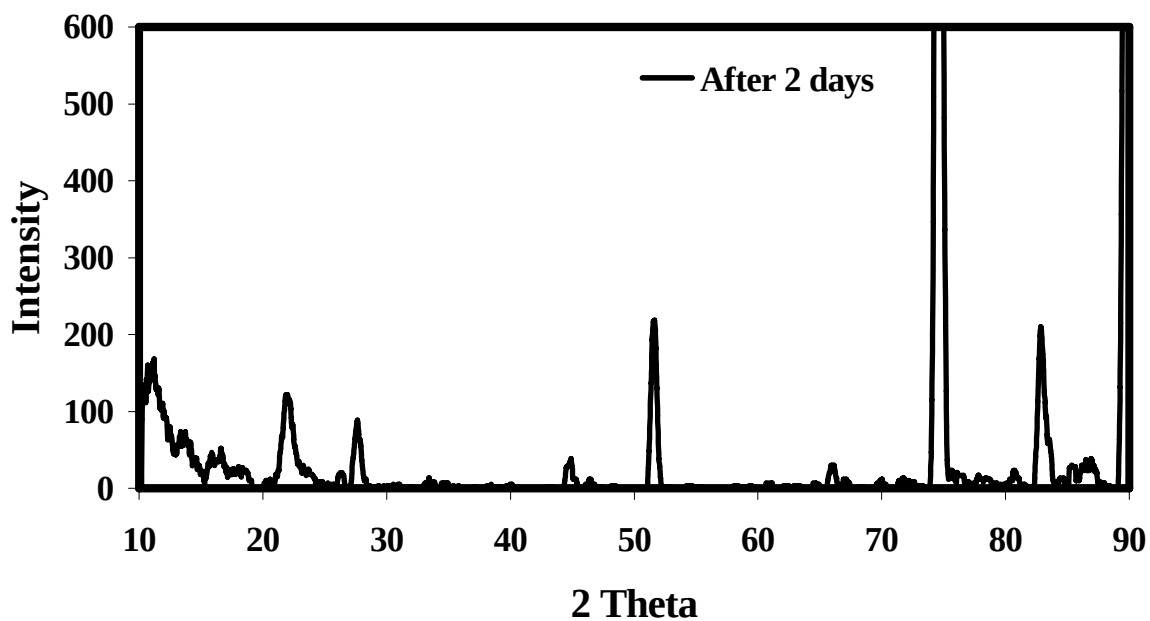


Figure 11. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 2 days.

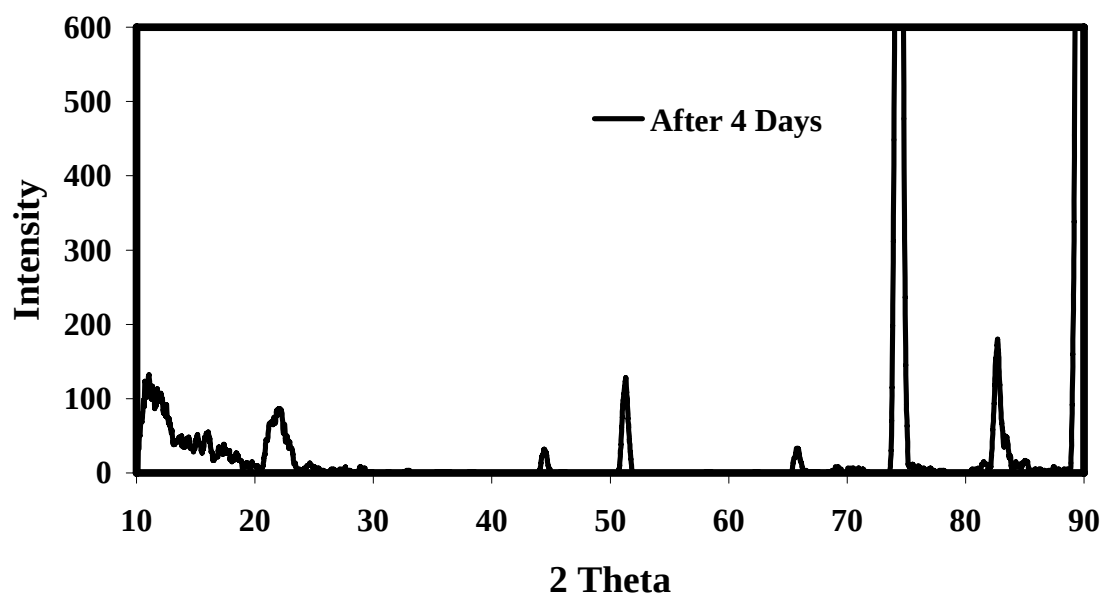


Figure 12. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 4 days.

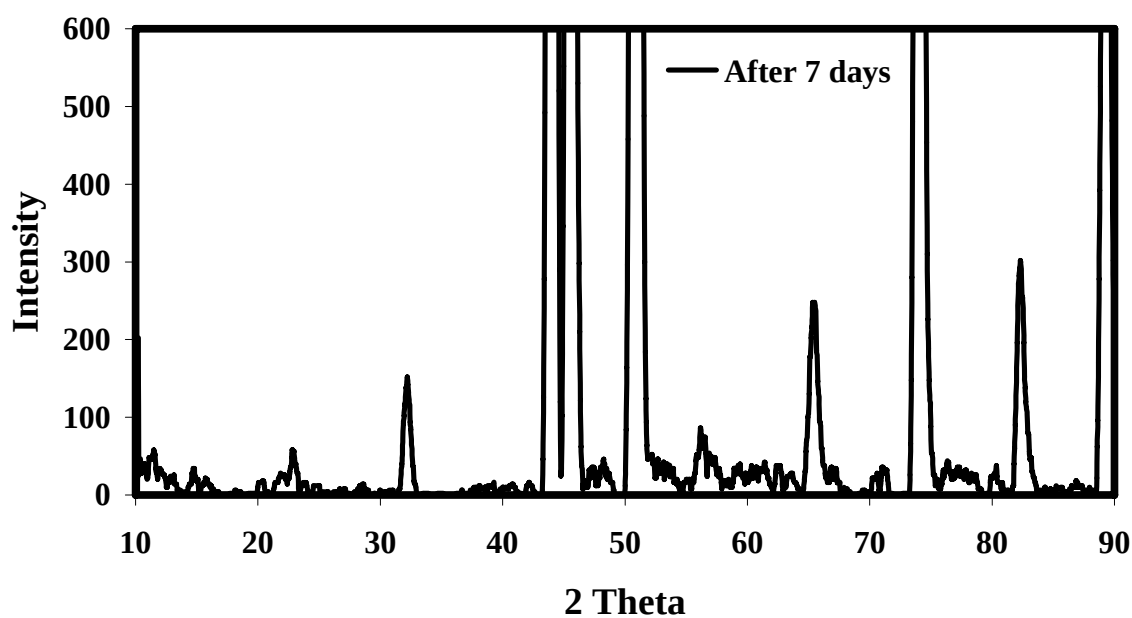


Figure 13. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 7 days.

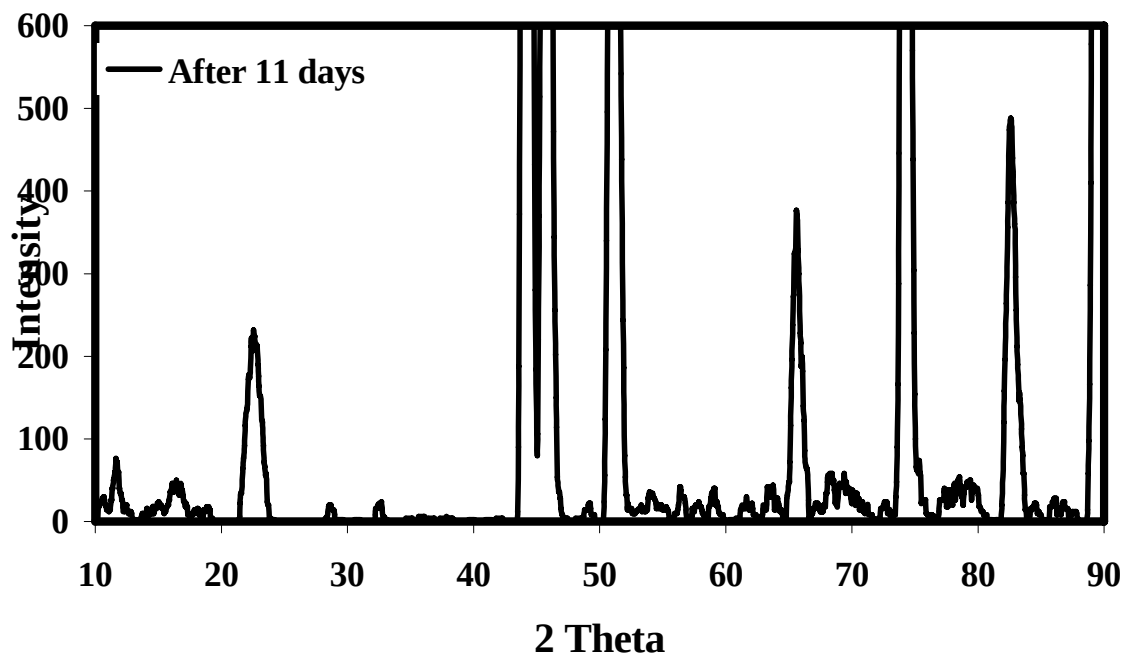


Figure 14. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 11 days.

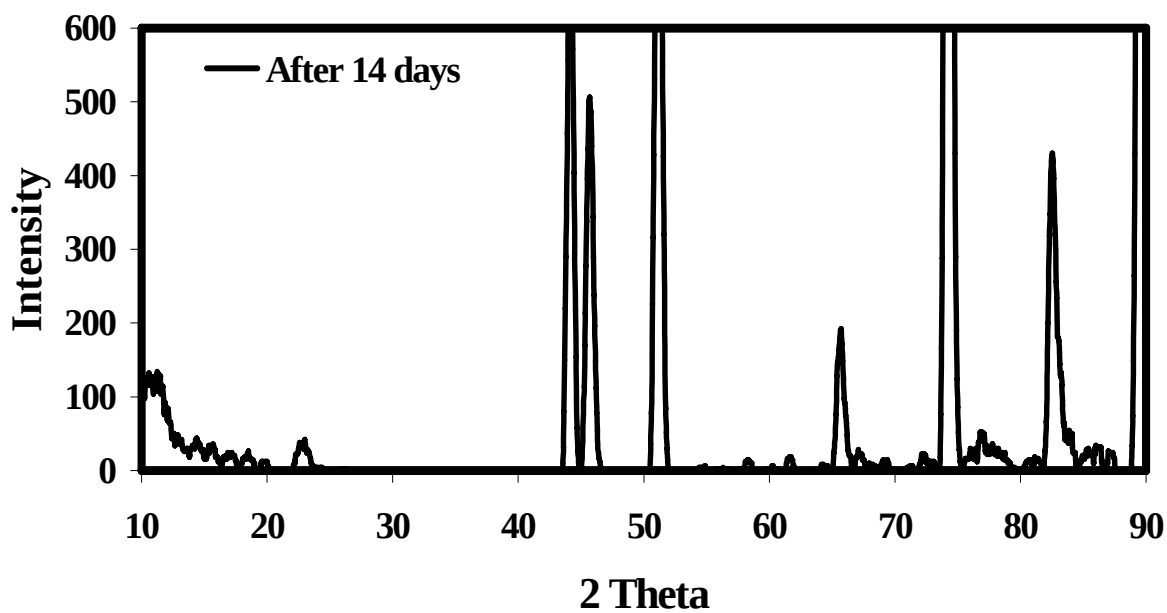


Figure 15. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 14 days.

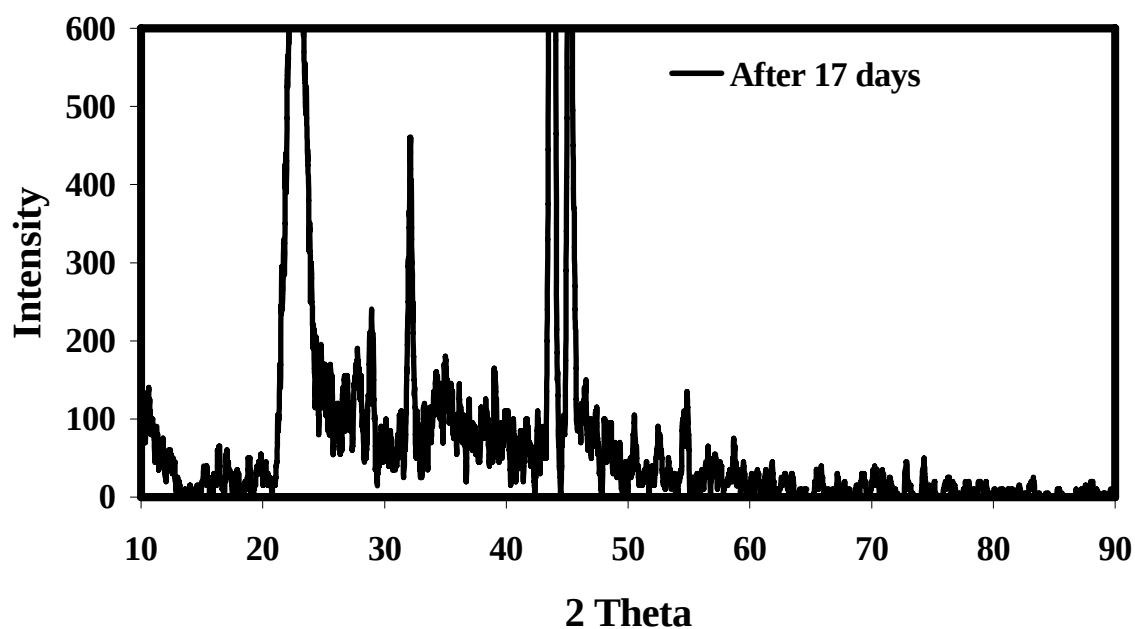


Figure 16. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 17 days.

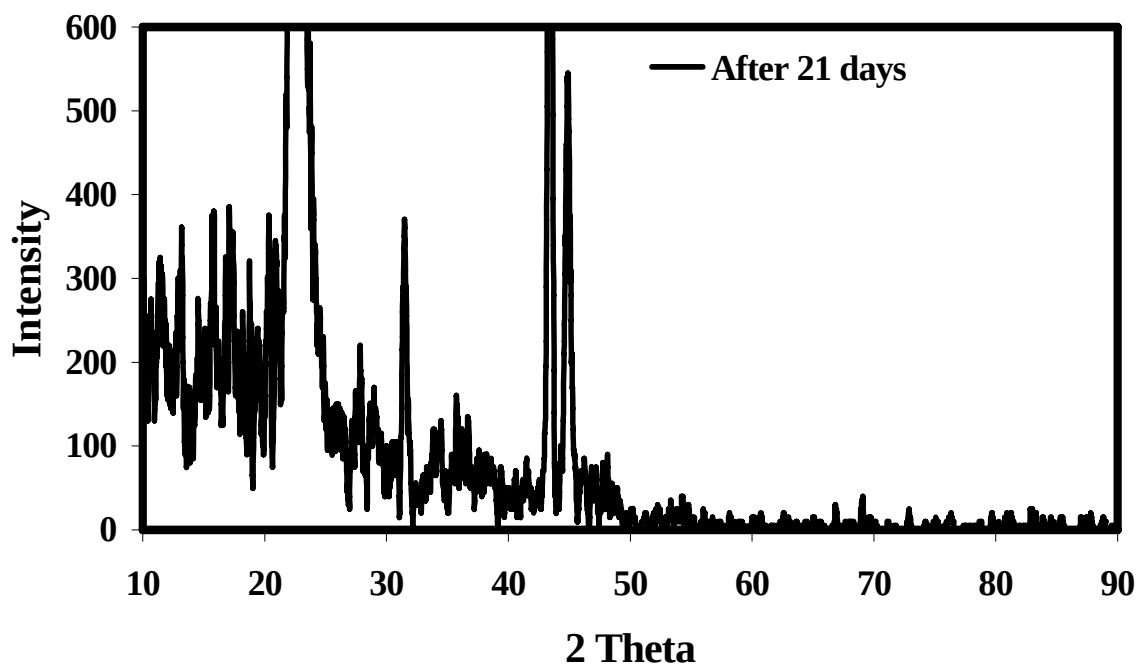


Figure 17. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 21 days.

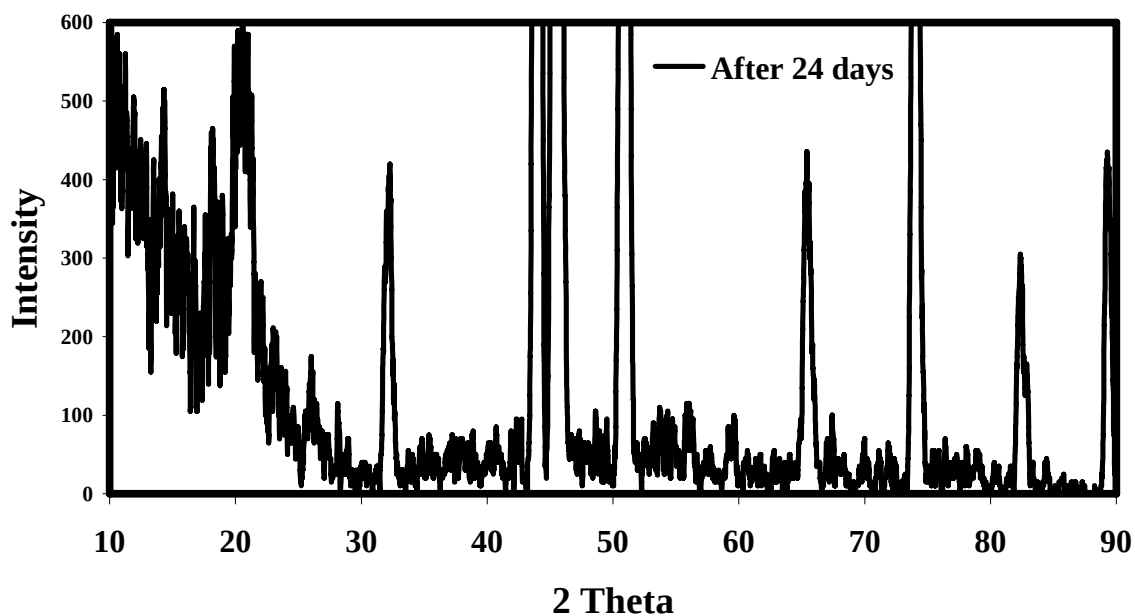


Figure 18. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 24 days.

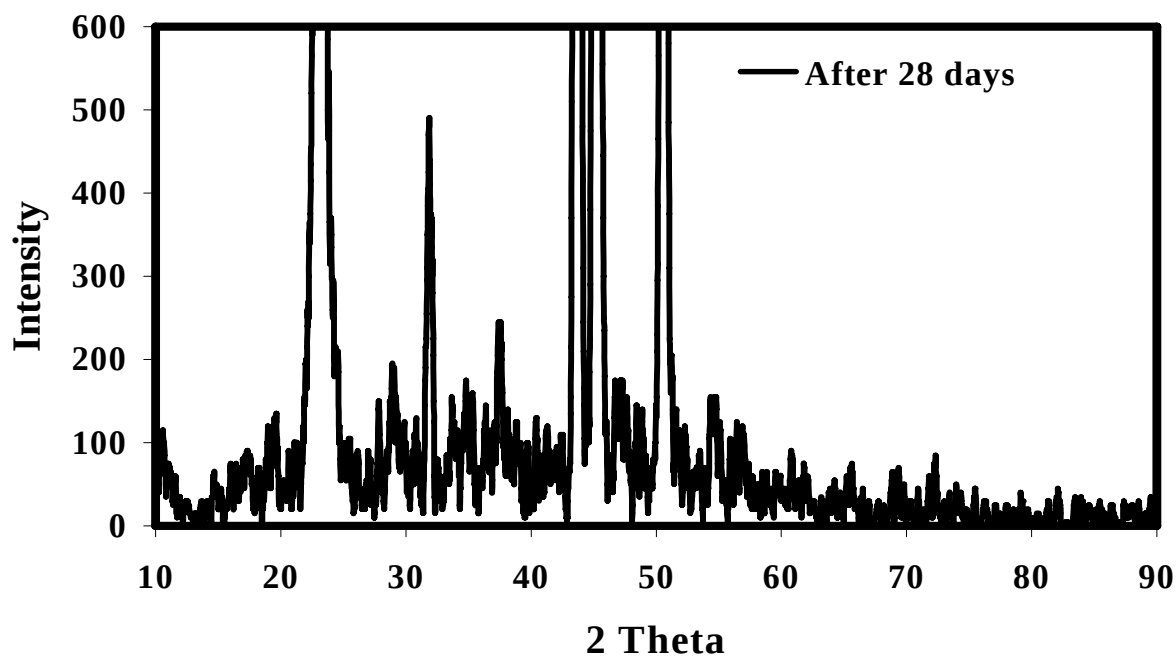


Figure 19. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 28 days.

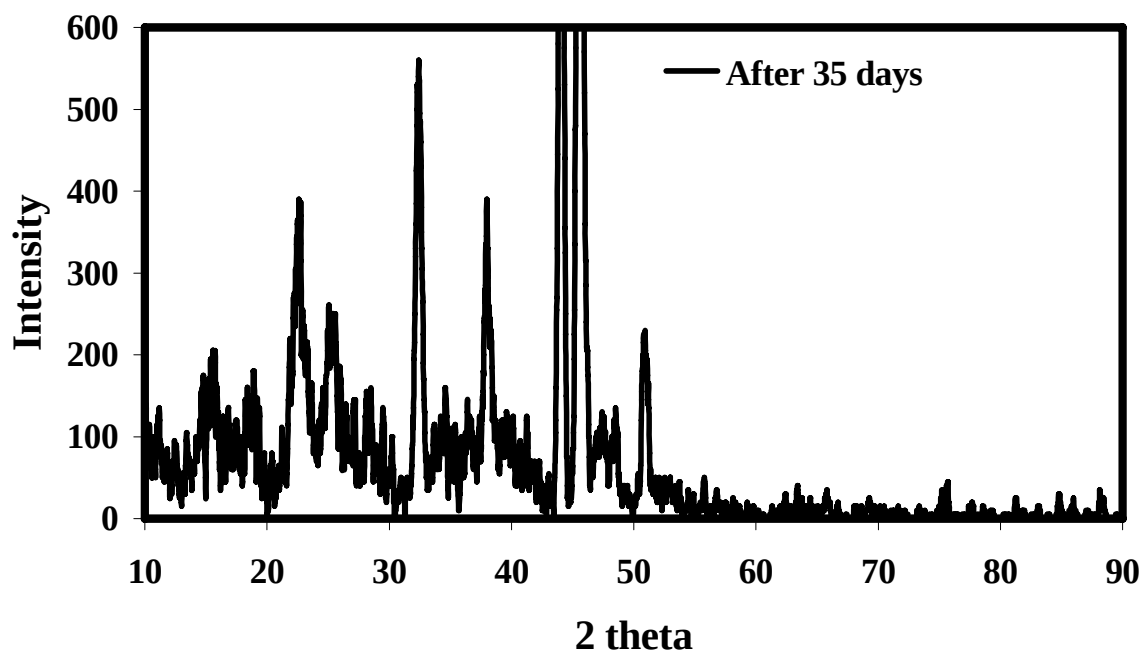


Figure 20. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 35 days.

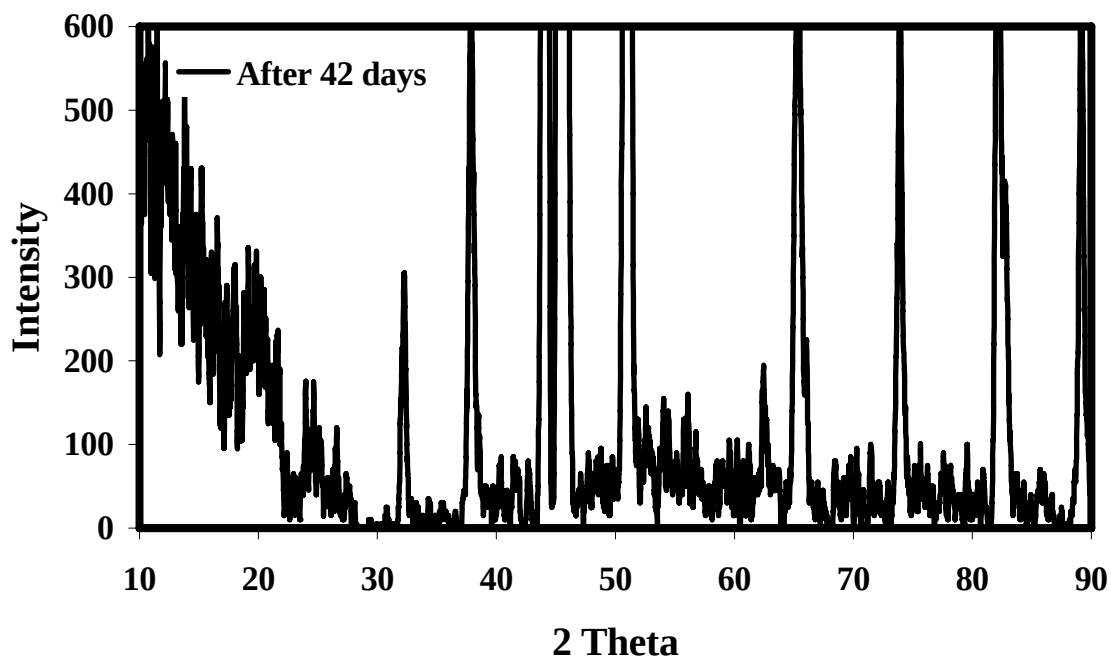


Figure 21. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 10% NH_4OH for 42 days.

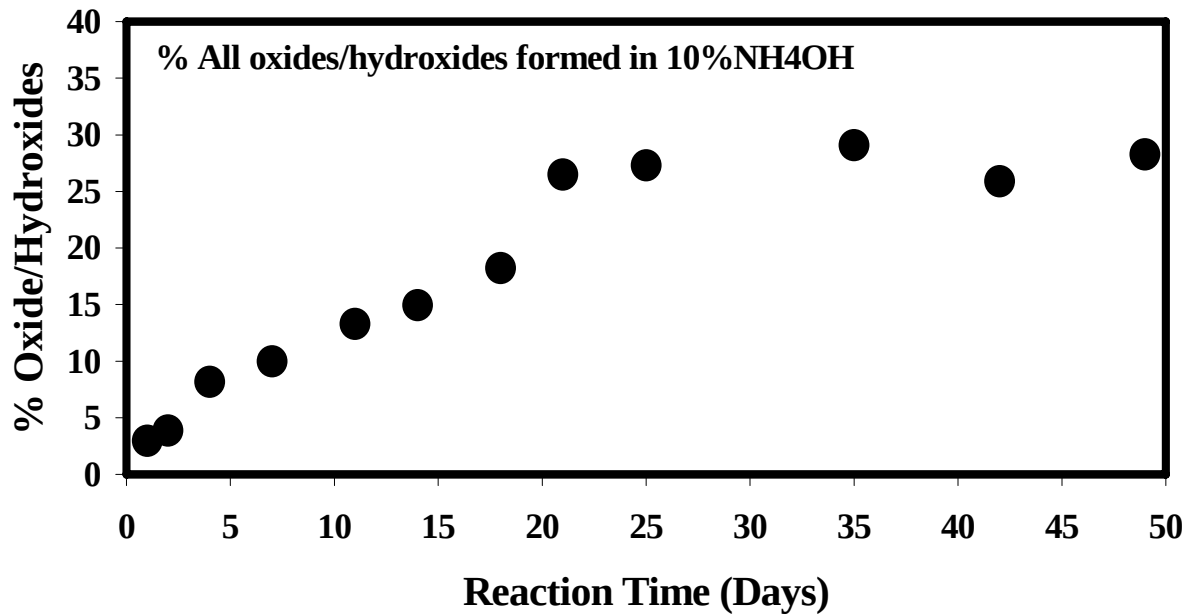


Figure 22. (%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.

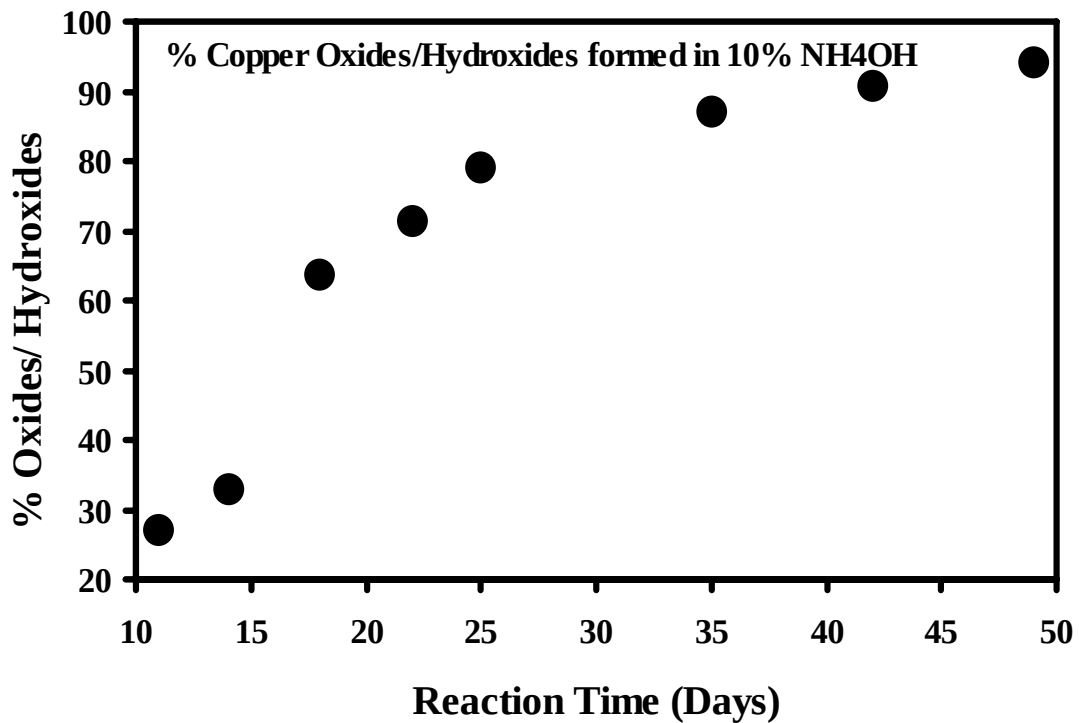


Figure 23. (%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.

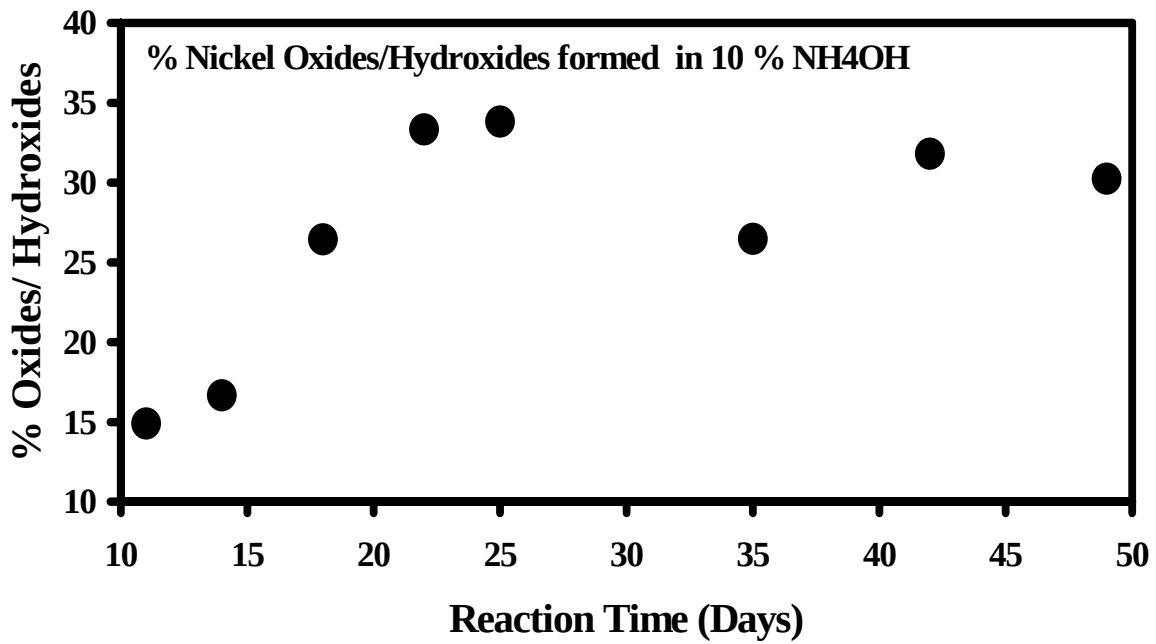


Figure 24. (%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH₄OH solution.

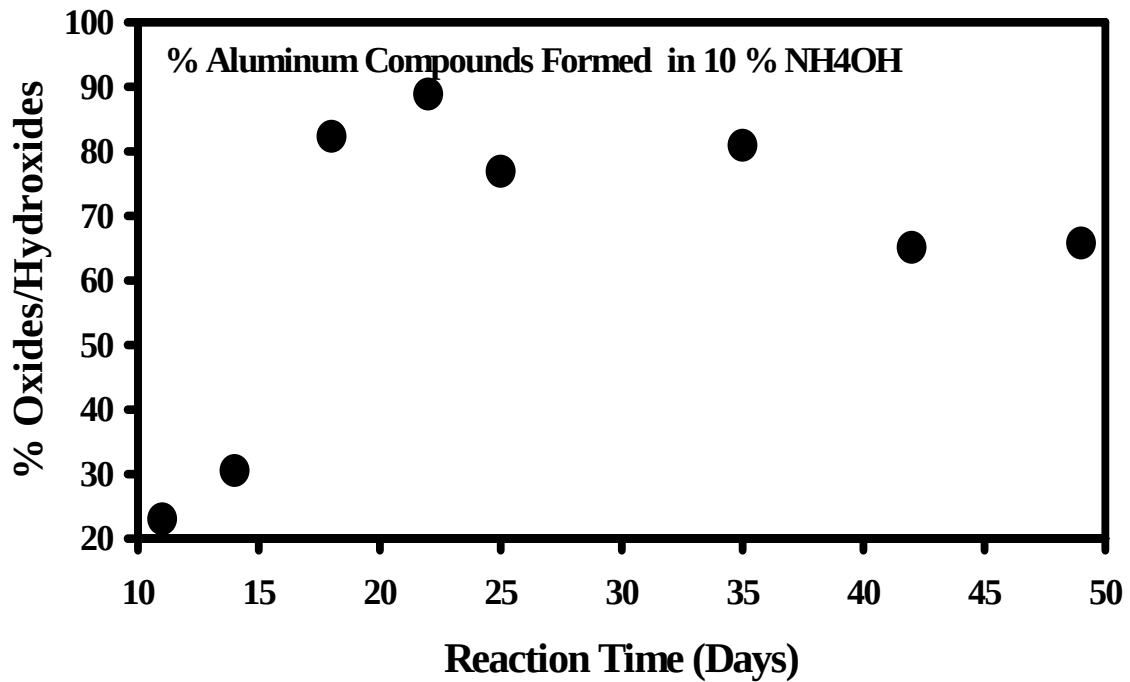


Figure 25. (%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH₄OH solution.

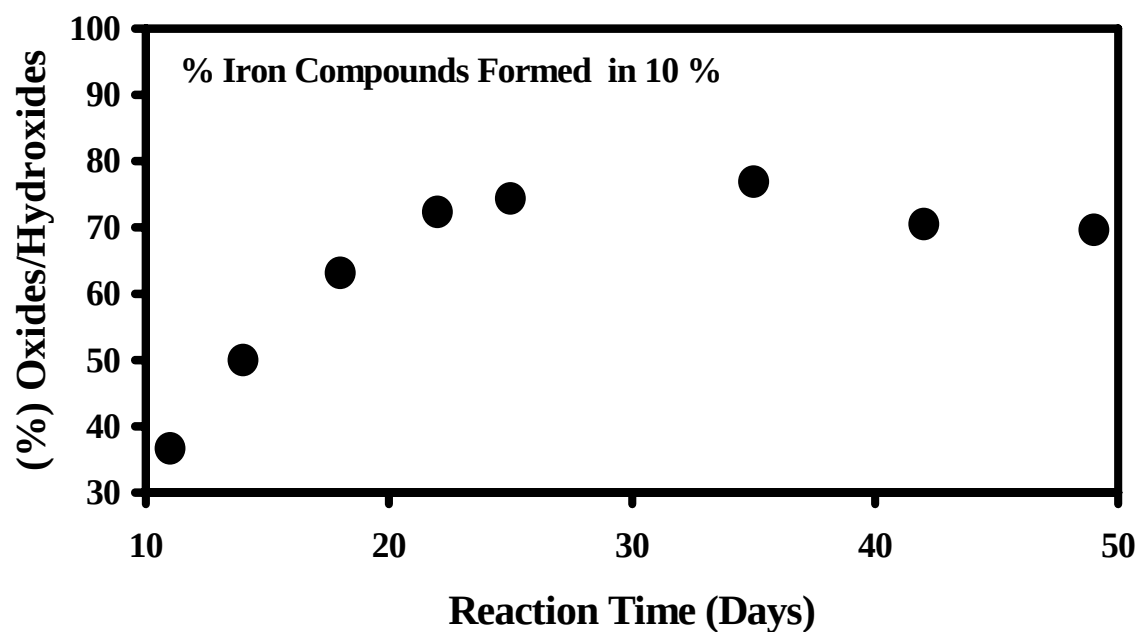


Figure 26. (%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 10% NH_4OH solution.

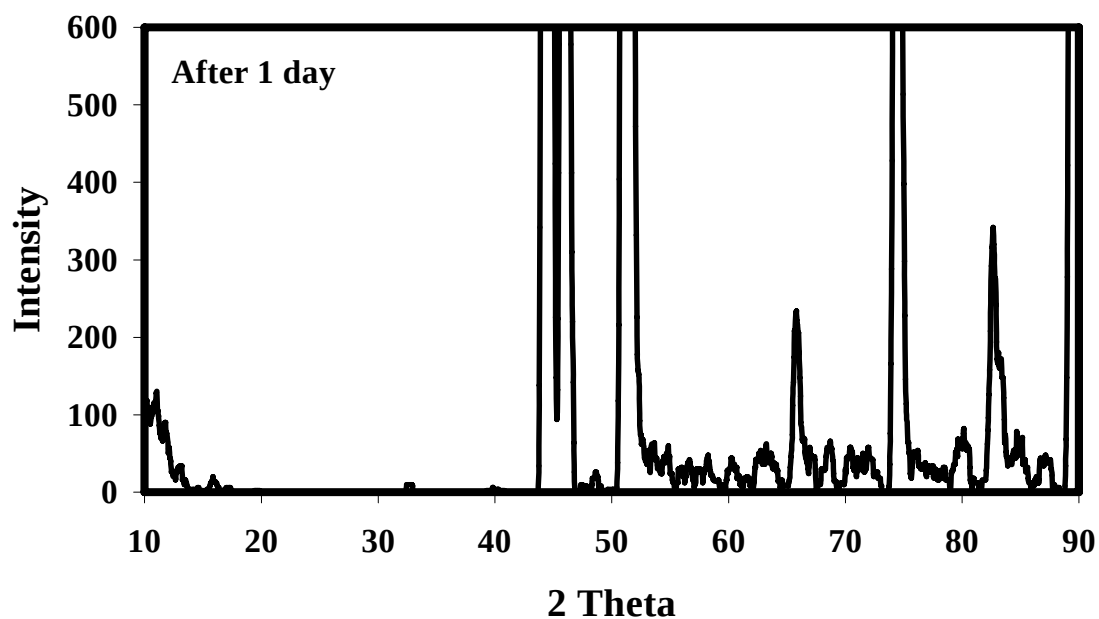


Figure 27. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 1 day.

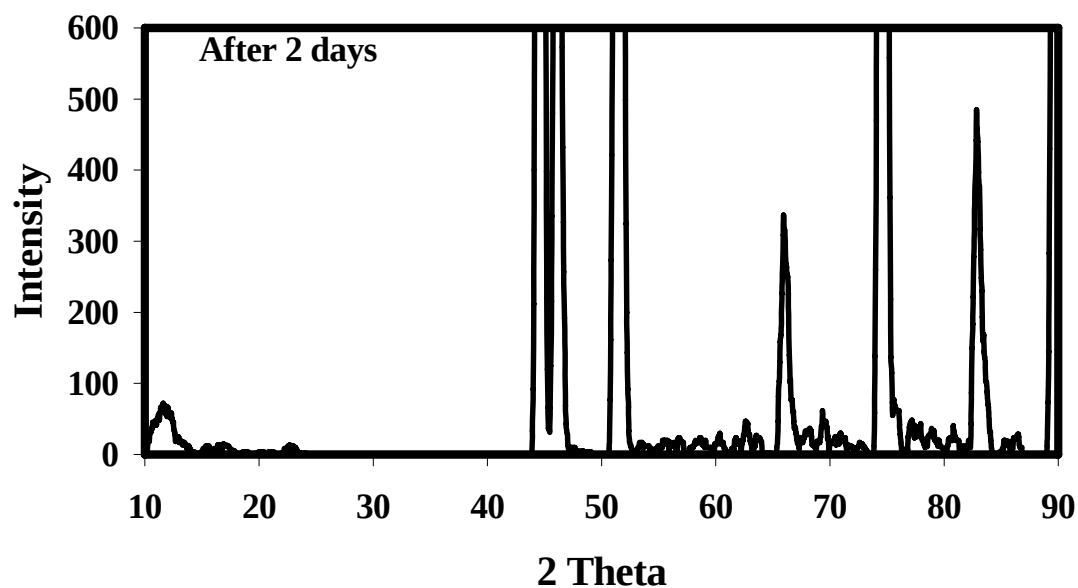


Figure 28. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 2 days.

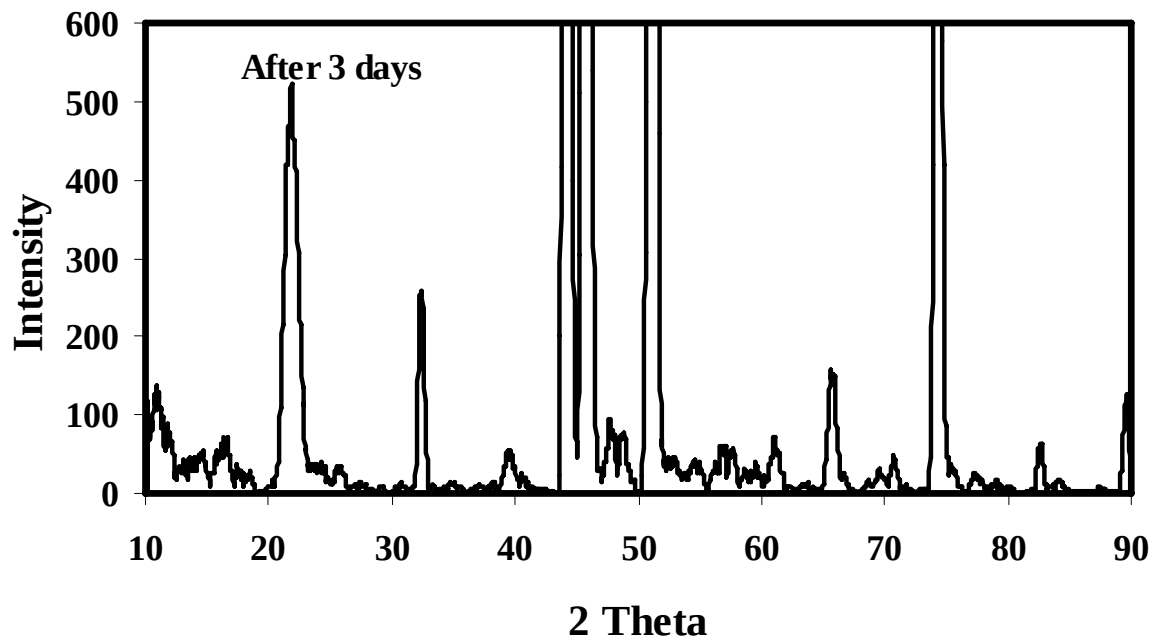


Figure 29. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 3 days.

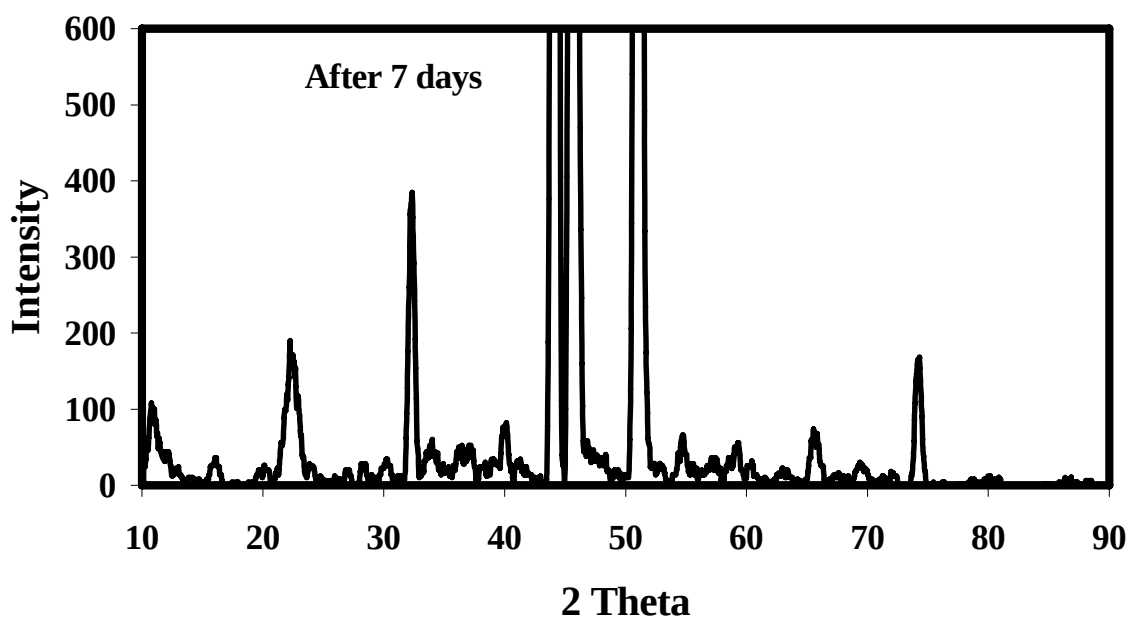


Figure 30. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 7 days.

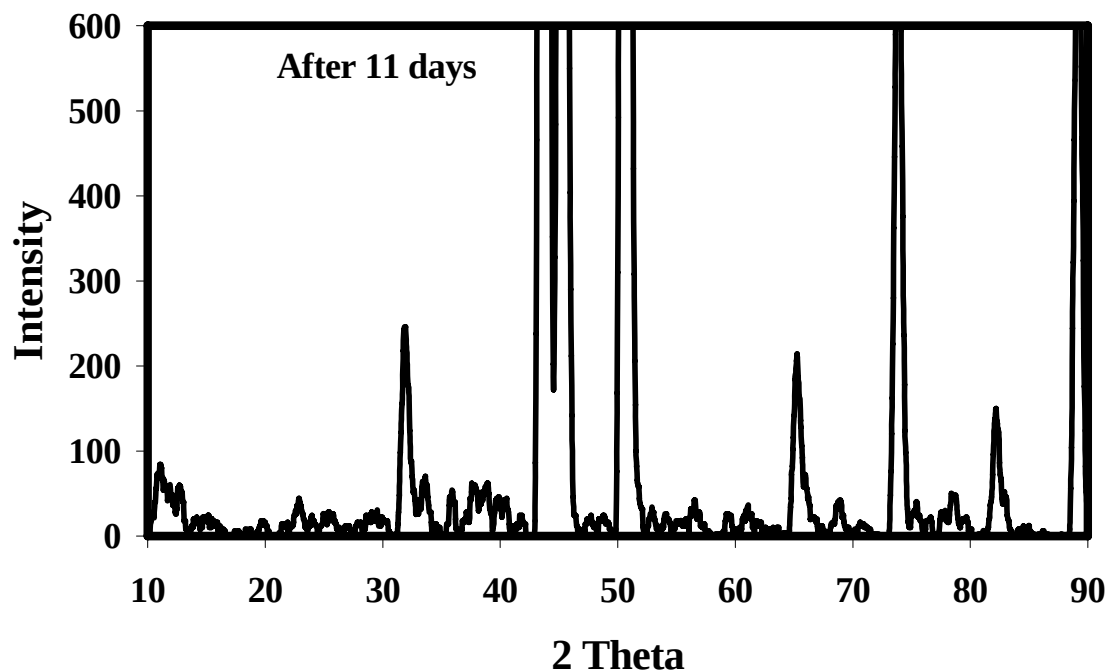


Figure 31. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 11 days.

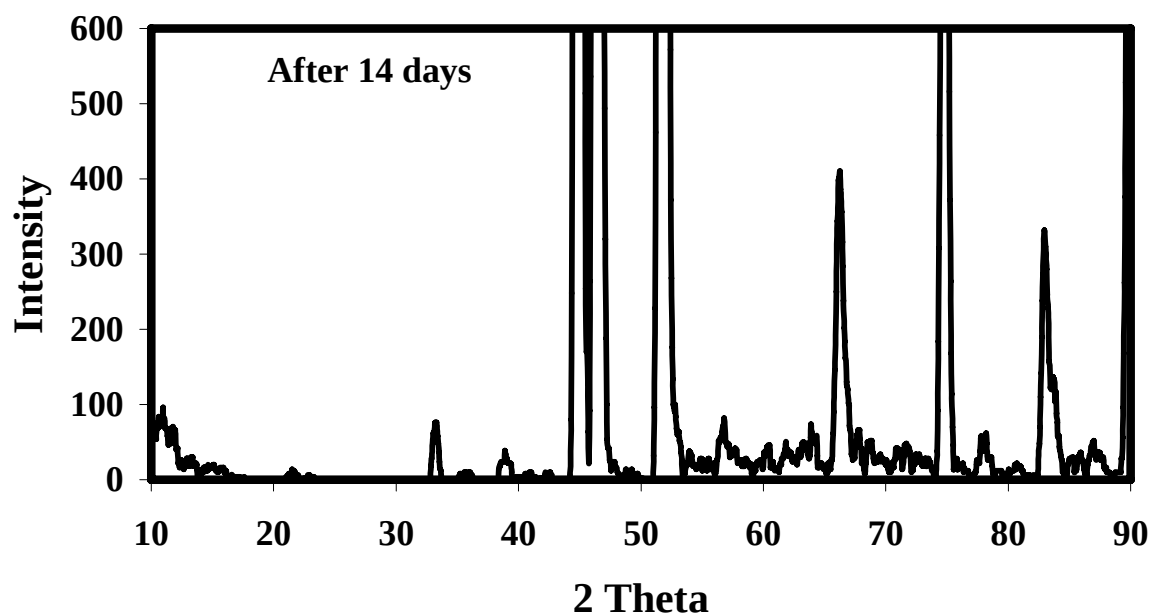


Figure 32. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 14 days.

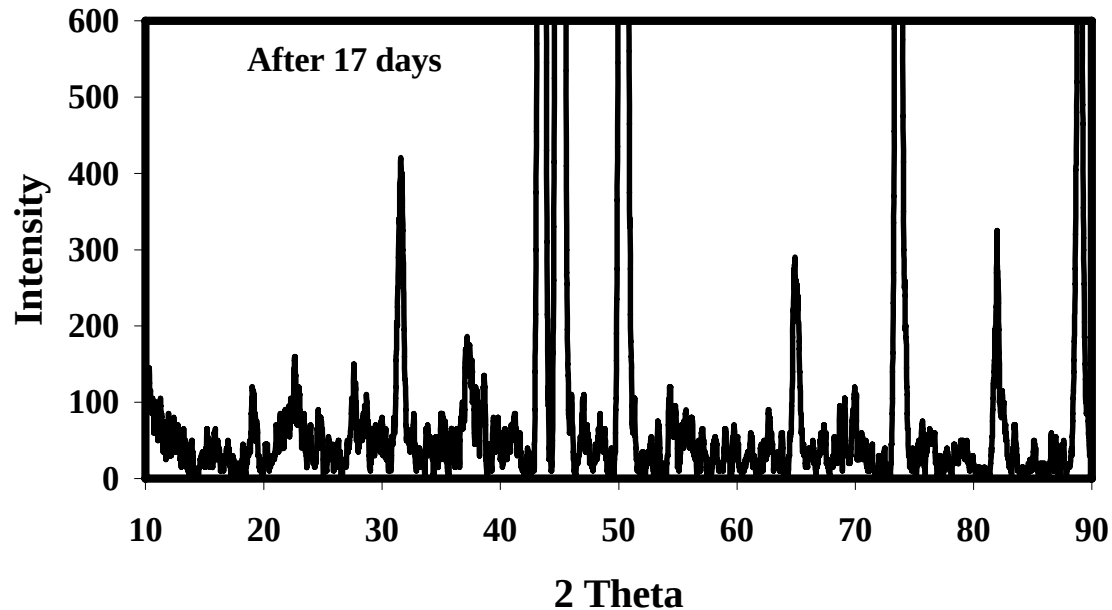


Figure 33. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 17 days.

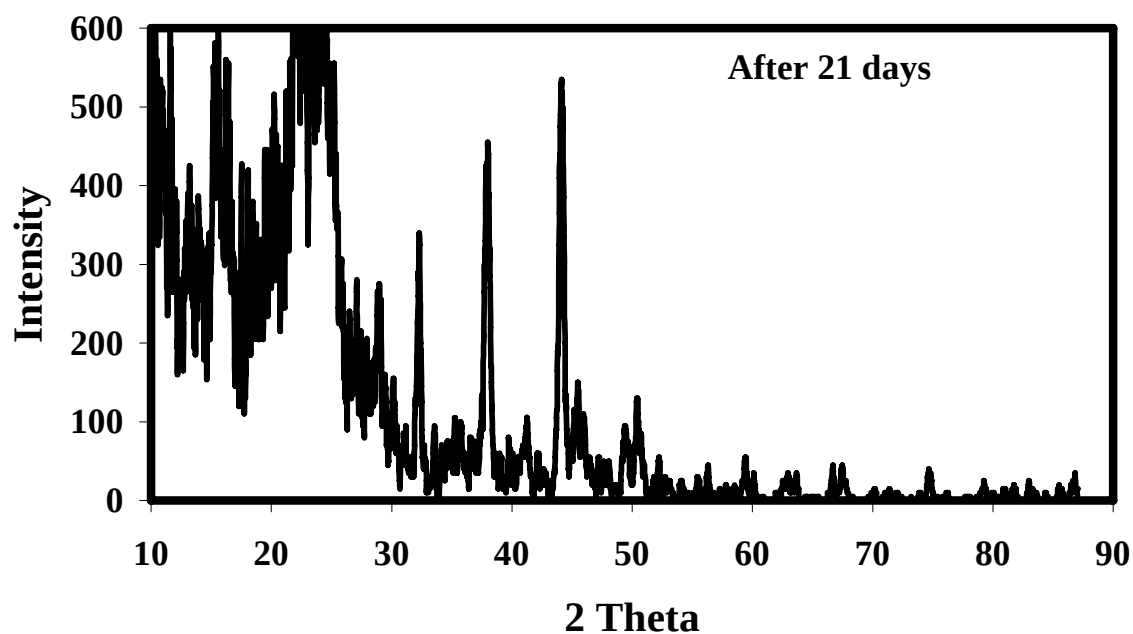


Figure 34. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 21 days.

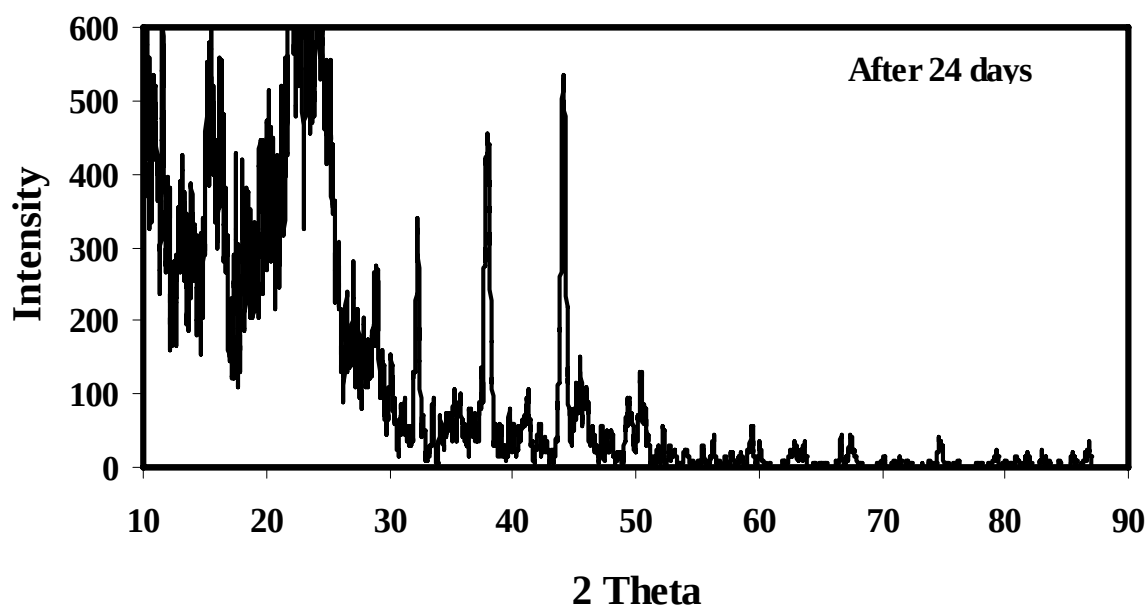


Figure 35. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 24 days.

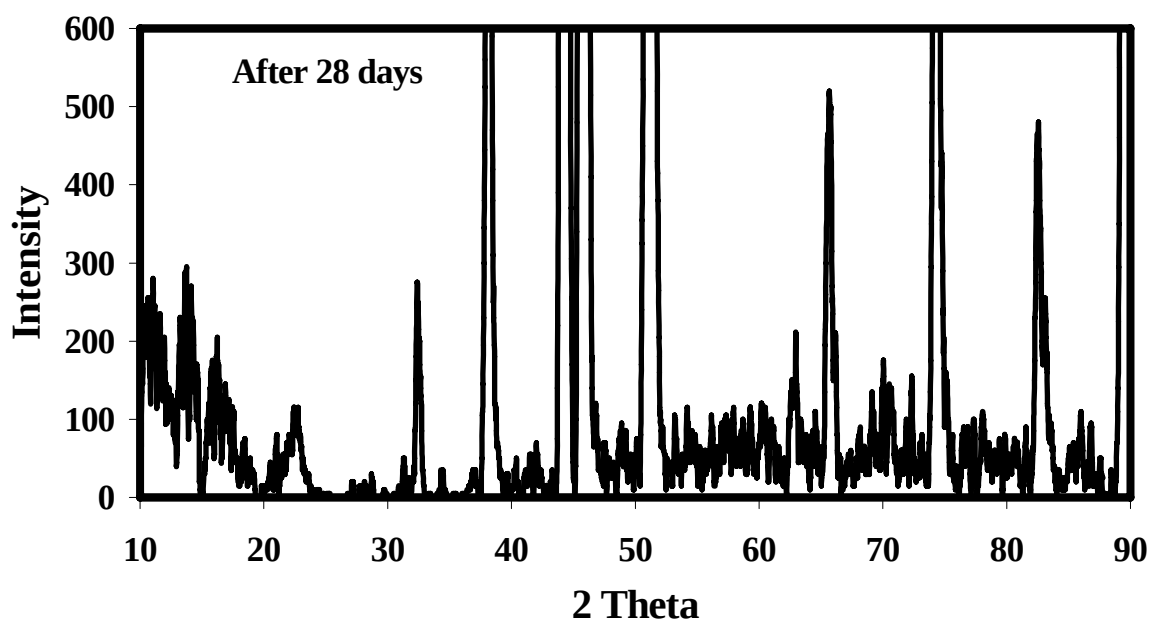


Figure 36. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 28 days.

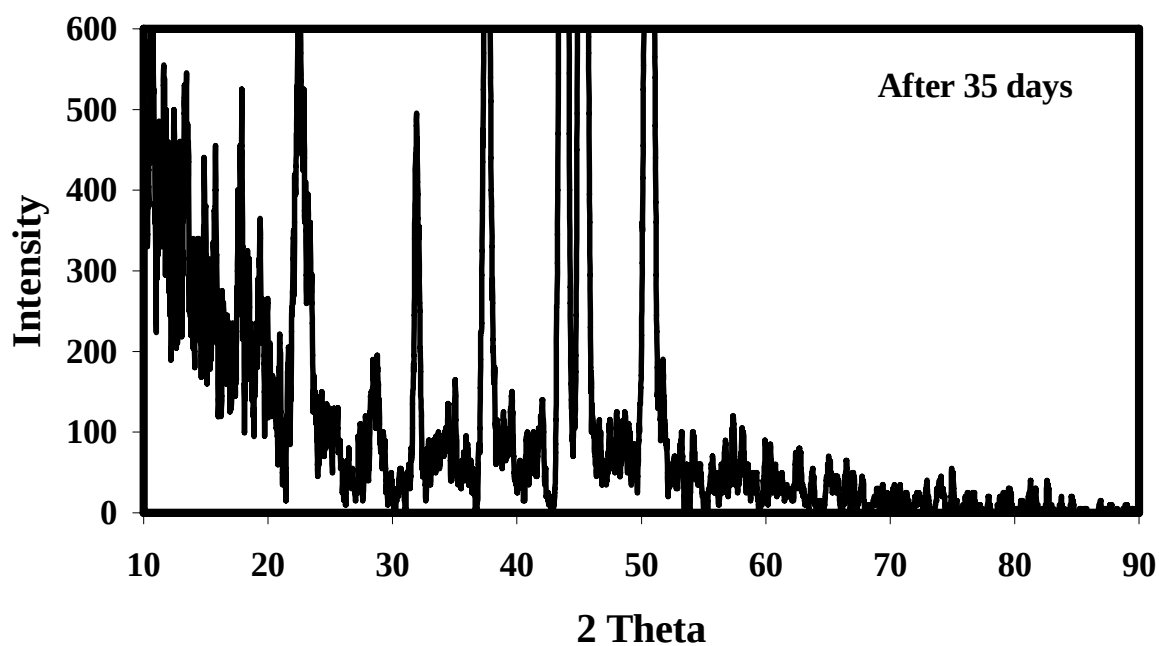


Figure 37. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 35 days.

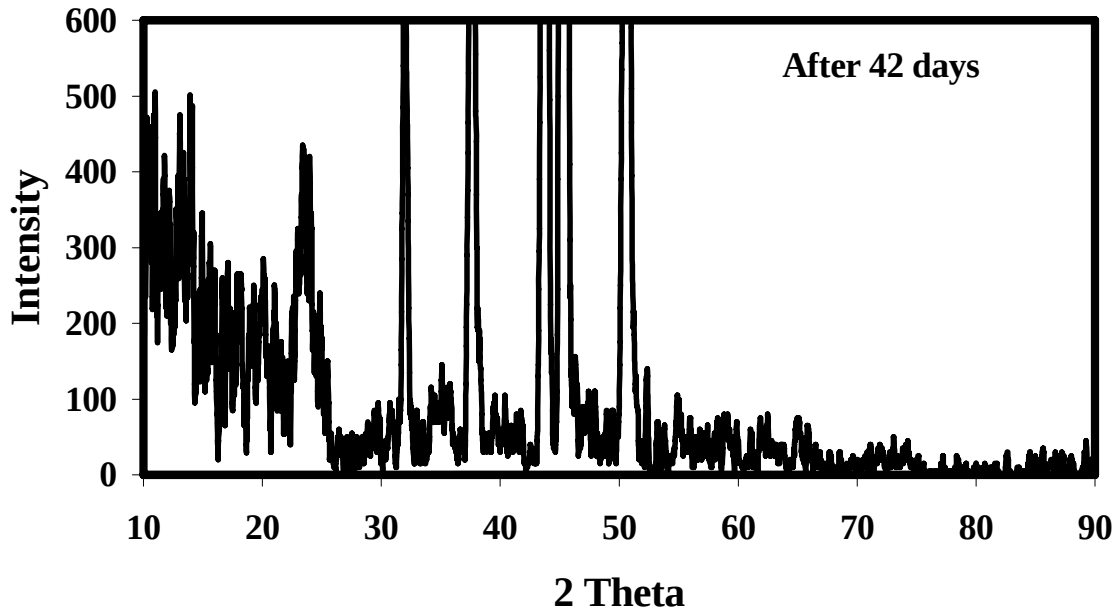


Figure 38. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 20% NH_4OH for 42 days.

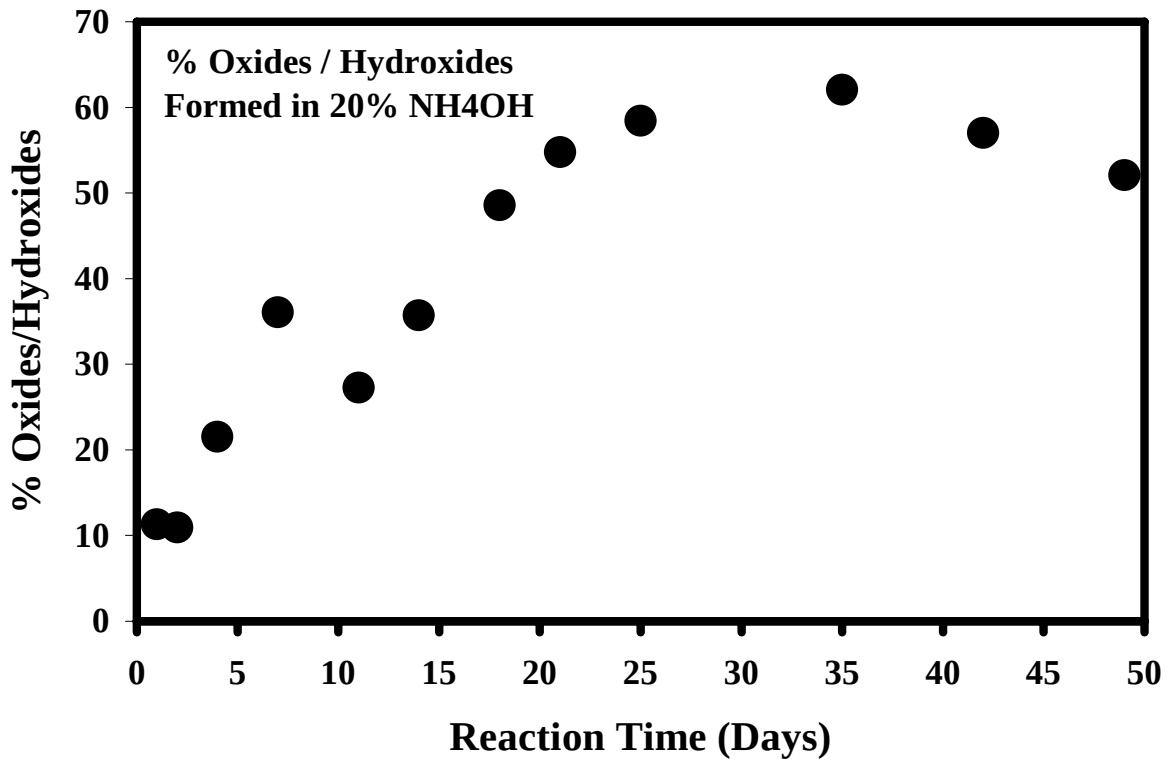


Figure 39. (%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH_4OH solution.

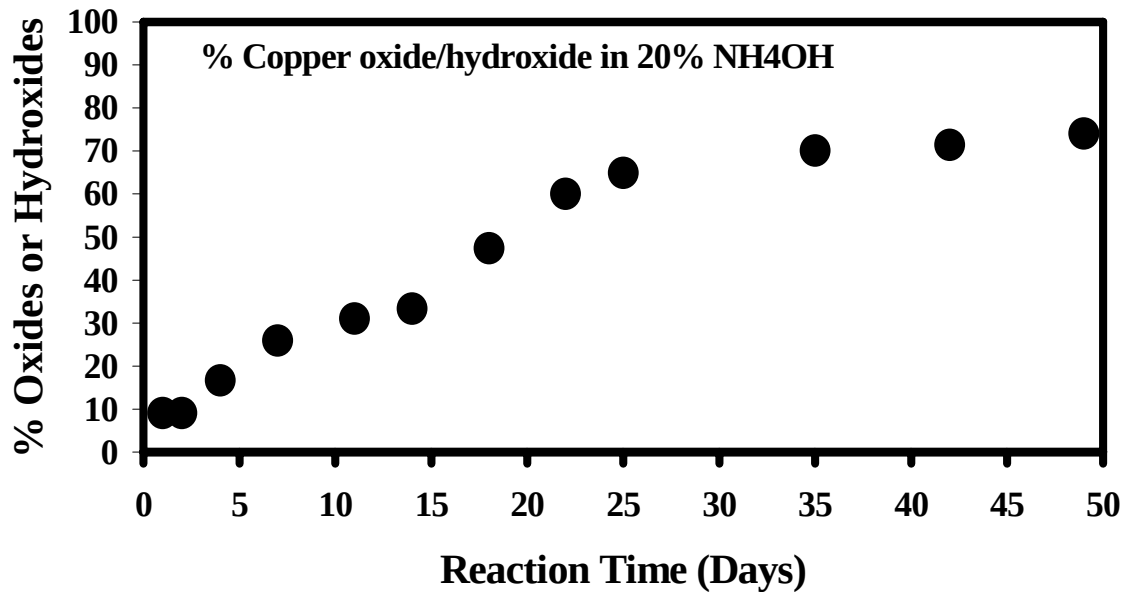


Figure 40. (%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH_4OH solution.

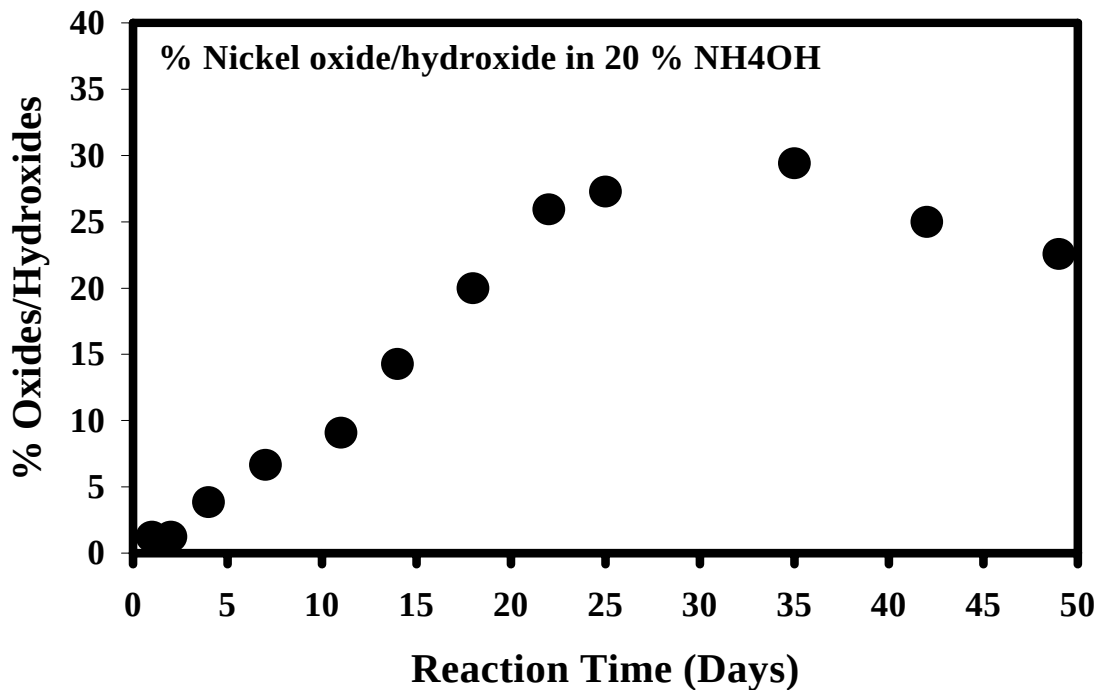


Figure 41. (%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH_4OH solution.

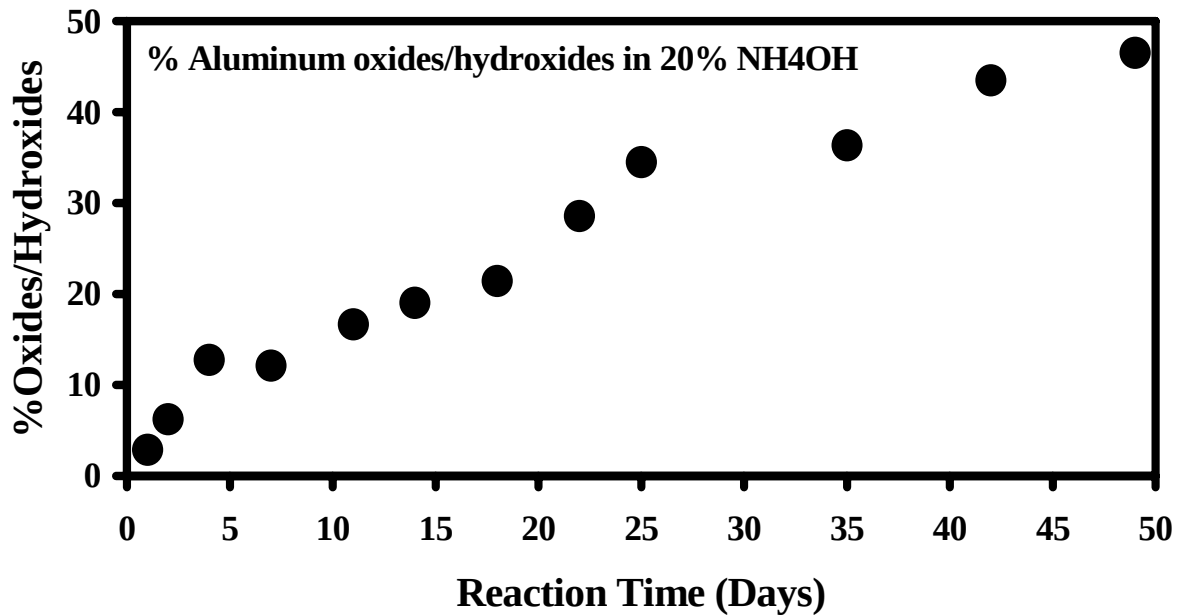


Figure 42. (%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH₄OH solution.

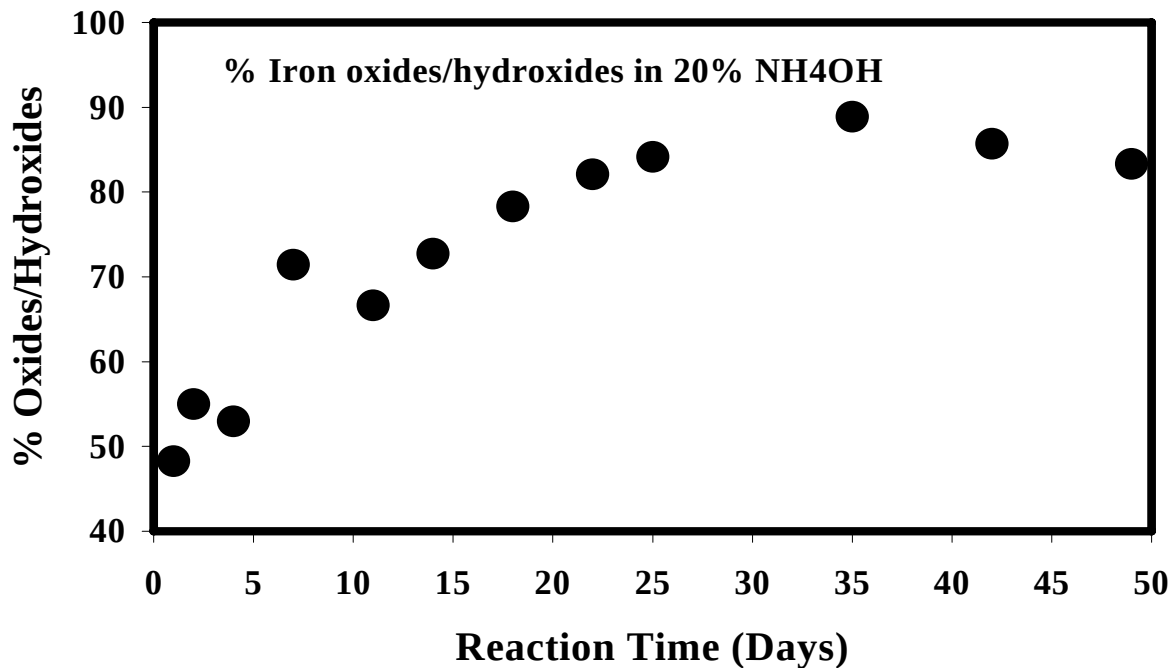


Figure 43. (%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 20% NH₄OH solution.

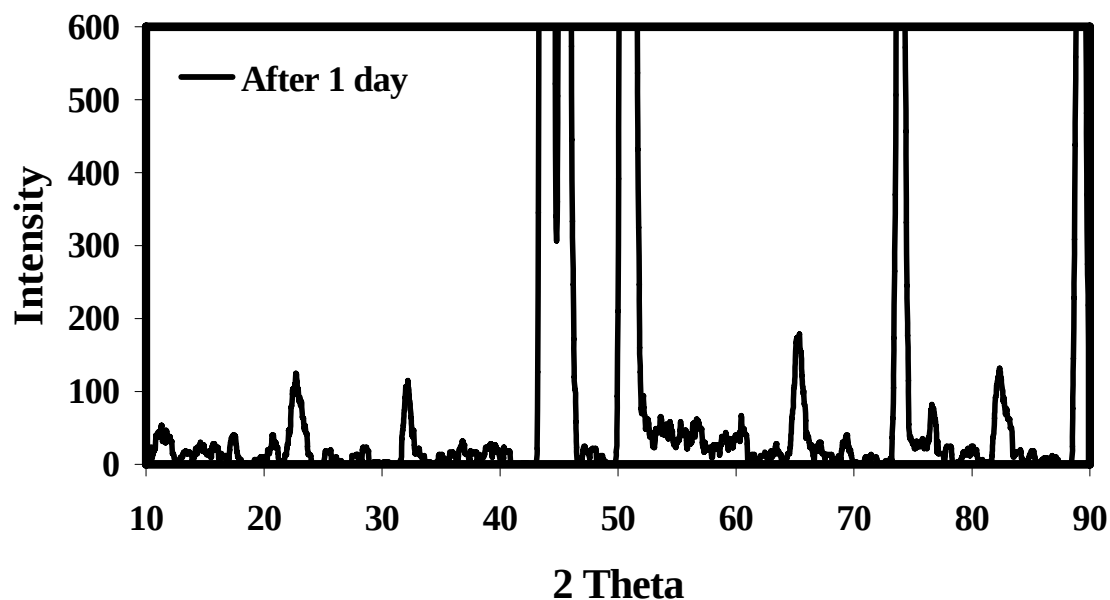


Figure 44. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 1 day.

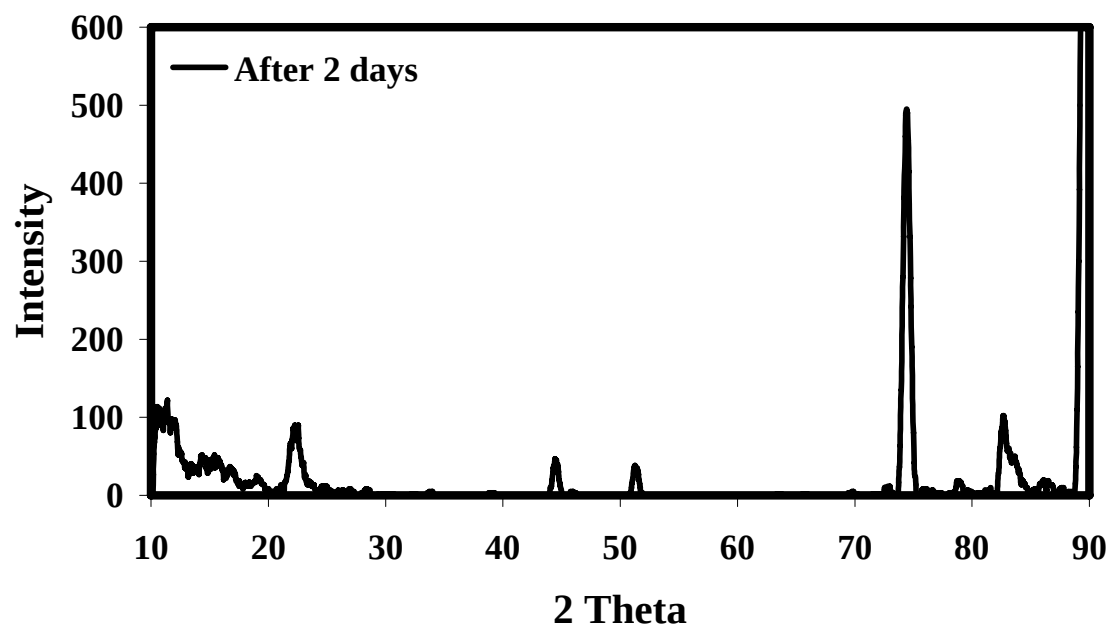


Figure 45. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 2 days.

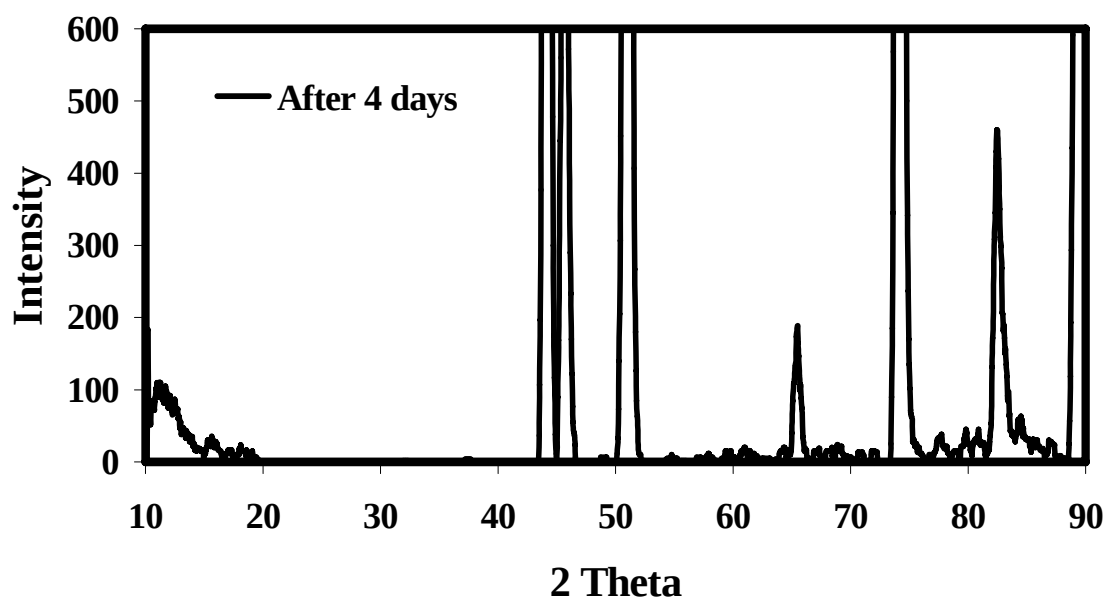


Figure 46. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 4 days.

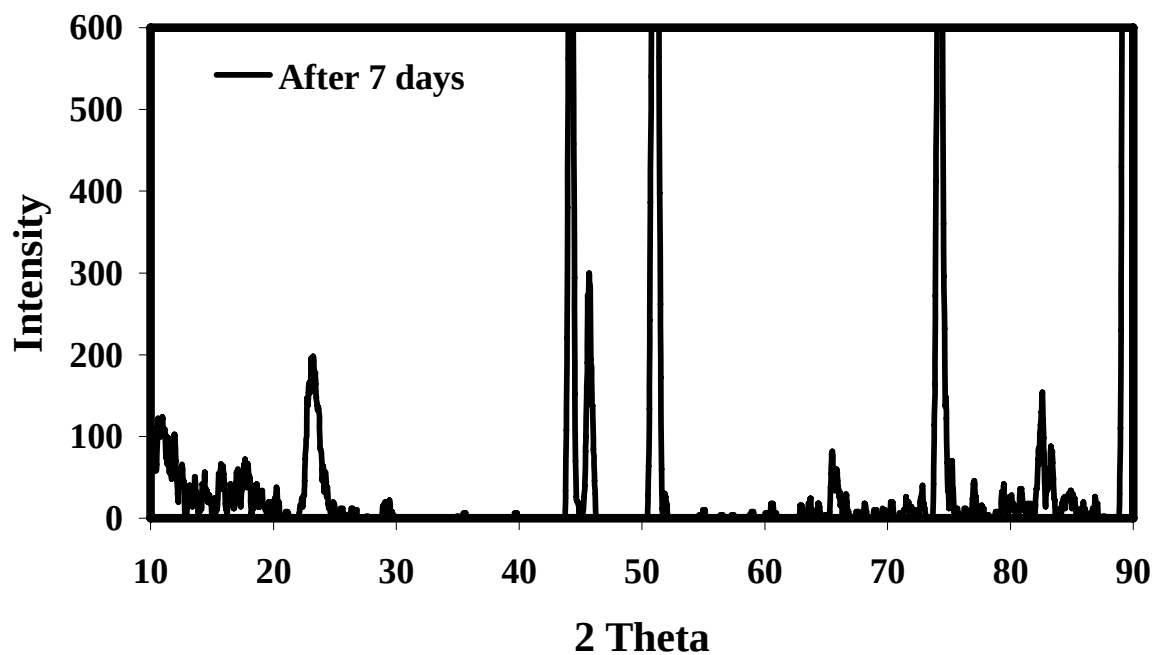


Figure 47. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 7 days.

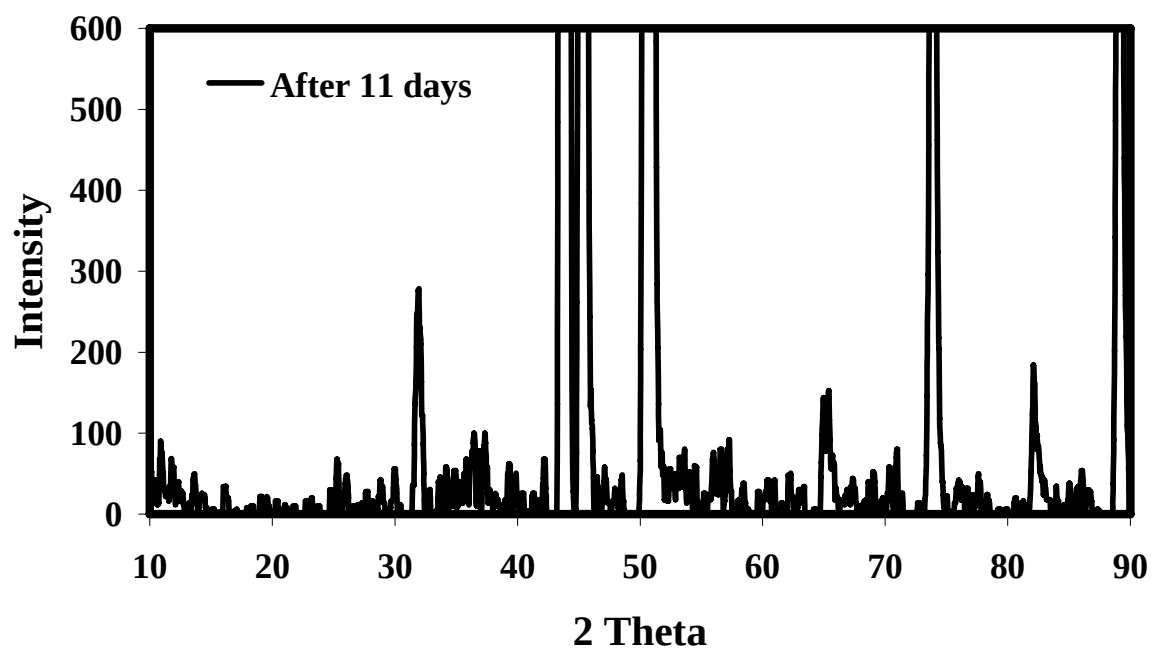


Figure 48. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 11 days.

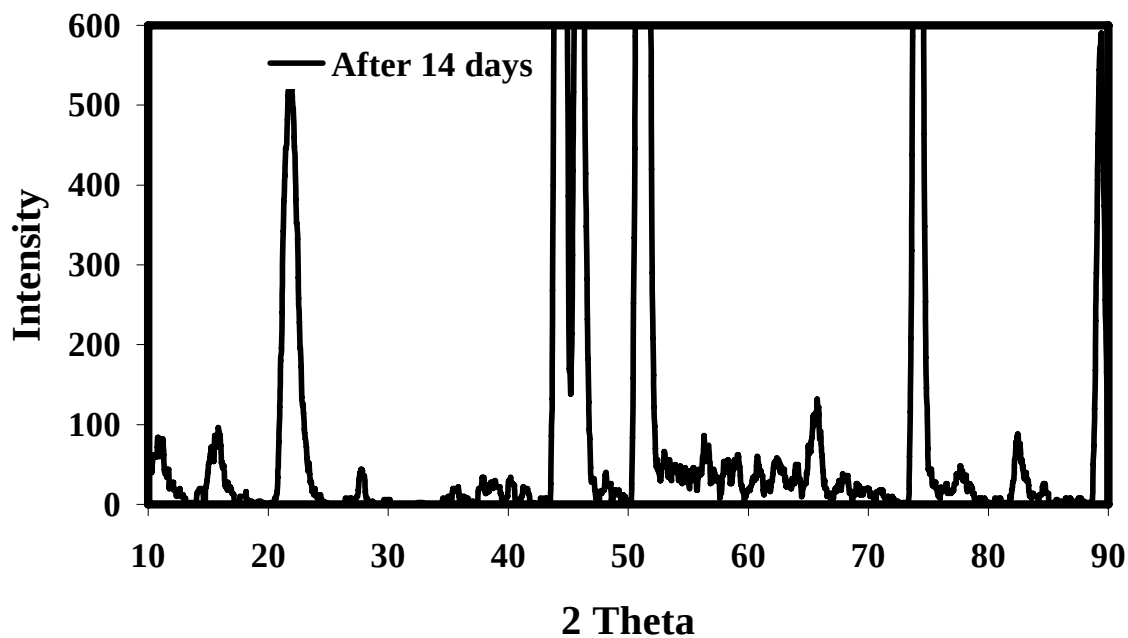


Figure 49. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 14 days.

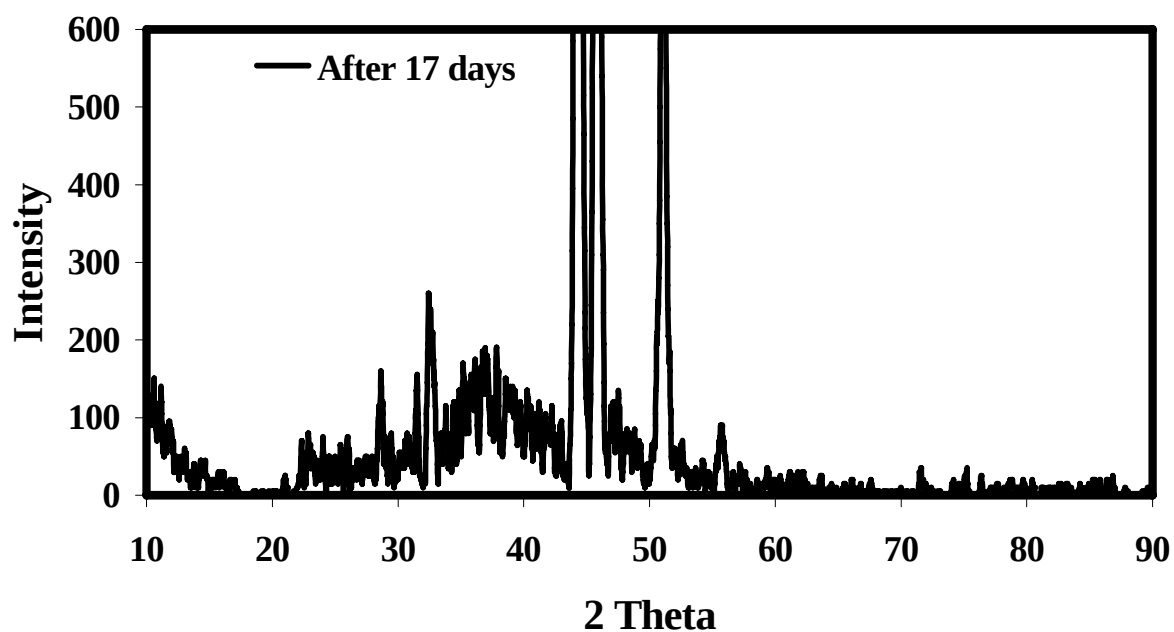


Figure 50. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 17 days.

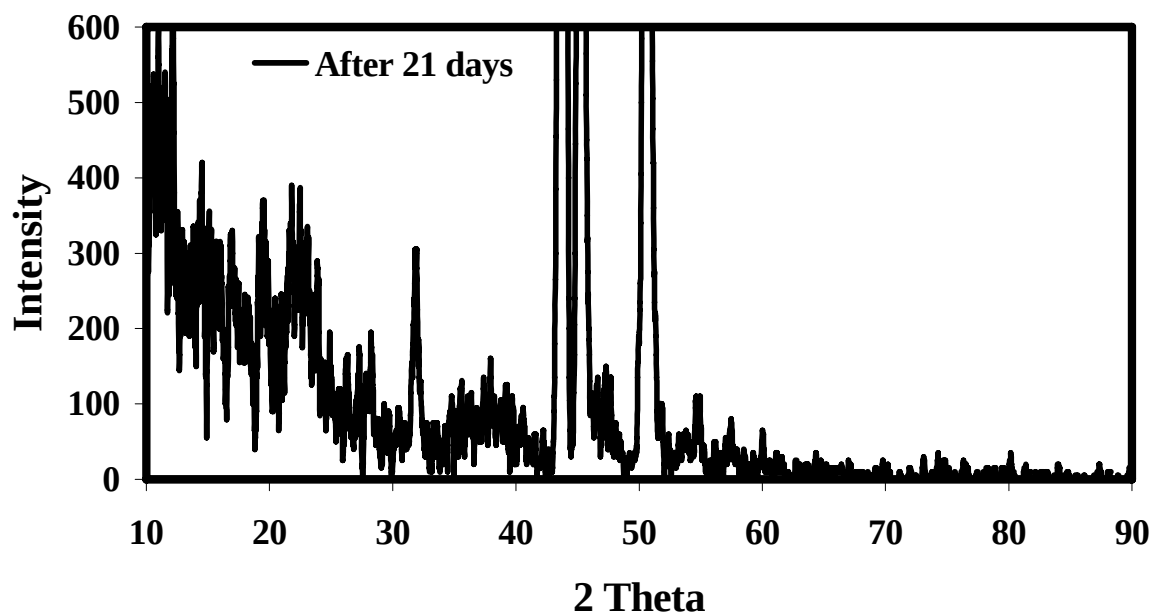


Figure 51. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 21 days.

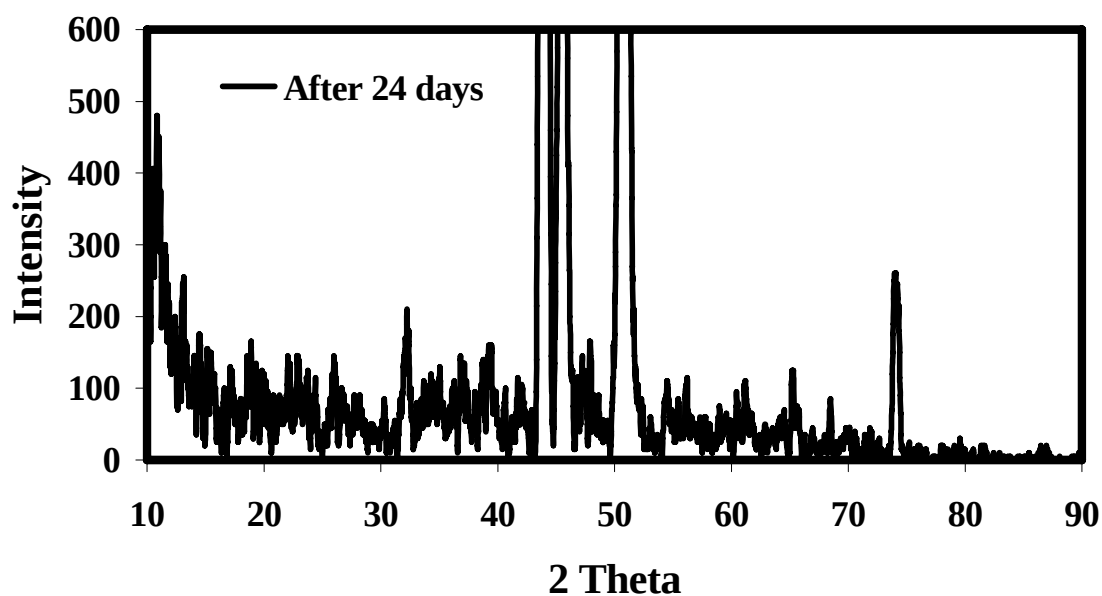


Figure 52. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 24 days.

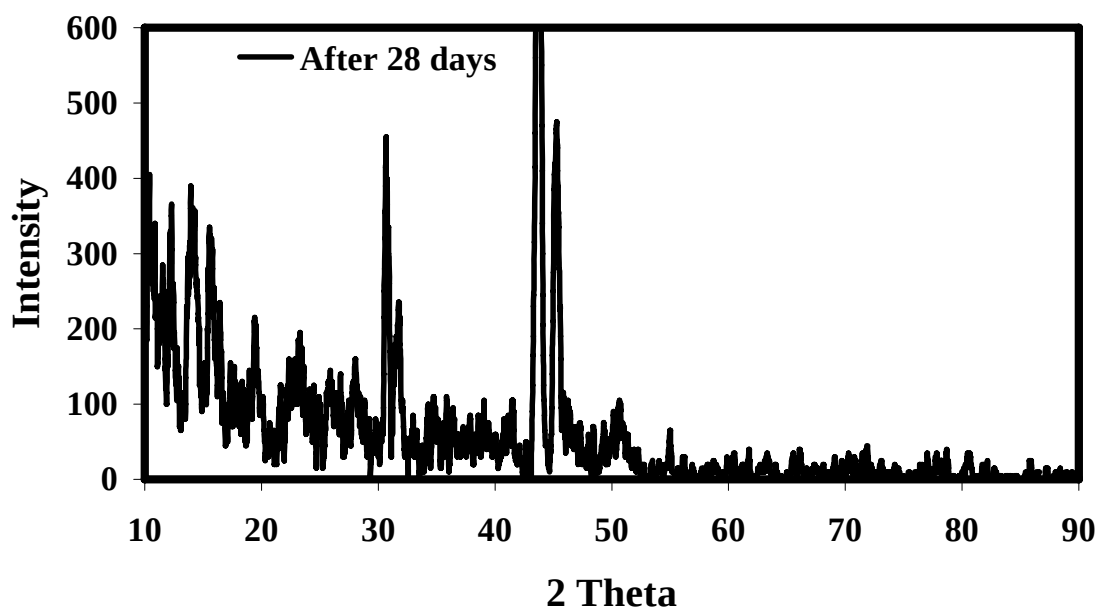


Figure 53. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 28 days.

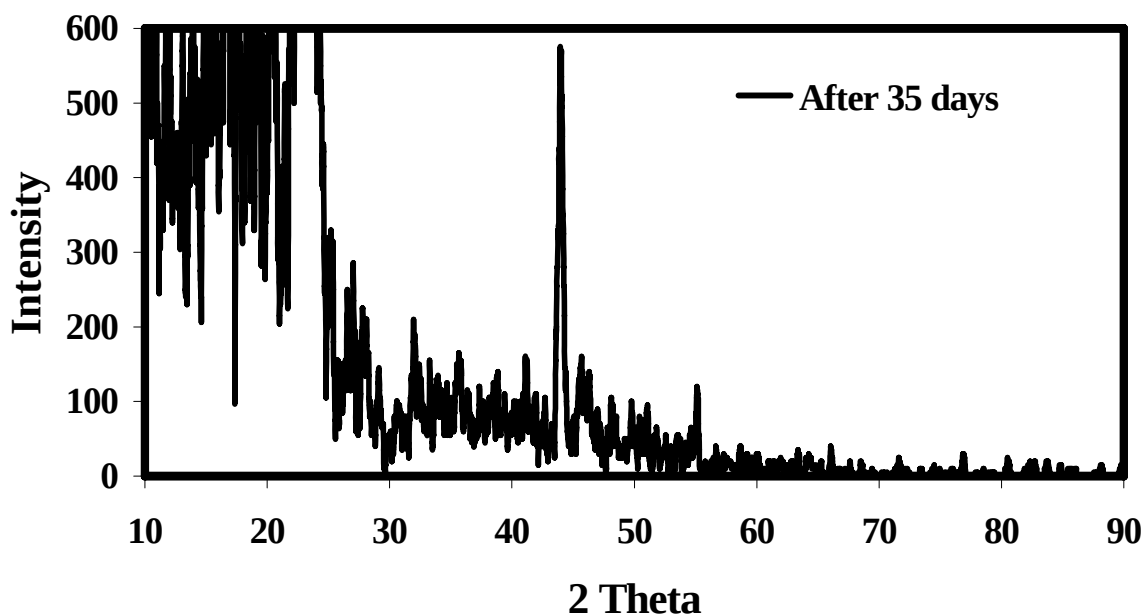


Figure 54. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 35 days.

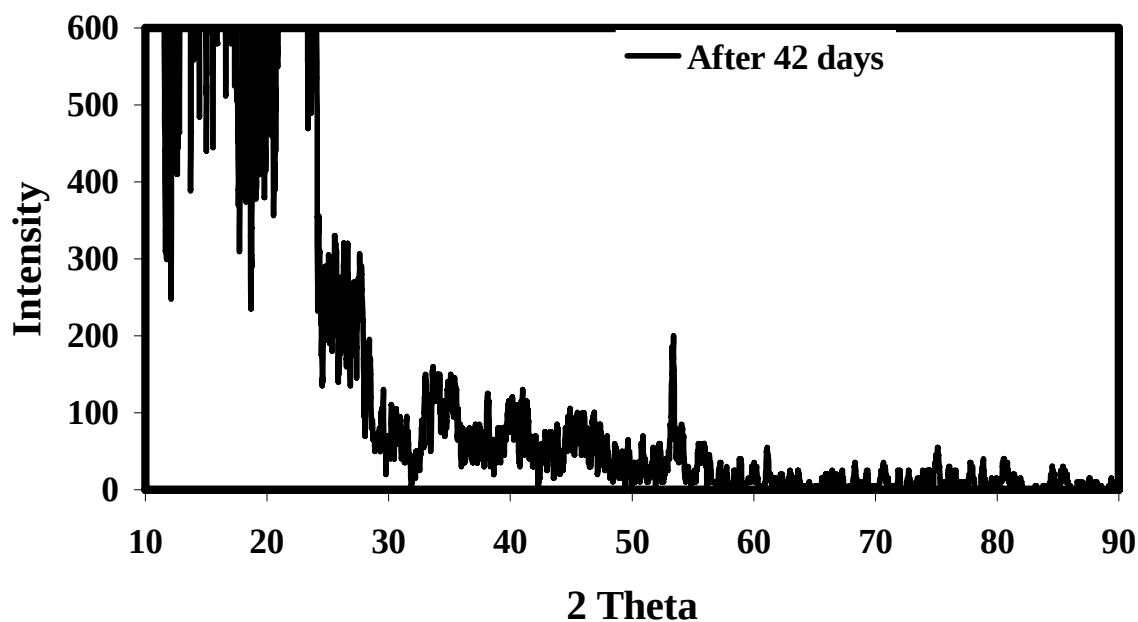


Figure 55. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with 50% NH_4OH for 42 days.

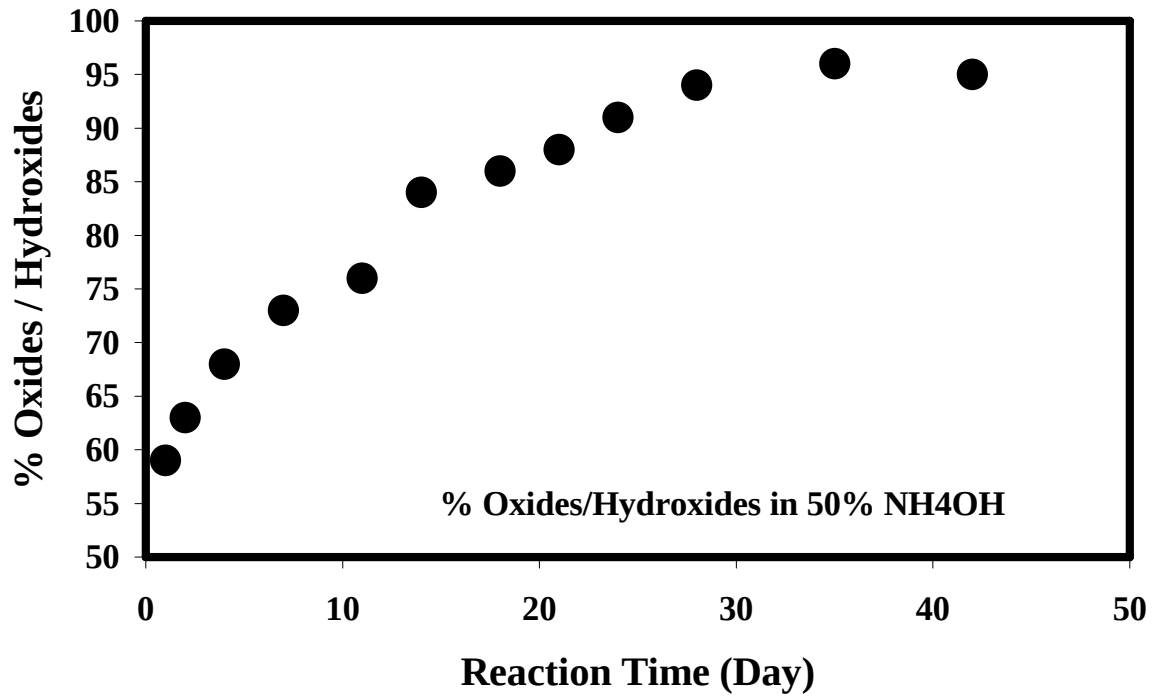


Figure 56. (%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH₄OH solution.

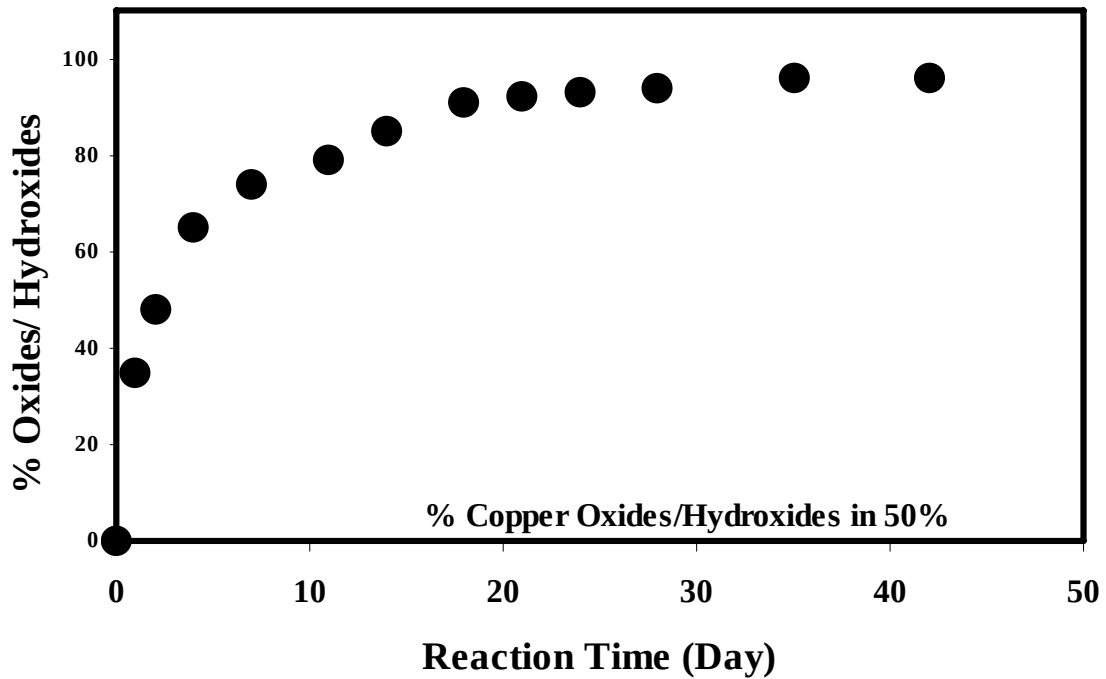


Figure 57. (%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH₄OH solution.

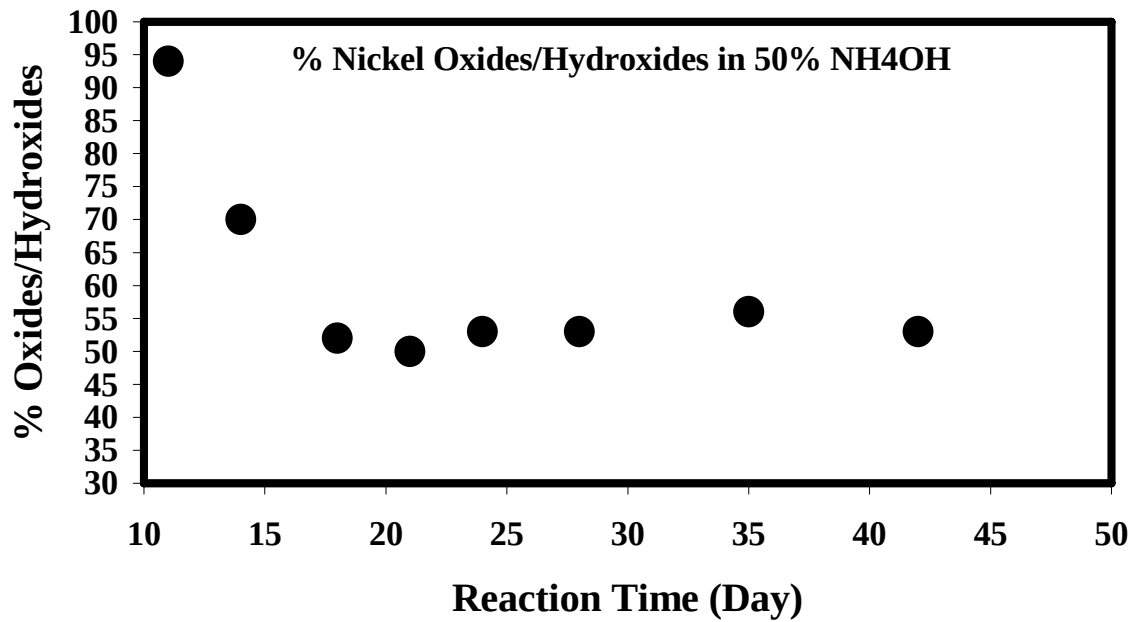


Figure 58. (%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH_4OH solution.

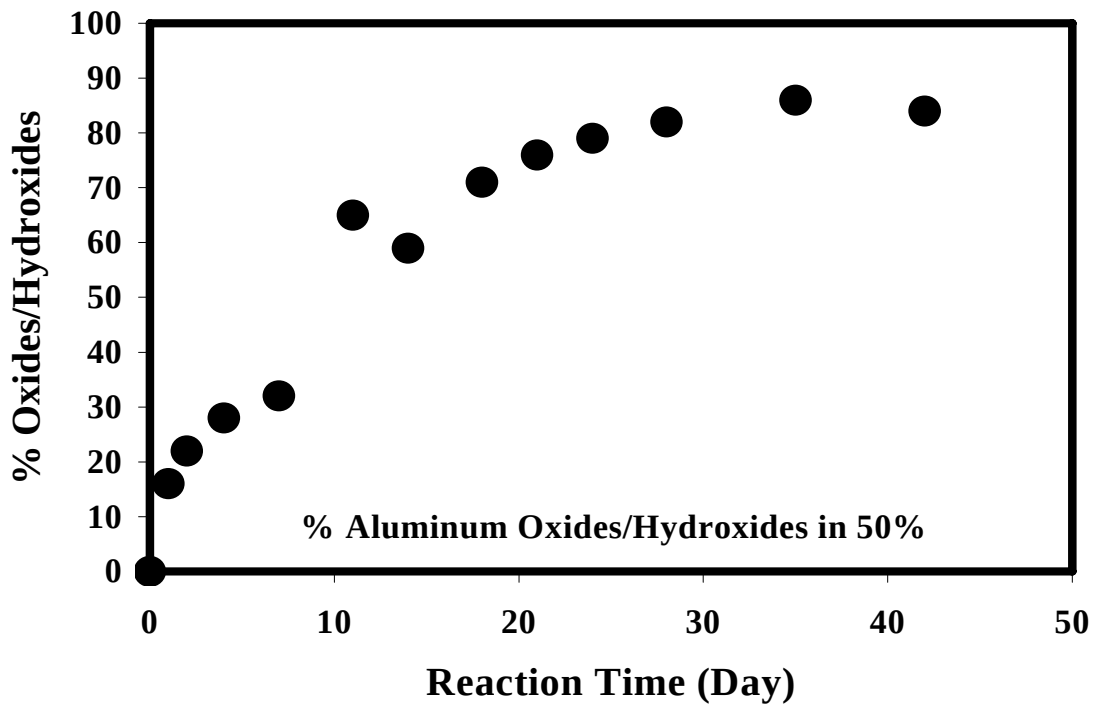


Figure 59. (%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH_4OH solution.

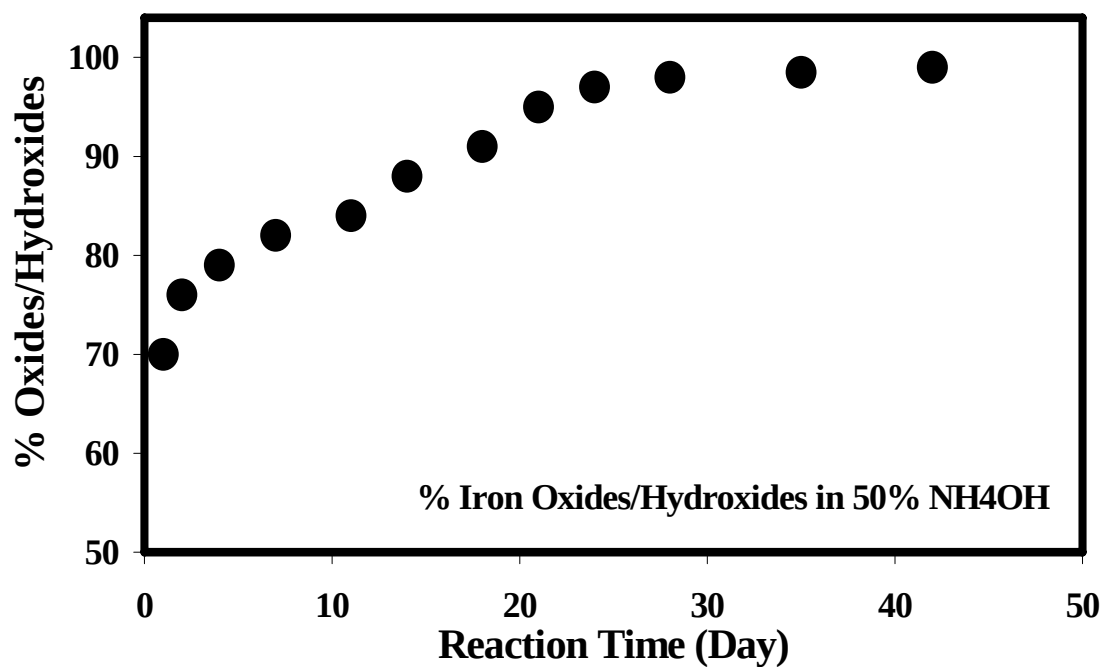


Figure 60. (%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% NH₄OH solution.

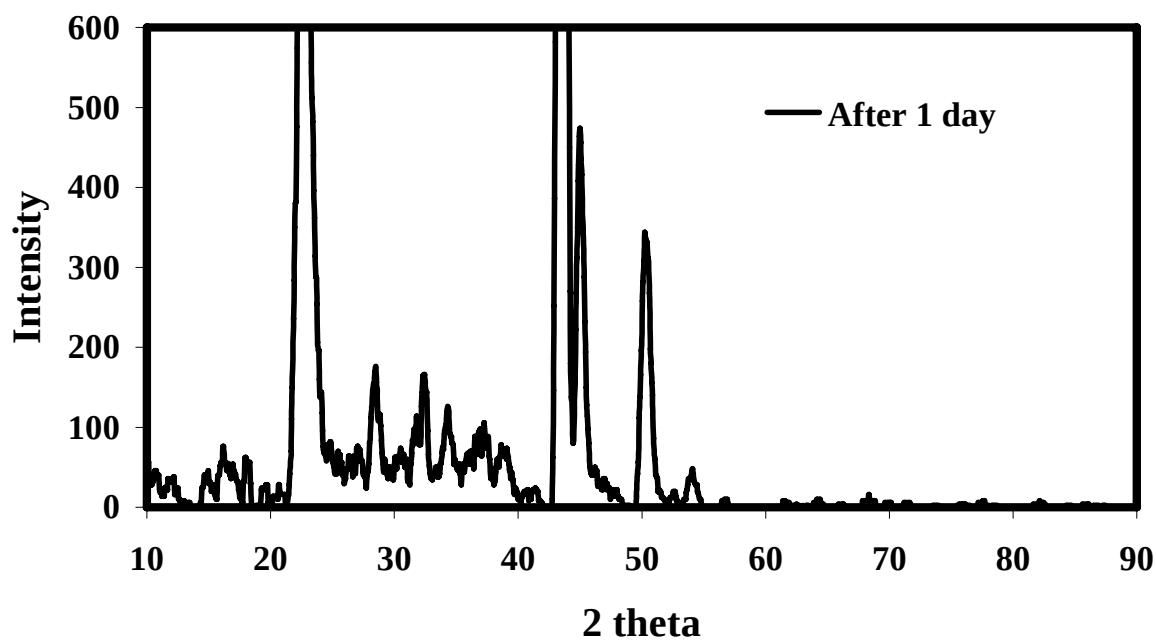


Figure 61. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 1 day.

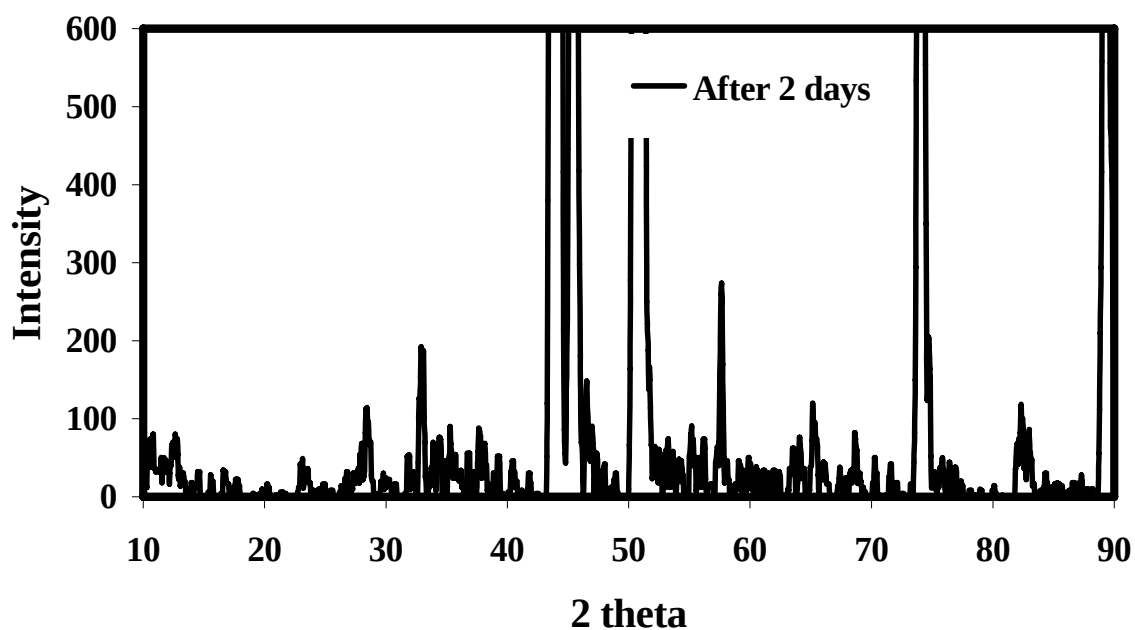


Figure 62. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 2 days.

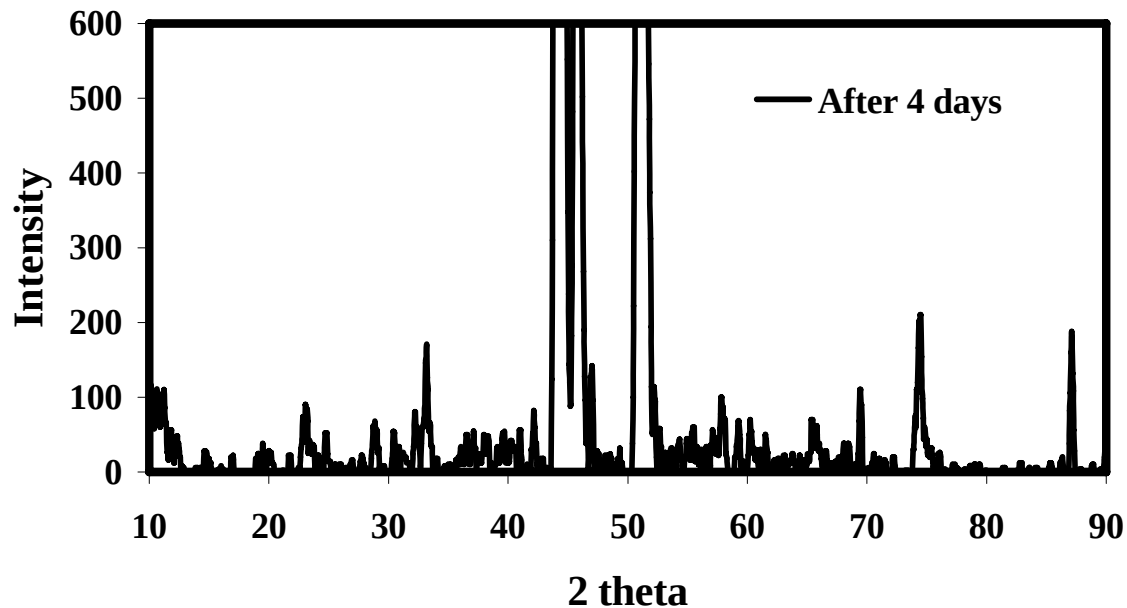


Figure 63. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 4 days.

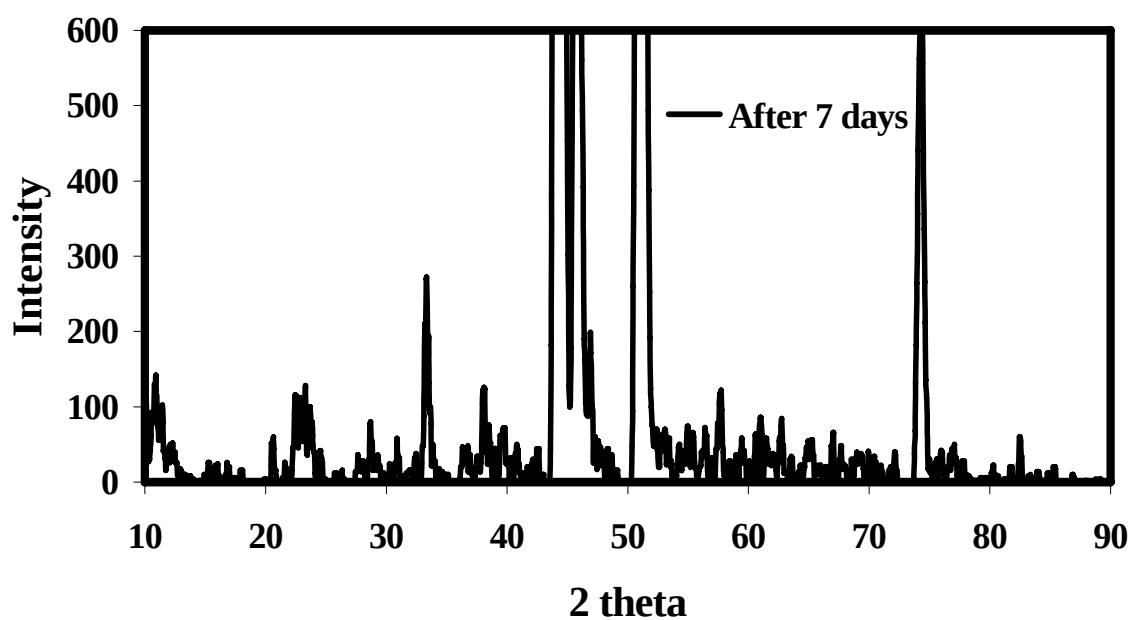


Figure 64. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 7 days.

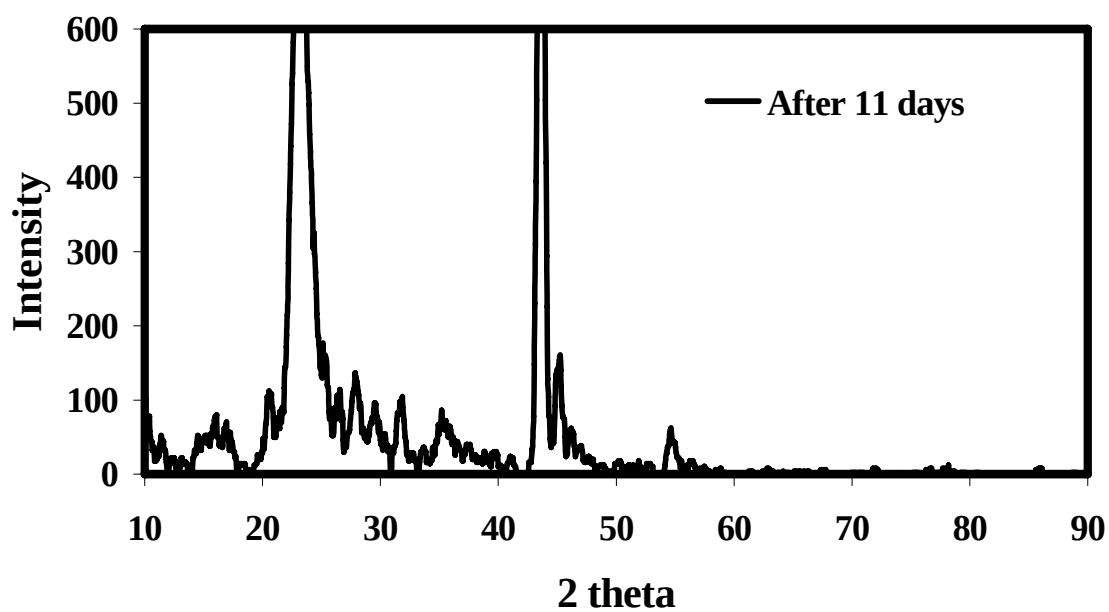


Figure 65. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 11 days.

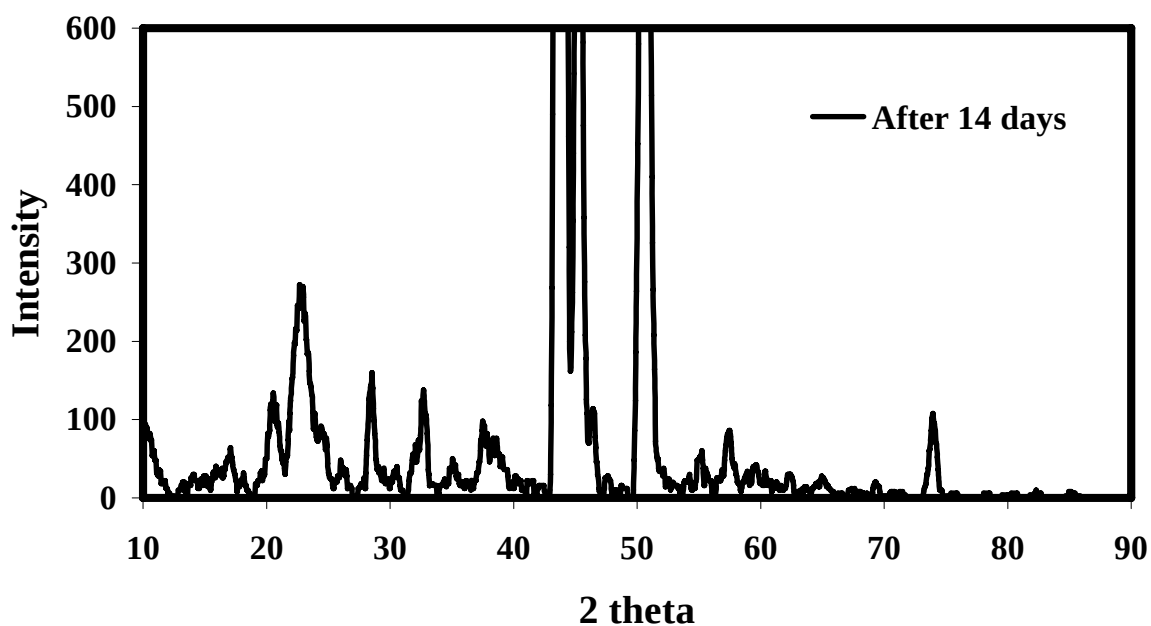


Figure 66. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 14 days.

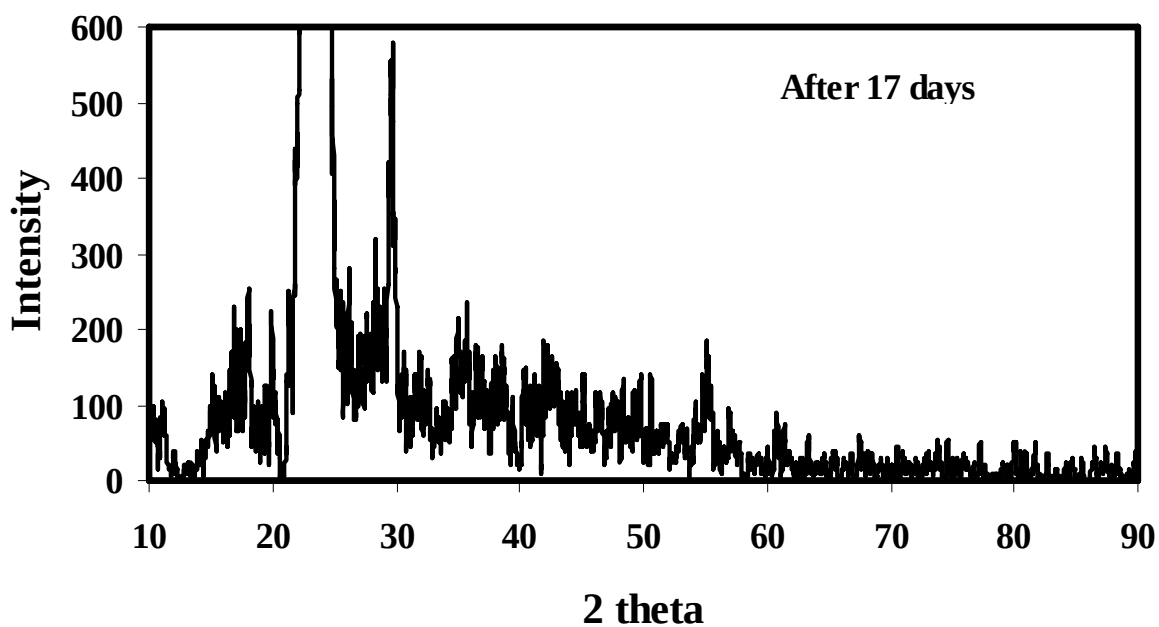


Figure 67. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 17 days.

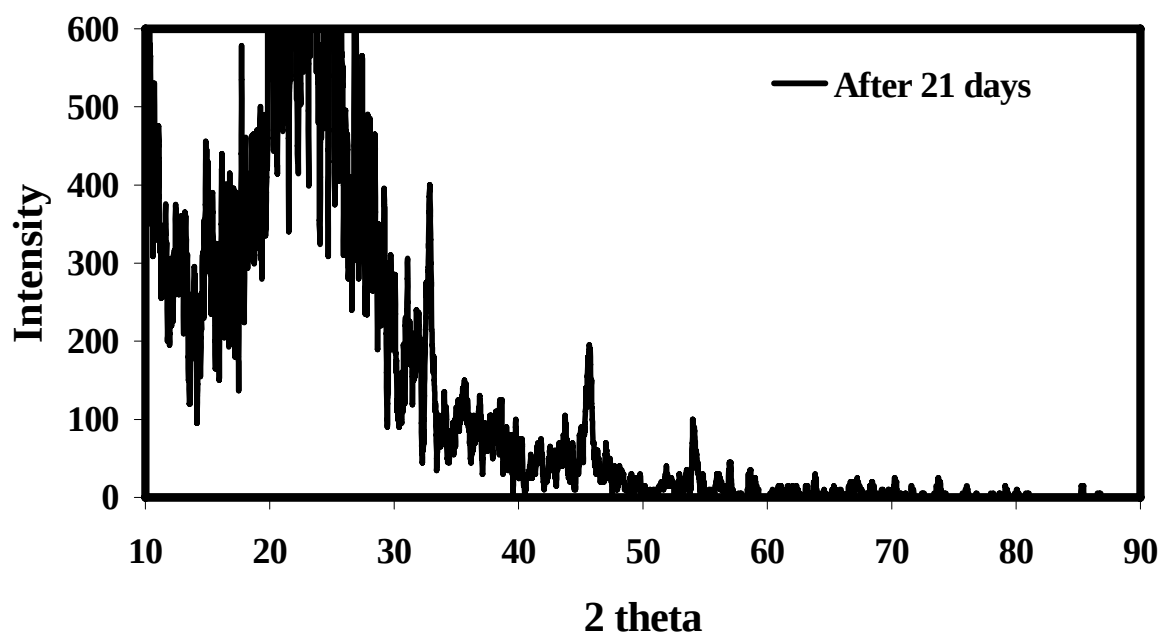


Figure 68. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 21 days.

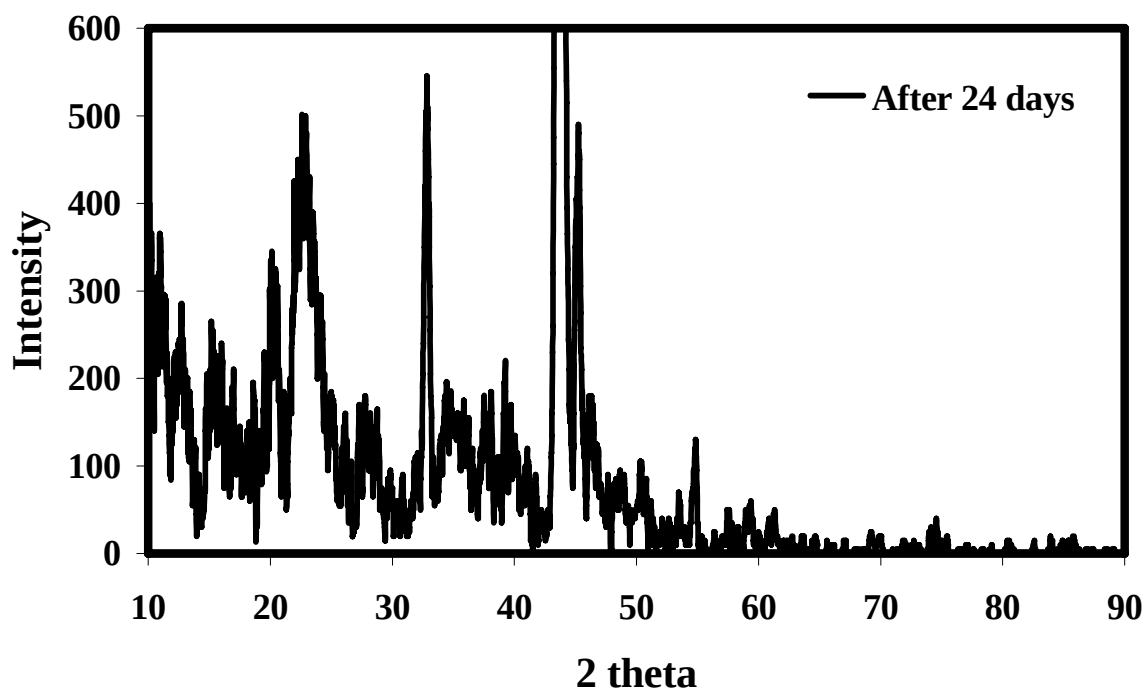


Figure 69. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 24 days.

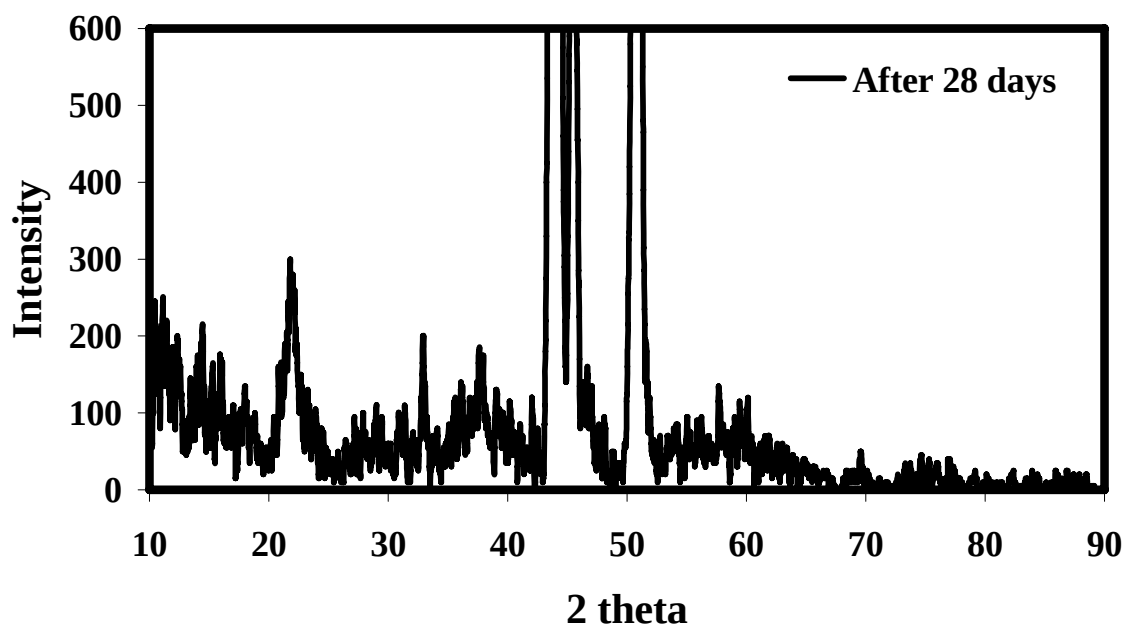


Figure 70. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 28 days.

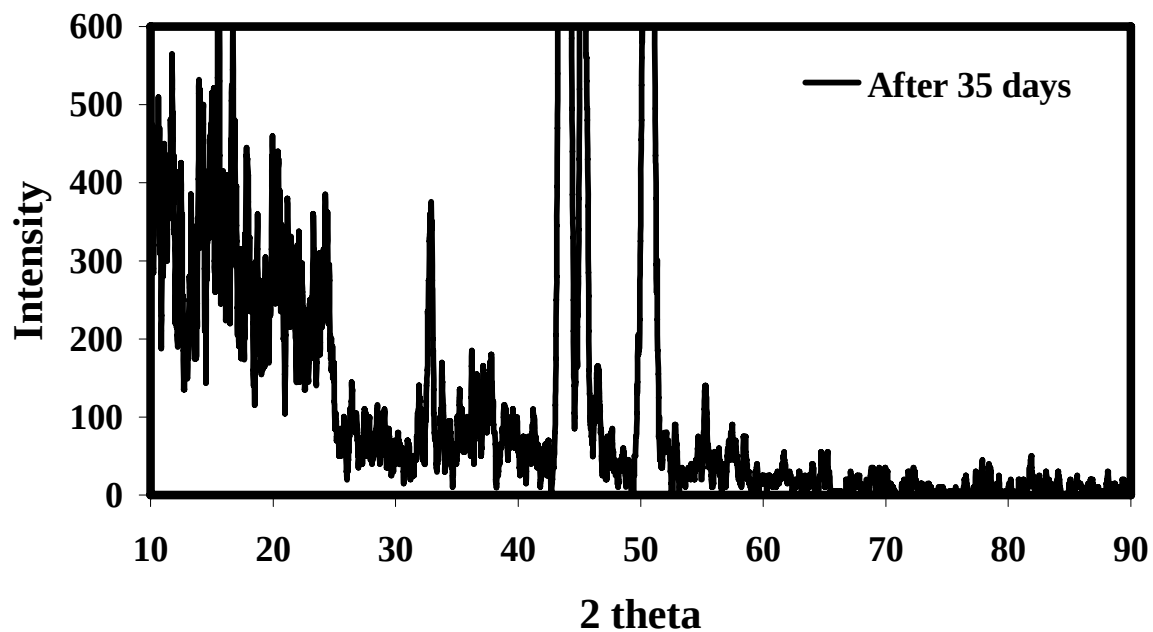


Figure 71. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 35 days.

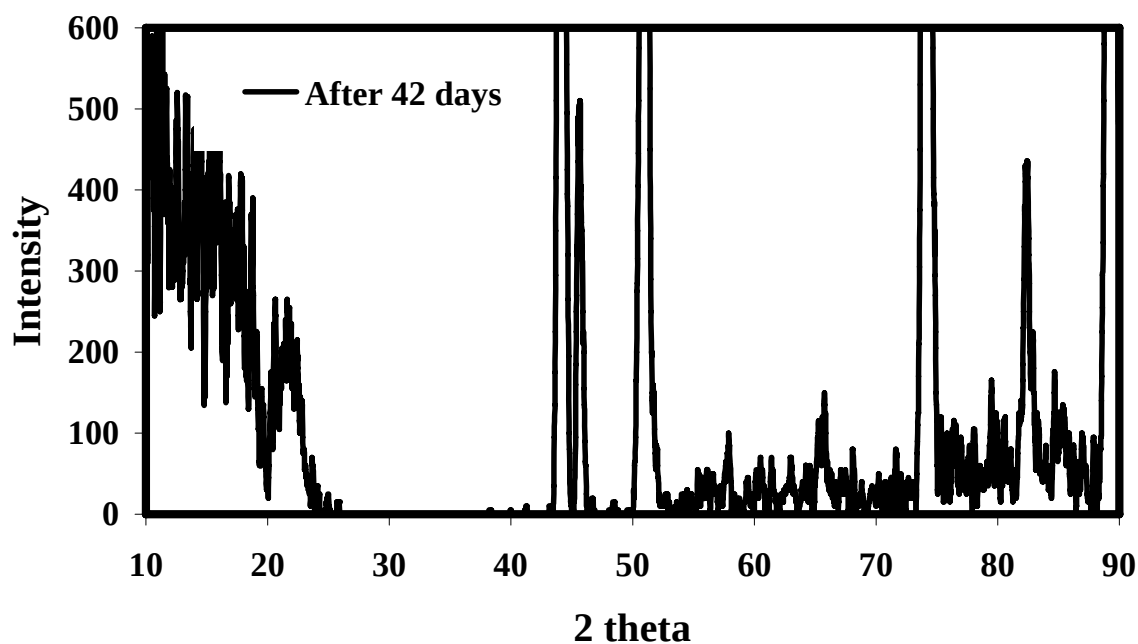


Figure 72. x ray diffraction pattern obtained from nickel aluminum bronze sample that was reacted with seawater for 42 days.

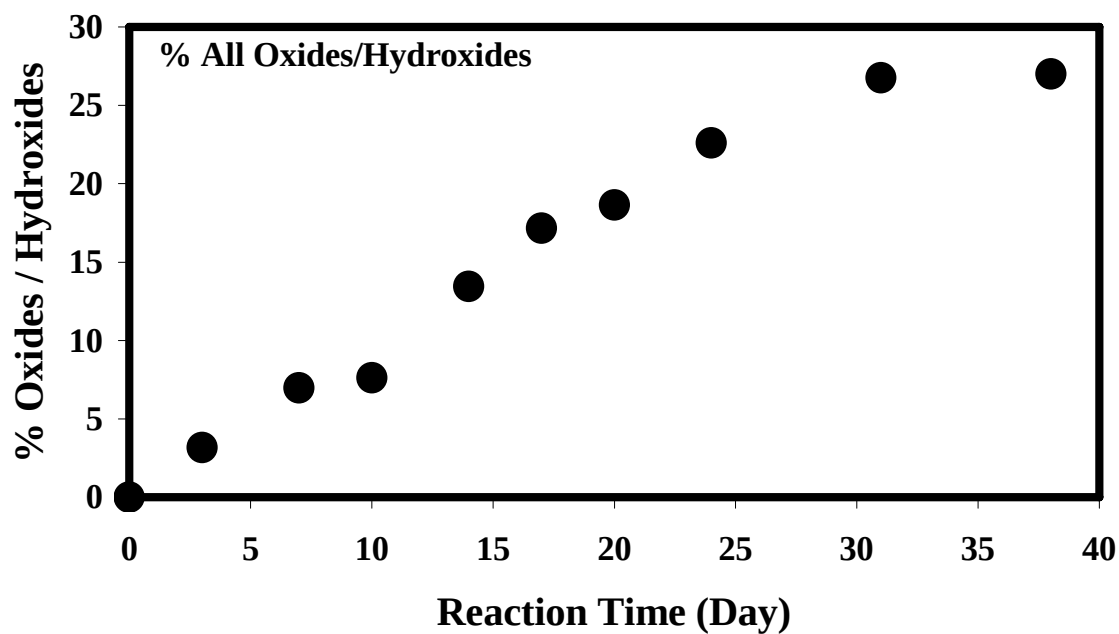


Figure 73. (%) of all oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.

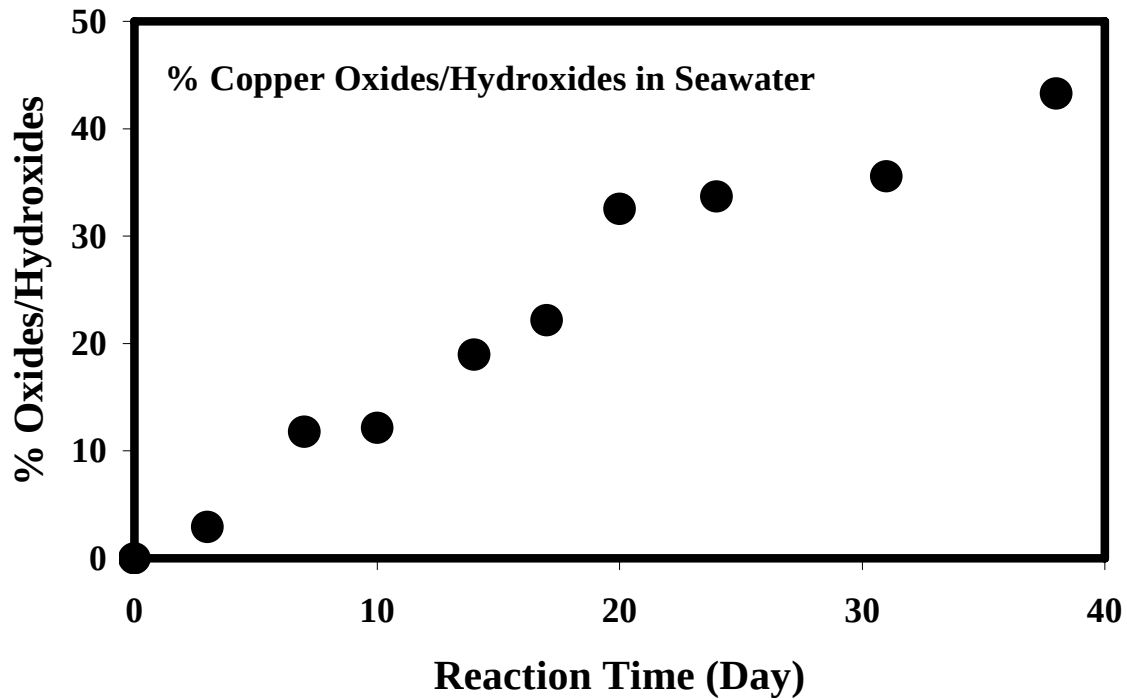


Figure 74. (%) Copper oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.

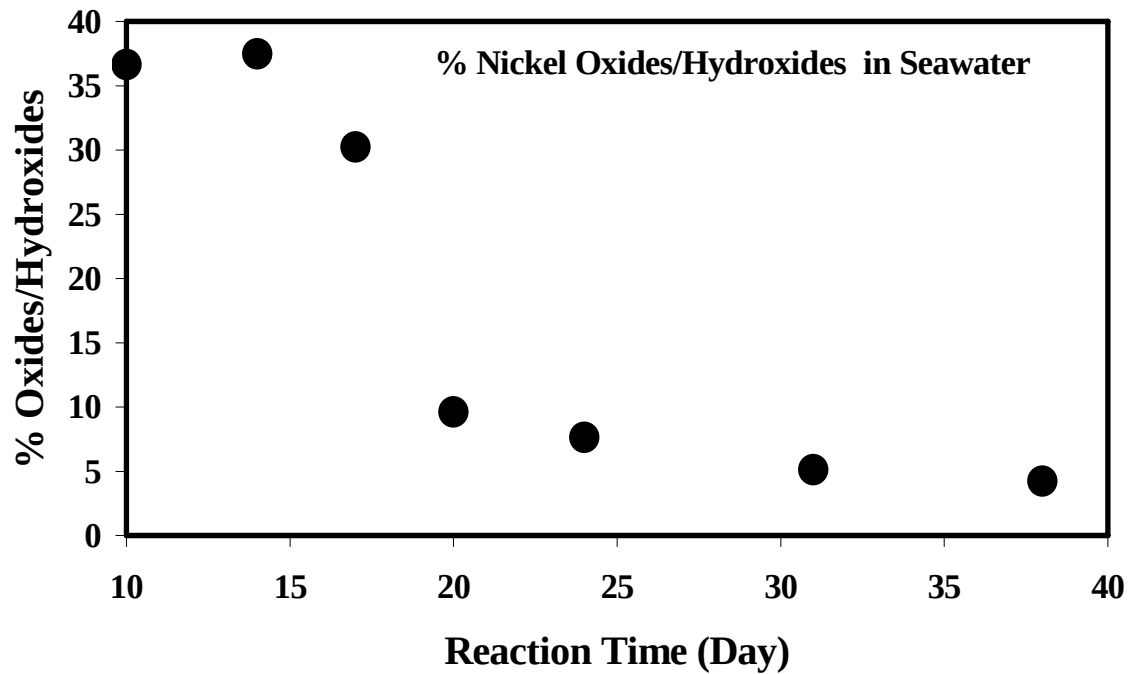


Figure 75. (%) Nickel oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.

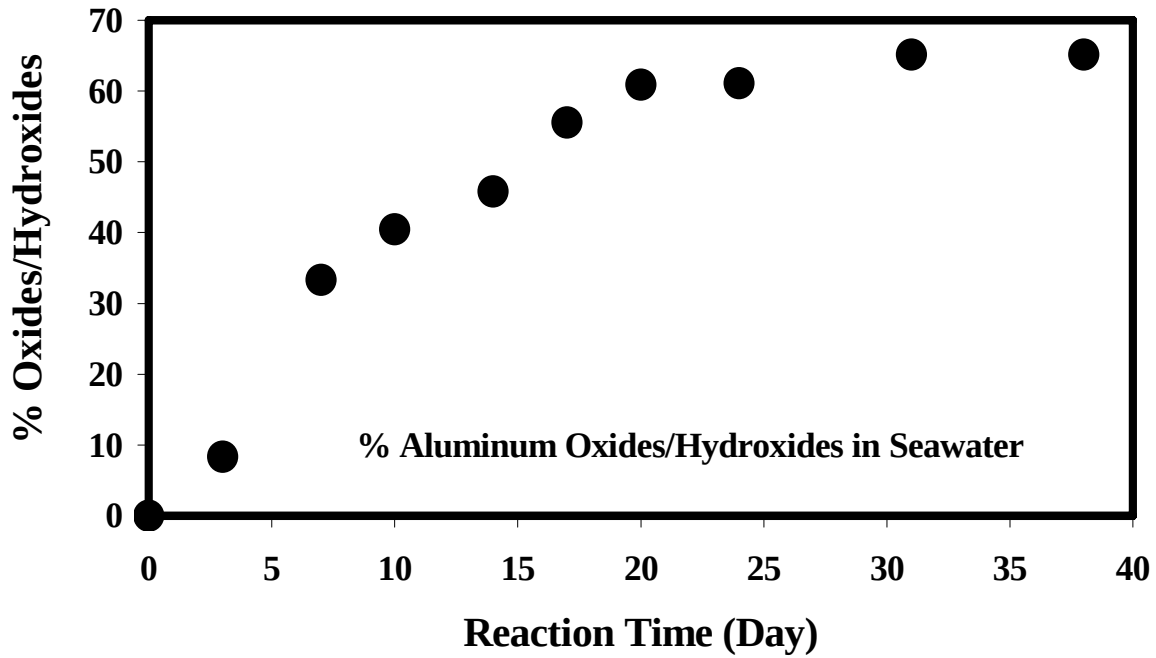


Figure 76. (%) Aluminum oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in seawater.

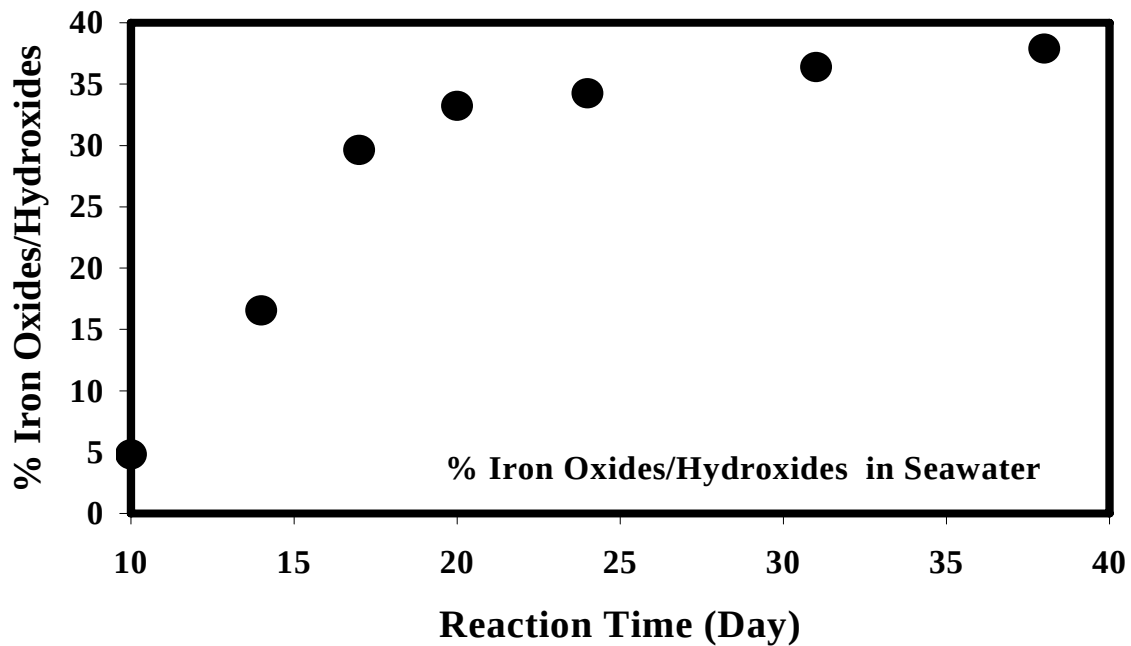


Figure 77. (%) Iron oxides/hydroxides formed on the surface of nickel aluminum bronze sample versus reaction time during corrosion in 50% seawater.

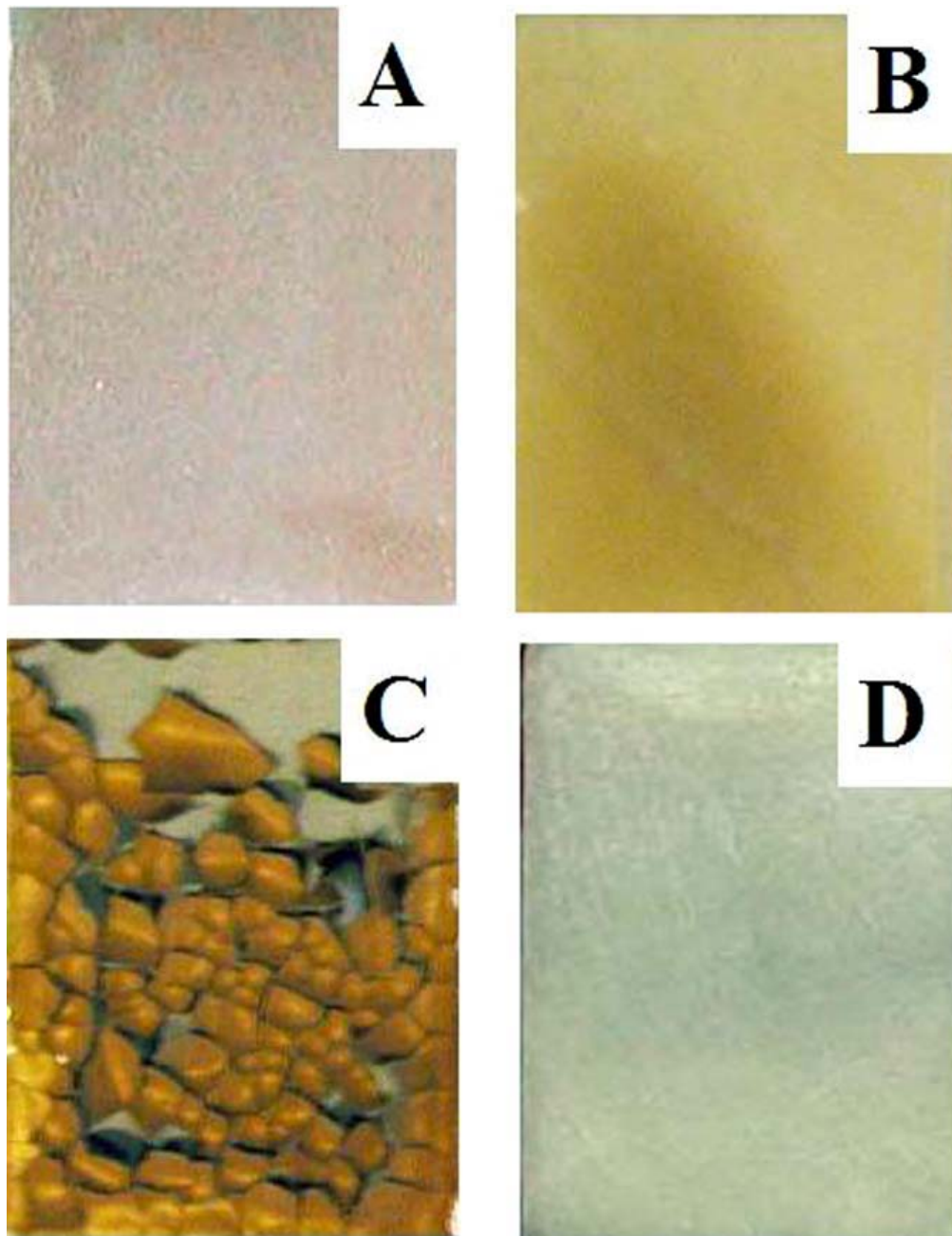


Figure 78. Scanning electron micrographs obtained from nickel aluminum bronze samples after reaction with (A) 10%, (B) 20%, (C) 50% NH_4OH solution and (D) seawater. Oxide characteristics (A) significant and tenacious corrosion, (B) severe corrosion, (C) dark brown corrosion product with severe “mud cracking” and (D) mild corrosion.

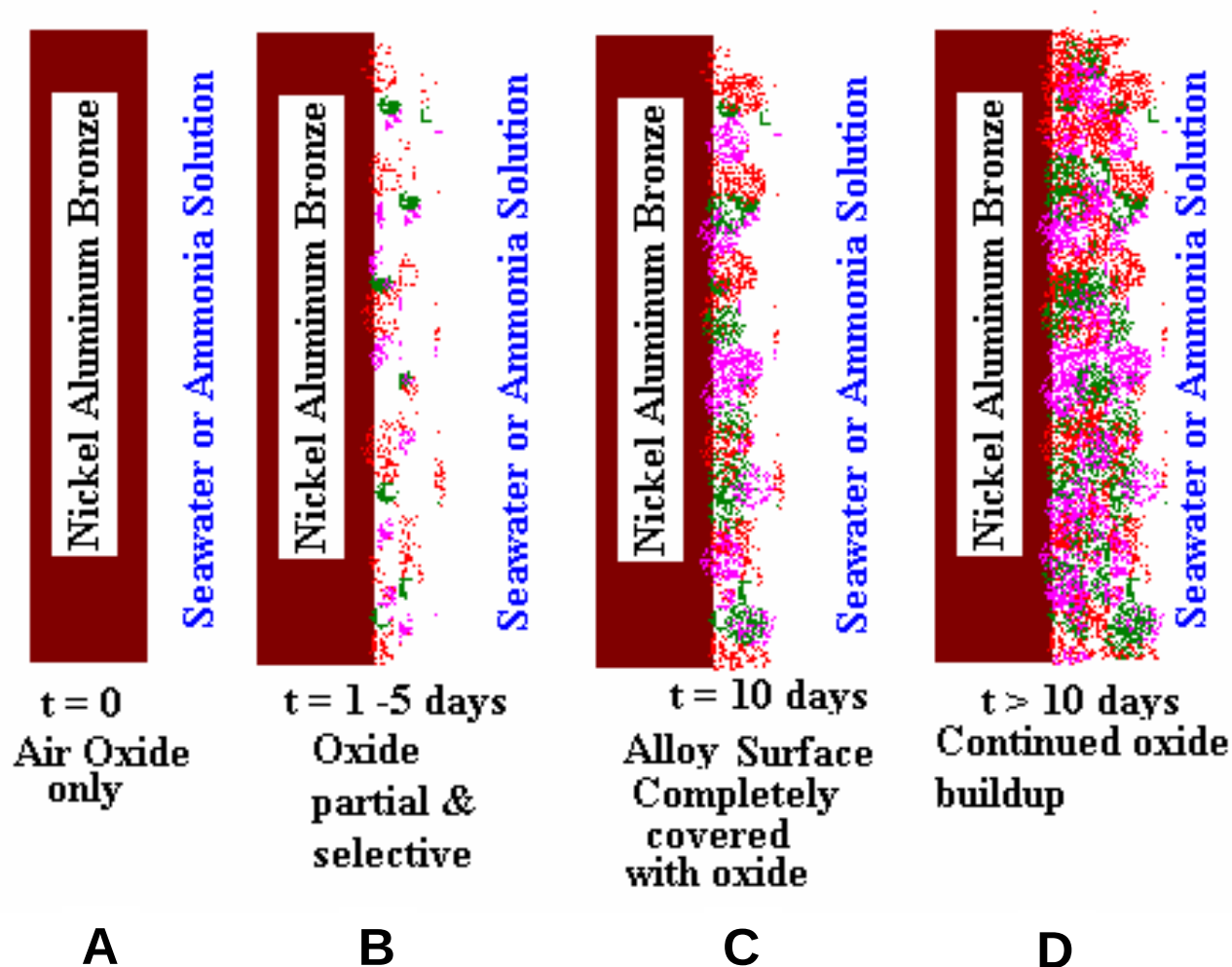


Figure 79. Schematic diagram of oxide growth on nickel aluminum bronze in seawater and or ammonia solution. Different colors represent different oxides such as copper oxide, nickel oxide and aluminum oxide.

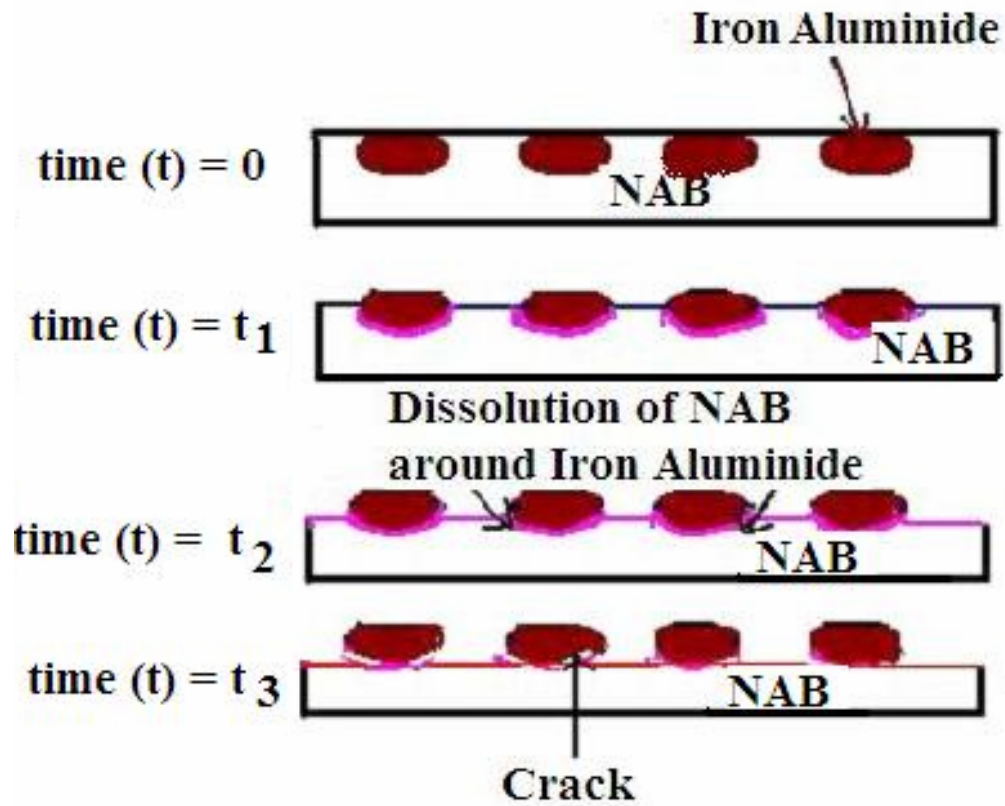


Figure 80. Schematic diagram depicting how the iron aluminide particles (kappa phase) are being exposed with time due to the corrosion of NAB sample surface in NH_4OH or seawater.

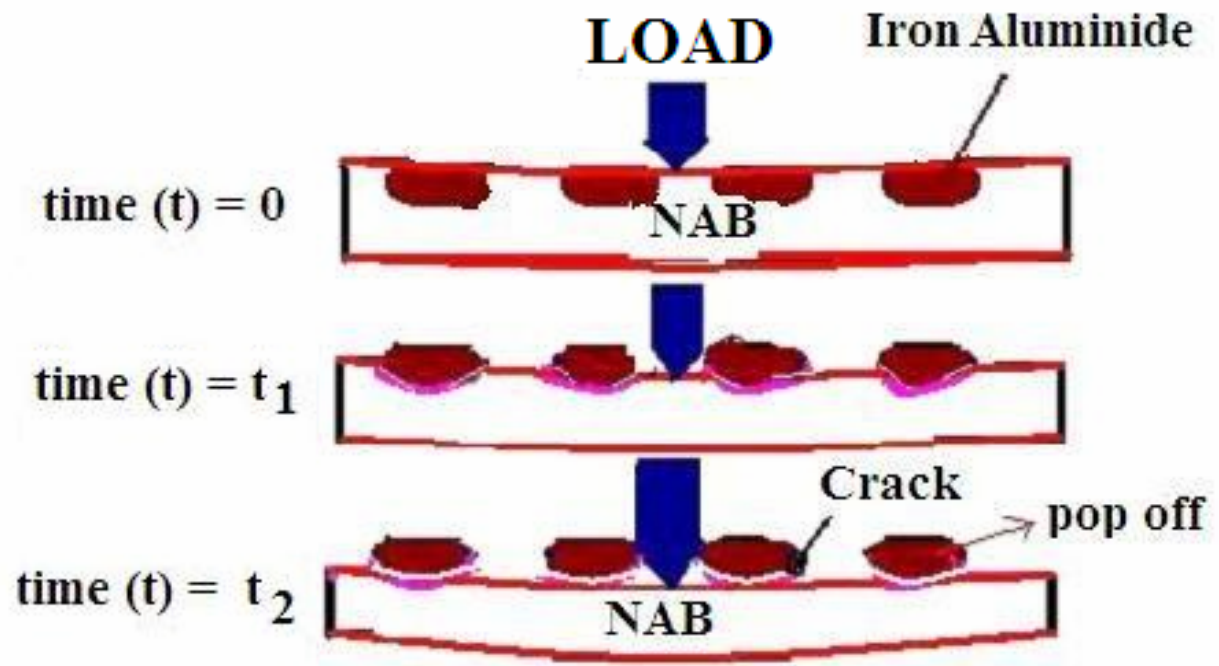


Figure 81. Schematic diagram of how the iron aluminide particles (kappa phase) are being weakened due to the corrosion of NAB matrix in NH_4OH or seawater and under applied stress.

Table 1. The rate of oxide formation and the order of the reaction estimated from the weight change measurement for nickel aluminum bronze in 10%, 20%, and 50% ammonia solution, and sea water.

Solution	Overall Reaction		Fast Reaction		Slow Reaction	
	Rate (%/day)	Order (%/day)	Rate (%/day)	Order	Rate (%/day)	Order
10% NH ₄ OH	0.11	0.5	0.17	0.5 -1.0	0.015	0.5 - 2.5
20% NH ₄ OH	0.22	0.5	0.32	0.5	0.02	2.5 - 3
50% NH ₄ OH	0.32	1 - 1.5	0.43	0.5 - 1	0.02*	1.5*-5.5
Seawater	0.0077	0.5	0.0089	1 .	- 0.0038	3-3.5

*[Intermediate Reaction Zone; Slow reaction zone (Rate k_3) = 0.032; (Order (n_3)) = 2.5]

Table 2. The rate of oxide formation and the order of the reaction estimated from the open circuit potential (OCP) values for nickel aluminum bronze in 10%, 20%, and 50% ammonia solution, and sea water.

Solution	Overall Reaction		Fast Reaction		Slow Reaction	
	Rate (%/day)	Order (%/day)	Rate (%/day)	Order	Rate (%/day)	Order
10% NH ₄ OH	5.6	0.5	7.38	0.5 -1.0	0.67	0 - 0.5
20% NH ₄ OH	4.8	0.5	5.45	0.5 - 1	1.25	0 – 2.5
50% NH ₄ OH	4.0	0.5 - 1	7.8	1 - 1.5	1.16*-2	1*-3.5
Seawater	4.8	0.5	5.45	0.5 – 1 .	- 1.25	2.5-3.5

*[Intermediate Reaction Zone; Slow reaction zone (Rate k_3) = 0.81; (Order (n_3)) = 2.5]

Table 3. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in 10% ammonia solution.

Oxides / Hydroxides	Overall Reaction		Fast Reaction		Slow Reaction	
	Rate (%/day)	Order (%/day)	Rate (%/day)	Order	Rate (%/day)	Order
Copper	4.3	0.5	7.2	0.5-1	0.375	0
Nickel	2.25	0.5	2.39	0.5 - 1	- 0.2	1
Aluminum	11.5	0.5	16.4	0.5	- 1.1	1
Iron	15.4	1 – 1.5	20.3	1.5 – 2.	- 0.83	3
All Oxides	4.5	0.5	6.8	1	0.125	0 – 3.5

Table 4. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in 20% ammonia solution.

Oxides / Hydroxides	Overall Reaction		Fast Reaction		Slow Reaction	
	Rate (%/day)	Order (%/day)	Rate (%/day)	Order	Rate (%/day)	Order
Copper	5.125	0.5	6.7	0.5-1	0.63	0
Nickel	2.17	0.5	2.46	0.5 - 1	- 0.26	1
Aluminum	13.8	0.5	15.65	0.5	5.8	0
Iron	18.0	1 – 1.5	24.0	1.5 – 2.	0.775	1.5-2.5
All Oxides	5.3	0.5	6.69	0.5 - 1	1.4	0 – 0.5

Table 5. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in 50% ammonia solution.

Oxides / Hydroxides	Overall Reaction		Fast Reaction		Slow Reaction	
	Rate (%/day)	Order (%/day)	Rate (%/day)	Order	Rate (%/day)	Order
Copper	8.5	1.5	10.62	1.5	1.25	2.0-2.5
Nickel	3.6	0.5	3.8	1	- 0.3	1
Aluminum	15.6	1	18.2	1	0.8	2.0-2.5
Iron	22.5	1.5	28.2	1.0 – 1.5.	1.5	2.5-3
All Oxides	8.75	1.5	11	1.5	1.75	2 – 2.5

Table 6. The rate of oxide formation and the order of the reaction estimated from x-ray diffraction patterns for nickel aluminum bronze in seawater.

Oxides / Hydroxides	Overall Reaction		Fast Reaction		Slow Reaction	
	Rate (%/day)	Order (%/day)	Rate (%/day)	Order	Rate (%/day)	Order
Copper	1.5	0.5	1.62	0.5	0.85	2-2.5
Nickel						
Aluminum	3.88	0.5	4.52	0.5	0.55	3-3.5
Iron	2.1	0.5	3.07	0.5 – 1.	0.25	2.5-3
All Oxides	0.94	0.5	1.07	0.5	0.4	2 – 2.5

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