

Effect of Temperature and Concentration of Ammonium Nitrate Solution on the Susceptibility of Mild Steel to Stress Corrosion Cracking

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ABSTRACT

The effect of varying the temperature and the concentration of ammonium nitrate solution on the stress corrosion cracking (SCC) susceptibility of mild steel is studied. An increase in the temperature causes a decrease in the stress corrosion life. It appears that the susceptibility in the range 368 K to 380 K was greater than at other temperatures. Near the boiling point corrosion and stress corrosion occurs, at the boiling point, the cracking was associated with a high rate of general corrosion. Microscopic examination after stress corrosion testing in 10Wt%, 20Wt%, and 52Wt% NH₄NO₃ solution revealed that in all cases there was severe intergranular attack, especially at the high concentration.

Keywords: Stress Corrosion Cracking, Ammonium Nitrate Solution, Mild Steel, Constant Load Test, Temperature Effect, Concentration Effect

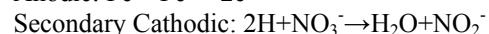
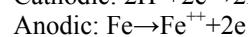
1. Introduction

In an attempt to determine what chemical and electrochemical properties of the corroding solution are required for stress corrosion cracking, previous researchers determined the potentiostatic polarization curves for single crystals in de-aerated boiling, 55% Ca (NO₃)₂, 30% NaOH, and other solutions [1]. The results revealed that iron exhibits passive behavior near the free corrosion potential in nitrate solution only. Although the surface film at the corrosion potential was stable, it required a long time to be restored if it was damaged.

Szklarska [2] stated that passivation phenomena were essential for the occurrence of the stress corrosion cracking of mild steel in nitrate solution. It was reported [3] that the sequence of the reaction of corroding iron in NH₄NO₃ solution was as follows:

- 1) Formation of a soluble complex salt of iron with ammonia, this salt being Fe (NH)₆ (NO₃)₂.
- 2) Production of nascent hydrogen which acts as a reducing agent.
- 3) Reduction of nitrate ions to NO₂⁻ as the main corrosion product.
- 4) Oxidation of ferrous ions to ferric ions.

The most probable cycle of reactions was considered to be:



Polarization studies on iron electrodes indicate that Fe₃C particles or carbon in interstitial solution may act as efficient sites for cathodic discharge during the corrosion reaction [4]. Intergranular penetration occurred in nitrates solution, but such penetration was limited to a depth of two grain diameters [5].

Most of the work regarding grain boundary attack of unstressed low carbon steel by nitrates has been carried out in NH₄NO₃ solution. Engell and Baumel [1] did produce this type of attack in boiling Ca (NO₃)₂ but only with the aid of anodic polarization. General overall attack in NH₄NO₃ is due to the high depolarizing power of the oxidizing NO₃⁻ ions on the cathodic local areas, coupled with the complexing action of the NH₄⁺ which facilitates the anodic reaction, i.e. iron dissolution of Fe⁺⁺ ions. Thus, the correlation of results from NH₄NO₃ solution with those from solutions of other cations (e.g. Ca⁺⁺, Na⁺, K⁺) probably has little significance.

Flis [6] proposed that after a small amount of grain boundary penetration, regions of stress concentration were produced. When the resulting strain in these regions was sufficiently large, the oxide film would be ruptured and the strain rate would be high enough to prevent the

reformation of the protective film. Thus, the crack propagation proceeded by an electrochemical process.

Whilst the various mechanisms of stress corrosion cracking were seldom proposed originally for the cracking of ferritic steels, they have all been suggested at different times as explaining the phenomenon of stress corrosion cracking in these materials. However, all the mechanisms are interpreted from data on the effects of various environmental and metallurgical parameters on stress corrosion. The susceptibility of the steel was remarkably affected by the concentration of the nitrate solution, this was noticed when cracking of mild steel in various nitrate solutions occurred. Baker and Singleterry [7] studied the stress corrosion cracking in u-bend specimens of A1S1 4340 steel. They reported that KNO_3 solutions show a systematic decrease in the time to failure with increasing concentration.

One of the reasons for the lack of appreciation of the chemical factors that affect SCC is the lack of understanding of the large influences that are produced by small change in the environment. A change of one unit of the pH changes the solubility of oxide by three order of magnitude for three valence ion such as Fe^{+3} and by two order of magnitude for a two valence ion such as Fe^{+2} [8].

Leferink [9] reported that the steel samples were subjected to aerated ammonium nitrate solution at 368 K with concentration ranging between 2% and 35%, after an exposure for 65 hours; cross sections of the steel were studied. When intergranular corrosion attack (IGA) occurs the steel was considered sensitive to ammonium nitrate within these concentrations.

2. Experimental Work

2.1 Material

The work was carried out on mild steel of the following composition (Wt%):

C	0.070
Mn	0.300
Si	0.093
S	0.044
P	0.019

The Material was supplied in the form of 19 mm diameters rods. Corroding solution was prepared by using ammonium nitrate.

2.2 Specimen Preparation

2.2.1 For Electrochemical Measurement

The steel rods supplied were hot-rolled at 1200 K to strip ~4mm thick. This was reheated to 1200 K in the furnace for 900 s, cooled slowly to 850 K, and then allowed to cool to room temperature. Most of the oxide film was removed by pickling in 30% HCl solution, and the surface was finally cleaned for cold-rolling by mechanical abrasion. The strip was reduced to 0.5 mm thick by cold-rolling.

Samples 20 mm by 13 mm were prepared. A 3 mm holes was drilled at one end to suspend the samples, then the specimen were degreased with ether, annealed at 1200 k for 3.6 ks after wrapping in thin foil to prevent oxidation. The specimens were attached to the holder and the whole assembly coated apart from an area of 100 mm² on one face.

2.2.2 For Stress Corrosion Testing

The steel rod was hot-rolled at 1200 k and swaged cold to approximately 10 mm diameter. It was then annealed at 1200 k for 900 s, furnace-cooled to 850 k, followed by air-cooling to room temperature. The specimens were machined from the rod as shown in Figure 1. They have a gauge length of 15.8 mm and a gauge diameter of 3.2 mm.

2.3 Apparatus

2.3.1 Electrochemical Measurements

For electrochemical measurements on unstressed specimens, a glass cell comprising two compartments was designed. The main compartment contained the working electrode and the platinum counter electrode. The reference compartments contained a saturated calomel electrode. The complete cell is shown in Figure 2. The two compartments were connected by a salt bridge with a Luggin capillary. The glass joints that carried the working and the counter electrodes also had a screw cap joint for the thermometer. There was another two openings in the main

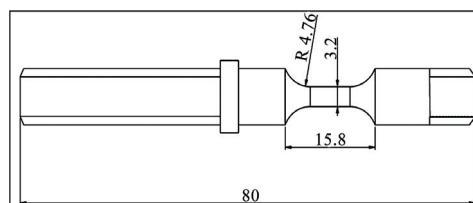


Figure 1. Stress corrosion test specimen (dimensions in mm)

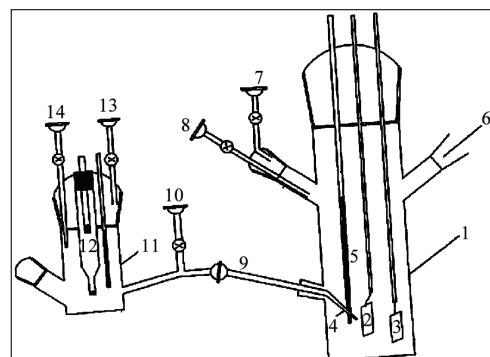


Figure 2. Electrochemical polarization cell (schematic): 1) Main compartment; 2) Specimen/working electrode; 3) Platinum electrode; 4) Luggin capillary; 5) Thermometer; 6) To condenser and gas outlet; 7, 13) Solution inlet; 8, 14) Gas inlet; 9) Salt bridge; 10) Gas Outlet; 11) Reference compartment; 12) Saturated calomel reference electrode

compartment, one for water condenser, and the other for gas and solution inlet, when working with de-aerated system. The reference compartment has a thermometer gas inlet and liquid inlet together with the saturated calomel electrode in one joint. The cell capacity was 0.4 dm^3 of test solution. Only the main compartment of the cell was immersed in an oil bath controlling the required temperature, the reference compartment being held at room temperature.

2.3.2 Stress Corrosion Measurements

The majority of the work was conducted using a constant load method. The tensile properties of the material were measured in triplicate, on an Instron Tensile Testing Machine. In all the constant load tests the load applied was 90% of the predetermined yield stress.

For electrochemical measurements on stressed specimens, a glass cell comprising of two compartments, the main compartment contained the stress corrosion specimen and the platinum counter electrode. The reference compartment contained saturated calomel electrode, similar to the reference compartment described before. The two compartments were connected by a salt bridge with a Luggin capillary. The capacity of the cell was 0.25 dm^3 , and the details are shown in Figure 3. To identify the reproducibility of the polarization curves, measurements were performed for three or more samples in one solution condition. Some scatter in the open circuit potential (OCP) and the active-passive transition potentials were found in the polarization curves determined in some tests.

3. Results and Discussions

The entire stress corrosion test carried out under a con-

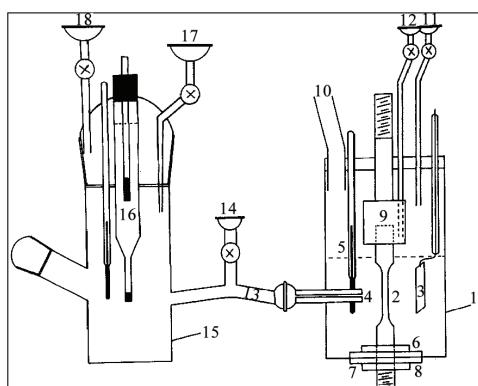


Figure 3. Stress corrosion test cell (schematic): 1) Main compartment; 2) Specimen/ working electrode; 3) Platinum electrode; 4) Luggin capillary; 5) Thermometer; 6) P.T.F.E nut; 7) Rubber washers; 8) Stainless steel nut; 9) Top shackle; 10) To condenser and gas outlet; 11, 18) Solution inlets; 12, 17) Gas inlets; 13) Salt bridge outlet; 14) Gas outlet; 15) Reference compartment; 16) Saturated calomel reference electrode

stant load of 90% of the yield stress (206.5 MNm^{-2}).

In this work effect of temperature and concentration were considered.

3.1 Effect of Temperature

3.1.1 Stress Corrosion Life

A solution of 52Wt% NH_4NO_3 at different temperature was used to determine the stress corrosion life. The results are summarized in Table 1.

Figure 4 shows the temperature dependence of stress corrosion life and general corrosion rate. This figure indicates that the stress corrosion life decreased as the temperature was increased. The general corrosion in 52Wt% NH_4NO_3 at the boiling point (383 K) was very severe, the gauge length of a stress corrosion specimen, left in such a solution for 108 ks without applied stress, dissolved to a point as shown in Figure 5. A similar specimen immersed in the solution at 368 K for about 1.3 Ms showed a reduction in Ultimate Tensile Stress (UTS) of only 13%, with maximum intergranular attack 3 grains in depth.

Table 1. Effect of temperature on stress corrosion life of mild steel in 52Wt% ammonium nitrate solution (stress= 206.5 MN m^{-2})

Temperature K	Number of Tests	Average Stress Corrosion Life ks	95% Confidence Limits of Life ks
303	2	>7300.0	-
323	3	352.0	± 108.0
343	4	145.8	± 57.2
358	4	69.8	± 32.0
368	7	27.3	± 9.6
375	4	22.3	± 20.9
380	4	23.4	± 9.7
383	5	18.3	± 7.8

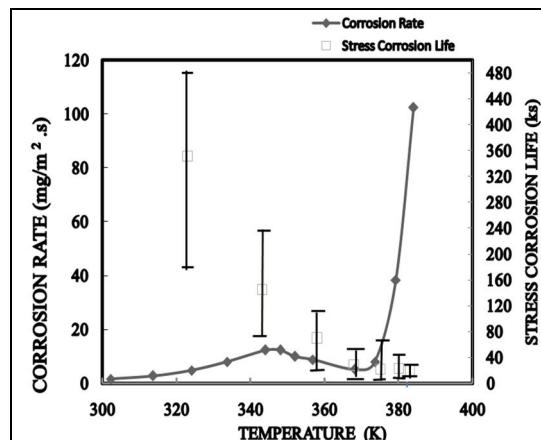


Figure 4. Effect of temperature on the general corrosion rate and stress corrosion life of mild steel in 52Wt% NH_4NO_3 solutions

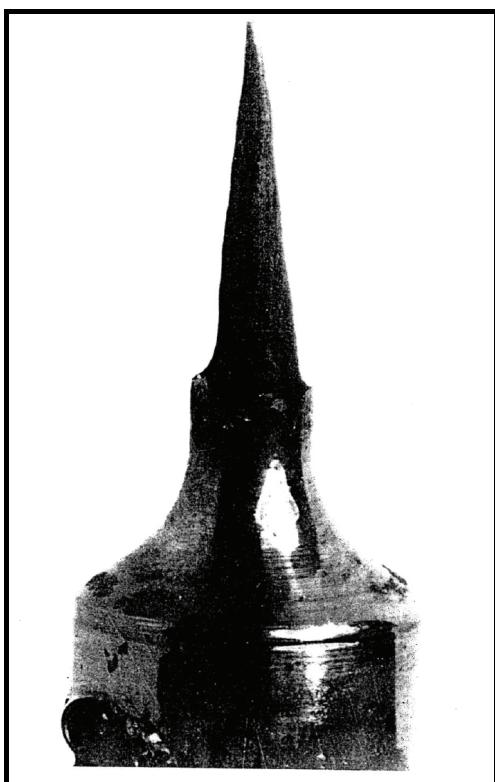


Figure 5. Stress corrosion test specimen after 108 ks immersion in 52Wt% NH_4NO_3 solutions at boiling point (383 K). Very high general corrosion attack X 12

Microscopical examination of longitudinal sections of specimens stress corroded at different temperatures showed the features indicated in Table 2.

Length of the section: 6.6 mm.

Grain diameter: 40 μm .

Width of the section: 2.5 mm.

Type A: Just detectable intergranular attack,

Type B: Fine cracks,

Type C: Wide cracks,

Type D: Cracks visible to the naked eye.

Table 2. Effect of temperature on the stress corrosion of mild steel in 52Wt% ammonium nitrate solution

Temperature K	Average Corrosion Life ks	Type of attack and No. of Loca- tions	Maximum Depth of Penetra- tion in Grains				Reduction in Dia- meter μm
			A	B	C	D	
323	352	3		1			-
343	145.8		7		6		203
358	698	3			6		76
368	27.3		6	1	44		8
375	22.3	3		1	15		-
380	23.4		4	1	18		-
383	18.3		3		-		228

It appears from Table 2 that the susceptibility in the range 368 K to 380 K was greater than at other temperatures. The higher susceptibility to cracking at higher temperature may be attributed to the nature of the corrosion product formed. Crack morphologies and crack features on the crack surface were observed by scanning electron microscope (SEM). Figure 6 shows the fracture surface morphology of specimen after stress corrosion failure in 52Wt% NH_4NO_3 solution at 368K which indicates high degree of intergranular attack. Previous work of Evans [10] showed that at high temperatures in the nitrate solution, anhydrous magnetite film that has high ionic conductivity is formed.

Our experiment illustrated that at the boiling point, the cracking was associated with a high rate of general corrosion while previous work reported that stress corrosion failure occurs only in hot and boiling nitrate solutions [1].

The 368 K was chosen as the test temperature because the stress corrosion life was reasonably short, with less scatter than at other temperatures, and the general corrosion attack was not severe.

Karthik *et al.* [11] reported that the temperature effect was hypothesized to be associated with oxygen presence, since the solubility at 333 K is greater than that at 368 K. These results confirm that the temperature effect in the presence of nitrate is associated with oxygen availability. Stress corrosion cracking usually occurs under the conditions where a component is exposed to a mildly corrosive environment while under stress (applied or residual) [12].



Figure 6. Fracture surface morphology of a specimen after stress corrosion failure in 52Wt% NH_4NO_3 solutions at 368 K, showing the high degree of intergranular attack X 250

Tang *et al.* [13] stated that a stress concentration is developed at the crack-tip and enhances significantly the local anodic dissolution. Also the presence of crack in steel would generate significant stress concentration, resulting in remarkable enhancement of local anodic dissolution rate.

3.1.2 Electrochemical Measurements of Mild Steel Specimen in Ammonium Nitrate Solution

1) Corrosion potential/time curves

Figure 7 shows variation of corrosion potential with time in 52Wt% NH_4NO_3 solutions at temperatures ranging from 298 K to 368 K.

At 368 K corrosion potential was nobler than at any other temperature. It appears that the aggressiveness of particular nitrate solution may well be indicated by measurement of the potential of metal in that solution. The corrosion potential behavior gives some indication of the processes which may be occurring. A lower general corrosion rate at higher temperature is indicated by the fact that the corrosion potential shifts to more noble values are greater at these temperatures. This shift could be due to the formation and growth of a Fe_2O_3 film on the corroding surface. At temperatures of 345 K and above, there was some oscillation in the corrosion potential before it attained a steady value. If the initial potential is considered, then the shortest life appears to correspond with nobler potential Figures 4 and 7.

2) Potentiodynamic polarization curves

Figure 8 shows the Potentiodynamic polarization curves in 52Wt% NH_4NO_3 solution at temperature ranging from 298 K to 368 K using a sweep rate of 0.33 mV.s^{-1} starting approximately 350 mV more negative than the open circuit potential (OCP) and scanning in the noble direction to more than 1200 mV.

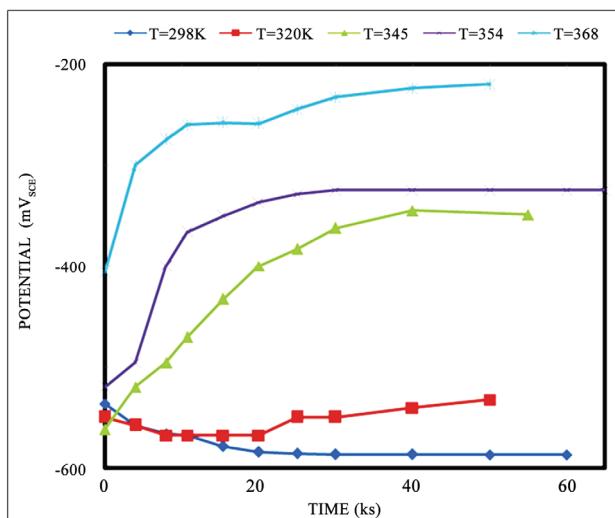


Figure 7. Effect of temperature on the corrosion potential/time behavior of mild steel in 52Wt% ammonium nitrate solutions

These curves indicate that decreasing the temperature promoted the formation of a more protective passivating film. The increase in temperature to 368 K shifted the corrosion potential to a higher value and increases the active peak current. Edgemon *et al.* [14] perform tests using mild steel in simulated waste solutions which primarily composed of ammonium nitrate and when held at approximately 370 K. Data characteristic of uniform and stress corrosion cracking are presented.

3.2 Effect of Concentration

3.2.1 Stress Corrosion Life

The influence of concentration of ammonium nitrate solution at 368 K on the stress corrosion life is shown in Table 3 and is plotted in Figure 9. The life decreases as the concentration increased. Microscopic examination of specimens after stress corrosion testing in 10Wt%, 20Wt% and 52Wt% NH_4NO_3 solution revealed that in all cases, there was severe intergranular attack, especially at the high concentrations.

3.2.2 Electrochemical Measurements on Unstressed Specimens

1) Corrosion potential/time curves

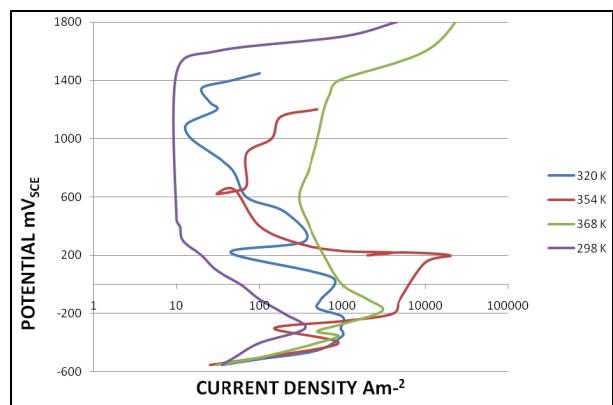


Figure 8. Effect of temperature on the Potentiodynamic polarization behavior of mild steel in 52Wt% ammonium nitrate solutions

Table 3. Effect of concentration of NH_4NO_3 solution on the stress corrosion life of mild steel at 368 K (stress=206.5 NM m^{-2})

Concentration of NH_4NO_3 Wt %	Number of Tests	Average Stress Corrosion Life ks	95% Confidence Limits of Life ks
10	4	45.0	\pm 30.0
20	9	60.5	\pm 23.7
30	4	27.4	\pm 16.6
40	4	27.4	\pm 13.0
52	7	27.3	\pm 9.6
70	4	20.9	\pm 9.4

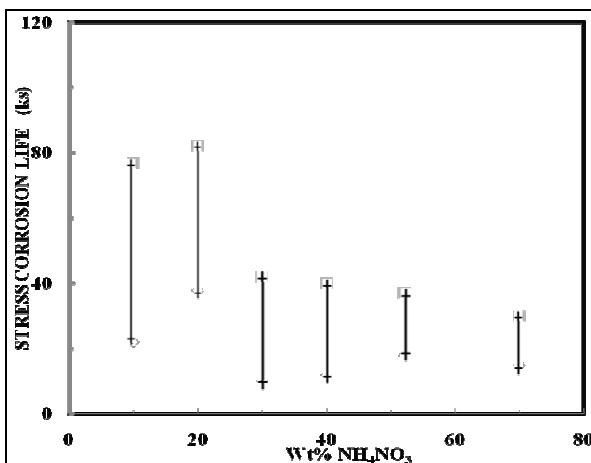


Figure 9. Effect of NH_4NO_3 concentration on the stress corrosion life of mild steel at 368 K

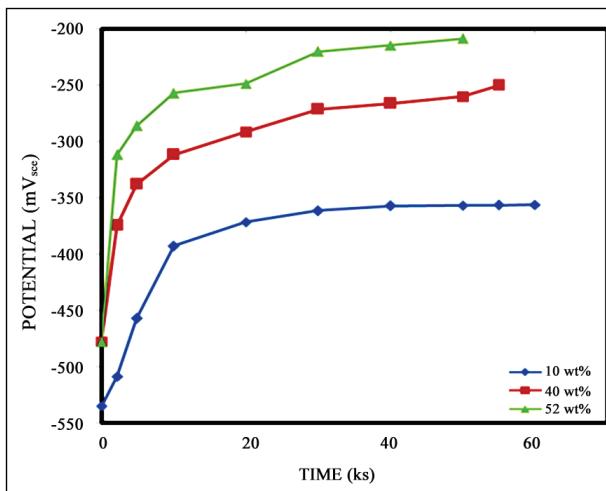


Figure 10. Effect of NH_4NO_3 concentration on the corrosion potential/time behavior of mild steel at 368 K

The variation of the corrosion potentials with time in 10Wt%, 40Wt%, and 52Wt% NH_4NO_3 solution at 368 K is plotted in Figure 10. At this temperature the oxide film apparently forms faster at high concentration and it has better protective properties. The corrosion potential became nobler as the concentration increased.

2) Potentiodynamic polarization curves

Figure 11 shows the Potentiodynamic polarization curves in different concentrations of ammonium nitrate solutions at 368 K using a sweep rate of 0.33 mV.s^{-1} starting approximately 300 mV more negative than the (OCP) and scanning in the noble direction to more than +1400mV. There are wide active regions, high passivation potentials and the high critical passivation current at lower concentrations. In all concentrations there was a very high rate of attack, but the morphology differed. In the following

sections 52Wt% NH_4NO_3 solution at 368 K was used as the aggressive environment. Preliminary work has shown that general corrosion was minimum at 368 K, a temperature at which the stress corrosion life was relatively short, with little scatter in the results Figure 4. The concentration of 52Wt% NH_4NO_3 was chosen as a compromise Figure 9, as too low concentration results in too long stress corrosion life, whilst the stress corrosion life in 70Wt% solution was approximately the same as that in 52Wt%.

At high concentrations, the passivating ability of the solution will increase, this means that the time required to produce a film having the critical properties required for crack initiation will decrease. These curves indicate a decrease in the stress corrosion life with increasing concentration as reported by previous workers for different nitrate solutions [7,14,15].

As a second stage of work, further areas in which investigation will be rewarding include:

- a) The effect of PH level.
- b) Oxygen concentration.
- c) The stages of stress corrosion failure.

This will help to define and establish effective and efficient corrosion mitigation strategies such as using inhibitors to stop this phenomenon.

3) Potentiostatic polarization

The behavior of specimens under different applied potentials ranging from -500mV to +900mV in 52Wt% ammonium nitrate solution at 368 K was investigated and the current was recorded during the test.

In Figure 12, the current behavior with the applied potential can be divided into three groups:

a) (-500 to -150 mV) high initial current density, followed by very fast decrease which indicates a high tendency for passivation.

b) (Zero to +100 mV) the initial current density is very high and remains at this high value for approximately 1 ks subsequently there are some periodic reduction in the rate

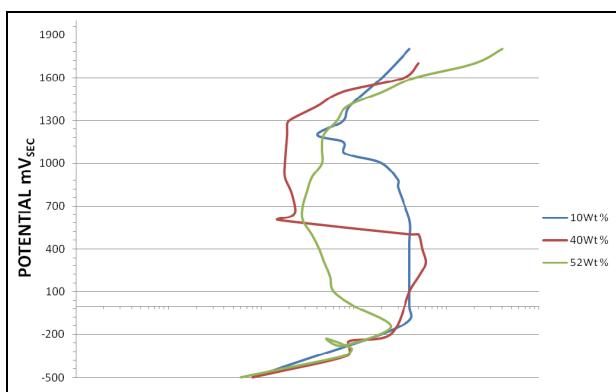


Figure 11. Effect of NH_4NO_3 concentration on the potentiodynamic anodic polarization behavior of mild steel at 368 K

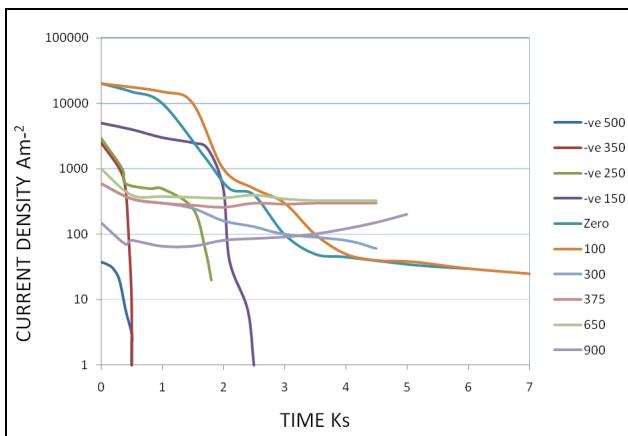


Figure 12. Potentiostatic anodic polarization behavior of mild steel in 52Wt% NH_4NO_3 solutions at 368 K

of current decrease at these potentials, with a relatively high value and current densities remain constant even after 6 ks. This indicates quite active conditions with very slow formation of oxide film, which are not favorable for stress corrosion, demonstrating that corrosion is probably occurring at these potential. Moderate decrease, indicates regions between active and passive state.

c) (+300 to 900 mV) Very slow decrease at the beginning, which indicates a very active state, followed by an approximately constant region.

4. Conclusions

The effect of temperature and concentration of ammonium nitrate solution on the stress corrosion life of mild steel is as follows:

- 1) An increase in temperature causes a decrease in the stress corrosion life. The relative roles of general corrosion and stress corrosion cracking in producing failure became difficult to separate at temperatures near the boiling point.
- 2) An increase in concentration (at 368 K) causes a decrease in the stress corrosion life.
- 3) The OCP of mild steel measured in 52% ammonium nitrate solution at 368 k was in the range -230 to -260 mV (SCE).
- 4) Stress corrosion cracking occurs only when the mild steel in particular solution conditions exhibits well defined active passive behavior.
- 5) Detailed study of the effect of pH level, oxygen concentration, stages of stress corrosion cracking failure and other factors is required. This will help in establishing effective corrosion mitigation to stop the stress corrosion cracking.

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