

ACKNOWLEDGEMENT

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List of abbreviations

AISI	American Iron and Steel Institute
ASM	American Society of Materials
ASTM	American Society of Testing and Materials
C	Carbon
CaCO ₃	Calcium Carbonate
CaCr ₂ O ₄	Calcium Chromium Oxide
CaFe ₂ O ₄	Calcium Iron Oxide
CaNiO ₂	Calcium Nickel Oxide
CaO	Calcium Oxide
CaSO ₄	Calcium Sulfate
Cl	Chlorine
CO	Carbon Oxide
CO ₂	Carbon Dioxide
Co ₃ O ₃	Cobalt Oxide
Cr	Chromium
Cr ₂ O ₃	Chromium Oxide
EDS	Energy dispersive X-ray spectroscopy
Fe	Iron
FeCl ₃	Iron Chloride
Fe ₂ O ₃	Iron Oxide
FeCr ₂ O ₄	Iron Chromium Oxide
FeO ₂ Cl ₂	Iron Oxide Chloride
H ₂	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen Sulfide
HCl	Hydrogen Chloride
HNO ₃	Hydrogen Nitrate
K	Potassium
K ₂ CO ₃	Potassium Carbonate
KCl	Potassium Chloride
KMnO ₄	Potassium Manganese Oxide
Li	Lithium
Li ₂ CO ₃	Lithium Carbonate
LiCrO ₂	Lithium Chromium Oxide
LiFeO ₂	Lithium Iron Oxide
M	Metal
MgCO ₃	Magnesium Carbonate
MgO	Magnesium Oxide
MgFe ₂ O ₄	Magnesium Iron Oxide
MgCr ₂ O ₄	Magnesium Chromium Oxide
MgNiO ₂	Magnesium Nickel Oxide
Mn	Manganese
MnO	Manganese Oxide
Mn _{1.5} Cr _{1.5} O ₄	Manganese Chromium Oxide

Mo	Molybdenum
MoO ₃	Molybdenum Oxide
Na	Sodium
NaCl	Sodium Chloride
Na ₂ O	Sodium Oxide
Na ₂ CO ₃	Sodium Carbonate
Na ₂ FeO ₄	Sodium Iron Oxide
NaNiO ₂	Sodium Nickel Oxide
NaNO	Sodium Nitrate
NaOH	Sodium Hydroxide
Na ₂ SO ₄	Sodium Sulfate
Ni	Nickel
NiO	Nickel Oxide
NiCr ₂ O ₄	Nickel Chromium Oxide
NiMoO ₄	Nickel Molybdenum Oxide
O ₂	Oxygen
P	Phosphorus
S	Sulfur
SEM	Scanning Electron Microscope
Si	Silicon
SO ₂	Sulfur Oxide
SUS	Steel Use Stainless
XRD	X-Ray Diffraction
ZnCl ₂	Zinc Chloride

List of symbols

g/cm ³	Gram per centimetre volume
g/mol	Gram per mole
⁰ C	Degree Celcius
K	Kelvin
hr	Hour
wt%	Weight percent
MPa	Mega Pascal
mg/cm ²	Milligram per centimetre square
ml	Millilitre
ml/min	Millilitre per minute
mm	Millimetre
psi	Pound per square inch
µm	Micronmetre

LIST OF APPENDIX

Appendix A The calculation to determine % of weight change

LIST OF PAPER PUBLISHED

1. Habsah Md Ishak, M.Misbahul Amin and Mohd Nazree Derman, (2009), Effect of temperature on corrosion behaviour of AISI 304 stainless steel with magnesium carbonate deposit. *Journal of Physical Science*, 19(2), 137-141
2. M.Misbahul Amin, Khairrel Refazie Ahmad, Habsah Md Ishak and Neelofar Amin (2009), Oxidation behaviour of SAE-1053 Alloy in presence of seawater. *Journal of Applied Science Research*, 5(1), 9-12

LIST OF PAPER PRESENTATION

1. Habsah Md Ishak, M.Misbahul Amin and Mohd Nazree Derman (2008), High temperature corrosion behaviour of steel with carbonate deposit at 1123K. *Science Technology and Science Social Conference (STSS 2008)*, 2nd – 4th June 2008, MS Garden Hotel, Kuantan, Pahang
2. Habsah Md Ishak, M.Misbahul Amin and Mohd Nazree Derman (2008), Effect of temperature on corrosion behaviour of AISI 304 stainless steel with magnesium carbonate deposit. 2nd USM Penang International Conference for Young Chemists (ICYC 2008), 18th – 20th June 2008, Universiti Sains Malaysia, Penang
3. Habsah Md Ishak, M.Misbahul Amin and Mohd Nazree Derman (2008), The hot corrosion of AISI 304 stainless steel with and without CaCO₃ deposit. *Malaysian Metallurgical Conference 2008*, 3rd – 4th December 2008, DANAU Golf Club, Bangi, Selangor
4. Habsah Md Ishak, M.Misbahul Amin and Mohd Nazree Derman (2009), High temperature corrosion behaviour of AISI 316L in presence of carbonate deposit. *Engineering Postgraduate Conference 2009*, 25th–26th July 2009, Dragon and Phoenix Jejawi, Universiti Malaysia Perlis

KELAKUAN KAKISAN SUHU TINGGI PADA KELULI TAHAN KARAT AUSTENIT DENGAN ENDAPAN CaCO_3 DAN MgCO_3

ABSTRAK

Kajian ke atas kelakuan kakisan suhu tinggi pada keluli tahan karat austenit dijalankan pada suhu 850°C , 900°C , 950°C dan 1000°C bagi tempoh pendedahan 24 hingga 120 jam dengan endapan kalsium karbonat (CaCO_3) dan magnesium karbonat (MgCO_3). Dua jenis keluli tahan karat austenit yang banyak terdapat di pasaran iaitu gred AISI 304 and AISI 316L dipilih dalam kajian ini. Keluli gred ini merupakan keluli yang banyak digunakan untuk komponen dalam industri petrokimia, loji kuasa haba, komponen dandang, pengandung tekanan dan lain-lain kerana rintangan kakisannya pada suhu tinggi dan dalam persekitaran menghakis secara umumnya adalah lebih baik dari aloi-aloi lain yang berasaskan besi. Kelakuan kakisan dan morfologi dinilai melalui kinetik perubahan berat, struktur morfologi endapan yang terbentuk diatas permukaan aloi dinilai dengan menggunakan mikroskop imbasan elektron (SEM), elemen komposisi yang wujud dalam keluli oksida dianalisis melalui tenaga penyebaran sinar-X (EDS) dan hasil kakisan dianalisa dengan menggunakan pembelauan sinar-X (XRD). Lengkung kinetik pengoksidaan aloi menunjukkan keadaan parabola bagi kedua-dua jenis aloi. Bagi aloi AISI 304 yang disalut dengan kalsium karbonat menunjukkan kehilangan berat pada semua suhu yang diuji manakala AISI 316L menunjukkan berat bertambah pada suhu 850°C dan 900°C . Bagaimanapun pada suhu 950°C dan 1000°C aloi ini mengalami kehilangan berat sepanjang masa pendedahan ujikaji dijalankan. Sementara itu, bagi aloi yang disalut oleh magnesium karbonat, AISI 304 mengalami pertambahan berat pada 850°C tetapi berat berkurangan pada suhu 900°C , 950°C dan 1000°C sama dengan AISI 316L. Ini menunjukkan AISI 316L mempunyai rintangan kakisan tinggi dibandingkan dengan AISI 304 kerana kehilangan berat yang sedikit pada aloi AISI 316L. Dengan pertambahan suhu dan masa pendedahan menyebabkan kehilangan berat keluli tahan karat juga bertambah. Pembentukan kerak padat dan rekat yang mempunyai retak dan liang pada aloi AISI 304 dan 316L disebabkan oleh pelepasan gas CO_2 dan CO . Fe_2O_3 , Cr_2O_3 , CaFe_2O_4 , CaCr_2O_4 dan NiMoO_4 merupakan hasil kakisan yang terbentuk pada AISI 304 dan 316L yang disalut dengan kalsium karbonat. Untuk aloi yang disalut dengan magnesium karbonat, hasil kakisan adalah Fe_2O_3 , Cr_2O_3 , MgCr_2O_4 dan NiMoO_4 . Morfologi kakisan suhu tinggi pada aloi yang disalut dengan kalsium karbonat menunjukkan serangan kakisan yang seragam dan mempunyai liang dan retak manakala bagi aloi yang disalut dengan magnesium karbonat menunjukkan serangan kakisan antara butir dengan retak dan liang.

HIGH TEMPERATURE CORROSION BEHAVIOUR OF AUSTENITIC STAINLESS STEEL WITH CaCO_3 AND MgCO_3 DEPOSIT

ABSTRACT

The high temperature corrosion behaviour of austenitic stainless steel was studied at 850⁰C, 900⁰C, 950⁰C and 1000⁰C for 24 to 120 hr exposure time with CaCO_3 and MgCO_3 deposit. Two commercial available austenitic stainless steel grade of AISI 304 and AISI 316L were selected. Austenitic stainless steel type AISI 304 and 316L are extensively and widely used in petrochemical, thermal power plants, boiler part, pressure vessel, etc. due to their improved corrosion resistance at elevated temperatures and corrosive conditions. The corrosion behaviour and morphological developments were investigated by weight change kinetics, morphological structures of deposits on the surface of alloy scales by scanning electron microscopy (SEM), elemental composition of oxide alloy was analyzed by energy dispersive X-Ray (EDS) analysis and the corrosion product was analyzed by X-ray diffraction. The oxidation kinetics curves of the alloy showing parabolic nature for both alloys. CaCO_3 coated AISI 304 revealed weight loss at all temperature while AISI 316L reveals weight gain at 850⁰C and 900⁰C. However at 950⁰C and 1000⁰C AISI 316L suffered weight loss through out the experiment period. Meanwhile MgCO_3 induced alloy AISI 304 suffered the weight gain at 850⁰C and weight loss at 900⁰C, 950⁰C and 1000⁰C as similar with AISI 316L. On the other hand, AISI 316L showed the highest corrosion resistance than AISI 304 because of the weight loss was relatively small than AISI 304 at 120hr. By increasing the temperature and exposure time the weight loss of alloys were increased. The developments of adherent, compact with pores and crack scale on the AISI 304 and 316L were due to evolution of CO and CO₂ gas. Fe₂O₃, Cr₂O₃ and CaFeO₂ are corrosion products formed on the AISI 304 and 316L coating with CaCO_3 . For MgCO_3 coated alloy, the corrosion product are Fe₂O₃, Cr₂O₃, MgFe₂O₂ and MgCrO₄. The hot corrosion morphology of the alloy induced by CaCO_3 coating shows a typical uniform attack, some pores and crack developed while on the MgCO_3 coated alloy shows some intergranular attack with crack and pores.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The studies reported here on high temperature corrosion behaviour of austenitic stainless steel in presence of carbonate deposit . High temperature corrosion in general terms refers to the accelerated attack of the hot gas path components of the equipment such as boiler, steam generator, heat exchanger, turbine etc due to the presence of certain compounds in the combustion products represent the most deleterious forms of surface degradation which can lead to the loss of mechanical strength and catastrophic failure of structural and engineering components.

High temperature corrosion are generally metal/gas or metal/vapour reaction involving nonmetals such as oxygen, halogens, hydrogen sulphide, sulphur vapour, etc. and oxidation, scaling and tarnishing are the more important forms. High temperature corrosion involves localized accelerated degradation of metal usually associated with deposition of salts or other compounds from hot gases contacting the metal surface. Several other corrosion phenomena are associated with high temperature corrosion as derivatives of the scaling. High temperature corrosion often occurs in process units using gases as feedstock or in the hot gas path. (Roberge, 1999)

In most industrial environments, predominant mode of corrosion often participates in the high temperature corrosion reactions is oxidation. Alloy often rely upon the oxidation reaction to develop a protective scale to resist corrosion attack such as

sulfidation, carburization and other form of high temperature attack. At high temperature metal can react directly with the gaseous atmosphere. The properties of high temperature oxide films such as their thermodynamics stability, ionic defect structure and detailed morphology play a crucial role in determining the oxidation resistance of a metal or alloy in a specific environment. High temperature corrosion is a widespread problem in various industries such as power generation, aerospace and gas turbine, heat treating, mineral and metallurgical processing, chemical processing, refining and petrochemical, automotive, pulp and paper and waste incineration.

High temperature corrosion is normally taken to apply to the reaction taking place between metals and gases at temperature above 100°C . In practical terms, it also usually means a temperature about 35% of the absolute melting range of a given metal or alloy (or up to 60% for some nickel and cobalt based alloys). For the conventional austenitic grades of stainless steel, such as type 304, this would be any temperature above 575°C (1050°F). At high temperature the changes can occur in the nature of the surface film of stainless steel. For example in an oxidizing gas, a protective oxide film is formed and in an environment containing sulfur bearing gases, the film will be form of sulfides. In more aggressive environments, with temperatures above 871°C (1600°F) the surface film may breakdown with a sudden increase in scaling.

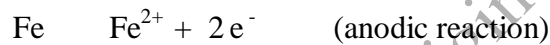
Corrosion problem normally related to the type of material for equipment used in industrial engineering or process plant. Without adequate corrosion resistance, components often fall short of the expected life. The additional cost usually associated with choosing increased corrosion resistance during the selection process is invariably less than that due to product contamination or lost production and high maintenance costs due to premature

failure. Austenitic stainless steels are widely used in industrial, because of their improved corrosion resistance at elevated temperatures and high temperature gaseous environments. However, when the iron based austenitic equipments or components are exposed with gas such as CO_2 , CO , H_2S and SO_2 or their complex multicomponent mixtures present in corrosive environments and/or medium under service condition extensively caused deterioration of materials. The serious consequences of the process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation and corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance and expensive over design, it is also jeopardizes safety and inhibits technological progress.

Thus, alloys for high temperature applications under aggressive environments must rely on the formation of protective oxide scales such as Cr_2O_3 . A Cr_2O_3 scale can usually loses its protective character at temperature above 1000°C , partially due to the formation of the volatile phase CrO_3 . Austenitic stainless steel are engineered to meet the demands of stability at high temperatures while retaining most of its ambient strength and exhibiting good creep and fatigue resistance. When exposed to a high temperature environment, austenitic stainless steel form a protective Cr oxide scale depending upon their composition. Austenitic alloys are now the principle material used for heat exchanger, steam generator, boiler part hot gas path section components because of their mechanical strength and surface stability at high temperatures. Austenitic stainless steel is mainly Fe-based alloys and may contain as many as eight or more alloying elements. The alloying elements play different roles. For example Cr is primarily alloys for environmental protection.

1.2 Corrosion

Corrosion is defined as the destruction or deterioration of material because of reaction with its environment (Fontana, 1987). Corrosion has been classified as wet corrosion and dry corrosion. Wet corrosion is corrosion in liquids or moist environments at temperatures up to 300°C usually in water-based. It is also called aqueous corrosion. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far. In the corrosion process the metal ions go into solution at anodic areas in an amount chemically equivalent to the reaction at cathodic areas.

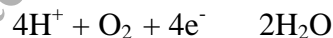


The reaction is rapid in most media, by the lack of pronounced polarization when iron is made an anode employing an external current. When iron corrodes, the rate is usually controlled by the cathodic reaction. The most common of cathodic reaction:-

- i. Hydrogen evolution



- ii. Oxygen reduction



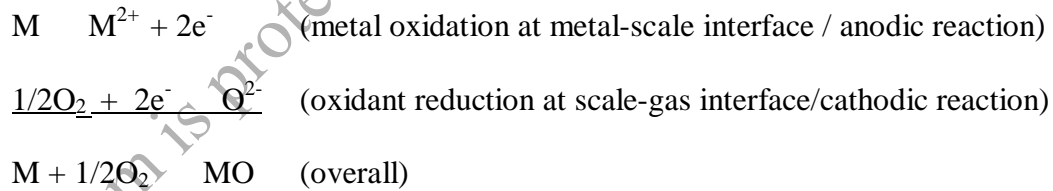
Dry corrosion is a form of corrosion that does not require the presence of liquid electrolyte or above the dew point of the environment at temperatures up to 1300°C. It is also called high temperature corrosion or hot corrosion. Vapor and gases are usually the corrodents. Meanwhile (Grubb et al., 2002) defined the dry corrosion as an accelerated corrosion of metal surfaces that results from the combined effect of oxidation and reactions with sulfur compounds and other contaminants such as chlorides, to form a molten salt on a metal surface that fluxes, destroys or disrupts the normal protective oxide.

According (Tsaur, 2005) the high temperature corrosion is commonly accompanied by the formation of a porous and non-protective oxide scale, which has attributed to the condensation of salts that attacks the protective oxide scale.

Corrosion rates can be divided into three categories: linear, decelerating, and accelerating. There are two methods for reporting corrosion rates: thickness of metal corroded per unit area, and % of weight (gain or loss) per unit area of exposed metal surface per unit time.

1.2.1 Reaction on high temperature corrosion

High temperature corrosion reaction proceeds by an electrochemical mechanism with some similarities to aqueous corrosion. The reaction proceeds by two basis separate reactions:



The most important of metal oxidation from an engineering view is the reaction rate. Oxide reaction product is generally retained on the metal surface, the rate of oxidation is usually measured and expressed as weight gain per unit area. Three basic kinetic laws have been used to characterize the oxidation rates of pure metals are illustrated in Fig. 1.1.

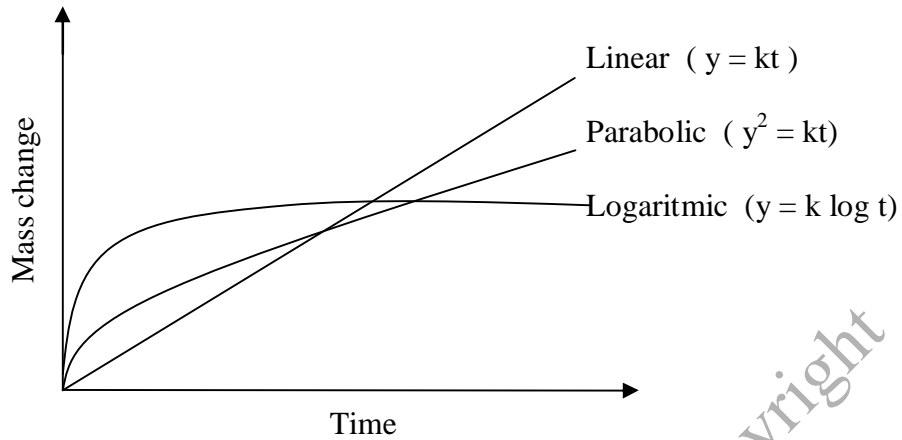


Figure 1.1 : Type of oxidation kinetics

At linear oxidation rate the metal surface is not protected by an oxide barrier layer, the oxidation rate usually remain constant with time. The characteristic of metals of this type of oxidation is a porous or cracked scale.

The linear oxidation rate is:

$$W = k_L t \quad (1.1)$$

where W is weight gain per unit area, t is time and k_L is the linear rate constant.

At low temperature when only a thin film of oxide is formed, the oxidation is usually observed to follow logarithmic or inverse logarithmic kinetic reaction rate:

$$W = k_e \log(Ct + A) \quad (1.2)$$

where W is weight gain per unit area, t is time and k_e , C and A are constant. The inverse logarithmic oxidation rate law is

$$1/W = C \circ k_i \log t \quad (1.3)$$

where W is weight gain per unit area, t is time and k_i and C are constant.

1.2.2 Mechanism of high temperature corrosion

The high temperature corrosion involves the processes oxidation, sulphidation, carburization and nitridation. Oxidation is generally described as the most commonly encountered form of high temperature corrosion. However, the oxidation process itself is not always detrimental. Most corrosion and heat resistant alloys rely on the formation of an oxide film to provide corrosion resistance whereas the chromium oxide is the most common of such films.

Oxidation which in the terminology used in gas metal reactions refers to the formation of oxides scales is the most frequent cause of high temperature corrosion of stainless steel. It can occur in oxygen, air, carbon dioxide or steam or in more complex industrial atmospheres containing significant quantities of these gases. Oxidation rate is depending to temperature and as temperature increased, the rate of oxidation also increased. Meanwhile the most common way of improving oxidation resistance is by increasing chromium contents. Apart from chromium, alloying additions used to enhance oxidation resistance include aluminium, silicon, nickel and some of the rare earth metals. Iron-nickel-chromium alloys are the most commonly employed materials for relatively low performance high temperature oxidation service because of their low cost, good mechanical properties and moderate oxidation resistance. In certain alloy systems, one or more dilute components that may form more stable oxides than the base metal may oxidize preferentially below the external surface of the metal. This is called internal oxidation and also occurs frequently in the iron, nickel and cobalts commonly used in high temperature applications.

Sulfidation is a common high temperature failure mechanism. As the name implies, it is describe the gaseous attack of metals by H_2S , S_2 , SO_2 and other gaseous sulfur species. A distinction can be made between sulfidation in gaseous environments and corrosion in the presence of salt deposits on corroding surfaces. At high temperature corrosion, hydrogen sulfide may act as an oxidizing agent in the formation of sulfide scales on metal substances. Iron base alloys are often used to contain hydrogen sulfide environments because of their low cost and good chemical resistance.

Carburization can occur when metals are exposed to carbon monoxide, methane, ethane or other hydrocarbons at temperature above $815^{\circ}C$. Carbon from the environment combines primarily with chromium but also with any other carbide formers (Nb, W, Mo, Ti, etc) present in the alloy to form internal carbides. Carburization is more common in the petrochemical industry. Apart from temperature, an increase in carbon potential of the gas mix is responsible for a higher severity of damage. Carburization has been identified as the most frequent failure mechanism of ethylene furnace tubes.

Thus, nitridation usually occurs when carbon, low alloy and stainless steel are exposed to an ammonia-bearing environment at elevated temperatures. It can also result from nitrogen atmospheres, especially under reducing condition and high temperatures.

There are many parallels to carburization; nitridation occurs when chromium and others elements combine with nitrogen to form embrittling nitrides in the microstructure.

1.3 Austenitic Stainless Steel

Austenitic stainless steels are complex alloys based on iron (Fe) and as a stable structure between 910 and 1400⁰C which have excellent strength characteristics at high temperatures. They have face centered cubic structure (fcc) with yield strength ranging from 200 to 275 MPa This structure is attained through the liberal use of austenitizing elements such as nickel, manganese and nitrogen. These steels are essentially nonmagnetic in the annealed condition and can be hardened only by cold working. Advantages include better corrosion resistance, excellent ductility, formality and toughness at extreme temperatures making them the largest stainless family in terms of number of alloys and usage. The austenite steels combine good corrosion resistance with ease of fabrication and thus are most widely used. Typical applications are furnace parts, heat exchangers, gas turbine parts, steam superheaters and piping, and chemical plant equipment for containing reactions and products at elevated temperatures.

Austenitic stainless steel grade known as 200 and 300 series, whereas 200 series defines as austenitic steels with manganese and nitrogen as nickel substitutes and 300 series as austenitic steels with nickel as the primary austenite stabilizer. The letter suffixes indicate other features in particular, -Lø denotes low carbon content. The carbon content is kept to 0.03% or less to avoid grain boundary precipitation of chromium carbide in the critical range 430 to 900⁰C.

1.4 The effect of carbonate deposit to corrosion behaviour

Deposit is defined as the material built up in a thin layer around the alloy surface. (Labuda, 1996). It is very well known that working equipment such as boiler, steam generator exhibit the presence of iron based deposits due to impurities in the water entering the boiler or steam generator (feedwater) and their increasing concentration and consolidation as the water boils as well as due to corrosion of boiler or steam generator materials. Water is the only medium for generate the steam for processing and manufacturing. In a boiler system, water is continuously fed as feed water that is converted into steam and delivered constantly to the main steam header. Common feed water contaminants that can form boiler deposits include calcium, magnesium, iron and silica. Deposit is formed by salts dissolved mainly calcium and magnesium carbonates or sulphates. When the boiler under operation, calcium and magnesium carbonate or sulphates are decomposed on hot metal surfaces forming hard scale deposits. These deposits usually form a dense layer that impedes heat transfer and cause costly boiler tube failures.

The formation of carbonate deposit is a common phenomenon in nature, as well as in many industrial processes. It may cause severe problem and economics loss. The deposit cause a drastic reduction in heat transfer rates in equipment such as boiler, steam generators, evaporators, heat exchangers, cooling jackets, etc. Boiler tube failures caused by overheating, increased fuel consumption and reduced efficiency of equipment. Equipment failure from corrosion as a result of under deposit corrosion can significantly add to cost. (Parsons, 2004)

Calcium carbonate (CaCO_3) precipitation is a primary process that leads to deposit of scale on metal surfaces. The formation of mineral scale is a persistent and expensive problem in industry. Most corrosion products that are deposited in the boiler originate in the pre-boiler system. The majority of corrosion products consist of colloidal and particulate metals and their oxides. The compounds are swept into the boiler and deposit on boiler tube surfaces. A major factor contributing to this problem is water used for boiler operating. Corrosion not only contributes to deposits but also results in metal damage.

Calcium and magnesium carbonate are also chief source of scale in heat-exchange equipment, boilers, pipelines, etc. It is may caused foaming and carryover of solids with steam and embrittlement of boiler steel caused by carbonate or bicarbonate produce CO_2 in steam, a source of corrosion in condensate lines. As will be discussed below, the calcium and magnesium carbonate may influenced the corrosion behavior of iron based alloy at high temperature.

The studies described here were mainly done on the high temperature corrosion of austenitic stainless steel with carbonate deposit. Molten alkali carbonates have drawn the attention of many research groups because their useful applications in environmentally safe fuel and the recent developments, including fuel recovery such as hydrogen methane and other hydrocarbons from natural bio-compounds (Attia et al., 2002). Water with high concentration of salts such as carbonate salts (MgCO_3 and CaCO_3) and fouling are often used to generate steam and cooling in industrial processes, resulting deterioration of structural materials. Due to fouling and inorganic ingredients are caused deposits on the surface of metallic-base alloy used under service. During operation at high temperature the

deposit can also form corrosion film which is affecting the equipment and lead to numerous technical and economical problem.

To date, a many studies on the high temperature corrosion behavior of austenitic stainless steel mostly deals only with carbonate salt Li_2CO_3 , K_2CO_3 , Na_2CO_3 (Amin et al., 2003; Perez et al., 2000; Azzi & Rameau, 1984; Frangini, 2000). It is obvious that there is a conspicuous lack of data on high temperature corrosion in presence of MgCO_3 and CaCO_3 deposit. Based on this conclusion, studies of the high temperature corrosion behaviour of austenitic stainless steel grade AISI 304 and 316L at different temperature 850°C , 900°C , 950°C and 1000°C and different time exposure 24, 48, 72, 96 and 120hr were done.

This information is very important for material selection in heat exchanger, boiler part or steam generator etc design for industrial application. It appears that for a better understanding of high temperature corrosion behaviour of austenitic stainless steel and for providing guidance to a component designer for a material selection, it is vital to study the high temperature corrosion behaviour of austenitic stainless steel and compare their resistance to degradation in different temperatures, time exposure, different type of steel grade and salt deposit. Thus, the results obtained from these alloys can perhaps be generalized to alloys that are similar in character. In this research, weight gain/loss data, scale morphologies and composition are used to establish the role of alloying elements contributing to high temperature corrosion resistance of the austenitic stainless steel under investigation.