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POLYTECHNIC SCHOOL  
DEPARTMENT OF MECHANICAL ENGINEERING



Diploma Thesis

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Pourbaix diagrams:  
Fundamentals & Applications for  
thermodynamic prediction of corrosion in  
the presence of Sulphur

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By

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## Abstract

It is well known that corrosion exists everywhere and its effects cause either loss of life, environmental problems or costly situations. Inevitably the metals used by engineers today will corrode, unless measures are taken in advance so as to control and thereby minimize the risk of corrosion within the expected service life of components and structures.

Indeed, the prevention is preferable than “cure”, Thus, in the present study preventive measures acquired by the Pourbaix diagrams, are discussed, in order to obtain an integrated supervision for control of corrosion in metallic structures. Marcel Pourbaix has developed a unique and concise method of summarizing the corrosion thermodynamic information for a given metal exposed in aqueous solutions in a characteristic E-pH (potential–pH) diagrams. Pourbaix diagrams in the presence of Sulphur have been analyzed and constructed for 3 different steels (Fe, P5, P9) at three temperatures through the ThermoCalc software. Besides these diagrams, comparative plots are also provided for the steels under consideration, indicating the “safe” operation regions for each environment. The critical value of the  $E_{corr}$  in each case has been determined.

The results may be used as a guidance for the design of Cathodic protection systems.

## Περίληψη

Έχει παρατηρηθεί ότι η διάβρωση υπάρχει παντού και η επίδρασή της μπορεί να προκαλέσει τόσο περιβαλλοντικές καταστροφές και απώλειες της ανθρώπινης ζωής, όσο και σημαντικά κόστη σε τομείς της βιομηχανίας και όχι μόνο. Αναπόφευκτα τα μέταλλα που χρησιμοποιούνται από τους μηχανικούς σε κατασκευές θα διαβρωθούν εφόσον δεν ληφθούν αξιόπιστα μέτρα αντιμετώπισης της διάβρωσης για όλο τον προδιαγεγραμμένο χρόνο λειτουργίας τους.

Πράγματι, “το προλαμβάνειν κρείττον του θεραπεύειν”, έτσι στην παρούσα διπλωματική εργασία μελετώνται τα μέτρα που μπορούν να ληφθούν για μια ολοκληρωμένη εποπτεία του ελέγχου και περιορισμού της διαβρωτικής δραστηριότητας στις μεταλλικές κατασκευές. Ο Marcel Pourbaix έχει αναπτύξει μια περιεκτική μέθοδο συνοψίζοντας τα θερμοδυναμικά δεδομένα της διάβρωσης για συγκεκριμένο μέταλλο μέσα σε διαγράμματα Ηλεκτροχημικού Δυναμικού-pH. Τα διαγράμματα αυτά κατασκευάζονται και αναλύονται για περιβάλλον με υψηλή περιεκτικότητα σε Θείου (S) για 3 χάλυβες (Fe, P5, P9) και για τρεις διαφορετικές θερμοκρασίες, με την χρήση του λογισμικού ThermoCalc που είναι εγκατεστημένο στο Εργαστήριο Υλικών. Τα αποτελέσματα παρουσιάζονται σε συγκριτικά διαγράμματα για τους τρεις χάλυβες που μελετήθηκαν προκειμένου να εξαχθούν συμπεράσματα για τα όρια χρήσης του κάθε υλικού στα αντίστοιχα διαβρωτικά περιβάλλοντα.

Προσδιορίστηκε για κάθε περίπτωση το δυναμικό διάβρωσης ( $E_{corr}$ ) που αποτελεί κύριο δεδομένο εισόδου για το σχεδιασμό συστημάτων καθοδικής προστασίας.

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## Chapter 1 Introduction

### 1.1 Aim and structure of the diploma thesis

The aim of this work is to apply the Pourbaix diagrams for the Thermodynamic prediction of the corrosion phenomena encountered in refineries in the presence of Sulphur rich environments. The thesis is divided in 5 chapters, which are briefly presented hereinafter.

*In Chapter One* general aspects of corrosion are reviewed and the motivation for the current work is discussed.

*In Chapter Two* the literature review is presented. The review presents the thermodynamic background of corrosion and the theory behind Pourbaix diagrams and explains how these diagrams can be utilized for the control of the several Corrosion phenomena.

*In Chapter Three* the Pourbaix's anatomy is provided.

*In Chapter Four* the Pourbaix diagrams calculated by employing the Thermo-Calc software are depicted.

*In Chapter Five*, the conclusions came out from this thesis are presented alongside to the future work recommendations.

An *Appendix* is included at the end, which provides the two different modules of Thermo-Calc involved in the calculations of the study.

## 1.2 Definition of Corrosion

Almost all metals and alloys are unstable in the earth's atmosphere and will always be susceptible to corrosion i.e., conversion to a lower energy inorganic compound, such as carbonate (salts of carbonic acid), sulfide or oxide. Thus, the metals and alloys used by engineers today are all in metastable state and will corrode, at a rate dependent on the environment, unless steps are taken to minimize the risk of corrosion for the expected service life of the component. Unfortunately, while this fact is known by the majority of engineers, corrosion resistance is often relegated to a lower priority when materials are selected on the basis of those properties essential to the specific application, such as strength, stiffness and electrical conductivity. The result is that corrosion is ubiquitous, occurring in all forms of engineering materials from microelectronics to orthopedic implants to major civil infrastructures and to the everyday objects in our lives. [1]

Corrosion can be defined in several ways: destruction or deterioration of the material because of reaction with its environment, destruction of materials by means other than straight mechanical and extractive metallurgy in reverse. Another definition [2] is: Corrosion is the result of an electrochemical process involving an anodic reaction, the metal goes into solution as an ion, and a cathodic reaction takes place where the electrons released by the anodic reaction are discharged to maintain electrical neutrality by reaction with ions in solution. Corrosion resistance or chemical resistance depends on many factors, and its complete and comprehensive study requires knowledge of several fields of sciences including chemistry, metallurgy and biology when microorganisms deteriorate the surfaces of metals. Like all technologies, corrosion science has its own jargon. The material or agent attacking a metal or other substrate is generally referred to as the corrosive and the material under chemical attack is the corrodent and the process is referred to as corrosion. For example, a corrodent is said to be corroded by a corrosive. The National Association of Corrosion Engineers (NACE) is an excellent source of additional published technical information and conferences of the subject of corrosion.

The most familiar and often used categorization of corrosion is probably the eight forms presented by Fontana [9]. This classification of corrosion was based on visual characteristics on the morphology of attack. The forms are discussed below.

#### *Uniform Attack*

- This is also called general corrosion, is the most common form of corrosion. The surface effect produced by most direct chemical attacks (e.g., as by an acid) is a uniform etching of the metal. The metal becomes thinner and eventually fails



*Fig 1: Uniform Attack*

#### *Galvanic Corrosion*

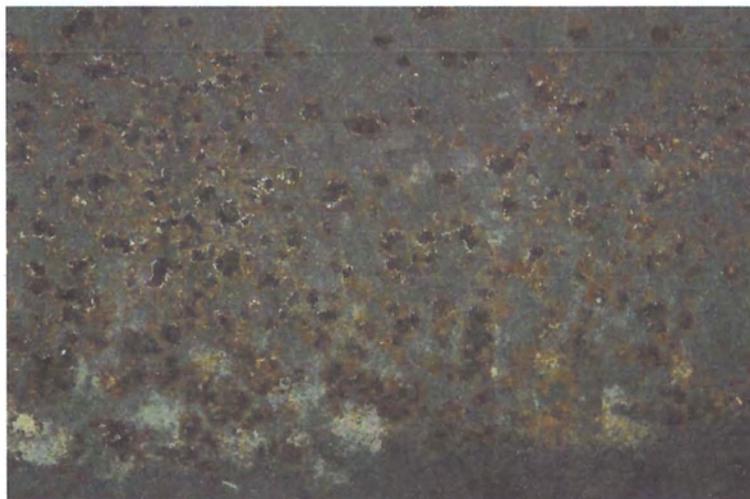
- A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact, this potential difference produces electron flow between them (in the presence of electrolyte). Corrosion of the less corrosion-resistance metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the cathodic metal corrodes very little or not at all in this type of couple. The Galvanic corrosion is also called Two-Metal Corrosion.



*Fig 2: Galvanic Corrosion*

### *Pitting Corrosion*

- Pitting corrosion is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally, a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth. Pitting is one of the most destructive and insidious forms of corrosion.



*Fig 3: Pitting Corrosion*

### *Crevice Corrosion*

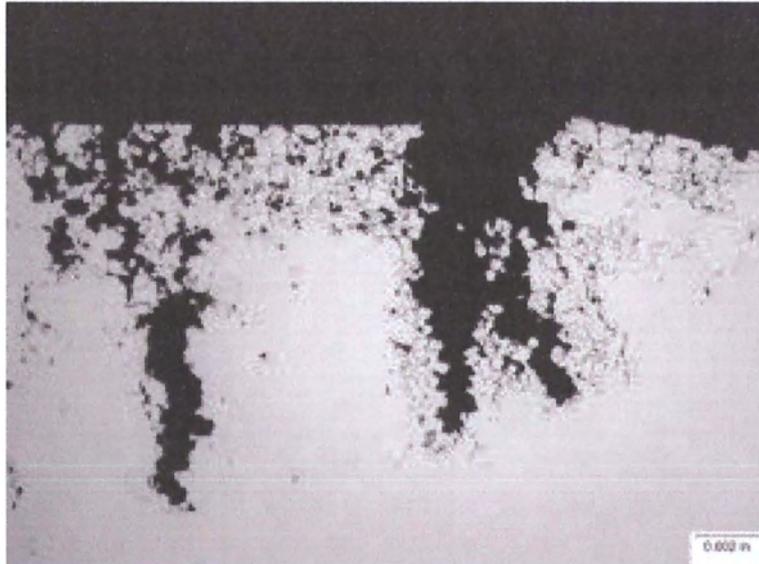
- Crevice is the corrosion produced at the region of contact of metals with metals or metals with nonmetals. It may occur at washers, under barnacles, at sand grains, under protective films, and at pockets formed by threaded joints. This type of attack is usually associated with small volumes of stagnant solution.



*Fig 4: Crevice Corrosion*

### *Intergranular Corrosion*

- Under certain conditions, grain interfaces are very reactive and intergranular corrosion results. Localized attack at grain boundaries with relatively little corrosion of the grains, is intergranular corrosion. Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain boundary areas.



*Fig 5: Intergranular Corrosion*

### *Erosion Corrosion*

- Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities.

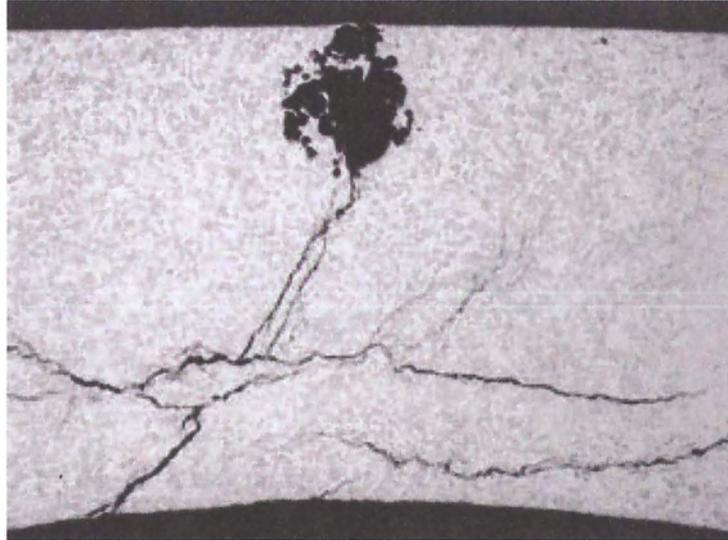


*Fig 6: Erosion Corrosion*

### *Stress Corrosion Cracking*

- Stress corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. During stress-corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it. This cracking phenomenon has

serious consequences since it can occur at stresses within the range of typical design stress.



*Fig 7: Stress Corrosion Cracking*

#### *Selective Leaching*

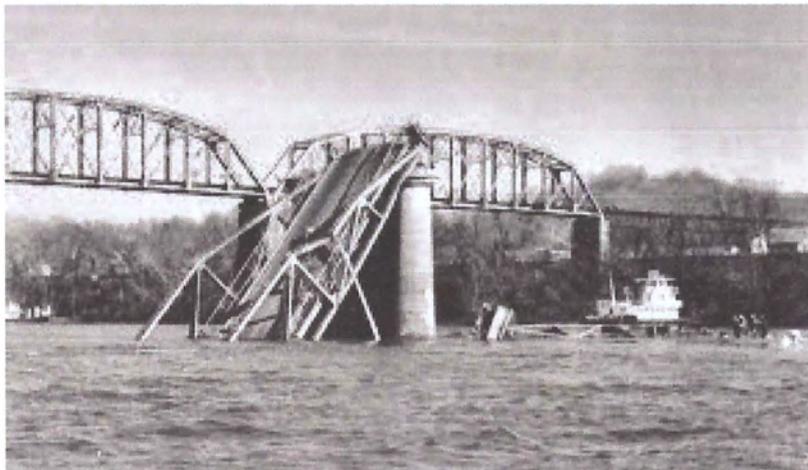
- Is the removal of one element from a solid alloy by corrosion processes. The most common example is the selective removal of zinc in brass alloys (dezincification). Similar processes occur in other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are removed. Selective leaching is the general term that describes these processes, and its use precludes the creation of terms such as dealuminumification, decobaltification,



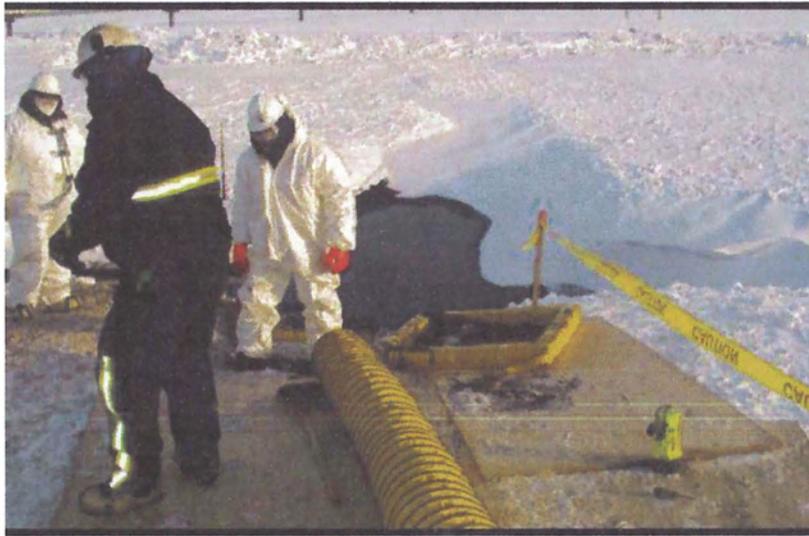
*Fig 8: Selective Leaching of zinc from brass*

### 1.3 Impact of Corrosion

The effects of corrosion in our daily lives can cause either loss of life, environmental problems or costly situations. For example, the sudden collapse because of corrosion fatigue of the Silver Bridge over the Ohio River at Point Pleasant, OH in 1967 resulted in the loss of 46 lives and cost millions of dollars (Fig 9). Another incident has been occurred in northern Alaska on 2 March, 2006 when approximately 1 million liters of crude oil leaked from a corroded transit pipeline and covered two acres of snow-covered tundra with environmental consequences (Fig 10).



*Fig 9: The collapse of Silver Bridge, Ohio 1967*



*Fig 10: Oil leak in Alaska, 2006*

Metallic corrosion is a major loss-producing phenomenon in many sectors of a nation's economy.

This is because corrosion results in loss of metals and materials, energy, labor, etc., which would have been contributively productive otherwise for some other useful purpose. Revie and Uhlig [3], [4] divide the losses due to corrosion into two categories:

- Direct loss
- Indirect loss

*Direct losses:*

- Cost of replacing corroded/failed structures/equipments/components,
- Painting and re-painting of corrosion-prone structures to prevent general atmospheric corrosion,
- Costs involved in all other protective measures, such as cathodic protection, inhibitor addition, protective coating/wrapping/cladding, galvanizing, electroplating, etc.,
- Extra cost involved in choosing corrosion-resistant alloys (CRAs) such as stainless steels, nickel base alloys, titanium, etc. in the place of carbon steels which would have been otherwise suitable from mechanical/ structural points of view, and

- Cost of dehumidifying storage rooms for storing metallic components/equipment and spare parts, etc. before they are put into use.

*Indirect losses* are like consequential losses that add heavily, many times very heavily, to the direct losses outlined above. These indirect losses include:

- Loss-of-Production (Downtime) Cost: This factor alone, many times, is orders of magnitude higher than the direct replacement cost,
- Product loss through leaks/failures due to corrosion: This also would be very heavy if the equipment is concerned is a pressure vessel and high pressure pipeline carrying huge quantities of finished products under pressure like utility gas separated from oil, purified potable water through water mains, high pressure steam, etc.,
- Loss of efficiency in heat transfer equipment and pipelines: Accumulation of corrosion product scales on pipelines and on heat transfer surfaces reduces the pumping and heat transfer efficiency, respectively, thereby necessitating increased power to the pumps and heat exchangers,
- Contamination and hence rejection of product: Heavy metal impurities as a result of corrosion of the container equipments and transfer pipelines would result in total rejection of several batches (huge quantities) of the carefully produced (value added) chemical product,
- Over-design: Giving “corrosion allowance,” thereby using vessels with thickness much greater than that demanded by mechanical requirements amounts to over-design and adds up to huge indirect cost involved in providing excess metal for corrosion to take place.

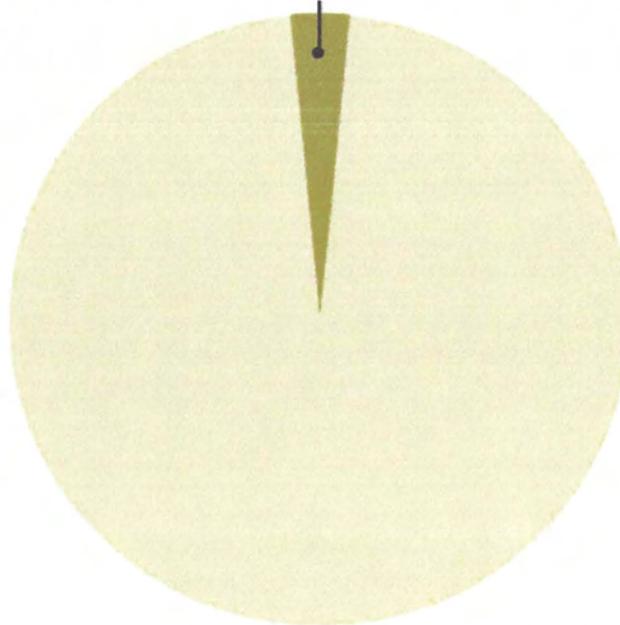
Discussing in numbers, a 2002 Federal study, initiated by NACE [6] provides economical details about corrosion costs in the United States. According to this study, the direct cost of metallic corrosion annually is \$276. This represents the 3.1% of the U.S. Gross Domestic Product (GDP) (Fig 11) in 1998. However, this report leaves out the enormous tally of the indirect costs, which is at least as much as the direct costs.

Also it is referred that Corrosion is so prevalent and takes so many forms that its occurrence and associated costs cannot be eliminated completely. However, it has been estimated that 25 to 30% of the annual corrosion costs in the U.S. could be saved if

optimum corrosion management practices were employed. Finally, in the results of the study it was mentioned that since metallic corrosion affects every U.S. industry sector, the development of Control programs remains a critical issue.

It should be also referred that the corrosion affects the Oil & Gas industry globally in a crucial economic level [7] as it is displayed in Table 1.

**Direct Corrosion Costs: \$276 billion (3.1% of U.S. GDP)**



**1998 U.S. GDP (\$8.79 trillion)**

*Fig 11: The impact of Corrosion on the U.S. economy*

*Table 1: Cost of Corrosion in Oil & Gas industry*

Region	Cost of Corrosion
Gas Pipeline Industry (North America)	\$80 million per year purchased in coatings to coat new pipelines and recoat existing pipelines
Oil and Gas (Agip/ General Italian Oil Company)	about \$0.40 per barrel of oil produced, the economic impact of corrosion
Oil and Gas (North Sea production platforms)	60% of all maintenance costs related to corrosion, directly or indirectly
Pipelines (Gas and Liquid Transmission, USA)	~ \$7 billion (in 1998)

## 1.4 Sulphur environments in Petroleum industry

The petroleum industry contains a wide variety of corrosive environments while some of these are unique to this industry. Corrosion problems occur in the petroleum industry in at least three general areas: (1) production, (2) transportations and storage, and (3) refinery operations.

In Production the sour oil wells handle oil with higher sulfur contents than sweet wells and represent a more corrosive environment. In high Hydrogen Sulphide wells there may be severe attack on the casing in the upper part of the well where the space is filled with gas. Water vapor condenses in this area picks up  $H_2S$  and  $CO_2$ .

Most of the corrosion difficulties in refineries are due to inorganics such as water,  $H_2S$ ,  $CO_2$ , sulfuric acid, and sodium chloride, and not to the organics themselves. For this reason, the petroleum industry has much in common with the chemical industry. Corrosive agents may be classified into general categories: (1) those present feedstock or crude oil, and (2) those associated with processes or control.

Furthermore, within Refinery Operations Hydrogen Sulphide, mercaptans and other Sulphide compounds are present in many of the crudes and gases processed by refineries. These are removed by reaction with sodium hydroxide, iron oxide, or sodium carbonate, but for various reasons they are frequently not removed until the final operation is approached. Corrosion problems are associated with the refining process itself or with processes utilized to remove Sulphur compounds.

It is also important to be mentioned that water is usually present in crude oils and complete removal is difficult. Water acts as an electrolyte and causes corrosion. It also tends to hydrolyze other materials, particularly chlorides, and thus forms an acidic environment. [9]

### *Hydrogen Sulphide impact:*

Hydrogen sulphide, when dissolved in water, is a weak acid and is therefore corrosive because it is a source of hydrogen ions. In the absence of buffering ions, water equilibrated with 1 atm of  $H_2S$  or  $CO_2$  (often referred to as acid gases) has a pH of about

4. However, under conditions of high-pressure hydrocarbon formations, pH values as low as 3 have been observed. In some cases, buffering species in produced water (such as bicarbonate) can result in higher pH values than expected based on just the amount of acid gases present. This can have a direct mitigating effect on corrosion rate and, in some cases, promote the formation of protective corrosion films, thus reducing the corrosion rate to very low levels.

Hydrogen sulphide can also play other roles in corrosion in oil and gas production. The sulphur on the metal surface resulting from the H<sub>2</sub>S corrosion reaction readily acts as a catalyst to promote absorption of atomic hydrogen into the corroding steel. Atomic hydrogen—also referred to as nascent hydrogen (H<sup>0</sup>)—is formed by the cathodic reduction of hydrogen ions. This accounts for its role in promoting SSC (*Sulphide Stress Cracking*), HIC (*Hydrogen Included Cracking*), and SOHIC (*Stress-oriented Hydrogen Included Cracking*) in steels. Stress-corrosion cracking is usually found in steel with a yield strength greater than approximately 550 MPa (80 ksi), whereas HIC and SOHIC are found in low-strength steels less than 550 MPa (80 ksi).

Hydrogen sulphide also reacts with elemental sulphur. In a gas phase with a high H<sub>2</sub>S partial pressure, sulphanes (free-acid forms of a polysulfide) are formed so that elemental sulphur is rendered mobile and is produced along with the remaining gaseous constituents. However, as the pressure decreases traveling up the production tubing, the sulphanes dissociate and elemental sulphur precipitates. Production environments with H<sub>2</sub>S and sulphur have been found to be more severe from the corrosion and EAC standpoint than environments with H<sub>2</sub>S alone. Various solvent treatments are used to avoid plugging by such sulphur, but their effect on corrosion and EAC need also to be considered during evaluation.

In the aqueous phase, under acidic conditions, sulphanes are also largely dissociated into H<sub>2</sub>S and elemental sulphur. However, enough strongly oxidizing species can remain either as polysulfide ions or as traces of sulphanes to play a significant role in corrosion reactions. Oxygen contamination of sour (H<sub>2</sub>S-containing) systems can also result in the formation of polysulfide and/or the precipitation of elemental sulphur generally leading to an increase in corrosivity.

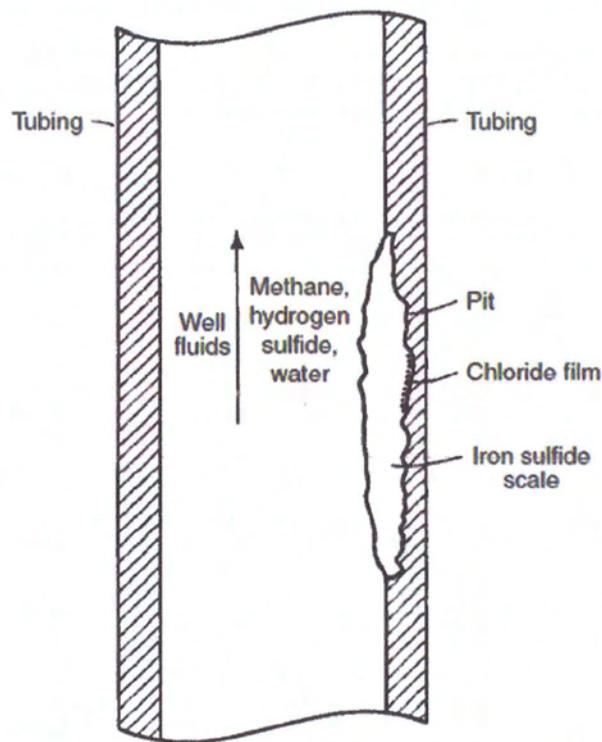
Iron sulphide corrosion products can be important in corrosion control. Because of the low solubility, rapid precipitation, and mechanical properties of such corrosion

products, velocity effects are not as commonly encountered in sour (H<sub>2</sub>S-containing) systems as in sweet (CO<sub>2</sub>-containing) systems. However, this effect can also be influenced by the morphology and actual crystalline form of iron sulphide, which can depend on temperature and H<sub>2</sub>S concentration, among other factors.

The great range of possible iron sulphide corrosion products and their possible effects on corrosion have been extensively studied. This continues to be an area of interest in corrosion control and prediction. At lower temperatures and very low H<sub>2</sub>S partial pressures, a somewhat protective sulphide film often forms. The absence of chloride salts strongly promotes this condition, and the absence of oxygen is absolutely essential. Under these conditions, the formation of a sulphide film often results in a remarkable decrease in corrosion rate when compared to similar conditions (CO<sub>2</sub> only) without H<sub>2</sub>S.

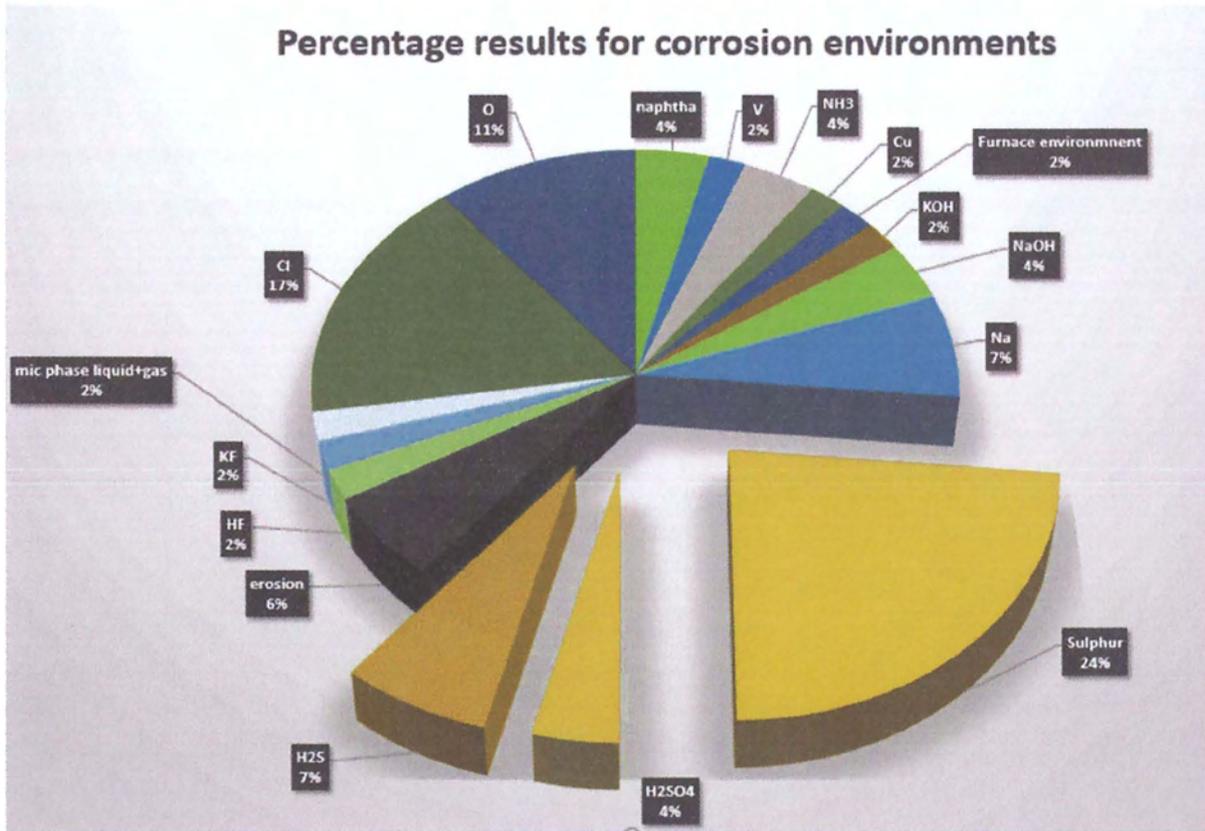
At the high temperatures (150 to 230 °C, or 300 to 450 °F) and H<sub>2</sub>S partial pressures (hundreds to thousands of pounds per square inch) encountered in deep sour gas wells, a so-called barnacle type of localized corrosion can occur, resulting in corrosion rates of several hundred mils per year. This type of attack is strongly promoted by sulfidic species and requires the presence of some minimum chloride concentration. Although initially recognized in deep sour well environments, this same mechanism may operate at lower temperature in pipelines where high levels of H<sub>2</sub>S and high chloride concentrations are observed.

In the barnacle mechanism ([Fig. 12](#)), corrosion can be sustained beneath thick but porous iron sulphide deposits (primarily pyrrhotite, FeS) because the FeS surface is an effective cathode. The anodic reaction beneath the FeS deposit is dependent on the presence of a thin layer of concentrated iron chloride (FeCl<sub>2</sub>) at the Fe/FeS interface. This intervening FeCl<sub>2</sub> layer is acidic due to ferrous ion hydrolysis, thus preventing precipitation of FeS directly on the corroding steel surface and enabling the anodic reaction to be sustained by the cathodic reaction on the external FeS surface. [\[10\]](#)



*Fig 12: Barnacle mechanism of sour pitting corrosion. [10, page 924]*

In a previous study conducted at the Laboratory of Materials in Mechanical Engineering Department of University of Thessaly [11], it was shown that the most frequent corrosion failure in oil refineries is the high temperature corrosion, including sulphidation and oxidation. The equipment most affected includes furnace equipment and heat exchangers. The type of materials that suffered more is the low-alloy steels as well as the carbon steels. Furthermore, it seems that the most corrosive environment among those under consideration in the case studies is that containing sulphur (Fig 13).



*Fig 13: Pie chart demonstrating several types of corrosion environments that lead to failure. [11]*

As shown clearly in [Fig. 13](#) the 35% of the failures are correlated to the sulphur containing environments, and this finding was motivated the current work.

## 1.5 Thermodynamic Prediction of Corrosion and Pourbaix diagrams

In order to obtain an integrated supervision for control and inhibition of corrosion rate in metallic structures, scientists are developing new methods to predict the results of every specific system, because the prevention is better than “cure”.

Marcel Pourbaix has developed a unique and concise method of summarizing the corrosion thermodynamic information for a given metal in a useful potential–pH diagram. These diagrams indicate certain regions of potential and pH where the metal undergoes corrosion and other regions of potential and pH where the metal is protected from corrosion. Such diagrams are usually called “Pourbaix diagrams” but are sometimes called “equilibrium diagrams” because these diagrams apply to conditions where the metal is in equilibrium with its environment. A deep knowledge upon these diagrams would be necessarily in corrosion control. Further detailed explanation and interpretation of Pourbaix diagrams will be conducted in the following chapters.

## Chapter 2 Literature Review

### 2.1 Thermodynamics of Corrosion

The thermodynamic aspects of corrosion, whether for aqueous corrosion or gaseous corrosion, are discussed first [12]. Thermodynamics set the framework of what is possible and what is not. It predicts the direction in which the changes of the system can occur. While does not provide any information on the rate of the reaction.

The corrosion of metals and alloys involves oxidation from their metallic state and therefore must obey the thermodynamic criteria. Apart from gold and platinum, the rest of the metals are found in nature as ores (oxide, sulphides, etc.). So, considerable amount of energy is consumed to convert the ores to metals and as a result, they remain at higher energy levels than their corresponding ores. Therefore, most of these metals tend to go back to their low energy state (oxides, chlorides, sulphates, etc.) on exposure to environments. Iron in a representative example is illustrated in [Fig.14](#). It is interesting

to note that corrosion, as a process, releases energy and so is spontaneous in nature. This indeed is a serious problem for almost all the engineering metals and alloys. [4]. The Gibbs free energy is given by the following equation:

$$\Delta G = -ve \text{ (negative)} \quad (2.1)$$

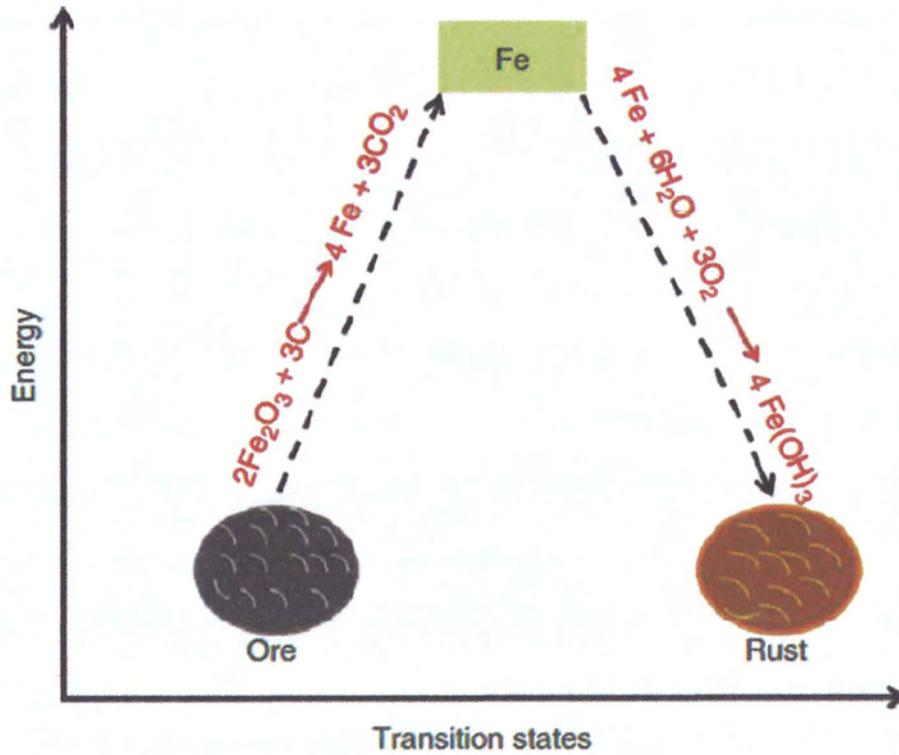


Fig 14: The physical meaning of corrosion

Regarding to the process of corrosion, on a corroding metal surface, anodic and cathodic reactions occur in a coupled manner at different places on the metal surface [Fig. 15].

For the example of iron, the reactions are as follows:



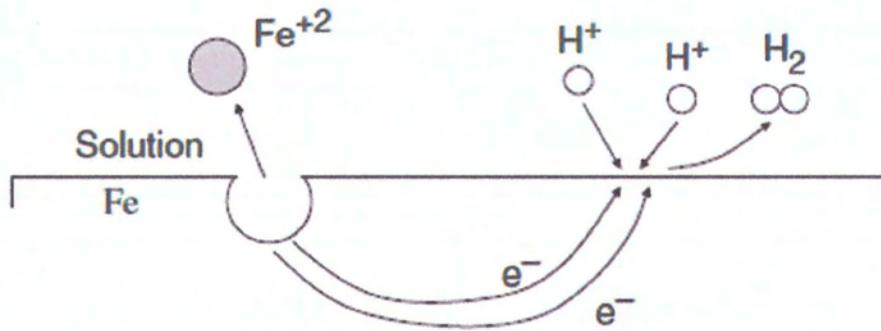


Fig 15: Coupled electrochemical reactions

An electron potential exists across the metal/solution interface as illustrated in Fig.16.

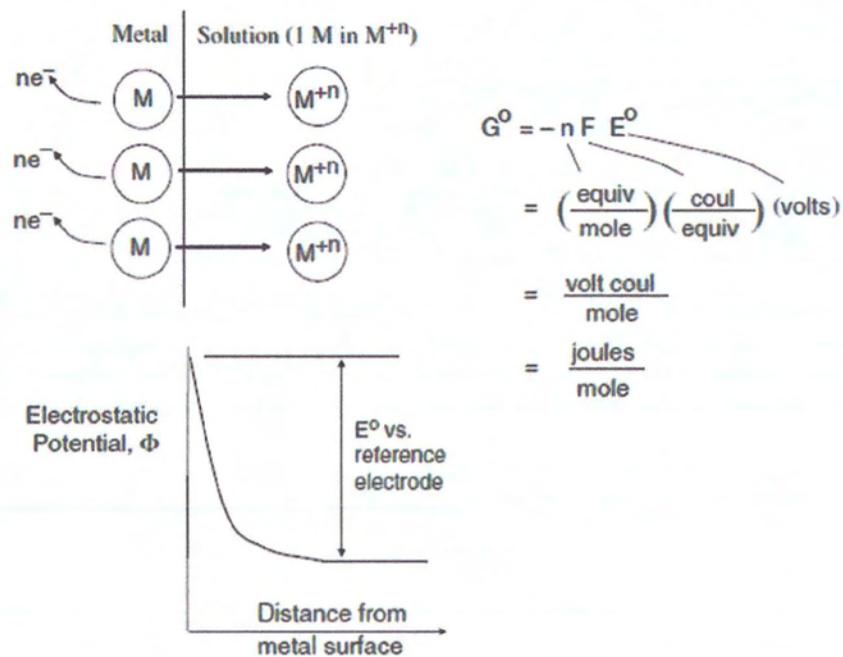


Fig 16: The free energy change for an electrochemical process

The free energy change for an electrochemical process when all the reactants and products are in their standard states is given by:

$$\Delta G = -nFE^0 \quad (2.2)$$

where  $n$  is the number of electrons transferred,  $F$  is the Faraday, and  $E^\circ$  is the electrode potential. The negative sign above is required to make spontaneous electrochemical reactions

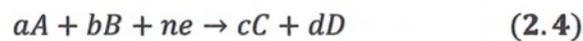
Its change is correlated to the change in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) associated with any corrosion reaction.

$$\Delta G = \Delta H - T\Delta S \quad (2.3)$$

### *The Nernst Equation*

The Nernst equation [18] allows calculation of the half-cell potential for some other concentration in terms of the standard electrode potential.

Consider a general electrochemical reaction:



Where  $a$  and  $b$  are the numbers of moles of the reactants  $A$  and  $B$  respectively.

Furthermore,

$$\Delta G = \sum_i \nu_i \mu_i (\text{products}) - \sum_i \nu_i \mu_i (\text{reactants}) \quad (2.5)$$

Or

$$\Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B \quad (2.6)$$

But for the solids and liquids the following equation is applied:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (2.7)$$

Thus,

$$\mu_C = \mu_C^\circ + RT \ln a_C$$

$$\mu_D = \mu_D^\circ + RT \ln a_D$$

$$\mu_A = \mu_A^\circ + RT \ln a_A$$

$$\mu_B = \mu_B^\circ + RT \ln a_B$$

Substitution of the equations above in **Eq. 2.6** gives

$$\Delta G = c[\mu_C^o + RT\ln a_C] + d[\mu_D^o + RT\ln a_D] - a[\mu_A^o + RT\ln a_A] - b[\mu_B^o + RT\ln a_B]$$

Grouping terms gives

$$\Delta G = [c\mu_C^o + d\mu_D^o - a\mu_A^o - b\mu_B^o] + \left[ RT\ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \right] \quad (2.8)$$

But from this equation:

$$\Delta G^o = c\mu_C^o + d\mu_D^o - a\mu_A^o - b\mu_B^o \quad (2.9)$$

The **Eq. 2.8** becomes

$$\Delta G = \Delta G^o + \left[ RT\ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \right] \quad (2.10)$$

With  $\Delta G = -nFE$  and  $\Delta G^o = -nFe^o$ , **Eq. 2.10** becomes

$$E = E^o - \frac{2.303RT}{nF} \log \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (2.11)$$

Which is the Nernst equation. This equation is very useful in the analysis of electrochemical cells and in the construction of Pourbaix diagrams.

At 25°C, the **Eq 2.11** can be written as

$$E = E^o - \frac{0.0591RT}{n} \log \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (2.12)$$

Moreover,

The equilibrium constant for **Eq. 2.4** is

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (2.13)$$

So that **Eq. 2.10** can be written as

$$\Delta G = \Delta G^o + RT\ln K \quad (2.14)$$

At equilibrium,  $\Delta G=0$  so that **Eq 2.14** becomes

$$\Delta G^o = -RT\ln K \quad (2.15)$$

or

$$\Delta G^{\circ} = -2.303RT \log K \quad (2.16)$$

This equation is useful because it is the link between the standard free energy change and the equilibrium constant for a reaction.

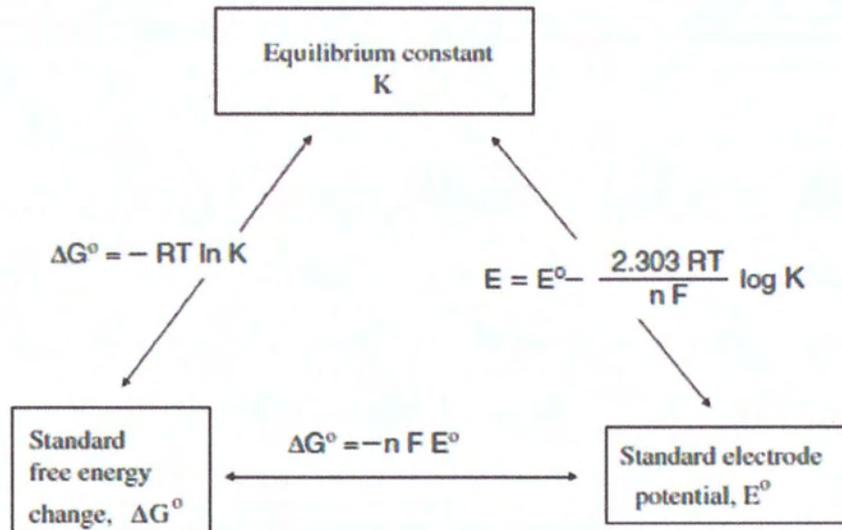


Fig 17: Summary of the relationship between  $\Delta G^{\circ}$ ,  $E^{\circ}$  and  $K$

## 2.2 Aqueous corrosion and Potential measurements

The corrosion of metallic materials at ambient or relatively low temperature is mainly due to the water in contact with them. The aqueous phase can be neutral, acid or basic. Aqueous corrosion is an electrochemical process with origins in the characteristics of electrical conduction of the two phases: electronic conduction in the metal phase and ionic conduction in the aqueous phase, also called the electrolyte. The electrochemical reactions enable the charge transfers on the interface between metal (electrode) and the electrolyte [8].

The reaction of the metal oxidation (anodic reaction) can be written as shown below:

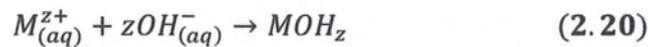


In the metal - electrolyte interface, the metal is oxidized to form positively charged ions that go into solution in the liquid or they can form solid compounds such as oxides, which remain on the metal. This reaction of oxidation releases electrons which must be consumed to ensure electrical neutrality. This is why one or more reactions of reduction of oxidizing chemical species (cathodic reactions) present in the aqueous phase necessarily happens simultaneously at the interface. If the solution is oxygenated, the dissolved O<sub>2</sub> gas is reduced to hydroxide ions, this reaction is favored in neutral or alkaline conditions, on the other hand, in acidic solutions, protons are reduced to form hydrogen gas.

The anodic reactions can be written as shown below:



The products of the reactions are ions which can remain in solution or react to give a precipitate (corrosion product) according to the reaction:



The corrosion in an aqueous environment up to the supercritical temperatures is influenced by the solution characteristics and material-related factors such as:

- Ph
- Temperature
- Density
- Electrochemical potential of the solution
- Activity of the anions
- Surface quality of the material
- Chemical Composition
- Heat treatment (If applied)
- Purity Level

*Use of Nernst Equation in aqueous solution:*

The best way to examine the application of Nernst equation to an electrochemical reaction is to apply this to the oxidation of iron. One can start with an (electrochemical) equilibrium process involving Fe and Fe<sup>2+</sup> (consider a piece of metallic iron immersed in an aqueous solution having Fe<sup>2+</sup> ions) and then examine what prompts the equilibrium to drift towards oxidation. This equilibrium can be represented:



The corresponding Nernst equation is:

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{Fe}}{a_{Fe^{2+}}} \quad (2.22)$$

Looking at **Eq. 2.21**, it can be said that the standard potential equals equilibrium potential, should the activity of Fe (product in any equilibrium) and Fe<sup>2+</sup> (reactants in any equilibrium) becomes unity. Such an equilibrium potential is called standard potential. Values of standard potential are displayed in Table 2. Such a series is called electro motive force (EMF) series. The following characteristics of the EMF series are important to understand the corrosion tendency of any metal.

- Hydrogen equilibrium bears zero value. This value, in fact, is not measured but assigned to this equilibrium.
- The other potentials are measured with respect to standard hydrogen electrode (SHE).
- Those equilibria having higher standard potential than that of H<sup>+</sup>/H will be noble while the others having lower standard potential will be active and corrode in acid solutions.

The points which need to be emphasized here are that the equilibrium potential (*E*) depends not only on the standard potential (*E*<sub>o</sub>) (which is unique to any electrochemical equilibrium), but also on the concentrations of the reactants and products. Therefore, the tendency of a metal to corrode can be altered irrespective of its inherent tendency to corrode.

Table 2: Standard Potential of Various Electrochemical Equilibria at 25 °C, Volts vs SHE

$\text{Au}^{3+} + 3e^- = \text{Au}$	+1.498
$\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}$	+1.229
$\text{Pt}^{2+} + 2e^- = \text{Pt}$	+1.20
$\text{Pd}^{2+} + 2e^- = \text{Pd}$	+0.987
$\text{Ag}^+ + e^- = \text{Ag}$	+0.800
$\text{Hg}^{2+} + 2e^- = \text{Hg}$	+0.854
$\text{Hg}_2^{2+} + 2e^- = 2\text{Hg}$	+0.789
$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	+0.771
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-$	+0.401
$\text{Cu}^{2+} + 2e^- = \text{Cu}$	+0.337
$2\text{H}^+ + 2e^- = \text{H}_2$	0.000 (Reference)
$\text{Pb}^{2+} + 2e^- = \text{Pb}$	-0.126
$\text{Sn}^{2+} + 2e^- = \text{Sn}$	-0.136
$\text{Ni}^{2+} + 2e^- = \text{Ni}$	-0.250
$\text{Co}^{2+} + 2e^- = \text{Ni}$	-0.277
$\text{Tl}^+ + e^- = \text{Tl}$	-0.336
$\text{In}^{3+} + 3e^- = \text{In}$	-0.342
$\text{Cd}^{2+} + 2e^- = \text{Cd}$	-0.403
$\text{Fe}^{2+} + 2e^- = \text{Fe}$	-0.440
$\text{Cr}^{3+} + 3e^- = \text{Cr}$	-0.744
$\text{Zn}^{2+} + 2e^- = \text{Zn}$	-0.763
$\text{Al}^{3+} + 3e^- = \text{Al}$	-1.662
$\text{Mg}^{2+} + 2e^- = \text{Mg}$	-2.363
$\text{Na}^+ + e^- = \text{Na}$	-2.714
$\text{K}^+ + e^- = \text{K}$	-2.925

The potential of an electrode can be determined only by measuring the voltage in an electrochemical cell between this electrode and an electrode of constant potential, called the reference electrode. [12] Many errors and problems can be avoided by careful selection of the best reference electrode for a specific case and by knowledge of the electrochemical principles that control the potential measurements in order to obtain meaningful measurements. A reference electrode, once selected, must be properly used, taking into account the stability of its potential and the problem of ohmic (*IR*) drop. Many different reference electrodes are available, and others can be designed by the users themselves for particular situations. Each electrode has its characteristic rest potential value, which is used to convert potential values measured with respect to this

reference into values expressed with respect to other references. In particular, the conversion of the potentials from or to the hydrogen scale is frequently required (see Table 2) for use of potential- pH diagrams (Pourbaix diagrams).

The Ph is a measure of the acidity (or alkalinity) of a solution and is defined as:

$$pH = -\log[H^+] = \log \frac{1}{[H^+]} \quad (2.23)$$

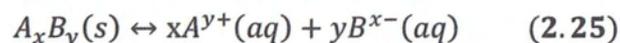
where  $[H^+]$  is the concentration of hydrogen ions in solution.

Neutral solutions have a pH value of 7.0, while acid solutions have pH values less than 7.0 and alkaline (basic) solutions have pH values greater than 7.0. Most solutions have pH values between 0 and 14, but lower and higher values are possible. For instance, the pH of 12 M HCl is -1.1.

$K_w$ : The ionization constant for water, which is the concentration of hydrogen ions and of hydroxyl ions ( $OH^-$ ) in aqueous solutions and are related by the following equation:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (2.24)$$

When an ionic solid (acid, base or salt) dissociates into ions in solution:



The solubility product  $K_{sp}$  is defined by

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y \quad (2.26)$$

where  $[A^{y+}]$  and  $[B^{x-}]$  are the concentrations of the dissolved ions.

If the ion product  $[A^{y+}]^x [B^{x-}]^y$  exceeds the tabulated value of  $K_{sp}$ , then precipitation of solid  $A_xB_y$  occurs. Otherwise, precipitation does not occur.

## 2.3 Cathodic Protection

It is well known that corrosion is electrochemical in nature [15]. Thus, an understanding of the mechanism of corrosion is relevant to the understanding of corrosion control measures. In most cases, the process of corrosion is unavoidable, however, in practice its control is possible and practicable. Corrosion control measures include the use of cathodic protection, coatings, inhibitors or pre-treatments, severally and jointly. The conjoint use of coatings and cathodic protection is an eminently powerful tool in corrosion protection, for while coatings will offer a first line of protection, the cathodic protection current will protect the substratum at imperfections in the coatings. Thus the cathodic current required for protection will be quite low.

*Cathodic protection (CP)* can be defined as a technique of reducing or eliminating the corrosion of a metal by making it the cathode of an electrochemical cell and passing sufficient current through it to reduce its corrosion rate. All CP systems require:

- Voltage
- Current
- Anode
- Cathode
- Return circuit
- Electrolyte

The application of cathodic protection requires the delivery of electrons to the structure to be protected. This may be achieved by two separate means:

- using impressed-current techniques
- using sacrificial anodes (a spontaneous galvanic effect)

The two techniques are discussed briefly below.

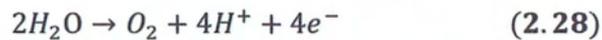
### *Impressed-current techniques*

The electrical current is delivered to the structure in this technique from a dc power source through an auxiliary anode (i.e., the current is forced in). The structure will act as a cathode in the cell thus formed, and will sustain the hydrogen evolution

reaction in the presence of an anaerobic aqueous environment. If the solution is aerated, the reduction of oxygen becomes possible and may occur in place of or together with the hydrogen evolution reaction depending on the potential to which the structure is depressed. The auxiliary electrode will necessarily become an anode in the cell. If this electrode is a base metal, then the anodic reaction will be



and the electrode will be steadily consumed. By contrast, if the electrode is a noble metal or an electrochemically inert but electrically conducting material, oxidation of the environment will occur in preference. In water, the reaction will be



or in brine possibly,



In either **Eq. 2.28** or **2.29**, the electrode will not normally be consumed. Consumable electrodes are cheap (e.g., scrap iron may be used), but they must be replaced at intervals. They contaminate the environment with dissolution products, and they cannot sustain high-current densities and must therefore be rather bulky. These disadvantages may be avoided by the use of non-consumable electrodes (silicon–iron, lead–antimony–silver, platinum–titanium, or platinum–tantalum), but with an unavoidable increase in first cost.

The magnitude of the driving voltage required from the dc source depends on a number of factors, including

1. The electrolytic conductivity of the environment
2. The area of structure to be protected
3. The nature of the electrode reaction at the auxiliary electrode
4. The resistance of the auxiliary electrode

In most cases, the electrolytic conductivity is the controlling factor, and the electrode reaction is of least importance. Clearly, if the environment does not have reasonable electrolytic conductivity, large IR (or voltage) drops will occur within it, creating the need for a higher driving voltage.

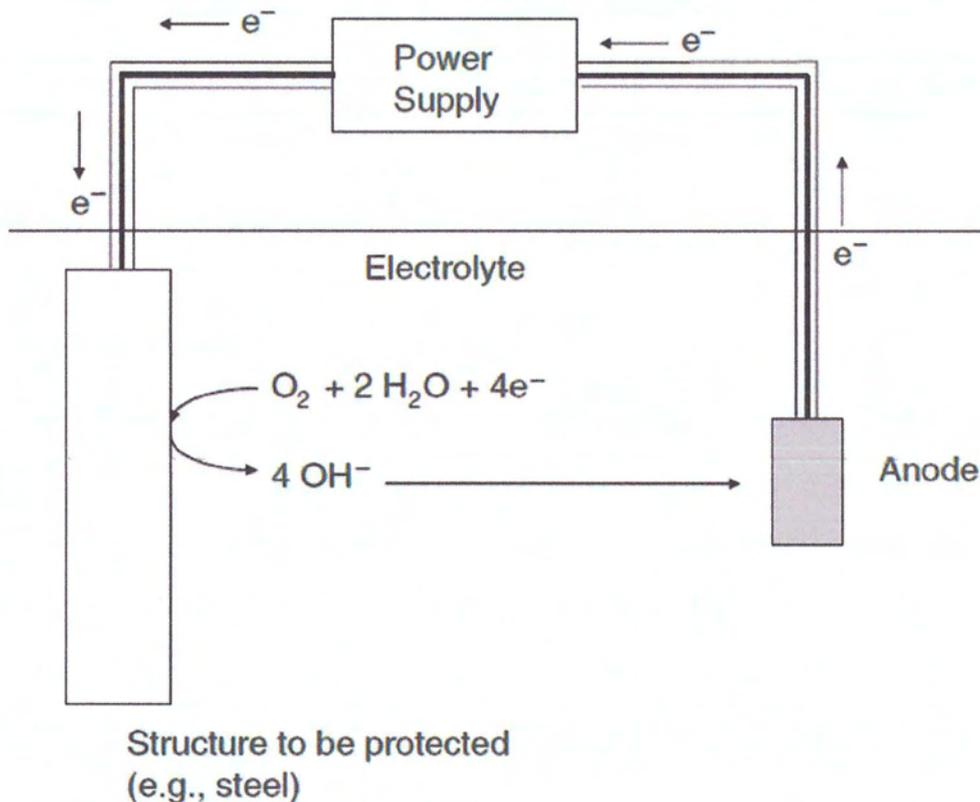
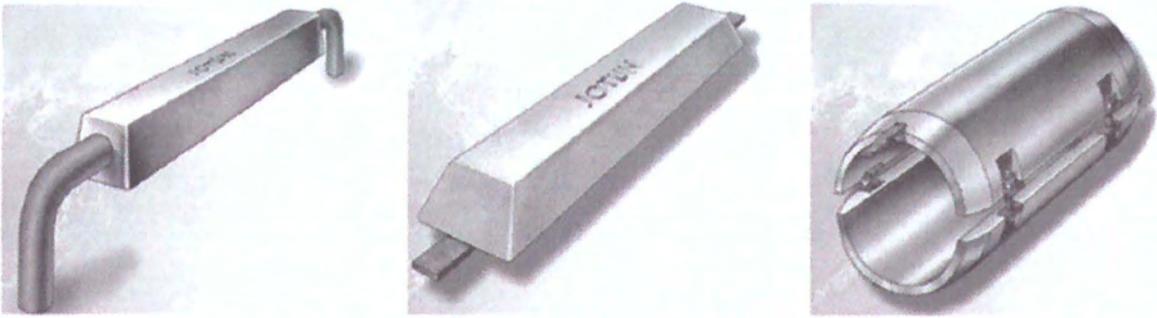


Fig 18: Schematic diagram of cathodic protection by an impressed current device

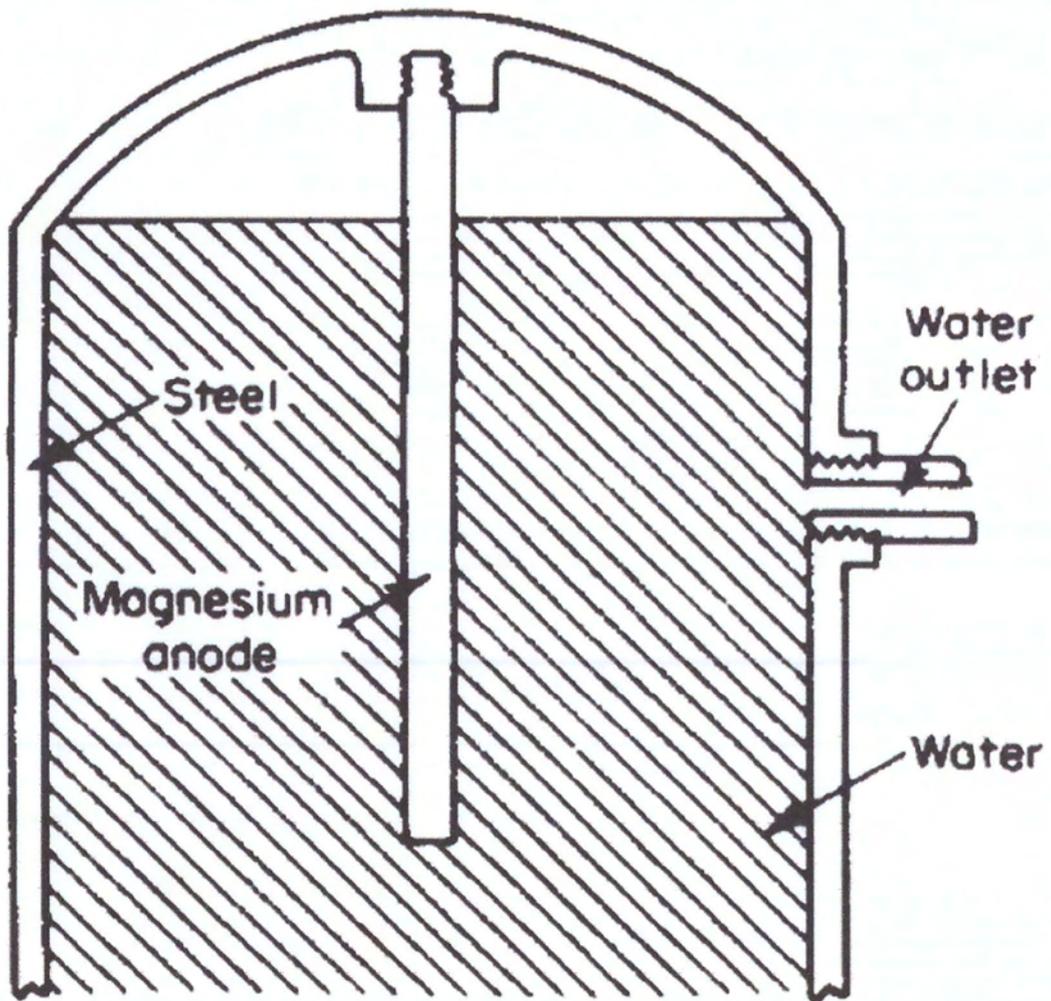
### *Sacrificial anode*

In contrast to the impressed-current technique, the use of sacrificial anodes does not depend on the creation of a driven electrochemical cell. A galvanic cell is formed between the structure and the sacrificial anode in which electrons pass spontaneously from the latter to the former. Thus, the source of the electrons (the sacrificial anode) must have a more negative electrode potential than the structure. It was for this reason that Humphrey Davy chose *zinc* or *iron* to protect copper, and explains why magnesium, aluminum, and zinc alloys are used to protect steel today.

With the sacrificial anode attached to the structure, the structure becomes the cathode and again sustains the hydrogen evolution and/or the oxygen reduction reaction. Meanwhile, the anode dissolves and may be said to be sacrificed in favour of protecting the structure. Hydrogen evolution will usually occur only when magnesium alloy anodes are used.



*Fig 19: Types of sacrificial anodes*



*Fig 20: Cathodic Protection of a domestic hot-water tank using a sacrificial anode*

### *Marine Cathodic Protection*

Both of the techniques that have been described above are common in marine applications. In recent years, hybrid systems combinations of impressed current and sacrificial anodes have been used for very large marine structures. Some marine commercial sacrificial anodes are magnesium, aluminum, or zinc or their alloys. Magnesium anodes have not been popular for offshore applications since the 1980s because of improvements in aluminum and zinc anodes. Several operators have experimented with composite sacrificial anode systems for offshore platforms. These designs use aluminum or zinc anodes for long-term performance and have magnesium anodes that are intended to provide an initially high current density and polarize the platform quickly to the desired protection potential. Results from the limited applications of this composite design are mixed, and this concept remains controversial.



*Fig 21: Cathodic Protection for Oil Rigs*

Aluminum anodes (aluminum-zinc alloys) are the preferred sacrificial anodes for offshore platform cathodic protection. This is because aluminum anodes have reliable long-term performance when compared to magnesium, which may be consumed before the platform has served its useful life. Aluminum also has better current/weight characteristics than zinc. Weight can be a major consideration for large offshore platforms.

The major disadvantage of aluminum for some applications (for example, the protection of painted ship hulls) is that aluminum is too corrosion resistant in many environments. Aluminum alloys will not corrode reliably onshore or in freshwaters. In marine environments, the chloride content of seawater depassivates some aluminum alloys and allows them to perform reliably as anode materials. Unfortunately, it is necessary to add mercury, antimony, indium, tin, or similar metals to the aluminum alloy to ensure that this depassivation occurs. Heavy-metal pollution concerns have led to bans on the use of mercury alloys in most locations. Aluminum-zinc-indium anodes have become the most popular choice for pipeline bracelets in seawater or seamud. The greater current capacity allows for much lighter weight anodes to be handled and installed. Additionally, although the alloy operates at a lower efficiency, it should be the only alloy used at temperatures above 60°C.

Zinc anodes are used on ship hulls because, unlike aluminum, zinc will continue to perform when ships enter the brackish water or freshwater of harbours. Tankers with combination ballast/product tanks use zinc anodes because of their lower tendency to cause sparks if they fall from their supports and strike steel. Zinc bracelet anodes are also used on pipelines. Again, they would be the preferred choice in brackish or freshwater and bottom mud. Because large-diameter marine pipelines must be buoyancy compensated, the increased weight of zinc can be an advantage. Zinc passivates above 60°C.

The Cathodic Protection designation in combination with the Pourbaix diagram's outcomes can give to the scientists and engineers an integrated control against corrosion development.



*Fig 22: Anodes on a ship hull*



*Fig 23: Zinc bracelets on a pipeline*

## Chapter 3 Pourbaix's Anatomy

### 3.1 Introduction

Under certain conditions, when a metal or alloy is exposed to an aqueous solution with a concentration of inorganic/organic mixture, corrosion phenomena occur at a corresponding degree. During corrosion, some metallic phases dissolve, the metal or alloy surface gets damaged and some secondary solid phases form at the solid-liquid interfaces (such as oxides, hydroxides, silicates, sulphides, sulphates, carbonates, nitrates, phosphates, borates, or halides). Such corrosive chemical or electrochemical reactions can be studied by means of the so-called Pourbaix diagrams if the reactions reach their equilibrium states.

Marcel Pourbaix in 1938 applied thermodynamics to predict materials corrosion resistance. He determined the phase stability relations in terms of varied pH and Eh values for an interaction system of metal and pure water or dilute aqueous solution. He presented the stability regions of metal and secondary phases (such as metal-oxides/hydroxides) on a pH-Eh diagram, which is now known as a Pourbaix diagram. A Pourbaix diagram is a kind of phase diagram that shows the stability boundaries for a metal-aqueous interaction system. The phase boundaries are shown as a function of pH (acidity) and Eh (standard hydrogen electronic potential). An aqueous solution phase is always present in such a system. At a given pH and Eh, a metal may lose its stability to a soluble or corrosive aqueous solution, or be in equilibrium with either the aqueous solution (insoluble/immune) or with a secondary-phase file that has formed (consisting of oxides, hydroxides, sulphides or other solids). In the latter case, further dissolution of the passive or protective metal is prevented. The speciation and partition in the aqueous solution and the interacting phases depend not only on pH and Eh, but also on other factors such as the bulk composition, temperature and pressure in the system. The interacting phases may be gas mixtures, stoichiometric solids or solid solutions.

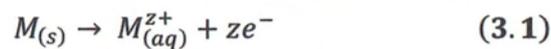
A Pourbaix diagram is divided in regions of "immunity", "corrosion" and "passivity". These regions provide information about the stability of a particular metal

or alloy in a specific aqueous electrochemical environment under certain pH, Eh, pressure and temperature conditions [13].

- The *immunity* region is the region in which there is no metal dissolution.
- The *corrosion* region is the region in which there is active metal dissolution.
- The *passivation* region is the region in which a protective metal-oxide film that prevents metal dissolution is formed.

A Pourbaix diagram plots the equilibrium potential ( $Eh$ ) between a metal and its various oxidised species as a function of pH.

The extent of half-cell reactions (anodic reaction) that describe the dissolution of metal



depend on various factors, including the potential,  $E$ , pH and the concentration of the oxidised species,  $M^{z+}$ . [16] The Pourbaix diagram can be thought of as analogous to a phase diagram of an alloy, which plots the lines of equilibrium between different phases as temperature and composition are varied.

### 3.2 Construction of a Pourbaix diagram

To plot a Pourbaix diagram the relevant Nernst equations are used (Eq 2.11). As the Nernst equation is derived entirely from thermodynamics, the Pourbaix diagram can be used to determine which species is *thermodynamically* stable at a given  $E$  and pH. But no information about the *kinetics* of the corrosion.

An example of a Pourbaix diagram [18] is given below which shows the Eh-pH diagram for aluminum. The abscissa in the diagram is the pH of the aqueous solution, which is a measure of the chemical environment. In a Pourbaix diagram, there are three possible types of straight lines:

1. Horizontal lines, which are for Reaction involving only the electrode potential
2. Vertical lines, which are for reactions involving only the pH
3. Slanted lines, which are reactions involving both the electrode potential  $E$  and the pH.

Pourbaix diagrams also contain regions between the various lines where specific chemical compounds or species are thermodynamically stable.

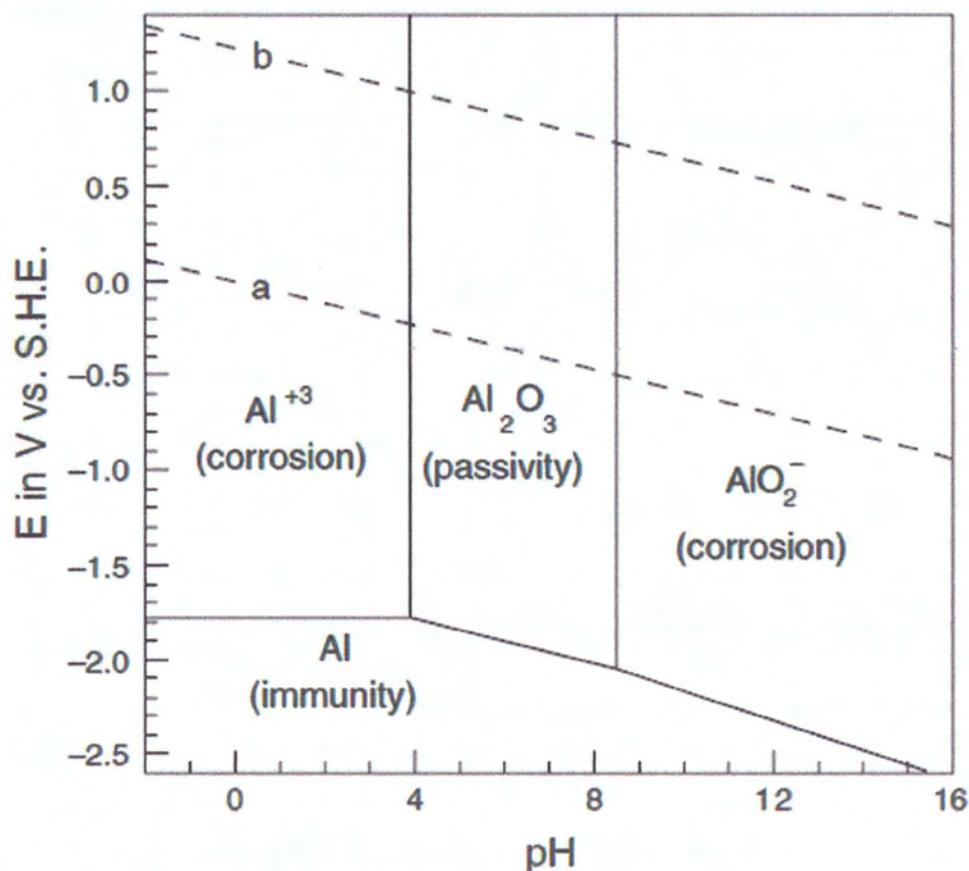


Fig 22: Pourbaix diagram for aluminum at 25°C

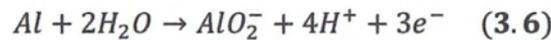
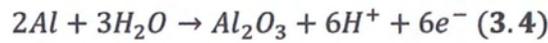
The diagram for the aluminum above identifies the various regions where the species Al (solid), Al<sub>2</sub>O<sub>3</sub> (solid), Al<sup>3+</sup> ions, and AlO<sub>2</sub><sup>-</sup> ions are each stable. When the stable species is a dissolved ion, the region on the Pourbaix diagram is labelled as a region of *Corrosion*. When the stable species is either a solid oxide or a solid hydroxide, the region on the Pourbaix diagram is labelled as a region of *Passivity*, in which the metal is protected by a surface film of an oxide or a hydroxide. When the stable species is the unreacted metal species itself, then region is labelled as a region of *Immunity*.

It is first necessary to assemble the appropriate chemical information about the specific metal being considered. Aluminum undergoes dissolution in acid solutions as Al<sup>3+</sup> ions and in basic solutions as aluminate ions (AlO<sub>2</sub><sup>-</sup>). In neutral or nearly neutral solutions, aluminum is covered with a protective oxide film.

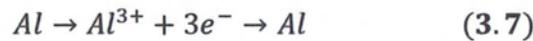
Thus, in the case of Al/H<sub>2</sub>O system, the various chemical entities and their chemical potentials are as follows [18]:

<i>Dissolved substances</i>	$\mu^{\circ}(\text{cal/mol})$
Al <sup>3+</sup>	-115,000
AlO <sub>2</sub> <sup>-</sup>	-200,710
H <sup>+</sup>	0
<i>Solid substances</i>	
Al	0
Al <sub>2</sub> O <sub>3</sub>	-384,530
<i>Liquid substances</i>	
H <sub>2</sub> O	-56,690

The chemical reactions involving these species are:



The dissolution of aluminum as Al<sup>3+</sup> ions by Eq. 3.2 is a reaction involving only the electrode potential E (but not only the pH). We first rewrite Eq. 3.2 as a reduction reaction. Then, for



The Nernst equation gives

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[Al^{3+}]} \quad (3.8)$$

For the reaction above, the Standard (reduction) potential is E<sup>o</sup>=-1.663 V vs SHE (Table 3), and 2.303RT/F=0.0591 V and n=3. Thus the Eq. 3.8 becomes

$$E = -1.663 + 0.0197 \log[Al^{3+}] \quad (3.9)$$

The numerical value of the electrode potential  $E$  for the dissolution of Al as  $Al^{3+}$  ions depends on the concentration of the dissolved ion. As seen in the Figure below, the electrode potential for Al/  $Al^{3+}$  reaction becomes more positive with increasing  $[Al^{3+}]$  concentration. Thus, for a given concentration of  $Al^{3+}$ , say  $10^{-6}$  M, the oxidized form ( $Al^{3+}$ ) is stable for potentials above the appropriate straight line at concentrations equal to or greater than  $10^{-6}$  M. Below the given straight line, the oxidized species does not exist at the concentration being considered. That is below the straight line, the reduced species (Al atoms) are stable. A clearer way to see this is to consider an electrode potential which is considerably below the straight line for  $[Al^{3+}] = 10^{-6}$  M, say  $E = -2.5$  V vs. SHE. Substituting this value of  $E$  into **Eq. 3.9** gives the concentration of  $[Al^{3+}]$  to be  $2.9 \times 10^{-43}$  M. This is a negligibly small value, so the oxidized species ( $Al^{3+}$ ) is not stable, and thus the reduced species (solid Al) is stable.

*Table 3: Standard (reduction) potentials for various electrochemical reactions involving Al & water*

Reaction (Oxidation)	$E^0$ (for reduction) (V vs. SHE)
$Al \rightarrow Al^{3+} + 3e^-$	-1.662
$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$	-1.550
$Al + 2H_2O \rightarrow AlO_2^- + 4H^+ + 3e^-$	-1.262
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.828

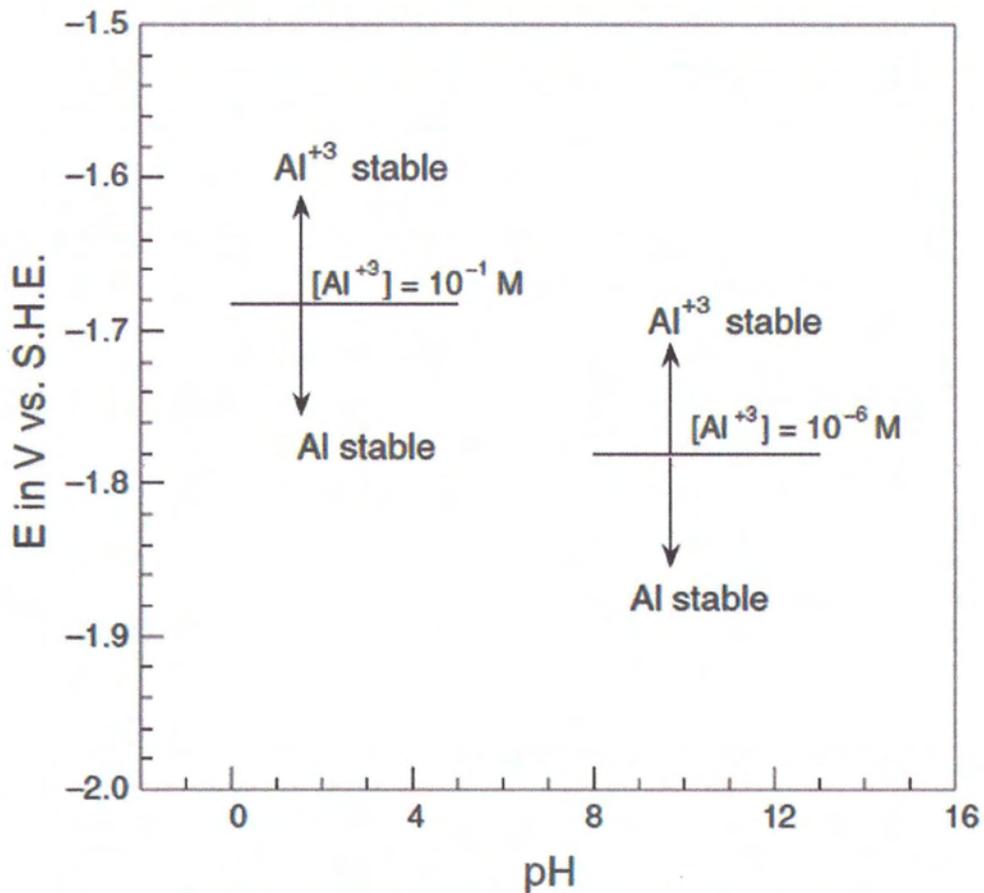


Fig 23: Partial Pourbaix diagram for aluminum at 25°C

In general, for any electrochemical reaction represented on a Pourbaix diagram, the oxidized species of the couple is stable above the straight line of the Nernst equation for the reaction, and the reduced species is stable below the straight line. By convention, Pourbaix diagrams are usually constructed under the condition that corrosion is considered to have occurred when the minimum concentration of the dissolved ion is  $1.0 \times 10^{-6}$  M. That convention is followed in this text.

**Eq. 3.3** is a chemical rather than an electrochemical reaction in that there is no electron transfer involved. The reaction depends on the pH but not on the electrode potential. Thus, from Eq. 2.9:

$$\Delta G^{\circ} = \mu^{\circ}(\text{Al}_2\text{O}_3(s)) + 6\mu^{\circ}(\text{H}^+(aq)) - [2\mu^{\circ}(\text{Al}^3(aq)) + 3\mu^{\circ}(\text{H}_2\text{O}(l))] \quad (3.10)$$

Using the various values of  $\mu^\circ$  given earlier gives  $\Delta G^\circ = +15,540$  cal/mol  $\text{Al}_2\text{O}_3$  for **Eq. 3. 3**.

Also from Chapter 2, The **Eq. 2. 16** is

$$\Delta G^\circ = -2.303RT \log K$$

Where the equilibrium constant K is

$$K = \frac{[H^+]^6}{[Al^{3+}]} \quad (3.11)$$

**Equation 2. 16** yields

$$+15,540 \frac{\text{cal}}{\text{mol}} = -2.303 \left( 1.98 \frac{\text{cal}}{\text{mol} \cdot K} \right) (298K) \log K \quad (3.12)$$

Or

$$\log K = -11.436 \quad (3.13)$$

Combining **3.11** and **3.13** gives

$$3pH + \log[Al^{3+}] = 5.718 \quad (3.14)$$

When  $[Al^{3+}] = 1.0 \times 10^{-6}$  M, then **Eq. 3.14** gives the result  $pH = 3.91$ . This is the pH which results when dissolved  $Al^{3+}$  ions of concentration  $1.0 \times 10^{-6}$  M react with water according to **Eq.3.3**. See the Figure below, which summarizes the thermodynamic results so far. It can be shown easily that  $Al^{3+}$  ions are stable to the left of the line  $pH = 3.91$  and  $Al_2O_3(s)$  is stable to the right of this line. For example, when the pH is 7.0, the concentration of  $Al^{3+}$  calculated from **Eq. 3.14** is  $[Al^{3+}] = 5.2 \times 10^{-16}$  M. That is, dissolved  $Al^{3+}$  ions are not stable for pH values greater than 3.91, but instead solid  $Al_2O_3$  is stable in that region.

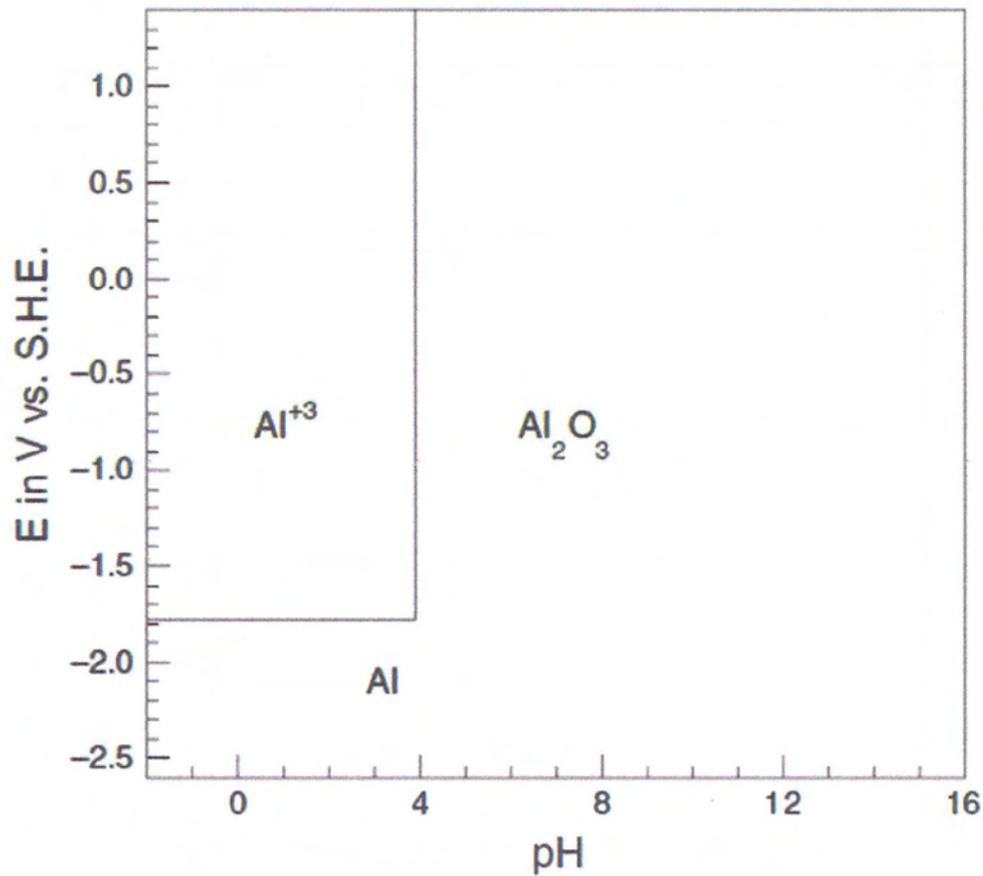


Fig 24: Partial Pourbaix diagram for aluminum at 25°C (2)

Continuing with the construction of the Pourbaix diagram for aluminum, we next turn to **Eq. 3.4**, which is a reaction depending on both the electrode potential and the pH. After **Eq. 3.4** is first recast as a reduction reaction, writing the corresponding Nernst equation gives

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[H^+]^6} \quad (3.15)$$

The value of  $E^{\circ}$  for **Eq. 3.4** is  $E^{\circ} = -1.550$  V vs. SHE. See Table 3 Alternately,  $E^{\circ}$  can be calculated from the free energy change for **Eq. 3.4** using the chemical potentials. With  $E^{\circ} = -1.550$  V and  $n = 6$ , **Eq. 3.15** gives

$$E = -1.550 - 0.0591pH \quad (3.16)$$

See figure below, which adds this line to the thermodynamic data accumulated so far and also summarizes the regions of stability for the various species as has been computed so far.

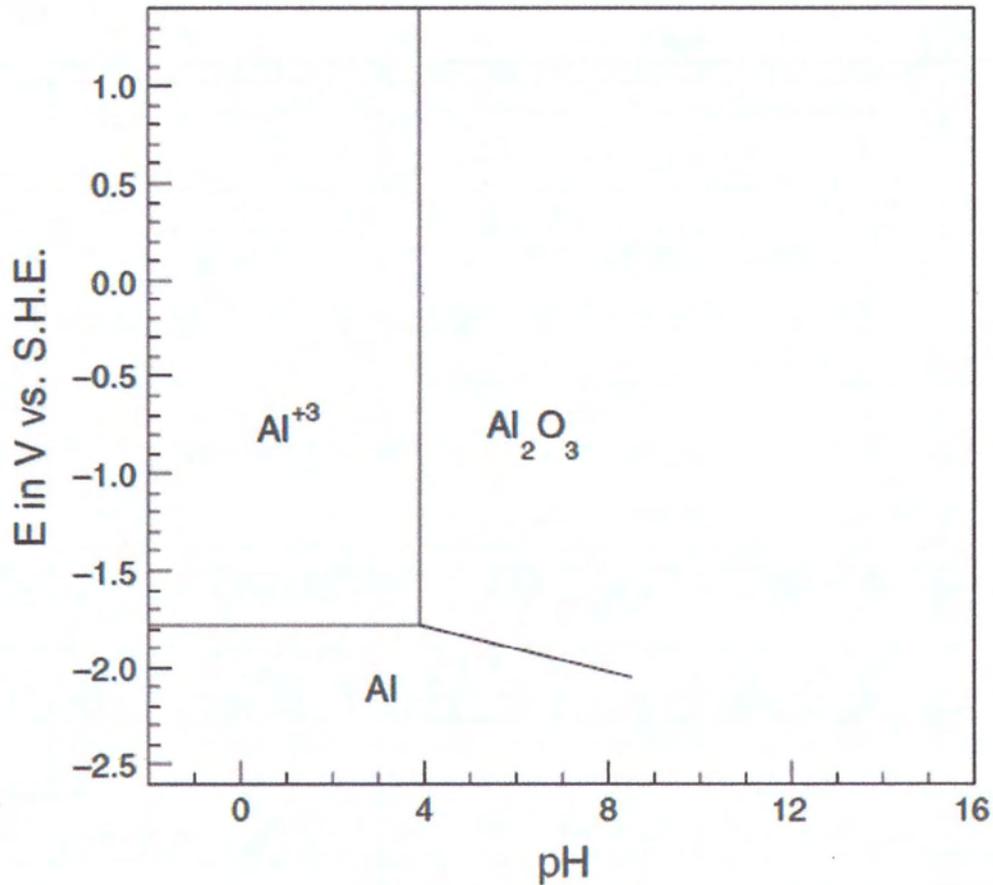


Fig 25: Partial Pourbaix diagram for aluminum at 25°C (3)

Eq. 3.5 in the set of possible reactions for the Al/H<sub>2</sub>O system can be treated in the same fashion as Eq. 3.3 because both are chemical (i.e., non-electrochemical reactions). The results for Eq. 3.5 is

$$-pH + \log[AlO_2^-] = -14.644 \quad (3.17)$$

When the concentration of the dissolved ion, in this case AlO<sub>2</sub><sup>-</sup>, is 1.0 × 10<sup>-6</sup> M, Eq. 3.17 gives the result

$$pH = 8.64 \quad (3.18)$$

The Nernst equation for the electrochemical reaction in 3.6 gives the following result

$$E = -1.262 + 0.0197 \log[AlO_2^-] - 0.0788 pH \quad (3.19)$$

When  $[AlO_2^-] = 1.0 \times 10^{-6} \text{ M}$ , **Eq. 3.19** gives

$$E = -1.380 - 0.0788 \text{ pH} \quad (3.20)$$

Addition of the straight lines for **Eq. 3.18** and **Eq. 3.20** to Figure above gives the completed Pourbaix diagram for aluminum shown in Fig. 24. When the diagram identifies only the regions of corrosion, passivity, and immunity (rather than citing the individual stable species), the diagram is said to be a “simplified Pourbaix diagram.”

### 3.3 Equilibrium states indications & interpretation

The phase boundaries define important regions that must be known for the corrosion mitigation, below is displayed the indications of the equilibrium states for three metals, (1) gold, (2) zinc and (3) aluminium through their Pourbaix diagrams [19].

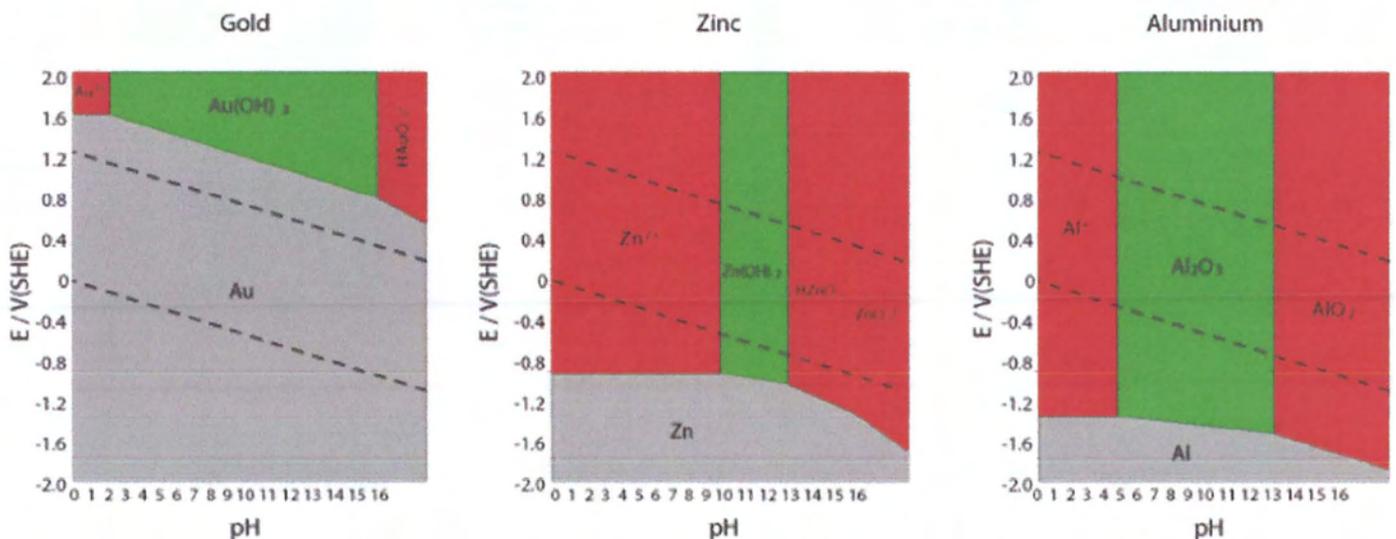


Fig 26: Pourbaix diagrams of gold, zinc and aluminium

Gold’s Pourbaix diagram explains why it is the most immune substance known. It is immune in all regions in which cathodic reactions can take place. Thus, gold never

corrodes (Since no ion complexes are present spontaneously to provide a cathodic half-cell reaction that occurs higher than +1.5 V vs SHE) in an aqueous environment.

Immunity of aluminum only occurs at lower potentials. Therefore, unless under conditions that cause it to passivate, it is much more susceptible to corrosion than gold or zinc.

## Chapter 4 Pourbaix diagrams of steel in the presence of Sulphur

### 4.1 Introduction

This is the main chapter of the present thesis, the Pourbaix diagrams calculated by the Thermo-Calc software and are presented below.

One important concept used in defining an aqueous-bearing heterogeneous interaction system is the so-called “Effective Interaction Ratio” between the initial alloy and the aqueous solution; as the initial aqueous solution is always based on 1 kg of water, this is why a calculated Pourbaix diagram is usually presented for an initial amount of the interacting metal (or alloy) at a certain level, e.g.,  $10^{-6}$ ,  $10^{-3}$ , 0.1 or 1 mole of metal/alloy.

The importance of this concept is double-fold:

- It has the implications of kinetic/dynamic effects (from e.g. chemical reaction mechanism and kinetics, fluid flow dynamics, surface area, interaction time and other factors)
- When it is started as at  $10^{-6}$  mole of metal (or alloy), it is not a completely-arbitrary choice for a “common standard”, thanks to that it has been regarded (by the materials corrosion society) as the “detectable” solubility limit for cathodic corrosion protection by immunity.

In the present thesis the *effective interaction ratio*, was kept constant at 1 gram of alloy in 1 kg of water, since the main purpose was to study the behavior of the Pourbaix diagrams of the selected materials at certain Temperatures i.e. (25°, 60°, 90°).

Thermo-Calc [13] suggest as a normal effective interaction ratio, of one to one, either 1 mol or 1 gram of initial bulk of the alloy, to 1 kg of water (dissolved substances included), thus for the present study an *effective interaction ratio* of 1 gram (equivalent to  $1.7906706 \cdot 10^{-2}$  molarity) in 1 kg of water was considered.

Another technical issue for the equilibrium calculations is to properly modify the numerical limits, this change is also recommended by Thermo-Calc. Such changes in

the numerical limits are essential and useful for making sure of finding a converged solution of stable equilibria, especially when the heterogeneous interaction system becomes more and more complicated. Thus, for the matter in hand calculations, the *Maximum number of iterations* was set to 2000, which enforces 4 times more iterations for each of the calculations in order to obtain stable equilibria. Furthermore, the *required accuracy* was set from the default value  $10^{-6}$  to  $10^{-4}$ , which allows less accurate calculations and it is easier to converge and the *Smallest fraction* remained  $10^{-12}$

Table 8 summarizes the data which were used for the construction of each Pourbaix diagram.

The diagrams have been constructed for 3 material's cases:

- Fe
- P5 steel
- P9 steel

in 1 kg of water with dissolved 5% H<sub>2</sub>S and S for 3 different temperatures (25°, 60°, 90°).

The first material under investigation was the St37 steel.

*Table 4: St37 Chemical Analysis (%wt)*

C	Mn	P	S
0.17	1.40 max	0.045 max	0.045 max

Carbon steel is one of the basic construction materials because its price is relatively low while it provides material properties that are acceptable for many applications.

P5 is a chromium alloy used for its strong resistance to hot sulphide corrosion cracking. 5% chromium material has a higher minimum mechanical properties than 1 1/4% and 2 1/4% chromium, which makes the material ideal for high temperature and

pressure applications. In addition, 5% chromium can be used for elevated temperatures and corrosion resistant process and service.

*Table 5: P5 (ASTM A335) Chemical Analysis (%wt)*

C	Mn	Si	Cr	Mo	P	S
0.15 max	.30-.60	0.50	4-6	.44-.60	0.030 max	0.030 max

Typical Applications of P5 steel:

- Petrochemical and refinery installations
- Delayed cokers
- Hydrocrackers
- Cat reformer Heater drain systems

P9 used primarily for NACE applications where sour environments under high temperature and pressure are expected. Chromium of 9% gives corrosion resistance similar to 400 series stainless steel, but provides higher tensile properties at hotter temperatures than 405 or 410 stainless. In addition, 9% chromium can be used for elevated temperatures and corrosion resistant process.

*Table 6: P9 (ASTM A335) Chemical Analysis (%wt)*

C	Mn	Si	Cr	Mo	P	S
0.15 max	.30-.60	0.25-1	8-10	.90-1.1	0.030 max	0.030 max

Typical Applications of P9 steel:

- Fluid cat crackers
- Crude distillation units

According to the literature the most possible corrosion products in Sulphur environment are those listed in Table 6, which were considered in the ThermoCalc calculations.

*Table 7: Iron sulphides*

Name	Chemical Formula	Crystal Structure	Properties
Troilite	FeS	Hexagonal	Stoichiometric end member of the $Fe_{1-x}S$ group ( $x=0$ )
Pyrrhotite	$Fe_{1-x}S$ ( $x=0$ to 0.17)	Monoclinic or Hexagonal	Thermodynamically stable, the most abundant iron sulphide in the Earth
Pyrite	$FeS_2$	Cubic	Thermodynamically stable iron sulphide, the most abundant mineral on the Earth's surface

*Pyrrhotite ( $Fe_{1-x}S$  ( $x=0$  to 0.17)) and Troilite ( $FeS$ )*

Pyrrhotite [14] is a non-stoichiometric group of iron sulphides with formulae corresponding to  $Fe_{1-x}S$  ( $x=0$  to 0.17), where Troilite is the stoichiometric end member of the pyrrhotite group when  $x=0$  (FeS). Pyrrhotite and Troilite are thermodynamically stable, these two co-exist below 150°C. Troilite and pyrrhotite are differentiated only because the crystals that nucleate seem to initially grow differently at temperatures below 150°C. Troilite can be viewed as low temperature and stoichiometric Pyrrhotite. A variety of different Pyrrhotites have been observed with different values of  $x$  resulting in changes in the unit cells of each.

*Pyrite ( $FeS_2$ )*

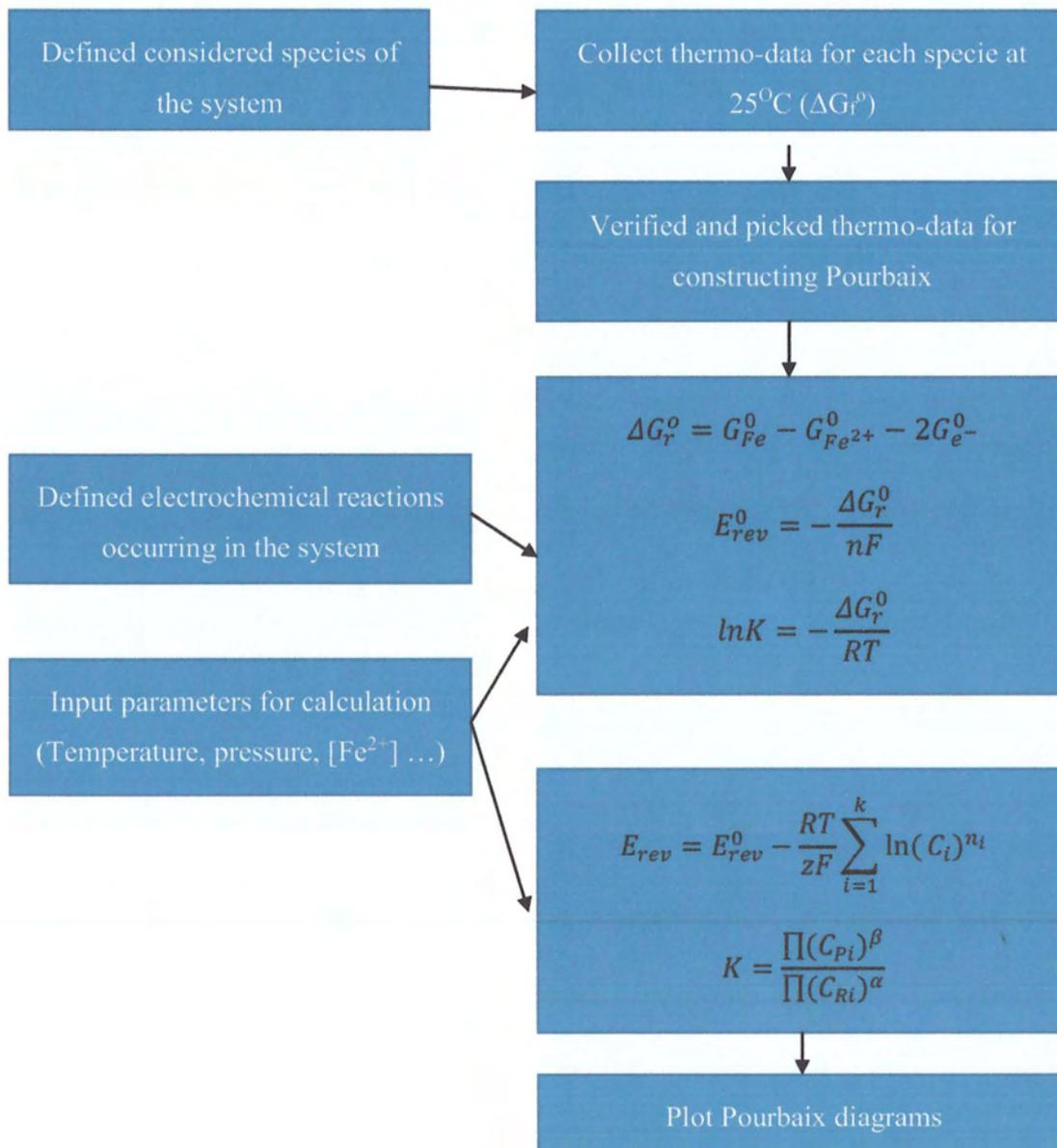
Pyrite is the most abundant sulphide mineral in nature, also known as "fool's gold". Pyrite and Pyrrhotite are the most stable iron sulphides, and considered to be the corrosion products seen in long exposures.

Table 8: The List of Pourbaix diagrams

System	Numerical Limits			Molarity
	<i>Max number of iterations</i>	<i>required accuracy</i>	<i>Smallest fraction</i>	Equal to 1gr
Pure Water 25°C	-	-	-	-
Pure Water 200°C/100 bar	-	-	-	-
Pure Water 340°C/700 bar	-	-	-	-
Fe-H <sub>2</sub> O-25°C	2000	1e-4	1e-12	1e-3 (≠1 gr)
Fe-H <sub>2</sub> O-60°C	2000	1e-4	1e-12	1e-3 (≠1 gr)
Fe-H <sub>2</sub> O-90°C	2000	1e-4	1e-12	1e-3 (≠1 gr)
Fe-H <sub>2</sub> O-5% S 25°C	2000	1e-4	1e-12	1.7906706e-2
Fe-H <sub>2</sub> O-5% S 60°C	2000	1e-4	1e-12	1.7906706e-2
Fe-H <sub>2</sub> O-5% S 90°C	2000	1e-4	1e-12	1.7906706e-2
Fe-H <sub>2</sub> O-15% S 25°C	2000	1e-4	1e-12	1.7906706e-2
Fe-H <sub>2</sub> O-5% H <sub>2</sub> S 25°C	2000	1e-4	1e-12	1.7906706e-2
Fe-H <sub>2</sub> O-5% H <sub>2</sub> S 60°C	2000	1e-4	1e-12	1.7906706e-2
Fe-H <sub>2</sub> O-5% H <sub>2</sub> S 90°C	2000	1e-4	1e-12	1.7906706e-2
P5-H <sub>2</sub> O-5% S 25°C	2000	1e-4	1e-12	N(Fe)=1.70e-2 N(Cr)=9.61e-4
P5-H <sub>2</sub> O-5% S 60°C	2000	1e-4	1e-12	N(Fe)=1.70e-2 N(Cr)=9.61e-4
P5-H <sub>2</sub> O-5% S 90°C	2000	1e-4	1e-12	N(Fe)=1.70e-2 N(Cr)=9.61e-4
P5-H <sub>2</sub> O-5% H <sub>2</sub> S 25°C	2000	1e-4	1e-12	N(Fe)=1.70e-2 N(Cr)=9.61e-4

P5-H <sub>2</sub> O-5% H <sub>2</sub> S 60°C	2000	1e-4	1e-12	N(Fe)=1.70e-2 N(Cr)=9.61e-4
P5-H <sub>2</sub> O-5% H <sub>2</sub> S 90°C	2000	1e-4	1e-12	N(Fe)=1.70e-2 N(Cr)=9.61e-4
P9-H <sub>2</sub> O-5% S 25°C	2000	1e-4	1e-12	N(Fe)=1.62e-2 N(Cr)=1.73e-3
P9-H <sub>2</sub> O-5% S 60°C	2000	1e-4	1e-12	N(Fe)=1.62e-2 N(Cr)=1.73e-3
P9-H <sub>2</sub> O-5% S 90°C	2000	1e-4	1e-12	N(Fe)=1.62e-2 N(Cr)=1.73e-3
P9-H <sub>2</sub> O-5% H <sub>2</sub> S 25°C	2000	1e-4	1e-12	N(Fe)=1.62e-2 N(Cr)=1.73e-3
P9-H <sub>2</sub> O-5% H <sub>2</sub> S 60°C	2000	1e-4	1e-12	N(Fe)=1.62e-2 N(Cr)=1.73e-3
P9-H <sub>2</sub> O-5% H <sub>2</sub> S 90°C	2000	1e-4	1e-12	N(Fe)=1.62e-2 N(Cr)=1.73e-3

The process of generating diagrams for an Fe-H<sub>2</sub>O-S or Fe-H<sub>2</sub>O-H<sub>2</sub>S system generally followed the steps shown in flow diagram below [14].



## 4.2 The calculated Pourbaix diagrams

The aim was to calculate the Pourbaix diagrams for three steels (Fe, P4, P9) exposed at certain temperatures (25°, 60°, 90°) under various Sulphur concentrations.

The **active corrosion field** is enclosed by the stable phases of water and the thermodynamically stable curves of the product of the corrosion. When the cathodic reactions take place due to the water under certain conditions of Eh and pH and are unable to form a stable phase (scale), then an active corrosion process begins.

# Pourbaix of Pure Water

Pourbaix Diagram (T=25 C)

2016.02.09.13.56.44  
H+1, H2O, ZE  
T=298.15, P=1E5, B(H2O)=1000.

25 C 1 bar

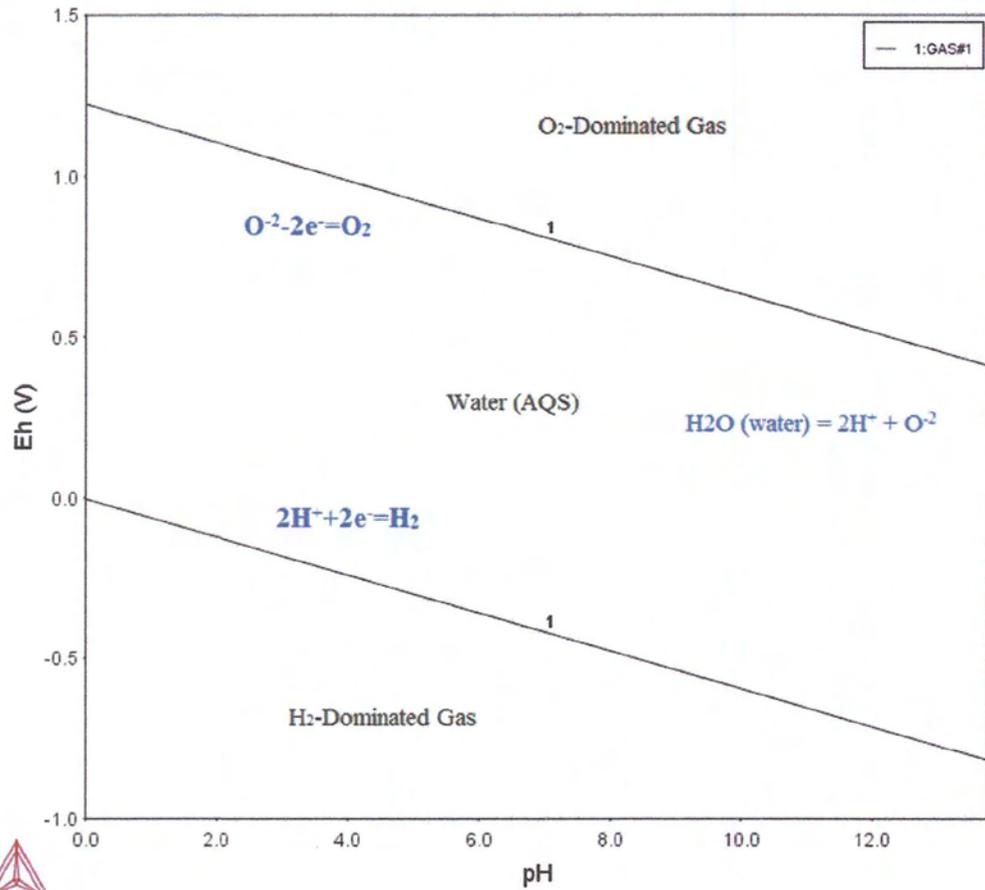


Fig 27: Pourbaix of pure water at 25°C and 1 bar

Pourbaix Diagram (P=100 bar T=200 C)

2016.02.09.14.00.38  
H+1, H2O, ZE  
T=473.15, P=1E7, B(H2O)=1000.

200 C 100 bar

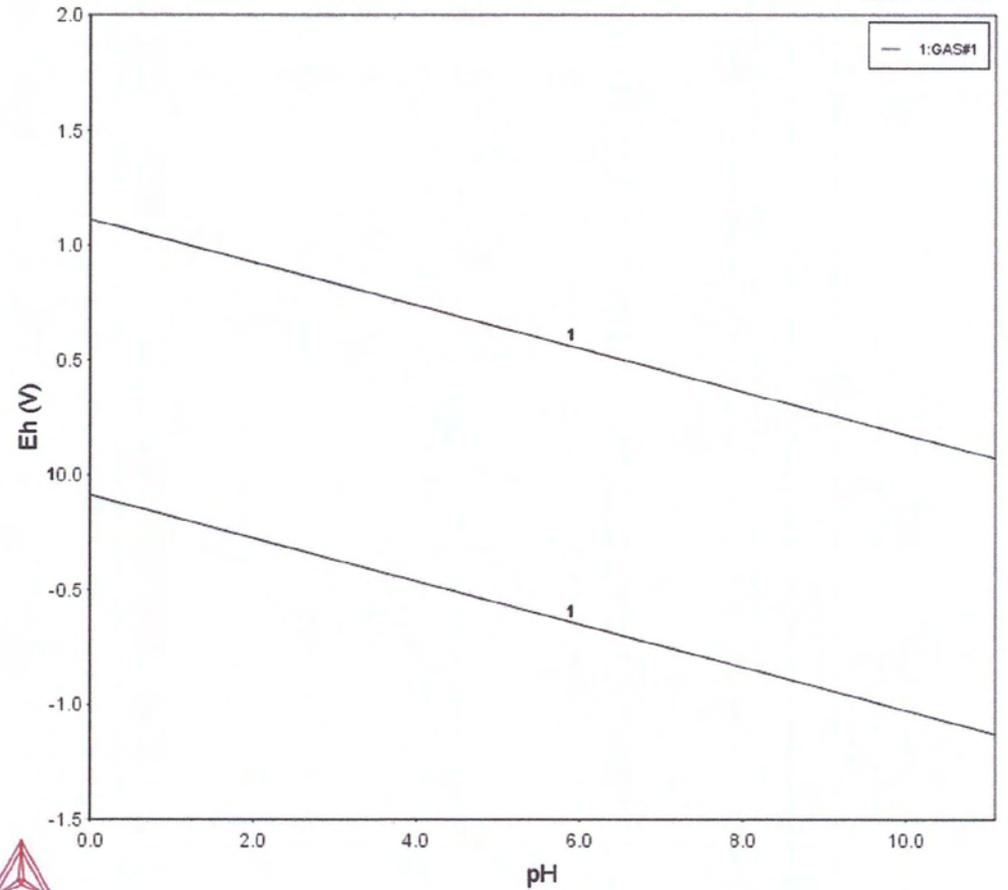


Fig 28: Pourbaix of pure water at 200°C and 100 bar

Pourbaix Diagram (P=700 bar T=340 C)

2016.02.09.14.01.56  
 H+1, H2O, ZE  
 T=613.15, P=7E7, B(H2O)=1000.

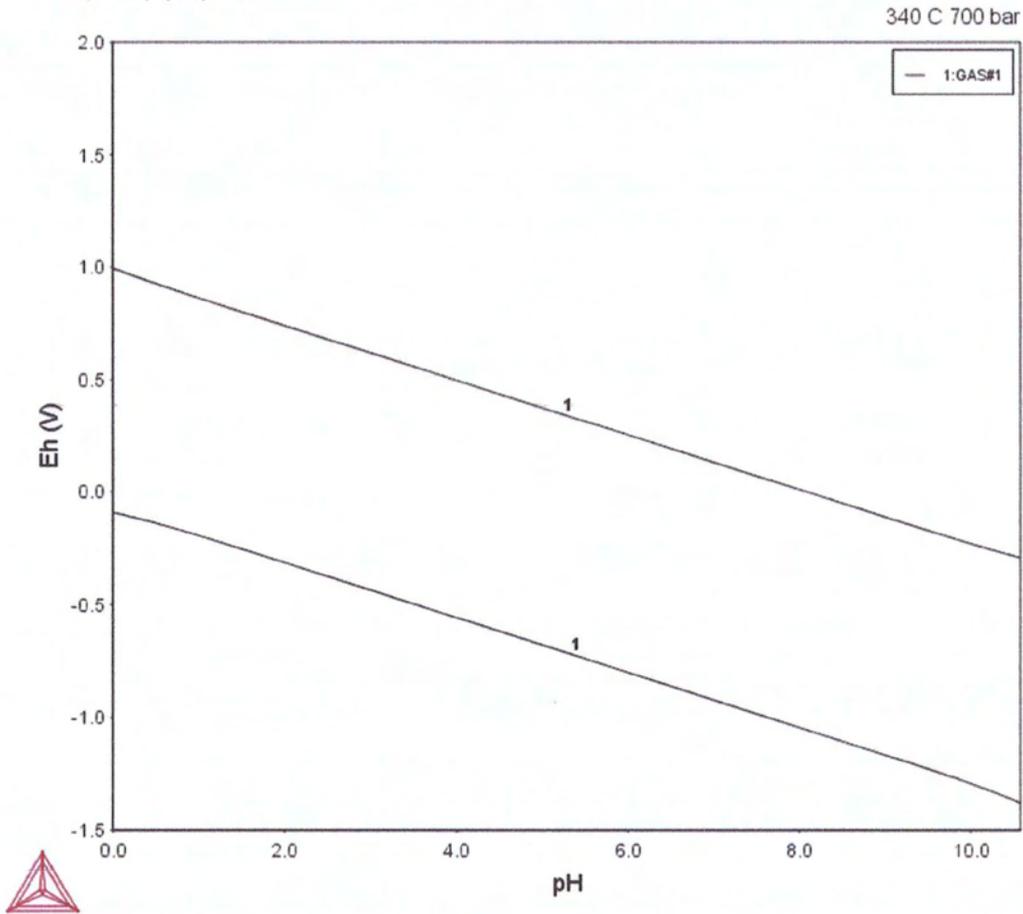


Fig 29: Pourbaix of pure water at 340°C and 700 bar

The Pourbaix diagrams above show the result of a calculation where the gaseous mixture phase was included. In the upper region (high Eh) and lower region (low Eh), the aqueous solution has been oxidised and reduced, respectively. Under defined conditions (pressure and temperature) the following electrochemical reactions occur:

- $\text{H}_2\text{O (water)} + 2\text{e}^- = \text{H}_{2(\text{gas})} + 2\text{OH}^{-1}$  (Formation of  $\text{H}_2$ -Dominated gas)
- $2\text{H}_2\text{O (water)} = \text{O}_{2(\text{gas})} + 4\text{H}^{+1} + 4\text{e}^-$  (Formation of  $\text{O}_2$ -Dominated gas)

The first reaction occurs under reducing conditions and the second under oxidising conditions. The system reaches global equilibrium, thus the water component is electrolyzed to  $\text{H}^+$  and  $\text{O}^{-2}$  at all pH conditions. [17] If Eh increases then the  $\text{O}^{-2}$  anion

will be oxidised to  $O_2$  (aq). On the other hand, if Eh decreases, then the  $H^+$  cation will be reduced to  $H_2$  (aq). The major electrolysis and redox reactions are the following:

- $H_2O$  (water) =  $H^+$  +  $OH^-$  (Electrolysis of water)
- $H_2O$  (water) =  $2H^+$  +  $O^{2-}$  (Electrolysis of water)
- $O^{2-} - 2e^- = 0.5O_2$  (aq) (Oxidation of  $O^{2-}$  at high Eh)
- $2H^+ + 2e^- = H_2$  (aq) (Reduction of  $H^+$  at low Eh)

Under a given pH condition at a critically high Eh an aqueous solution with a high enough  $O_2$  will become less stable than an  $O_2$ -Dominated gaseous mixture phase. At this point, the gas phase replaces the aqueous solution phase in the system. Similarly happens of a critically low Eh value for the  $H_2$ -Dominates gaseous mixture.

These diagrams above, show that the upper and lower boundaries between the aqueous phase (water) and the gas phase ( $O_2$  or  $H_2$  dominated) can shift when the temperature and pressure change.

# Pourbaix of Fe-H<sub>2</sub>O system

## Pourbaix Diagram

2015.10.21.13.34.56  
 FE, H+1, H2O, ZE  
 T=298.15, P=1E5, B(H2O)=1000., N(Fe)=1E-3

25 C 1 bar .001mFE

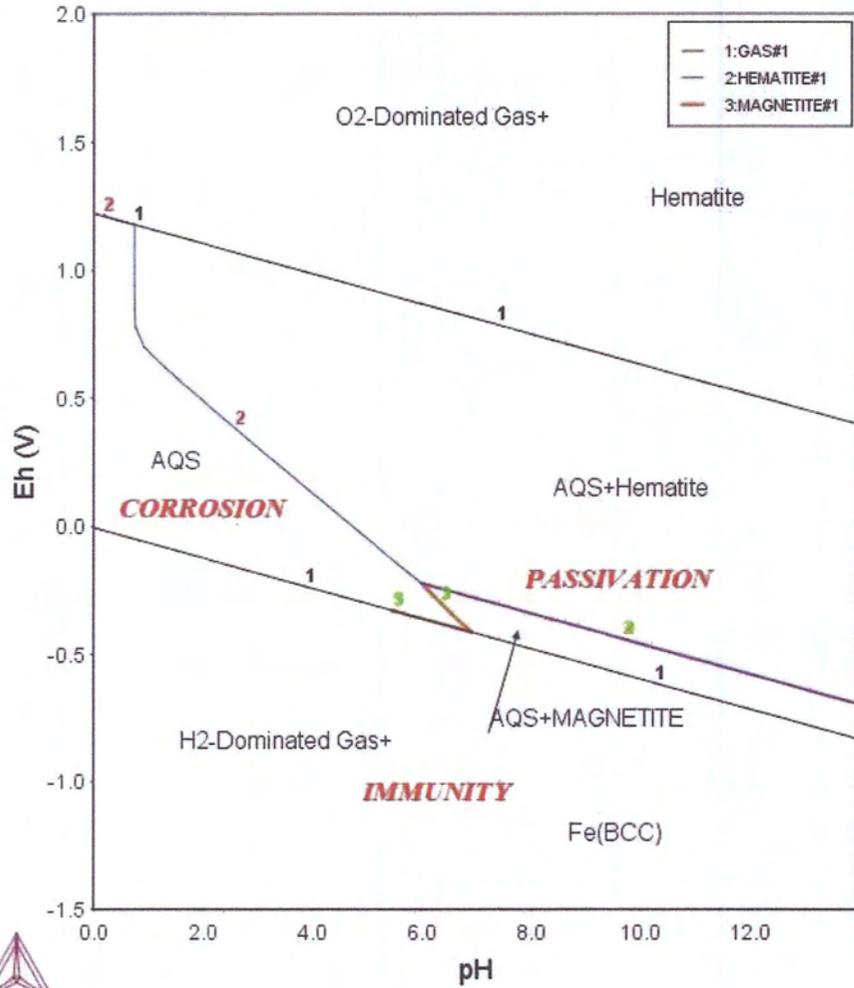


Fig 30: Fe in 1 kg of H<sub>2</sub>O at 25°C

60 C 1 bar .001mFE

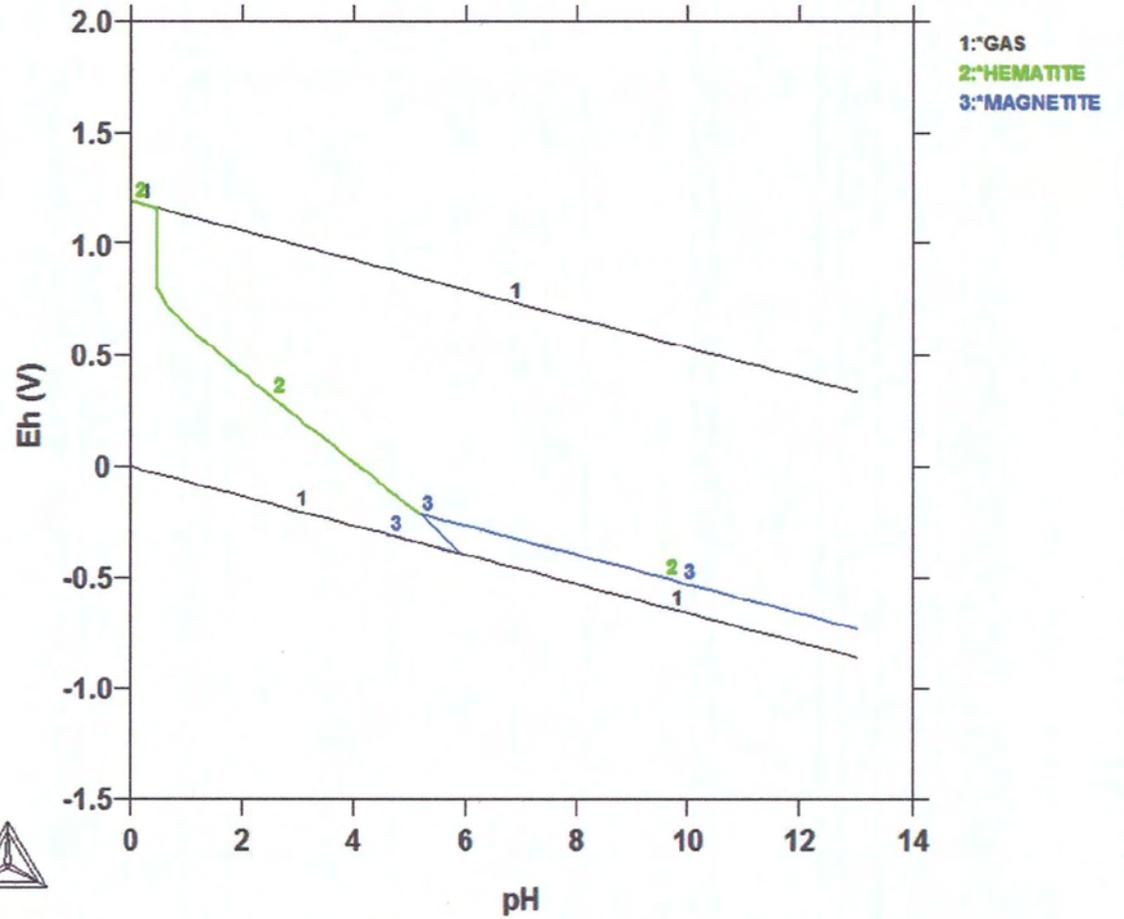
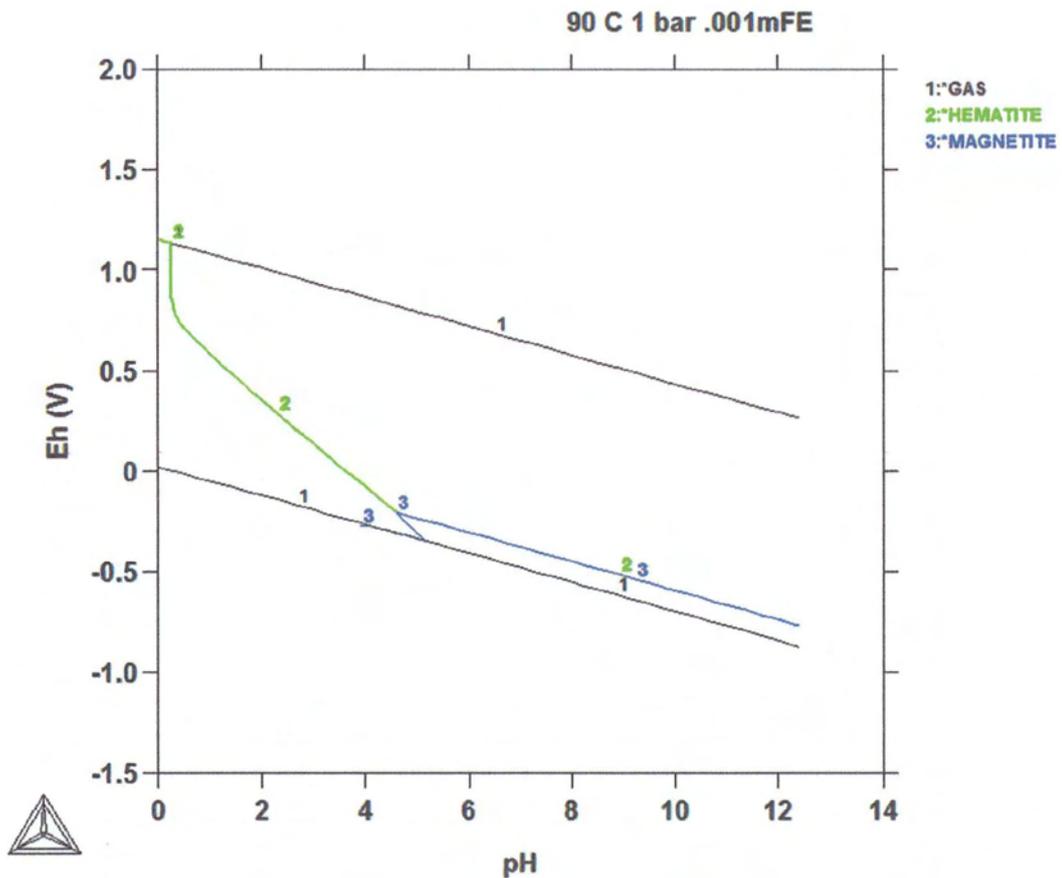


Fig 31: Fe in 1 kg of H<sub>2</sub>O at 60°C



*Fig 32: Fe in 1 kg of H<sub>2</sub>O at 90°C*

In the diagrams above, 1e-3 m Fe actively reacted with 1 kg of pure water at 1 bar with increasing temperature. As shown, the aqueous-gas phase boundaries shift as the temperature in the interaction system change. The lower is the temperature the more the active metal corrosion region enlarges.

An active metal corrosion region exists where the products of the redox reactions dissolve and therefore, do not create a protective scale. In this case, exists below the Hematite line, approximately from 0 to 6 pH.

# Pourbaix of Fe-H<sub>2</sub>O-5% S

1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=25 C)

2016.02.22.10.33.54  
 FE, H+1, H2O, S, ZE  
 T=298.15, P=1E5, B(H2O)=1000., N(Fe)=1.79067E-2, N(S)=1.55958E-2 25 C 1 bar .017907mFE .015596mS

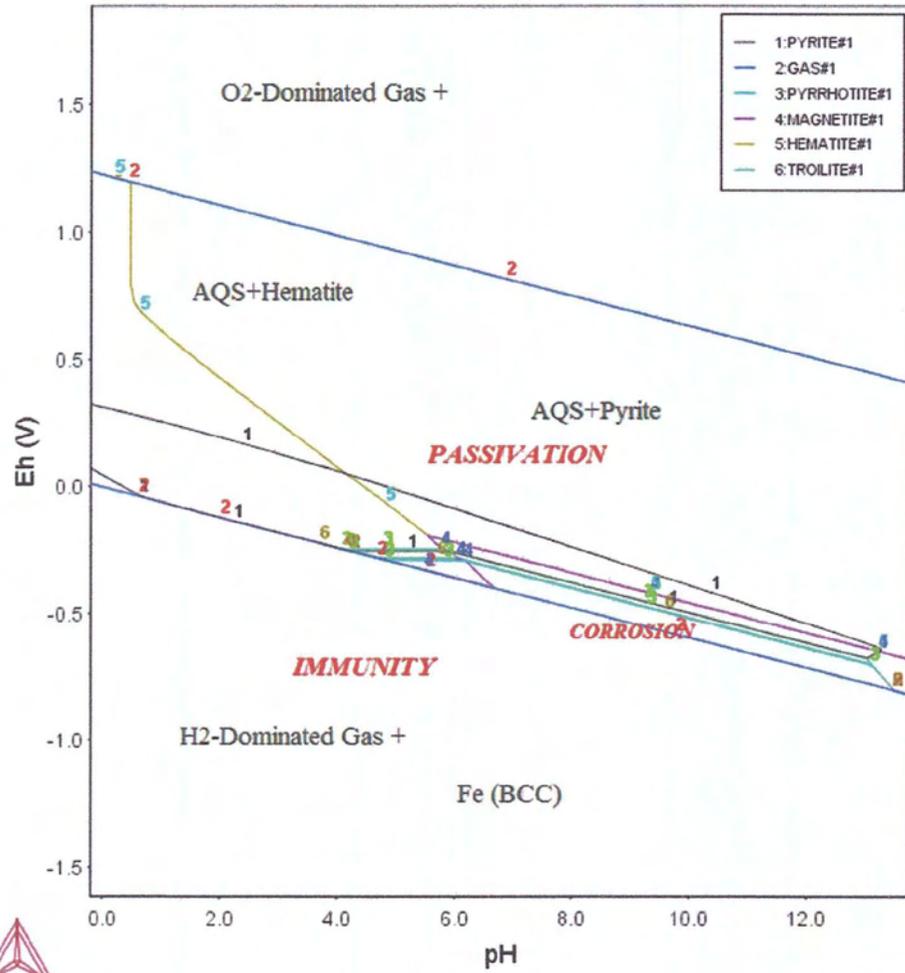


Fig 34: Fe in 1 kg of H<sub>2</sub>O with 5% S at 25°C

1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=60 C)

2016.02.22.12.14.39  
 PAQ2: H2O, H+1, ZE, FE, S  
 P=1E5, T=333.15, B(H2O)=1000., N(Fe)=1.79067E-2, N(S)=0.155958

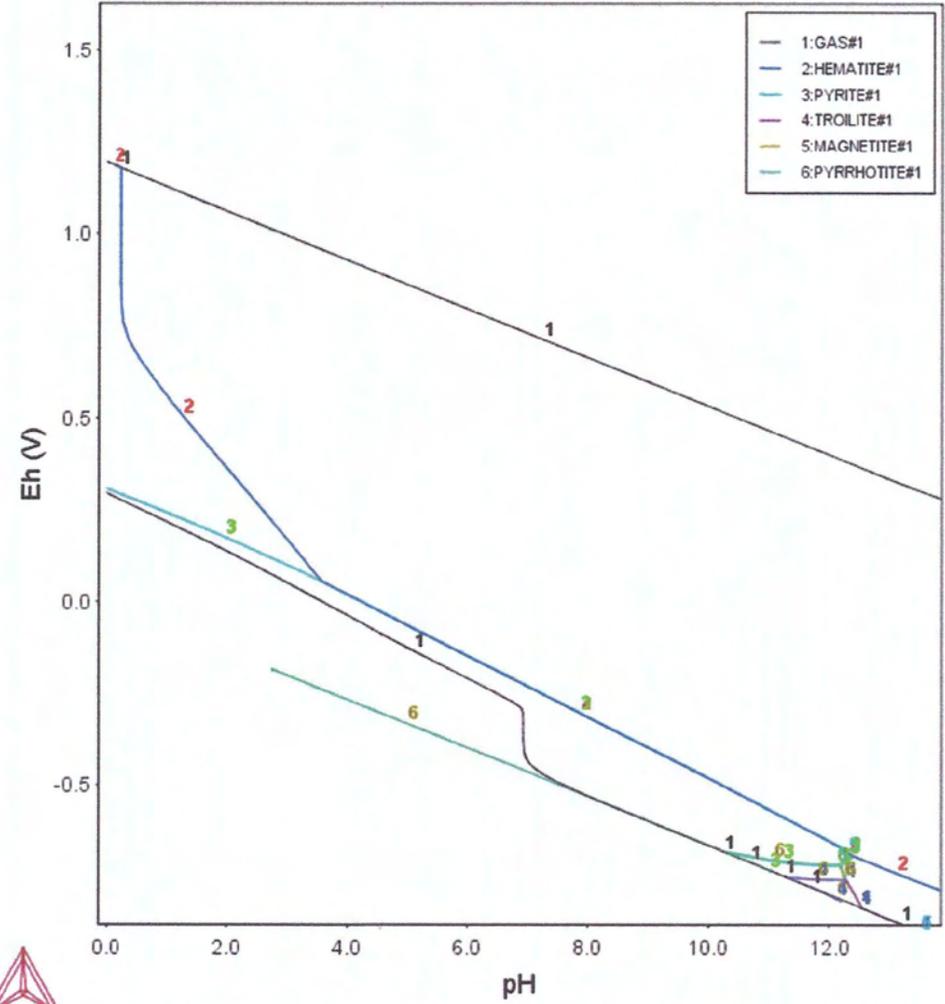


Fig 33: Fe in 1 kg of H<sub>2</sub>O with 5% S at 60°C

1 gr Fe in 1 Kg H2O-5% S (T=90 C)

2016.02.22.11.25.06  
 PAQ2: H2O, H+1, ZE, FE, S  
 P=1E5, T=363.15, B(H2O)=1000., N(Fe)=1.79067E-2, N(S)=0.155958

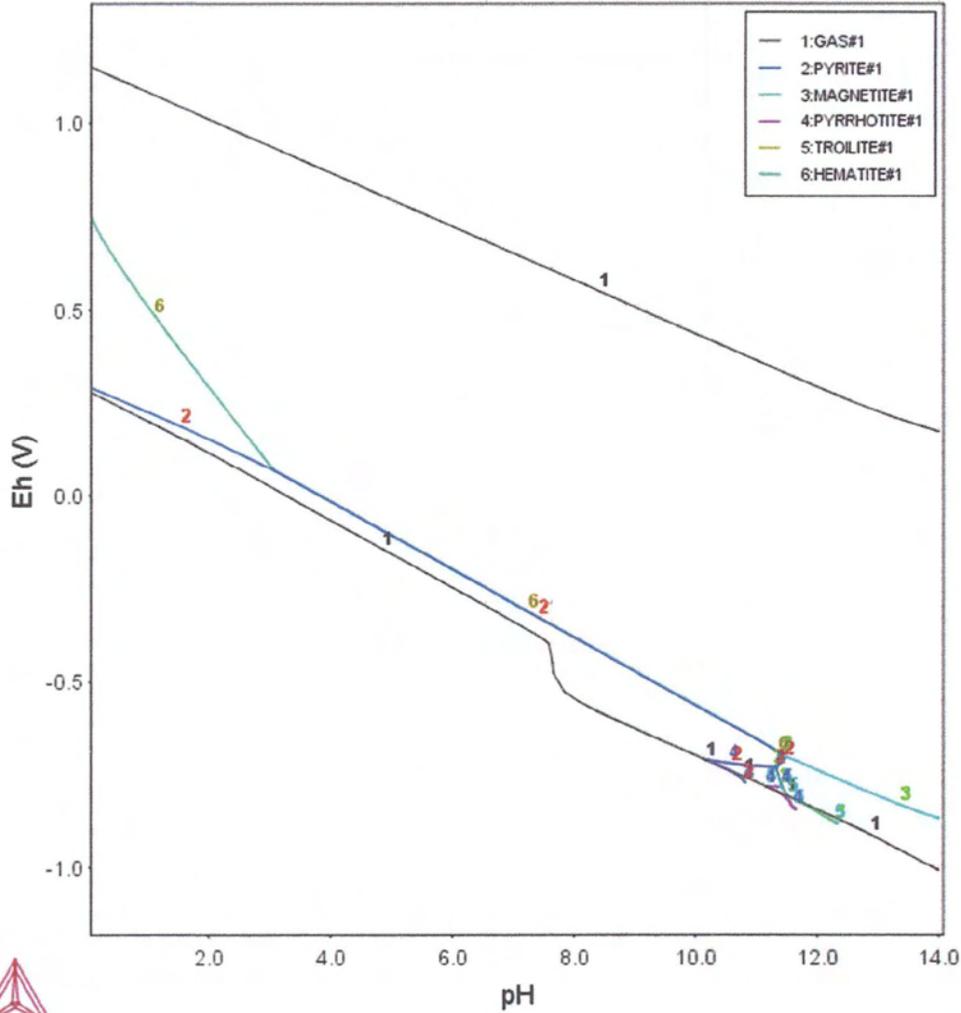


Fig 35: Fe in 1 kg of H2O with 5% S at 90°C

1 gr Fe in 1 Kg H2O-5% S (T=90 C)

2016.02.22.11.25.06  
 PAQ2: H2O, H+1, ZE, FE, S  
 P=1E5, T=363.15, B(H2O)=1000., N(Fe)=1.79067E-2, N(S)=0.155958

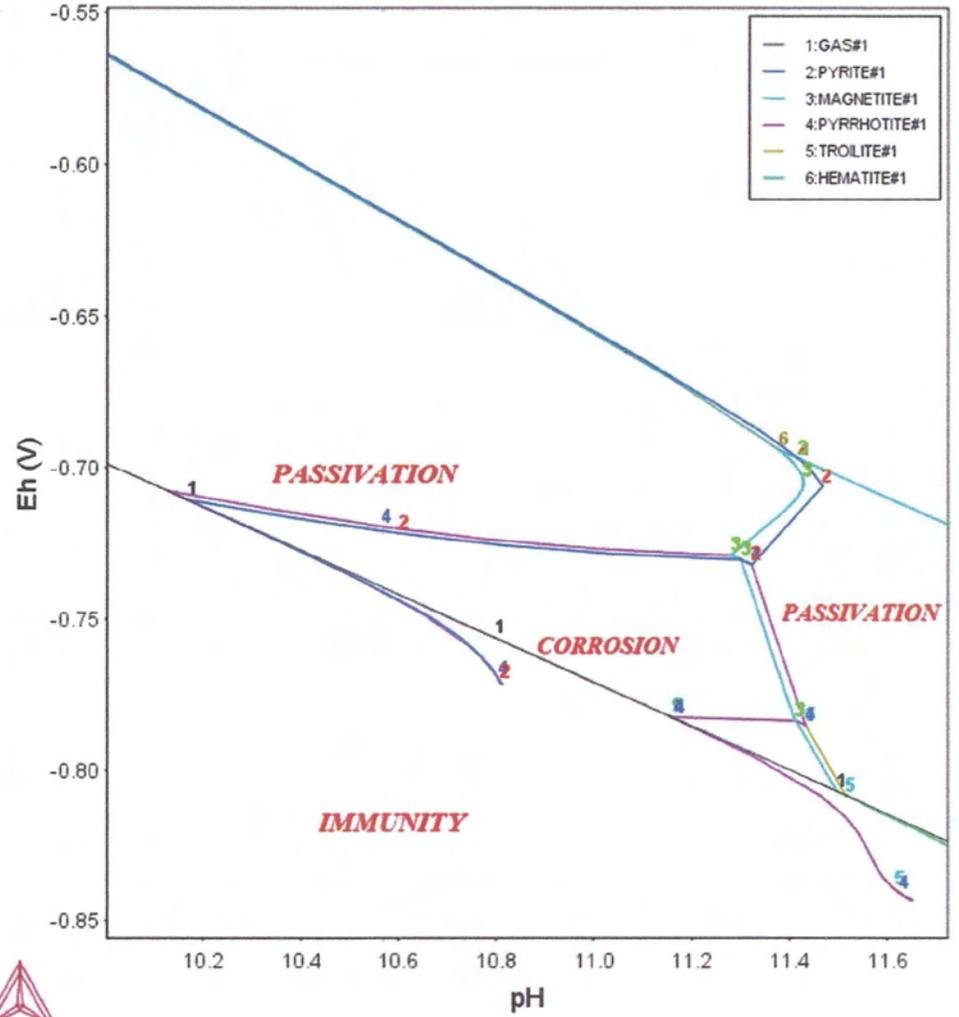


Fig 36: Fe in 1 kg of H2O with 5% S at 90°C-Zoom-In

# Pourbaix of Fe-H<sub>2</sub>O-5% H<sub>2</sub>S

1 gr Fe in 1 Kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=25 C)

2016.02.26.11.56.51  
 PAQ2: H<sub>2</sub>O, H+1, ZE, H<sub>2</sub>S, FE  
 P=1E5, T=298.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(H<sub>2</sub>S)=0.146732

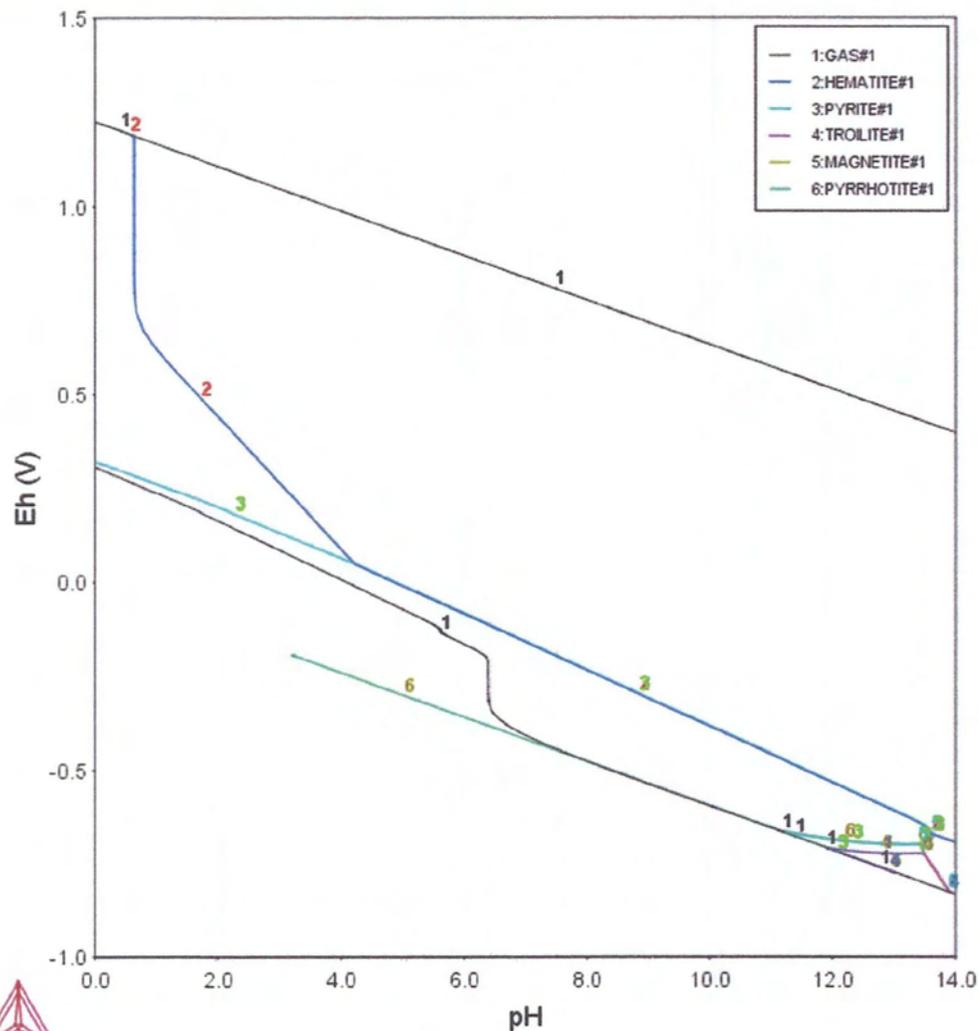


Fig 37: Fe in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 25°C

1 gr Fe in 1 Kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=60 C)

2016.02.26.12.11.06  
 PAQ2: H<sub>2</sub>O, H+1, ZE, FE, H<sub>2</sub>S  
 P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(H<sub>2</sub>S)=0.146732

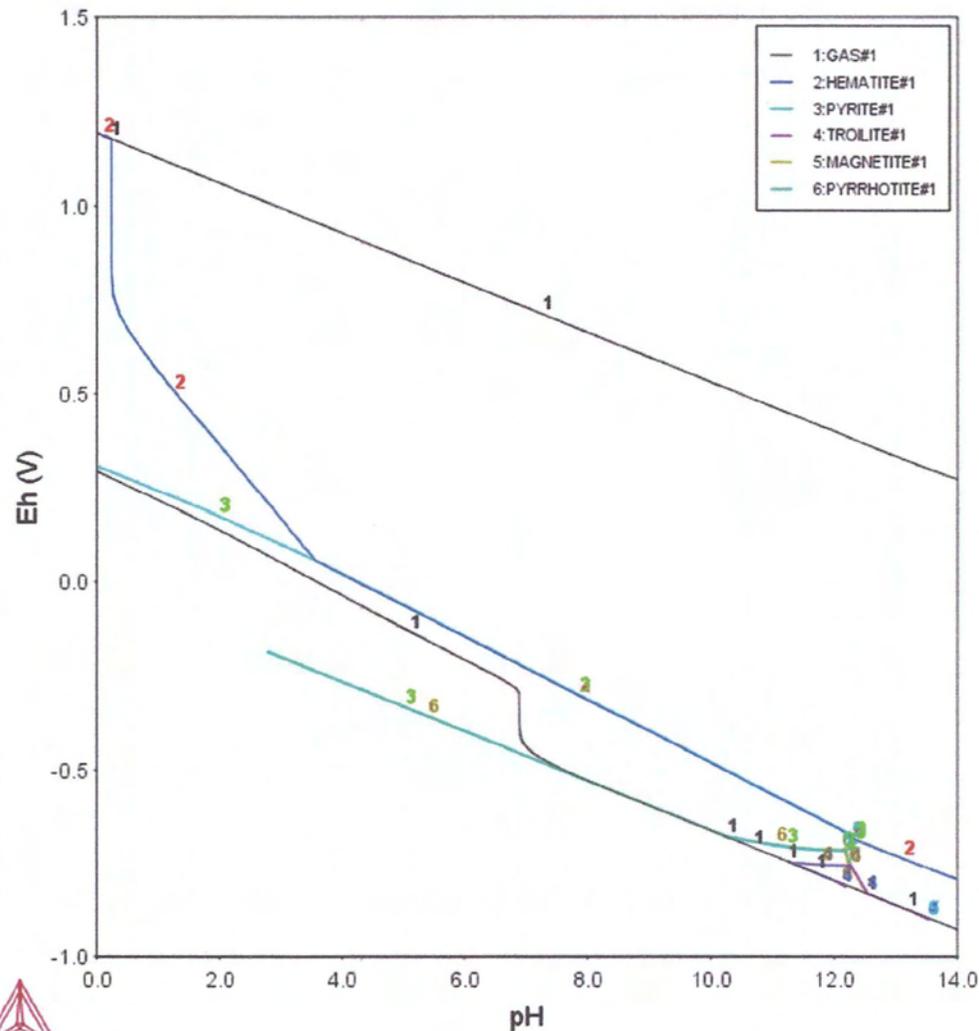


Fig 38: Fe in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 60°C

1 gr Fe in 1 Kg H2O-5% H2S (T=90 C)

2016.02.26.12.31.17  
 PAQ2: H2O, H+1, ZE, FE, H2S  
 P=1E5, T=363.15, B(H2O)=1000., N(Fe)=1.79067E-2, N(H2S)=0.146732

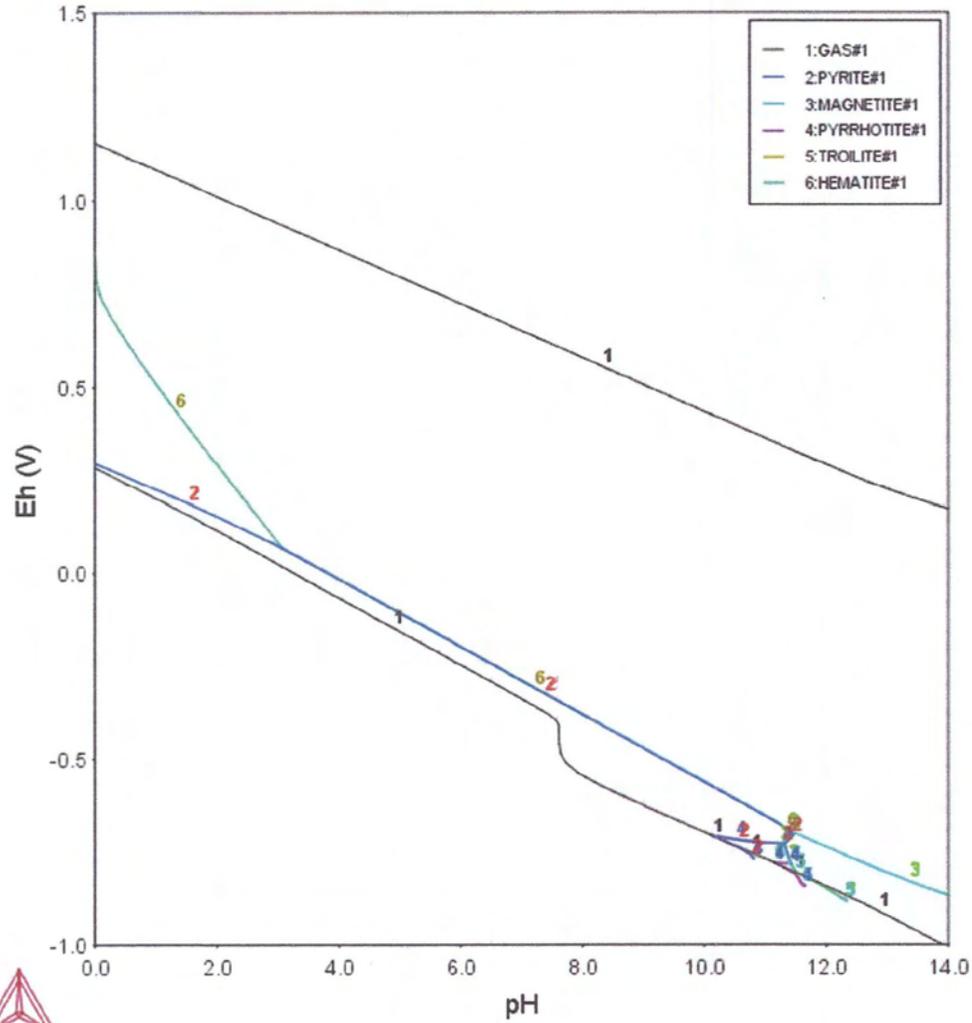


Fig 40: Fe in 1 kg of H2O with 5% H<sub>2</sub>S at 90°C

1 gr Fe in 1 Kg H2O-5% H2S (T=90 C)

2016.02.26.12.31.17  
 PAQ2: H2O, H+1, ZE, FE, H2S  
 P=1E5, T=363.15, B(H2O)=1000., N(Fe)=1.79067E-2, N(H2S)=0.146732

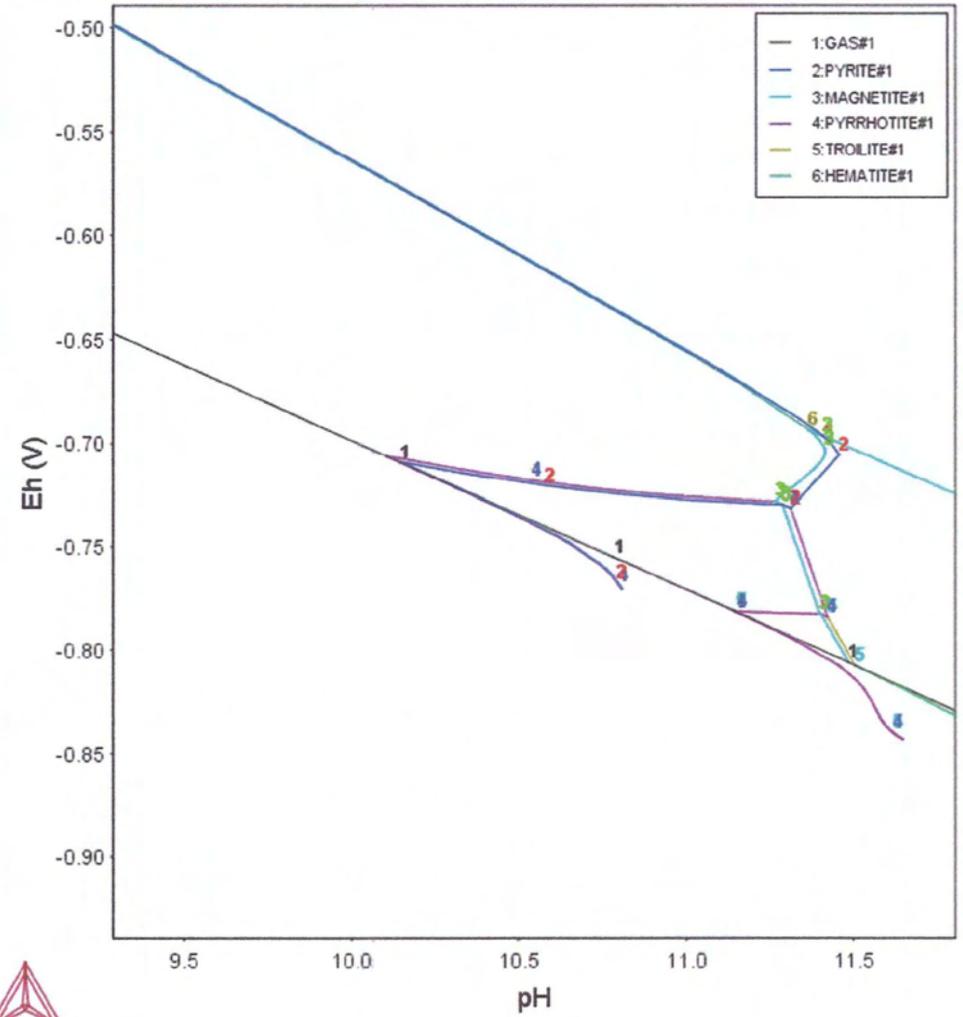


Fig 39: Fe in 1 kg of H2O with 5% H<sub>2</sub>S at 90°C-Zoom-In

# Fe-SULPHUR INCREASES

1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=25 C)

2016.02.22.10.33.54

FE, H+1, H<sub>2</sub>O, S, ZE

T=298.15, P=1E5, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(S)=1.55958E-2 25 C 1 bar .017907mFE .015596mS

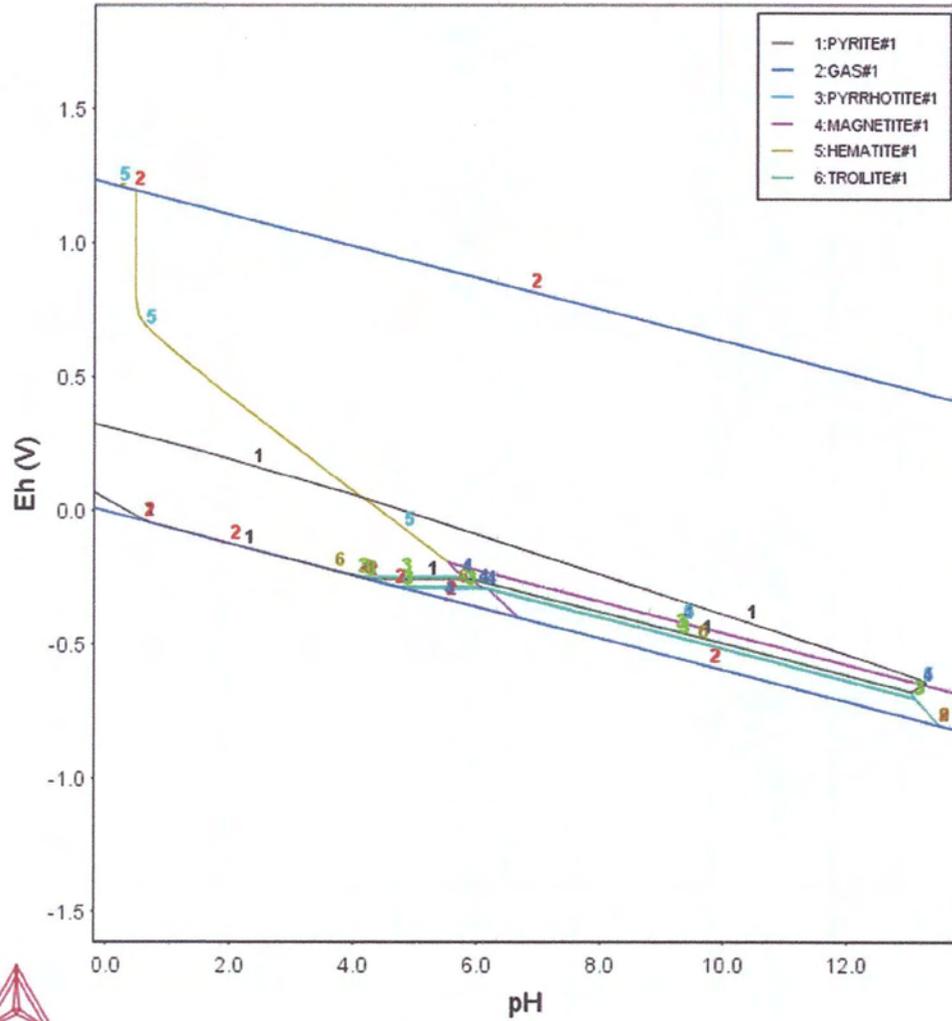


Fig 42: Fe in 1 kg of H<sub>2</sub>O with 5% S at 25°C

1 gr Fe in 1 Kg H<sub>2</sub>O-15% S (T=25 C)

2016.02.22.12.17.57

FE, H+1, H<sub>2</sub>O, S, ZE

T=298.15, P=1E5, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(S)=0.935746

25 C 1 bar .017907mFE .46787mS

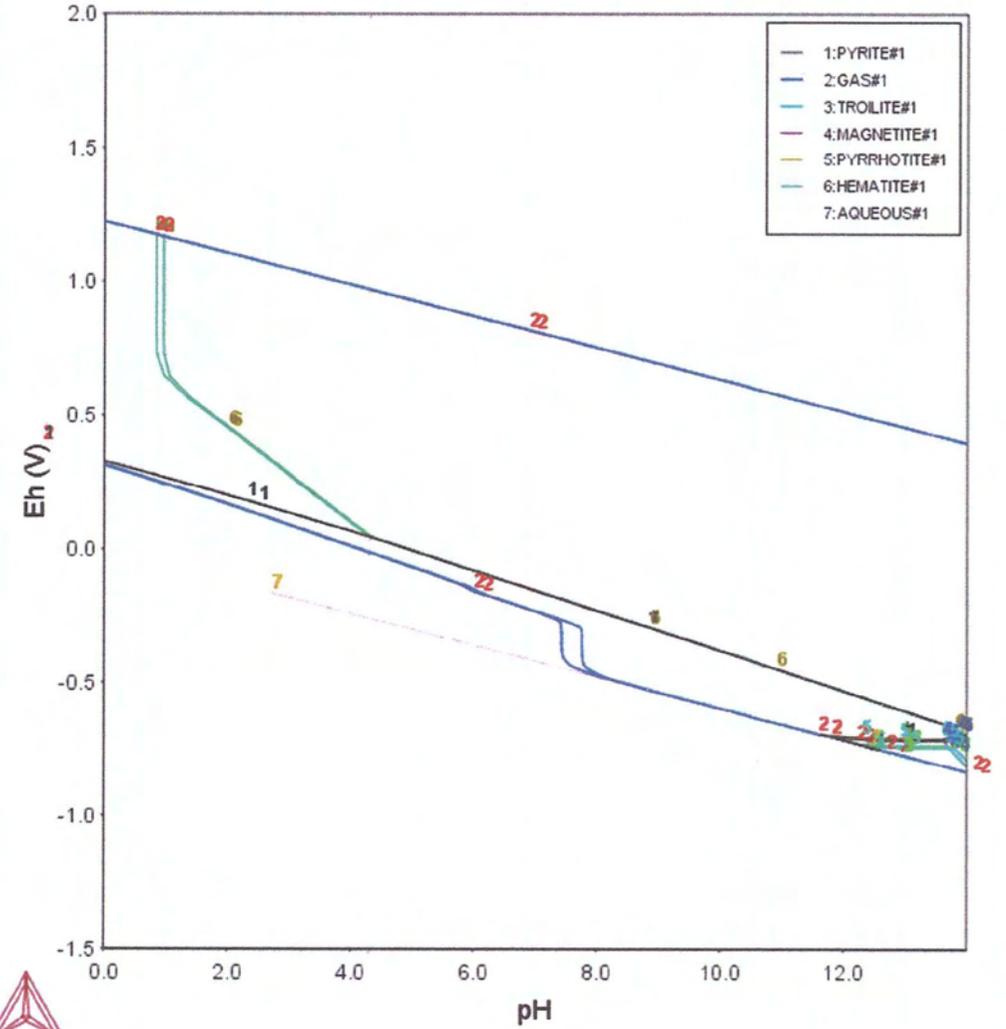


Fig 41: Fe in 1 kg of H<sub>2</sub>O with 15% S at 25°C

The diagrams above differ from the simplified Pourbaix diagram of Fe in water. If the working environment contains sulphur (S) or hydrogen sulphide (H<sub>2</sub>S) there is formation of various metal-sulphides, mainly Pyrite, Pyrrhotite and Troilite is expected.

It is clear that both in S and H<sub>2</sub>S Pourbaix diagrams, iron sulphides coexist with some iron oxides, in particularly with Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and Hematite (Fe<sub>2</sub>O<sub>3</sub>). It is important to be mentioned that the entire range of pH values is covered by stability fields (curves) of corrosion products (either sulphides or oxides) above the phase boundaries of H<sub>2</sub>-Dominated Gas stability line, this indicates that for long exposures the stabilized corrosion scales on the interface Metal-Solution will lead to passivation of the system, even though it is not possible to calculate the Kinetics of the process through Pourbaix diagrams. Another remarkable indication is the shift of the phase boundaries (curves) to the left, as the temperature of the system increases. That indicates the change of the range of the stability field for each corrosion product, for instance the thermodynamically stable region of Hematite enlarges as the temperature increases, this enlargement indicates bigger activation range of pH and Eh, where Hematite is likely growing up.



In comparison with the simplified Fe-H<sub>2</sub>O system, there isn't uncovered pH-Eh field, where Fe will eventually completely dissolve into the aqueous solution phase, that definitely causes a delay for the corrosion process of the system in the presence of sulphur.

Regarding to the Sulphur increase from 5% to 15% the stability curves of Troilite Magnetite and Pyrrhotite are shifted to the right towards the alkaline region of the aqueous solution. In general, the two diagrams do slightly differ and the phase boundaries of the gas remain steady.

# Pourbaix of P5-H<sub>2</sub>O-5% S

1 gr P5 steel in 1 Kg H<sub>2</sub>O-5% S (T=25 C)

2016.02.23.11.19.24  
 CR, FE, H+1, H<sub>2</sub>O, S, ZE  
 T=298.15, P=1E5, B(H<sub>2</sub>O)=1000., N(CR)=9.61612E-4, N(Fe)=1.70108E-2, N(S)=0.155958  
 25 C 1 bar 9.6161E-04mCR .017011mFE .15596mS

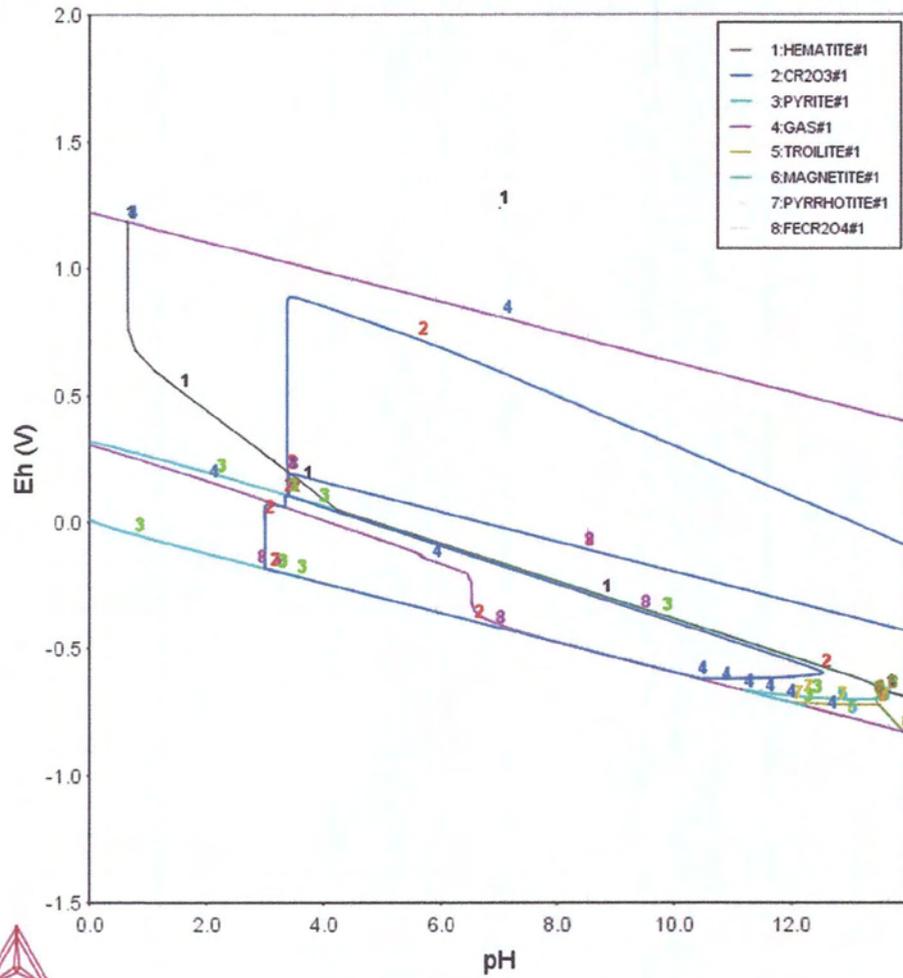


Fig 44: P5 in 1 kg of H<sub>2</sub>O with 5% S at 25°C

1 gr P5 steel in 1 Kg H<sub>2</sub>O-5% S (T=60 C)

2016.02.23.10.23.23  
 PAQ2: H<sub>2</sub>O, H+1, ZE, FE, CR, S  
 P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.70108E-2, N(CR)=9.6163E-4, N(S)=0.155958

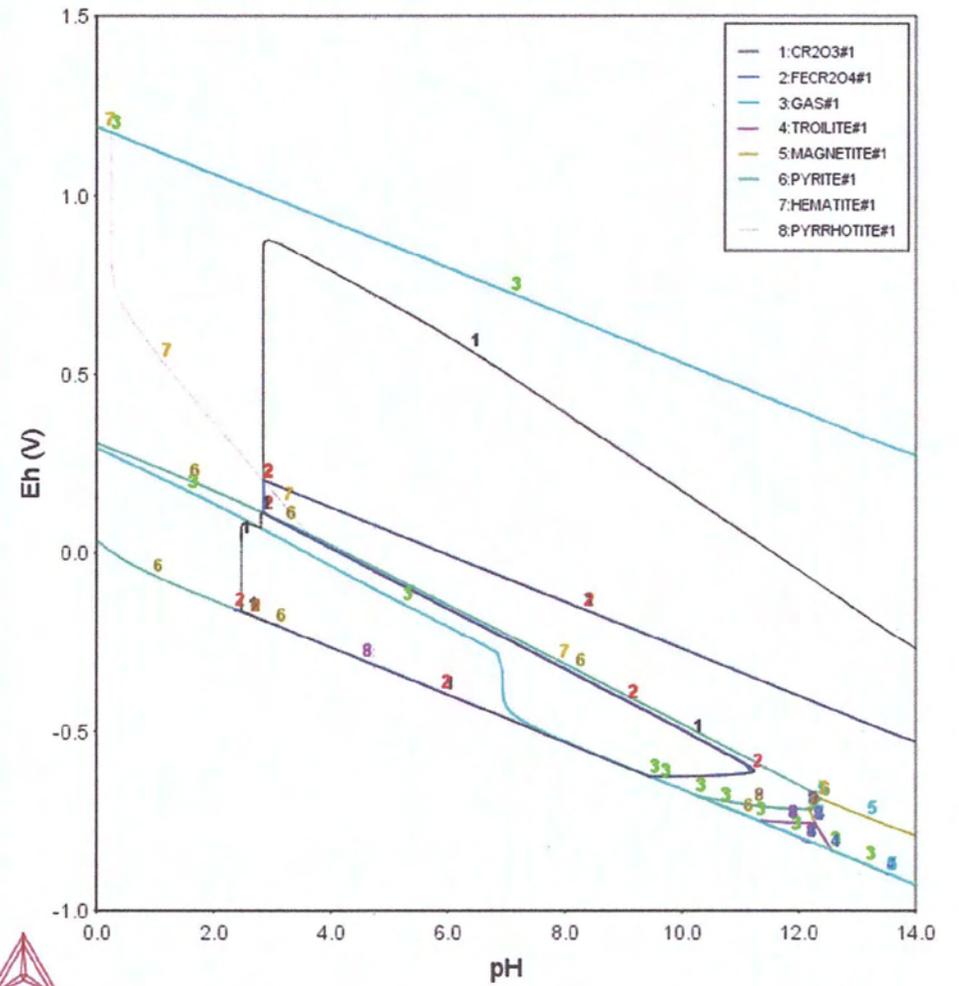


Fig 43: P5 in 1 kg of H<sub>2</sub>O with 5% S at 60°C

1 gr P5 steel in 1 Kg H2O-5% S (T=90 C)

2016.02.23.10.39.50

PAQ2: H2O, H+1, ZE, FE, CR, S

P=1E5, T=363.15, B(H2O)=1000., N(Fe)=1.70108E-2, N(CR)=9.61626E-4, N(S)=0.155958

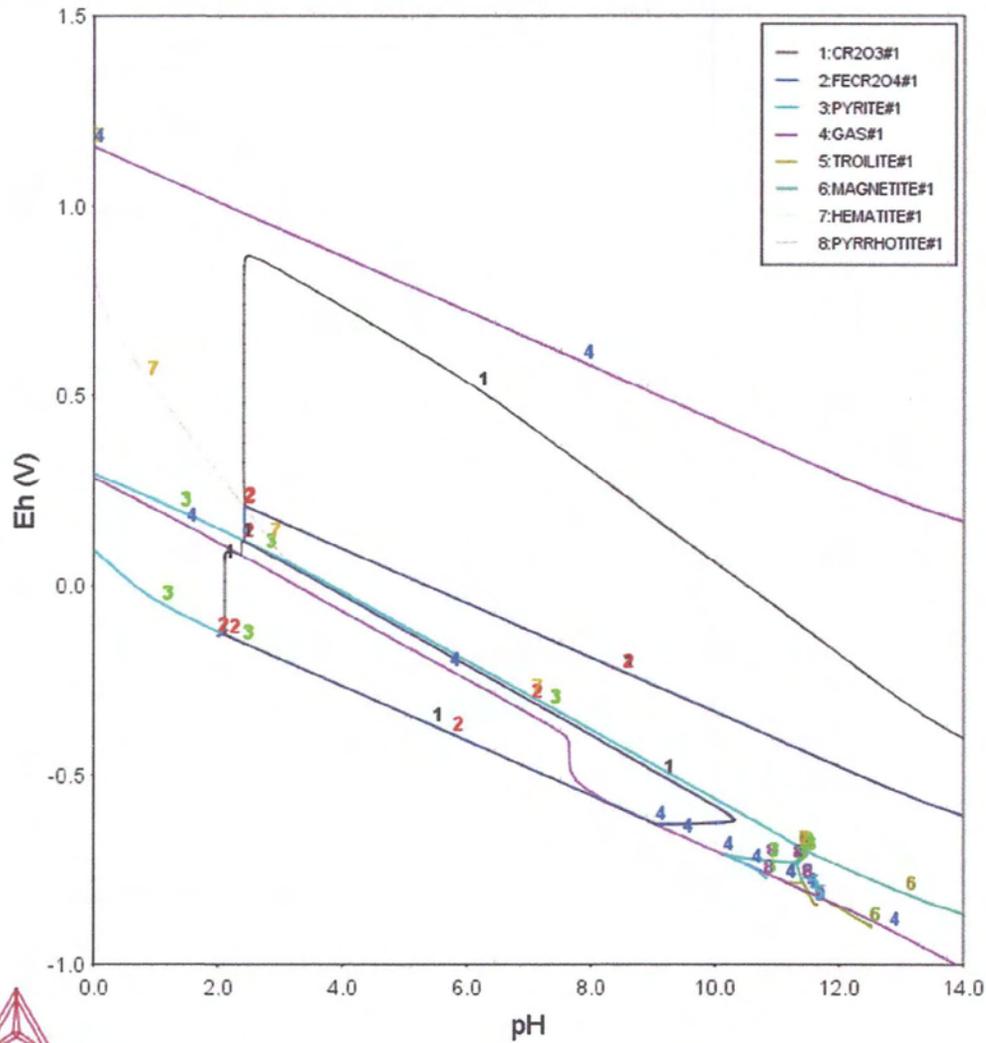


Fig 45: P5 in 1 kg of H2O with 5% S at 90°C

1 gr P5 steel in 1 Kg H2O-5% S (T=90 C)

2016.02.23.10.39.50

PAQ2: H2O, H+1, ZE, FE, CR, S

P=1E5, T=363.15, B(H2O)=1000., N(Fe)=1.70108E-2, N(CR)=9.61626E-4, N(S)=0.155958

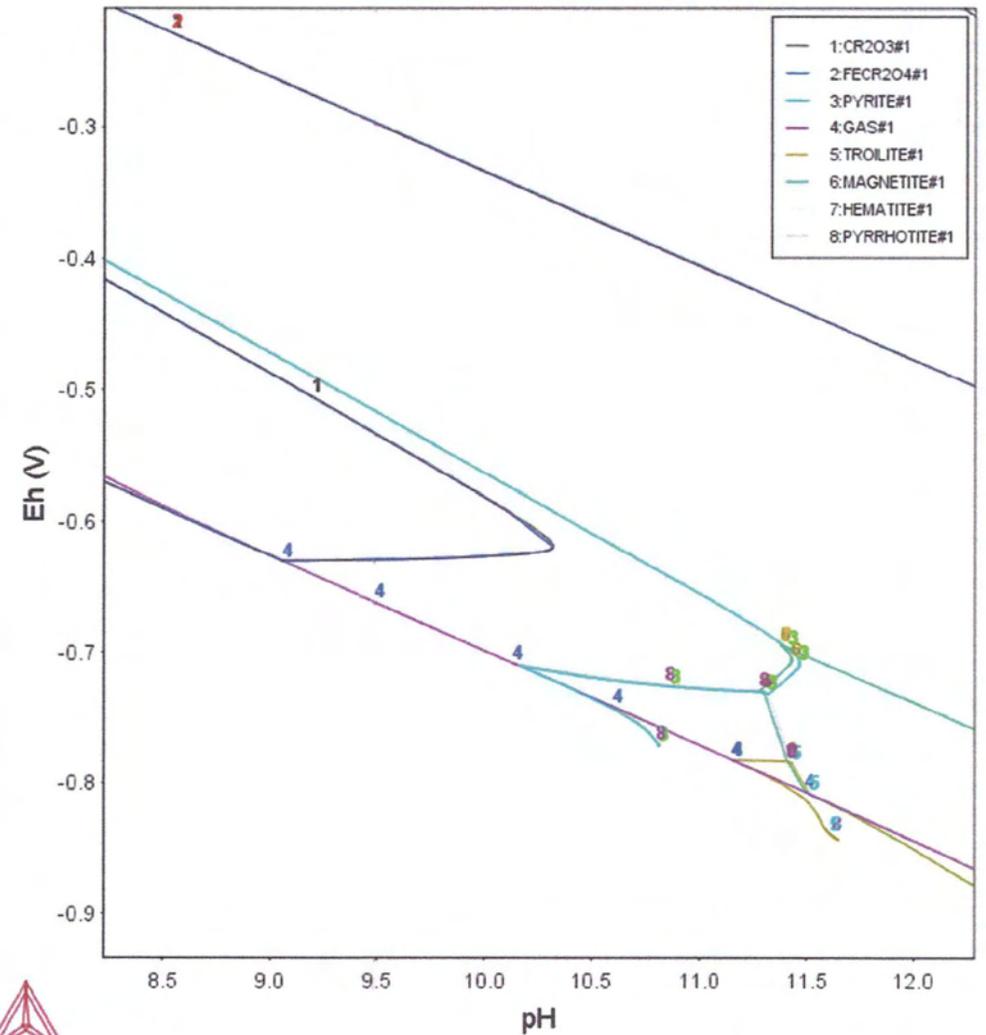


Fig 46: P5 in 1 kg of H2O with 5% S at 90°C -Zoom-In

# Pourbaix of P5-H<sub>2</sub>O-5% H<sub>2</sub>S

1 gr P5 steel in 1 kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=25)

2016.03.16.10.10.00

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, H<sub>2</sub>S1

P=1E5, T=298.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.70108E-2, N(Cr)=9.61636E-4, N(H<sub>2</sub>S1)=0.146732

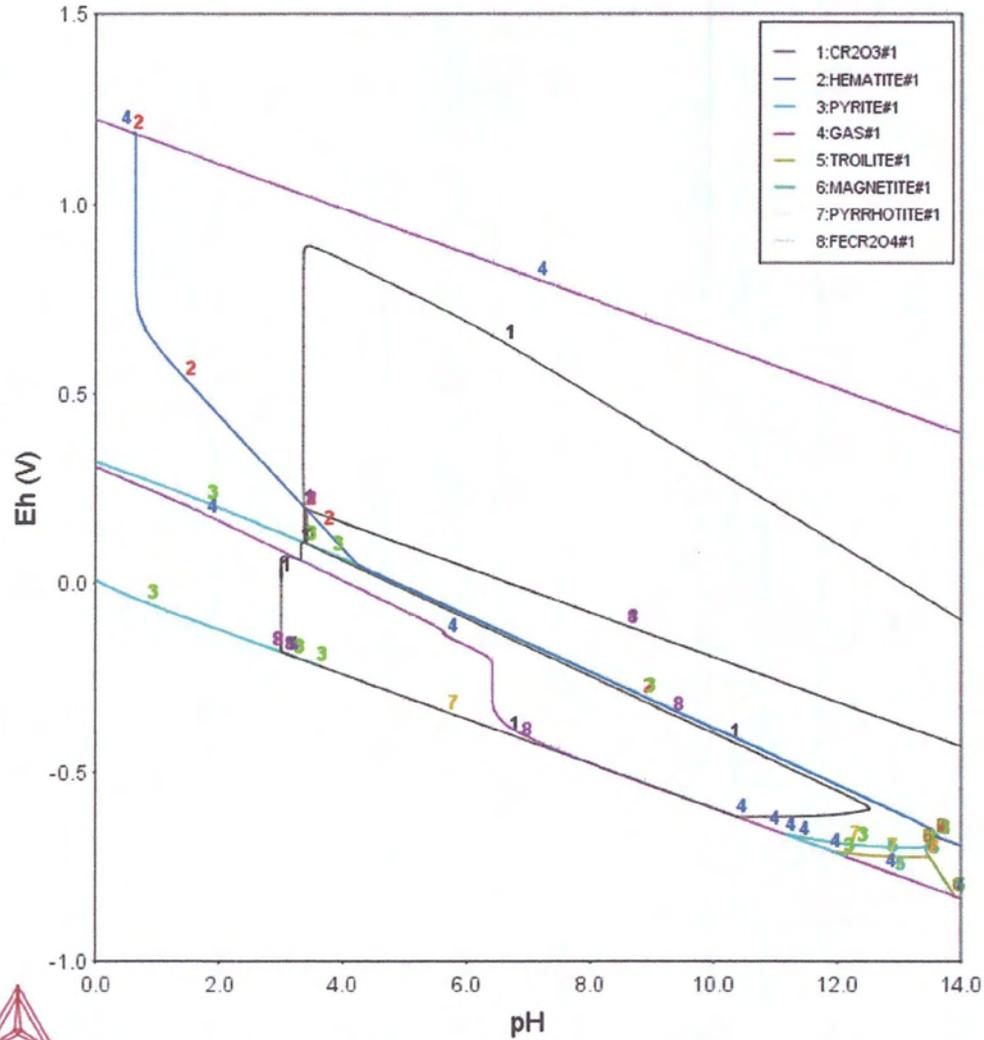


Fig 48: P5 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 25°C

1 gr P5 steel in 1 kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=60)

2016.03.16.10.26.10

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, H<sub>2</sub>S1

P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.70108E-2, N(Cr)=9.6163E-4, N(H<sub>2</sub>S1)=0.146732

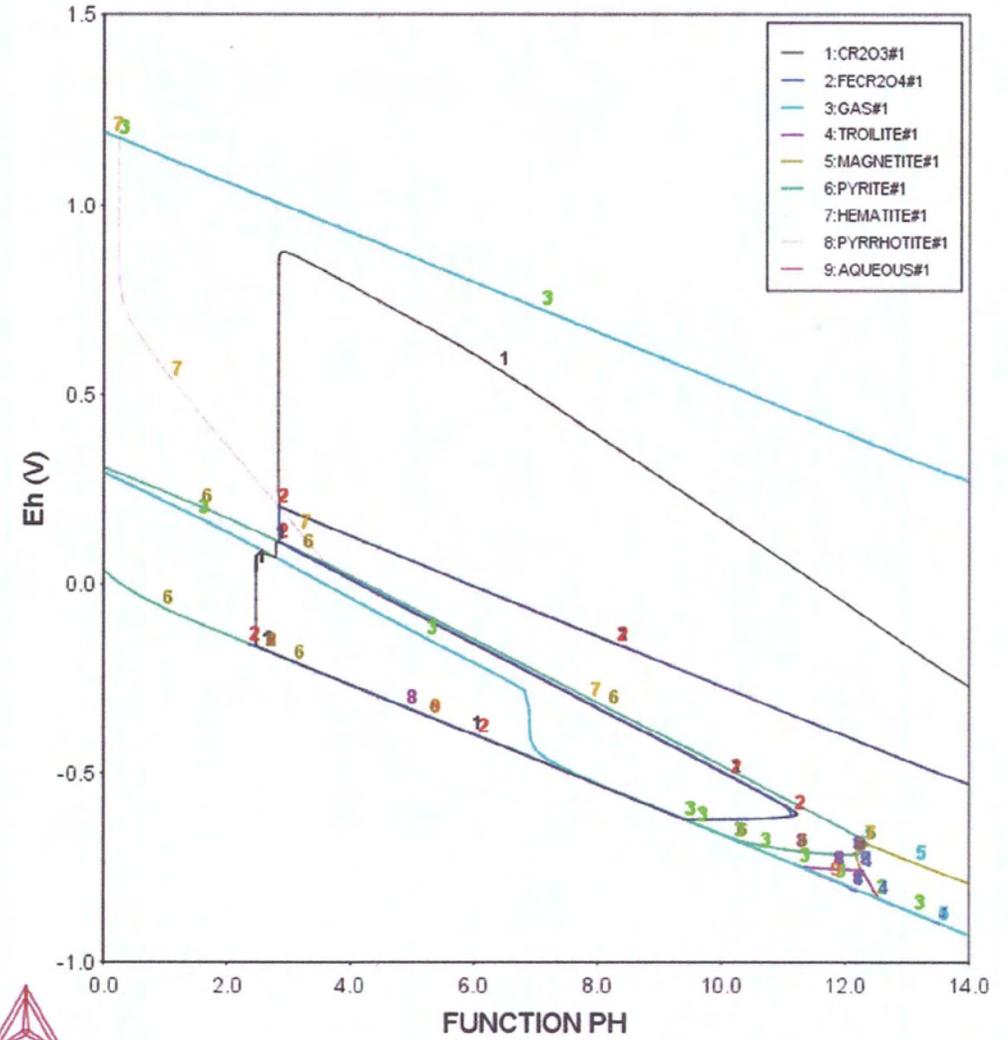


Fig 47: P5 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 60°C

1 gr P5 steel in 1 kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=90)

2016.03.16.10.57.49

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, H<sub>2</sub>S<sup>1</sup>

P=1E5, T=363.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.70108E-2, N(Cr)=9.61626E-4, N(H<sub>2</sub>S<sup>1</sup>)=0.146732

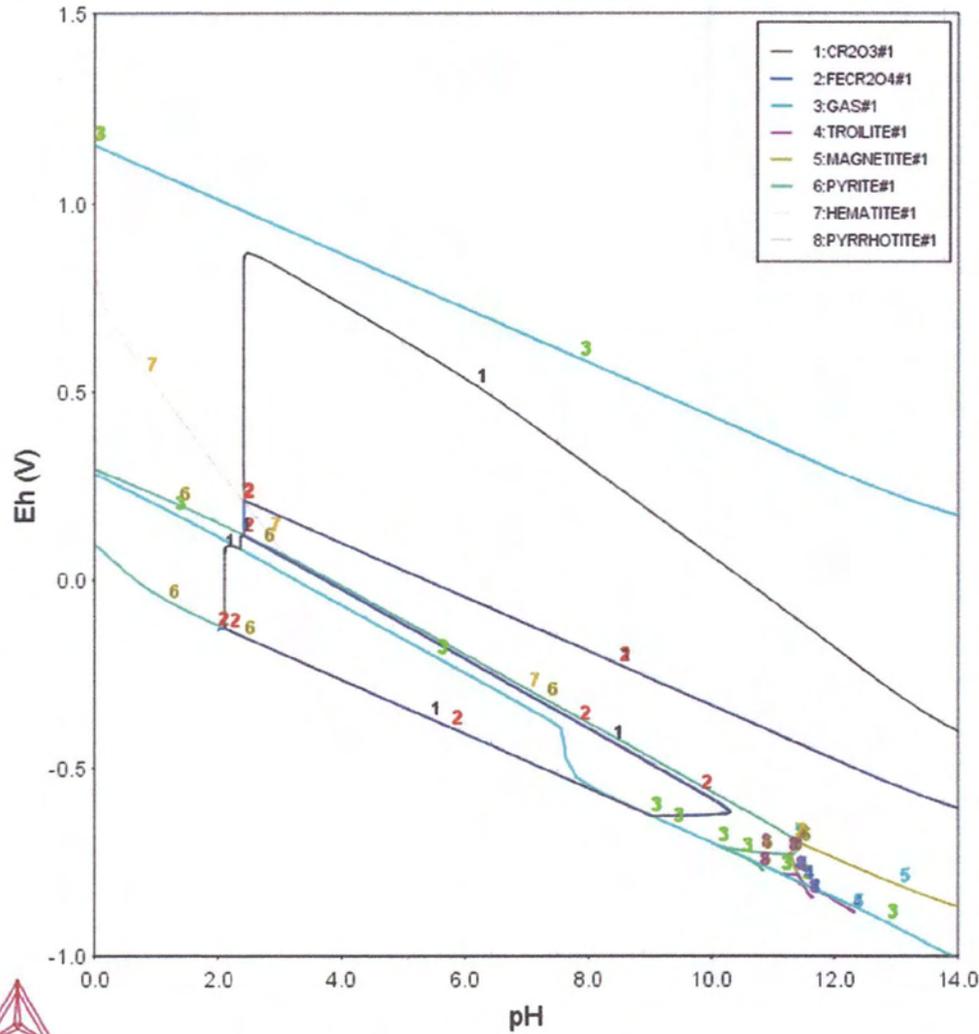


Fig 49: P5 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 90°C

1 gr P5 steel in 1<sup>3</sup>kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=90)

2016.03.16.10.57.49

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, H<sub>2</sub>S<sup>1</sup>

P=1E5, T=363.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.70108E-2, N(Cr)=9.61626E-4, N(H<sub>2</sub>S<sup>1</sup>)=0.146732

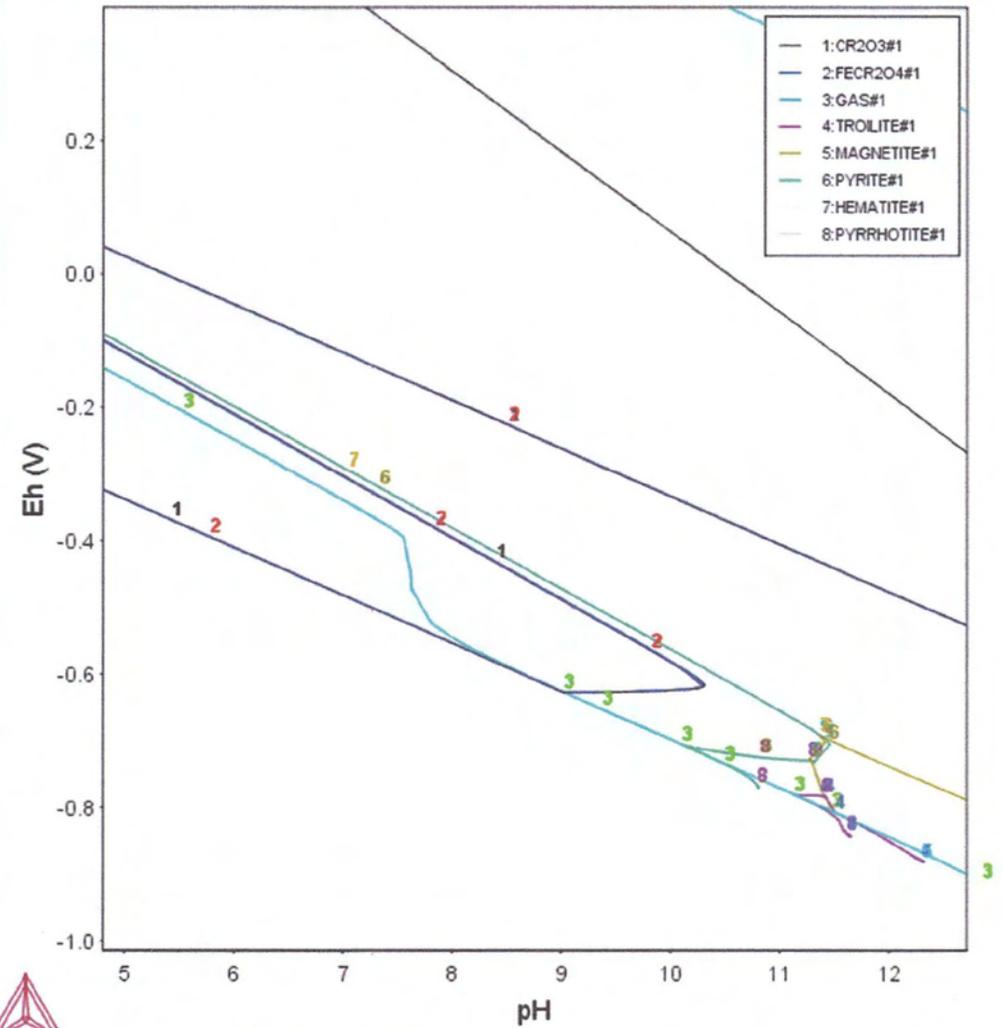


Fig 50: P5 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 90°C-Zoom-In

The P5 stainless steel contains approximately 4-6% in Chromium (Cr). Thus, introducing Cr into the interaction system causes the formation of  $\text{FeCr}_2\text{O}_4$  and  $\text{Cr}_2\text{O}_3$ , both of those compounds are thermodynamically stable and coexist in the diagrams with the other Sulphide products that have been mentioned above. Of course, once again all the curves shift to the left as the temperature is increasing.

At relatively high electrochemical potentials and for the majority of the pH range the chromium oxide ( $\text{Cr}_2\text{O}_3$ ) may be reached as a product on the scale. On the contrary, at low Eh, the corrosion product depends more from the pH of the solution. In P5 Pourbaix diagrams also there is nowhere bare field without a stable phase.

It is also observed, the same shift of the equilibrium curves to left when the temperature increases.

# Pourbaix of P9-H<sub>2</sub>O-5% S

1 gr P9 steel in 1 Kg H<sub>2</sub>O-5% S (T=25 C)

2016.02.23.11.01.06

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, S

P=1E5, T=298.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.62945E-2, N(CR)=1.73093E-3, N(S)=0.155958

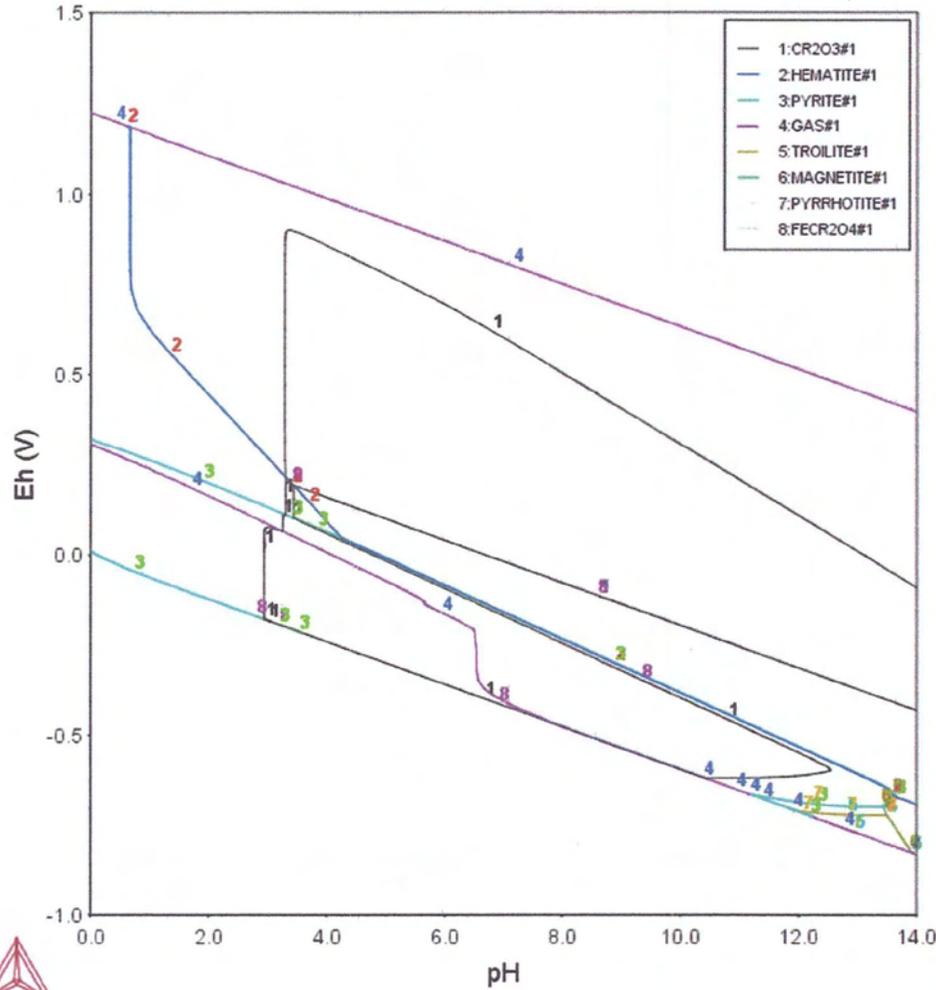


Fig 51: P9 in 1 kg of H<sub>2</sub>O with 5% S at 25°C

1 gr P9 steel in 1 Kg H<sub>2</sub>O-5% S (T=60 C)

2016.02.23.11.37.25

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, S

P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.62945E-2, N(CR)=1.73092E-3, N(S)=0.155958

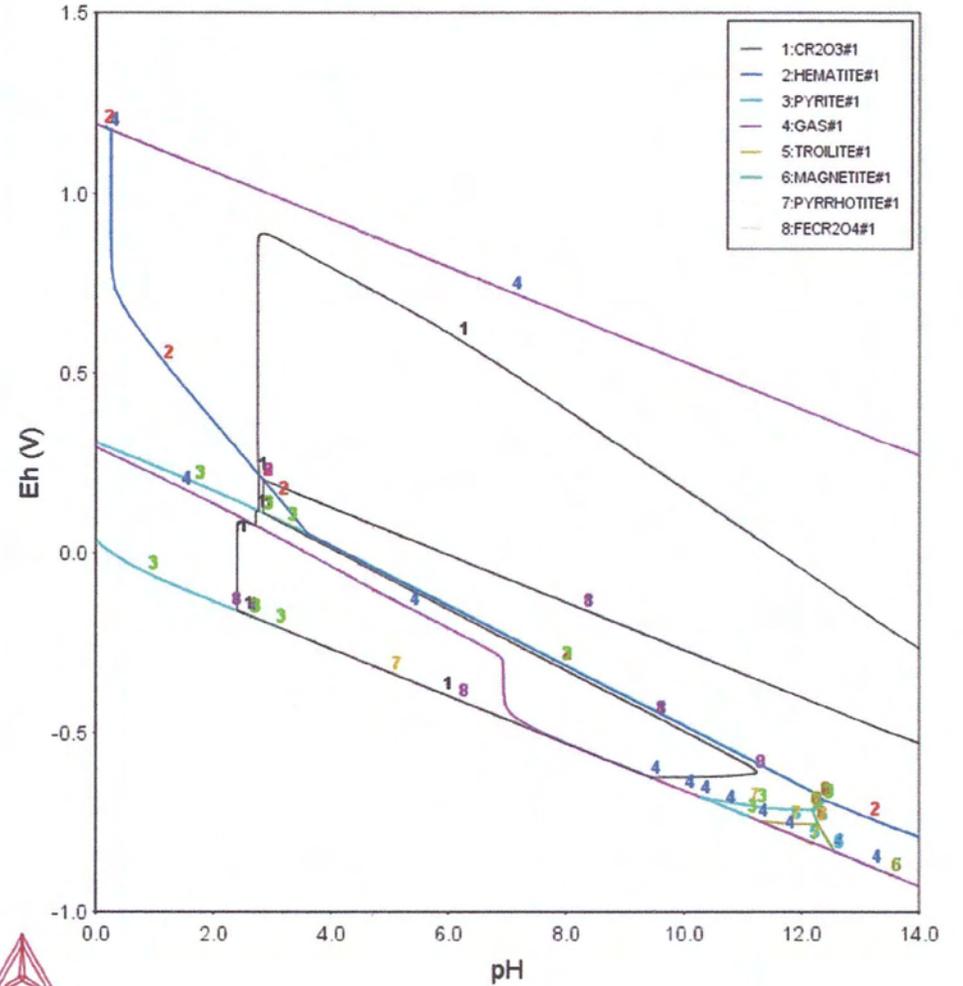


Fig 52: P9 in 1 kg of H<sub>2</sub>O with 5% S at 60°C

1 gr P9 steel in 1 Kg H2O-5% S (T=90 C)

2016.02.26.11.23.58

PAQ2: H2O, H+1, ZE, FE, CR, S

P=1E5, T=363.15, B(H2O)=1000., N(FE)=1.62945E-2, N(CR)=1.73092E-3, N(S)=0.155958

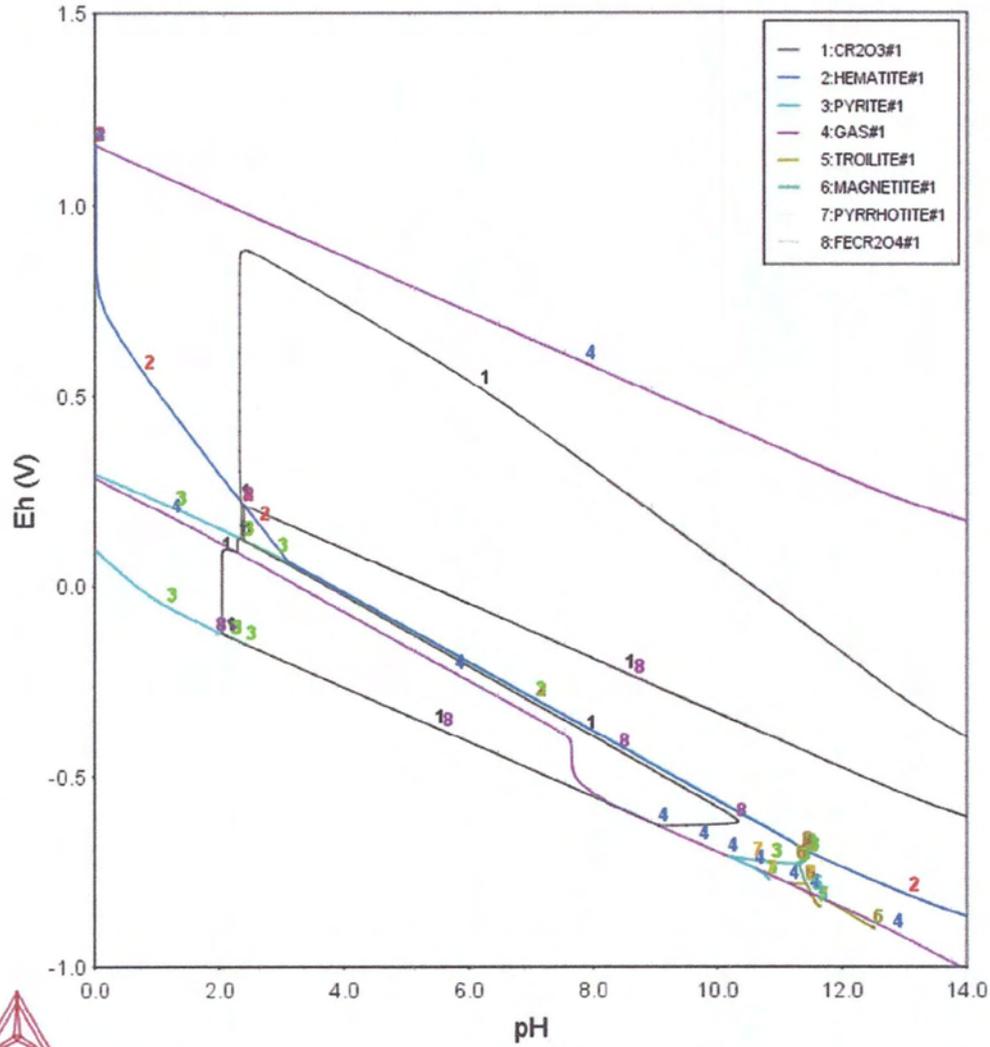


Fig 54: P9 in 1 kg of H2O with 5% S at 90°C

1 gr P9 steel in 1 Kg H2O-5% S (T=90 C)

2016.02.26.11.23.58

PAQ2: H2O, H+1, ZE, FE, CR, S

P=1E5, T=363.15, B(H2O)=1000., N(FE)=1.62945E-2, N(CR)=1.73092E-3, N(S)=0.155958

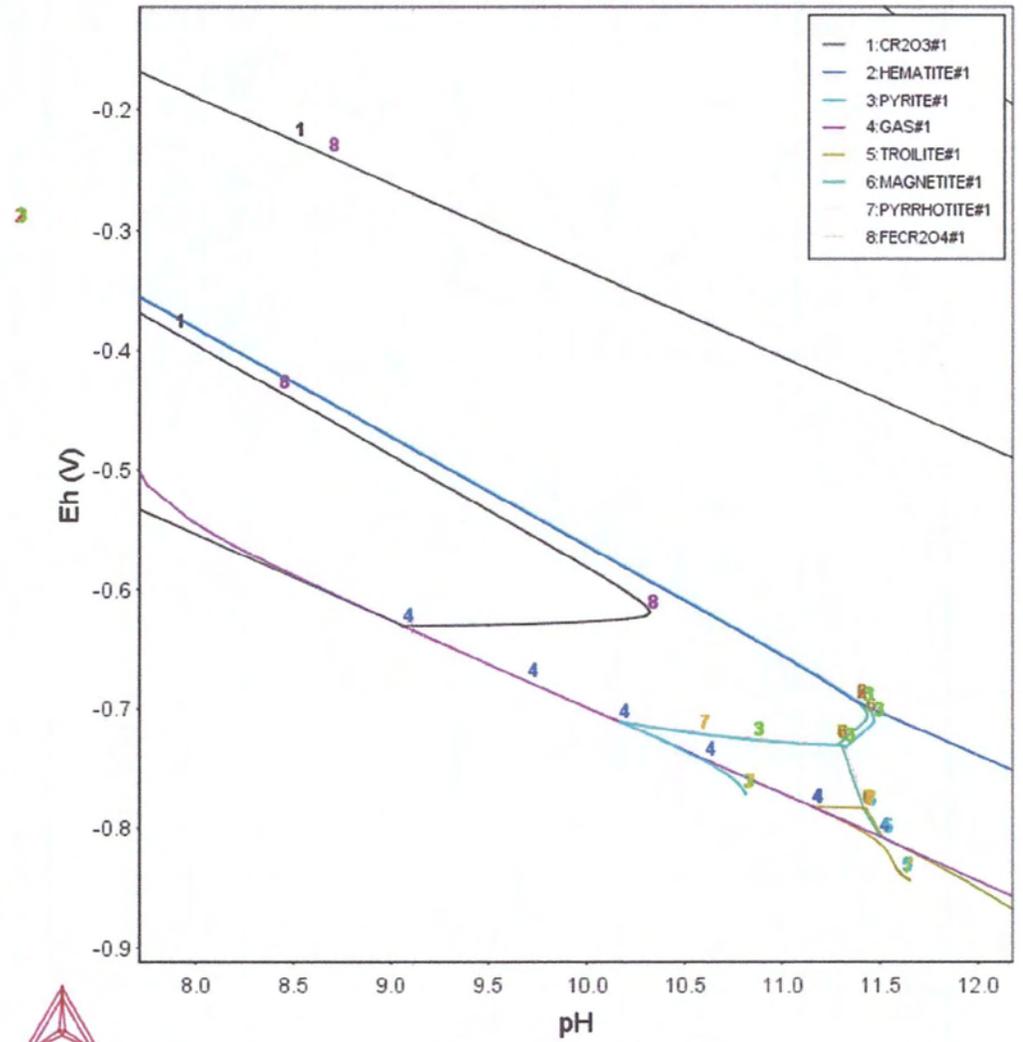


Fig 53: P9 in 1 kg of H2O with 5% S at 90°C -Zoom-In

## Pourbaix of P9-H<sub>2</sub>O-5% H<sub>2</sub>S

1 gr P9 steel in 1 kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=25)

2016.03.16.11.05.41

PAQ2: H<sub>2</sub>O, H+1, ZE, FE, CR, H<sub>2</sub>S1

P=1E5, T=298.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.62945E-2, N(Cr)=1.73093E-3, N(H<sub>2</sub>S1)=0.146732

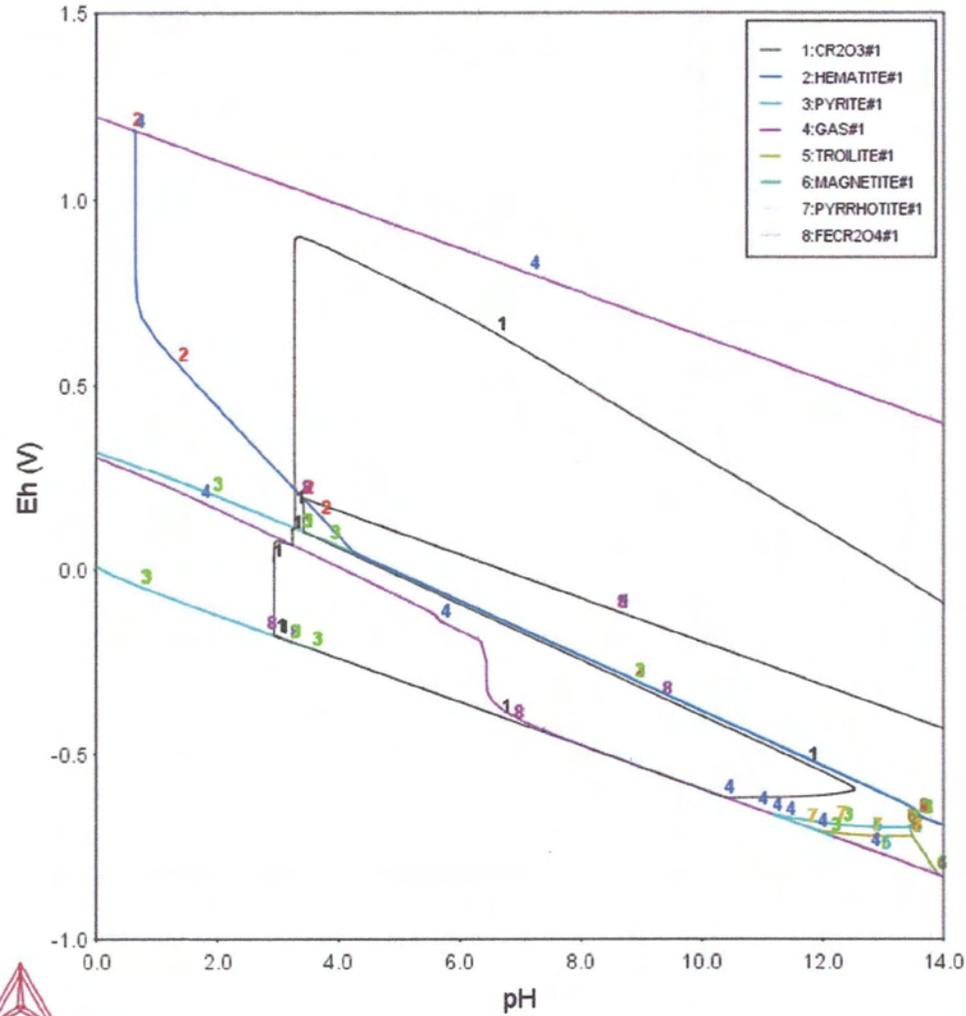


Fig 56: P9 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 25°C

1 gr P9 steel in 1 kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=60)

2016.03.16.11.47.53

PAQ2: H<sub>2</sub>O, H+1, ZE, FE, CR, H<sub>2</sub>S1

P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.62945E-2, N(Cr)=1.73092E-3, N(H<sub>2</sub>S1)=0.146732

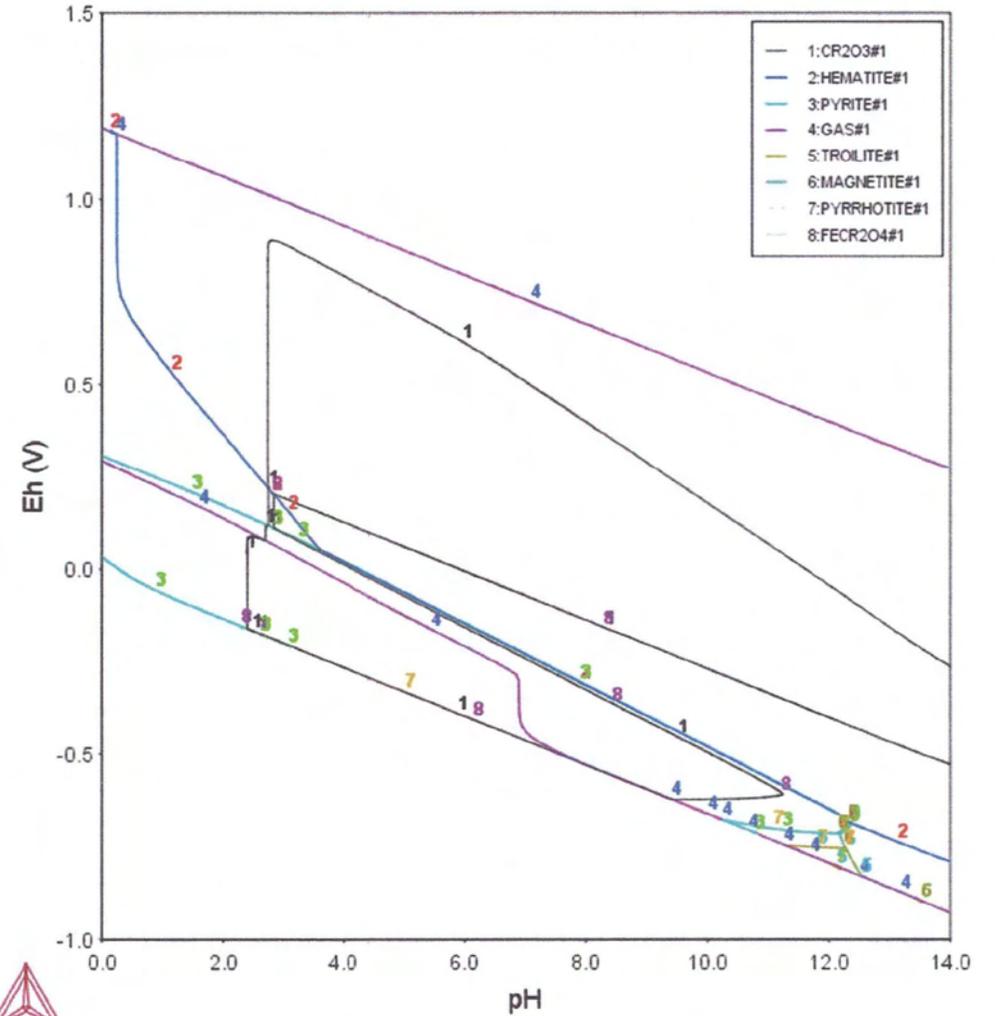


Fig 55: P9 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 60°C

1 gr P9 steel in 1 kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=90)

2016.03.16.12.29.52

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, H<sub>2</sub>S1

P=1E5, T=363.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.62945E-2, N(Cr)=1.73092E-3, N(H<sub>2</sub>S1)=0.146732

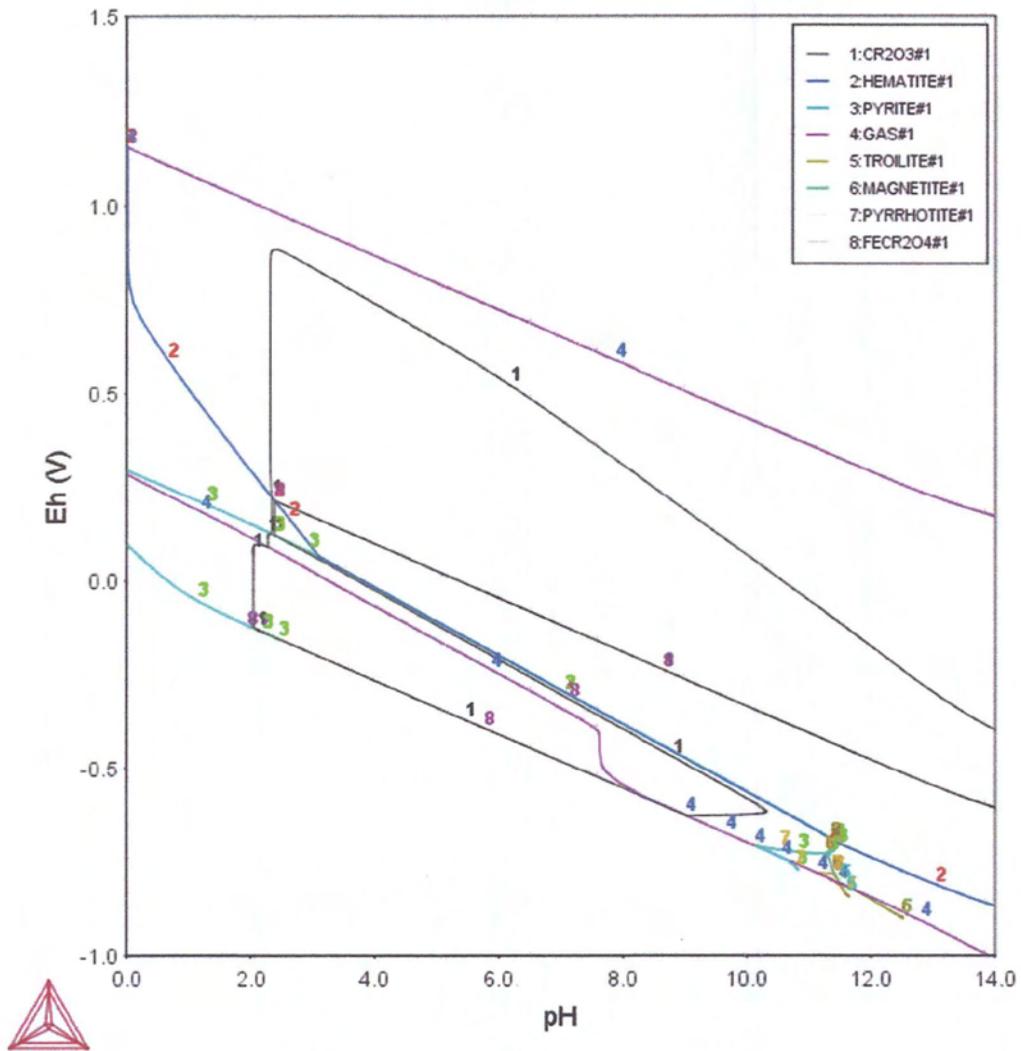


Fig 58: P9 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 90°C

1 gr P9 steel in 1 kg H<sub>2</sub>O-5% H<sub>2</sub>S (T=90)

2016.03.16.12.29.52

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, FE, CR, H<sub>2</sub>S1

P=1E5, T=363.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.62945E-2, N(Cr)=1.73092E-3, N(H<sub>2</sub>S1)=0.146732

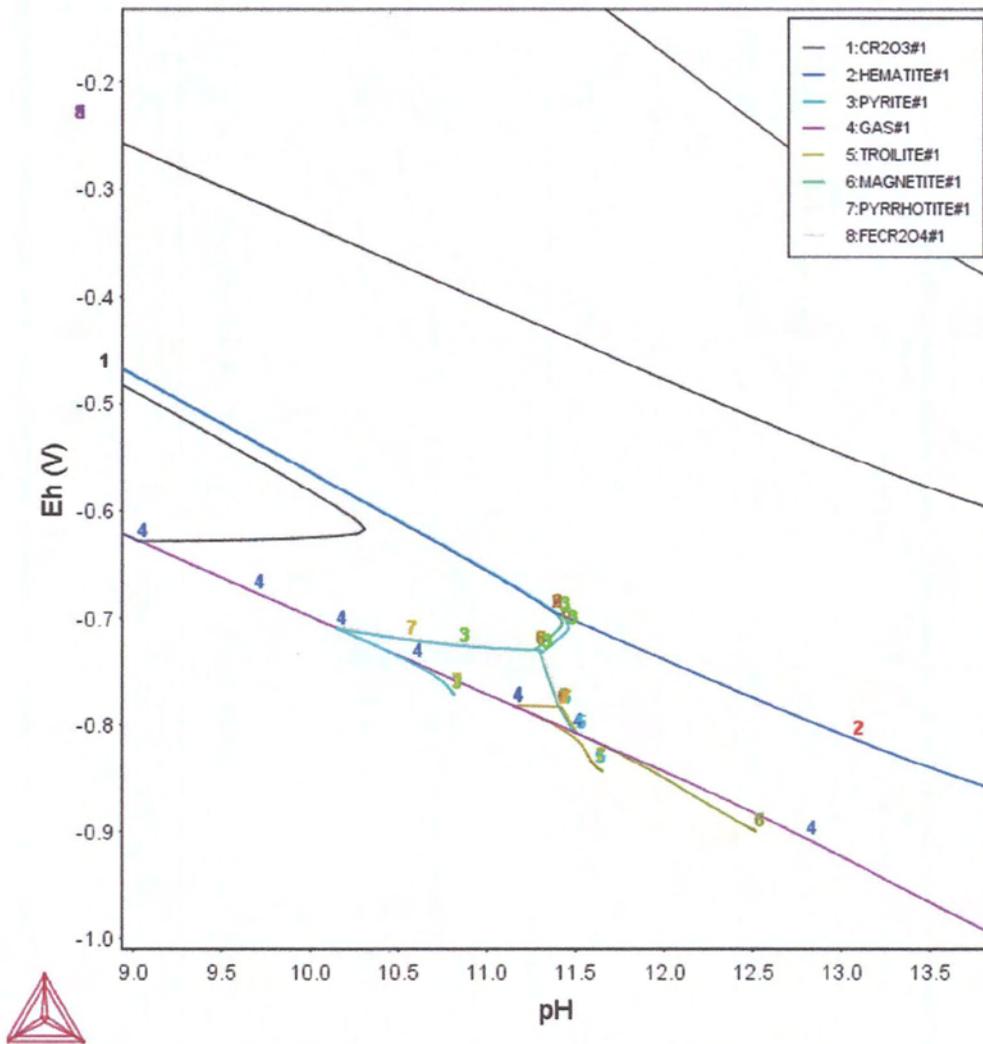


Fig 57: P9 in 1 kg of H<sub>2</sub>O with 5% H<sub>2</sub>S at 25°C -Zoom-In

In Pourbaix diagrams of the P9 steel which contains 8-10 % Cr, one can find the same corrosion products (Sulphides and oxides), like the previous P5 Pourbaix diagrams, in comparison with the P5 diagrams, there is not much that changed except to the percentage contribution of Chromium, that is why the Pourbaix diagrams of these two grades of steel are similar.

In the next section, the comparative diagrams will provide an integrated aspect of the changes that were observed with a detailed study on the diagrammatic schemes.

### 4.3 Results & Discussion

In order to achieve an integrated approach about the parameters that affect Pourbaix diagrams, some comparative diagrams have been constructed by the OriginPro software and are mainly divided into 2 regions:

- Low pH Solutions (Acidic Solutions)
- High pH Solutions (Alkaline Solutions)

The study focuses to the temperatures, i.e. 25°C, 60°C and 90°C.

The aim of using Pourbaix diagrams in industry is to create design rules against corrosion, for the Fe-H<sub>2</sub>O system, these corrosion control measures are as follows (for a specific point):

1. If the electrode potential is changed in the negative direction to a value below - 0.3 V vs SHE, the iron electrode is forced into a region of immunity. (Cathodic Protection)
2. If the electrode potential is changed in the positive direction to values above - 0.1 V vs SHE, the iron electrode is forced into a region of passivity. (Anodic Protection)
3. If the Ph of the aqueous solution is increased to 7 or higher, the iron electrode will then also reside in a region of passivity.

# Pourbaix Diagram

2015.10.21.13.34.56

FE, H+1, H2O, ZE

T=298.15, P=1E5, B(H2O)=1000., N(FE)=1E-3

25 C 1 bar .001mFE

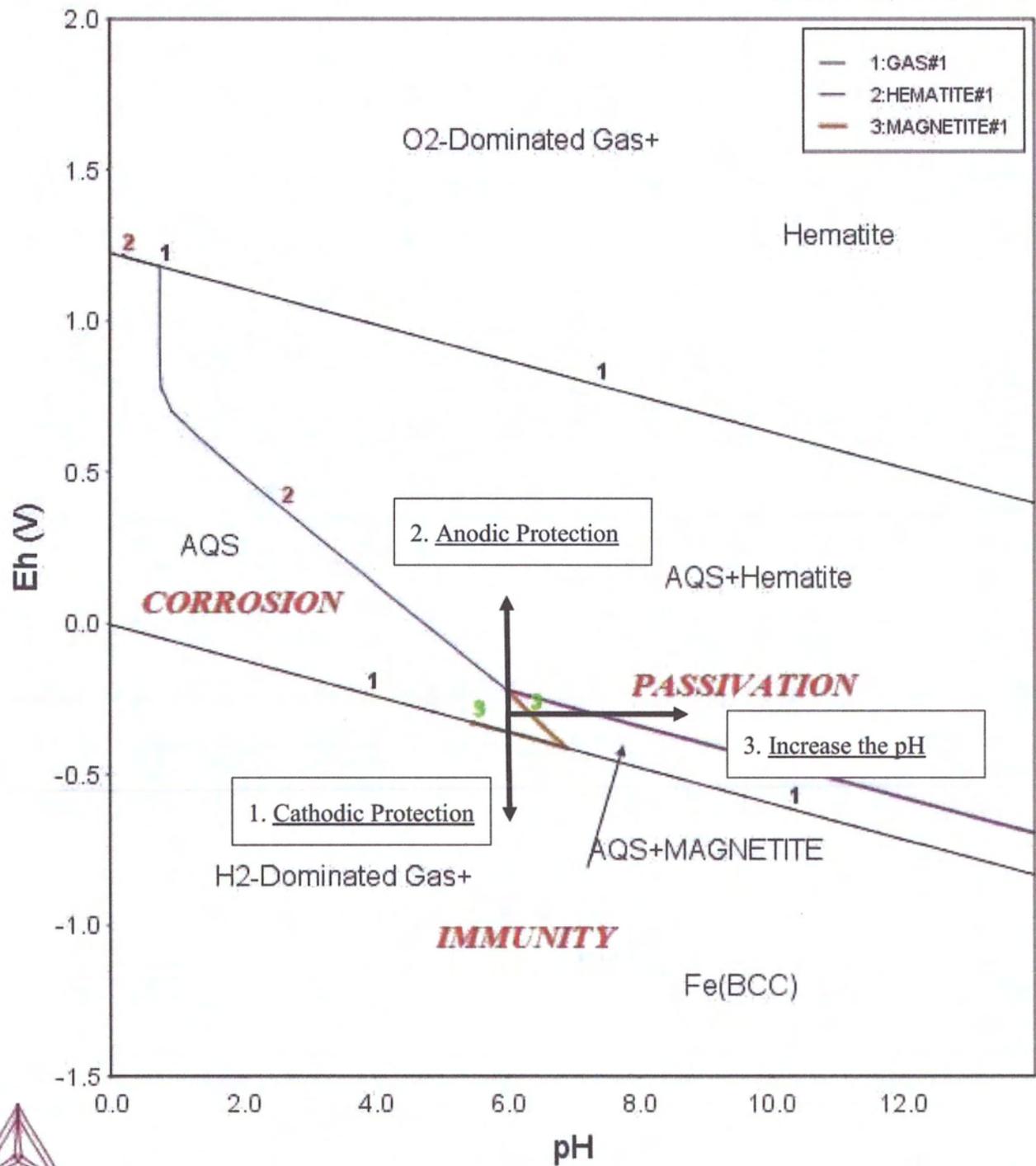


Fig 59: Corrosion Control Measures on the Fe-H<sub>2</sub>O system

When a metal-solution system operates on a certain electrode potential-pH and undergoes corrosion, this Eh is called potential of corrosion ( $E_{corr}$ ).

In this region any stable phase is able to create a protective scale on the interface of metal-solution, thus the electrochemical reactions do not stop.

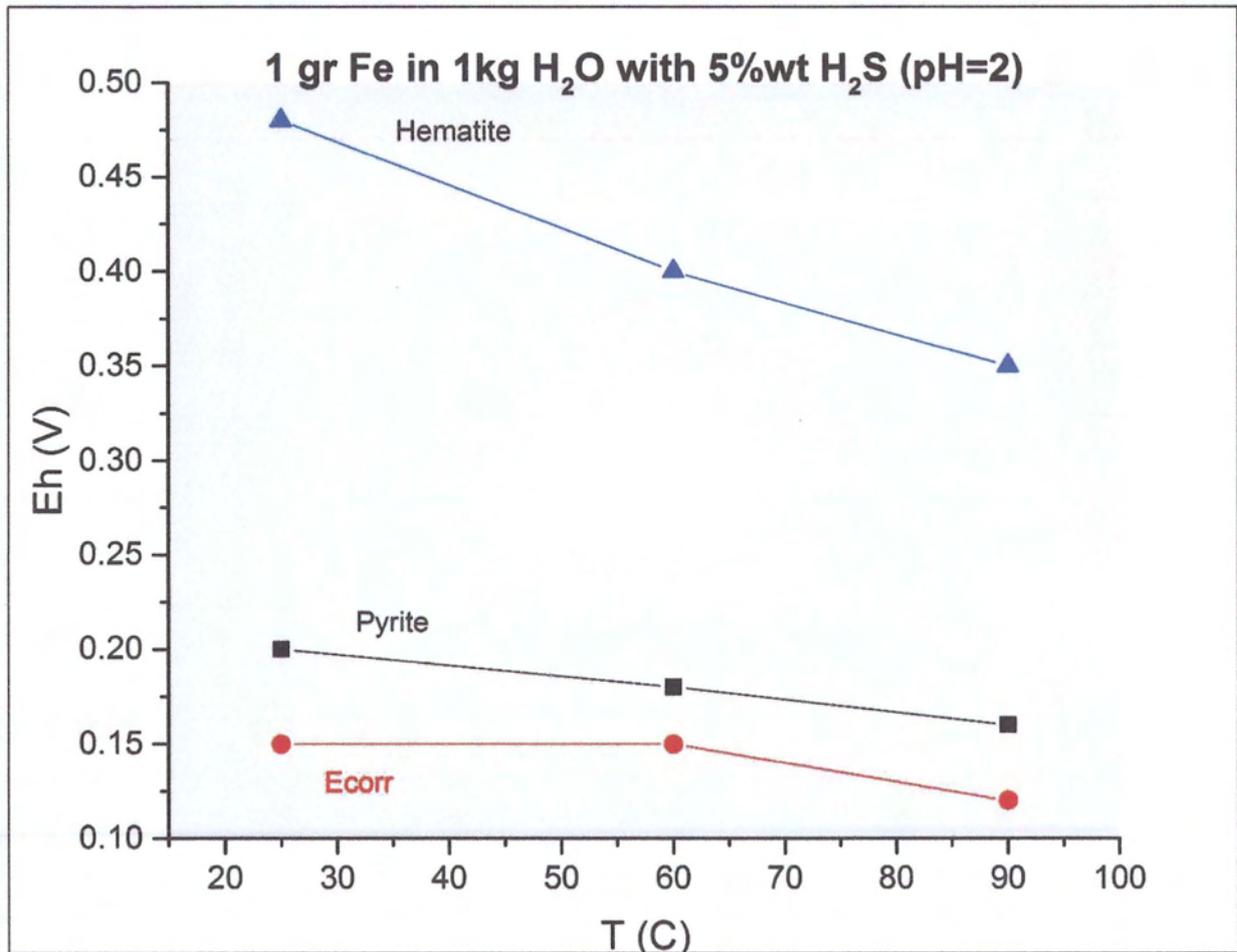


Fig 60: Compounds of Fe in acidic solution

Above is shown the compounds by the change of electrode potential. The  $E_{corr}$  potential is the critical point, below this any electrochemical reaction occurs, thus the system remains in immunity.

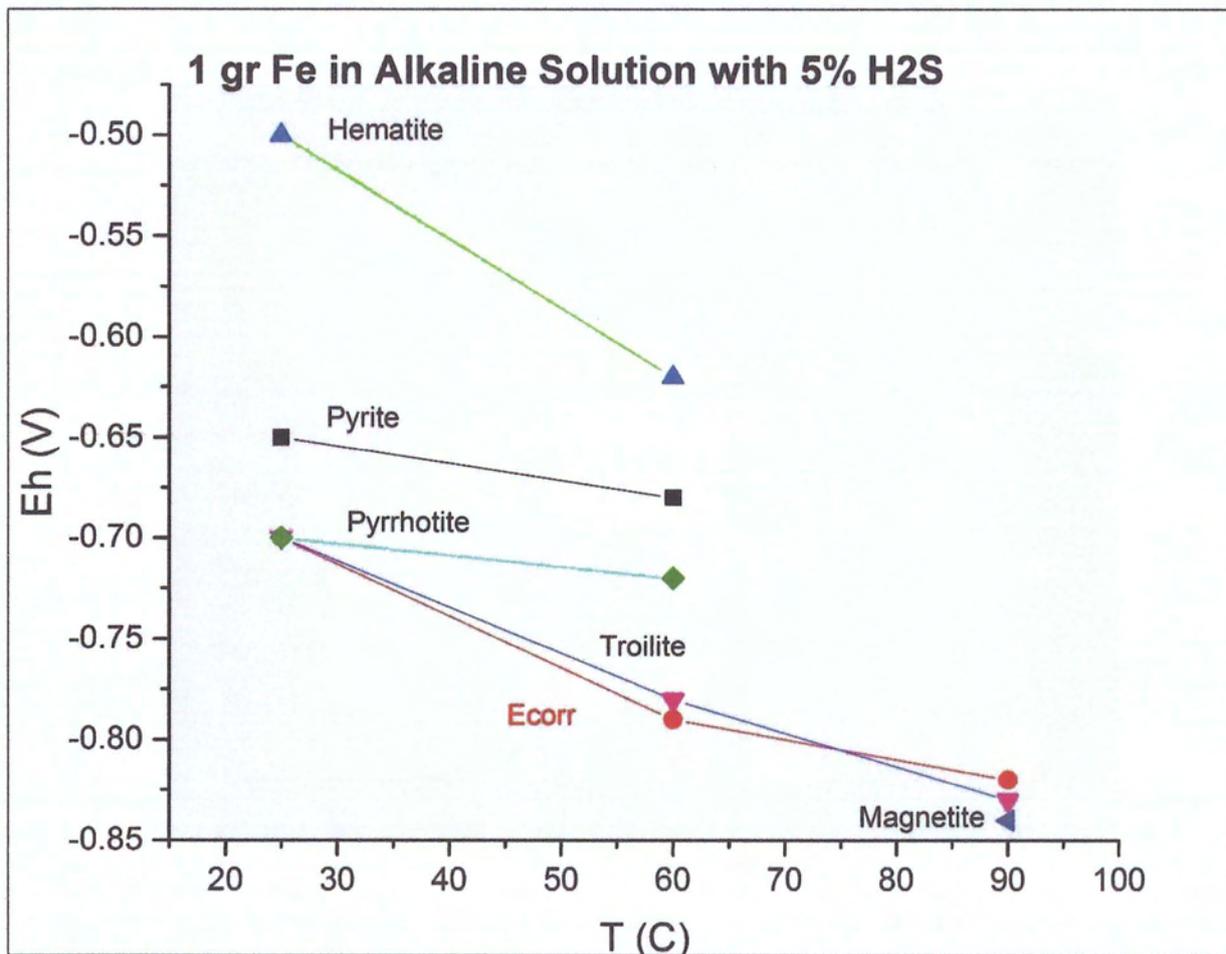
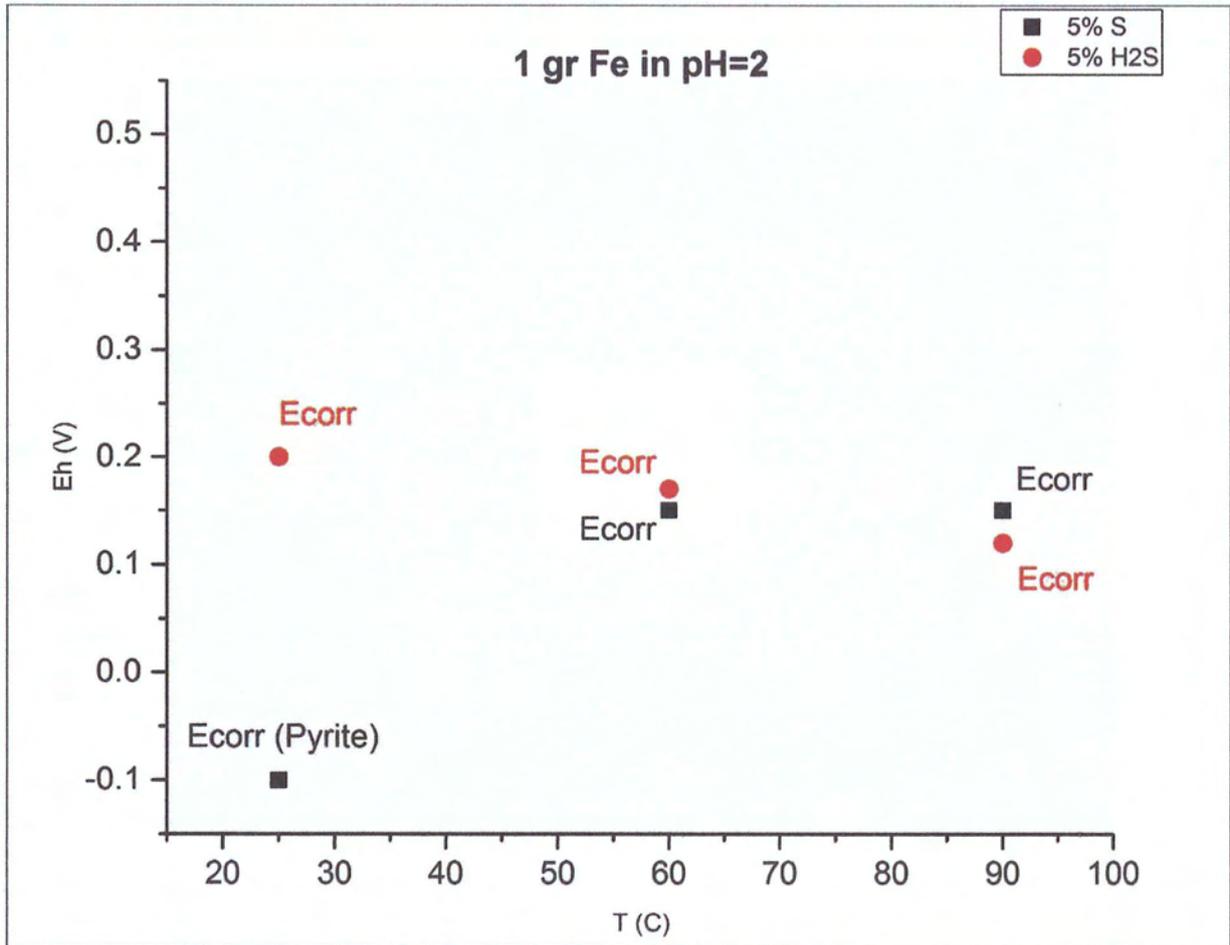


Fig 61: Compounds of Fe in Alkaline Solution

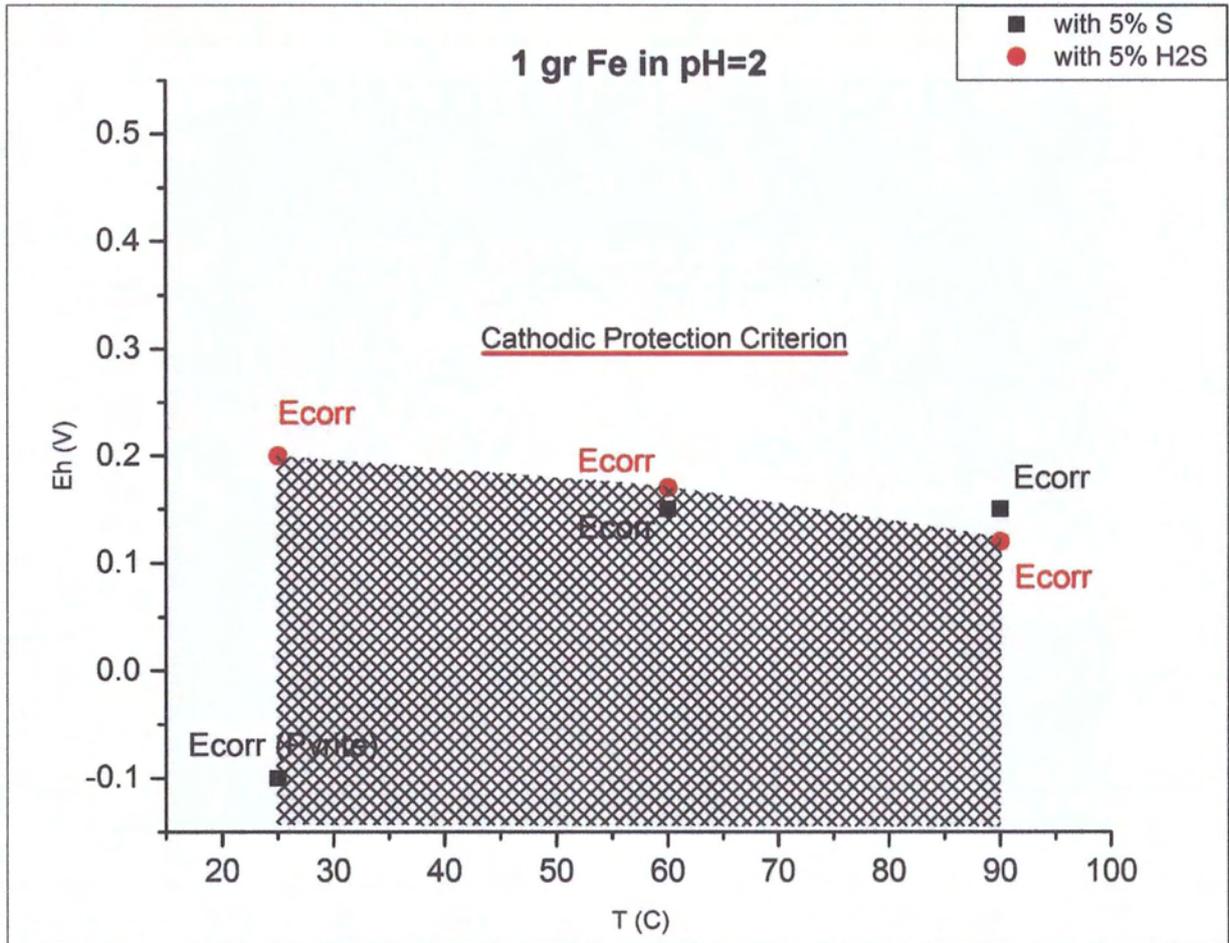
The same happens also for the alkaline solution, but in this case, more products can be found.



*Fig 62: Comparison-Fe with H<sub>2</sub>S & S in Acidic Solution*

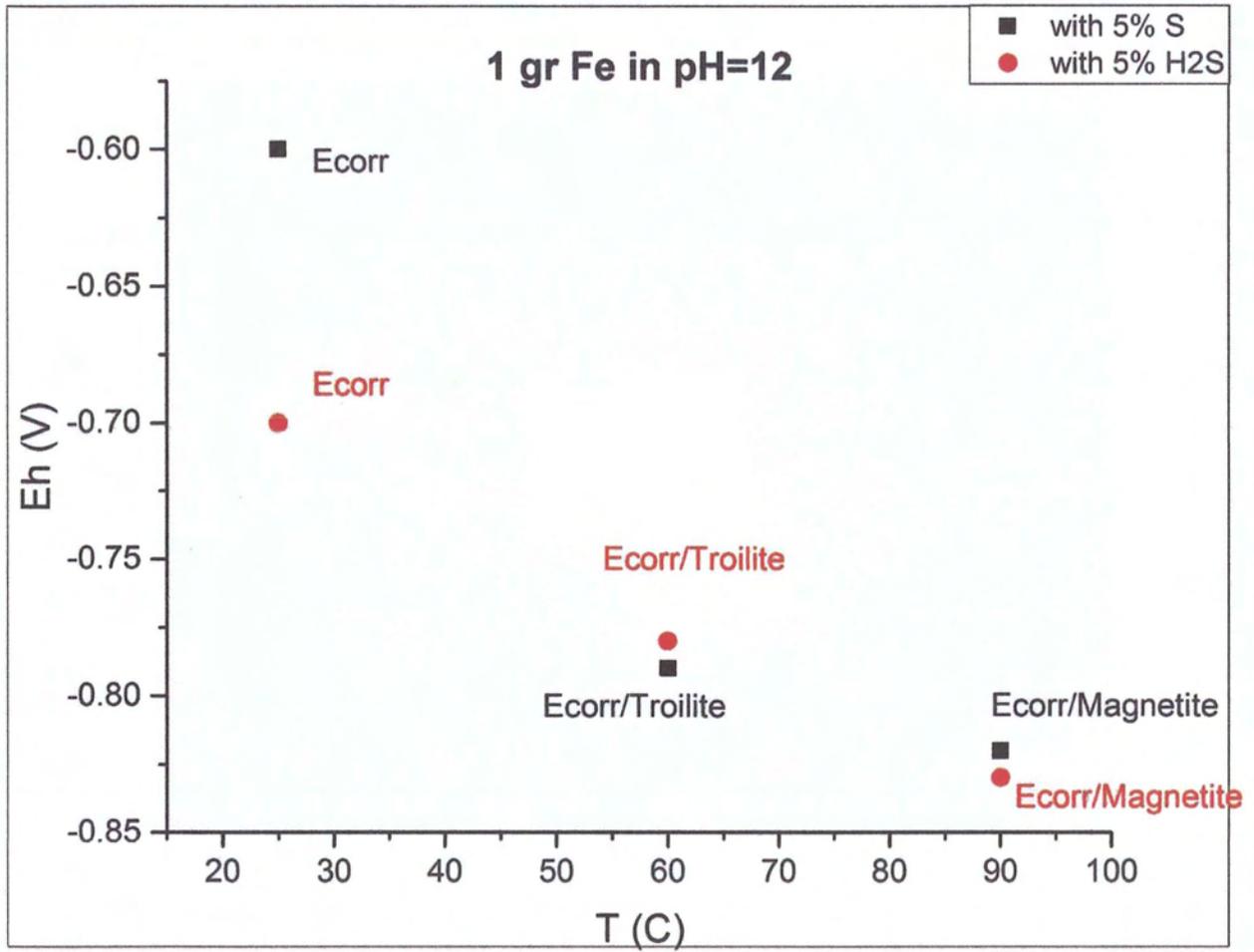
The diagram above indicates the first corrosion potential, which comes up for any of 2 solutions (either with S or with H<sub>2</sub>S).

At the temperature points of 60 and 90°C the phases are almost coincident, also at 25°C there is a small range of  $\Delta E_h = 0.3V$ , this is a very significant detail for the designation of a protection criterion which covers the two cases simultaneously.



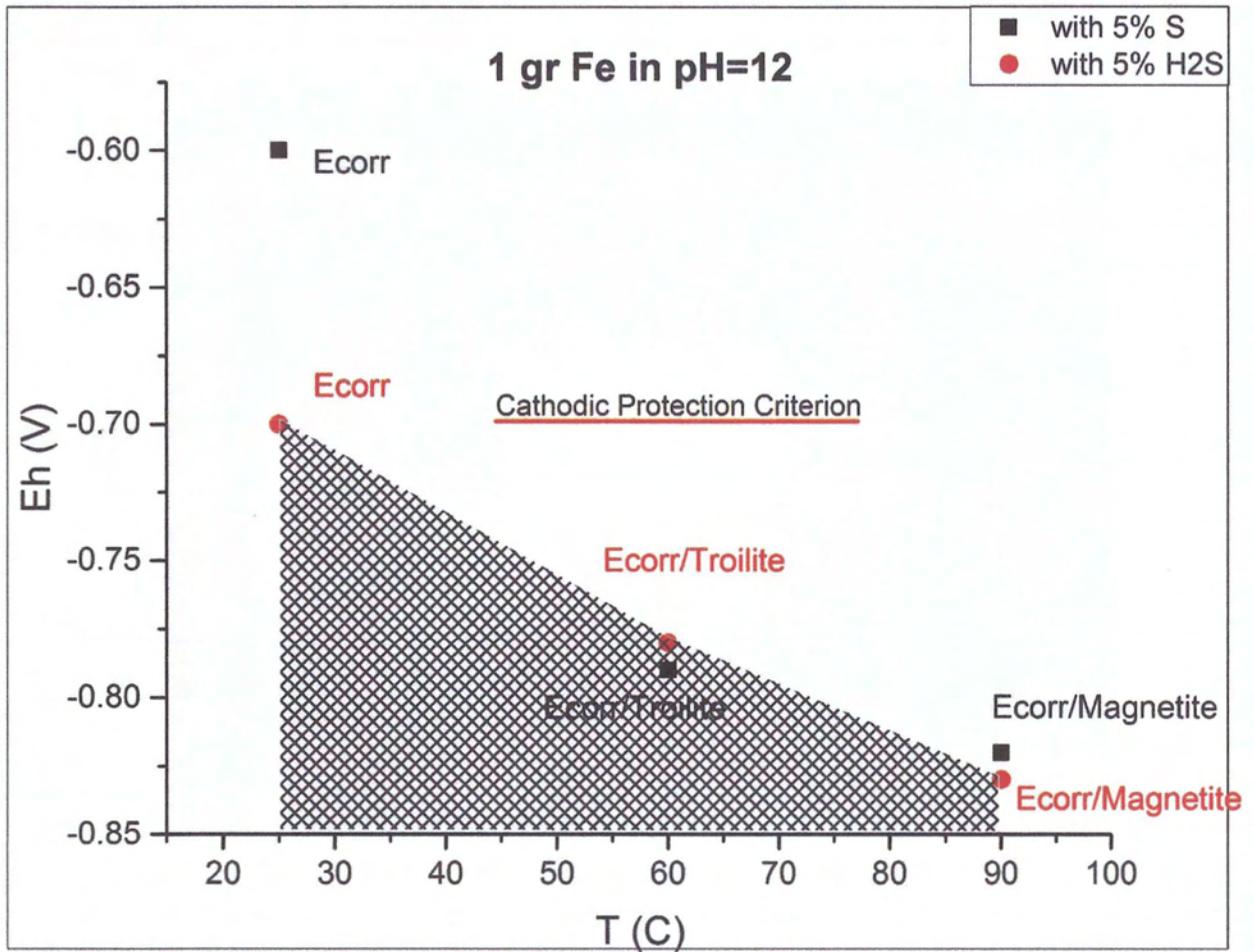
*Fig 63: Cathodic Protection Criterion-Fe with H<sub>2</sub>S & S in Acidic Solution*

The Cathodic Protection Criterion above, which designed for the specifics of the system either for H<sub>2</sub>S or for S, would be implemented by the cathodic techniques which were described in Literature Review (Chapter 2)



*Fig 64: Comparison-Fe with H<sub>2</sub>S & S in Alkaline Solution*

Once again in this diagram the phases for every of the 3 temperature points are almost coincident with the maximum range of Eh to be 0.1V, therefore, only one Cathodic protection criterion could be considered.



*Fig 65: Cathodic Protection Criterion-Fe with H<sub>2</sub>S & S in alkaline Solution*

This grid on the Cathodic Protection Criteria design, indicates the 'Safe' region, where the specific interaction system can operate properly.

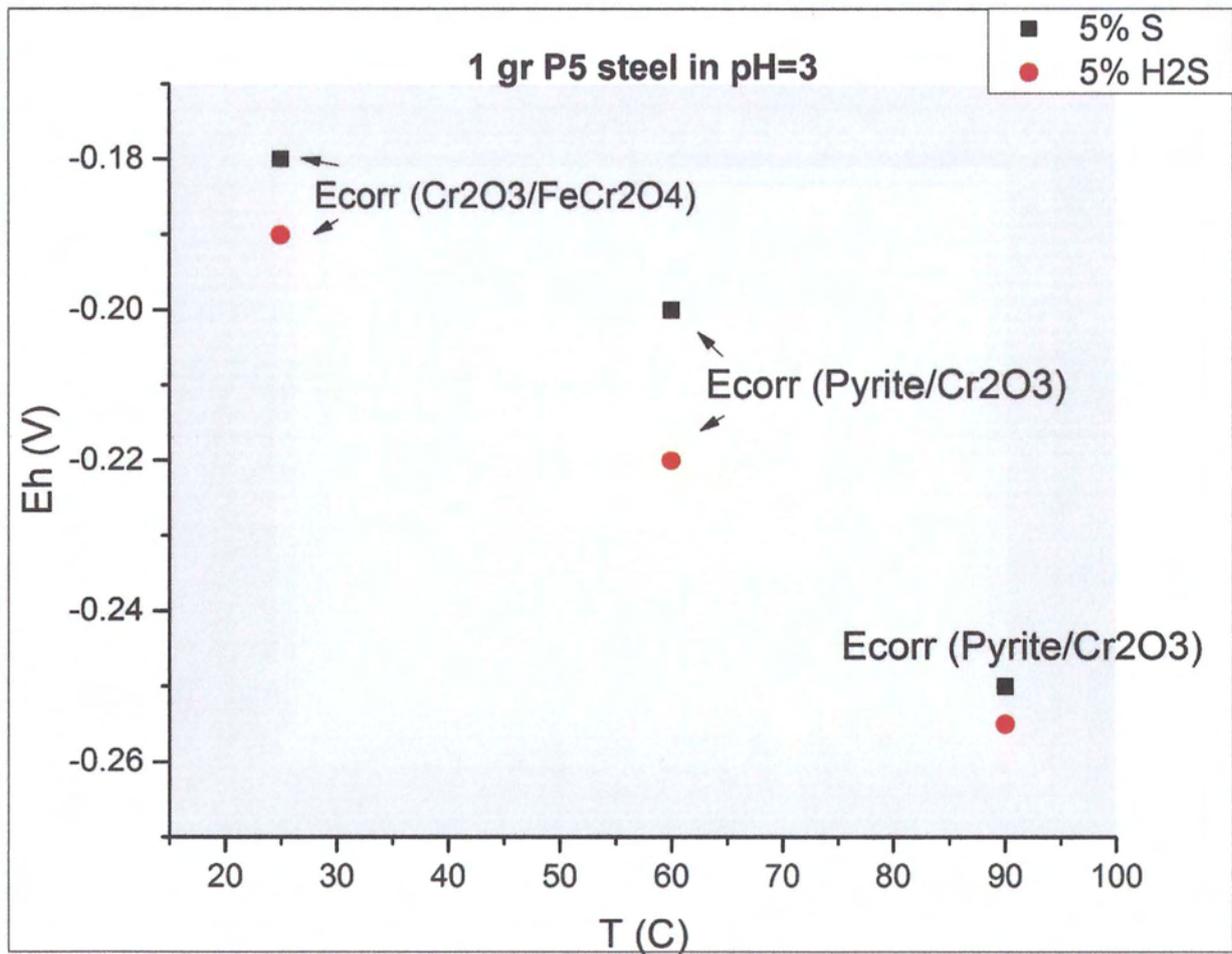
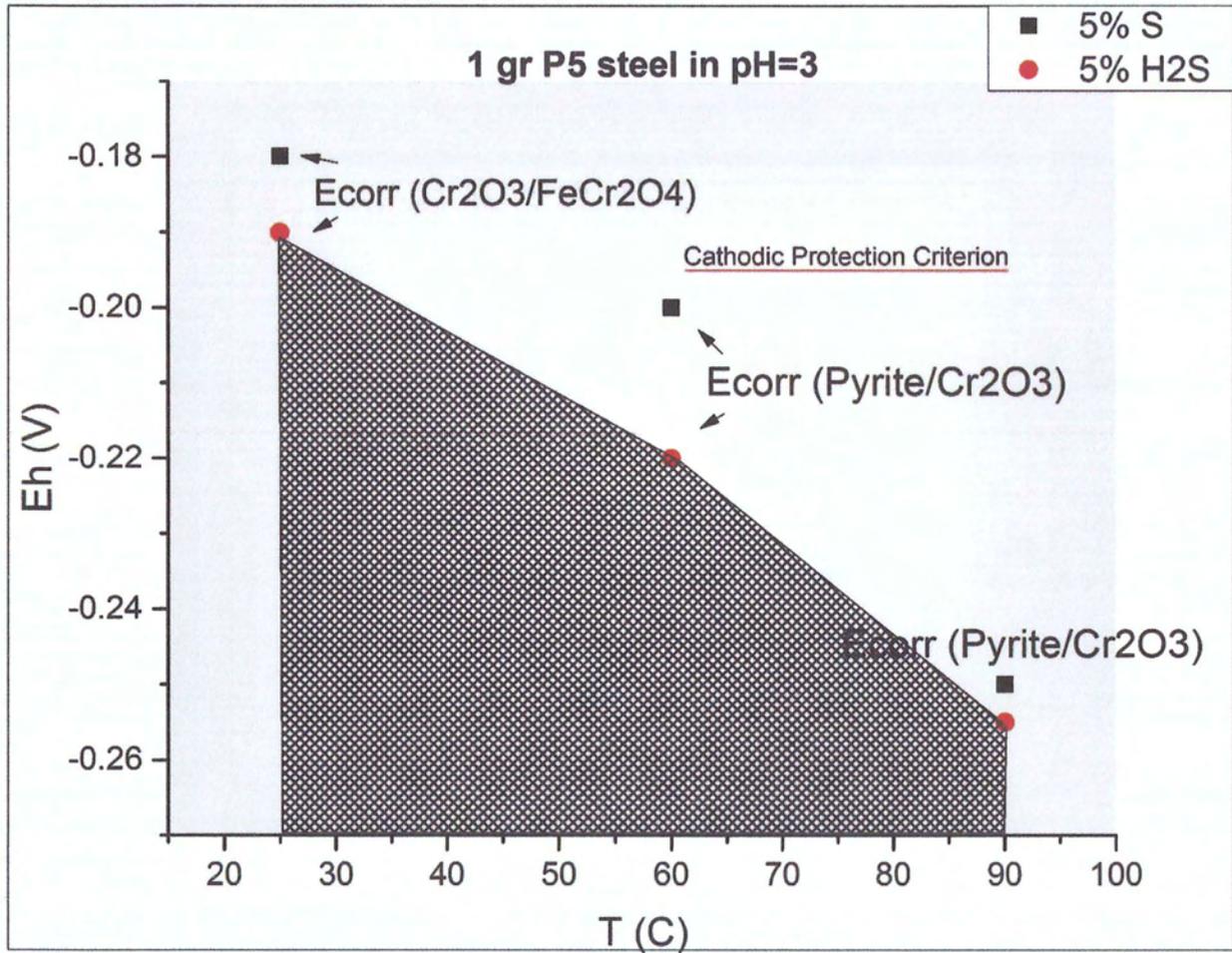


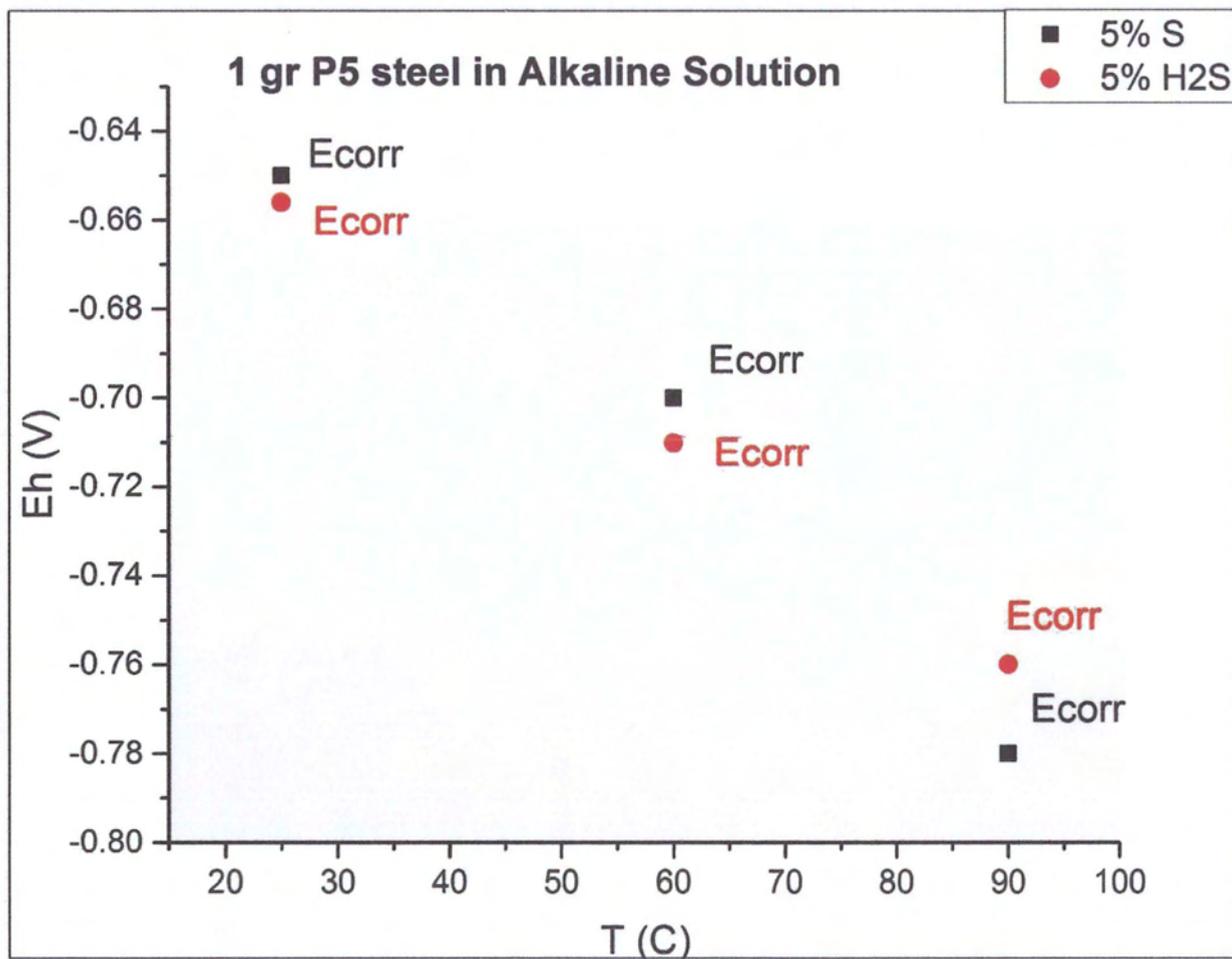
Fig 66: Comparison-P5 with H<sub>2</sub>S & S in Acidic Solution

For the P5 system the first phases at the lowest Eh are either Pyrite or Cr<sub>2</sub>O<sub>3</sub>. The maximum range of electrochemical potential between the two cases is  $\Delta E_h = 0.02V$ , thus, the phases could be considered as coincident.



*Fig 67: Cathodic Protection Criterion-P5 with H<sub>2</sub>S & S in Acidic Solution*

The 'Safe' pH-Eh region for the corrosion prevention is slightly bigger for the low temperatures below 60°C



*Fig 68: Comparison-P5 with H2S & S in Alkaline Solution*

The **E<sub>corr</sub>** situation for each of the 3 temperature points are coincident, with the maximum range of Eh to be 0.02V.

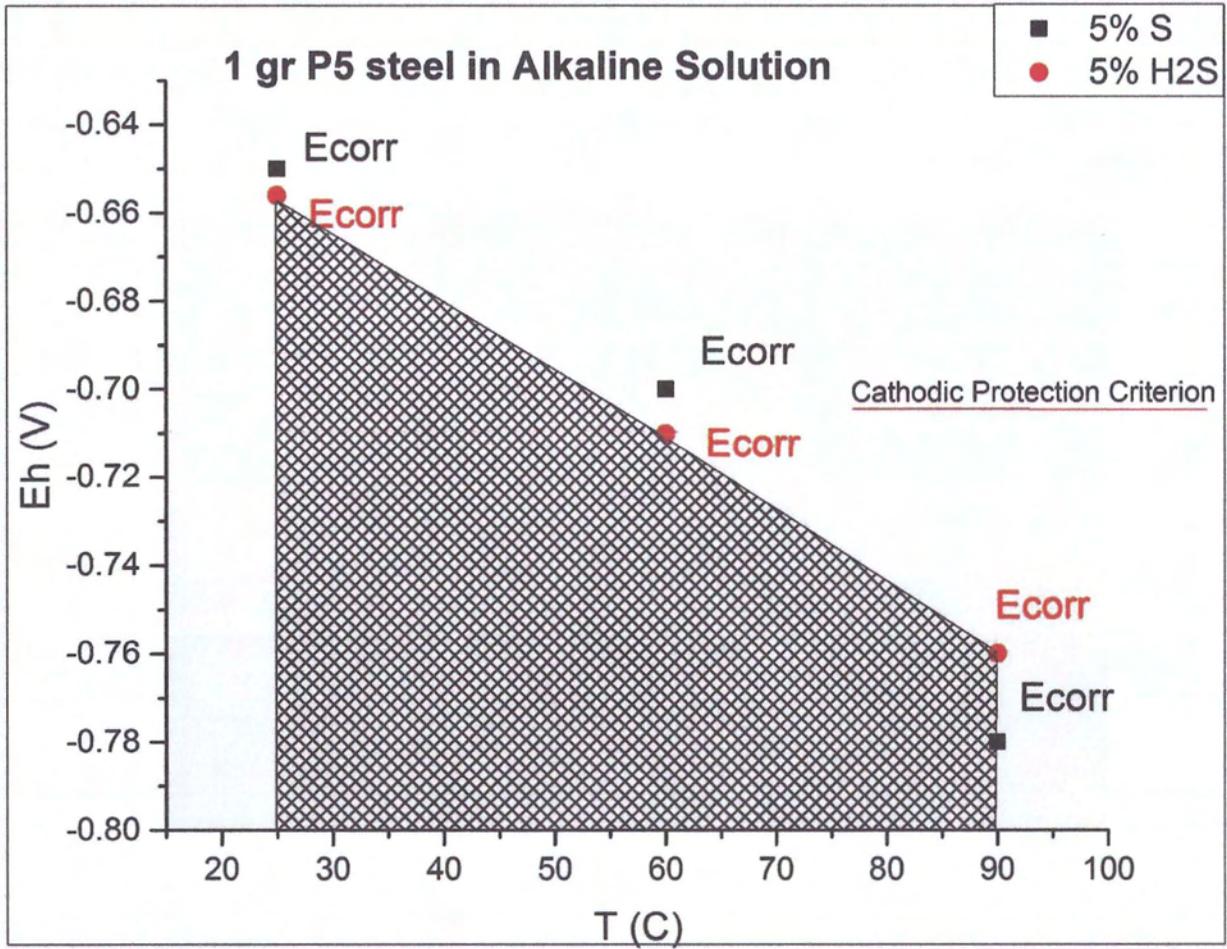


Fig 69: Cathodic Protection Criterion-P5 with H<sub>2</sub>S & S in alkaline Solution

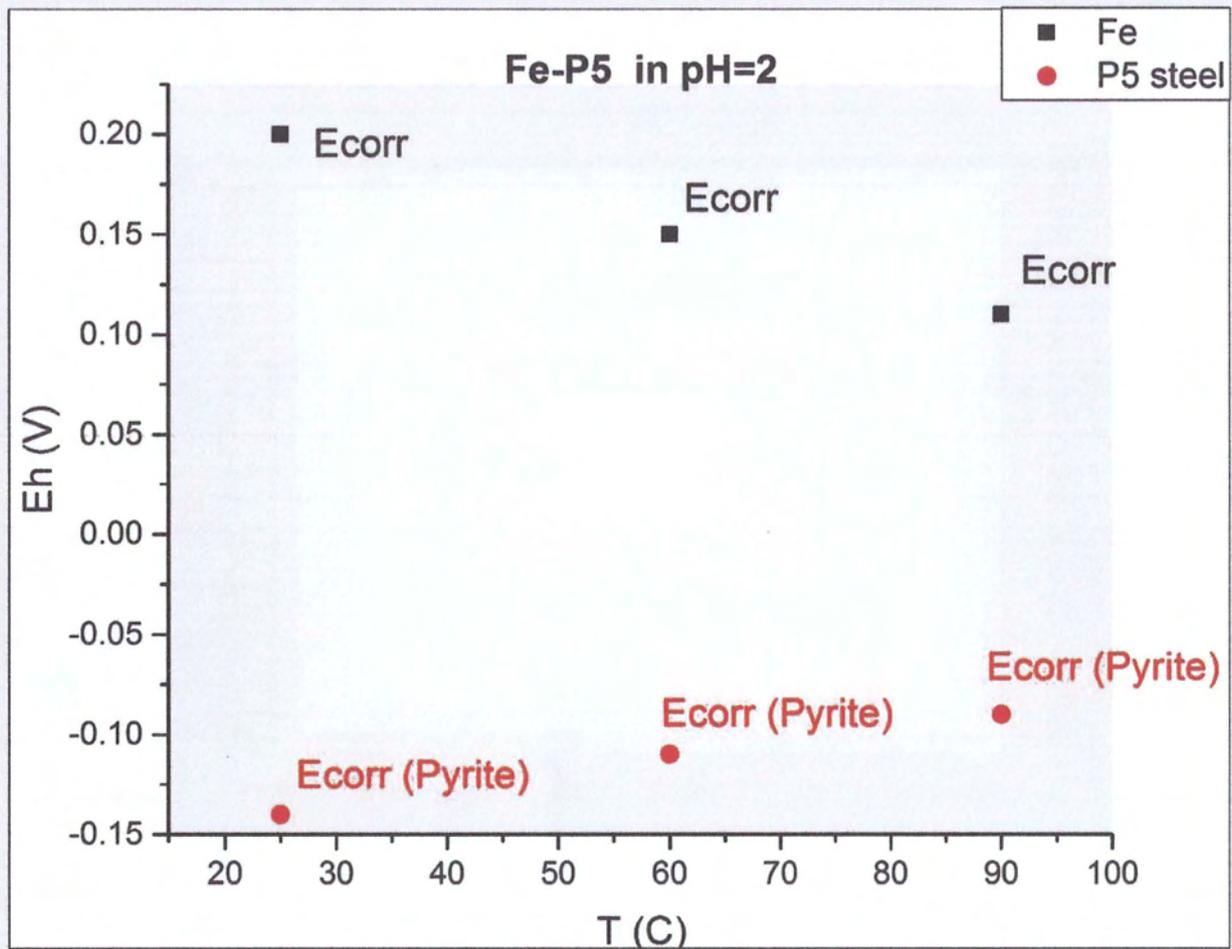


Fig 70: Comparison-Fe & P5 in Acidic Solution

In Fe-P5 comparison, a different type of phase comes up in every temperature, for the P5 steel (Pyrite).

The range of the electrochemical potential is pretty small again, with a maximum value of  $\Delta E_h = 0.35V$  at  $25^\circ C$ . Thus, is possible to design a protection criterion for both, but the corrosion is more favoured for Fe.

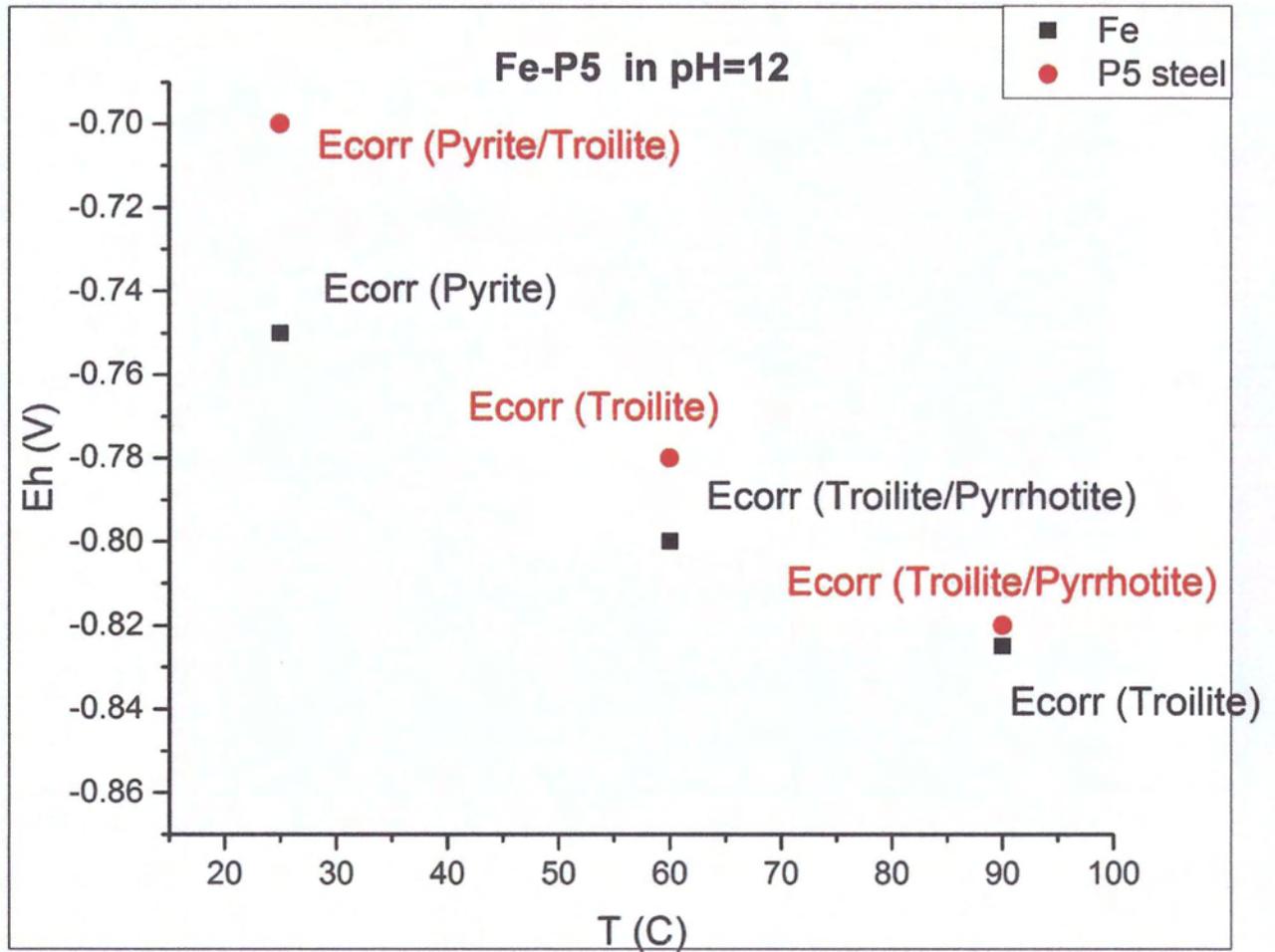


Fig 71: Comparison-Fe & P5 in Alkaline Solution

It is shown that the phase formation is similar and the range of the electrochemical potential is pretty small.

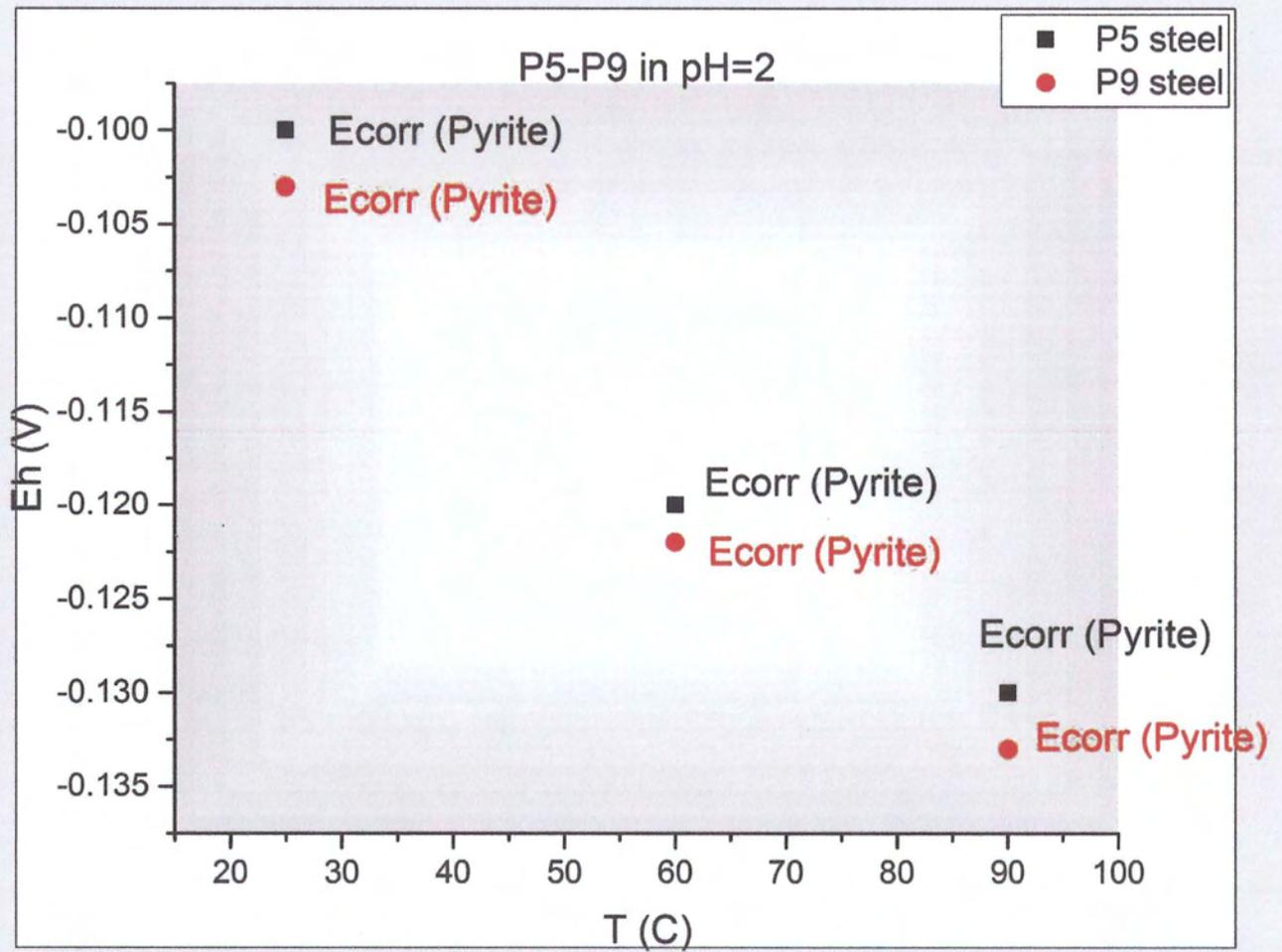


Fig 72: Comparison-P5 & P9 in Acidic Solution

The P9 steel differs from the P5 only in Cr composition. The behavior of each. Is similar in acidic solution. (same phase format, tiny Eh ranges)

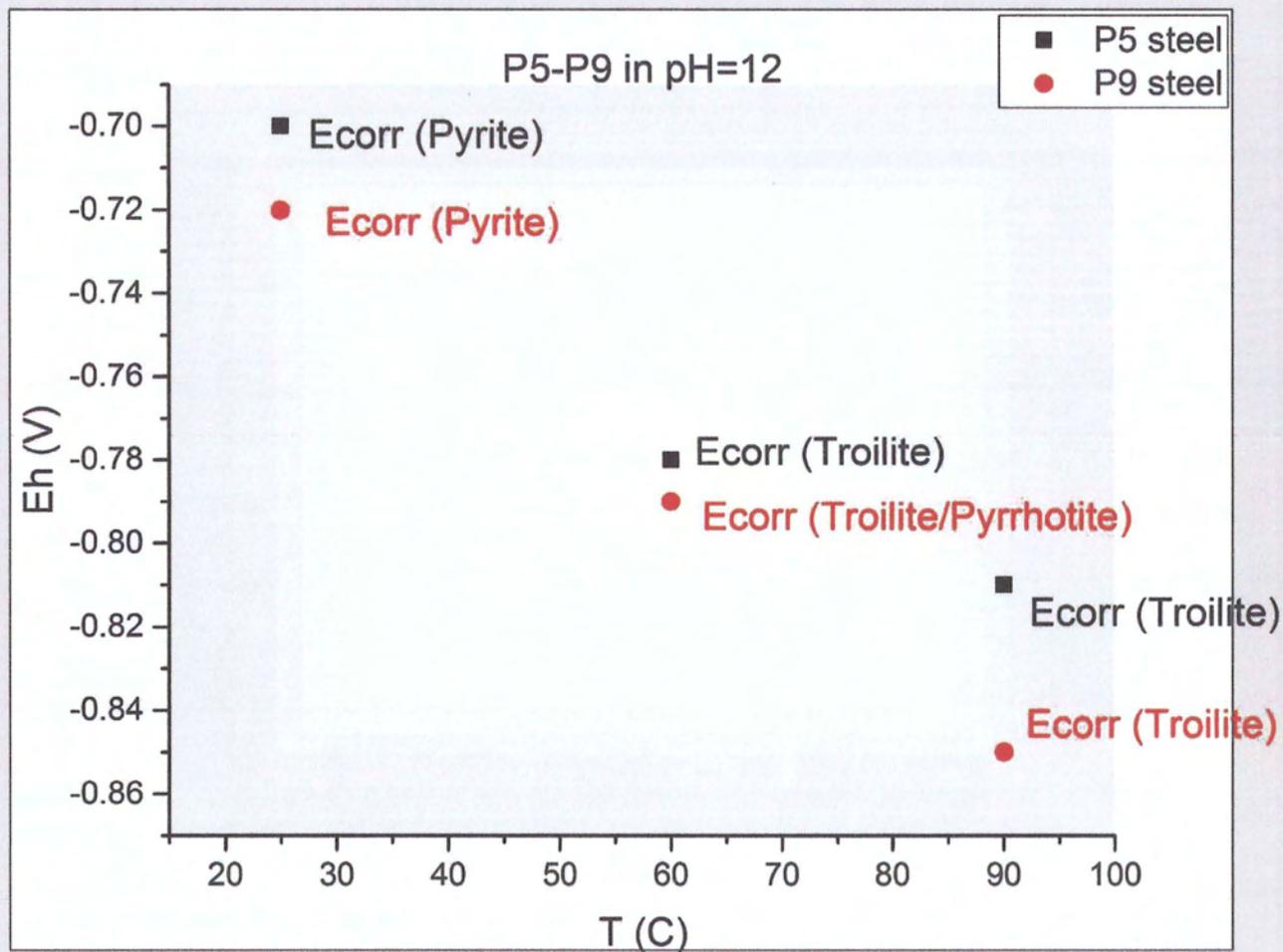


Fig 73: Comparison-P5 & P9 in Alkaline Solution

The same happens for the alkaline region. P5 and P9 steels are quite similar at all ranges of pH. Thus, they can be treated the same regarding to the corrosion protection criteria.

## Chapter 5 Conclusions & Future work

### 5.1 Conclusions

Summarizing the results presented above, a Pourbaix diagram is a highly useful tool for understanding the corrosion susceptibility of a metal in aqueous solution and defining the areas of immunity, corrosion and passivation over the whole range of pH and potential values. These information help to the corrosion mitigation over the global industry, as well as to a safer working environment.

It is important to note that the information gathered by those diagrams concern only the thermodynamic prediction and do not provide any indication on the kinetics of the reactions. Thus, a Pourbaix diagram is the first but significant step for the prediction of the corrosion behaviour of a given metal/aqueous solution system.

### 5.2 Future Recommendations

The theory of Pourbaix diagrams can definitely be used as an extra tool to the determination/investigation of corrosion

As a complementary tool will be useful in order to define the safe operational conditions where a system is allowed to 'work' without unexpected failures due to corrosion.

In particular, for buried pipeline projects or for maritime applications, where the aqueous corrosion dominates, Pourbaix diagrams are the key for the cathodic protection design.

Furthermore, the conclusions that come from the Pourbaix diagrams study will create more integrated and reliable suggestions for the corrosion control at the investigated case studies.

- A further recommendation is the construction of more complex Pourbaix diagrams at higher temperatures and involving more corrosion compounds as the Cr-sulphides like the Cr<sub>5</sub>S<sub>8</sub> for the P5 and the P9 grades.
- The input data for the further investigations may be found at the Case studies conducted at the Laboratory of Materials.
- EDX as well as XRD analyses may also be used in order to determine the corrosion products of the scale formed. In this case, one knows the exact chemical compounds which are formed during corrosion process. Thus, this clue will be also an input data for the construction process of Pourbaix diagrams.
- The combination of the computational and laboratory data will provide an extraordinary package of knowledge (theoretical and actual), which can be the base of the more reliable Pourbaix diagram construction.

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[http://www.doitpoms.ac.uk/tlplib/pourbaix/pourbaix\\_construction.php](http://www.doitpoms.ac.uk/tlplib/pourbaix/pourbaix_construction.php)
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[http://www.doitpoms.ac.uk/tlplib/pourbaix/pourbaix\\_construction.php](http://www.doitpoms.ac.uk/tlplib/pourbaix/pourbaix_construction.php)

## APPENDIX

### A: Thermo-calc Console

#### 1. Pourbaix module: *E-pH diagram for Fe-H<sub>2</sub>O-5%S system in 25 °C*

---

- In this example has been defined a Fe-water system, with initial molarity for the iron  $1.7906706 \cdot 10^{-2}$  (equal to 1 gram) in 1 kg of water (H<sub>2</sub>O) (figure), it could be reconstructed for the temperatures 60°C & 90°C ([figure](#) & respectively).

#### **SYS: GO POURBAIX**

WELCOME TO THE POURBAIX MODULE

!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

for Quick Calculations of Pourbaix Diagrams

=====

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Thermo-Calc Software AB  
Norra Stationsgatan 93  
SE-113 47 Stockholm, Sweden

(Version 7.0, Mar. 2014)

Need any instruction on the POURBAIX module? /N/:

Enforce a PAUSE after plotting when running a MACRO? /N/:

-----

| |

| 1. Start a completely new POURBAIX diagram calculation |

- | 2. Open an old file & plot other property diagrams |
- | 3. Open an old file & make another POURBAIX calculation |
- | 4. Open an old file & make another STEPPING calculation |
- | |

-----

**Select option /1/: 1**

1 -- Make a completely new POURBAIX diagram calculation  
and automatically plot a pH-Eh diagram.

- i.e., define a new chemical system;
- specify the T-P-X conditions;
- calculate the initial equilibria;
- perform the pH-Eh mapping calculation;
- plot pH-Eh & various property diagrams.

**Consider the GAS phase in calculating a Pourbaix diagram? /Y/: Y**

**Use single database? /Y/: Y**

**Combined Database: /PAQ2/: PAQ2**

THERMODYNAMIC DATABASE module

Current database: TCS Public Aqueous Soln (SIT) TDB v2.4

```

H          O          ZE
VA DEFINED
LIQUID:L REJECTED
GRAPHITE    DIAMOND_A4    FC_ORTHORHOMBIC
MONOCLINIC REJECTED
CBCC_A12    CUB_A13    CHI_A12
FE4N        FECN_CHI REJECTED
CEMENTITE    M23C6    M7C3
M5C2        M3C2    KSI_CARBIDE
PI REJECTED
FE3C        NI3C    CR3C2

```

CR7C3	CR23C6 REJECTED	
COCO3	FECO3	NAHCO3
NA2CO3	NA2CO3_S2	NICO3
CRC6O6	REJECTED	
CO3N	CRN	CR2N
FE2N	NI3N REJECTED	
NANO2	NANO2_S2	NANO3
	REJECTED	
COCL2	CRCL2	CRCL3
FECL2	FECL3	NICL2
	REJECTED	
FECLO	NACLO4	NACLO4_S2
	REJECTED	

DEFINE A CHEMICAL SYSTEM AND ITS INITIAL BULK COMPOSITION:

=====

Normally a POURBAIX diagram and related equilibrium property in a heterogeneous interaction system are calculated under a certain bulk composition which is usually 1 kg of water with defined amounts of dissolving solute substances. The solutes may either be completely dissolved into the aqueous solution, or be partially dissolved and simultaneously form some solid phases.

CHEMICAL SYSTEM (ELEMENTS):

Default defined elements (solvent H2O): H & O  
and specially assigned ZE(electron) & VA(vacancy).

Prompt specified elements (solutes ELEM):

Fe Ni Co Cr C N S Na Cl

INITIAL BULK COMPOSITION:

Default defined composition (solvent): 1.0 kg of H2O

Prompt specified composition (solutes): x mole of ELEM

-----

Notes: For accepting a default value, just RETURN at prompt;  
For changing to a specific value, enter it at prompt.

=====

IMPORTANT NOTE for Entering Solutes in Chemical Formulas:  
First element letter in UPPER case, and second lower case!  
such as NaCl CO2 CoCl3 Fe0.93S NaSO4-1 H2SO4

-----

Mass of Water (weight) = 1 kg

**First solute: Fe 0.0179067060614**

**Second solute: S 0.1559576**

Outside current composition limits

Molality of S (mole/kg) /.001/:0.01559576

Next solute:

-----

Defined chemical system and initial bulk composition:

Note: Solutes have been split up into chemical elements  
and their mole numbers. If confirmed, the POURBAIX  
Module will, in further steps, count the initial  
bulk composition in terms of chemical elements.

-----

H2O	1.00000000	kg
ZE	(specially assigned)	
FE	0.1790670606E-01	mole
S	0.1559576000E-01	mole

**Confirm defined system and initial bulk composition? /Y/: Y**

RETRIEVE THERMODYNAMIC DATA FROM THE DATABASE: PAQ2

H            O            ZE

VA DEFINED

LIQUID:L REJECTED

GRAPHITE          DIAMOND\_A4          FC\_ORTHORHOMBIC

MONOCLINIC REJECTED

CBCC\_A12          CUB\_A13          CHI\_A12

FE4N          FECN\_CHI REJECTED

CEMENTITE          M23C6          M7C3

M5C2          M3C2          KSI\_CARBIDE

PI REJECTED

FE3C          NI3C          CR3C2

CR7C3          CR23C6 REJECTED

COCO3          FECO3          NAHCO3

NA2CO3          NA2CO3\_S2          NICO3

CRC6O6 REJECTED

CO3N          CRN          CR2N

FE2N          NI3N REJECTED

NANO2          NANO2\_S2          NANO3

REJECTED

COCL2          CRCL2          CRCL3

FECL2          FECL3          NICL2

REJECTED

FECLO          NACLO4          NACLO4\_S2

REJECTED

REINITIATING GESS .....

FE DEFINED

S DEFINED

/- DEFINED

This database has following phases for the defined system

AQUEOUS:A          REF\_ELECTRODE          GAS:G

FCC\_A1          BCC\_A2          HCP\_A3

WUSTITE          MAGNETITE          HEMATITE

FE2O3_GAMMA	FEO2H2	FEO3H3
FEOOH	FE2O2O2H2	PYRRHOTITE
PYRRHOTITE_S2	TROILITE	TROILITE_S2
TROILITE_S3	PYRITE	MARCASITE
FESO4	FE2S3O12	

**Reject phase(s) /NONE/: FCC SIGMA**

FCC\_A1          SIGMA REJECTED

**Reject phase(s) /NONE/:**

**Restore phase(s): /NONE/:**

.....

The following phases are retained in this system:

AQUEOUS:A	REF_ELECTRODE	GAS:G
BCC_A2	HCP_A3	WUSTITE
MAGNETITE	HEMATITE	FE2O3_GAMMA
FEO2H2	FEO3H3	FEOOH
FE2O2O2H2	PYRRHOTITE	PYRRHOTITE_S2
TROILITE	TROILITE_S2	TROILITE_S3
PYRITE	MARCASITE	FESO4
FE2S3O12		

.....

OK? /Y/:

ELEMENTS .....

SPECIES .....

PHASES .....

PARAMETERS ...

FUNCTIONS ....

List of references for assessed data

'TCS public data set for gaseous mixture in the Fe-Co-Cr-Na-Ni-C-H-O-N-S  
-Cl system.'

'TCS public data set for liquid mixture and alloy solutions in the Fe-Co  
-Cr-Na-Ni-C-H-O-N-S-Cl system.'

'TCS public data set for stoichiometric solids and liquids in the Fe-Co-Cr  
-Na-Ni-C-H-O-N-S-Cl system.'

'TCS Aqueous Solution Database, TCAQ2, v2.0 (2002/2003). Extracted data  
only for Fe-Co-Cr-Na-Ni-C-H-O-N-S-Cl bearing aqueous solution species  
from TCAQ2 which covers totally 83 elements and contains many more  
aqueous solution species.'

-OK-

***Should any phase have a miscibility gap check? /N/: N***

..... Reinitializing POLY3 workspaces .....

***Enforce Global Minimization Technique in calculations? /N/: N***

***Save all functions, variables and tables in POLY3 file? /Y/: Y***

***Set numerical limits? /N/: N***

SET CALCULATING PARAMETERS:

List of Default and Pre-defined Calculation Conditions:

-----

Units: T in K, P in Pascal, B(H2O) in gram, N(ELEM) in mole

-----

T=298.15, P=1E5, B(H2O)=1000, N(H+1)=0, N(ZE)=0, N(Fe)=1.79067E-2,  
N(S)=1.55958E-2

DEGREES OF FREEDOM 0

***Confirm defined conditions? /Y/: Y***

Calculating start points; please be patient!

LIST THE FIRST DEFAULT STARTING EQUILIBRIUM POINT:

Output from POLY-3, equilibrium = 1, label A0 , database: PAQ2

Conditions:

T=298.15, P=1E5, B(H2O)=1000, N(Fe)=1.79067E-2, N(S)=1.55958E-2,

LNACR(H+1)=-16.1181, MUR(ZE)=100

DEGREES OF FREEDOM 0

Temperature 298.15 K ( 25.00 C), Pressure 1.000000E+05

Number of moles of components 5.55107E+01, Mass in grams 1.00132E+03

Total Gibbs energy -1.70184E+07, Enthalpy -1.58621E+07, Volume 0.00000E+00

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
FE	1.7907E-02	3.2258E-04	4.6065E-26	-1.4462E+05	SER
H+1	-1.7849E-01	-3.2153E-03	1.0000E-07	-3.9956E+04	SER
H2O	5.5508E+01	9.9996E-01	9.9963E-01	-9.2228E-01	AQUEOUS#
S	1.5596E-02	2.8095E-04	2.7694E-25	-1.4018E+05	SER
ZE	1.4729E-01	2.6534E-03	1.0412E+00	1.0000E+02	REF_ELEC

AQUEOUS#1 Status ENTERED Driving force 0.0000E+00

Moles 5.5466E+01, Mass 9.9989E+02, Volume fraction 0.0000E+00 Mole fractions:

H2O 1.00028E+00 S 2.81177E-04 H+1 -2.24941E-03

ZE 1.68706E-03 FE 8.56728E-12

Constitution:	SiteFraction	Molality	Activity	log10Act
H2O	9.99719E-01	5.55084E+01	9.99639E-01	-0.0002
SO4-2	2.81334E-04	1.56208E-02	8.11315E-03	-2.0908
OH-1	2.13405E-09	1.18491E-07	1.00590E-07	-6.9974
H+1	2.12154E-09	1.17796E-07	1.00000E-07	-7.0000
HSO4-1	1.69843E-09	9.43038E-08	8.00566E-08	-7.0966

FE+2	4.35199E-12	2.41640E-10	1.25503E-10	-9.9013
FEOH+1	4.21411E-12	2.33985E-10	1.98635E-10	-9.7019
S4-2	1.00000E-15	0.00000E+00	1.3293E-104	-103.8764
S2O8-2	1.00000E-15	0.00000E+00	3.09594E-70	-69.5092
S2O4-2	1.00000E-15	0.00000E+00	6.73356E-51	-50.1718
S2O3-2	1.00000E-15	0.00000E+00	6.78461E-38	-37.1685
S2-2	1.00000E-15	0.00000E+00	1.20446E-60	-59.9192
S-2	1.00000E-15	0.00000E+00	7.48686E-39	-38.1257
S4O6-2	1.00000E-15	0.00000E+00	2.37340E-74	-73.6246
O3	1.00000E-15	0.00000E+00	2.6324E-113	-112.5797
O2	1.00000E-15	0.00000E+00	2.56845E-58	-57.5903
S5-2	1.00000E-15	0.00000E+00	6.3714E-127	-126.1958
HSO3-1	1.00000E-15	0.00000E+00	1.94275E-20	-19.7116
HS-1	1.00000E-15	0.00000E+00	6.11898E-33	-32.2133
HO2-1	1.00000E-15	0.00000E+00	7.74601E-51	-50.1109
H2SO3	1.00000E-15	0.00000E+00	1.17209E-25	-24.9310
H2S	1.00000E-15	0.00000E+00	5.38521E-33	-32.2688
H2O2	1.00000E-15	0.00000E+00	3.66028E-46	-45.4365
SO2	1.00000E-15	0.00000E+00	1.12350E-25	-24.9494
H2	1.00000E-15	0.00000E+00	5.46000E-18	-17.2628
SO3-2	1.00000E-15	0.00000E+00	1.42378E-17	-16.8466
FESO4+1	1.00000E-15	0.00000E+00	1.62530E-21	-20.7891
FEOH+2	1.00000E-15	0.00000E+00	9.25319E-19	-18.0337
S3-2	1.00000E-15	0.00000E+00	1.67139E-82	-81.7769
FEO3H3-1	1.00000E-15	0.00000E+00	1.70618E-51	-50.7680
FE2O2H2+4	1.00000E-15	0.00000E+00	3.70031E-35	-34.4318
FE+3	1.00000E-15	0.00000E+00	1.53038E-23	-22.8152

Solution Properties: pH = 7.0000 Eh = 0.0010 V I = 0.0312

pe = 0.0175 Ah = 0.1000 kJ m\* = 0.0156

Aw = 0.9996 Os = 1.2845 pKw = 13.9973

At1= 1.0000E-15 At2= 1.1849E-07 (equiv\_mol/kg\_H2O)

HEMATITE#1 Status ENTERED Driving force 0.0000E+00

Moles 4.4767E-02, Mass 1.4298E+00, Volume fraction 0.0000E+00 Mole fractions:

ZE 1.20000E+00 FE 4.00000E-01 H+1 -1.20000E+00

H2O 6.00000E-01 S 0.00000E+00

Constitution:

FE2O3 1.00000E+00

LIST THE DEFINED SYMBOLS:

DEFINED CONSTANTS

TSLIMIT0=99, AH2O=55.508435, WH2O=1.80152E-2, RNL=2.3025851, R=8.31451,

RNF=96485.309

DEFINED FUNCTIONS AND VARIABLES%

TC%=T-273.15

PBAR%=P\*1E-05

PKB%=P\*1E-08

RT%=R\*T

EH=MUR(ZE)/RNF

PH=- LOG10(ACR(H+1,AQUEOUS#1)\*AH2O )

....

....

....

MUR(ZE) is the electrochemical potential (ECP; in the unit of J/mol; w.r.t. the standard hydrogen electrode).

ACR(H+1,AQUEOUS) is the site-fraction-based activity of the H+1 aqueous species in AQUEOUS solution phase, but AI(H+1,AQUEOUS) [that equals ACR(H+1,AQUEOUS)\*AH2O] is the molality-based activity of the H+1 aqueous species that should be used for defining the pH quantity.

Within an aqueous-bearing heterogeneous interaction system, the fundamental system-components must be H2O, H+1 and ZE, which are corresponding to the basic elements O & H and the hypothetical electron (ZE) in the aqueous solution phase. For the additional chemical elements in the system, their corresponding system-components shall be defined as in their element forms (such as Fe, Cr, Mn, Ni, Na, Cl, S)

or (for some) in their molecular forms (e.g., NaCl, H<sub>2</sub>S).

The reference state for the H<sub>2</sub>O component must always be defined as the solvent species H<sub>2</sub>O in the AQUEOUS solution phase under the current temperature (\*) and 100000 Pascal (i.e., 1 bar). The reference states for the H+1 and ZE components are by default set as their SER.

Various conventional properties of aqueous solute species I are converted in the following manners:

$$ML = Y(\text{AQUEOUS}, I) * AH_{2O} / YH_{2O}$$

$$RC = ACR(I, \text{AQUEOUS}) * YH_{2O} / Y(\text{AQUEOUS}, I)$$

$$AI = RC * ML$$

$$= ACR(I, \text{AQUEOUS}) * AH_{2O}$$

where YH<sub>2</sub>O [i.e., Y(AQUEOUS, H<sub>2</sub>O)] and Y(AQUEOUS, I) are the site-fractions of solvent H<sub>2</sub>O and solute species I.

LIST THE DEFINED AXIS-VARIABLES:

Axis No 1: LNACR(H+1)      Min: -34.532535 Max: 2.3025851 Inc: 0.8

Axis No 2: MUR(ZE)      Min: -150000 Max: 200000 Inc: 7718.85

NOTE: The default settings (listed above) for two mapping variables [in terms of lnACR(H+1) and MUR(ZE), and their minimum/maximum values and increment steps] are covering the following pH-Eh ranges/steps:

pH: 0.00 -> 14.00, at a step of 0.35

Eh: -1.55 -> 2.07, at a step of 0.08 (V)

The maximum pH limit has been calculated precisely and determined automatically by the POURBAIX-Module, as a function of the temperature-pressure conditions and initial bulk compositions of the current defined interaction system.

**Accept the default settings for two mapping variables? /Y/: Y**

MAP THE POURBAIX DIAGRAM:

Version S mapping is selected

Organizing start points

Using ADDED start equilibria

Tie-lines not in the plane of calculation

Generating start point 1

Generating start point 2

...

...

Generating start point 42

Phase region boundary 1 at: -1.612E+01 7.816E+04

\*\* GAS#1

AQUEOUS#1

HEMATITE#1

Calculated.. 26 equilibria

Terminating at axis limit.

Phase region boundary 2 at: -3.453E+01 3.295E+04

\*\* GAS#1

AQUEOUS#1

HEMATITE#1

Calculated. 44 equilibria

...

...

...

Phase region boundary 55 at: -2.102E+01 6.600E+04

\*\* GAS#1

AQUEOUS#1

HEMATITE#1

Calculated.            26 equilibria

Terminating at known equilibrium

\*\*\* BUFFER SAVED ON FILE: C:\Users\Student3\Documents\POURBAIX.POLY3

CPU time for mapping            25 seconds

POSTPROCESSOR VERSION 3.2

Setting automatic diagram axes

CURRENT DEVICE: TC-UNITE Driver

Plotting the diagram; please be patient!

***Any missing phase boundary you could possibly think of? /N/: N***

***Change the pH/Eh steps for smoother curves? /N/: N***

***Zoom in? /N/: N***

***Change Curve-Label Option for the diagram? /N/: N***

1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=25 C)

2016.02.22.10.33.54

FE, H+1, H<sub>2</sub>O, S, ZE

T=298.15, P=1E5, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(S)=1.55958E-2 25 C 1 bar .017907mFE .015596mS

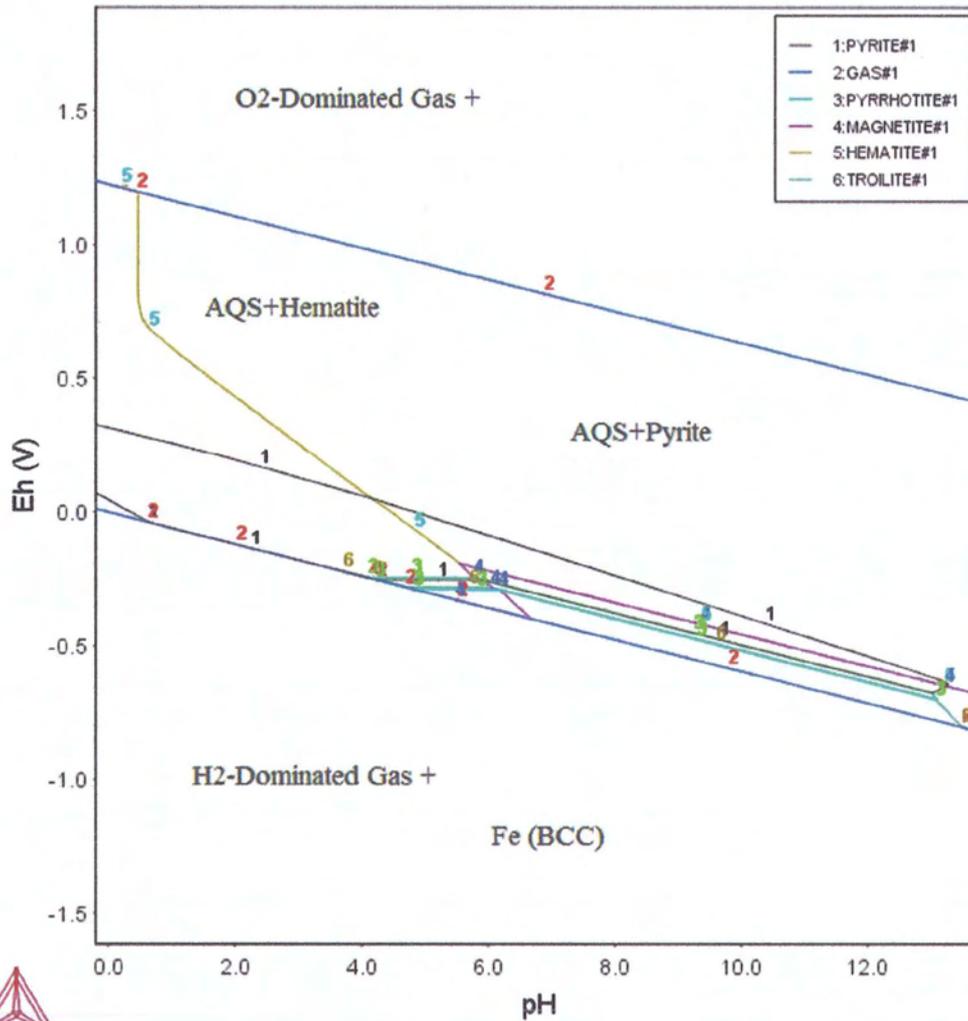


Fig 74: 1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=25°C)

➤ Now the temperature has been changed for performance

SET CALCULATING PARAMETERS:

List of Default and Pre-defined Calculation Conditions:

-----

Units: T in K, P in pascal, B(H<sub>2</sub>O) in gram, N(ELEM) in mole

-----

T=298.15, P=1E5, B(H2O)=1000, N(H+1)=0, N(ZE)=0, N(FE)=1.79067E-2  
DEGREES OF FREEDOM 0

**Confirm defined conditions? /Y/: N**

RE-DEFINE CALCULATION CONDITIONS:

=====

Notes: For accepting a default value, just RETURN at prompt;

For changing to a specific value, enter it at prompt.

-----

Initial Bulk Composition:

Mass of Water (weight) = 1 kg

**Molality of FE (mole/kg) /1.790/: 1.79067E-2**

Pressure and Temperature:

**System Pressure (bar) /1/: 1**

Calculating applicable temperature limit. Please be patient!

Testing result with global minimization

The Applicable Temperature Limit at given X and P is **94.81 C**.

**System Temperature (C) /25/: 60**

List of Default and Pre-defined Calculation Conditions:

-----

Units: T in K, P in pascal, B(H2O) in gram, N(ELEM) in mole

-----

T=298.15, P=1E5, B(H2O)=1000, N(FE)=1.79067E-2, N(S)=1.55958E-2,

LNACR(H+1)=-16.1181, MUR(ZE)=100

DEGREES OF FREEDOM 0

**Confirm defined conditions? /Y/: Y**

1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=60 C)

2016.02.22.12.14.39

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, Z<sub>e</sub>, FE, S

P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(S)=0.155958

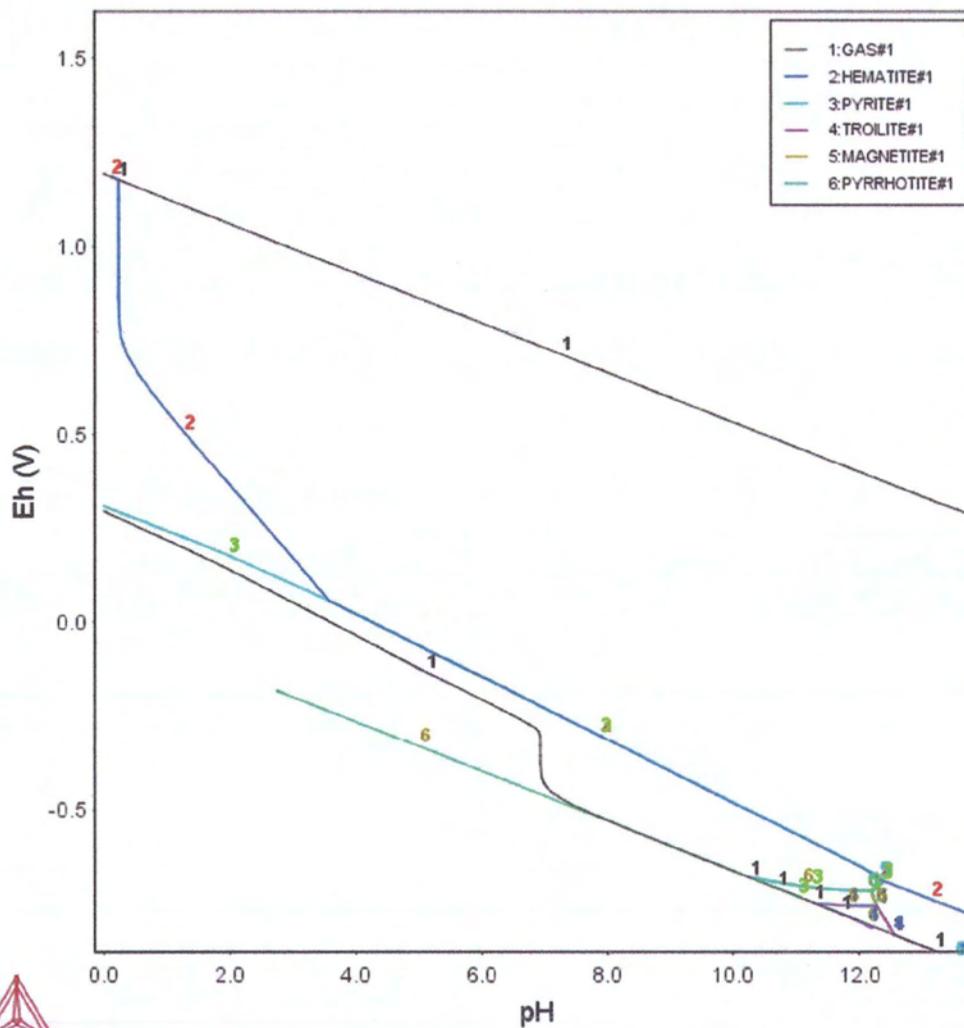


Fig 75: 1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=60°C)

1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=60 C)

2016.02.22.12.14.39  
PAQ2: H<sub>2</sub>O, H<sup>+</sup>, Z<sub>e</sub>, FE, S  
P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(S)=0.155958

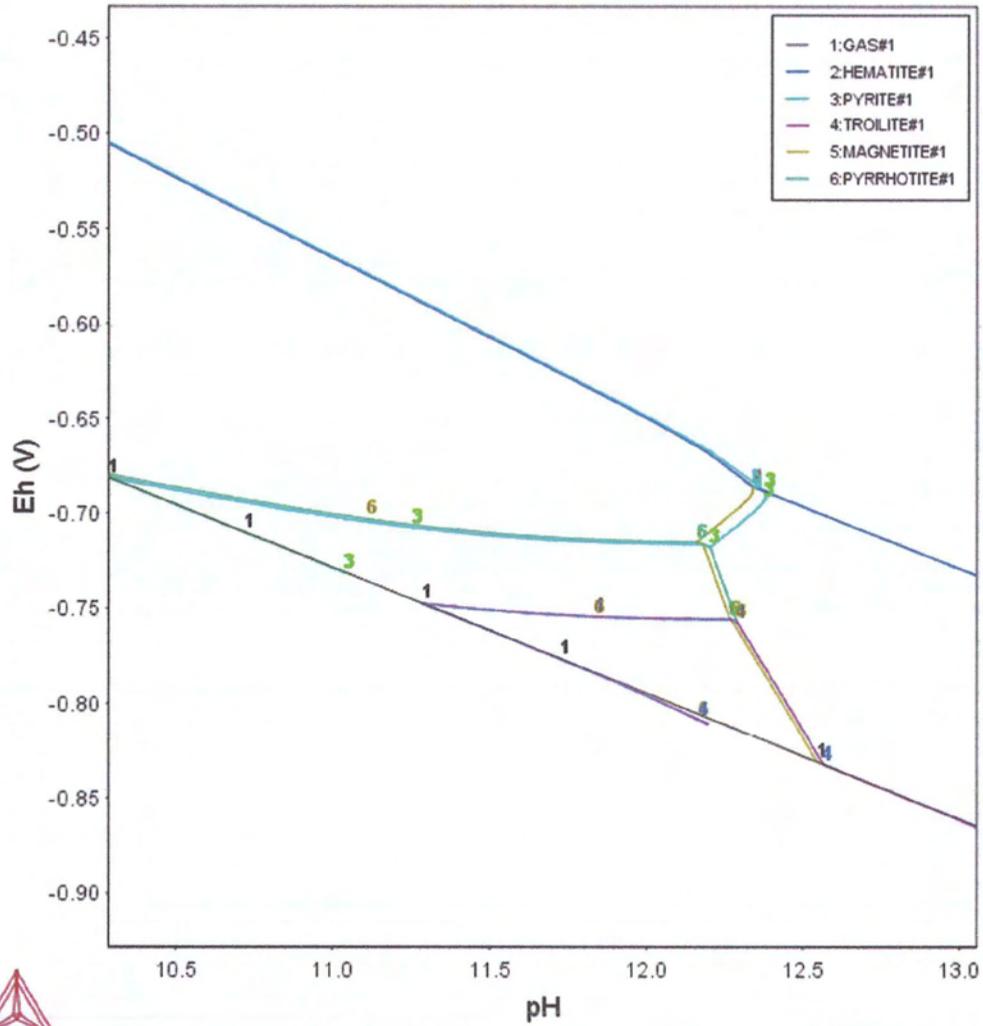


Fig 76: 1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=60°C)-Zoom In

1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=90 C)

2016.02.22.11.25.06

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, Z<sub>e</sub>, FE, S

P=1E5, T=363.15, B(H<sub>2</sub>O)=1000., N(Fe)=1.79067E-2, N(S)=0.155958

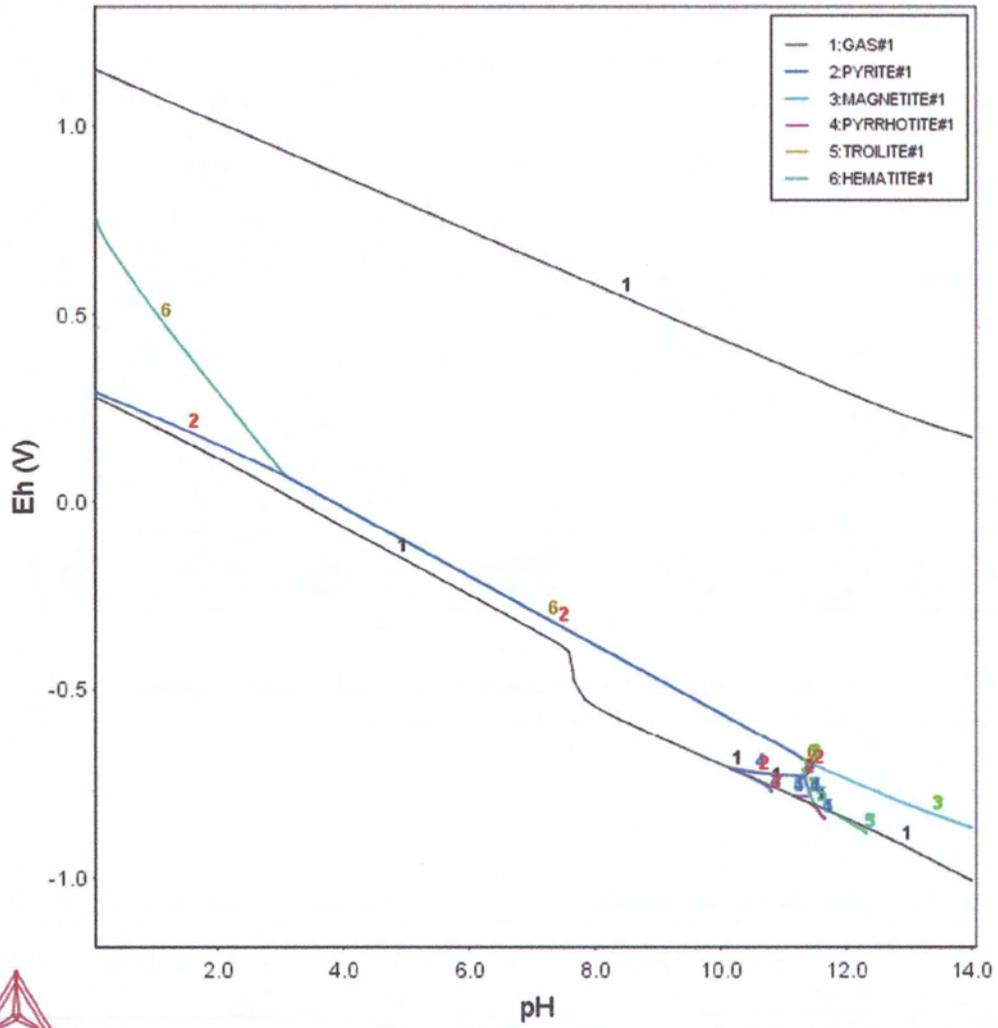


Fig 77: 1 gr Fe in 1 Kg H<sub>2</sub>O-5% S (T=90°C)

## 2. TDB-POLY-POST routine: *E-Ph diagram for 304L-H<sub>2</sub>O-5% NaCl system in 25°C*

---

- In this example has been defined a low carbon stainless steel (304L)-water system, with 5% dissolved sodium chloride in 1 kg of water (figure) , it could be reconstructed for the temperatures 60°C & 90°C (figure & respectively ).

### **SYS: go da**

THERMODYNAMIC DATABASE module

Current database: TCS Steels/Fe-Alloys Database v6.2

VA DEFINED

IONIC\_LIQ:Y      L12\_FCC      B2\_BCC  
B2\_VACANCY      HIGH\_SIGMA      DICTRA\_FCC\_A1  
REJECTED

### **TDB\_TCFE6: rej sys**

VA DEFINED

IONIC\_LIQ:Y      L12\_FCC      B2\_BCC  
B2\_VACANCY      HIGH\_SIGMA      DICTRA\_FCC\_A1  
REJECTED

REINITIATING GES5 .....

### **TDB\_TCFE6: sw PAQ2**

Current database: TCS Public Aqueous Soln (SIT) TDB v2.4

H            O            ZE

VA DEFINED

LIQUID:L REJECTED

GRAPHITE      DIAMOND\_A4      FC\_ORTHORHOMBIC

MONOCLINIC REJECTED

CBCC\_A12      CUB\_A13      CHI\_A12

FE4N      FECN\_CHI REJECTED

CEMENTITE      M23C6      M7C3

M5C2      M3C2      KSI\_CARBIDE

PI REJECTED

FE3C            NI3C            CR3C2  
 CR7C3            CR23C6 REJECTED  
 COCO3            FECO3            NAHCO3  
 NA2CO3            NA2CO3\_S2            NICO3  
 CRC6O6 REJECTED  
 CO3N            CRN            CR2N  
 FE2N            NI3N REJECTED  
 NANO2            NANO2\_S2            NANO3  
 REJECTED  
 COCL2            CRCL2            CRCL3  
 FECL2            FECL3            NICL2  
 REJECTED  
 FECLO            NACLO4            NACLO4\_S2  
 REJECTED

**TDB\_PAQ2: d-sys H O Na Cl Fe Cr Ni**

NA            CL            FE  
 CR            NI DEFINED

**TDB\_PAQ2:l-sys const**

AQUEOUS:A :H2O H2 H+1 OH-1 H2O2 HO2-1 O2 O3 CL2 CL-1 CLO2 CLO-1 CLO2-1  
 CLO3-1 CLO4-1 HCLO HCLO2 CR+2 CR+3 CROH+2 CRO+1 CRO2-1 HCRO2 HCRO4-1 CRO4  
 -2 CR2O7-2 FE+2 FE+3 FEOH+1 FEOH+2 FEO3H3-1 FE2O2H2+4 FECL+2 NA+1 NI+2  
 NIOH+1:

> Aqueous Solution: using the SIT Model (from TCAQ2 database)

**REF\_ELECTRODE :ZE:**

> Reference Electrode for ZE potential; always SUSPENDED in POLY.

GAS:G :CL CL2 CL1H1 CL1O1 CL1O2 CL1H1O1 CL2O1 CL1CR1 CL1CR1O1  
 CL1CR1O2 CL1FE1 CL1NA1 CL1NI1 CL2CR1 CL2CR1O1 CL2CR1O2 CL2FE1 CL2NA2  
 CL2NI1 CL3CR1 CL3CR1O1 CL3FE1 CL3NA3 CL4CR1 CL4CR1O1 CL4FE2 CL5CR1 CL6CR1  
 CL6FE2 CR CR1H1 CR1H1O1 CR1H1O2 CR1H1O3 CR1H2O2 CR1H2O3 CR1H2O4 CR1H3O3  
 CR1H3O4 CR1H4O4 CR1H4O5 CR1O1 CR1O2 CR1O3 CR2 CR2O1 CR2O2 CR2O3 FE FE1H1O1  
 FE1H1O2 FE1H2O2 FE1O1 FE1O2 H H1NA1 H1NA1O1 H1NI1 H1NI1O1 H1O1 H1O2 H2  
 H2NA2O2 H2NI1O2 H2O1 H2O2 NA NA1O1 NA2 NA2O1 NA2O2 NI NI1O1 O O2 O3:

> Gaseous Mixture, using the ideal gas model

FCC\_A1 :CR FE NA NI O:VA:

> This is also the MX (X=C,N) solution phase.

BCC\_A2 :CR FE NA NI O:VA:

> This is also the MX3 (X=C,N) solution phase.

HCP\_A3 :CR FE NA NI:VA:

> This is also the M2X (X=C,N) solution phase.

SIGMA :FE NI:CR:CR FE NI:

HALITE :NA1CL1:

WUSTITE :FE0.947O1:

MAGNETITE :FE3O4:

HEMATITE :FE2O3:

FE2O3\_GAMMA :FE2O3:

FEO2H2 :FE1H2O2:

FEO3H3 :FE1H3O3:

FEOOH :FE1H1O2:

FE2O2O2H2 :FE2H2O4:

CRO2 :CR1O2:

CRO3 :CR1O3:

CR2O3 :CR2O3:

CR5O12 :CR5O12:

CR8O21 :CR8O21:

NAO2 :NA1O2:

NA2O :NA2O1:

NA2O\_S2 :NA2O1:

NA2O\_S3 :NA2O1:

NA2O2 :NA2O2:

NA2O2\_S2 :NA2O2:

NAOH :H1NA1O1:

NAOH\_S2 :H1NA1O1:

NIO :NI1O1:

NIO\_S2 :NI1O1:

NIO2H2 :H2NI1O2:

NIOOH :H1NI1O2:

FECR2O4 :CR2FE1O4:

NICR2O4 :CR2NI1O4:

NA2CR2O4 :CR2NA2O4:

NIFE2O4 :FE2NI1O4:

NA2CRO4 :CR1NA2O4:

NA2CRO4\_S2 :CR1NA2O4:

NA2FEO2 :FE1NA1O2:

**TDB\_PAQ2: rej ph HCP\_A3 CBCC\_A12 CUB\_A13 CHI\_A12 Fe4N**

HCP\_A3 REJECTED

**TDB\_PAQ2: rej ph SIGMA**

SIGMA REJECTED

**TDB\_PAQ2: rej ph NaH**

**TDB\_PAQ2: get**

REINITIATING GESS .....

ELEMENTS .....

SPECIES .....

PHASES .....

PARAMETERS ...

FUNCTIONS ....

List of references for assessed data

'TCS public data set for gaseous mixture in the Fe-Co-Cr-Na-Ni-C-H-O-N-S  
-Cl system.'

'TCS public data set for liquid mixture and alloy solutions in the Fe-Co  
-Cr-Na-Ni-C-H-O-N-S-Cl system.'

'TCS public data set for stoichiometric solids and liquids in the Fe-Co-Cr  
-Na-Ni-C-H-O-N-S-Cl system.'

'TCS Aqueous Solution Database, TCAQ2, v2.0 (2002/2003). Extracted data  
only for Fe-Co-Cr-Na-Ni-C-H-O-N-S-Cl bearing aqueous solution species  
from TCAQ2 which covers totally 83 elements and contains many more  
aqueous solution species.'

-OK-

**TDB\_PAQ2: go p-3**

POLY version 3.32

**POLY\_3: d-com H2O H+1 ZE Na Cl Fe Cr Ni**

**POLY\_3: s-r-s H2O AQUEOUS \* 1e5**

**POLY\_3: s-r-s Ze REF\_ELE \* 1e5**

**POLY\_3: l-st c**

\*\*\* STATUS FOR ALL COMPONENTS

COMPONENT	STATUS	REF. STATE	T(K)	P(Pa)
VA	ENTERED	SER		
H2O	ENTERED	AQUEOUS#1 *		100000
H+1	ENTERED	SER		
ZE	ENTERED	REF_ELECTRODE# *		100000
NA	ENTERED	SER		
CL	ENTERED	SER		
FE	ENTERED	SER		
CR	ENTERED	SER		
NI	ENTERED	SER		

**POLY\_3: ent-sym const AH2O=55.508435**

**POLY\_3: ent-sym const RNF =96485.309**

**POLY\_3: ent-sym funct Eh = mur(ZE)/RNF;**

**POLY\_3: ent-sym funct pH = -log10(acr(H+1));**

**POLY\_3: l-sym**

DEFINED CONSTANTS

AH2O=55.508435, RNF=96485.309

DEFINED FUNCTIONS AND VARIABLES%

EH=MUR(ZE)/RNF

PH=- LOG10(ACR(H+1) )

**POLY\_3: s-c p=1e5 t=298.15**

**POLY\_3: s-c b(H2O)=1000**

**POLY\_3: s-c n(Na)=0.085554 n(Cl)=0.085554**

**POLY\_3: s-c n(Fe)=1.3250488E-2 n(Cr)=3.4618048E-3**

**POLY\_3: s-c n(Ni)=1.3630942E-3**

**POLY\_3: s-c lnacr(H+1)=-16.11809565 mur(Ze)=0**

**POLY\_3: l-c**

P=1E5, T=298.15, B(H2O)=1000, N(NA)=8.5554E-2, N(CL)=8.5554E-2,  
N(Fe)=1.32505E-2, N(CR)=3.4618E-3, N(NI)=1.36309E-3, LNACR(H+1)=-16.1181,  
MUR(ZE)=0

DEGREES OF FREEDOM 0

**@@ Setting Numerical Limits:**

**POLY\_3: s-n-l 2000 1e-4 1e-12 n**

LIMITATIONS of the present version of Thermo-Calc

Max number of elements : 40

Max number of species :5000

Max number of sublattices in a phase : 10

Max number of constituents in a phase: : 200

Max number of constituents in an ideal phase :5000

**@@ Calculating an initial equilibrium with only AQUEOUS presented:**

**POLY\_3: c-st p \*=sus**

**POLY\_3: c-st p AQUEOUS=ent 55.8**

**POLY\_3: l-st p**

\*\*\* STATUS FOR ALL PHASES

PHASE	STATUS	DRIVING FORCE	MOLES
-------	--------	---------------	-------

AQUEOUS#1	ENTERED	0.000000E+00	5.580000E+03
-----------	---------	--------------	--------------

SUSPENDED PHASES:

WUSTITE#1 REF\_ELECTRODE#1 NIO\_S2#1 NIOOH#1 NIO2H2#1 NIO#1 NIFE2O4#1 NICR2O4#1

NAOH\_S2#1 NAOH#1 NAO2#1 NA2O\_S3#1 NA2O\_S2#1 NA2O2\_S2#1 NA2O2#1 NA2O#1

NA2FEO2#1 NA2CRO4\_S2#1 NA2CRO4#1 NA2CR2O4#1 MAGNETITE#1 HEMATITE#1

HALITE#1

FEOOH#1 FEO3H3#1 FEO2H2#1 FECR2O4#1 FE2O3\_GAMMA#1 FE2O2O2H2#1 FCC\_A1#1

CRO3#1

CRO2#1 CR8O21#1 CR5O12#1 CR2O3#1 BCC\_A2#1 GAS#1

**POLY\_3: c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 4 grid points in 0 s

84 ITS, CPU TIME USED 0 SECONDS

**POLY\_3: l-e ,x**

Output from POLY-3, equilibrium = 1, label A0 , database: PAQ2

Conditions:

P=1E5, T=298.15, B(H2O)=1000, N(NA)=8.5554E-2, N(CL)=8.5554E-2,  
N(Fe)=1.32505E-2, N(CR)=3.4618E-3, N(NI)=1.36309E-3, LNACR(H+1)=-16.1181,  
MUR(ZE)=0  
DEGREES OF FREEDOM 0

Temperature 298.15 K ( 25.00 C), Pressure 1.000000E+05  
Number of moles of components 5.57250E+01, Mass in grams 1.00599E+03  
Total Gibbs energy -1.70642E+07, Enthalpy -1.59025E+07, Volume -7.58845E-08

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
H2O	5.5508E+01	9.9611E-01	9.9606E-01	-9.7749E+00	AQUEOUS#
H+1	-1.2256E-02	-2.1994E-04	1.0000E-07	-3.9956E+04	SER
ZE	3.9613E-02	7.1086E-04	1.0000E+00	0.0000E+00	REF_ELEC
NA	8.5554E-02	1.5353E-03	1.5221E-50	-2.8436E+05	SER
CL	8.5554E-02	1.5353E-03	1.1830E-30	-1.7082E+05	SER
FE	1.3250E-02	2.3778E-04	1.0841E-18	-1.0254E+05	SER
CR	3.4618E-03	6.2123E-05	2.9897E-45	-2.5415E+05	SER
NI	1.3631E-03	2.4461E-05	9.6340E-14	-7.4297E+04	SER

AQUEOUS#1 Status ENTERED Driving force 0.0000E+00

Moles 5.5725E+01, Mass 1.0060E+03, Volume fraction 1.0000E+00 Mole fractions:

H2O 9.96114E-01 NA 1.53529E-03 FE 2.37784E-04 NI 2.44611E-05  
CL 1.53529E-03 ZE 7.10858E-04 CR 6.21233E-05 H+1 -2.19937E-04

Constitution:	SiteFraction	Molality	Activity	log10Act
H2O	9.96603E-01	5.55084E+01	9.96160E-01	-0.0017
CL-1	1.53630E-03	8.55682E-02	6.59873E-02	-1.1805
NA+1	1.53630E-03	8.55681E-02	6.60024E-02	-1.1804
FE+2	1.38015E-04	7.68713E-03	2.72477E-03	-2.5647
FEOH+1	9.99243E-05	5.56555E-03	4.29714E-03	-2.3668
CRO+1	5.41433E-05	3.01566E-03	2.32838E-03	-2.6329
NI+2	2.44566E-05	1.36217E-03	4.85058E-04	-3.3142

CROH+2	6.08166E-06	3.38734E-04	1.20412E-04	-3.9193
HCRO2	1.90785E-06	1.06263E-04	1.06253E-04	-3.9737
NIOH+1	2.05375E-08	1.14389E-06	8.83196E-07	-6.0539
CR+3	2.00706E-08	1.11788E-06	1.09420E-07	-6.9609
CRO2-1	1.11015E-08	6.18327E-07	4.77408E-07	-6.3211
OH-1	2.33373E-09	1.29983E-07	1.00231E-07	-6.9990
H+1	2.32492E-09	1.29492E-07	1.00000E-07	-7.0000
O3	1.00000E-12	0.00000E+00	2.0445E-113	-112.6894
H2	1.00000E-12	0.00000E+00	5.91876E-18	-17.2278
FEOH+2	1.00000E-12	0.00000E+00	1.92263E-11	-10.7161
H2O2	1.00000E-12	0.00000E+00	3.35254E-46	-45.4746
FEO3H3-1	1.00000E-12	0.00000E+00	3.66478E-44	-43.4360
FECL+2	1.00000E-12	0.00000E+00	5.98607E-16	-15.2229
FE2O2H2+4	1.00000E-12	0.00000E+00	1.59752E-20	-19.7966
FE+3	1.00000E-12	0.00000E+00	3.19121E-16	-15.4960
HCLO	1.00000E-12	0.00000E+00	2.78953E-45	-44.5545
HCLO2	1.00000E-12	0.00000E+00	1.00471E-87	-86.9980
CRO4-2	1.00000E-12	0.00000E+00	3.01208E-26	-25.5211
HCRO4-1	1.00000E-12	0.00000E+00	9.10293E-27	-26.0408
HO2-1	1.00000E-12	0.00000E+00	7.09476E-51	-50.1491
CR2O7-2	1.00000E-12	0.00000E+00	3.01216E-51	-50.5211
O2	1.00000E-12	0.00000E+00	2.17016E-58	-57.6635
CR+2	1.00000E-12	0.00000E+00	5.24730E-15	-14.2801
CLO4-1	1.00000E-12	0.00000E+00	5.4469E-133	-132.2639
CLO3-1	1.00000E-12	0.00000E+00	1.0470E-105	-104.9800
CLO2-1	1.00000E-12	0.00000E+00	1.05154E-82	-81.9782
CLO2	1.00000E-12	0.00000E+00	1.1402E-100	-99.9430
CLO-1	1.00000E-12	0.00000E+00	6.04737E-46	-45.2184
CL2	1.00000E-12	0.00000E+00	3.87747E-50	-49.4115

Solution Properties: pH = 7.0000 Eh = 0.0000 V I = 0.1086

pe = 0.0000 Ah = 0.0000 kJ m\* = 0.1892

Aw = 0.9962 Os = 1.1287 pKw = 13.9973

At1= 1.0000E-12 At2= 1.2998E-07 (equiv\_mol/kg\_H2O)

**POLY\_3: l-st p**

\*\*\* STATUS FOR ALL PHASES

PHASE	STATUS	DRIVING FORCE	MOLES
AQUEOUS#1	ENTERED	0.000000E+00	5.572498E+01

SUSPENDED PHASES:

WUSTITE#1 REF\_ELECTRODE#1 NIO\_S2#1 NIOOH#1 NIO2H2#1 NIO#1 NIFE2O4#1 NICR2O4#1  
NAOH\_S2#1 NAOH#1 NAO2#1 NA2O\_S3#1 NA2O\_S2#1 NA2O2\_S2#1 NA2O2#1 NA2O#1  
NA2FEO2#1 NA2CRO4\_S2#1 NA2CRO4#1 NA2CR2O4#1 MAGNETITE#1 HEMATITE#1  
HALITE#1

FEOOH#1 FEO3H3#1 FEO2H2#1 FECR2O4#1 FE2O3\_GAMMA#1 FE2O2O2H2#1 FCC\_A1#1  
CRO3#1

CRO2#1 CR8O21#1 CR5O12#1 CR2O3#1 BCC\_A2#1 GAS#1

**POLY\_3: sh b n n (\*)**

B=1005.9877

N=55.724975

N(H2O)=55.508435, N(H+1)=-1.2255986E-2, N(ZE)=3.9612563E-2, N(NA)=8.5554E-2,

N(CL)=8.5554078E-2, N(Fe)=1.3250495E-2, N(CR)=3.4618194E-3,

N(NI)=1.3630942E-3

**@@ Calculating an initial equilibrium with all phases presented:**

**POLY\_3: c-st p \*=ent 0**

**POLY\_3: c-st p AQUEOUS=ent 55.8**

**POLY\_3: c-st p REF\_ELE=sus**

**POLY\_3: l-st p**

\*\*\* STATUS FOR ALL PHASES

PHASE	STATUS	DRIVING FORCE	MOLES
WUSTITE#1	ENTERED	0.000000E+00	0.000000E+00
NIO_S2#1	ENTERED	0.000000E+00	0.000000E+00
NIOOH#1	ENTERED	0.000000E+00	0.000000E+00
NIO2H2#1	ENTERED	0.000000E+00	0.000000E+00
NIO#1	ENTERED	0.000000E+00	0.000000E+00
NIFE2O4#1	ENTERED	0.000000E+00	0.000000E+00
NICR2O4#1	ENTERED	0.000000E+00	0.000000E+00
NAOH_S2#1	ENTERED	0.000000E+00	0.000000E+00
NAOH#1	ENTERED	0.000000E+00	0.000000E+00
NAO2#1	ENTERED	0.000000E+00	0.000000E+00

NA2O_S3#1	ENTERED	0.000000E+00	0.000000E+00
NA2O_S2#1	ENTERED	0.000000E+00	0.000000E+00
NA2O2_S2#1	ENTERED	0.000000E+00	0.000000E+00
NA2O2#1	ENTERED	0.000000E+00	0.000000E+00
NA2O#1	ENTERED	0.000000E+00	0.000000E+00
NA2FEO2#1	ENTERED	0.000000E+00	0.000000E+00
NA2CRO4_S2#1	ENTERED	0.000000E+00	0.000000E+00
NA2CRO4#1	ENTERED	0.000000E+00	0.000000E+00
NA2CR2O4#1	ENTERED	0.000000E+00	0.000000E+00
MAGNETITE#1	ENTERED	0.000000E+00	0.000000E+00
HEMATITE#1	ENTERED	0.000000E+00	0.000000E+00
HALITE#1	ENTERED	0.000000E+00	0.000000E+00
FEOH#1	ENTERED	0.000000E+00	0.000000E+00
FEO3H3#1	ENTERED	0.000000E+00	0.000000E+00
FEO2H2#1	ENTERED	0.000000E+00	0.000000E+00
FECR2O4#1	ENTERED	0.000000E+00	0.000000E+00
FE2O3_GAMMA#1	ENTERED	0.000000E+00	0.000000E+00
FE2O2O2H2#1	ENTERED	0.000000E+00	0.000000E+00
FCC_A1#1	ENTERED	0.000000E+00	0.000000E+00
CRO3#1	ENTERED	0.000000E+00	0.000000E+00
CRO2#1	ENTERED	0.000000E+00	0.000000E+00
CR8O21#1	ENTERED	0.000000E+00	0.000000E+00
CR5O12#1	ENTERED	0.000000E+00	0.000000E+00
CR2O3#1	ENTERED	0.000000E+00	0.000000E+00
BCC_A2#1	ENTERED	0.000000E+00	0.000000E+00
AQUEOUS#1	ENTERED	0.000000E+00	5.583656E+01
GAS#1	ENTERED	0.000000E+00	0.000000E+00

SUSPENDED PHASES:

REF\_ELECTRODE#1

**POLY\_3: c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 3913 grid points in 0 s

465 ITS, CPU TIME USED 1 SECONDS

**POLY\_3: l-e ,x**

Output from POLY-3, equilibrium = 1, label A0 , database: PAQ2

Conditions:

P=1E5, T=298.15, B(H2O)=1000, N(NA)=8.5554E-2, N(CL)=8.5554E-2,  
N(FE)=1.32505E-2, N(CR)=3.4618E-3, N(NI)=1.36309E-3, LNACR(H+1)=-16.1181,  
MUR(ZE)=0

DEGREES OF FREEDOM 0

Temperature 298.15 K ( 25.00 C), Pressure 1.000000E+05

Number of moles of components 5.56976E+01, Mass in grams 1.00595E+03

Total Gibbs energy -1.70630E+07, Enthalpy -1.59012E+07, Volume -6.20719E-15

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
H2O	5.5508E+01	9.9660E-01	9.9654E-01	-8.5924E+00	AQUEOUS#
H+1	-5.2837E-02	-9.4864E-04	1.0000E-07	-3.9956E+04	SER
ZE	5.2863E-02	9.4911E-04	1.0000E+00	-4.4035E-12	REF_ELEC
NA	8.5554E-02	1.5360E-03	1.5537E-50	-2.8431E+05	SER
CL	8.5554E-02	1.5360E-03	1.2078E-30	-1.7077E+05	SER
FE	1.3251E-02	2.3790E-04	5.2232E-26	-1.4431E+05	SER
CR	3.4618E-03	6.2154E-05	1.2572E-53	-3.0196E+05	SER
NI	1.3631E-03	2.4473E-05	1.0073E-15	-8.5603E+04	SER

AQUEOUS#1 Status ENTERED Driving force 0.0000E+00

Moles 5.5653E+01, Mass 1.0045E+03, Volume fraction 1.0000E+00 Mole fractions:

H2O 9.96925E-01 NA 1.53727E-03 NI 2.36160E-07 CR 1.00000E-11

CL 1.53727E-03 ZE 4.71032E-07 FE 1.68577E-11 H+1 -3.11048E-10

Constitution:	SiteFraction	Molality	Activity	log10Act
H2O	9.96925E-01	5.55084E+01	9.96603E-01	-0.0015
CL-1	1.53727E-03	8.55948E-02	6.73703E-02	-1.1715
NA+1	1.53727E-03	8.55947E-02	6.73703E-02	-1.1715
NI+2	2.35950E-07	1.31376E-05	5.07139E-06	-5.2949
OH-1	2.28889E-09	1.27444E-07	1.00279E-07	-6.9988
H+1	2.27916E-09	1.26903E-07	1.00000E-07	-7.0000

NIOH+1	2.10599E-10	1.17261E-08	9.23842E-09	-8.0344
FE+2	6.13590E-12	3.41644E-10	1.31278E-10	-9.8818
FEOH+1	4.72178E-12	2.62907E-10	2.07132E-10	-9.6838
O3	1.00000E-12	0.00000E+00	2.0474E-113	-112.6888
HCLO2	1.00000E-12	0.00000E+00	1.02675E-87	-86.9885
HCLO	1.00000E-12	0.00000E+00	2.84935E-45	-44.5453
H2O2	1.00000E-12	0.00000E+00	3.35574E-46	-45.4742
HCRO2	1.00000E-12	0.00000E+00	4.47228E-13	-12.3495
H2	1.00000E-12	0.00000E+00	5.91876E-18	-17.2278
HCRO4-1	1.00000E-12	0.00000E+00	3.83517E-35	-34.4162
FEOH+2	1.00000E-12	0.00000E+00	9.26752E-19	-18.0330
HO2-1	1.00000E-12	0.00000E+00	7.10153E-51	-50.1486
FEO3H3-1	1.00000E-12	0.00000E+00	1.76819E-51	-50.7525
FECL+2	1.00000E-12	0.00000E+00	2.94449E-23	-22.5310
FE2O2H2+4	1.00000E-12	0.00000E+00	3.71177E-35	-34.4304
FE+3	1.00000E-12	0.00000E+00	1.53750E-23	-22.8132
O2	1.00000E-12	0.00000E+00	2.17223E-58	-57.6631
CROH+2	1.00000E-12	0.00000E+00	5.06585E-13	-12.2953
CRO4-2	1.00000E-12	0.00000E+00	1.26903E-34	-33.8965
CRO2-1	1.00000E-12	0.00000E+00	2.00946E-15	-14.6969
CRO+1	1.00000E-12	0.00000E+00	9.79571E-12	-11.0090
CR2O7-2	1.00000E-12	0.00000E+00	5.34416E-68	-67.2721
CR+3	1.00000E-12	0.00000E+00	4.60120E-16	-15.3371
CR+2	1.00000E-12	0.00000E+00	2.20654E-23	-22.6563
CLO4-1	1.00000E-12	0.00000E+00	5.5717E-133	-132.2540
CLO3-1	1.00000E-12	0.00000E+00	1.0705E-105	-104.9704
CLO2-1	1.00000E-12	0.00000E+00	1.07460E-82	-81.9688
CLO2	1.00000E-12	0.00000E+00	1.1652E-100	-99.9336
CLO-1	1.00000E-12	0.00000E+00	6.17706E-46	-45.2092
CL2	1.00000E-12	0.00000E+00	4.04171E-50	-49.3934

Solution Properties: pH = 7.0000 Eh = -0.0000 V I = 0.0856

pe = -0.0000 Ah = -0.0000 kJ m\* = 0.1712

Aw = 0.9966 Os = 1.1033 pKw = 13.9973

At1= 1.0000E-12 At2= 1.2745E-07 (equiv\_mol/kg\_H2O)

HEMATITE#1            Status ENTERED    Driving force 0.0000E+00  
Moles 2.6376E-02, Mass 8.4242E-01, Volume fraction 0.0000E+00 Mole fractions:  
ZE 1.20000E+00 FE 4.00000E-01 CL 0.00000E+00 NI 0.00000E+00  
H2O 6.00000E-01 CR 0.00000E+00 NA 0.00000E+00 H+1 -1.20000E+00

NIFE2O4#1            Status ENTERED    Driving force 0.0000E+00  
Moles 9.4497E-03, Mass 3.1640E-01, Volume fraction 0.0000E+00 Mole fractions:  
ZE 1.14286E+00 FE 2.85714E-01 CR 0.00000E+00 CL 0.00000E+00  
H2O 5.71429E-01 NI 1.42857E-01 NA 0.00000E+00 H+1 -1.14286E+00

CR2O3#1            Status ENTERED    Driving force 0.0000E+00  
Moles 8.6546E-03, Mass 2.6308E-01, Volume fraction 0.0000E+00 Mole fractions:  
ZE 1.20000E+00 CR 4.00000E-01 CL 0.00000E+00 NI 0.00000E+00  
H2O 6.00000E-01 FE 0.00000E+00 NA 0.00000E+00 H+1 -1.20000E+00

**POLY\_3:sh b n n(\*)**

B=1005.9468

N=55.697645

N(H2O)=55.508435, N(H+1)=-5.2836909E-2, N(ZE)=5.2863107E-2, N(NA)=8.5554E-2,  
N(CL)=8.5554078E-2, N(FE)=1.3250503E-2, N(CR)=3.4618286E-3,  
N(NI)=1.3630942E-3

**POLY\_3: s-a-v 1 lnacr(H+1) -32.22994 0 0.5**

**POLY\_3: s-a-v 2 mur(Ze) -150000 200000 5000**

**POLY\_3: l-a-v**

Axis No 1: LNACR(H+1)            Min: -32.22994 Max: 0            Inc: 0.5

Axis No 2: MUR(ZE)                Min: -150000 Max: 200000        Inc: 5000

**POLY\_3: add 2**

**POLY\_3: add -2**

**POLY\_3: li-in-eq**

No 1 +2 P=100000, T=298.15, B(H2O)=1000., N(NA)=8.5554E-2,  
N(CL)=8.5554078E-2, N(FE)=1.3250503E-2, N(CR)=3.4618286E-3,  
N(NI)=1.3630942E-3, LNACR(H+1)=-16.118096, MUR(ZE)=-4.4035374E-12  
No 2 -2 P=100000, T=298.15, B(H2O)=1000., N(NA)=8.5554E-2,  
N(CL)=8.5554078E-2, N(FE)=1.3250503E-2, N(CR)=3.4618286E-3,

N(NI)=1.3630942E-3, LNACR(H+1)=-16.118096, MUR(ZE)=-4.4035374E-12

**POLY\_3: MAP**

Version S mapping is selected

INITIATED WORKSPACES ON FILE C:\Users\Anna\Documents\RESULT\_002.POLY3

Organizing start points

Using ADDED start equilibria

Tie-lines not in the plane of calculation

Generating start point 1

Generating start point 2

Generating start point 3

Generating start point 4

Phase region boundary 1 at: -1.612E+01 5.889E+04

AQUEOUS#1

\*\* CR2O3#1

HEMATITE#1

NIFE2O4#1

Calculated.. 34 equilibria

Terminating at axis limit.

Phase region boundary 2 at: -3.223E+01 -8.162E+03

AQUEOUS#1

\*\* CR2O3#1

HEMATITE#1

NIFE2O4#1

Calculated. 38 equilibria

...

Phase region boundary 87 at: -1.612E+01 -1.748E+03

AQUEOUS#1

CR2O3#1

\*\* FECR2O4#1

HEMATITE#1

NIFE2O4#1

Calculated. 6 equilibria

Terminating at known equilibrium

\*\*\* BUFFER SAVED ON FILE: C:\Users\Anna\Documents\RESULT\_002.POLY3

CPU time for mapping 227 seconds

**POLY\_3: post**

POLY-3 POSTPROCESSOR VERSION 3.2

Setting automatic diagram axes

**POST: l-sym**

DEFINED CONSTANTS

AH2O=55.508435, RNF=96485.309, ZERO=0

DEFINED FUNCTIONS AND VARIABLES%

EH=MUR(ZE)/RNF

PH=- LOG10(ACR(H+1) )

TEMP\_C=T-273.15

**POST: s-d-a x pH**

**POST: s-a-text x n pH**

**POST: s-s-s x n 0 14**

**POST: s-d-a y Eh**

**POST: s-a-text y n Eh (V)**

**POST: s-s-s y n -1.0 1.5**

**POST: s-l-c e**

**POST: s-font , .32**

**POST: s-t-m-s y**

**POST: s-title 304L stainless steel (Fe-18Cr-8Ni wt%) in H2O-5%NaCl System (T=25 C)**

**POST: pl,,,**

The composition set AQUEOUS#3 created from the store file

304L stainless steel (Fe-18Cr-8Ni wt%) in H<sub>2</sub>O-5%NaCl System (T=25 C)

2016.02.09.13.25.41

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, NA, CL, FE, CR, NI

P=1E5, T=298.15, B(H<sub>2</sub>O)=1000., N(NA)=8.5554E-2, N(CL)=8.55541E-2, N(FE)=1.32505E-2, N(CR)=3.46183E-3, N(NI)=1.36309E-3

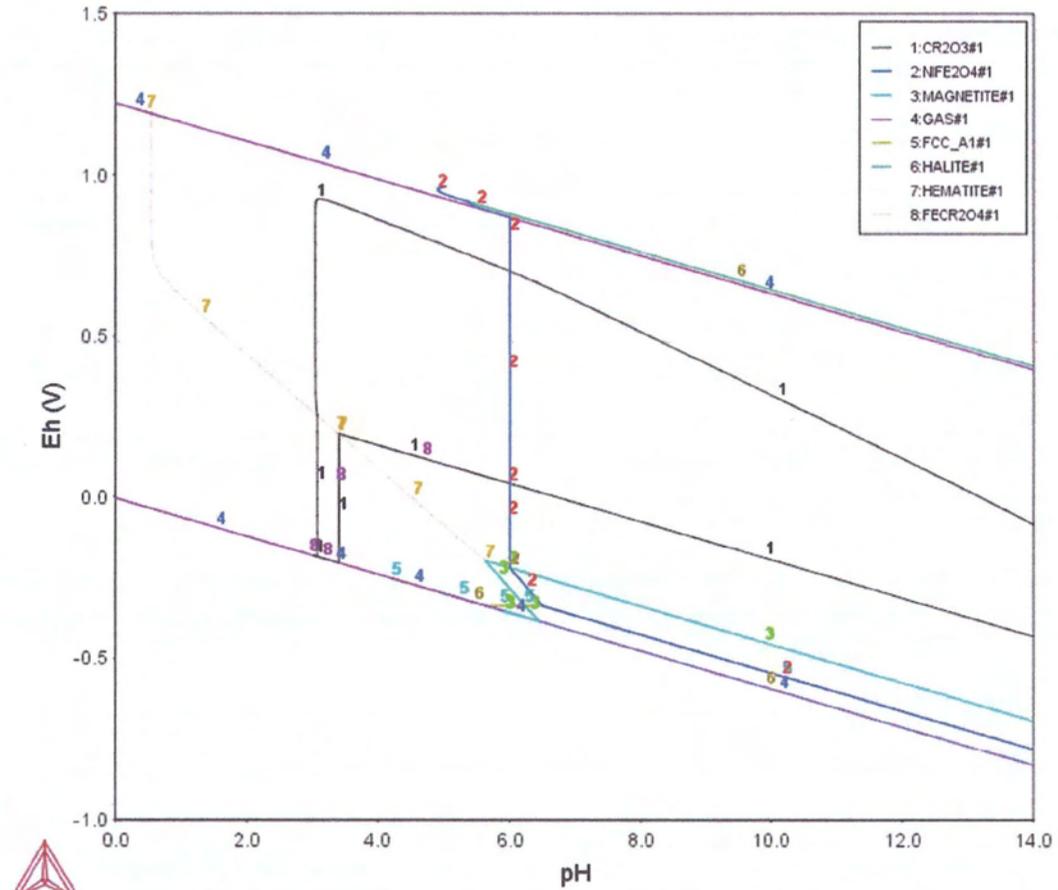


Fig 78: 304L stainless steel in 1 Kg H<sub>2</sub>O-5% NaCl (T=25 °C)

304L stainless steel (Fe-18Cr-8Ni wt%) in H<sub>2</sub>O-5%NaCl System (T=60 °C)

2016.02.09.14.17.20

PAQ2: H<sub>2</sub>O, H<sup>+</sup>, ZE, NA, CL, FE, CR, NI

P=1E5, T=333.15, B(H<sub>2</sub>O)=1000., N(NA)=8.5554E-2, N(CL)=8.55541E-2, N(FE)=1.32505E-2, N(CR)=3.46182E-3, N(NI)=1.36309E-3

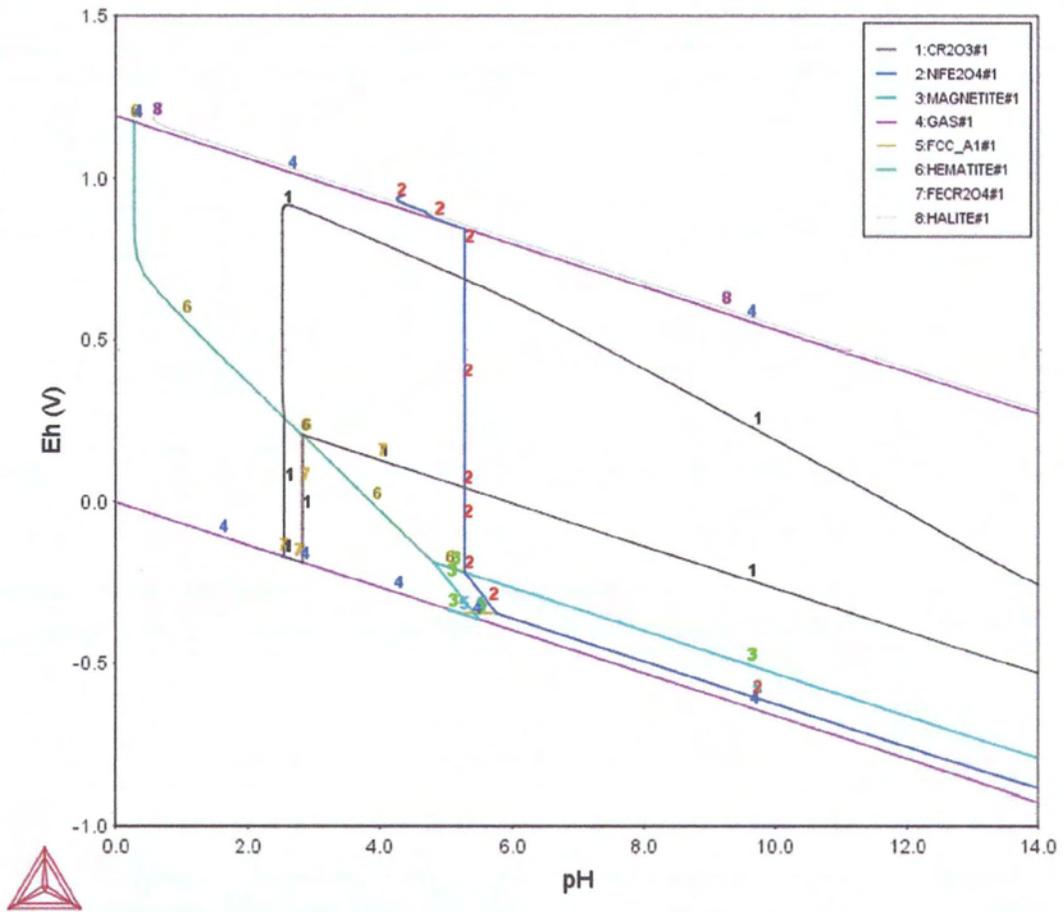


Fig 79: 304L stainless steel in 1 Kg H<sub>2</sub>O-5% NaCl (T=60 °C)

304L stainless steel (Fe-18Cr-8Ni wt%) in H<sub>2</sub>O-5%NaCl System (T=90 C)

2016.02.09.14.37.20

PAO2: H<sub>2</sub>O, H+1, ZE, NA, CL, FE, CR, NI

P=1E5, T=363.15, B(H<sub>2</sub>O)=1000., N(NA)=8.5554E-2, N(CL)=8.55541E-2, N(FE)=1.32505E-2, N(CR)=3.46182E-3, N(NI)=1.36309E-3

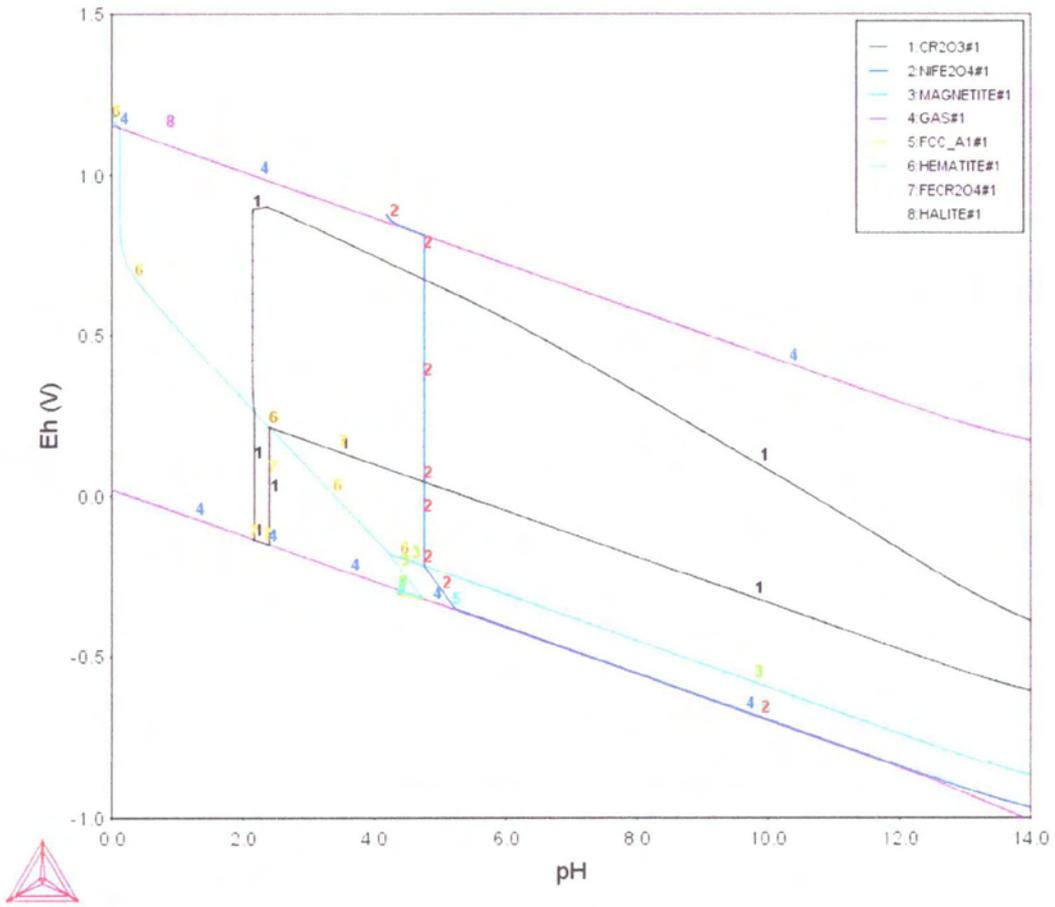


Fig 80: 304L stainless steel in 1 Kg H<sub>2</sub>O-5% NaCl (T=90 °C)

ΠΑΝΕΠΙΣΤΗΜΙΟ ΘΕΣΣΑΛΙΑΣ  
ΒΙΒΛΙΟΘΗΚΗ



004000135180

