

**ELECTROCHEMICAL DISSOLUTION AND PASSIVATION
BEHAVIOR OF IRON IN AMMONIACAL CARON LEACHING
SOLUTION**

by

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ABSTRACT

The electrochemical passivation of pure Fe in ammoniacal solution was investigated to determine the stability of both Fe-oxides and Fe-ammines during anodic polarization. The potentiodynamic experiments were done in 6M total NH_3 [3M NH_4OH and 1.5M $(\text{NH}_4)_2\text{CO}_3$] solution. Different experimental parameters such as temperature (15° , 25° , 35° , 45° and 55°C) and pH (6, 8, 10 and 12) were used. Pure oxygen and argon gas was sparged during the experiment to oxygenate or de-oxygenate the solution with no stirring in either case. Polarization plots show that both active anodic dissolution and passive regions are present for pure iron in ammoniacal solution. It also shows that as the temperature increased the dissolution rate increased in both anodic and passive regimes. At the same time, the active region for iron dissolution is present across a wider potential range. For pH 10 the highest dissolution rate is around $0.025\text{A}/\text{cm}^2$ or $260\text{ g}/\text{m}^2\text{hr}^1$ at 55°C and passivation of iron generally occurs at ca. -0.36 V (SHE) irrespective of the temperature. The peak anodic dissolution rate ($0.2\text{ A}\cdot\text{cm}^{-2}$ or $2080\text{ g}/\text{m}^2\text{hr}^1$) surprisingly occurs at pH 6.

Potentiostatic experiments were done at different fixed potentials at pH 9 and 25°C . The highest current density was registered at -0.6 V . The peak dissolution current observed for the potentiostatic tests is roughly two orders of magnitude lower than that observed in the potentiodynamic test for pH 9 and at 25°C . Solution and morphological analyses were done by ICP and SEM, respectively for pH 6 and 9 solutions. The current efficiency for pH 6 is far lower than at pH 9 which implies that the current registered at

pH 6 is used for the formation of a product film. Speciation calculations indicate that this film may be siderite (FeCO_3) at low potential. From XPS analyses, it is believed that the passive layer formed at higher potentials (more than 0.40V) is Fe_2O_3 . Speciation diagrams point to the stability of iron tetra-ammines at pH 10. It was shown that metastable Eh-pH diagrams for $\text{Fe}/\text{NH}_3/\text{CO}_3/\text{H}_2\text{O}$ system can be generated through potentiodynamic measurements aimed at active and passive behavior of iron.

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DEDICATION

The word I never said to my parents

“I love you MA, BABA”

1. INTRODUCTION

The mining of nickel started around 160 years ago in Sweden and Norway where nickel sulphide minerals were the main source for nickel [Torries 1995]. Since that time, the production from sulphide deposits in Canada, Russia and Australia has competed with the production from massive laterite deposits in New Caledonia, Indonesia, Brazil, Cuba and the Philippines [Torries 1988, 1995]. About 55% of world nickel has been extracted from sulphide deposits while the other 45% has been recovered from laterite deposits [Anthony and Flett 1997].

The sulphide deposits are divided into two unique geological locations: one is the subvolcanic mafic-intrusion at Noril'sk, Siberia, and the other is astrobleme-associated mafic-intrusion deposits at Sudbury, Canada [Elias 2002]. The subvolcanic mafic-intrusion is related to flood basalts. These two geological areas represent about 42% of the total global nickel sulphide resources [Hoatson et al. 2006] [Watling 2008]. As the global reserves of high-grade sulphide deposits are diminished and as demand for nickel continues to increase, low grade laterite ores are increasingly economically attractive [Simons 1988].

Depending on the mineralogy of laterites, different nickel extraction routes can be considered. The commercial recovery of nickel and cobalt from laterites occurs both pyrometallurgically and hydrometallurgically. The grade (percentage of Ni and Co in the ore) of the laterite and presence of Mg and Fe in the ore body are the most important

factors in determining the optimal processing route. The pyrometallurgical processes are suitable for high magnesium (Mg) laterites (known as saprolite $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) which contain lower concentrations of cobalt and iron than limonitic laterites [Dalvi et al. 2004]. The saprolitic laterites typically contain 20-50% water which is driven out by drying and calcination. Fe and Ni are reduced to their metallic state in reduction furnaces where coke, coal or fuel oil (such as at Falcondo) are used as reducer [Li et al. 2009].

Also, Mg and Si have a high affinity to follow the slag and the ferro-nickel matte can be easily removed from the slag [Steyl et al 2008]. The characteristics of the slag and matte largely depend on the ratio of Si to Mg in the ore. This matte/crude metal is further processed to get final metal. This pyrometallurgical process is used at the Falcondo operation in Dominican Republic. Pyrometallurgical processes have some distinct advantages such as they are suitable for high magnesium and silica containing laterite ores and the amount of reducing agent used is low and inexpensive related to the value of the metal produced [Dalvi et al. 2004]. In general pyrometallurgical processes also operate at high throughput which is a significant factor in plant economics [Hayes 1993]. They also have some limitations. Calcining and drying are energy intensive since all the moisture in the feed must be removed and all the materials need to be calcined and melted to form a slag at about 1600°C. Pyrometallurgical processes for laterites thus require high grade ores, consume significant energy and are not suitable for high cobalt recovery as this metal often reports to slag [Xiaokuia 2010] [Jones et al. 1996] [Dalvi et al. 2004] [Georgiou and Papangelakis 1998] [Guo et al. 2009].

Hydrometallurgical processes are more suitable for the high iron laterite known as limonite. The hydrometallurgical processes include high acid atmospheric leaching and high pressure acid leaching (HPAL) [Georgiou and Papangelakis 1998] [Rubisov and Papangelakis 2000]. The HPAL process provides high recoveries of nickel and cobalt, has acceptable acid consumption and produces low residual iron in solution, but requires expensive autoclaves and has high maintenance costs [Anthony and Flett 1997]. The HPAL process is usually suitable for laterites with low Mg (not more than 4%) and Al because these elements consume acid. The HPAL process is carried out in pachuka tanks or in autoclaves with leaching temperatures ranging from 250-270°C [Dalvi et al. 2004]. Solid-liquid separation then occurs by counter current decantation (CCD) while final separation and recovery methods vary [Loveday 2008]. HPAL has been used successfully at Moa Bay since the 1950s and also currently operates at Murrin Murrin [Moskalyk and Alfantazi 2002]. Vale is currently building a new HPAL facility with unique downstream processing at Goro in New Caledonia [Xavier and Ciminelli 2008].

A third option, the Caron mixed pyro- hydrometallurgical process for the recovery of nickel, cobalt and copper from limonitic laterites in ammoniacal solution was developed in 1950 by M.H. Caron [Caron 1950]. The Caron leaching process is the oxidative dissolution of pre-reduced iron based nickel and cobalt alloys in ammoniacal carbonate solution at atmospheric pressure [Caron 1950]. The main advantages of the Caron process are the selective dissolution of nickel and cobalt and the recyclability of ammonia [Kumbasar 2009]. However, the energy requirements and operating costs are high and recoveries of nickel and cobalt are low [McDonald and Whittington 2008]. For

example, the Yabulu refinery in Australia reports recoveries of ca. 80 and 50 % for Ni and Co, respectively. While specific losses during leaching are not well documented it is believed that a significant portion of the paymetal loss occurs during this step [Caron 1950, Senanayake et al. 2010]. There are currently two mechanisms which are believed to contribute to Ni and Co losses in the Caron process leach: (a) cobalt adsorption or co-precipitation onto/with iron oxides/hydroxides and (b) iron passivation during the leach [Osseo-Asare and Fuerstenau 1979, 1980] [Osseo-Asare et al. 1983]. The latter is the subject of this thesis.

The first published work of Fe-alloy passivation in ammoniacal solution is attributed to Osseo-Asare and his co-workers [Osseo-Asare et al. 1983]. The typical anodic polarization curves for iron and cobalt in ammoniacal solution containing 2 M NH_3 and 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 9.7 with a scan rate of 0.1 mV s^{-1} in oxygenated solution are shown in Fig 1.1 [Osseo-Asare et al. 1983]. The active dissolution of iron and cobalt starts at around -0.6 and -0.5 V (SHE), respectively, and continues up to -0.45 V (SHE) for iron and 0.18 V (SHE) for cobalt. This region of anodic dissolution is often referred to as an anodic nose. At higher potentials, iron and cobalt start to passivate, and passivation continues until around 1.1 V (SHE) in the case of iron. Iron has a wider potential window of passivity than cobalt.

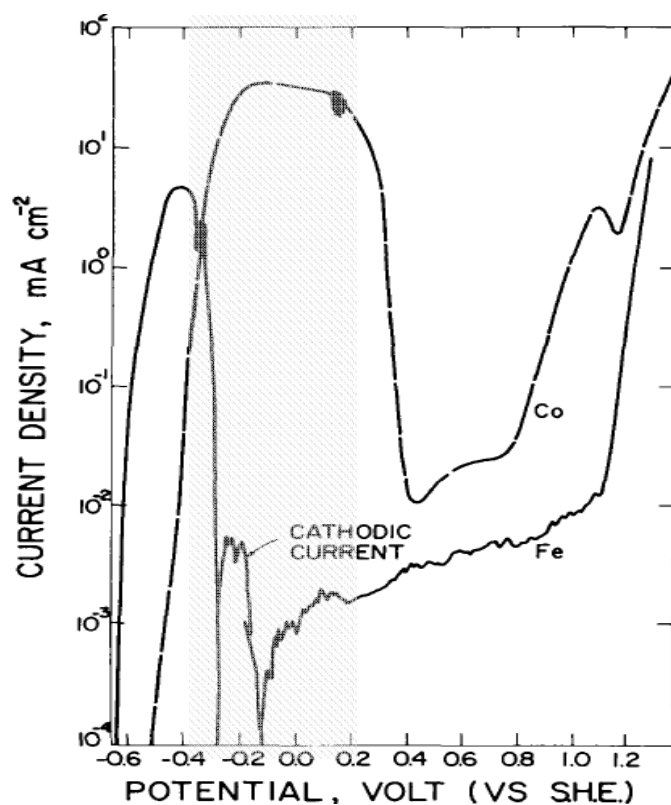


Figure 1.1: Anodic polarization curves of bulk Fe and Co in ammoniacal solution at pH 9.7 [Osseo-Asare et al. 1983].

During the dissolution of nickel and cobalt bearing iron-based alloys in the leaching stage of the Caron process, iron and cobalt can both dissolve at lower potential but as potential increases with the presence of air (oxygen) iron easily forms a passive layer (highlighted zone in Fig. 1.1) which isolates the cobalt and nickel from the ammoniacal solution. Thus the cobalt and nickel associated with reduced goethite (i.e. iron), which is expected to dissolve in solution by complexing with ammonia, does not leach resulting in diminished cobalt and nickel recoveries. The net cathodic current observed at -0.3 V in Fig 1.1 corresponds to oxygen reduction.

As the particular information of electrochemical and dissolution behavior of iron in ammoniacal solution is very limited, the following pages will give a brief description of the electrochemical response of iron to ammoniacal solution. As noted, iron passivation is believed to contribute to nickel and cobalt losses in the Caron process. Thus it is also relevant to review the Caron process literature. Both of these reviews will take place in Chapter 2. Chapter 3 will discuss the specific research objectives of this work while Chapters 4 and 5 will present the experimental methods and discuss the results, respectively. Polarization curves, surface analysis by SEM and XPS, metastable Pourbaix diagrams and speciation diagrams for iron at different temperature and pH will form the basis of this work. Finally, Chapter 6 will provide some conclusions and recommendations for future work.

2. LITERATURE REVIEW

2.1. Limonitic laterites

The word laterite comes from a Latin word "later" which means "bricks or tiles". The laterites are mainly oxide ores that are rich in iron and aluminum. These ores are widely distributed in the equatorial regions and are formed during laterization [Georgiou et al. 1998, 2009], [Krause 2009] [Monhemius 1987] [Kerfoot and Weir 1988]. The laterization process occurs when ultramafic rocks undergo a chemical weathering process [Helgren and Butzer 1977]. The tropical weathering process is favoured by warm climate and high rainfall. The parent rocks are typically dunite or peridotite. Lateritic deposits have not been discovered in northern regions with the exception of northern Oregon which is laterized and contains nickeliferous magnesium silicates. Laterites have mainly been found in tropical locations such as Cuba, Dominican Republic, Guatemala, New Caledonia, Indonesia, Philippines, Australia, Papua New Guinea, Brazil, Madagascar, Southwest Europe, Turkey, India, Southwest Asia and China.

During the laterization process, carbon dioxide is dissolved from the atmosphere and organic acids acidify the underground water. The gradual decomposition of peridotite ($X_3Y_2(SiO_4)_3$) occurs with possible bacterial activity, which leads to percolating of elements such as Fe, Al, Cr, Ni, Mg and Si. Under these conditions, iron oxides can easily form and start to precipitate, thus forming goethite ($\alpha\text{-FeO}\cdot\text{OH}$) [Pickles 2004]. Aluminum can also precipitate either in the goethite matrix or as gibbsite

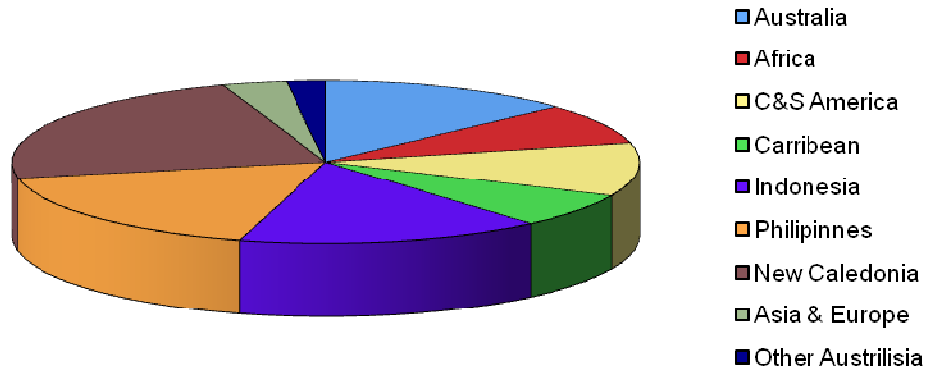
(Al(OH)₃). Chromium is found as a spinel associated to goethite. Also, cobalt and nickel can be precipitated together with iron forming part of the crystalline lattice in the goethite [Pickles 2004]. Cobalt is also often found as asbolane ((Ni,Co)_{2-x}Mn⁴⁺(O,OH)₄ nH₂O) in laterites in association with manganese [Fittock 1993].

Lateritic deposits usually consist of three layers, namely the limonitic, the saprolitic and the garnieritic layers [Dalvi et al. 2004].

- a. Limonitic zone: This has abundant goethite (~50 wt % iron), nickel ~1 - 1.5 wt % and Cobalt ~0.1 - 0.2 wt %. Limonitic laterites are the top layer of a laterite deposit, which is a homogeneous ore consisting mainly of goethite (FeO*OH) in association with other valuable metals such as nickel, cobalt and copper. These ores are not well crystallized and are very fine grained on average 50-60 µm [Tang and Valix 2006]. Limonite also contains gibbsite, chromite and asbolane that are complex Mn IV oxide phases (~20 wt % Ni + Co).
- b. Saprolitic zone: This is located between the limonitic and garnieritic zones; it contains several magnesium silicates and intermediate amounts of Ni, Fe, Mg and Si. This ore typically contains ~1- 2 wt % Ni and ~ 0.05 - 0.07 wt % Co. Pyrometallurgical processes (ferronickel and matte smelting) are used to process this kind of ore.
- c. Garnieritic zone: This is located at the bottom of the ore body. It is rich in Ni (~ 1.8 - 3.0 wt %) and magnesium silicates. It is very heterogeneous in

mineralogical and chemical composition. Pyrometallurgical processes are also used to treat these types of ore.

World Nickel Laterite Resources (Distribution by Contained Nickel)



Location	Mt	% Ni	Mt Ni	% of Total
Australia	2452	0.86	21	13.1
Africa	996	1.31	13	8.1
C&S America	1131	1.51	17	10.6
Carribean	944	1.17	11	6.9
Indonesia	1576	1.61	25	15.7
Philipinnes	2189	1.28	28	17.4
New Caledonia	2559	1.44	37	22.9
Asia & Europe	506	1.04	5	3.3
Other Austrilisia	269	1.18	3	2
Total Laterites	12621	1.28	161	100

Figure 2.1: Distribution of Nickel Laterite resources all over the world. [Dalvi et al. 2004]

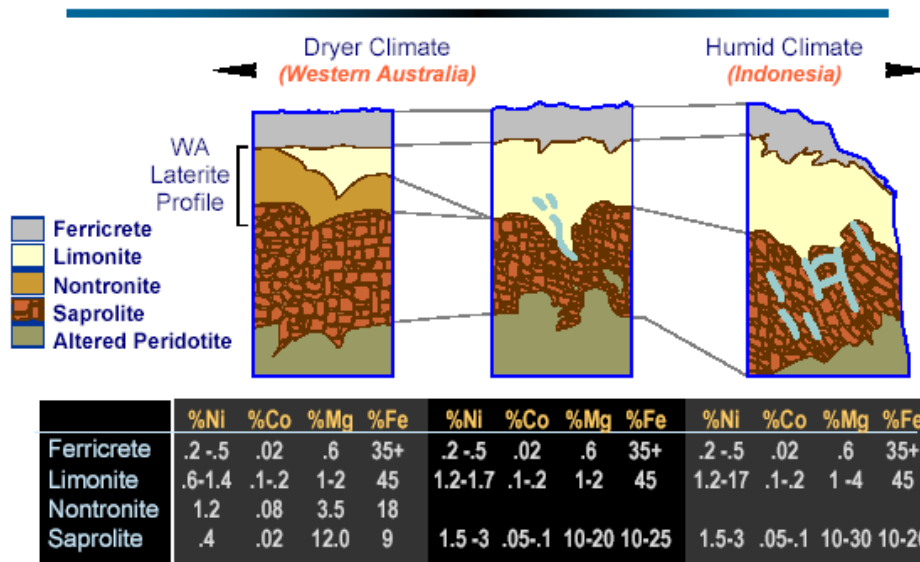


Figure 2.2: Laterite Profiles: Wet and Dry Laterites [Dalvi et al. 2004]

A general description of laterites processing has been discussed by [Caron 1950], [Burkin 1987], [Moskalyk and Alfantazi 2002], [Dalvi et al. 2004] and [Bingol et al. 2005]. In general the processing of laterites falls in three different classes.

- Pyrometallurgical (High carbon ferronickel, matte smelting etc).
- Hydrometallurgical (High pressure acid leaching, acid leaching etc).
- Mixed pyro-hydrometallurgical (Caron process)

There are two processes used economically which contain significant hydrometallurgical unit operations. One is the Caron leaching process and the other is HPAL (High pressure acid leaching) [Richardson et al. 1981]. HPAL is the preferred process to recover nickel and cobalt from limonitic laterites as it functions well with a fine, moist feed and it is considered to be the best option for selective dissolution of

nickel and cobalt where iron is precipitated as hematite [Loveday 2008] [Whittington et al. 2003]. Although several projects for Ni and Co recovery from laterites by high pressure acid leaching are now under consideration, particularly in Australia and New Caledonia [Dalvi et al. 2004], only a handful of operations are currently employing this process such as at New Caledonia by Vale Inco, Moa Bay, Cuba, by Moa Nickel [Moskalyk and Alfantazi 2002] and Murrin Murrin by Minara Resources Ltd (60%), Glencore International (40%) [Krause 2009]. Advantages of the acid pressure leaching process include [Georgiou and Papangelakis 1998]:

- a. No drying and reduction steps are needed, since raw laterite ‘as mined’ is used.
- b. High selectivity is obtained due to hydrolytic iron re-precipitation as hematite.
- c. No sulphur dioxide emissions are produced.
- d. Recoveries of more than 95% for nickel and more than 90% for cobalt can be achieved.

2.2. Ammoniacal environment

A number of leaching systems in which ligands are used to complex metal cations in solution have been commercially applied [Sato et al. 1978]. Ammonia is one such ligand which has seen significant attention in extractive metallurgy [Osseo-Asare et al. 1983] [Kmetova et al. 1985] [Jana et al. 1999]. Ammonia is an effective complexing agent which has inherent advantages over alternative reagents. Ammoniacal leach

solutions are generally basic in nature which alleviates several corrosion problems encountered in the acidic systems [Park et al. 2007]. Also, the ammoniacal leaching medium is selective to nickel and cobalt and offers the rejection of major waste components like iron through their removal during the leaching step as insoluble oxy/hydroxyl compounds [Power and Geiger 1977] [Caron 1950].

There are a few commercial operations that have been established based on ammoniacal leaching processes such as the Sherritt Gordon process, the Nicaro process, [Sato et al. 1978], [Bogacki et al. 1997] and the Caron process. The Sherritt Gordon process is historically important as it is the first commercially successful hydrometallurgical process to extract nickel from sulphide ores [Wadsworth 1987]. In the Sherritt process, nickel is recovered by the reduction of hexamminenickel (II) sulphide solution with compressed hydrogen [Sato et al. 1978]. In the Nicaro process, nickel oxide is recovered by the thermal decomposition of nickel carbonate produced by heating the hexamminenickel (II) carbonate solution and purging ammonia gas [Sato et al. 1978].

2.3. Caron leaching process

The Caron process is a combined process of pyrometallurgical and hydrometallurgical steps. The process can be defined as the oxidative dissolution of pre-reduced iron based nickel-cobalt-copper in ammoniacal carbonate solution at atmospheric temperature [Caron 1950]. The Caron process has been used commercially at Nicaro (Cuba), Punta-Gorda (Cuba), Yabulu (Australia), Nonoc (Philippines - now closed) and

Tocantins (Brazil) [Dalvi et al. 2004]. The advantages of the Caron process are described clearly by A. R. Burkin, 1987:

- a. The recyclability of the leaching reagent. Theoretically, ammonia and carbonate are not consumed during the process. Ammonia is recovered by the ammonia stripper.
- b. The selectivity of nickel and cobalt over iron is very high. The iron which is present as goethite ($\text{FeO} \cdot \text{OH}$) in laterites, and represents the major component of the ore, is roasted in a reduction furnace. During this reductive roasting stage Ni and Co are selectively reduced.
- c. Corrosion of materials of construction is not a significant issue in ammonia-based processes

2.3.1. Ore dressing and reductive roasting

Ore drying and grinding, reductive roasting, leaching with ammoniacal carbonate solution and metal recovery from the solution are the main processing steps in the Caron process.

A considerable amount of energy is required in the rotary kiln to reduce the moisture content of the raw ore from more than 30% to 2-3% [Burkin 1987]. After drying the ore is ground to obtain a constant size and composition. The ore is then roasted in a reductive roaster to reduce nickel and cobalt selectively at about 750- 850°C [Mckay and

Swinkels 1975] [Weir et al. 1973] [Zuniga and Asselin 2009]. In this temperature range most of the nickel bearing goethite forms metallic nickel and cobalt and only some of the iron is reduced [Tolley and Laughlin 1982]. The final product of this stage is an iron based alloy (Fe-Ni-Co) where the larger portion of the remaining iron forms magnetite (Fe_3O_4) [Fittock 1993] [Feng and Van Deventer 2002] [Mohapatra et al. 2002] [Li et al. 2009]. Also, cobalt is often found in association with asbolane in laterites [Georgiou and Papangelakis 2009]. The chemical formula of asbolane is $(\text{Ni-Co})_{2-x} \text{Mn}^{4+}(\text{O,OH})_4^- n\text{H}_2\text{O}$. During the reductive roasting, the Co associated with manganese phases is liberated to form the metallic alloy with iron [Georgiou and Papangelakis 2009].

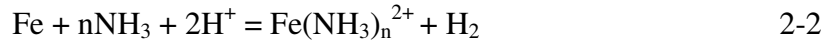
The reductive roasting reaction can be given as follows equation no 2-1.



2.3.2. Leaching reaction

After the reduction stage, the hot reduced calcine is cooled to about 150-200°C and then it is quenched in a tank which contains the ammoniacal ammonium carbonate leach solution [Miller and Wiewiorowski 1976]. This solution is recycled from leach residue by washing. The solution may contain about 6.5 wt% NH_3 , 3.5 wt% CO_2 and 1 wt% Ni [Francis et al. 2008]. Quenching is done in the absence of air to dissolve most of the iron in ammoniacal solution according to reaction 2-2 [Anand et al. 1986] [Das and Anand 1995]. During leaching air is supplied to oxidize and dissolve the nickel and cobalt from the iron based alloy e.g. reaction 2-3. The soluble nickel and cobalt ammine complex ions are formed in this stage [Senanayake and Das 2004] [Senanayake 2007].

Iron, which is initially dissolved as a ferrous ammine complex, is now oxidized quickly to the ferric state and precipitates as ferric hydroxide, eventually leaving the process in the leach residues [Jandova and Pedlik 1994], [Das and Anand 1995], [Chang et al. 2010].



2.3.3. Extraction and metal recovery

After roasting and leaching, separation of metal ions is effected via solvent extraction, precipitation of mixed sulfides or cobalt oxide/carbonate and nickel carbonate, calcination of nickel carbonate to nickel oxide, and hydrogen reduction of nickel oxide to yield nickel metal. A modern plant such as Yabulu incorporates a cobalt-recovery step in the Caron process due to high demand and price of cobalt usually by semi selective sulphiding and mixed nickel cobalt sulphide intermediate with Ni:Co >2. [Senanayake et al. 2010] [Mckay and Swinkels 1975] [Parhi et al. 2008]. The remaining cobalt bearing raffinate from the solvent extraction circuit is put into contact with hydrogen sulphide or ammonium hydrosulfide to precipitate out the cobalt, zinc and nickel as a mixed sulphide. This sulphide precipitate actually contains negligible amounts of nickel because most of the nickel was already extracted before in solvent extraction circuit. The precipitated material is thickened, washed in counter current circuit to remove any dissolve magnesium and calcium. The cobalt sulphide slurry is transferred to stripping stills where

steam is injected to recover ammonia and carbon dioxide gas [Fittock 1993] [Chander and Sharma 1981] [Price and Reid 1992].

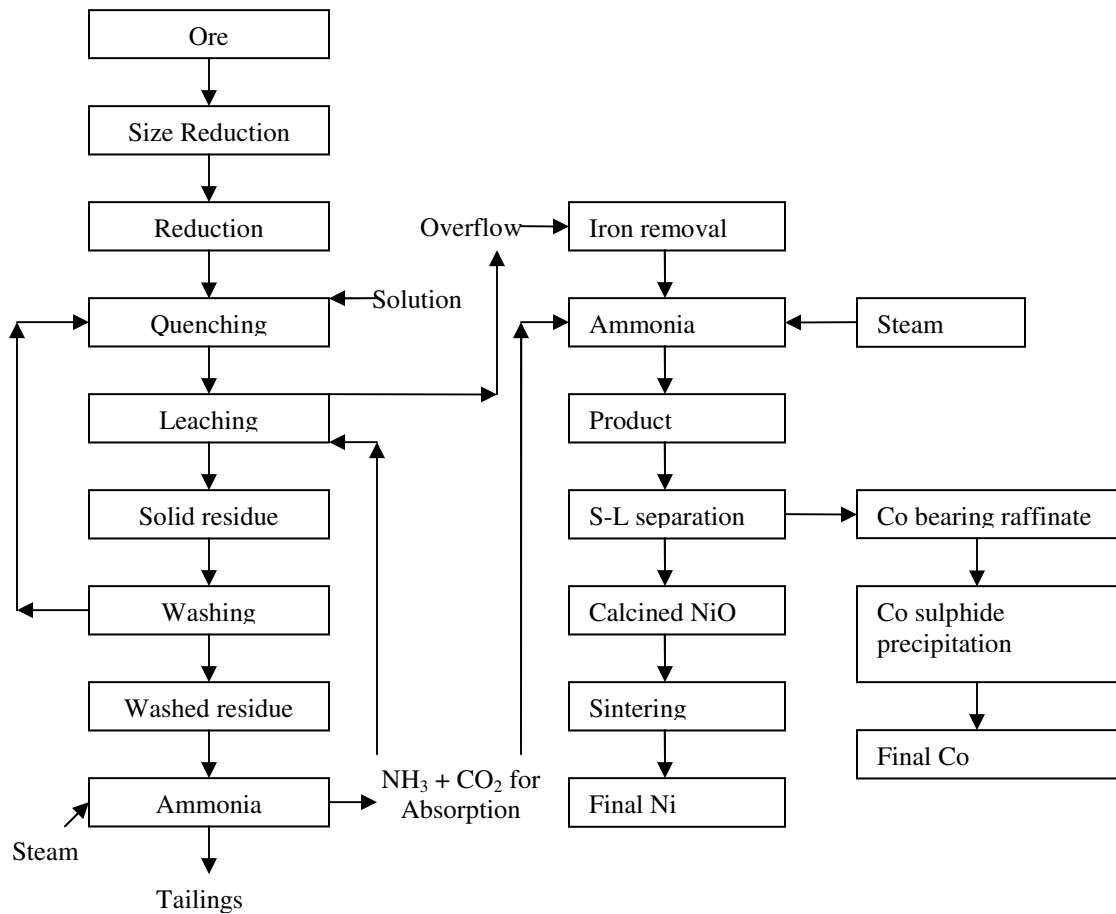


Figure 2.3: Flow-sheet of the Caron process [Burkin 1987]

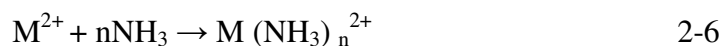
Ammonia and carbon dioxide are recovered from the top of the stripping still by water absorption. These ammonia and carbon dioxide gases are used again to makeup the ammonium carbonate solution to the counter current decantation washing circuit. The overall process flow sheet of the Caron plant is given in Fig 2.3. The Caron leaching process has some significant disadvantages [Senanayake et al. 2010] [Nikoloski and Nicol 2006] [Nicol et al. 2003]:

- a. The initial infrastructure is expensive. The temperature in the reductive roasting stage is about 800-850°C. So, energy requirements for drying and reduction roasting are higher. The front-end operations consume more than 60% of the energy input to the entire process.
- b. Recoveries are on the order of 50-60% for cobalt and 70-90% for nickel [Senanayake et al. 2010]
- c. The process is mainly applicable to high iron limonitic laterites. The amount of serpentinitic silicate ore (high Mg and Si) that can be accepted is limited due to losses of nickel caused by forsterite (Mg_2SiO_4) formation during roasting. The unreduced Ni-Co-oxides can entrapped forsterite (Mg_2SiO_4) depending upon the mineralogy and roasting temperature.

2.4. Chemical reaction consideration for Caron process

Both corrosion and many metal extraction processes from ores involve electrochemical reactions [Nikoloski et al. 2006] [Wadsworth 1984]. Understanding these reactions can shed light on process fundamentals and improve process outcomes such as final recovery.

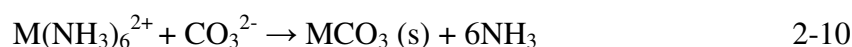
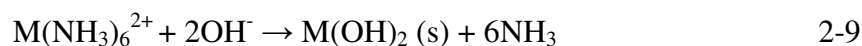
The dissolution of the Fe-Ni-Co alloy formed during reductive roasting is an electrochemical process which, in the presence of oxygen, includes the following cathodic (reduction) reaction (equation 2-4) and anodic (oxidation) reactions equations 2-5 and 2-6 (where ammonia is present).



Electrochemical reactions occurring in ammoniacal solution are subject to constraints related to the speciation of ammonia. Ammonia assumes three different forms (a) free aqueous ammonia (NH_3), (b) ammonium ions (NH_4^+) and (c) metal ammines ($\text{M}(\text{NH}_3)_n^{2+}$) [Osseo-Asare 1981], [Osseo-Asare and Fuerstenau 1979, 1980 and 1987]. These metal ammines can be precipitated as follows depending on the leach conditions:



Or,



Ammonium is more stable than ammonia at low pH and the reverse is true at high pH. In order to obtain good metal extraction both ammonia and ammonium ions must be present in solution to minimize the tendency to precipitate out the dissolved metal from the solutions. Ideal conditions can thus be created at pH 9.25 where ammonia and ammonium ions are in equilibrium at 298K [Osseo-Asare et al. 1983]. In practice, most Caron leaches operate near pH 9.5-10. According to the Eh-pH diagram of cobalt-water-

ammines and iron-water-ammines studied by Osseo-Asare (1983) and Asselin (2008), it is shown that the stability regions of dissolved cobalt ammine species $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{NH}_3)_5]^{2+}$ are centered near pH 9.25 and span a wide range of potentials.

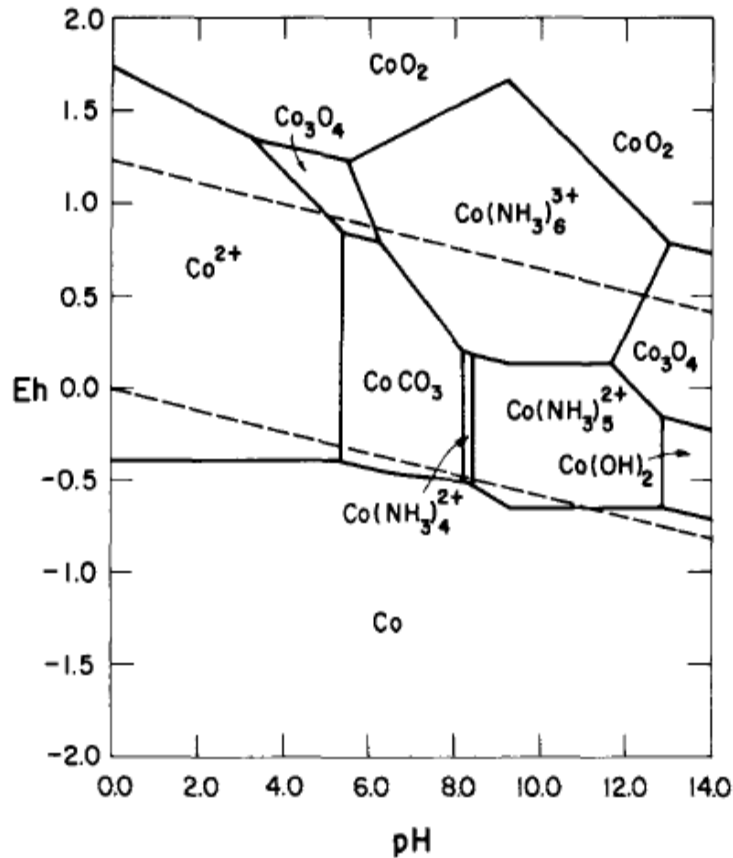


Figure 2.4: Eh-pH diagram of Co-NH₃-H₂O-CO₂ at 298K $[\text{Fe}] = 1.0 \times 10^{-4} \text{ kmol m}^{-3}$, $[\text{NH}_3] = 4.0 \text{ kmol m}^{-3}$, $[\text{CO}_2] = 1.0 \text{ kmol m}^{-3}$. [Osseo-Asare et al. 1983]

From Fig 2.5 for the iron-ammonia-water-carbonate system, it is evident that the stability region of iron ammines is narrow: from pH 9.2-9.7 with limited stability as Eh is increased [Osseo-Asare et al. 1983]. Reducing or mildly oxidizing conditions are needed for the stability of ferrous ammines and cobalt can only be extracted from the the Fe-

based alloy when iron forms this weak ammine complex else passivation might occur.

Fig 2.5 also shows a passivity region where Co cannot be extracted.

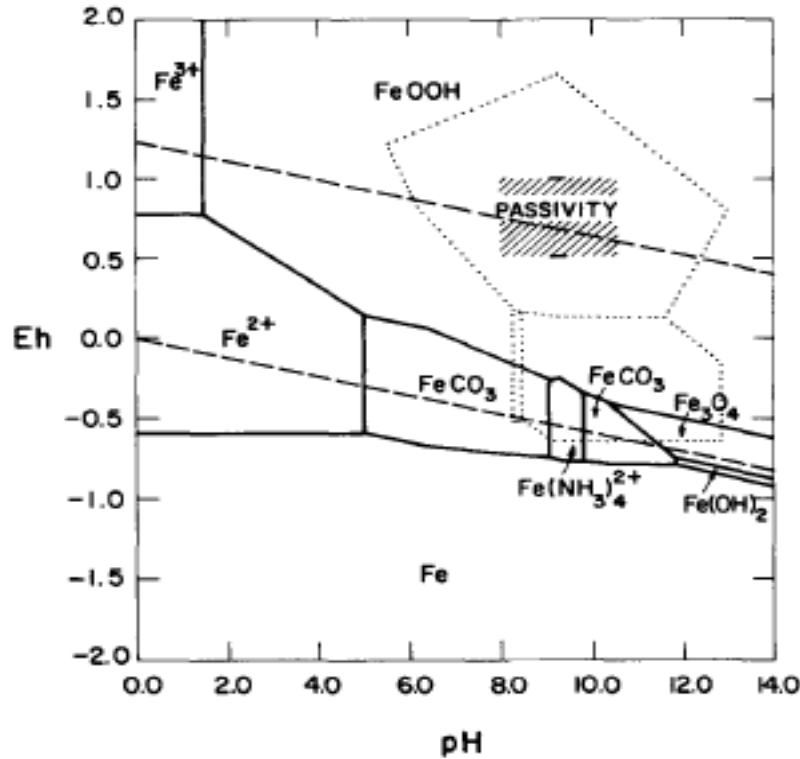


Figure 2.5: Eh-pH diagram for the Fe-(Co)-NH₃-H₂O-CO₃ system at 298K, [Fe] = 1.0×10^{-4} kmol m⁻³, [NH₃] = 4.0 kmol m⁻³, [CO₂] = 1.0 kmol m⁻³. The dotted lines represent the superposition of the corresponding Co-NH₃-H₂O-CO₃ system (Fig 2.4). [Osseo-Asare et al. 1983]

2.5. Electrochemical passivation of iron

Over last few decades, extensive research has been undertaken to find the mechanism and kinetics of anodic dissolution of iron in different aqueous media. Studies have been performed over a wide range of pH, in different electrolytes and different mechanisms have been proposed. Bockris et al. in 1962, suggested that iron dissolution in acid solution (in dilute H₂SO₄) is a consecutive mechanism [Bockris et al 1961] [Bockris

and Drazic 1962] [Takahashi et al. 1992]. According to this mechanism iron forms an absorbed intermediate $(\text{FeOH})_{\text{ad}}$ in the initial step and the rate determining step is the discharge of this absorbate. Heusler also proposed a catalytic mechanism where the intermediate $(\text{FeOH})_{\text{ad}}$ behaves as a catalyst in the initial step of Fe dissolution [Folleher and Heusler 1884] [Heusler 1985].

The idea of passivity can be best described by $\log(\text{current})$ vs. potential diagram. Sato (1978) described the polarization behavior of iron in sodium phosphate solution [Sato 1978]. With reference to Fig 2.6, the current density of iron increases exponentially at first when the potentials go in the positive (toward the right) direction. This means that iron dissolved readily within this exponential region and that the predominant reaction is anodic iron dissolution (region I in Fig 2.6). This region is known as the active region. When the current density reaches a peak, further increase in potential results in a decrease in observed current and any further increase in potential results in no added current: this is iron passivation (or region II in Fig 2.6).

The nature of the passive films depends on the type of electrolytes. Such as in 0.1m L^{-1} sodium borate solution iron forms $\gamma\text{-Fe}_2\text{O}_3$ [Martini and Muller 2000]. Also, according to Ammar and Khalil, the passive film of iron in alkaline solution (NaOH) is a mixture of the Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ [Ammar and Khalil 1970]. After continued increase in potential, the current density of iron starts to increase again due to the breakdown of the passive film. This region is known as the transpassive region (III).

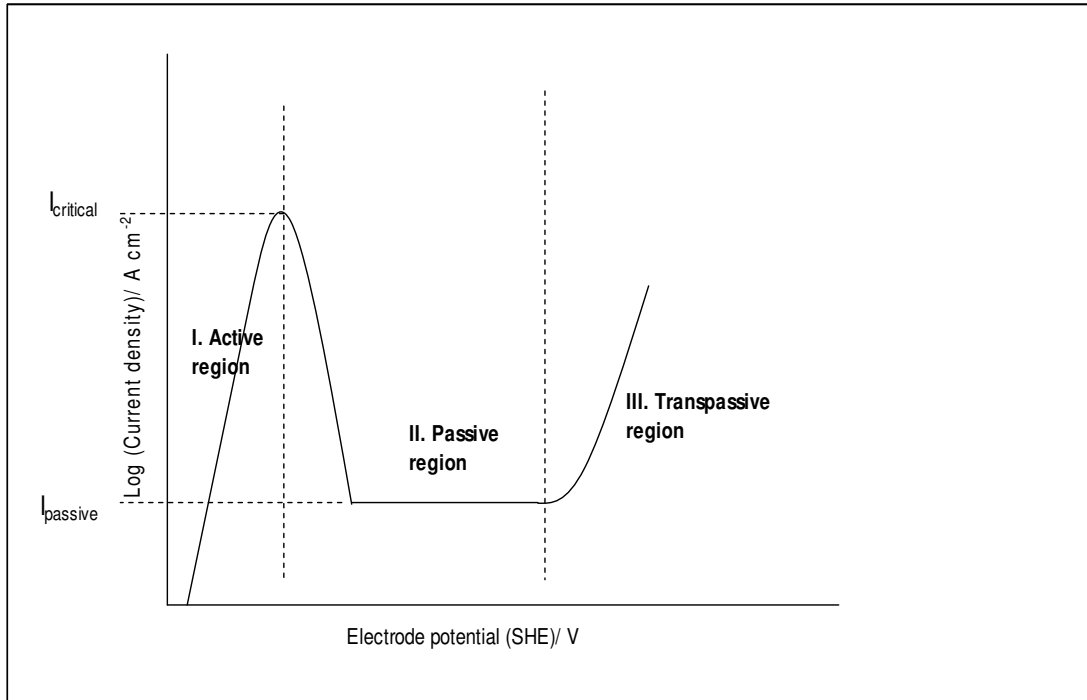


Figure 2.6: The typical anodic polarization curve for iron shows electrode potential vs log (current density).

Due to the typical anodic, passive and transpassive behavior of iron, the dissolution of iron constitutes an important research field. In many practical fields, iron bearing components are exposed to corrosive environments wherein they are attacked. In the primary metals processing industry, such as during recovery of Ni and Co from the Caron leaching process, iron is considered gangue which can effect the recovery of nickel and cobalt [Osseo-Asare et al. 1983], [Osseo-Asare 1981], [K. Osseo-Asare and DW. Fuerstenau 1979, 1980, 1987].

During the last few decades, the corrosion research of iron has been performed at high temperature and pressure in weak and strong alkaline solutions to obtain more information about the oxide formation reaction mechanism [Huijbregts et al. 1969]

[Macdonald and Owen 1973] [Hurlen 1963]. Huijbregts et al. performed polarization experiments on iron in alkaline solutions (10^{-4}N NaOH) at 250°C [Huijbregts et al. 1969]. According to their experiments, HFeO_2^- formed at low potential (Table 2.1 a), then magnetite developed on the surface at -290mV/SHE (Table 2.1 b), Fe_2O_3 formed at -40mV/SHE (Table 2.1c) and finally oxygen evolution occurred according to reaction Table 2.1(d).

The HFeO_2^- ions transports to the magnetite layer via the pores and will dissociate at the more alkaline oxide-solution interface. Any iron anions formed during reaction will consume hydroxyl ions, such that the pH at the oxide-metal interface will decrease [Huijbregts et al. 1969]. Thus, the oxide layer consisted of a very porous inner layer and a more compact outer layer consisting of coarse magnetite crystals. Also, in weakly alkaline medium, magnetite will form at higher corrosion potentials by oxidation of ferrous and ferric ions and by generating hydrogen gas [Huijbregts et al. 1969].

Table 2.1: Different reactions of iron in alkaline solution.

Reactions	Reaction No.
$\text{Fe} + 3\text{OH}^- \leftrightarrow \text{HFeO}_2^- + \text{H}_2\text{O} + 2\text{e}^-$	(a)
$2\text{Fe} + 4\text{OH}^- + \text{FeO}_2^- \leftrightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 6\text{e}^-$	(b)
$2\text{Fe} + 6\text{OH}^- \leftrightarrow \alpha\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 6\text{e}^-$	(c)
$4\text{OH}^- \leftrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	(d)

The active anodic behavior of iron in alkaline solution is a significant concern for electrochemical cells such as rechargeable anodes (Fe-Ni, Fe-Air etc). However, the polarization mechanism of iron in alkaline solution is difficult to elucidate due to

difficulties related to reproducibility. The difficulty of steady state polarization reproducibility of iron in alkaline solution was encountered by Macdonald and Owen [Macdonald and Owen 1973] in 1M LiOH solution.

The corrosion layer formed on carbon steel surface plays a important role on the corrosion rate during the corrosion of steel in CO₂ aqueous solutions [Lopez et al. 2003] [Liu et al. 2009]. Carbon steel in CO₂/amines such as di-glycolamines at higher temperature shows higher corrosion rate because the carbamate forms a soluble chelate with Fe²⁺ and also accelerate the electrochemical anodic and cathodic reaction [Guo and Tomoe 1999]. Also, it is believed that FeCO₃ behaves as a protective layer which implies the lower corrosion rate. [Ikeda et al. 1983] [Waard and Lotz 1993].

2.6. Effects of iron passivation on Caron leaching in various aerated solutions

To understand the anodic characteristics of iron in the Caron leach environment, a study was performed by Nikoloski et al., 2003. The following electrolytes were used to investigate the effect of thiosulfate and cobalt on the dissolution rate of iron (Table 2.2).

Table 2.2: Composition of Solution (Nikoloski et al., 2003)

Species (g/dm ³)	Barren	Barren Thiosulphate	with Loaded Thiosulphate	without Loaded
NH ₃ (NH ₄ ⁺)	90	90	90	90
CO ₂	45	45	45	45
Ni	-	-	9	9
CO	-	-	0.7	0.7
S ₂ O ₃ ²⁻	-	2.5	-	2.5
SO ₄ ²⁻	-	-	15.8	15.8

According to Nikoloski et al., iron can spontaneously passivate in Caron leaching solution. They tried to find out the effects of thiosulfate and nickel/cobalt in ammoniacal Caron solution. The results of CV tests obtained by Nikoloski et al. are reproduced in Fig 2.7. The peak anodic current density of $\sim 80 \text{ mA/cm}^2$ was achieved at -340 mV/SHE in barren solution with thiosulphate. Iron passivation is apparent at potentials above -300 mV/SHE [Nikoloski et al. 2003]. The dissolution current density of iron is higher for the solution which contains thiosulfate and lower when the solution contains cobalt and nickel ion in solution. At pH 9.9 and assumed sulphide ion concentration of 10^{-6} M , the reduction potential of thiosulfate is -392 mV/SHE . This potential is more positive than that for iron dissolution (-1051 mV/SHE) and measured OCP of -730 mV/SHE in loaded aerated solution [Nikoloski et al. 2003]. However, the thiosulfate ion is a metastable ion, it can be expected that thiosulfate ion will be oxidized to more stable sulfur species in the bulk solution with higher redox potentials in aerated solution resulting the faster oxidation and consequently delaying the iron passivation. So, in absence of thiosulfate, passivation of iron in Caron leaching solution needs a very high concentration of dissolve oxygen and does not take place in solution subject to aeration.

According to Nikoloski and Nicol study, nickel and cobalt can exhibit passivation at higher potentials than iron in ammoniacal solution [Nikoloski et al. 2003]. It was also demonstrated that the iron-nickel-cobalt alloy can passivate at lower potentials which results in the inhibition of valuable metal dissolution. They also established the potential region for anodic dissolution for iron, nickel and cobalt in ammoniacal carbonate solution. Although they studied the actual (pH 9.7 and temperature 45°C) of Caron process condition they didn't use any other temperature or pH.

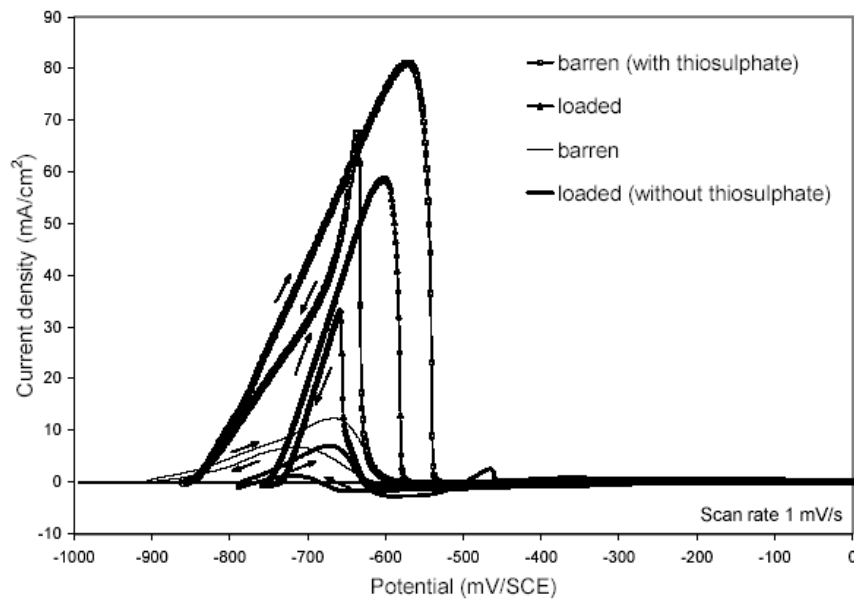


Figure 2.7: Anodic behavior of iron in various aerated solutions [Nikoloski et al. 2003]

Also, to investigate the polarization behaviour of iron in ammoniacal solution, Osseo-Asare and his co-workers performed many experiments with disc-shaped specimens of bulk Fe, Co and sintered Fe-Co mixtures [Kho 1989] [Kho et al. 1992]. All experiments were done at 298K at pH 9.7 in 2M NH_3 and 1M $(\text{NH}_4)_2\text{CO}_3$.

As previously shown in Fig 1.1, the polarization curves exhibit three distinct regions: active (I), passive (II), and at higher potential above ~ 0.8 V/SHE is characteristics a general break down of passive film (transpassivity), follows by oxygen evolution at above ~ 1.2 V/SHE (III) [Osseo-Asare et al. 1983]. It was shown that from Fig 1.1 when iron is polarized at -0.6 V/SHE below the initial open circuit potential (-0.14 V/SHE), maximum dissolution of iron occurs at -0.52 V/SHE. Cathodic current loops were observed over a potential range of -0.28 V/SHE to -0.10 V/SHE Cobalt showed a relatively wider range of active dissolution than iron (Fig. 1.1). The value of the maximum anodic current for cobalt (32 mA/cm^2) was much higher than that of the iron (4 mA/cm^2) electrode.

Fig 2.8 describes the concentration variation of dissolved iron and cobalt in ammoniacal solution with respect to applied potential as measured by Osseo-Asare et al. (1983). The dissolution rate of cobalt is initially high up to -0.34 V/SHE, at which point the maximum current (32 mA/cm^2) is observed. After this point, cobalt starts to passivate as well. But iron dissolves only in the active region (*i.e.*, below -0.4 V) and in the passive region it gives a nearly constant aqueous concentration. Fig 2.8 also gives some information about the effect of oxygen on the dissolution rate of cobalt and iron in ammoniacal solutions [Osseo-Asare et al. 1983]. The dissolution rate of cobalt is not greatly changed by oxygen. But the dissolution rate of iron is decreased with aeration in ammonia-ammonium carbonate solution. Because during aerated condition pure O_2 gas is sparged to the solution which implies the increased rate of oxygen reduction the iron can easily passivate in presence of oxygen.

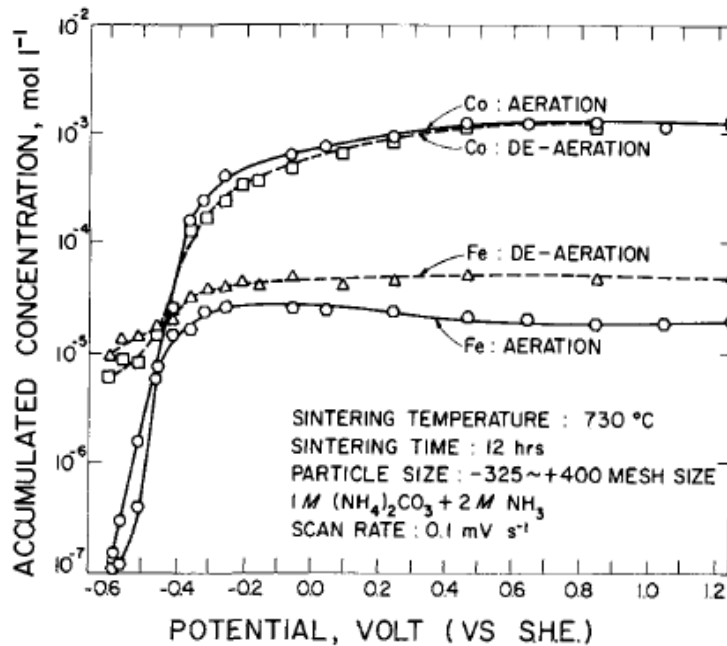


Figure 2.8: Concentration variation of dissolved Fe and Co during potentiodynamic polarization of a sintered Fe-50 wt% Co specimen in an aqueous ammoniacal solution containing $2 \text{ kmol m}^{-3} \text{ NH}_3$ and $1 \text{ kmol m}^{-3} (\text{NH}_4)_2\text{CO}_3$. [Osseo-Asare et al. 1983]

From the above discussion it can be said that the tendency of passivation of iron is greater than that of cobalt and iron can passivate at lower current/potential. The lower tendency of passivation of cobalt means that its ammine complexes are more stable than iron amines (cf. Fig 2.5). From Fig 2.8 it is apparent that, as the value of E_h is increased, cobalt (II) ammine complexes are oxidized to cobalt (III) amines but iron (II) amines become insoluble through oxidation as either Fe_2O_3 or FeO^*OH . Practically no cobalt dissolution can be done below 0.5 V (SHE). Thus to obtain good dissolution of cobalt, aeration must be controlled carefully to get a minimum tendency of iron passivation.

Despite the fact that Osseo-Asare et al. performed detailed electrochemical studies pertaining to the dissolution of iron in ammoniacal solutions, their work was constrained to a temperature of 25°C at pH 9.7 in 4M total ammonia. In fact, the Caron leach is operated at higher total ammonia concentrations and temperatures. Furthermore, the effect of pH may be important given the thermodynamic predictions reported by Asselin (cf. section 2.7). The study by Nikoloski et al., while thorough and performed in actual Caron solutions, did not report the effect of temperature or pH on measurements such that variations in process conditions could not be predicted.

2.7. Thermal stability of species at different condition

The Caron leach is carried out in an ammoniacal carbonate solution at about pH ~10 and concentration of 6M. According to Osseo-Asare, dissolve iron-containing species is expected to be at activity 10^{-4} at 25°C [Osseo-Asare 1981]. After reduction, the ore is cooled down to less than 200°C and then quenched with leach solution. As it is an exothermic reaction it is expected that the leach temperature may be changed during leaching. Apparently, the Caron leach reactors are cooled with large refrigeration units to maintain a moderate temperature ($< 40^{\circ}\text{C}$) during leaching. Thus it is important to evaluate the thermodynamic stability of different ammine complexes as a function of temperature. Thermodynamic data is necessary to evaluate the thermodynamic stability of various species. However, very few studies aimed at measuring ammine complex thermodynamic data have been conducted in solutions relevant to Caron (or any other

hydrometallurgical process) leach. Most studies have been performed at atmospheric temperature in nitrate environments.

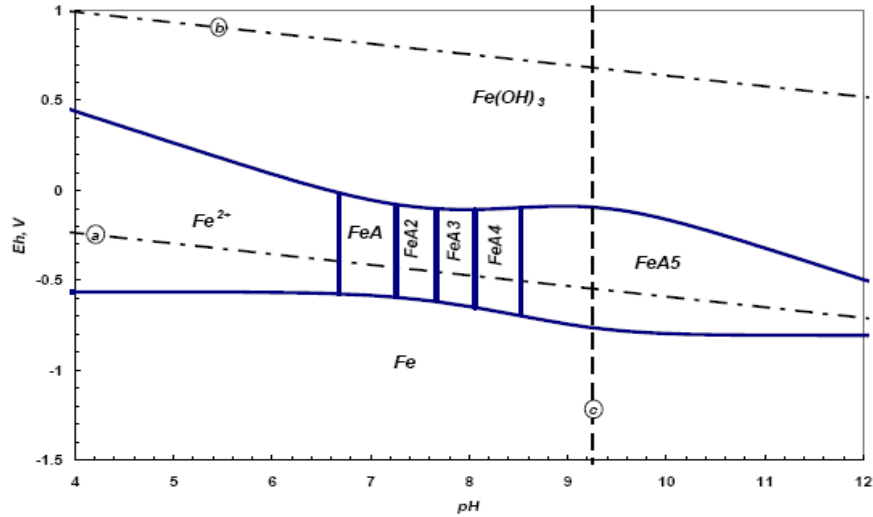


Figure 2.9: Quasi-equilibrium diagram for Fe-NH₃-H₂O at 298K. $[Fe] = 10^{-3}$ and $[NH_3]_T = 6M$. [Asselin 2008]

Mironov et al. have published a good review paper of the thermodynamic data of metal ammine complexes in aqueous media [Mironov et al. 1992]. Asselin (2008) and Nazari and Asselin (2010) have determined the stability regions of iron, nickel and cobalt ammines at different elevated temperatures based on the data by Isaev et al. and in ammoniacal solution [Isaev et al. 1990]. Also, the thermodynamics of metal ammine complexes in hydrometallurgical extraction processes have been investigated in terms of predominance diagrams such as Pourbaix diagrams and $\log[M]$ -pH (speciation diagrams) [Osseo-Asare 1981] [Zhong and Hepworth 1995]. However these predominance diagrams have some limitations in practical applications because they reflect equilibrium situations with pure components. Real leaching operations often do not reach

equilibrium and passive films, for example, are rarely pure or of predictable stoichiometry.

Fig 2.9 and 2.10 (Asselin 2008, using data from Isaev et al.) describe the stability region for iron amines at 298 and 333 K relative to redox potentials and pH. From these two diagrams it is clear that if temperature is increased, the window of stability for the iron amines is reduced in size. The constrained window of iron ammine stability indicates that passivation of the Fe-Ni-Co alloy is very likely to occur, particularly as the Caron leach is oxidative in nature with typical operating condition at -0.2 and +0.2V [Asselin 2008]. Passivation can be mitigated by maintaining low leach temperatures and performing a preliminary anaerobic leach where the objective is to preferentially extract iron from the underlying alloy. Typically this occurs in quenching tanks where the hot, reduced, roaster calcine is immersed in recycled leach liquor [Nikoloski 2006].

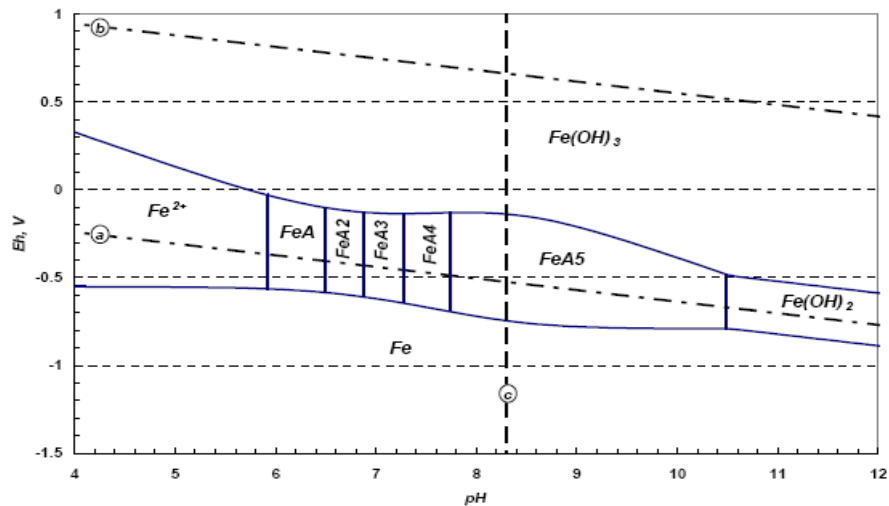


Figure 2.10: Quasi-equilibrium diagram for Fe-NH₃-H₂O at 333K. $[Fe] = 10^{-3}$ and $[NH_3]_T = 6M$. [Asselin 2008]

3. RESEARCH OBJECTIVES

The literature review section has shown that iron passivation can be a contributor to the poor recovery of nickel and cobalt from the Caron process. However, the electrochemical dissolution and passivation behavior of iron in ammoniacal solution needs more study. Although Osseo-Asare et al. performed detailed electrochemical studies pertaining to the dissolution of iron in ammoniacal solutions; their work was constrained to a temperature of 25°C at pH 9.7 in 4M total ammonia. In fact, the Caron leach is operated at higher total ammonia concentrations and temperatures. The study by Nikoloski et al., while thorough and performed in actual Caron solutions, did not report the effect of temperature or pH on measurements.

Furthermore, the effect of pH may be important given the thermodynamic predictions reported by Asselin (cf. section 2.7). The thermodynamics of the Fe-NH₃-CO₃-H₂O system have not been consistently described in the past because of a paucity of relevant data. Thus, the approach taken here, which was the overall objective of the work, was to demonstrate that relevant thermo-kinetic predictions could be generated through the use of electrochemical techniques. This approach would generate thermo-kinetic Eh-pH diagrams that could be used for process optimization. Specifically, the objectives were to:

- a. Determine the active and passive behavior of iron in various ammoniacal solutions with relevance to the Caron process

- b. Correlate this active and passive behavior of iron with the known thermodynamic data.
- c. Evaluate whether metastable (thermo-kinetic) Pourbaix diagrams (Eh-pH) can be generated with the electrochemical data generated from different polarization tests.

4. EXPERIMENTAL PROCEDURES

4.1. Electrochemical study

Specimens of pure iron measuring 1cm x 1cm x 1cm were cut from Armco iron bar stock. The chemical composition of the iron was obtained through ICP and is presented in table 4.1.

Table 4.1: Chemical composition of Armco iron electrodes

Elements	Contents (%)
Iron (Fe)	99.82
Nickel (Ni)	0.0084
Cobalt (Co)	0.0013
Copper (Cu)	0.015
Zinc (Zn)	0.015
Manganese (Mn)	0.0233
Zirconium (Zr)	0.0937

The electrodes were mounted in epoxy resin so as to present a planar surface to the solution. The electrodes were polished to 600 and then 1200 grit SiC. The polished electrodes were then rinsed with methanol and washed with de-ionized water.

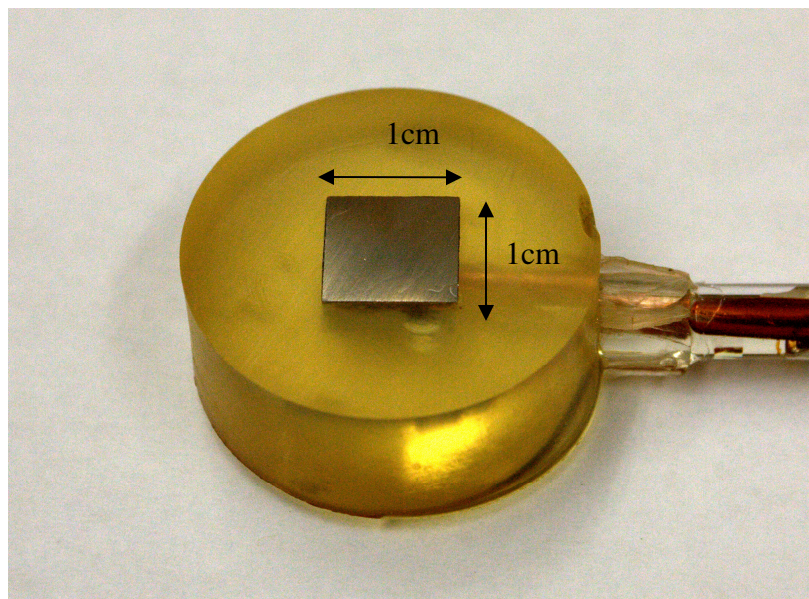


Figure 4.1: Epoxy mounted iron sample

The electrolytic solution was prepared with reagent grade chemicals and doubly distilled water. The standard test solution consisted of 3M ammonium hydroxide (NH_4OH) and 1.5 M ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$). The total ammonia concentration was 6M and pH was around 10. Sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used to adjust the pH and concentration of the solutions. Two different aeration conditions were used. The test solutions were either de-oxygenated or oxygenated by sparging argon or oxygen gas, respectively, for at least 20 minutes before starting any experiment. Sparging was continued during the tests.

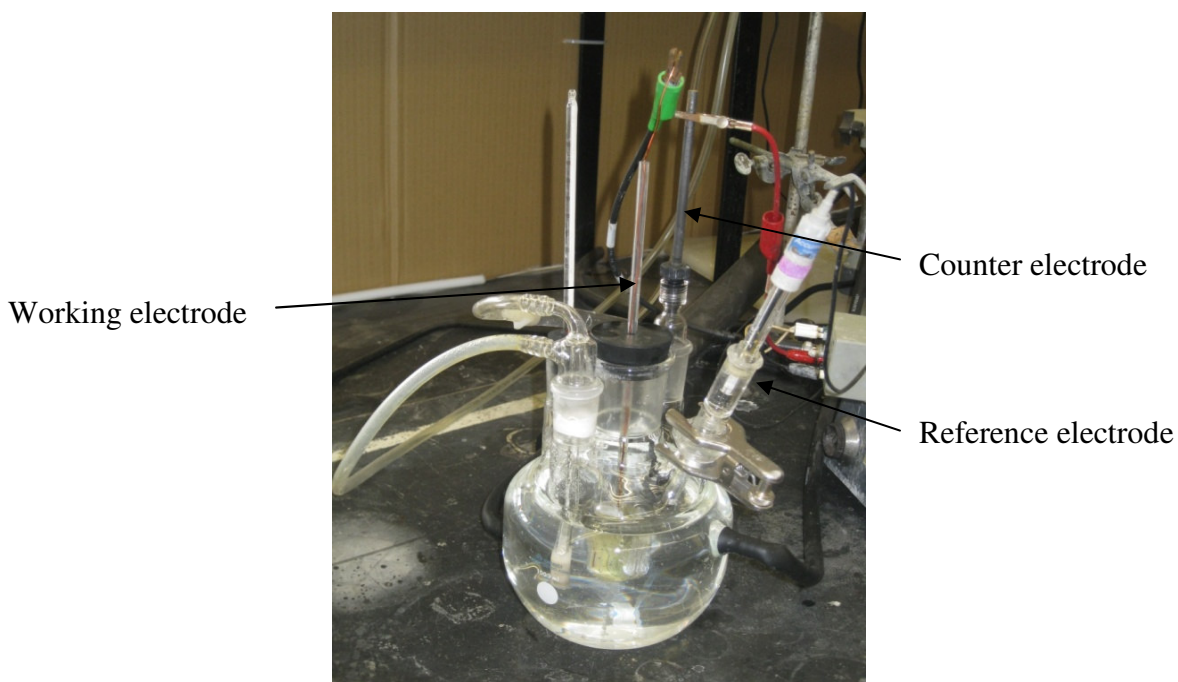


Figure 4.2: Glass jacketed three cell electrodes

A standard three electrode jacketed glass cell was used for the experiments (Fig 4.2). A graphite counter electrode and Calomel reference electrode (SCE) were used. The electrochemical experiments were computer controlled by PowerCORR software through a 273A potentiostat (Princeton Applied Research). Open circuit potential was measured as a function of time before each experiment to establish electrode stability and free corroding potential for further comparison with potentiodynamic tests. After pouring the ammoniacal solution in the electrochemical cell, pure oxygen and argon gas was sparged for 20 min to to either fully oxygenate or de-oxygenate the test solution. The electrode potential was swept potentiodynamically (0.5 mV/s) or potentiostatically at different temperature, pH and as a function of aeration. Sparging was continued throughout the duration of the tests.

4.2. XPS, SEM and ICP analysis

The corroded iron sample was analyzed by XPS and SEM. During the potentiodynamic experiments at pH 6 and 9, ca. 20ml of solution was sampled from the cell by pipette at different potentials. These samples were analyzed by ICP (Inductively Coupled Plasma) to determine the extent of iron dissolved in the solution. XPS was used to gain insight into the nature of the passive film formed after potentiostatic polarization. XPS spectra were measured by Leybold max 200 spectrometer using monochromatic AlK α radiation (1486.6 eV) operated at 15 keV. The areas of component peaks were estimated after Shirley background subtraction. XPS spectra were de-convoluted by using XPSPEAK4.1 curve fitting software.

5. RESULTS AND DISCUSSION

5.1. Microstructure of Armco iron

The microstructure of the iron sample prior to any electrochemical testing is shown in Fig. 5.1 and 5.2 at 300 and 200 times magnification, respectively. The iron is composed of ferrite grains with an average size of 10-15 μm . ICP analysis of the Armco iron revealed that it was 99.82% Fe with trace amount of carbon and some other element. So, the Armco iron used for these experiments contains ferrite with 12-15 μm grain size.

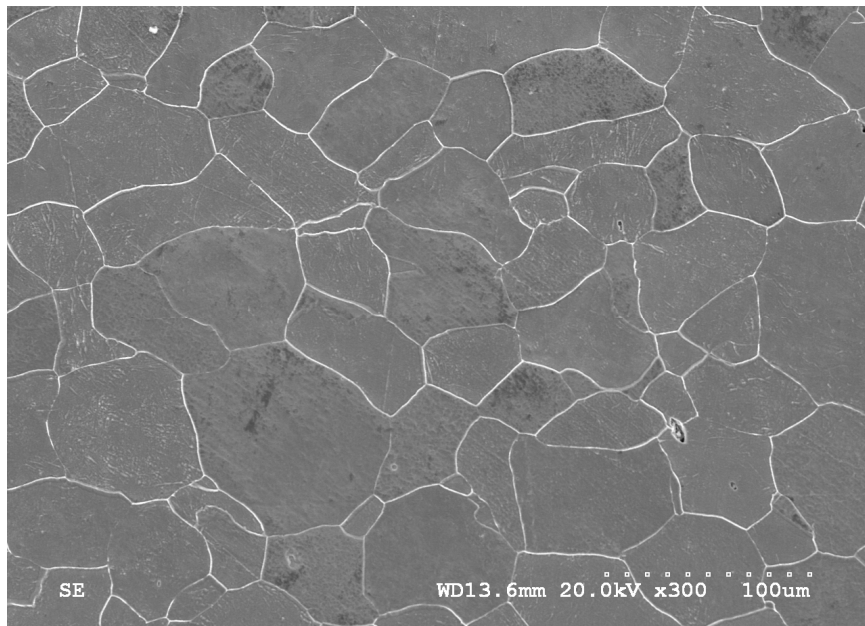


Figure 5.1: Microstructure of Armco iron X300 magnification (2% nital solution for 2-3 min etching)

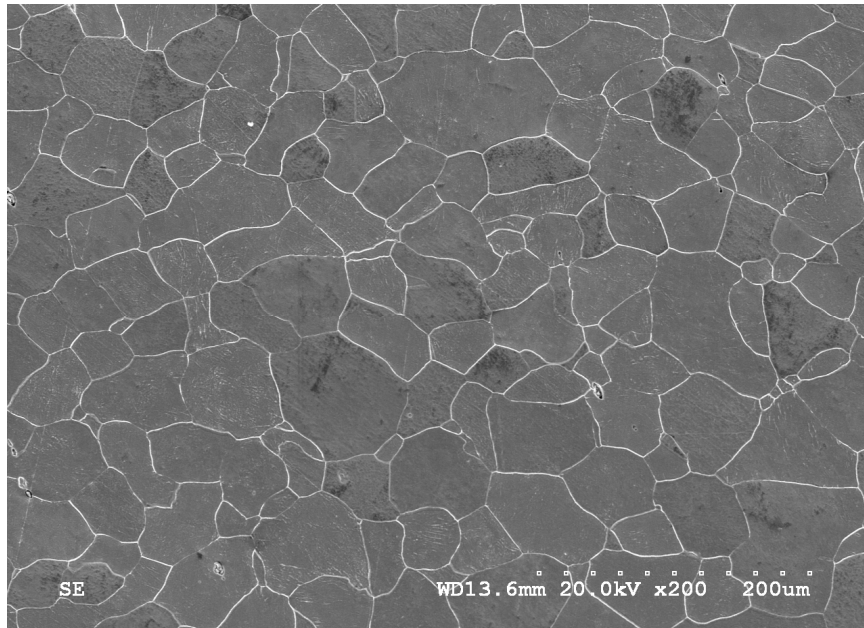


Figure 5.2: Microstructure of Armco iron: X200 magnification (2% natal solution for 2-3 min etching)

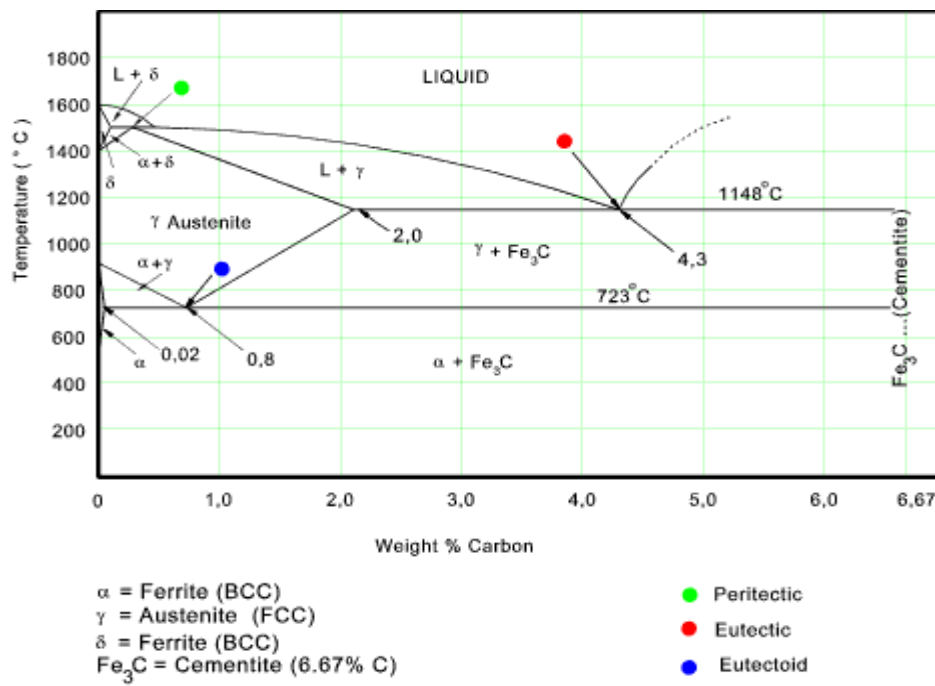


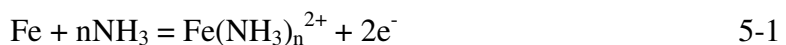
Figure 5.3: Fe-Fe₃C Phase Diagram [Kostyleva et al. 2000]

5.2. Effects of temperatures

Fig 5.4 and 5.5 show the effects of electrode potential and temperature on current densities of an iron electrode, respectively, in oxygenated and de-oxygenated ammonium carbonate solution at pH 10. For both oxygenated and de-oxygenated solutions, active and passive current densities increased with increasing temperature, and the maximum oxidation current densities occurred over a wider potential range between ca -0.65V to -0.36V (SHE). The highest oxidation current density was ca. 0.025 A cm^{-2} ($260 \text{ g m}^{-2} \text{ hr}^{-1}$), with iron beginning to passivate at potential larger than ca. -0.40 V (SHE). The pourbaix diagram of Fe-NH₃-CO₃-H₂O [Osseo-Asare et al. 1983] reported in Fig 2.5, implies a good agreement with the potentials found in potentiodynamic tests which demonstrates that iron can dissolve in solution by forming $\text{Fe}(\text{NH}_3)_4^{2+}$ at pH 10 and at potentials higher than ca. -0.40V iron starts to passivate.

The cathodic current loops were found in oxygenated ammonium carbonate solutions and these are due to the oxygen reduction reaction occurring between ca. -0.3 V to -0.1 V (SHE).

During active oxidative dissolution at potentials of ca. -0.40 V (SHE) in ammonium carbonate solution at pH 10, iron (II) ammine complexes are expected to form by:



At higher potentials (> ca. -0.40 V), passivation of iron can occur by reactions such as:

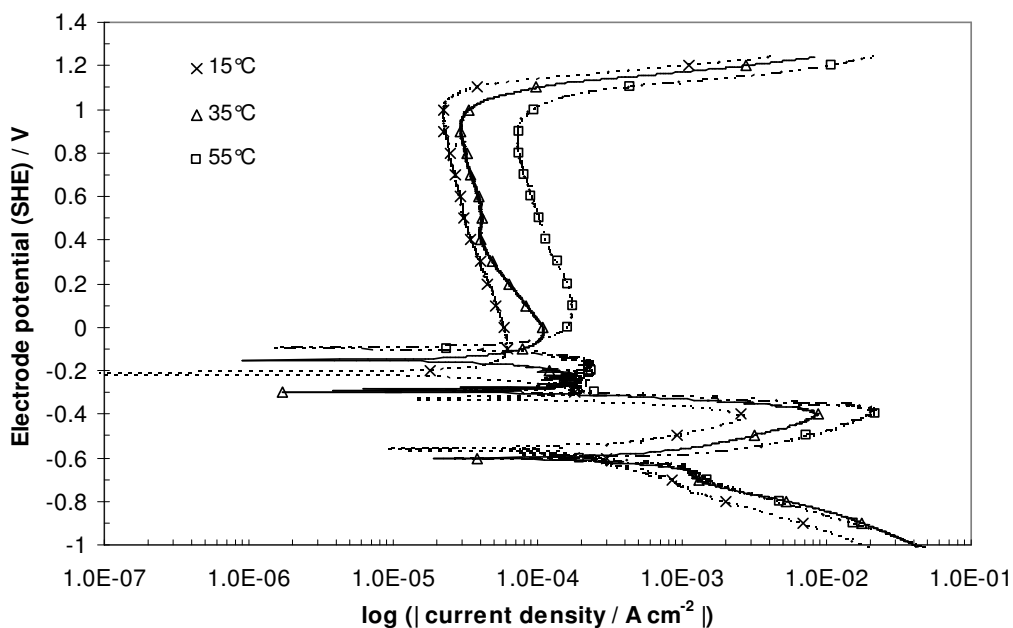
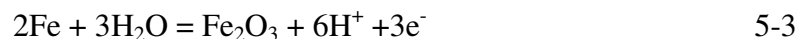
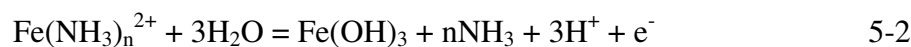


Figure 5.4: Effect of electrode potential and temperature on current densities of iron in oxygenated ammonium carbonate solution at pH 10.

Table 5.1: Electrochemical parameters of the anodic dissolution and passivation region of iron at different temperatures and oxygenated conditions.

Parameters		Temperature, °C		
		15	35	55
Deoxygenated condition	E_{corr} , V (SHE)	-0.66	-0.65	-0.63
	I_{corr} , (A/cm ²)	5.0×10^{-5}	2.0×10^{-4}	2.0×10^{-4}
	E_{pass} , V (SHE)	-0.40	-0.38	-0.37
	I_{pass} , (A/cm ²)	2.8×10^{-5}	8.9×10^{-5}	2.4×10^{-4}
Oxygenated condition	E_{corr} , V (SHE)	-0.56	-0.60	-0.59
	I_{corr} , (A/cm ²)	2.0×10^{-4}	7.0×10^{-4}	6.0×10^{-4}
	E_{pass} , V (SHE)	-0.40	-0.38	-0.37
	I_{pass} , (A/cm ²)	5.5×10^{-5}	9.5×10^{-5}	1.6×10^{-4}

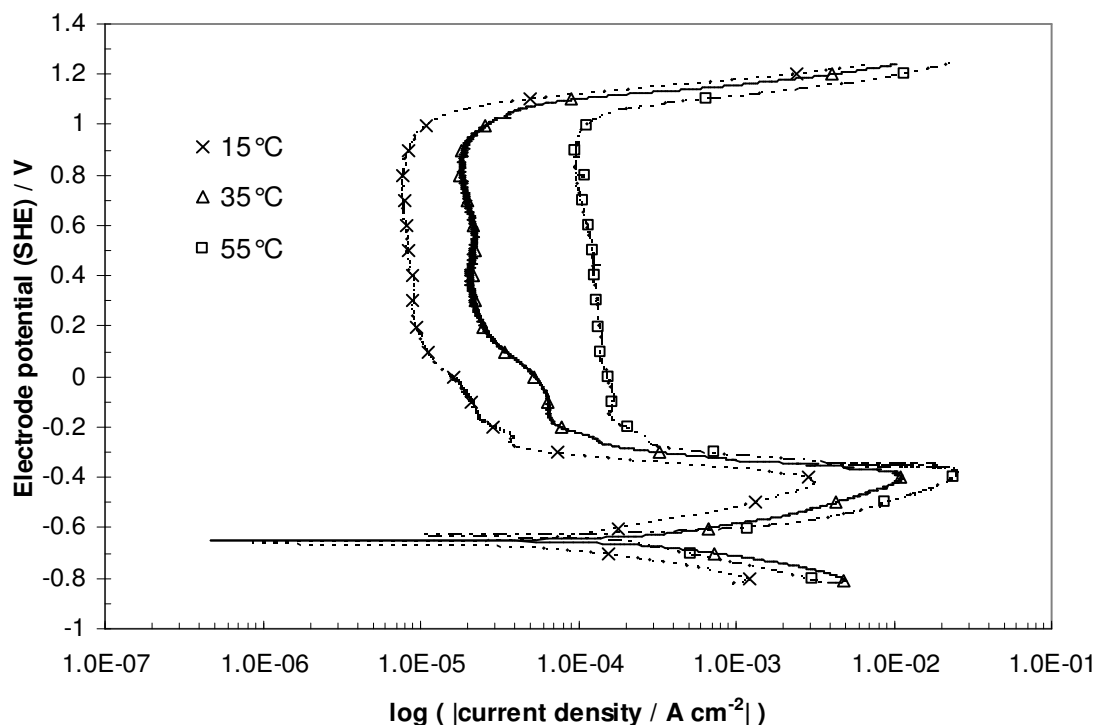


Figure 5.5: Effect of electrode potential and temperature on current densities of iron in de-oxygenated ammonium carbonate solution at pH 10.

These diagrams (Fig 5.4 and 5.5) give the corresponding potential where iron starts to dissolve and passivate in ammoniacal solution in oxygenated and de-aerated environments. According to the reaction scheme highlighted above, it is believed that ferrous ions or ammine complexes are generated during anodic dissolution and ferric oxide or oxy-hydroxide compounds are generated at potentials commensurate with passivation. The overall electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), passivation potential (E_{pass}), passivation current density (I_{pass}) of iron in ammoniacal carbonate solution at different temperatures and in oxygenated vs. de-oxygenated conditions are reported in Table 5.1. I_{pass} for oxygenated and deoxygenated condition was measured at 380mV and 170mV, respectively, above

the potential corresponding to critical passivation current. This information can be used to draw a metastable potential-pH diagram for the Fe-H₂O-NH₃ system at different temperatures.

5.3. Effects of pH

The Caron leaching process is operated typically at pH 9.5-10 [Kho et al. 1992]. In the experiments reported here, solutions of pH 6, 8, 10 and 12 were used to understand the effects of pH at different temperatures on iron oxidation processes. Fig 5.6 and 5.7 show the effect of potential and pH on current densities for iron in de-oxygenated solutions at 25°C and 40°C, respectively. Comparison of the data in Fig 5.6 and 5.7 at constant pH showed that increasing temperature increased oxidation current densities, as for the data in Fig 5.5.

Peak oxidation current densities were ca. 0.2, 0.002, 0.01 and 0.0006 A/cm² at pH 6, 8, 10 and 12, respectively (Fig 5.7). At pH 6, iron dissolution current densities increased exponentially in the potential range -0.5 to 0 V (SHE), before reaching what appeared to be a mass transport controlled limit, which was followed by passivation at 0.70 V (SHE).

The speciation and Eh-pH diagram of C-H₂O (Fig 5.8 and 5.9) system at 40°C provides the stability region of different species with varying pH 0 to 14. Aqueous

carbonic acid (H_2CO_3) is present below pH 6.3. When carbonic acid dissolves in water it always stays in equilibrium with carbon dioxide gas (CO_2).

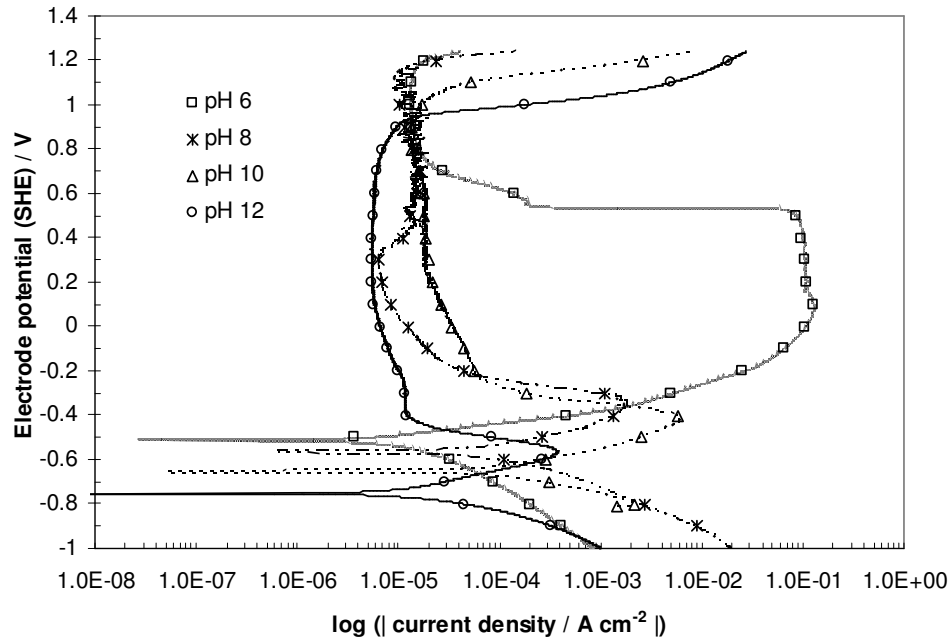
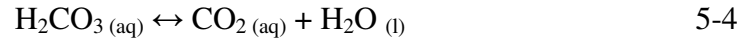
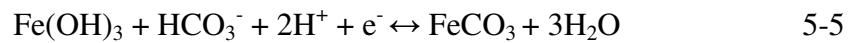


Figure 5.6: Dissolution rate as a function of potential at different pH in Carbon solution at 25°C in de-oxygenated condition.

Previous work has found that dissolved $\text{CO}_{2(\text{g})}$ in aqueous solution can cause corrosion failure of steel pipelines in the oil/gas transportation [Yin et al. 2009], [Zhang and Cheng 2009] [Lopez et al. 2004]. The mechanism of CO_2 corrosion depends on various environmental parameters such as temperature, pH, solution chemistry etc [Xue and Cheng 2010]. Equation 5-4 shows the dissolution reaction of carbonic acid to carbon dioxide and water. The overall reaction of iron in CO_2 environment can be: (a) anodic, iron dissolution and (b) cathodic, reactions involved one or more following steps; hydrogen ion reduction, carbonic acid reduction and water reduction. Temperature is also

an influencing factor for CO₂ corrosion of iron surface. At low temperature (below 60°C) and pH below 6, no protective layer has been formed because the solubility of iron carbonate is high enough [Yin et al. 2009]. Also, at low temperature, the corrosion layer formed is loose and porous, which leads to corrosion rates. So, the dissolution rate of iron in ammoniacal carbonate solution at pH 6 is higher than pH 8-12. At higher temperature above 60°C, the corrosion product becomes more compact, dense and adherent to the surface.

Fig 5.7 shows a very small ($\sim 0.01 \text{ A/cm}^2$) decrease in dissolution current density just above 0.20 V and the dissolution current density remains high (at the mass transport limit) till ca. 0.70 V. This is believed to be due to the formation of a porous layer of Fe(OH)₃ that does not significantly impede the high dissolution current density observed [Gayer and Wootner 1957]. The Nernst equation (Eq. 5-6) can be used to calculate the theoretical reduction potential for Fe(OH)₃/FeCO₃ at 40°C for pH 6. This calculation results in a value of 0.20 V which agrees with the observation above.



$$E (\text{SHE}) / \text{V} = -\Delta G^\circ/nF - 2.303(\text{RT}/nF) \log Q - 2.303(\text{RT}/F) (m/n)\text{pH} \quad 5-6$$

Also, at higher over-potentials for (ca. > 0.70 V) it is believed that this porous and unstable Fe(OH)₃ layer breaks down and start to form a more stable passive layer such as Fe₂O₃, FeO*OH, Fe₃O₄ etc.

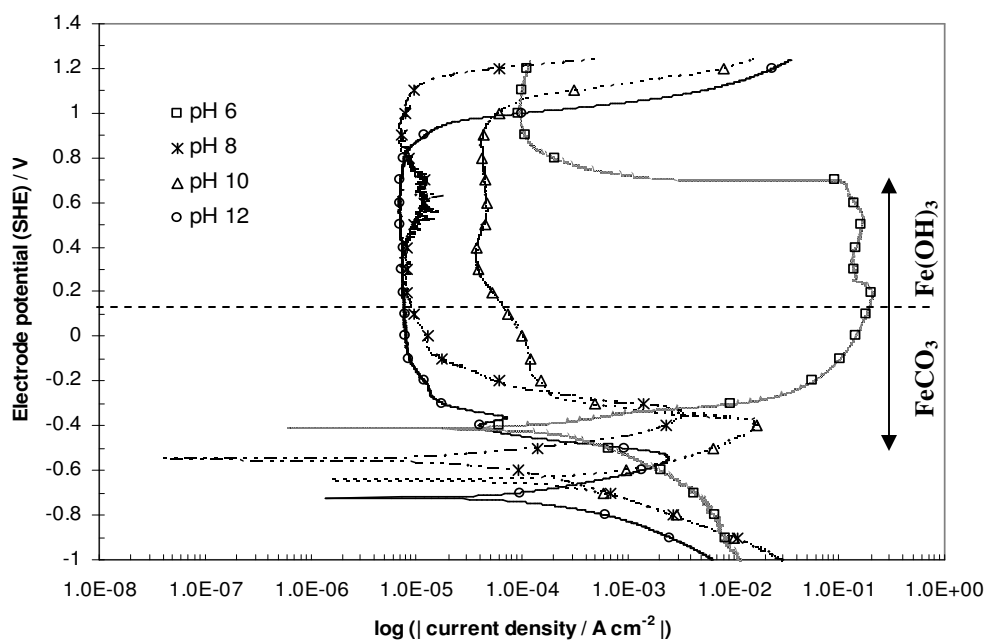


Figure 5.7: Dissolution rate as a function of potential at different pH in Caron solution at 40°C in de-oxygenated condition.

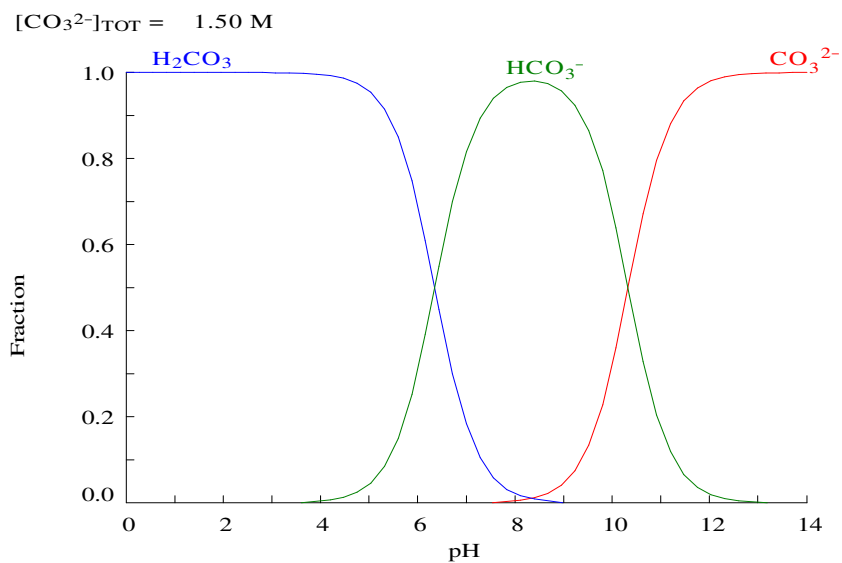


Figure 5.8: Speciation diagram of C-H₂O with [CO₃²⁻] = 1.5M produced by MEDUSA.

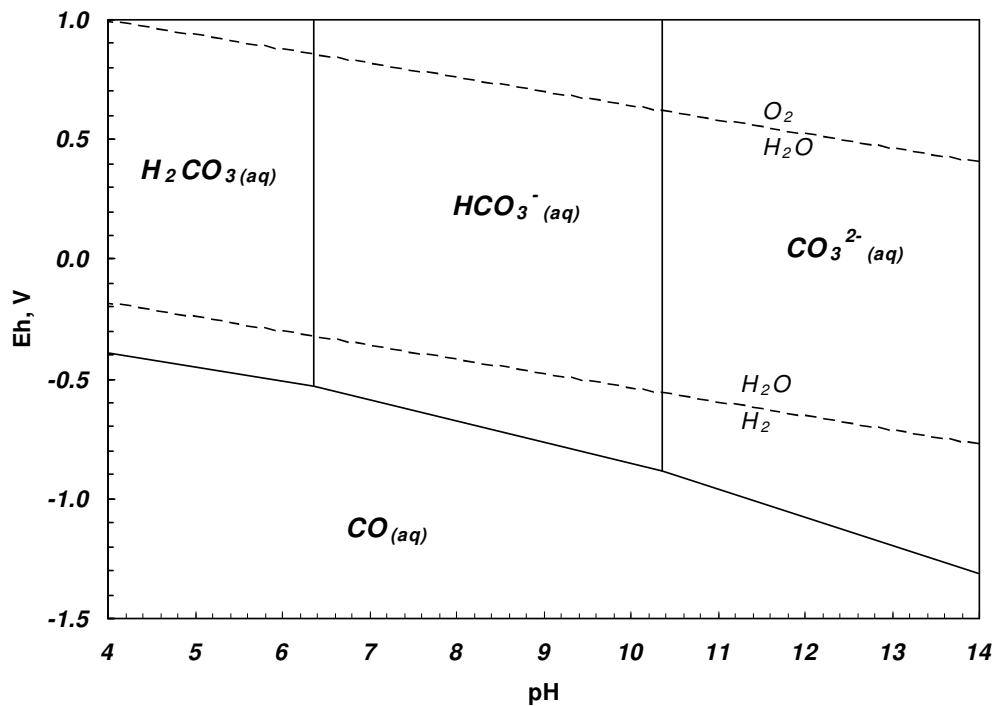


Figure 5.9: The Eh-pH diagram of C-H₂O system at 40°C.

5.4. Potentiostatic experiments

Fig 5.10 shows the time dependence of current densities for an iron electrode in de-oxygenated ammonium carbonate solution at pH 9 and 25°C at different potentials. Fig 5.10 shows only 5 of the 14 potentiostatic measurements taken for a given condition. Steady state current densities were achieved for each potential after a maximum of ca. 1000 s, with the highest current density of ca. 4 mA/cm² at 1.24 V (SHE).

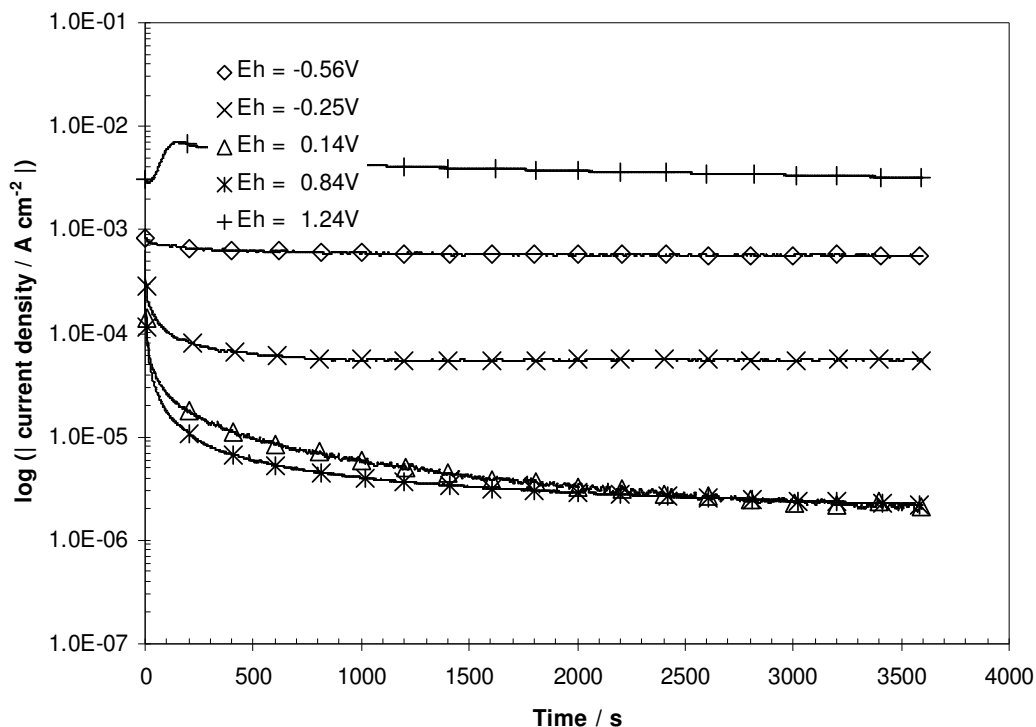


Figure 5.10: Effect of potential on time dependent current densities for iron in de-oxygenated ammonium carbonate solution at pH 9 and 25°C.

The steady state current density data in Fig 5.10 was used to construct the polarization curve shown in Fig 5.11 which also shows potentiodynamically obtained potential-current density data (potential scan rate 0.5mV s^{-1}) for the same conditions. The passive current densities obtained potentiostatically are roughly two orders of magnitude lower than those measured in the potentiodynamic experiment for pH 9 and 25°C. Fig. 5.11 demonstrates the impact of scan rate on the formation of the passive film. Clearly, the film formed on iron is increasingly protective with time.

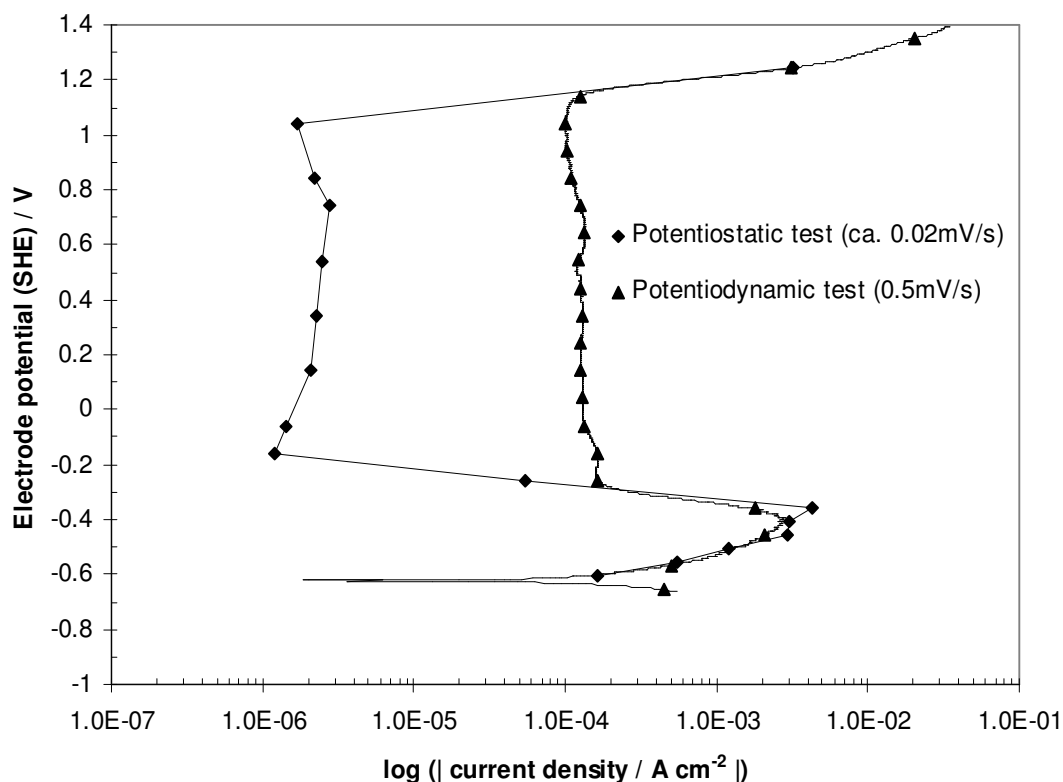


Figure 5.11: Electrode potential – (steady state) current density data from potentiostatic experiments with iron in de-oxygenated ammonium carbonate solution at pH 9 and 25°C.

Despite of the difference in current densities observed in the passive region, the dissolution current densities and potentials measured in the active region are nicely fitted between the potentiodynamically and potentiostatically measured potential-current density data. This implies that the data extracted from the potentiodynamic curves is largely representative of the time-scale used for leaching (1-2 hours for example). For this reason the potential range of active dissolution, as measured potentiodynamically and as a function of pH, may be used to represent the metastable potential-pH region for soluble Fe (II) species.

5.5. Comparison of direct scan and steady-state condition

To compare the effect of time on the potentiodynamic test results, both a direct scan and steady-state condition potentiodynamic test were performed at pH 10 and 25°C (Fig 5.12). In the direct scan the iron sample was polarized directly from -1.25 V versus the reference electrode without any prior immersion time in solution. In the steady-state scan, the iron sample was immersed in solution at open circuit for 4 hrs and before being polarized from -0.25 V versus open circuit. In case of the steady-state scan, the iron sample was spontaneously passivated while the direct scan reveals a distinct anodic nose at ca. -0.4 V followed by passivation of iron at higher potentials. Clearly, the response observed in the direct scan condition is contingent on high cathodic overpotentials and would not be observed in a leach environment without the existence of a significantly reducing environment. In oxygenated conditions iron passivates spontaneously.

With regards to the Caron leach, and to minimize the effects of iron passivation, reducing conditions must be maintained at the initial stages of leaching to dissolve most of the iron by forming ammine complexes and consequently enable the dissolution of nickel and cobalt at higher potential in the presence of oxygen.

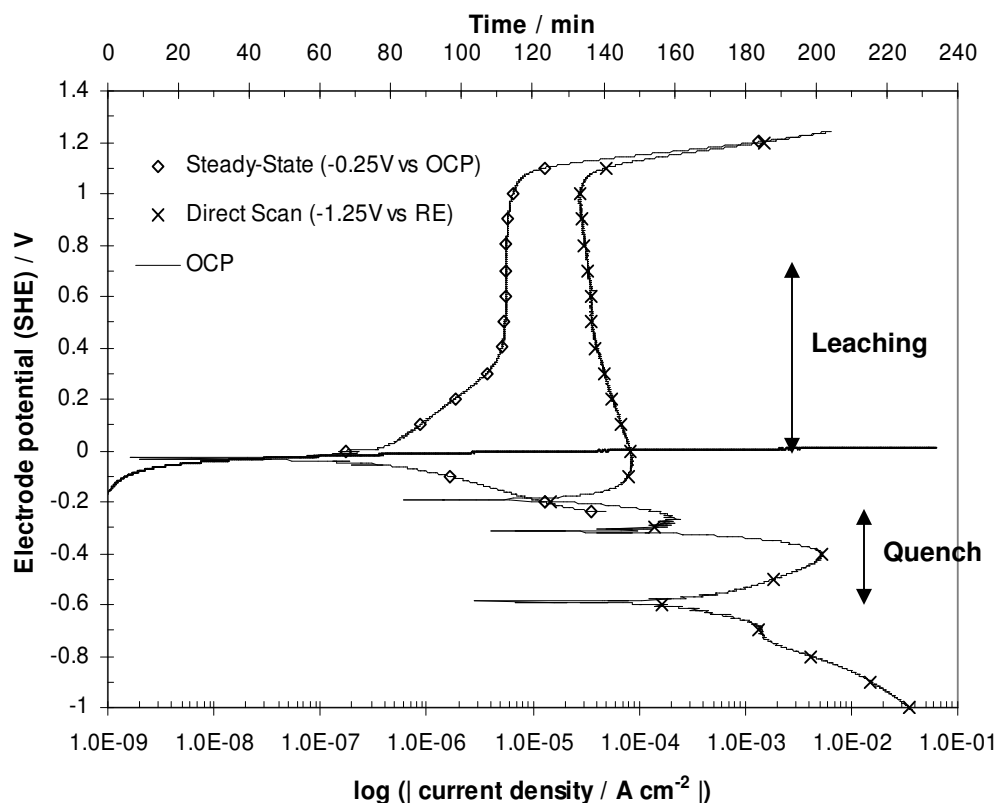


Figure 5.12: Comparison of direct scan and steady-state condition on polarization curve for iron in oxygenated ammonium carbonate solution at pH 10 and 25°C.

5.6. Solution analysis

20 cm³ samples of solution were taken by pipette during a potentiodynamic experiment at pH 9 and 6, and subsequently analyzed for dissolved iron by ICP. Results are listed in Table 5.2, showing that for pH 6 ca. 7.55 mg dm⁻³ iron dissolved over ca. 1 hour, the background dissolved iron concentration being <0.03 mg dm⁻³ at pH 6 and 9 prior to potentiostatic experiments. Approximately 0.37 and 82.45 C was passed between the corrosion potential and beginning of the passive region at pH 9 and 6, respectively. Based on the ICP analysis in table 5.2, the current efficiency for active Fe^{II} dissolution

was calculated to be approximately 79% and 15% for pH 9 and 6 respectively. The current efficiency is lower for pH 6, which implies that much of the iron was precipitated at the electrode surface. The mean ionic flux of Fe^{II} as measured by ICP corresponded to the current density of ca. 1×10^{-3} at pH 9 and $2 \times 10^{-2} \text{ A/cm}^2$ at pH 6. These last numbers are in good agreement with the potentiodynamic potential-current data presented in Fig 5.11 and 5.6 for pH 9 and 6, respectively.

Table 5.2: Solution analysis by ICP at different potentials during potentiodynamic test for pH 9 and 6.

Potential,(V)	Fe	Current	Potential, (V)	Fe	Current
pH 9	(mg dm ⁻³)	Efficiency, %	pH 6	(mg dm ⁻³)	Efficiency, %
-0.60	0.07		-0.52	<0.03	
-0.36	0.13	79.1	-0.01	2.48	37.2
-0.20	0.21	45.4	0.18	5.06	15.3
0.44	0.22	46.4	0.34	5.37	12.6
1.01	0.26	54.3	0.51	2.88	6.1
1.10	0.44	91.7	0.95	7.55	15.8

5.7. Surface analysis

After potentiostatic oxidation of iron electrodes at -0.38 V (SHE) and 0.35 V (SHE), for 1.5 hours, they were gently rinsed with distilled water and surfaces imaged by scanning electron microscopy. The resulting photomicrographs are shown in Fig 5.13, showing that for -0.38 V (SHE), in the active dissolution region, the surface appeared corroded, whereas for 0.35 V (SHE), in the passive region, the surface is largely un-attacked and smooth, due to the passive film being protective.

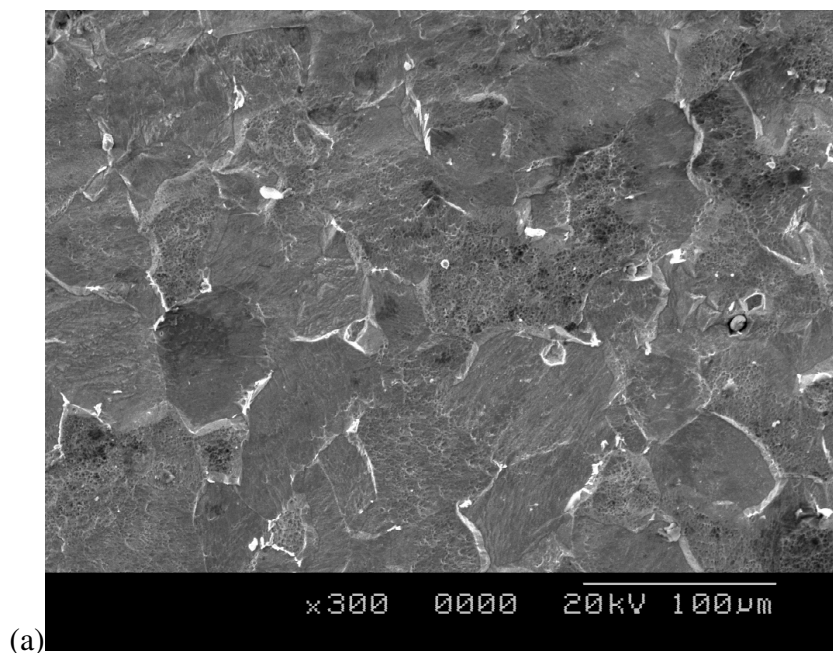


Figure 5.13 (a): Photomicrographs of surfaces of oxidized iron after potentiostatic exposure for 1.5 hrs at -0.38 in de-oxygenated ammonium carbonate solution at pH 9 and 25°C with 300X magnifications.

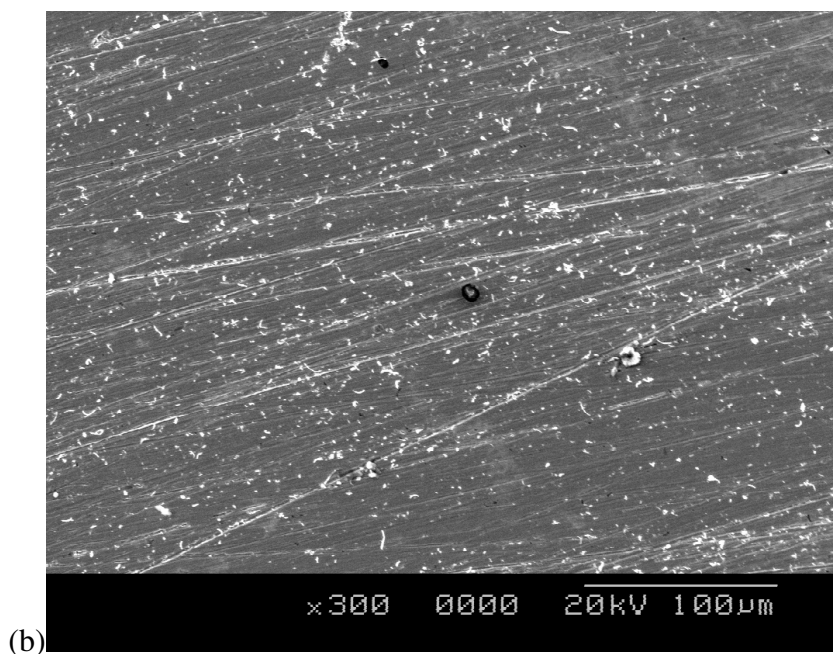


Figure 5.13 (b): Photomicrographs of surfaces of oxidized iron after potentiostatic exposure for 1.5 hrs at 0.35 V in de-oxygenated ammonium carbonate solution at pH 9 and 25°C with 300X magnifications.

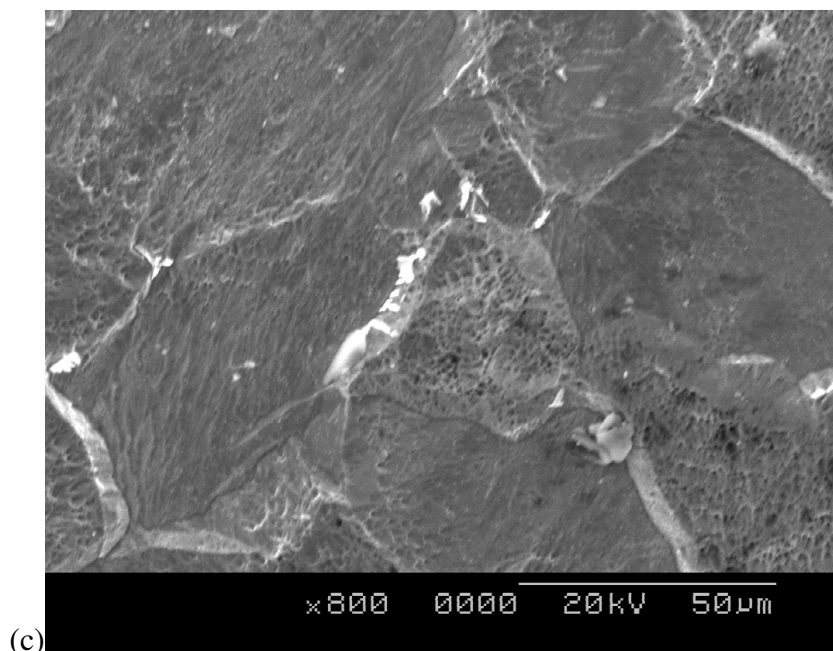


Figure 5.13 (c): Photomicrographs of surfaces of oxidized iron after potentiostatic exposure for 1.5 hrs at -0.38 V in de-oxygenated ammonium carbonate solution at pH 9 and 25°C with 800X magnifications.

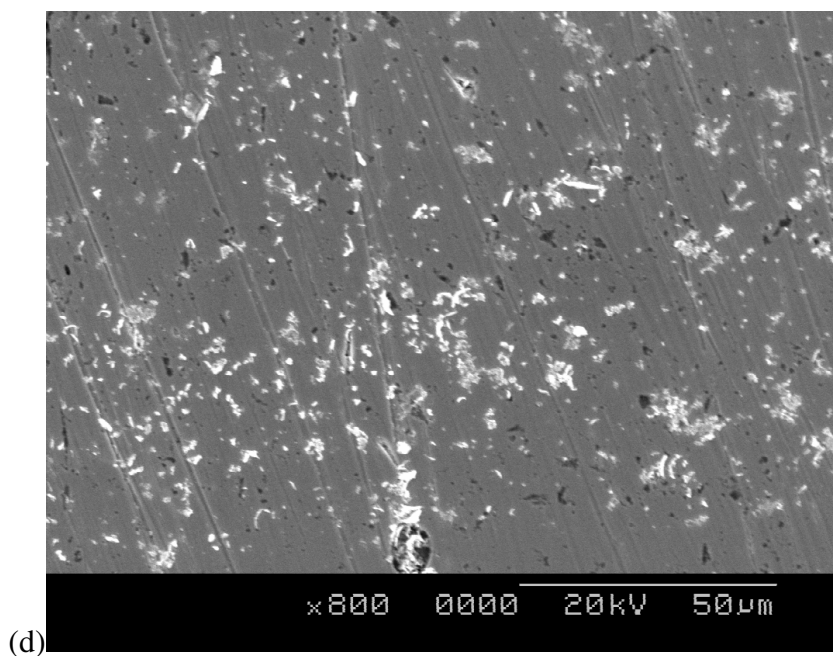


Figure 5.13 (d): Photomicrographs of surfaces of oxidized iron after potentiostatic exposure for 1.5 hrs at 0.35 V in de-oxygenated ammonium carbonate solution at pH 9 and 25°C with 800X magnifications.

5.8. XPS analysis

To ascertain the nature of the passive film formed, one iron sample was immersed in de-oxygenated ammonium carbonate solution of pH 9 at a potential of 0.44 V (SHE) for 4 hours and another was polished, rinsed and exposed in air i.e. no treatment applied. Fe2p, O1s and C1s spectras were reported in Fig 5.14 (a–c) respectively. According to online data available from the UK surface analysis forum, if the Fe2p and O1s binding energies are 710.8 and 530.2 eV, respectively, then the compound is Fe₂O₃. Fig 5.14(a) show two different energy peaks found at 706.9 and 710.72 eV. Peak (706.9 eV) is for pure Fe metal and 710.72 eV is likely the Fe₂O₃ peak.

These two peaks were found in both conditions (with and without treatment) used in the lab. Thus, in both conditions iron build-up a passive layer on its surface, this is believed to be Fe₂O₃. But the Fe/Fe^{II} area ratio under the peaks for the two different conditions is not same. As calculated, this ratio for the air-only exposed sample is 8.23 and for the immersed sample the ratio is 9.84. Thus it would appear that the oxide thickens upon exposure to solution.

Heuer and Stubbins have studied the XPS characterization of FeCO₃ films in the context of CO₂ corrosion of pipeline steel [Heuer and Stubbins 1999]. Using FeCO₃ standards they determined that the Fe2p_{3/2} peak for siderite was at 710.32eV and the the Fe2p_{1/2} was at 723.7eV. Also, the O1s peak was found to lie at 531.9eV. For the C1s spectra the peak was found at a binding energy of 289.4eV [Heuer and Stubbins 1999].

When siderite was allowed to “ripen” by for 48 hours at 75°C, these same authors noted that it converted to hematite.

Wu et al. studied the characteristics of surface film of N80 steel during carbon dioxide corrosion [Wu et al. 2004]. They used simulant stratum water and crude oil as corrosion medium with water to oil ratio of 9:1. The corrosion test was carried out under turbulent flow condition for 72 h at 80°C with a carbon dioxide partial pressure of 0.5 MPa. The binding energies of four elements iron, oxygen, carbon and calcium in the surface and subsurface of the film were characterized by fitting those with high resolution spectra [Wu et al. 2004] [Claassen and Sandenbergh 2007]. According to these authors, the C1s spectra revealed that the main peaks at 289.52 eV (surface) and 288.72 eV (subsurface) corresponded to iron carbonate (FeCO_3). Also, the O1s spectrum revealed that the peaks at 529.95 eV (surface) and 529.83 eV (subsurface) corresponded to $\text{Fe}(\text{OH})_2$ or FeOOH , and that the peaks at 531.60 eV (surface) and 531.43 eV (subsurface) was close to 531.9 eV, which corresponded to pure iron carbonate [Wu et al. 2004] [Heuer and Stubbins 1999]. However, $\text{Fe}(\text{OH})_2$ transformed quickly into $\alpha\text{-FeO*OH}$ in an air environment. In the present case there is no peak for siderite in the measured XPS spectra because we are just in the maximum pH range (pH 9) region where siderite stability diminished. According to the speciation diagrams (Fig 5.8 and 5.15), FeCO_3 formation occurs below pH 9.

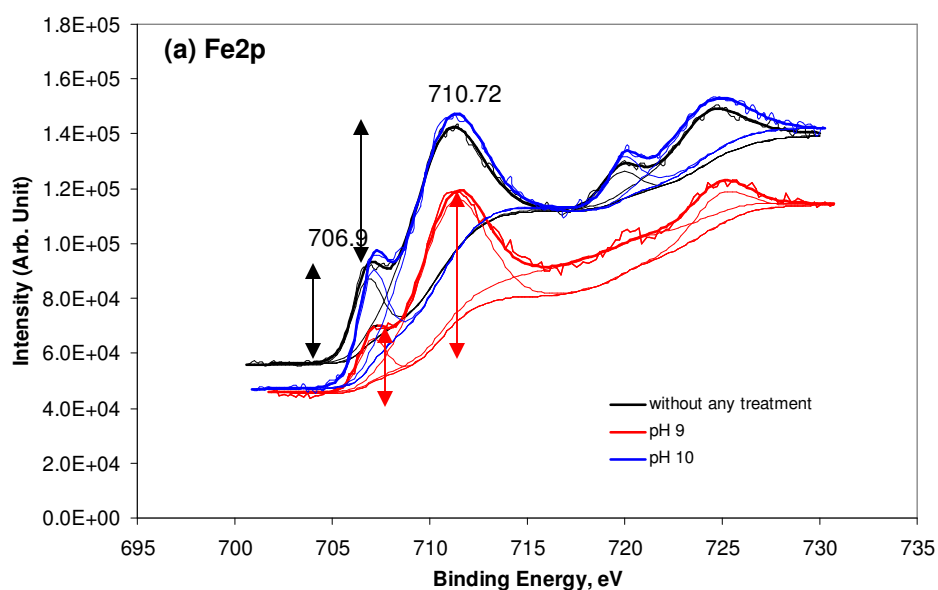


Figure 5.14 (a) De-convoluted XPS spectra for Fe2p (Shirley background) obtained after 4 hours at 0.44 V (SHE) potentiostatic polarization at pH 9 and 25°C (red spectra). The black spectra are for Fe exposed only to air i.e. no treatment.

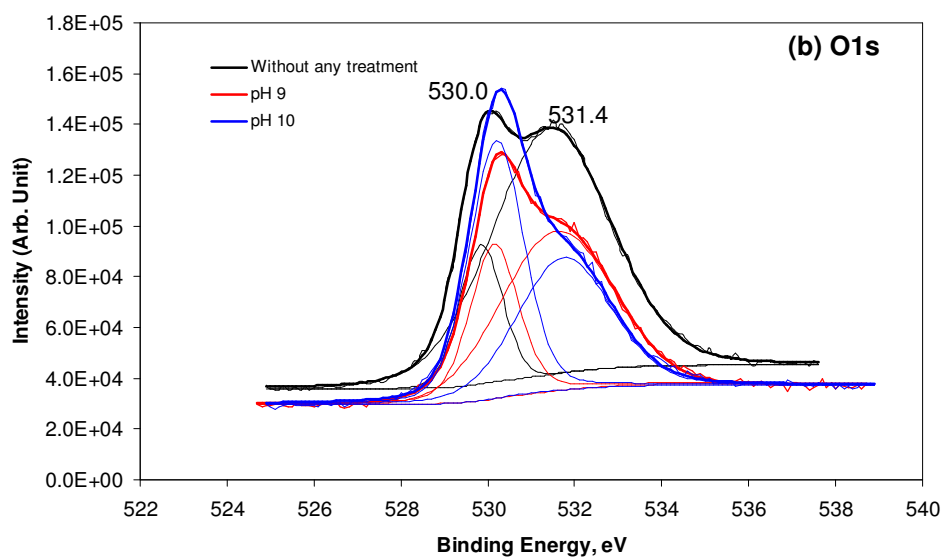


Figure 5.14 (b) De-convoluted XPS spectra for O1s (Shirley background) obtained after 4 hours at 0.44 V (SHE) potentiostatic polarization at pH 9 and 25°C (red spectra). The black spectra are for Fe exposed only to air i.e. no treatment.

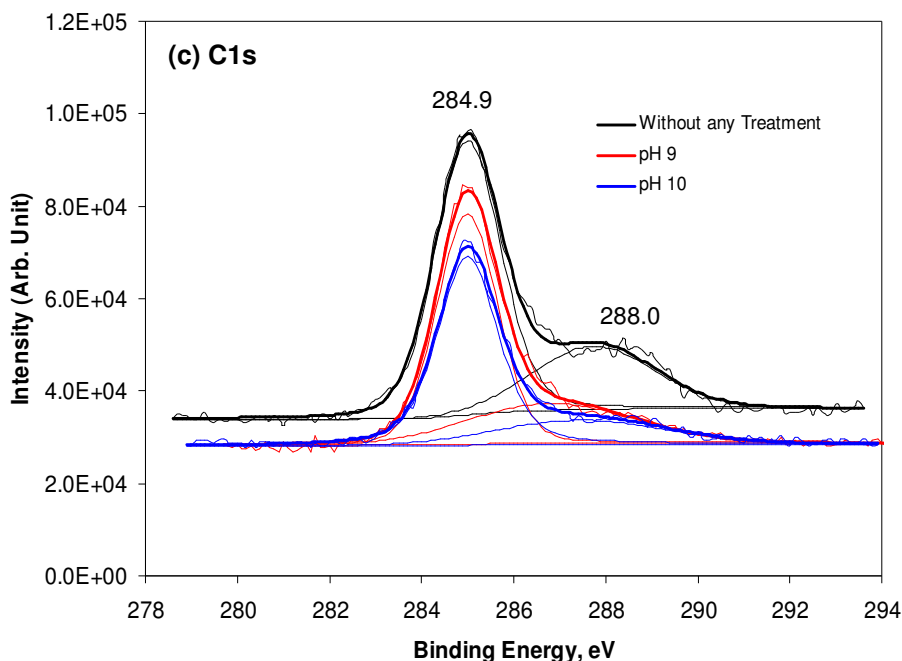


Figure 5.14 (c): De-convoluted XPS spectra for C1s (Shirley background) obtained after 4 hours at 0.44 V (SHE) potentiostatic polarization at pH 9 and 25°C (red spectra). The black spectra are for Fe exposed only to air i.e. no treatment.

5.9. Potential-pH and speciation diagrams of iron

Potential-pH diagrams have been published [Asselin 2008], [Osseo-Asare et al. 1983] for iron-ammonia-carbonate-water systems relevant to the Caron process. One purpose of the results reported in Fig 5.4-5.5 was to enable comparison of kinetic behavior with thermodynamic predictions. For example, the potential range over which active dissolution is implied should correspond to the conditions in which iron(II) is predicted to be soluble as Fe^{2+} or $\text{Fe}(\text{NH}_3)_n^{2+}$ ions; above such potentials, Fe(III) oxides / hydroxides should form, causing passivation.

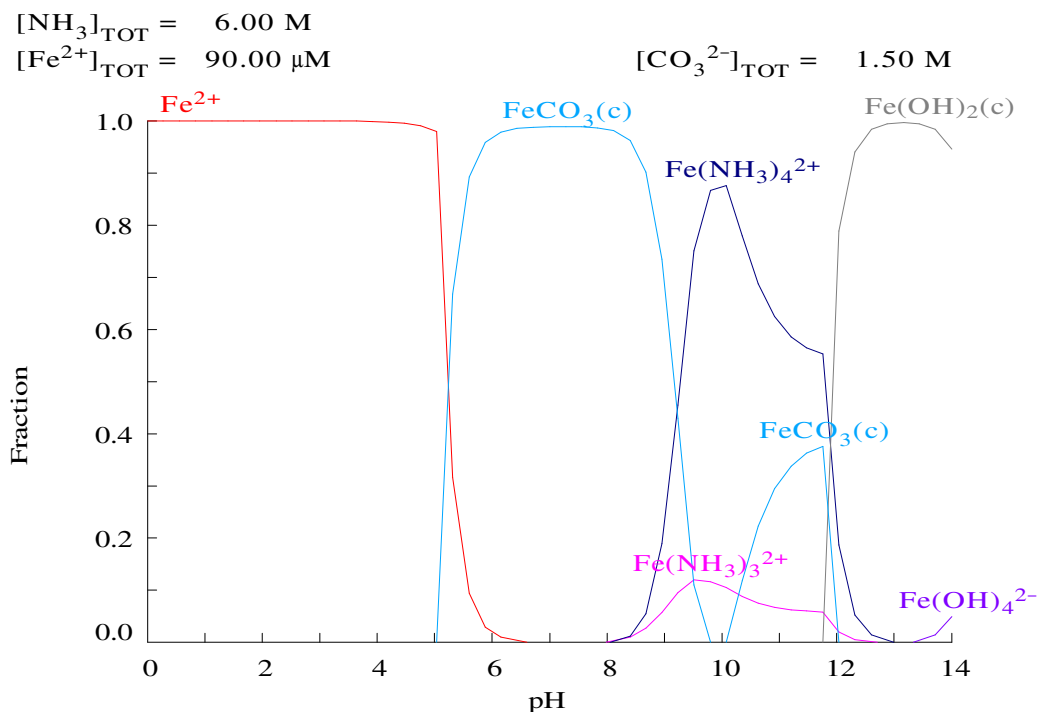


Figure 5.15: Speciation diagram of iron calculated at $[\text{Fe}^{2+}] = 9 \times 10^{-5} \text{ M}$, $[\text{NH}_3] = 6 \text{ M}$ and $[\text{CO}_3^{2-}] = 1.5 \text{ M}$ at 25°C

According to Fig 5.15 (speciation diagram of Fe^{2+}) iron dissolution in ammoniacal carbonate solution through the formation of ammine complexes is achieved between pH 9 and 12 at 25°C . This is in agreement with the previous work presented by Asselin (2008) and Osseo-Asare et al. (1983). Here the concentration of total $[\text{Fe}^{2+}] = 9 \times 10^{-5} \text{ M}$, $[\text{NH}_3] = 6 \text{ M}$ and $[\text{CO}_3^{2-}] = 1.5 \text{ M}$. The iron concentration used to generate these diagrams was based on the ICP analysis (presented above table 5.2) which gave a maximum Fe concentration of ca. $9 \times 10^{-5} \text{ M}$. Below pH ~ 9.0 , FeCO_3 which known as siderite is the major stable species down to pH 5.10. Also, $\text{Fe}(\text{OH})_2$ is stable at higher pH ~ 12 which implies the passivation of iron.

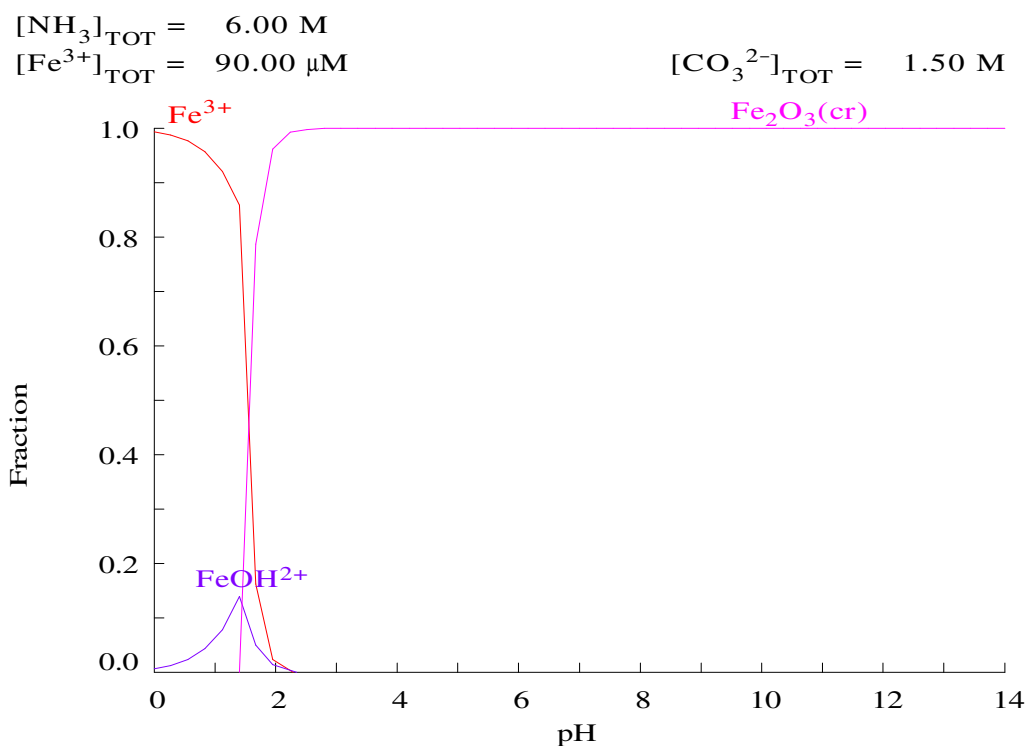


Figure 5.16: Speciation diagram of iron calculated at $[\text{Fe}^{3+}] = 9 \times 10^{-5} \text{ M}$, $[\text{NH}_3] = 6 \text{ M}$ and $[\text{CO}_3^{2-}] = 1.5 \text{ M}$ at 25°C .

Fig 5.17 (a) and (b) show the metastable potential-pH diagram for the $\text{Fe-NH}_3\text{-CO}_3\text{-H}_2\text{O}$ system overlaid onto the potential ranges through which active dissolution as Fe (II) species was implied in potentiodynamic experiments at pH 6, 8, 9, 10 and 12 at two different temperatures. Agreement between the thermodynamic and thermo-kinetic potential ranges was generally acceptable, except for significant deviation at pH ca. 6, at which Fe(II) solubility was evidently higher than predicted, in that passivation required significantly higher potentials than predicted (cf. Fig 5.7 above). As explained before, a porous layer of iron hydroxide (III) is believed to have formed at potentials exceeding 0.20 V (SHE) which would explain the mass transport limitation observed in Fig 5.7

This porous layer controlled the higher dissolution current rate in that predicted (ca. > 0.20V) higher potential area. It is also of note that the real stability of soluble ferrous species is less than expected at pH 8 to 10 (Fig 5.17). This may have implications for the leaching process. Thus the solution redox potential has to be controlled carefully during the leaching process.

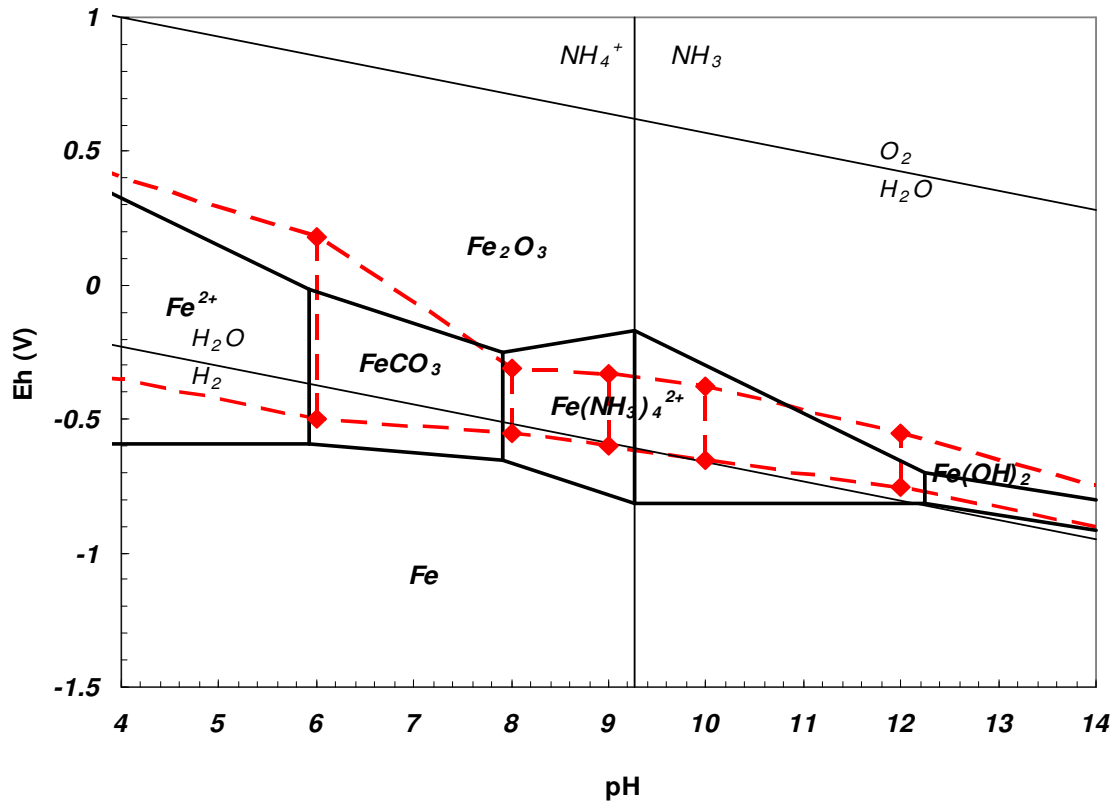


Figure 5.17 (a): Meta-stable potential-pH diagram for the Fe-NH₃-CO₃-H₂O system with [Fe] = 9×10⁻⁵ M (5ppm), [NH₃]_T = 6M and [CO₃²⁻] = 1.5M at 25°C. The solid and dotted lines indicate respectively the theoretical and measured values from potentiodynamic test.

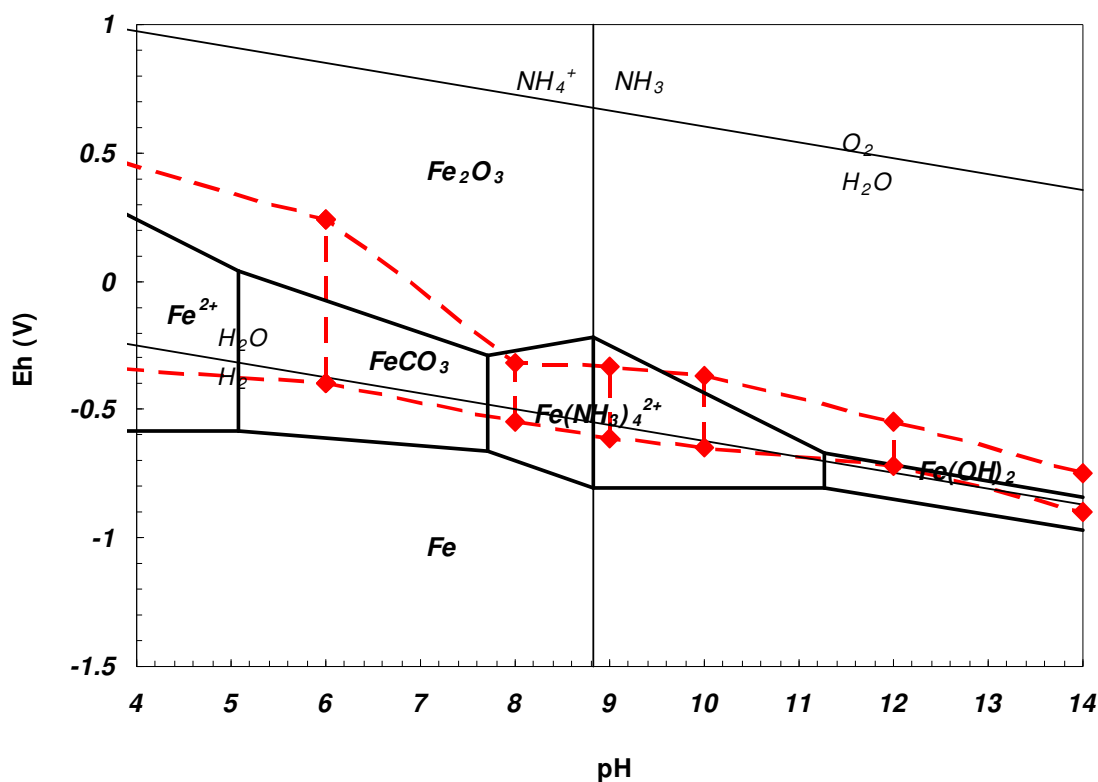


Figure 5.17 (b): Meta-stable potential-pH diagram for the Fe-NH₃-CO₃-H₂O system with [Fe] = 9×10⁻⁵ M (5ppm), [NH₃]_T = 6M and [CO₃²⁻] = 1.5M at 40°C. The solid and dotted lines indicate respectively the theoretical and measured values from potentiodynamic test

Figs 5.17 (a) and (b) also show that the potential for dissolution of iron in ammoniacal solution from metallic iron is higher than the predicted theoretical values. For both cases (25°C and 40°C) the actual dissolution potential is around 100-200mV higher. This is of course consistent with mixed-potential theory as applied to these thermo-kinetic diagrams.

According to the speciation and potential-pH diagram of Fe-NH₃-CO₃-H₂O system, siderite (FeCO₃) is a stable compound between pH 6-9) at 25°C. Siderite formation in carbonate solution has been investigated by Han et al. (2009), Osseo-Asare

(1981), Zhang and Cheng (2009) and Cui et al. (2006). Han et al. studied the chemistry and structure of the passive film on mild steel in CO₂ corrosion environments at 80°C and pH 8. As the iron/steel sample is immersed in a CO₂ containing electrolyte, the iron carbonate can form a surface film when FeCO₃ super saturation has been attained [Han et al. 2009], [Osseo-Asare 1981].

According to the speciation diagram (Fig 5.15), in the range of pH 9-12 and Eh - 0.6 to -0.1V, the metallic iron is assumed to be dissolved by forming different ammine complexes:

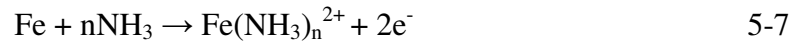


Table 5.3 shows a comparison of the theoretical and measured values of the potentials for Fe/Fe(NH₃)₄²⁺ and H⁺/H₂ at different temperature. It has been found that the measured corrosion potentials (E_{corr}) are between the reversible potentials of H⁺/H₂ and Fe/Fe(NH₃)₄²⁺ as expected by mixed potential theory. So, it is believed that in reality hydrogen reduction occurs in cathode and iron oxidation in anode. The reaction can be written as follows.

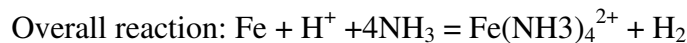
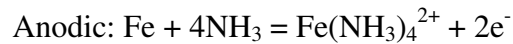


Table 5.3: Comparison of measured corrosion potential (E_{corr}) and theoretical (calculated) values for hydrogen reduction ($E_{\text{H}^+/\text{H}_2}$) and ferrous tetra-ammine formation ($E_{\text{Fe}/\text{FeA4}^*}$)

Temperature, °C	E_{corr} , (V/SHE)	$E_{\text{H}^+/\text{H}_2}$, (V/SHE)	$E_{\text{Fe}/\text{FeA4}^*}$, (V/SHE)
15	-0.66	-0.52	-0.83
25	-0.65	-0.54	-0.84
35	-0.65	-0.56	-0.84
45	-0.64	-0.58	-0.85
55	-0.63	-0.60	-0.86

*FeA4= Iron tetra ammine, $\text{Fe}(\text{NH}_3)_4^{2+}$

Table 5.4 shows a comparison of theoretical and calculated G°_{298} values for different amines based on the assumption that the corrosion potential represents the reversible potential for the Fe-ammine formation reactions. While it is clear from Table 5.3 that this is not the case (in fact the cathodic overpotential seems to be smaller than the anodic overpotential), this analysis was undertaken for comparison purposes. The E° values were calculated from equation 5-8 by using the E_{corr} from the potentiodynamic test for 298K at pH 10. Then ΔG°_{298} has been derived from equation 5-9 for the corresponding reaction. This ΔG°_{298} can then be used to calculate G°_{298} for the related amines. G°_{298} for the related amines, as calculated from measured values of E_{corr} , are similar to the theoretical G°_{298} values found in literature [Isaev 1990] [Asselin 2008]. The smallest relative difference between calculated vs. measured values is observed for the mono-ammine.

$$E = E^\circ - (2.303RT/nF) \log\{[\text{NH}_3]^n/[\text{Fe}^{2+}]\} \quad 5-8$$

$$\Delta G^\circ_{298} = -E^\circ nF \quad 5-9$$

Table 5.4: Comparison of theoretical and calculated G°_{298} values for different amines at 25°C and pH 10

Amines	Calculated E° , V	G°_{298} (Theory)	G°_{298} (Calculated)	Log β
		KJ/mol	KJ/mol	
FeA	-0.509	-128.65	-124.79	10.41
FeA2	-0.486	-162.11	-146.85	0.345
FeA3	-0.463	-193.23	-169.00	-0.41
FeA4	-0.445	-222.13	-190.97	-1.21
FeA5	-0.417	-248.34	-213.03	-1.97

Table 5.5 shows the corrosion rate (I_{corr}) and exchange current densities (I_0) as obtained by Tafel extrapolation. Based on speciation calculations presented above (Fig 5.15) we assume that the anodic process exchange current density is that of the tetra-amine formation reaction. An Arrhenius diagram (Fig 5.18) has been drawn from the potentiodynamic data by taking the average corrosion current (I_{corr}) at the mixed/corrosion potential and at the anodic nose (i.e. the maximum anodic current). Measurements of these data were accomplished through calculating an average of three Tafel extrapolations as obtained from three distinct but reasonable Tafel slopes (cf. Appendix A).

From the Arrhenius diagram (Fig 5.18) it has been calculated that the apparent activation energy is ~ 48.30 KJ/mol for the overall process (at the mixed potential) and ~ 44.06 KJ/mol at the anodic nose region. These calculations show that these activation energies are significantly different to that measured previously for Armco iron in 1M HCl at pH ~ 0 in deaerated solutions (~ 85.6 KJ/mol) [Chebabe et al. 2003].

Table 5.5: Exchange current densities for Fe/FeA4*, H₂/H⁺ and overall reactions at different temperature for pH 10.

Temperature, °C	$I_{(corr)}$, A/cm ⁻²	Exchange current density $I_{(H_2/H^+)}$, A/cm ⁻²	Exchange current density $I_{(Fe/FeA4^*)}$, A/cm ⁻²
15	5.0×10^{-5}	2.0×10^{-6}	4.5×10^{-6}
25	8.0×10^{-5}	1.5×10^{-6}	4.0×10^{-6}
35	2.0×10^{-4}	2.0×10^{-5}	2.2×10^{-5}
45	3.0×10^{-4}	1.0×10^{-4}	2.7×10^{-5}
55	2.0×10^{-4}	1.0×10^{-4}	2.9×10^{-5}

*FeA4= Iron tetra ammine, $Fe(NH_3)_4^{2+}$

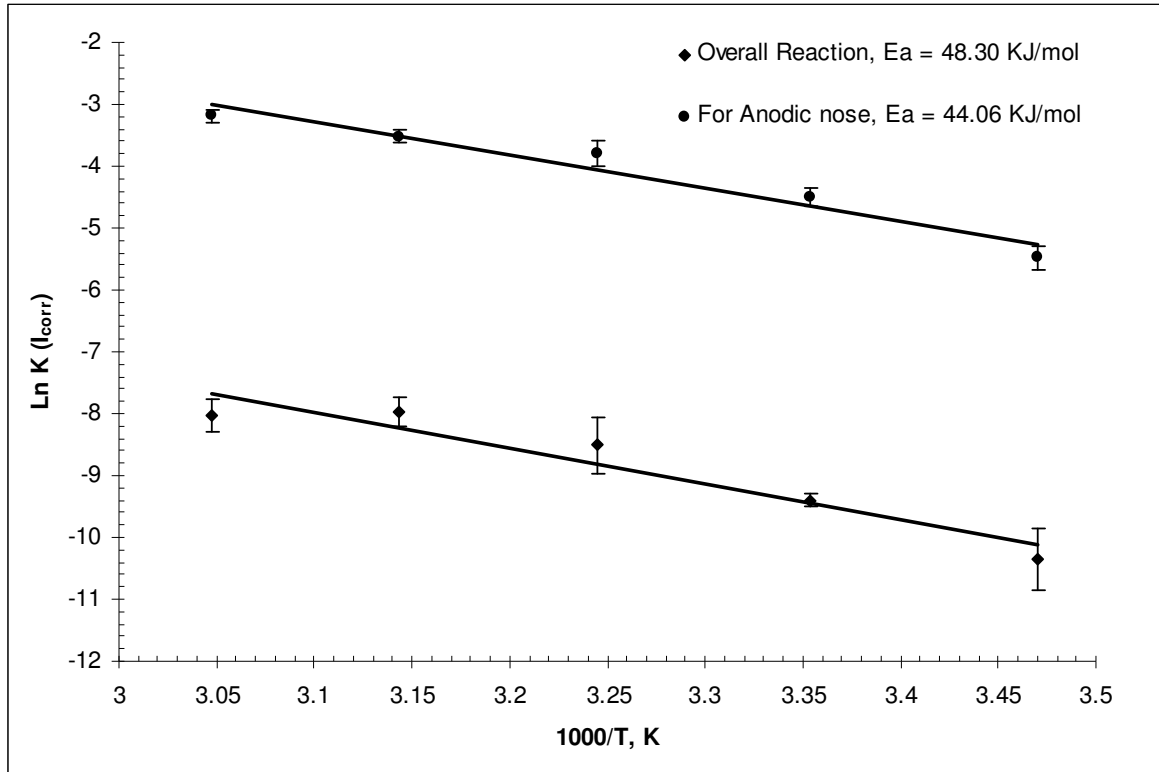


Figure 5.18: Arrhenius plot for different reactions in ammoniacal solution (pH 10).

6. CONCLUSIONS

The passivation of iron begins at around -0.40 V (SHE) in the 15°C - 55°C temperature range in oxygenated and de-oxygenated solutions at pH 9.0-10. The highest oxidation current density was ca. 0.025 A cm⁻² (260 g m⁻²hr⁻¹) for pH 10 at 55°C, with iron beginning to passivate at potential > ca. -0.40 V (SHE). In oxygenated ammonium carbonate solutions, oxygen reduction reactions occur at ca. -0.3 V to -0.1 V (SHE). Under the tested conditions the maximum anodic dissolution rate of amines increased with temperature up to a maximum of 0.20 A/cm² (2100 g m⁻²hr⁻¹) at 40°C for pH 6.

At pH 6, iron dissolution current densities increased exponentially in the potential range -0.5 to 0 V (SHE), before reaching what appeared to be a mass transport controlled limit, which was followed by passivation at 0.70 V (SHE). The speciation and Eh-pH diagram of C-H₂O system at 40°C provides that aqueous carbonic acid (H₂CO₃) is the suitable species below pH 6.3. When carbonic acid dissolves in water it always stays in equilibrium with carbon dioxide gas (CO₂). At lower temperature (below 60°C) with suitable condition FeCO₃ (siderite) is believed to form a loose and porous film which does not suppress corrosion. This implies that the high current densities observed at pH 6 may result from the absence of a protective film. ICP and SEM analysis have shown that the dissolution rate is highest at around -0.450V (SHE) in the anodic nose region at pH 6.

The passive current densities obtained potentiostatically are roughly two orders of magnitude lower than those measured potentiodynamically at a scan rate of 0.5 mV/s at pH 9, 25°C. Thus the passive film at this pH thickens considerably (or becomes more

protective) with time. Despite of the difference in current densities observed for the passive region, the dissolution current densities and potentials measured for the active region are nicely fitted between the potentiodynamically and potentiostatically measured potential-current density data. This implies that the data extracted from the potentiodynamic curves is largely representative of the time-scale used for leaching (1-2 hours for example). For this reason the potential range for active dissolution as measured potentiodynamically and as a function of pH was suitable for use in the generation of the metastable potential-pH diagrams, particularly for Fe (II) species.

The comparison of the direct scan and steady-state experiments showed that on iron is passivated easily in Caron solutions. To minimize the effects of iron passivation on the leach, very careful potential control must be employed at the initial stages of leaching and in the absence of oxygen.

Based on the ICP analysis, the current efficiency for active Fe(II) dissolution was calculated to be approximately 79% and 15% for pH 9 and 6, respectively. The current efficiency is lower for pH 6 despite high overall currents implying that a porous and un-protective passive film was forming. From the speciation diagram of Fe (II), it shows the complete dissolution of iron can be achieved in between pH ~ 9.0- 12.0 by forming iron (II)- tetra-ammines and siderite (FeCO_3) is stable species in between pH ~ 5.10 - 9.0. The complete passivation of iron can be achieved at higher pH above ~ 12 by forming $\text{Fe}(\text{OH})_2$. XPS analyses of corroded surfaces after the potentiostatic test established that hematite forms at high Eh at pH 9.

Finally, it was shown that metastable or thermo-kinetic Eh-pH diagrams for the Fe-NH₃-CO₃-H₂O system can be measured electrochemically. These diagrams may be more useful in predicting the outcome of practical leaching scenarios than solely thermodynamic diagrams.

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APPENDICES

Appendix A- Example of Tafel slopes used for measurement of I_{corr} and I_0

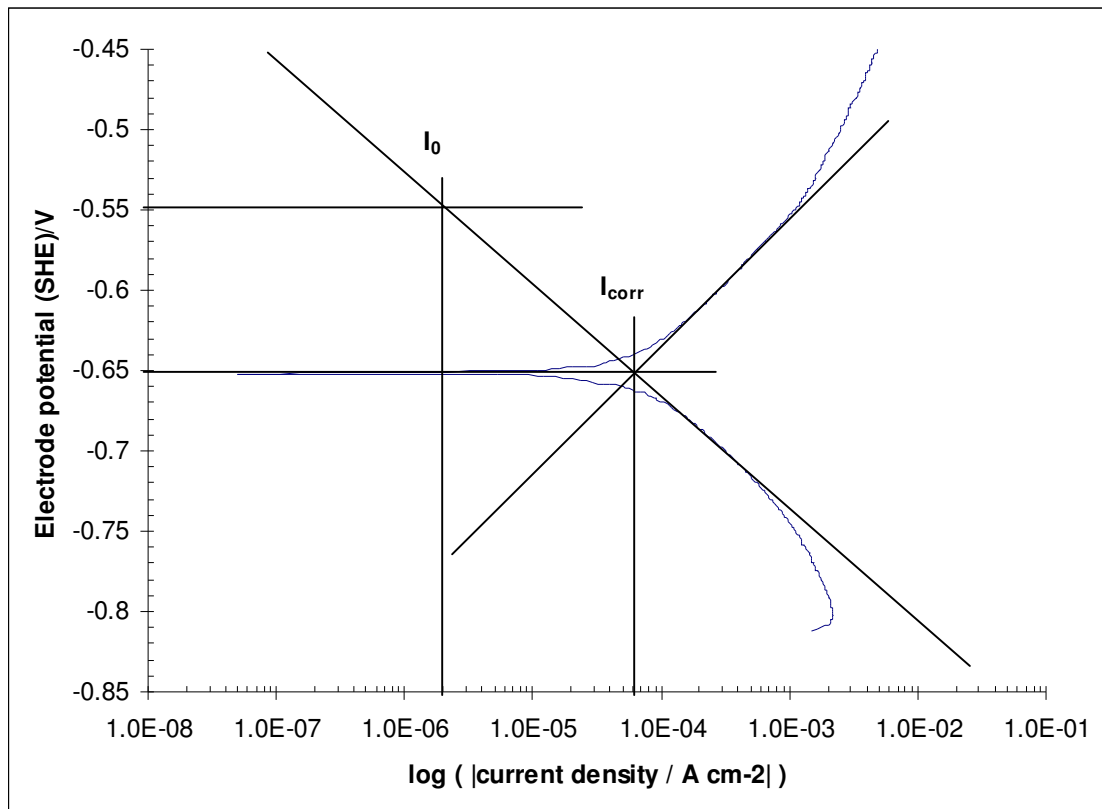


Figure A-1. Tafel slopes of iron in ammoniacal solution with total $[\text{NH}_3] = 6\text{M}$, $[\text{CO}_3] = 1.5\text{M}$ at pH 10 and 25°C in deoxygenated conditions

Appendix B- Measured I_{corr} values for different temperatures

Table B-1: I_{corr} values for overall reaction at different temperature for pH 10.

1/T, (1/K)	I_{corr}, A/cm⁻²	T (K)	ln (I_{corr})
3.470415	5.0×10^{-5}	288.15	-9.90349
3.354016	8.0×10^{-5}	298.15	-9.43348
3.245173	2.0×10^{-4}	308.15	-8.51719
3.143171	3.0×10^{-4}	318.15	-8.11173
3.047387	2.0×10^{-4}	328.15	-8.51719

FeA4* = $\text{Fe}(\text{NH}_3)_4^{2+}$

Appendix C- ΔG° values calculations

Table C-1: Thermodynamic data for NH_3 , Fe and H_2O species used in the calculation of the Pourbaix diagrams

Species	$\Delta G^\circ_{f,(298)}$ KJ/mol	$C_p(T) = A+B \times 10^{-3}T + C \times 10^{-5}T^2 + D \times 10^{-6}T^3$, J.[mol.K] ⁻¹				S°_{298} J.[mol.K] ⁻¹	$G^\circ_{(313)}$ KJ/mol
		A	B	C	D		
Fe	0	31.87	-22.33	-3.51	40.07	-22.333	25.018
Fe^{2+}	-91.564	LIHCA: b = 0.40				-105.86	-88.59 ^a
CO_3^{2-}	-528.134	69525	-287938	-12200	334778	-49.99	-520.364 ^a
CO_2	-386.148	-35770	159740	5462	-200297	117.6	-384.63 ^a
HCO_3^-	-587.117	20291	-83794	-3547	97286	98.45	-581.63 ^a
FeCO_3	-666.957	48.66	112.19	-0.001	0.009	92.885	-662.95 ^a
Fe_2O_3	-741.363	143.56	-36.32	-31.43	71.79	87.53	-747.57 ^a
$\text{Fe}(\text{OH})_2$	-491.68	95.10	28.47	-5.86	0.001	93.00	-495.25 ^a
$\text{Fe}(\text{NH}_3)_4^{2+}$	-222.13	K measured upto 328K(Isaev 1990 ^b)				305.23	-225.02 ^b
H_2O	-237.2	186.9	-464.2	-19.6	548.6	69.95	21.99
H_2	0	22.49	17.04	0.36	11.12	130.68	-1.97
O_2	0	22.49	20.88	1.62	-8.20	205.15	-3.09
H^+	0	Criss Cobble				0	-0.04
NH_3	-26.5	507.81	-1522	-107.9	1656.8	111.3	-28.14
NH_4^+	-79.406	LIHCA: b = 0.40				113.4	-81.05

^a G°_{313} value calculated from HSC software using the HSC database. ^bCalculated from Log K and ΔS data (Isaev 1990).