

Chlorine-Induced High Temperature Corrosion:

I. Metals and Alloys – A Review

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ABSTRACT

A review is presented on the available results of the corrosion of Co, Ni, Cr, Fe and their alloys in oxidizing and in oxidizing/sulphidizing atmospheres in the presence of chlorine. The thermodynamic aspect of the reactions between the metal and chlorine or hydrogen chloride are discussed using stability diagrams. The saturated vapour pressures of some chlorides are also reported.

It was clear from the results on the high temperature corrosion of metals and alloys in oxidizing environments that small additions of hydrogen chloride or chlorine accelerate the (oxidation) corrosion reactions. A mechanism has been proposed describing this "active oxidation" by several reaction steps and transport phenomena. The "active oxidation" is based on two simultaneous processes: 1) solid state diffusion, and 2) vapour phase transport of metal species. In oxidizing/sulphidizing environments, contradictory results have been obtained, but it is suggested that in this case, too, the corrosion is based on solid state diffusion and vapour phase transport of the metal species.

KEY WORDS

oxidation, sulphidation, hydrogen chloride, chlorine, high temperature corrosion, metals, cobalt, iron, nickel, chromium, alloys.

1. INTRODUCTION

During the operation of fossil-fuel-fired boilers, waste incinerators, coal gasification systems, and gas turbines, most of the used materials are exposed to severe and complex corrosive gases at high temperatures. These gases contain compounds of carbon, sulphur, oxygen and chlorine, often resulting in a rapid attack of the materials.

In the past, corrosion research in coal gasification systems was focussed on the oxygen and sulphur content of coal gasification atmospheres. This means that much effort was spent on finding materials with a good corro-

sion resistance against environments with low oxygen and high sulphur partial pressures. Several materials and also various protective coatings have been developed and tested, resulting in the design of several commercially available alloys with adequate mechanical and chemical properties in coal gasification atmospheres.

Due to the increased tendency to use coals contaminated with significant amounts of chlorine, additional problems occur in connection with the high concentration of chlorine in coal /26/. It was suggested /12,26/ that chlorine was present mostly as inorganic chlorides, such as sodium, potassium and calcium. More recent studies reported /26/ that chlorine is partly present as sodium chloride but that a part is also associated with weakly bonded chloride ions, for example, in British coals. Chlorine in the coals will rapidly be released as hydrogen chloride during the initial stage of gasification or combustion processes.

The mechanisms of attack by oxygen and sulphur are more or less understood today, but the effect of chlorides on corrosion is not clear /12/. At present there is a growing interest in knowledge regarding the corrosion behaviour in chlorine-containing environments. Due to the presence of chlorine, additional research is necessary, because other gaseous species next to oxygen and sulphur can have considerable effects on the long-term performance of the used materials.

From the literature it is known that the presence of chlorine causes an accelerated attack in oxidizing environments. See also an earlier review by Daniel and Rapp /96/. This is explained by a vapour phase transport of reactants which plays a dominant role at high temperatures and high concentrations of chlorine. The effect of chlorine on the sulphidation is not yet well understood. Only a few studies have been published on the effect of chlorine on the sulphidation rate, but more research is necessary to reveal the effect of the presence of chloride on the corrosion mechanism.

In this report, a review on high temperature corrosion influenced by chlorine or hydrogen chloride is presented. From the literature concerning the effect of chlorine/hydrogen chloride on the high temperature corrosion, it becomes apparent that much research has been focussed on the oxidation of various metals and alloys. In general, oxidation is accelerated by the

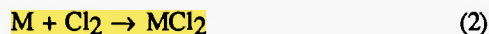
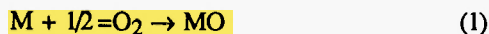
presence of hydrogen chloride or chlorine due to what is called "vapour phase induced accelerated underdeposit corrosion". The oxidation mechanism is proposed to consist of solid state diffusion and vapour phase transport of the metal-ions, forming an oxide scale. Whether an oxide scale will be formed depends on the process parameters. Also sublimation of the metal and/or oxide scale can have an effect on the total corrosion rate.

Finally, a mechanism is proposed concerning chlorine-induced accelerated corrosion in order to understand the influence of the presence of the aggressive gas components.

2. THERMODYNAMIC (AND KINETIC) FUNDAMENTALS

2.1 Thermodynamic and Kinetic Aspects

The high temperature corrosion of metals and alloys in an atmosphere containing oxygen and hydrogen chloride or chlorine will, depending on the gas composition, lead to several reactions between the metal or alloy and the gas compounds. Parallel and/or consecutive reactions will determine the overall corrosion, depending on the standard free energies, calculated from thermodynamic data [45]. Whether a reaction can occur is answered by the second law of thermodynamics, mostly written in terms of the Gibbs Free Energy (G). If only oxygen and chlorine containing species are present, the following reactions are considered:



where M is a divalent metal.

The reaction between the metal M and hydrogen chloride is almost identical due to the fact that hydrogen chloride is always in equilibrium with chlorine. The equilibrium oxygen and chlorine partial pressures can be calculated by equations derived from the second law of thermodynamics:

$$(pO_2)^{1/2} = a_{MO}/a_m \cdot \exp(\Delta G^\circ_{MO}/RT) \quad (3)$$

$$(pCl_2) = a_{MCl_2}/a_m \cdot \exp(\Delta G^\circ_{MCl_2}/RT) \quad (4)$$

where:

- P_x = partial pressure of gas x in equilibrium
- a_y = thermodynamic activity of component y
- ΔG°_x = standard free energy of formation of component x
- R = gas constant
- T = absolute temperature.

Some thermodynamic aspects with reference to iron, chromium and nickel have been reported by Ihara et al [5,36,37,38,39]. The authors assume a set of reactions which will play a role during the corrosion by the gas compounds. The standard free energy changes of the reactions are calculated from thermodynamic data and given as a function of the temperature. From the thermodynamic data [45], stability diagrams can be constructed. These diagrams are normally calculated at unit activity of the condensed phases, but in general, alloys are used and mixed products are formed, which means that the activity of the components is different from unity.

In such diagram the equilibrium dissociation pressures and the stable condensed phases, such as metal oxides, chlorides, and oxychlorides are shown.

In practice the thermodynamically stable phases are not always formed: kinetic factors are very important, too. If these factors are also accounted for in the stability diagrams, the boundaries will in general shift to higher partial pressures. If the solid phase activities are taken into account, the stability field boundaries result in an increase of the stability field of the metal component. Thus the equilibrium dissociation pressures of chlorine and/or oxygen increase. It was, furthermore, reported [36,71,72] that during the experiments sometimes a discrepancy was found between the formed corrosion products and the thermodynamically stable compounds. A major disadvantage of the thermodynamic phase stability diagrams [71,72] is that in the case of the formation of metal chlorides, the vapour pressures of the volatile species in equilibrium with the corresponding solids are neglected, resulting in the observed discrepancy between the detected and predicted corrosion products.

2.2. Vapour Pressures of Some Chlorides in Equilibrium with the Solid/Liquid Phase

It is clear from the literature that the addition of hydrogen chloride or chlorine to gaseous atmospheres in almost all cases leads to accelerated corrosion. **Hydrogen chloride- or chlorine-induced corrosion is due to the formation of volatile metal chlorides.** Due to the high vapour pressures of these species, **the metals or alloys and even the formed oxides will react with the aggressive gas compounds.** This was confirmed by the presence of metal chlorides deposited on the walls of reaction tubes. **In practice a vapour pressure of $1 \cdot 10^{-6}$ atm is used as the critical value. Above this value evaporation will become important.**

A review of vapour pressures and related data for the principal corrosion products of the metals Fe, Cr, Ni, and Co has been given by W.D. Halstead [32]. The vapour pressures of chlorides in equilibrium with the solid or liquid phase are given in Fig. 1. It is clear that FeCl_3 has the highest vapour pressure.

It is, of course, well-known that not only the vapour pressure value but also the change in free energy (ΔG) is of importance to predict the corrosion products. Other parameters are the local partial pressure of, for example, oxygen and sulphur, which also play a role in the total corrosion process.

3. THE HIGH TEMPERATURE CORROSION OF METALS AND ALLOYS IN ENVIRONMENTS CONTAINING OXYGEN AND HYDROGEN CHLORIDE OR CHLORINE

3.1. Cobalt

3.1.1. Introduction

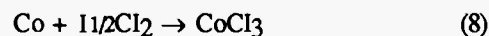
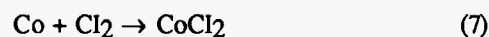
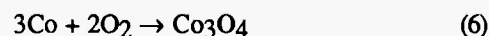
When cobalt is exposed at high temperatures to a gas mixture containing oxygen and chlorine, possible reaction products are: $\text{CoCl}_2(\text{g})$, $\text{CoCl}_3(\text{g})$, $\text{Co}_2\text{Cl}_4(\text{g})$, $\text{CoCl}_2(\text{s})$, $\text{CoO}(\text{s})$ and $\text{Co}_3\text{O}_4(\text{s})$. From the literature [11,41,44,46,53,59-64] it is known that the oxidation kinetics and mechanisms change significantly if chlorine is added to the oxidizing atmosphere. Depending on process parameters such as the temperature and the relative

activities of several gas components, different results were obtained.

In atmospheres containing chlorine and high partial pressures of oxygen, some mechanisms of induced accelerated oxidation by chlorine have been proposed [11,41,44,46,53,61-63] which can be described by the following three stages: initiation, propagation and termination.

3.1.2. Initiation

During the initial stage of the corrosion process the cobalt reacts at high temperatures with oxygen and chlorine, forming cobalt oxide and cobalt chloride, respectively. The following reactions are supposed to play a role:



During this stage, no protective oxide scale is formed on the specimen. The direct attack of cobalt by chlorine, according to reactions 7 and 8, results in a high amount of volatile cobalt chloride. After some time a high concentration of cobalt chloride will be present in the gas phase. This was confirmed by Jacobson et al [41] who used a mass spectrometer to determine the reaction products in the gas phase. These authors studied the reaction of cobalt with 1% chlorine in 1, 10 and 50% oxygen/argon atmospheres at 650 °C. In the case of 10 and 50% oxygen, volatilization occurred only in the first few minutes of the reaction. In 1% oxygen atmosphere, continuous volatilization took place. This may imply that a dense oxide scale is formed on the surface of the specimen in the case of 10 and 50% oxygen [41].

The scale formed in gas mixtures ($T = 650$ °C) with 10 and 50% oxygen and 1% chlorine consists mainly of CoO with only a thin layer of Co_3O_4 at the gas-scale interface. No condensed chlorides were detected. In a gas mixture containing 1% oxygen and 1% chlorine the scale cracked upon cooling and element mapping clearly indi-

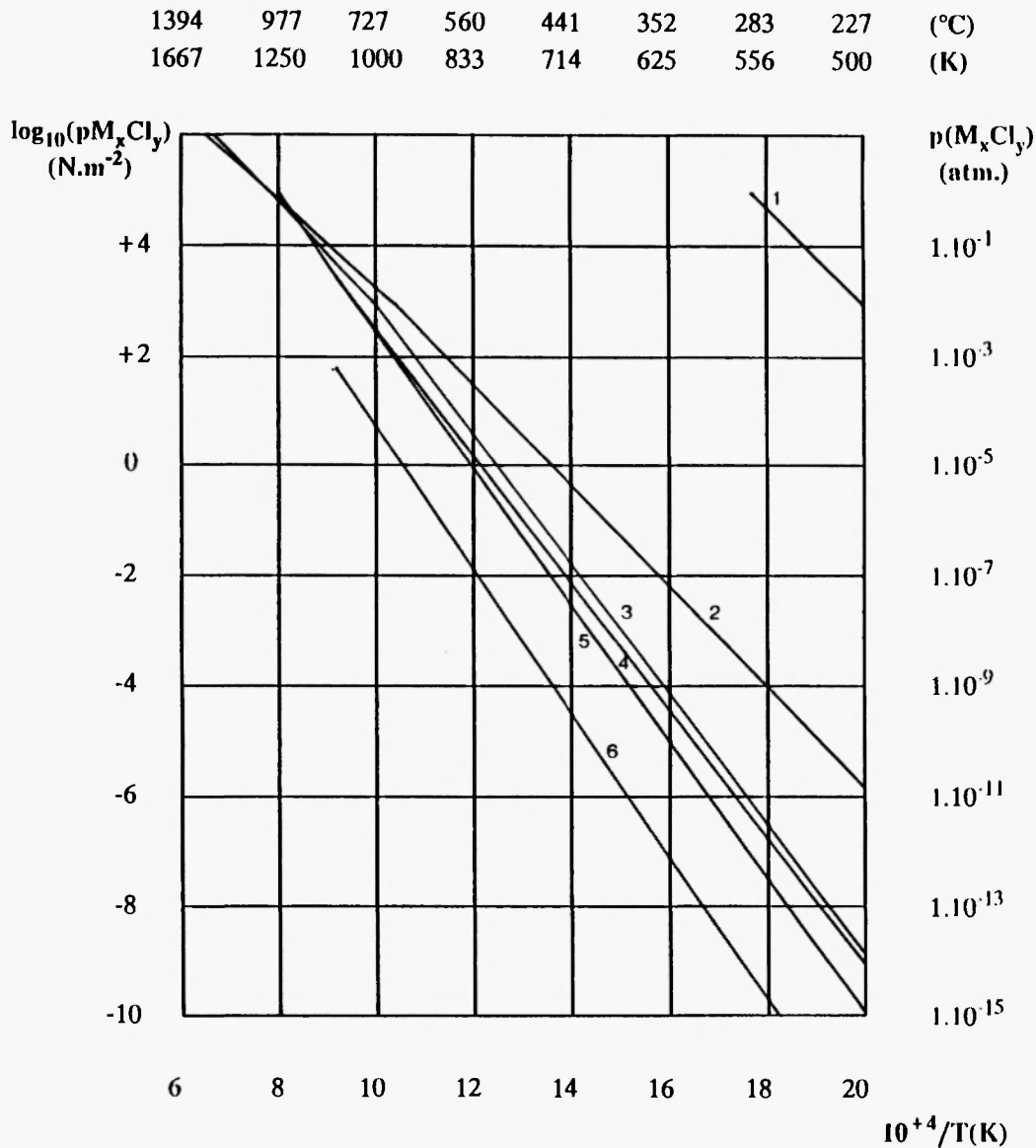


Fig. 1: Saturated vapour pressure of several chloride compounds [32], 1) FeCl_3 , 2) FeCl_2 , 3) CoCl_3 , 4) CrCl_3 , 5) NiCl_2 , 6) CrCl_2 .

cated the presence of chlorides below the product layer. T.G.A. experiments showed that in this gas mixture only a weight decrease was observed [41,59,63], probably due to the volatilization of cobalt chloride. It was assumed that no (semi-)protective oxide scale is formed but only a porous oxide scale which does not hinder the transport of volatile chlorides to the gas phase. This means that vapour species play an important role in the

accelerated complex corrosion process.

3.1.3. Propagation

The void fraction in the CoO scale and the corrosion rate are known to be much higher in the presence than in the absence of chlorine [63]. If it is suggested that only lattice diffusion plays a role, the corrosion would be much lower due to a lower contact area

between the oxide and the underlying metal. Since accelerated corrosion is found, other mechanisms, for example, vapour phase transport, should also play a role in the corrosion process induced by the penetration of chlorine /63/. McNallan /59/ proposed that the vapour-phase transport of the metal species is governed by the formation of volatile chlorides.

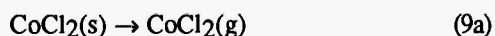
In oxide scales on the corroding cobalt, the partial pressure of oxygen falls from a high value at the gas-scale interface to a very low value at the scale-metal interface. This leads to an opposing gradient in the equilibrium partial pressure of the volatile chloride which produces a driving force for diffusion of chloride vapour. The chlorides are formed at the scale-metal interface or in the inner part of the scale and then diffuse to the gas-scale interface where they are converted to oxides.

The presence of metal chlorides (confirmed by EDS-analysis) at the scale-metal interface can be explained by:

- a) the overgrowing of the initially formed chloride by the oxide, and
- b) the diffusion of chlorine or hydrogen chloride through the oxide scale, probably by the pre-existing pores, or by bulk diffusion.

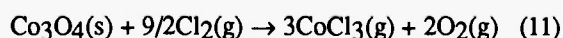
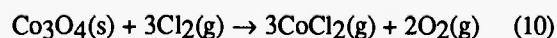
A general mechanism for the steady-state chlorine- or hydrogen chloride-induced accelerated oxidation, which is also called "active oxidation", can now be considered to consist of the following steps /11,39,44,46,53,59-64/:

- 1) the transport of chlorine through a laminar diffusion boundary layer;
- 2) the diffusion of the reactants through the oxide scale (in which form the chlorine is transported through the scale, for example, as Cl_2 or Cl^- , is not well understood. Several mechanisms may play a role, such as diffusion through pores and defects or lattice diffusion, but this has not yet been studied in detail);
- 3) the reaction of the chlorine with the metal or with the oxide;
- 4) the formation of a volatile chloride, e.g.:



- 5) the diffusion of volatile chlorides through the oxide scale;
- 6) the formation of chlorine and Co_3O_4 from CoCl_2 and oxygen;
- 7) the diffusion of the reformed chlorine to the metal-scale interface.

Because CoCl_2 and CoCl_3 (as the volatile species) were still detected, although in much smaller quantities after the formation of an oxide scale /41/, other mechanisms may also play a role. It is, therefore, assumed that, if the metal chlorides do not react with the oxygen in the oxide scale, metal chlorides can diffuse outward by the presence of little pits or cracks, acting as fast diffusion paths. Since it is also assumed that the vapour species are in equilibrium with the oxides in the latter stage of the reaction, the following reactions between cobalt oxide and chlorine are considered /39,61-63/:



These reactions were investigated by McNallan and W.W. Liang /61/ who studied cobalt oxide specimens exposed to different gas mixtures ($T = 727^\circ\text{C}$). Analogous experiments were described by Jacobson /39/ and McNallan et al /59,62,63/. The results showed a linear weight loss rate, presumably due to the evaporation of cobalt chlorides (Fig. 2) /61/. These experiments were performed in oxygen ($T = 727^\circ\text{C}$, 1% Cl_2 , 15% O_2) containing environments.

Another aspect that could exert an effect on the oxidation mechanism is the influence of chlorine on the defect concentration in the oxide scale. It is known /11,28/ that the oxidation of pure cobalt in oxygen is controlled by the diffusion of cobalt cations through the oxide scale and characterized by a p-type semi-conduction. McNallan et al /62/ assumed that, if the solubility of Cl in CoO is significant, the chloride ions may be incorporated and replace the oxygen ions on anionic lattice sites:

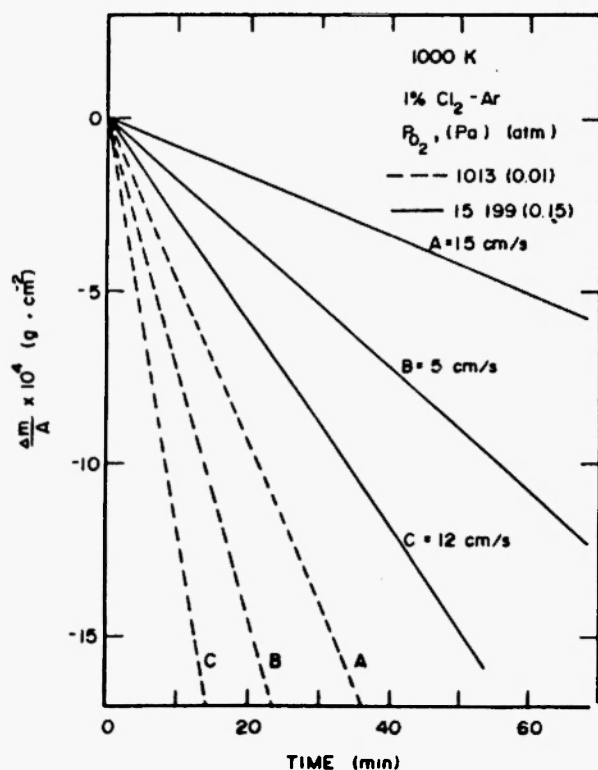
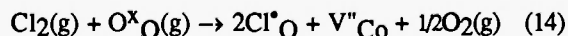


Fig. 2: Weight change of CoO in a 1% Cl_2 -Ar mixture as a function of the O_2 partial pressure and the gas velocity [61].



It was proposed that according to this equation the oxidation rates would be higher in the presence of chlorine. However, experiments [61] performed at 627 and 727 °C in a gas mixture of oxygen (0.01-50%) and chlorine (0-1%) showed that no significant effect was observed on the electrical resistance of the cobalt oxide. This means that a change of the defect concentration of the cobalt oxide by the presence of chlorine in this case may be neglected.

3.1.4. Termination

McNallan et al [63] reported that at the final stage of the experiments, e.g., withdrawing the furnace and quenching the system to room temperature in a chlorine-containing atmosphere, chloride products were detected. The condensed chlorides could have formed during this cooling period from volatile chlorides, which are known to be present at high temperatures.

By flushing the system by argon and subsequently cooling the specimen to room temperature (thus cooling under a protective argon atmosphere), no chlorides were detected in the corrosion products. McNallan et al [63] suggested that the chlorides might have evaporated into the argon stream during the flushing and cooling procedure.

3.1.5. Evaluation

The oxidation rate of cobalt is increased by a very complex corrosion mechanism in the presence of chlorine. The formation of a "protective" oxide scale depends on several process parameters, such as the partial pressures of oxygen and chlorine. The accelerated oxidation is probably due to the formation of cobalt oxide from chloride vapour, beneath the oxide scale or/and due to a change of the defect structure of the cobalt oxide. The mechanism of chlorine penetrating through the oxide scale is a point of wild speculations and further detailed study is necessary before a detailed explanation is available.

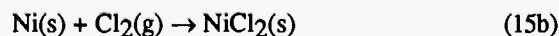
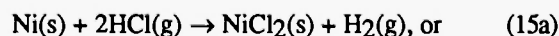
3.2. Nickel

3.2.1. Introduction

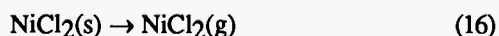
The corrosion of pure nickel in atmospheres containing hydrogen chloride or chlorine can in principle lead to altering the corrosion mechanism and the formation of a number of different compounds. If oxygen and chlorine or hydrogen chloride are the only aggressive components, the compounds which can be formed are NiO and NiCl_2 , depending on the process parameters [16,31,33,36,45,49,56,57,63,71,72,85].

3.2.2. Corrosion in Pure Hydrogen Chloride

A study on the corrosion behaviour of nickel in pure hydrogen chloride was carried out by Ihara et al [36]. At temperatures up to about 450 °C a parabolic rate was found, probably due to the formation of a dense, adherent "protective" nickel chloride scale, according to:



If the temperature is raised, the sublimation of the reaction products will play a dominant role. Sublimation of the corrosion products has been detected, and linear kinetics of evaporation has been found above 550 °C, following the reaction:



This was also reported by Hauffe and Hinrichs /33/. It is known /32/ that the vapour pressure of nickel chloride at 550 °C is about $1 \cdot 10^{-6}$ atm, implying an appreciable evaporation rate of nickel chloride (see also Fig. 1).

3.2.3. Corrosion in Atmospheres Containing Oxygen and Cl_2/HCl

Experiments in a gas mixture with high concentration of hydrogen chloride or chlorine and a low concentration of oxygen in general showed the formation of nickel chloride. For example, at lower temperatures, between 400 and 700 °C, it was found /36/ that there was no fundamental difference in the corrosion products of nickel in gas mixtures either consisting of 100% hydrogen chloride or of 25/75 hydrogen chloride/oxygen. In all cases only nickel chloride was formed. The same results were obtained by Sowney et al /16/ studying the kinetics of a Ni- Cl_2 system between 350 and 600 °C. If nickel is tested in hydrogen chloride with 20% oxygen, the corrosion rate in this temperature range is higher than in pure hydrogen chloride. If the temperature is further increased the corrosion is suppressed by the presence of oxygen. This phenomenon of suppressed corrosion was also found by Hauffe and Hinrich /33/ who studied the corrosion of nickel in chlorine-oxygen mixtures between 700 and 800 °C. Ihara /36/ suggested that the presence of oxygen results in a modification of the defect structure in the nickel dichloride scale by dissolution of oxygen.

If the temperature is further increased, a NiCl_2 -scale can hardly be formed. Experiments performed at 900 °C in a gas mixture containing 10% hydrogen chloride ($p_{\text{Cl}_2} = 3 \cdot 10^{-11}$ atm), and a low oxygen pressure ($2 \cdot 10^{-20}$ atm) have been performed by Prescott et al /71,72/. Only nickel chloride crystals were found, but at these high temperatures a substantial scale could not be

detected. This is in accordance with Ihara's experimental results /36/ which revealed that hardly any scale can be thermodynamically stable with respect to the compounds. This was also found by Strafford et al /83/.

It is known that in pure oxidizing environments the nickel will be oxidized to NiO , according to:



Under these circumstances, the oxidation rate of nickel decreases with time, implying that the oxidation process of the formation of nickel oxide is controlled by a solid state diffusion mechanism /43,28/. If a small amount of chlorine or hydrogen chloride is added to the gas mixture, the corrosion and kinetics change /16,31,33,36,40,43,45,47,49,56,57,59,63,64,71,72,83, 85/.

The morphology of the corrosion products on nickel after attack in an argon (49%)-oxygen(50%)-chlorine(1%) mixture at 727 °C was studied by McNallan et al /63/. The gas mixture contained a much smaller quantity of chlorine compared with that used in the experiments by Prescott /71,72/ and Ihara et al /36/. In this gas mixture, the reaction with nickel showed combustion-like characteristics, resulting in a temperature increase of the specimen above the furnace temperature. These observations were also found by Lee and McNallan /49/ and Hauffe and Hinrichs /33/. Lee and McNallan /49/ reported the corrosion behaviour of nickel in environments containing oxygen (4-50%) and chlorine (0-5%) at temperatures between 623 °C and 923 °C. At 923 °C with a gas mixture of 20% oxygen and different contents of chlorine, the thermogravimetric results showed a linear decrease in mass of the specimens. The rate of this mass loss increased with the chlorine content (Fig. 3). The porous scale formed under these process conditions consists only of nickel oxide and contains no condensed chlorides. Two regimes of the kinetic behaviour were found: a passive corrosion in which an oxide film is present and where the rate is controlled by transport of the volatile reaction products between the gas phase and the oxide, and an ignition-like attack. It is assumed that the oxide film is penetrated by chlorine and

that the corrosion occurs by a rapid formation of a porous oxide layer by nickel chloride transport through

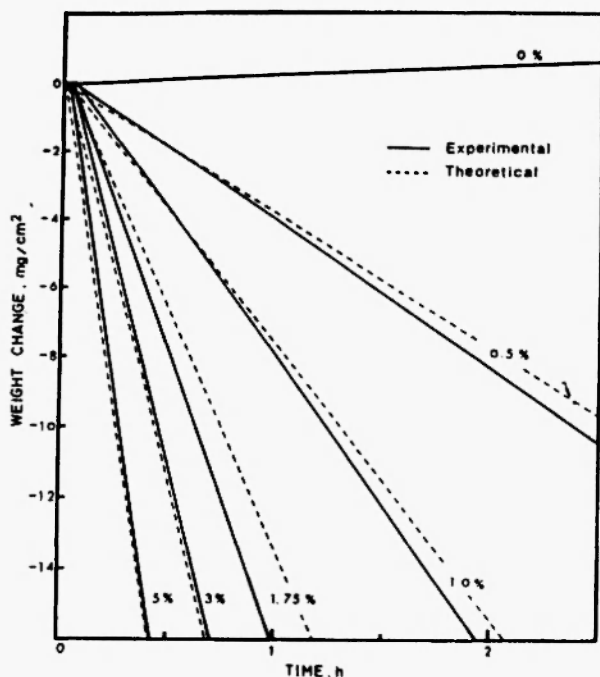


Fig. 3: Thermogravimetric results /49/ at 1200 K of Ni in Ar-50%O₂-Cl₂ gas mixtures, showing an agreement with theoretical calculations. The numbers on the curves refer to the Cl₂ percentage in the gas.

the gas phase in the pores. In Lee and McNallan /49/ a model is presented which will predict the process conditions under which an ignition-like attack will occur. Kinetic studies were also performed by Hauffe and Hinrichs /33/ and Halfdanarson and Hauffe /31/ quantifying the corrosion of nickel by chlorine-containing gas mixtures, using the Tedmon equations next to mass transport and diffusion rate equations.

3.2.4. Evaluation

The corrosion of Ni in pure hydrogen chloride is determined by the formation and evaporation of NiCl₂. If the gaseous environments have a high oxygen potential resulting in the formation of the thermodynamically stable NiO, combustion-like corrosion will take place under controlled process conditions. The mechanism for the accelerated oxidation of nickel corresponds well with the mechanism of active oxidation of cobalt (see Section 3.1.).

3.3. Chromium

3.3.1. Introduction

Only a few studies /36,75/ have been performed on the corrosion behaviour of chromium at high temperatures in aggressive environments containing hydrogen chloride or chlorine. In environments where only oxygen and/or hydrogen chloride or chlorine are present, the following products /36,75/ may form: Cr₂O₃(s), CrCl₂(g), CrCl₃(g), CrCl₄(g), CrO₂Cl₂(g), CrO₃(g), CrCl₂(s) and CrCl₃(s).

A kinetic study of the corrosion of chromium in a gas mixture of hydrogen chloride and oxygen (1 atm) was reported by Ihara et al /36/ in which the partial pressure of oxygen was varied from 0 to 75% between 400 and 800 °C. Chlorination kinetics of chromium between 650 and 800 °C in gaseous environments with pCl₂ between 2.6.10⁻² and 2.6.10⁻¹ atm were studied by Reinhold and Hauffe /75/. The effect of chlorine or hydrogen chloride on Cr₂O₃ was also noted /36,75/.

3.3.2. Corrosion in Pure HCl/Cl₂

In pure hydrogen chloride, only CrCl₂ was formed /36/. At temperatures of up to 600 °C, corrosion showed a nearly parabolic weight gain, but above 600 °C sublimation of the reaction product will play a role. These observations, the parabolic weight increase due to the formation of a "protective" CrCl₂-scale dominant at temperatures lower than about 600 °C and the linear weight loss due to the evaporation of CrCl₂, which has a significant effect above 600 °C, can be described by the Tedmon equation /31,33/.

Sublimation plays a role only at T > 600 °C and is explained by the fact that the vapour pressure of CrCl₂ reaches a critical value of 1.10⁻⁶ atm at this temperature. This value is determined empirically. Analogous observations were also obtained by studying nickel /37/ and iron /38/ in pure hydrogen chloride.

Reinhold and Hauffe /75/ also reported a weight loss during exposure of Cr at 700 °C in chlorine containing gas mixtures. In the aggressive gas mixture with pCl₂ < 5.10⁻² atm, the sublimate was CrCl₃. At higher chlorine partial pressures also CrCl₄ has been found. It was proposed /75/ that the aggressive component of the reaction between Cr in a gas mixture with

hydrogen chloride or chlorine can be described by the following steps:

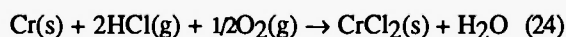
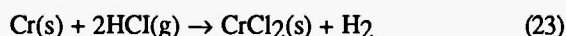
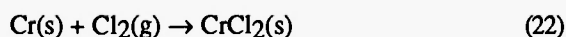
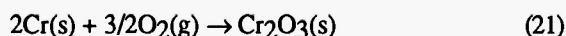
- 1) diffusion of reactants through a laminar boundary layer;
- 2) diffusion of reactants across the scale;
- 3) formation of CrCl_2 , CrCl_3 , or CrCl_4 , depending on temperature and gas composition;
- 4) formation of volatile products, according to:



- 5) diffusion of the volatile products across the laminar boundary layer.

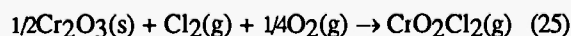
3.3.3. Corrosion in Atmospheres Containing Oxygen and Cl_2/HCl

In oxygen-containing gas mixtures with hydrogen chloride or chlorine, where Cr_2O_3 is the thermodynamically stable phase, corrosion changes significantly. In the initial stage of the corrosion process, simultaneous formation of chromium chlorides and oxide will take place, and the chlorides may be overgrown by the oxide. In the initial stage of the corrosion process, the following reactions will probably take place, depending on the gas composition [36,75]:



Whether a "protective" oxide scale will effectively form depends among others on the oxygen content of the gas mixture. Reinhold and Hauffe [75] reported that, during the simultaneous attack of chlorine and oxygen on chromium at 700 °C, three oxygen pressure regions were determined. With a chlorine pressure of $2.6 \cdot 10^{-2}$ atm and an oxygen pressure up to $2.6 \cdot 10^{-3}$ atm, a con-

siderable initial weight loss is found due to the fact that no protective oxide scale has formed. At an oxygen pressure of $2.6 \cdot 10^{-2}$ atm, a mass gain was observed, explained by the formation of Cr_2O_3 on the surface. At higher oxygen pressures a weight loss is found again. This last weight loss is according to Reinhold and Hauffe [75] due to the formation of CrO_2Cl_2 :



Experiments [36] at temperatures up to 500 °C but with much higher $p\text{O}_2$ (0.2 - 1 atm) showed that the addition of oxygen to the gaseous atmosphere resulted in a reasonable protective behaviour of the reaction products, probably due to the formation of a chromia scale covering the specimen surface. At higher temperatures (>500 °C), severe corrosion was observed, probably due to the formation of chromium(III)chloride and water according to the reaction (see Fig. 4):

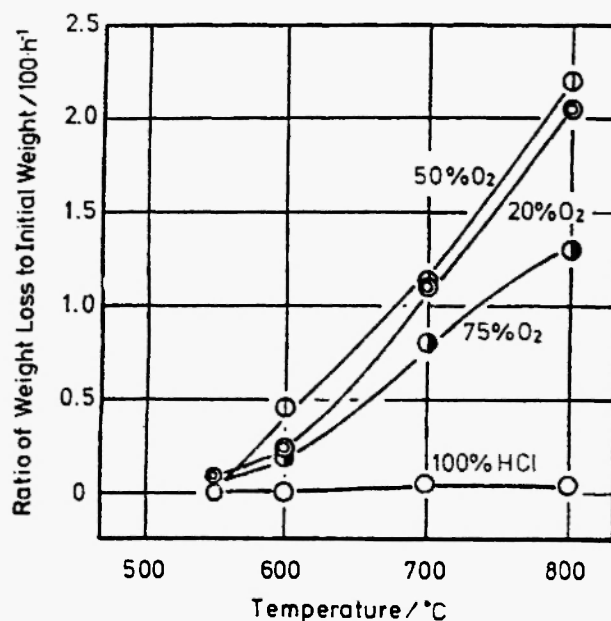
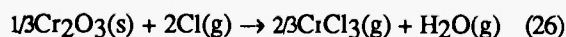
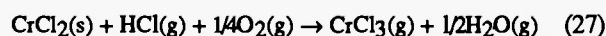


Fig. 4: Changes of relative weight losses of Cr_2O_3 measured by a quartz microbalance when 200 mg of Cr_2O_3 powder in a quartz basket was exposed to reaction gases for 2 h [36].



Other possible surface reactions resulting in the evaporation of chromium in oxygen rich atmospheres are:

- conversion of Cr_2O_3 with Cl_2 and O_2 /75/, according to reaction Equation (25);
and
- oxy-chlorination /36/, according to:



The steady state corrosion of chromium in the presence of hydrogen chloride or chlorine and oxygen can be described by a mechanism consisting of several steps and corresponding with those also described earlier for cobalt.

3.3.4. Evaluation

In general, the corrosion behaviour of chromium in pure hydrogen chloride or in a gas mixture with chlorine as the aggressive component is characterized by the formation and evaporation of chromium chloride, depending on temperature and relative activities of the gas components. In a mixed oxygen-chlorine atmosphere with chromia as the thermodynamically stable product, a protective chromia scale may be formed. Accelerated oxidation may still occur, probably due to reactions between the substrate c.q. oxide and the hydrogen chloride or chlorine.

3.4. Iron

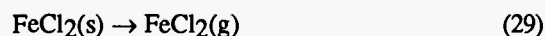
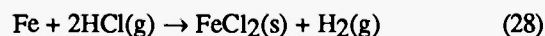
3.4.1. Introduction

The reactions of iron with hydrogen chloride and/or chlorine/oxygen gas mixtures have been studied by many authors /10,15,16,22-25,38,39,48,64,72,84,87-92/. Depending on process parameters such as the temperature and the relative activities of the gas components, the following products may be formed: $\text{FeO}(\text{s})$, $\text{Fe}_3\text{O}_4(\text{s})$, $\text{Fe}_2\text{O}_3(\text{s})$, $\text{FeCl}_2(\text{g})$, $\text{FeCl}_3(\text{g})$, $\text{FeCl}_2(\text{s})$, and $\text{FeCl}_3(\text{s})$.

3.4.2. Corrosion in Pure HCl/Cl_2

Corrosion studies of Fe in pure hydrogen chloride gas between 300 and 800 °C were performed by Ihara et al /38/. In pure hydrogen chloride almost parabolic

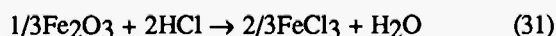
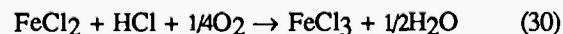
reaction kinetics are obtained at temperatures up to about 450 °C, due to the formation of a “protective” ferrous chloride scale. Sublimation occurs if the temperature is further increased, and at temperatures higher than 600 °C, the specimen weight decreases linearly with time. If the temperature is further increased, no surface scaling is found /84/. Similar results were obtained by Jacobson /10/ who studied the corrosion behaviour of Fe at 550 °C in an argon atmosphere with 1% Cl_2 . At 550 °C a linear weight decrease was observed (see Fig. 5). Jacobson /10/ and Fruehan et al /22,23,24/ proposed that in pure hydrogen chloride the process at the metal surface can be described by a two-step process with the transport of iron chloride (g) rate limiting, according to:



That sublimation of iron chloride will become dominant at higher temperatures is ascribed /38/ to reaching a critical saturated vapour pressure of FeCl_2 of $1 \cdot 10^{-6}$ atm. See also the results with Ni /37/ and Cr /36/ in pure hydrogen chloride.

3.4.3. Corrosion in Atmospheres Containing Oxygen and HCl/Cl_2

If oxygen is added to the gas mixture, the corrosion alters significantly. At lower temperatures (550 °C), Ihara et al /38/ and Jacobson /10/ found an increase in the formation of FeCl_3 . It seems plausible that the addition of oxygen would lead to a protective oxide scale, thus limiting the formation of FeCl_2 , but Ihara et al /38/ found that the corrosion increased, probably due to the formation of ferric chloride.



Ihara et al /38/ also found that the chlorination of the oxide with a consequent sublimation was confirmed from their measurements (400 - 800 °C) of the weight loss of $\alpha\text{-Fe}_2\text{O}_3$ powder. This means that, probably due to the high vapour pressure of FeCl_3 , the corrosion of

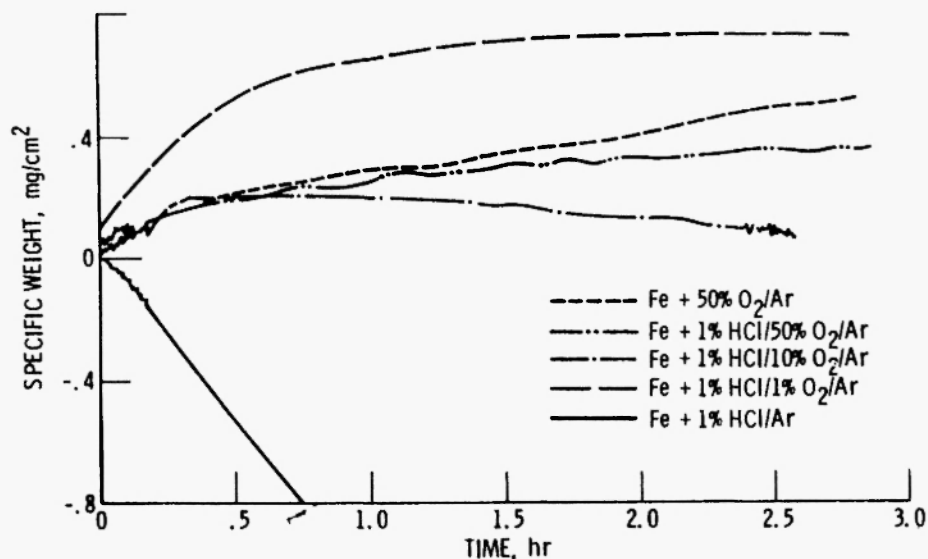


Fig. 5: Thermogravimetric results of iron in a HCl/O₂ gas mixture at 550 °C /39/.

iron is greatly accelerated by a small addition of oxygen to the hydrogen chloride.

At higher oxygen partial pressures /10/, the scale becomes more protective due to the formation of an oxide scale. Jacobson /10/ reported that condensed phases were found on the metal-scale interface where the oxygen potential is low. In 1% HCl/10% O₂/Ar and 1% HCl/50% O₂/Ar-mixtures ($T = 550$ °C), the reaction behaves similarly to oxidation with some deviation due to volatilization. This was evident from the weight gain curves, which revealed that a lower specific weight gain was obtained after three hours. This was also found by Lee and McNallan /48/ who studied the oxidation of Fe in 1% HCl/15% O₂/Ar and 1% HCl/50% O₂/Ar-mixtures at 827 and 927 °C and Prescott et al /72/ who studied the degradation of metals in an Ar/25% H₂/10% HCl/5% CO/1% CO₂ gas mixture at 900 °C. From weight gain experiments it seems that, at these temperatures, the oxidation rate of iron is reduced by the presence of chlorine. Lee and McNallan /48/ attributed this effect to the increasing amount of volatile corrosion products at these temperatures.

3.4.4. Evaluation

The corrosion of Fe in HCl-gas is determined by the formation and evaporation of FeCl₂. Which process dominates depends strongly on the temperature. If small

amounts of oxygen are added to the gas mixture, the corrosion rate usually increases. This can be explained by the fact that formation of the highly volatile product ferric chloride (FeCl₃) and/or oxy-chlorination will probably occur. At higher temperatures and oxygen partial pressures, an oxide scale was reported to have formed, characterized by a porous structure, indicating to an oxide scale of poor protective quality. Since chlorides are also present beneath the oxide scale, "active oxidation" will take place. This means that the mechanism of Fe oxidation in the presence of chlorine or hydrogen chloride is very complex. Next to the enhanced oxidation, other surface reactions can also take place, resulting in an evaporation of the iron compounds. In other words, the mechanism of hydrogen chloride induced oxidation of iron agrees well with the hydrogen chloride induced oxidation mechanism discussed for cobalt.

3.5. Alloys

3.5.1. Introduction

In this part of the report, the effects of hydrogen chloride or chlorine in oxidizing environments on commercially available alloys are discussed. Next to the studies on pure metals, which is of major importance for determining kinetics and mechanisms, commercially

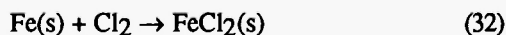
available industrial metallic materials are also an interesting subject for study. A number of alloys are discussed in order to find if there is a general corrosion mechanism which is applicable to all metallic materials.

Special attention is paid to the effect of the presence of elements such as Cr, Al, Ni, W, Mo, and Co on the corrosion resistance of alloys in hydrogen chloride or chlorine containing gas mixtures. Also the effect of nitrogen and water vapour on corrosion behaviour are discussed.

3.5.2. Effect of Chromium on the Chlorination

Bramhoff et al [4,5,6] studied the corrosion behaviour of the low chromium alloy 10CrMo9.10 in an 87% H_2 /13% O_2 /HCl atmosphere with hydrogen chloride contents between 0 and 3000 ppm ($T = 500^\circ C$) and the high chromium alloy Fe-20Cr at $900^\circ C$ in atmospheres with a $pO_2 = 1.10^{-20}$ atm and varying the HCl-concentration between 0 and 2000 ppm.

The experimental results revealed that for 10CrMo9.10 in an oxidizing atmosphere the mass gain increased with increasing amounts of HCl up to about 1000 ppm HCl. A further increase of the hydrogen chloride content resulted in a decrease of the mass gain (Fig. 6). This was explained by evaporation of the reaction products. The scale morphology on 10CrMo9.10 formed in hydrogen chloride-containing environments was characterized by a porous structure consisting of Fe_3O_4 and some Fe_2O_3 . $FeCl_2$ was detected only at the metal-scale interface. Evaporation was in this case explained by the formation of $FeCl_2$ from Fe and HCl or Cl_2 diffusing through pores and cracks in the oxide scale to the metal-scale interface, and reacting with the underlying alloy:



A porous structure of the oxide scale was also observed by Elliot and Marsh [19] who studied the oxidation behaviour of Incoloy 800H in moist air containing 500 ppm $HCl(g)$ at $800^\circ C$. They assumed that the low chemical potential of the HCl and the high potential of the oxygen used favoured the formation of Cr_2O_3 which is resistant to further reaction. The for-

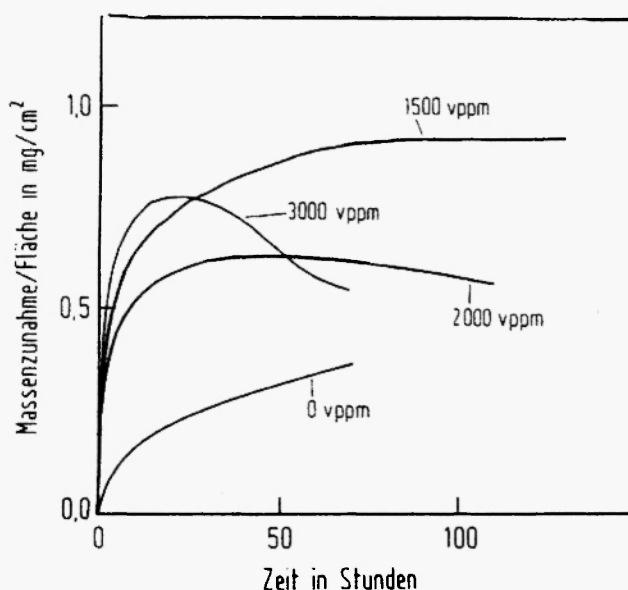
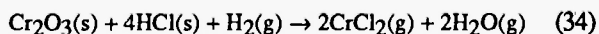


Fig. 6: Mass increase of 10CrMo9.10 at $500^\circ C$ as a function of time in He- O_2 -HCl atmospheres with different HCl pressures at constant $pO_2/5$.

mation of $FeCl_2(g)$ and $FeCl_3(g)$ is, according to these authors, responsible for the reactive evaporation. The same authors reported nothing about the possibility of Cr_2O_3 reacting with HCl or Cl_2 . In the literature [36] it is reported that this reaction still occurred since volatile compounds can be formed in case of very low pressures of these compounds in the gas phases.

At higher temperatures and lower oxygen partial pressures the evaporation rate will play a more dominant role. For example, the oxidation behaviour of Fe-20Cr in a gas mixture earlier reported by Bramhoff et al [4,6] showed that the rate of mass increase decreased with increasing amount of hydrogen chloride (Fig. 7). The effect on evaporation of the oxide scale by reactions between the oxide and hydrogen chloride or chlorine becomes more important.

It is assumed [4,6] that in the initial stage of the oxidation also chlorination will take place, but eventually the oxides overgrow the chlorides. Since the oxidation of Fe-20Cr resulted in a dense chromia scale, evaporation is assumed by the reaction of chromia with hydrogen chloride, according to:



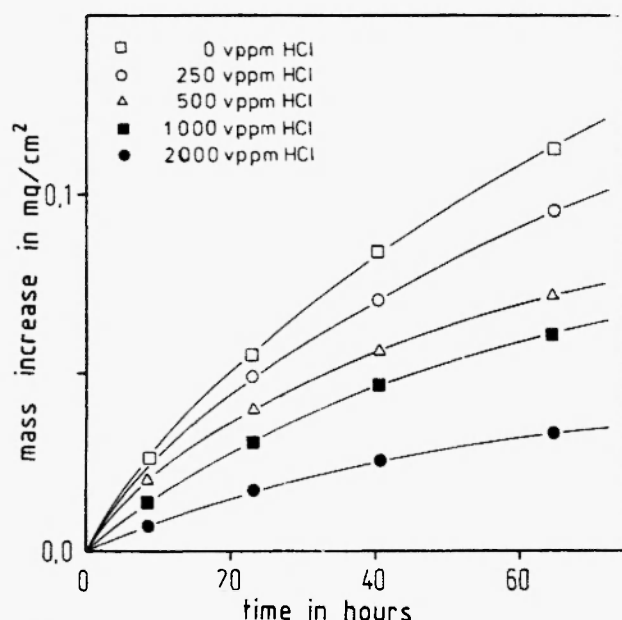


Fig. 7: Mass increase vs time of Fe-20Cr oxidized at 900 °C in different He-H₂-H₂O-HCl gas mixtures [6].

After some time a stationary state is reached, resulting in a linear mass decrease.

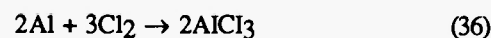
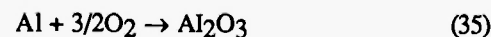
That a steady state may be established between scale growth and sublimation was also observed by Gesmundo et al [27], who tested Ni-29Mo-4Fe at 600 and 700 °C in atmospheres containing HCl, water vapour and some free oxygen. The alloy showed a linear weight loss as a function of time, due to the formation of several volatile compounds.

Three binary alloys, Fe-1Cr, Fe-5Cr, and Fe-20Cr, were tested in Ar/50%O₂/1%Cl₂ gas mixtures between 627 and 927 °C [42]. In all cases an iron-rich (at the scale-gas interface) porous oxide scale was detected. This was explained by a rate controlling mechanism of diffusion of FeCl₂ or CrCl₂ vapour through the pores, and eventually the reoxidation of FeCl₂. For higher alloyed steels, chromia has been detected at the metal-scale interface, resulting in a much higher resistance against oxidation. It is also known that the diffusion rate of Fe in chromia is much higher than of Cr [43]. This could play a role in the formation of an iron-rich layer at the outside, as was also found by Strafford et al [83] who studied the corrosion of binary Fe-Cr alloys containing 2, 5, 9, 14, and 25% Cr at 1000 °C (pO₂ = 10⁻¹⁶, pCl₂

= 10⁻⁸ atm). It can be concluded that increasing levels of Cr gradually suppress the corrosion. Corrosion products were FeCl₂ vapour and Cr₂O₃. Attack occurred initially via the grain boundaries.

3.5.3. Effect of Aluminium on Chlorination

If Al is added to the alloy, the protectiveness of the formed oxide scale is in general more pronounced than if only chromium is present [18,74,80,82]. Elliot et al [18], for example, studied the behaviour of selected commercial alloys in gaseous environments containing 20% O₂ and 2% Cl₂ at 900 and 1000 °C. The aluminium containing alloys showed a better corrosion resistance than the chromia forming alloys, although spallation can occur on cooling to ambient temperature. This better corrosion resistance of the aluminium containing alloys was also observed [52,80,95] for chromium and aluminium oxide formed on high temperature Ni, Co, and Fe alloys in a gas mixture of Ar-25%H₂-10%HCl-5%CO-1%CO₂ at 900 °C. Here, the rates of attack were fairly low for Al₂O₃-forming alloys in comparison with Cr₂O₃-forming ones. The corrosion increased by thermal cycling, due to a further disruption of the protective oxide scale. The presence of voids was explained [18] by the generation of volatile halides which can provide a gradient for transporting cations away from the metal. Due to the counterflow of vacancies, these condensed out as an accumulation of voids. An internal penetration was also observed. In all cases, aluminium containing alloys and alloys with refractory metals such as Mo, W, or Co showed that chlorides were present at the alloy surface. For the aluminium containing alloys, Elliot et al [18] suggested that in the initial corrosion stage two competitive reactions play a role:



Elliot et al [18] reported that alumina cannot be transformed to chloride since this reaction is thermodynamically impossible. This is not true since volatile products can be formed in case of very low pressures of the products in the gas phase [97].

Here we note that reactions between the oxide and hydrogen chloride still can play a role in the total corro-

sion process, e.g., if the vapour pressure of the metal chloride is high enough ($> 10^{-6}$ atm). It is necessary to perform additional experiments to substantiate this and to obtain a correct definition of the used system.

Oh et al /68/ investigated several commercially available superalloys in an Ar/20%O₂/2%Cl₂ gas mixture at 900 °C. Alloys with sufficient Al or Ti showed the smallest attack, indicating to an Al₂O₃ scale protecting the underlying metal from exposure. No chlorination was detected beneath the scale.

Alumina is thus a more effective barrier than chromia to the inward penetration of aggressive gas components /82/. Small additions of SO₂ do not play an obvious role in the process /95/.

3.5.4. Effect of Nitrogen in Oxidation

Bramhoff /4,6/ investigated the difference in oxidation behaviour at 900 °C of Fe-20Cr in He-H₂-H₂O-HCl and N₂-H₂-H₂O-HCl. During the exposure of the specimens to nitrogen containing atmospheres, the oxidation is faster and the evaporation is enhanced in comparison with He-containing gas mixtures. The different behaviour is attributed to the formation of chromium nitride in the initial stage of the corrosion which react probably very rapidly with oxygen to chromia. The chromium nitride moreover adversely affected the structure and protectiveness of the overgrowing oxide.

3.5.5. Effect of Other Components in the Alloy

Alloys containing small amounts of Co showed less severe corrosion. However, the attack is more severe if the alloys also contain small amounts of Mo or W. Increased corrosion due to the presence of W or Mo was confirmed by Stott et al /80/ who studied several high temperature alloys in an Ar/5.5%O₂/1%HCl/0.86%SO₂ gas mixture at 900 °C ($p_{\text{Cl}_2} = 8 \cdot 10^{-4}$, $p_{\text{O}_2} = 5.5 \cdot 10^{-2}$, and $p_{\text{S}_2} = 5 \cdot 10^{-27}$ atm, resp.). Volatile corrosion products formed, particularly from nickel, cobalt and molybdenum. Mo and W showed a rapid corrosion. The severe attack due to the presence of Mo was also reported by Ruedl et al /78/ who investigated Mo-4Ni foils in 21% HCl at 400-820 °C. Weight losses were due to MoO₃ volatilization (above 600 °C).

An increasing Ni content of iron-nickel alloys reduced the corrosion rate /84/ at 800 and 1000 °C ($p_{\text{Cl}_2} = 10^{-8} - 10^{-12}$ atm, $p_{\text{O}_2} = 10^{-16} - 10^{-20}$ atm). A limi-

ting content of 50% nickel confers excellent chlorination resistance to Fe /84/.

3.5.6. Effect of Water on the Protectivity

Hossain et al /35/ studied the effect of moist (12,800 ppm H₂O) and dry air containing 0-2000 ppm HCl on the oxidation resistance of Ni-Cr-Al alloy at 850 °C. Cracking of the oxide during the early stage of the oxidation process was detected when water was added to the gas. In dry air containing hydrogen chloride no cracking was observed. In dry or moist air free from hydrogen chloride an adherent protective oxide was formed. Spalling did not occur during cooling. Cracking of the scale in hydrogen chloride-containing atmospheres induced by water addition was explained by the reaction of H₂O vapour with Al and Cr in the alloy under the formation of hydrogen which dissolved in the alloy at 850 °C. On cooling the hydrogen was released, causing the oxide scale to blister and spall. This was attributed to the fact that the hydrogen chloride removed the NiO-scale and it thus may facilitate penetration of water through the oxide.

This behaviour of the oxide scale in moist atmospheres is in agreement with the results of Elliot and Marsh /19/ who studied the oxidation of Incoloy 800H in moist air containing 500 ppm hydrogen chloride at 800 °C.

The explanation given by Hossain et al /35/ should be put in question marks because other mechanisms /98/ may probably also play a role. During the condensation (cooling) period the chloride compounds may become partly transformed into hydrated chloride compounds, such as FeCl₂ · 6H₂O or similar hydroxide compounds. Condensation may also cause an increased strain in the sulphide scale, which eventually would lead to cracking of the scale.

3.5.7. Evaluation

Small influences, such as small additions of SO₂ to the gas /71/, moist and dry air /35/, additions of Al, Co, W, and Mo to the alloy, and thermal cycling /18,52,80,95/, were investigated. Small additions of SO₂ resulted in no effect compared to the results obtained under purely oxidizing circumstances. The effect of water was described as enhancing the susceptibility for cracking. If Al is added to the metal, the corrosion

susceptibility decreases, probably due to the formation of the very stable alumina, but thermal cycling has a detrimental effect on the protection by the alumina scale. The addition of Ni gives a slight decrease of the corrosion rate, in contrast to W or Mo, which lead to a severe attack of the alloys.

It is clear from the results that the corrosion rate increases in the presence of hydrogen chloride or chlorine. With respect to the enhanced corrosion rate, a model was discussed /42/ calculating the kinetics for oxide growth controlled by solid state diffusion and in pores where vapour transport may take place. Quantification of the model led to the conclusion that the oxide growth by vapour transport is also possible. Due to this conclusion, it is clear that k_p , the parabolic rate constant, differs when HCl or Cl_2 is used, resulting in "active" oxidation. This means that the Tedmon equation in its most simple form cannot always be used, especially when k_p was determined in oxidizing atmospheres only. The kinetics of oxidation might include solid state diffusion, and the formation, diffusion and reoxidation of volatile iron chlorides. The formed

chlorides act as a gas phase carrier transporting the metal atoms. In other words, the proposed mechanism regarding the increased corrosion rate by addition of hydrogen chloride or chlorine agree well with those from pure metals as described for cobalt. A schematic overview of several reactions considering the corrosion influenced by hydrogen chloride or chlorine is given in Fig. 8.

4. THE EFFECT OF HCL OR Cl_2 ON HIGH TEMPERATURE CORROSION OF ALLOYS UNDER COAL GASIFICATION CONDITIONS

4.1. Introduction

Relatively little information has been published /1-4,7,8,12,14,26-30,51,55,65,67,69,70,73,79/ regarding the influence of chlorine or hydrogen chloride on the corrosion behaviour of alloys in atmospheres with low oxygen and high sulphur pressures. Chlorides are common contaminants in many high temperature environments, such as coal gasification plants, coal fired

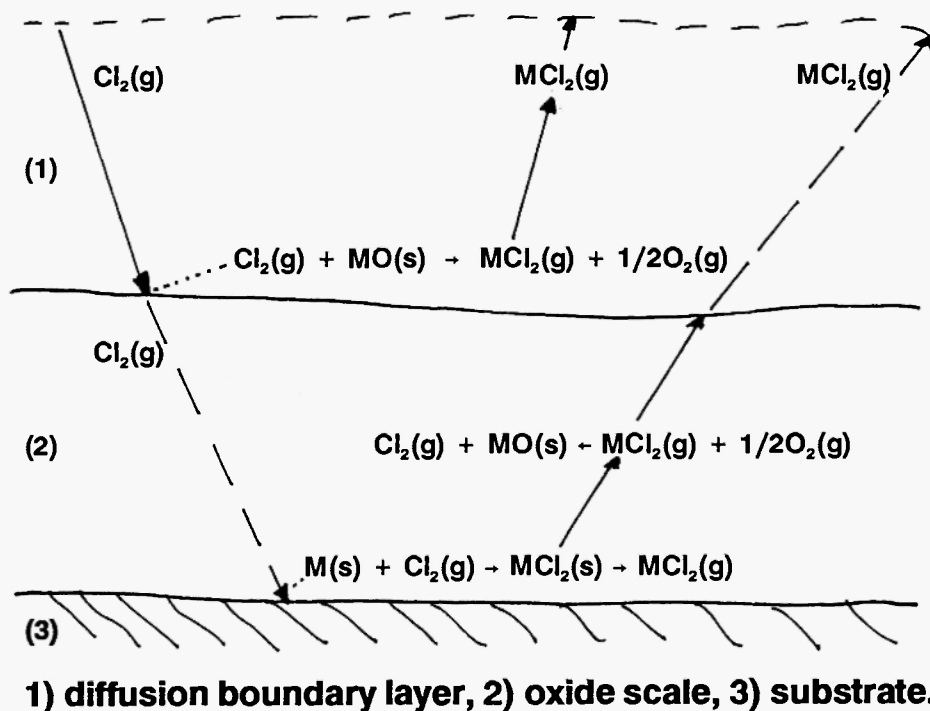


Fig. 8: Schematic overview of several reactions considering the induced corrosion attack by the presence of hydrogen chloride or chlorine.

boilers and waste incinerators. Gibb /26/ reported that the chlorine content of British coals lies between 0.02 and 0.75%. Due to the high concentration of chlorine in the coal, the gaseous atmosphere inside the plant will, therefore, also contain a significant amount of chlorine, probably released by the dechlorination of the coal. The gaseous transport of chlorine compounds is predominantly responsible for the alteration of the corrosion mechanism /26/. A detailed mechanism of the effect of chlorides in oxidizing/sulphidizing environments has been the subject of considerable speculations and discussions. In only oxidizing atmospheres, mechanisms have, been proposed if hydrogen chloride or chlorine is added to the oxidizing gas mixture, as reported in Section 3.1.3. It is also worth noting that the addition of hydrogen chloride increases the syngas dewpoint. This is the lowest temperature at which a plant can operate without the condensation of moisture on the metal surfaces.

4.2. High Temperature Corrosion in Coal Gasification Atmospheres

Bakker and Perkins /3/ reported the effect of adding 600 ppm hydrogen chloride to the syngas on the corrosion behaviour of low alloy steels. The experiments were performed in a syngas containing 0.6% H₂S at 350 °C. The rate of sulphidation was reduced by almost one third. The effect of reduced sulphidation rate at 1 atmosphere was explained on the basis that the chloride in the sulphide scale acts too slow for the required outward diffusion of Fe to form the sulfide. No chlorides were found on the outer FeS scale. Chlorides were only found in the underlying sulfide/oxide scale as red whiskers and at the interface with the outward growing sulfide scale. Bakker and Perkins /3,69/ reported that this was also found by other authors /73/ who studied the reaction of Fe with mixtures of hydrogen sulphide and hydrogen chloride where the hydrogen sulphide attack reduced in the temperature range between 200 and 399 °C. But at higher operating pressures, i.e. at a pressure of 40.8 atmosphere, it is found that the hydrogen chloride accelerates the rate of sulfidation. Similar phenomena were observed with protective alumina scales which are severely attacked at high pressures. In their paper nothing is reported about the

experimental procedure to determine the corrosion rate. The weight gain was only measured at the end of the experimental procedure. However, the extent of the reaction may be measured by the amount of metal consumed, the amount of sulphide consumed, or the amount of sulphide produced. Furthermore, it is known that the formed metal chloride may evaporate at the temperature at which the experiments are carried out and during the cooling period in an inert gas atmosphere, resulting in a much "lower" weight gain /63/. If the specimens were cooled in the aggressive environment, down-time corrosion may occur. From this point of view, it is highly speculative in this case to discuss the obtained results of reduced sulphidation attack by the addition of hydrogen chloride.

Gohil and Saunders /29,79/ studied the corrosion resistance of FeCrAl steels in coal gasification atmospheres at 450 °C containing 300 and 1000 ppm hydrogen chloride ($p_{O_2} = 3.8 \cdot 10^{-30}$ atm, $p_{S_2} = 5.4 \cdot 10^{-12}$ atm). The experiments were focussed on the surface finish of the samples: one involved a simple 600 grit SiC finish, the other a final finishing with 1 µm diamond paste. In cases of a 1 µm surface finish, the alloys were relatively severely attacked when 1000 ppm hydrogen chloride was added to the gas mixture. The specimens with only a 600 grit SiC finish showed small mass gains, except FeCrAl steel. If the amount of hydrogen chloride was reduced, corrosion also decreased. From these results, it is clear that the modification of the surface finish has a pronounced effect on the corrosion resistance. The addition of silicon and chromium also improved the corrosion resistance.

Brooks and Meadowcroft /7,8/ studied the role of chlorine on the corrosion behaviour of mild steel, 21/4Cr1Mo and 9Cr1Mo. The presence of 0-2000 ppm hydrogen chloride in an oxidizing/sulphidizing atmosphere ($p_{O_2} = 1 \cdot 10^{-30} - 1 \cdot 10^{-34}$ atm, $p_{S_2} = 1 \cdot 10^{-9}$ atm) was examined. At 400 and 500 °C the alloys showed linear kinetics when 400 or 2000 ppm hydrogen chloride was added. At 550 °C and in a gas mixture containing 200 ppm hydrogen chloride, the 21/4Cr1Mo exhibited protective kinetics (Fig. 9), and the scale was multi-layered. In general, the addition of hydrogen chloride resulted in the formation of a thicker, more porous, less adherent scale, mostly consisting of FeS. Above 200 ppm hydrogen chloride, hardly any effect was detected on

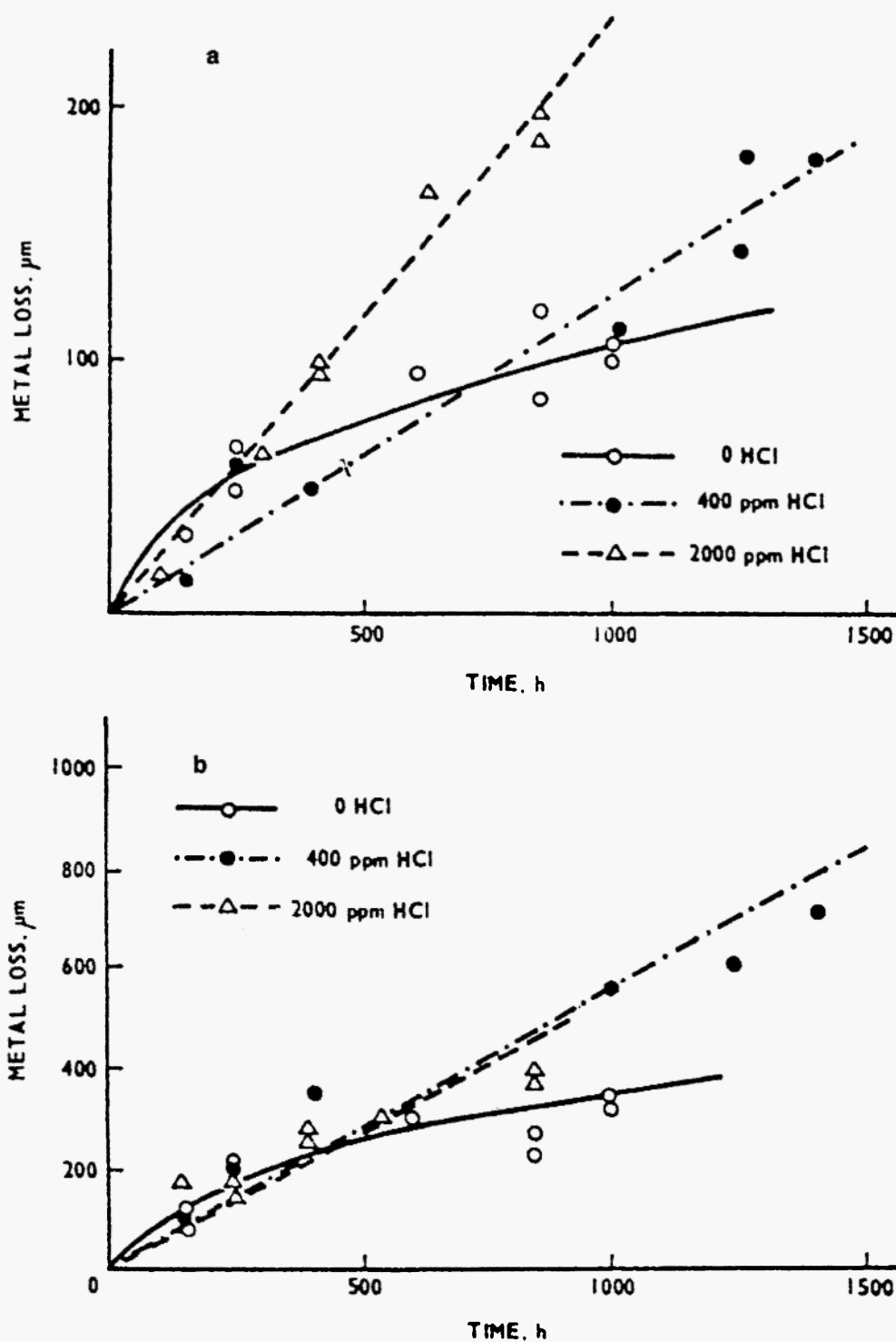


Fig. 9: Metal loss vs time [7] for mild steel exposed to 10%CO, 10%H₂O, 0.5%SO₂, Bal. N₂ with additions of HCl, a) 400 °C, b) 500 °C.

the corrosion rate as a function of the amount of hydrogen chloride. The authors suggested that the small dependence of the corrosion rate of the hydrogen chloride content was due to a scale failure mechanism. The presence of hydrogen chloride induced a repeated scale failure which increased the porosity of the scale by the formation of iron (II) chloride at the scale/metal interface /1,2,51,65/. Iron chloride was detected at the metal-scale interface which was also confirmed by van Liere /51/ and Bakker /1/. The high corrosion rates were ascribed to a repeated rapid parabolic sulphidation kinetics. Because no dependence of HCl concentration was detected above 200 ppm HCl, it was proposed that the rate of volatilisation of iron chloride (II) reached an upper limit for the level of hydrogen chloride content on the metal surface beneath the scale. Assuming that hydrogen chloride diffuses through the scale to form iron chloride at the metal-scale interface, the maximum rate occurs when there is a continuous presence of FeCl_2 at this interface. A higher HCl-concentration than 200 ppm does not lead to a higher corrosion rate. Calculations predicting the maximum concentrations of hydrogen chloride were performed by mathematical modelling /7,8/.

Cutler et al /14/ made a study on 18Cr/12Ni/Nb steels in an oil-fired combustion rig where the coal combustion atmosphere was simulated between temperatures of 450 and 720 °C. Addition of hydrogen chloride considerably increased the rate of corrosion.

Coley et al /4/ studied FeCrAl-alloys (polished with 1 μm diamond paste) in the same atmosphere as Saunders and Gohil /29,79/, but in this case 1000 and 2200 ppm hydrogen chloride was added at temperatures of 450 °C. It is clear from these results that the addition of hydrogen chloride decreased the time of breakaway and resulted in the formation of oxide dendrites which were iron rich. It was also shown that preoxidation had no effect on the long term corrosion rate in the presence of hydrogen chloride. According to Coley /4/, the mechanism of the increase of breakaway corrosion by hydrogen chloride is not well understood, but it is proposed, also by others, that the formation of volatile chlorides under the oxide film leads to its fracture and subsequent loss of protection. Coley also discussed an iron and oxygen rich dendrite formation at the early stage of the corrosion process. After some time, these dend-

rites became overgrown by a porous sulphide scale (when no hydrogen chloride was present no dendrites formed and a thin featureless oxide film was formed). An exact mechanism is still an item for further investigation.

4.3. Evaluation

From the results obtained from experiments performed in oxidizing/sulphidizing environments with a small addition of hydrogen chloride, it is speculative as yet which corrosion mechanism will play a dominant role, but it is still assumed that there is a similarity between the corrosion mechanism of metals or alloys under purely oxidizing circumstances with the addition of hydrogen chloride and the phenomena detected in simulated coal gasification atmospheres with small additions of hydrogen chloride or chlorine.

In some studies /3,69,73/, a reduction in the corrosion rate was found, but others showed an increase in corrosion. A thorough discussion of the obtained results is at this moment not possible, and further laboratory work in a range of simulated coal gasification plant atmospheres and temperatures is required to obtain a detailed mechanism of corrosion in hydrogen chloride or chlorine containing gas atmospheres.

5. CONCLUDING REMARKS

At present it is generally known that small amounts of chlorine or hydrogen chloride in high temperature processes increase the corrosion rate of metals and alloys significantly. Based on the available results, a number of concluding remarks can be made concerning the effect of hydrogen chloride or chlorine on the high temperature corrosion of metals and alloys.

1. In pure hydrogen chloride or chlorine a "semi-protective" scale of metal chloride may form at low temperatures. At higher temperatures, evaporation of the products will become more dominant. This depends strongly on the saturated vapour pressure of the volatile chlorides (evaporation will become more pronounced above $1 \cdot 10^{-6}$ atm).
2. Addition of hydrogen chloride or chlorine to oxi-

dizing atmospheres increases the oxidation rate of metals and alloys under formation of a porous oxide scale. The supposed mechanism (see also Fig. 8) for "active oxidation" is based on the following steps: a) transport of reactants through a laminar diffusion boundary layer, followed by diffusion through the oxide scale; b) reaction with the metal or alloy forming volatile metal chlorides; c) diffusion of the reaction products through the pores in the oxide scale; and d) formation of chlorine and metal oxide whereafter the reformed chlorine diffuses again to the metal-scale interface.

3. At higher temperatures volatilization of the metal chloride compounds will also take place, due to the fact that the formed metal chlorides diffuses through the pores to the metal-scale interface. Also reactions between the oxide scale and chlorine or hydrogen chloride can play a role.
4. The effect of hydrogen or chlorine on the high temperature corrosion of alloys in oxidizing/sulphidizing atmospheres is still speculative. In general, the sulphidation rate is increased in the presence of hydrogen chloride or chlorine, but a few results were published showing a decreased corrosion rate. Proposed explanations are: 1) chlorine or hydrogen chloride influences the defect concentration when incorporated in the lattice /43/. The Cl⁻ ions may replace the S²⁻ ions on anionic lattice sites, increasing the number of Fe²⁺-vacancies, and thus increasing the diffusivity of iron-ions (not occurring in oxides /61/; 2) the vapour phase accelerated underdeposit corrosion /4,5,6,42,43,48/; and 3) a repeated scale failure mechanism /7,8/.

REFERENCES

1. Bakker, W.T., Materials for Coal Gasification. An EPRI Perspective, EPRI Gasification Conference (1990).
2. Bakker, W.T. and Perkins, R.A., The Effect of Coalbound Chlorine on Corrosion Control in Coal Gasification Plants, Proc. of the 1st International Conf. on Chlorine in Coal, Chicago, October (1989).
3. Bakker, W.T. and Perkins, R.A., Beyond Mixed Oxidant Corrosion-Corrosion Phenomena in Gasifiers, EPRI Gasification Conference (1990).
4. Bramhoff, D., Grabke, H.J. and Schmidt, H.P., *Werkst. Korros.*, **40**, 642 (1989).
5. Bramhoff, D., Grabke, H.J., Reese, E. and Schmidt, H.P., *Werkst. Korros.*, **41**, 303 (1990).
6. Bramhoff, D., Grabke, H.J. and Schmidt, H.P., in: The Role of Active Elements in the Oxidation Behaviour of High Temperature Metals & Alloys, *Appl. Sci. Publ.*, E. Lang (Ed.), 335, London (1989).
7. Brooks, S. and Meadowcroft, D.B., The Role of Chlorine in the Corrosion of Mild and Low Alloy Steels in Low pO₂, Proc. Symp. High Temperature Corrosion in Energy Systems, *Met. Soc. AIME-ASM*, M.F. Rothman (Ed.), 515 (1985).
8. Brooks, S. and Meadowcroft, D.B., in: Corrosion Resistant Materials for Coal Conversion Systems, *Appl. Sci. Publ.*, D.B. Meadowcroft and M.I. Manning (Eds.), London, 105 (1983).
9. Boettger, H. and Umland, F., *Werkst. Korros.*, **25**, 805 (1974).
10. Brown, M.H., DeLong, W.B. and Auld, J.R., *Ind. Eng. Chem.*, **39**, 839 (1947).
11. Carter, R.E. and Richardson, F.D., *J. Met.*, **7**, 336 (1955).
12. Clarke, F. and Morris, C.W., in: Corrosion Resistant Materials for Coal Conversion Systems, *Appl. Sci. Publ.*, D.B. Meadowcroft and M.I. Manning (Eds.), London, 47 (1983).
13. Coley, K.S., Blick, K. and Rhoades-Brown, J.E., *Werkst. Korros.*, **40**, 175 (1989).
14. Cutler, A.J.B., Grant, C.J., Laxton, J.W., Price, D.D. and Stevens, C.G., in: Corrosion Resistant Materials for Coal Conversion Systems, *Appl. Sci. Publ.*, D.B. Meadowcroft and M.I. Manning (Eds.), 159, London (1983).
15. Daniel, P.L. and Rapp, R.A., in: Advances in Corrosion Science and Technology, R.A. Staehle and M.G. Fontana (Eds.), *Plenum Press*, New York, **5**, 155 (1976).
16. Downey, B.J., Bermel, J.C. and Zimmer, P.J., *Corrosion*, **25**, 502 (1969).

17. Elliot, P., Ansari, A.A. and Marsh, G., *Proc. Int. Congr. Met. Corros., NRCC, Ottawa, Ont.*, **3**, 330 (1984).
18. Elliot, P., Ansari, A.A., Prescott, R. and Rothman, M.F., *Corr. Sci.*, **44**, 544 (1988).
19. Elliot, P. and Marsh, G., *Corr. Sci.*, **44**, 397 (1984).
20. Elliot, P., Tyreman, C.J. and Prescott, R., *J. Met.*, **37**, 20 (1985).
21. Fraud, C. and Vincent, L., *Oberfläche-Surf.*, **23**, 230 (1982).
22. Fruehan, R.J., *Metallurg. Trans.*, **3**, 2585 (1972).
23. Fruehan, R.J. and Martonik, L.J., *Metallurg. Trans.*, **4**, 2789 (1973).
24. Fruehan, R.J. and Martonik, L.J., *Metallurg. Trans.*, **4**, 2793 (1973).
25. Fujita, K., Onoue, H. and Sakiyama, K., *Corros. Engng.*, **19**, 340 (1970).
26. Gibb, W.H., in: *Corrosion Resistant Materials for Coal Conversion Systems*, *Appl. Sci. Publ.*, D.B. Meadowcroft and M.I. Manning (Eds.), London, 25 (1983).
27. Gesmundo, F., de Asmundis, C., Coen-Porisini, F. and Ruedl, E., *Br. Corros J.*, **15**, 14 (1980).
28. Koel, G.J., Thesis, University of Twente, The Netherlands (1971).
29. Gohil, D.D., Saunders, S.R.J., Bennett, M.J., in: *Proc. High Temperature Materials for Power Engineering*, Luik 1990, E. Bachelet et al (Eds.), Reidel Publishing Company, 189, Dordrecht (1990).
30. Haanappel, V.A.C., Haanappel, N.W.J., Fransen, T. and Gellings, P.J., *Annual Report COST 501/2 Round II*, University of Twente, The Netherlands (1990).
31. Halfdanarson, J. and Hauffe, K., *Werkst. Korros.*, **24**, 8 (1973).
32. Halstead, W.D., *Corr. Sci.*, **15**, 603 (1975).
33. Hauffe, K. and Hinrichs, J., *Werkst. Korros.*, **21**, 954 (1970).
34. Hossain, M.K., Noke, A.C. and Saunders, S.R.J., *Oxid. Met.*, **12**, 451 (1978).
35. Hossain, M.K. and Saunders, S.R.J., *Oxid. Met.*, **12**, 1 (1978).
36. Ihara, Y., Ohgame, H., Sakiyama, K. and Hashimoto, K., *Corr. Sci.*, **23**, 167 (1983).
37. Ihara, Y., Ohgame, H., Sakiyama, K. and Hashimoto, K., *Corr. Sci.*, **22**, 901 (1982).
38. Ihara, Y., Ohgame, H., Sakiyama, K. and Hashimoto, K., *Corr. Sci.*, **21**, 805 (1981).
39. Jacobson, N.S., *Oxid. Met.*, **25**, 157 (1986).
40. Imai, Y. and Tagano, H., *Boshoko Gijutsu*, **30**, 259 (1981).
41. Jacobson, N.S., McNallan, M.J. and Lee, Y.Y., *Metallurg. Trans. A*, **17A**, 1223 (1986).
42. Kim, A.S. and McNallan, M.J., *Corrosion*, **46**, 746 (1990).
43. Kofstad, P., *High Temperature Corrosion*, Elsevier Applied Science Publishers, Ltd. (1988).
44. Krueger, J., Melin, A. and Winterhager, H., *Cobalt*, **33**, 176 (1966).
45. Kubaschewski, O., Evans, E.L. and Alcock, C.B., *Metallurgical Thermochemistry*, Pergamon Press (1958).
46. Liang, W.W. and Yun, K.H., *Proceedings of the Symposium on Corrosion-Erosion Behavior of Materials*, K. Natesan (Ed.), *American Institute of Mechanical Engineers*, Warrendale, Penn., 60 (1980).
47. Lee, Y.Y., *Diss. Abstr. Int. B.*, **48**, 3092 (1988).
48. Lee, Y.Y. and McNallan, M.J., *J. Electrochem. Soc.*, **137**, 472 (1990).
49. Lee, Y.Y. and McNallan, M.J., *Metallurg. Trans. A.*, **18A**, 1099 (1987).
50. Lewis, E.C., Bakker, W.T. and Perkins, R.A., *Proc. ASM Conference, Materials for Coal Gasification*, Chicago (1987).
51. van Lieere, J., Kip, J.B.M. and Bakker, W.T., *Materials Performance at the SAR Coal Gasification Plant*, EPRI Gasification Conference (1990).
52. Liu, J., *Diss. Abstr. Int. B.*, **49**, 4510 (1989).
53. Maloney, M.J. and McNallan, M.J., *Metallurg. Trans. B.*, **16B**, 751 (1985).
54. Mayer, P., Manolescu, A.V. and Thorpe, S.J., in: *Corrosion Resistant Materials for Coal*

- Conversion Systems, *Appl. Sci. Publ.*, D.B. Meadowcroft and M.I. Manning (Eds.), 87, London (1983).
55. McKee, D.W., Shores, D.A. and Luthra, K.L., *J. Electrochem. Soc.*, **125**, 411 (1978).
 56. McKinley, J.D., *J. Chem Phys.*, **40**, 120 (1964).
 57. McKinley, J.D. Jr. and Shuler, K.E., *J. Chem. Phys.*, **28**, 1207 (1958).
 58. Kofstad, P., High Temperature Corrosion, Elsevier Applied Science Publishers Ltd. (1988).
 59. McNallan, M.J., NATO ASI Ser., Ser. C (*Thermochem. Alloys*), **286**, 495 (1989).
 60. McNallan, M.J., Kang, C.T. and Liang, W.W., *Metallurg. Trans. A*, **15A**, 403 (1984).
 61. McNallan, M.J., and Liang, W.W., *J. Amer. Cer. Soc.*, **64**, 302 (1981).
 62. McNallan, M.J., Liang, W.W., Kim, S.H. and Kang, C.T., in: Proc. International Conference on High Temperature Corrosion (National Association of Corrosion Engineers), Houston, Texas (1983).
 63. McNallan, M.J., Liang, W.W., Oh, J.M. and Kang, C.T., *Oxid. Met.*, **17**, 371 (1982).
 64. McNallan, M.J., Oh, J.M. and Liang, W.W., *Energy Res. Abstr.*, **8**, Abstr. No. 29875 (1983).
 65. Meadowcroft, D.B., *Werkst. Korros.*, **39**, 45 (1988).
 66. Misra, R.D. and Sivakumar, R., *Oxid. Met.*, **25**, 83 (1986).
 67. Mulet, J.C., Prebende, C., Devisme, F. and Flament, T., First Annual Progress Report, Project No. 4F1 COST 501 Round II, Work Package WP4 (1990).
 68. Oh, M.J., McNallan, M.J., Lai, G.Y. and Rothman, M.F., *Metallurg. Trans. A*, **17A**, 1087 (1986).
 69. Perkins, R.A. and Bakker, W.T., in: Materials for Coal Gasification, *ASM International*, W.T. Bakker, S. Dapkunas and V. Hill (Eds.), 85 (1987).
 70. Pourbaix, A., *Werkst. Korros.*, **40**, 157 (1989).
 71. Prescott, R., Stott, F.H. and Elliott, P., *Oxid. Met.*, **31**, 145 (1989).
 72. Prescott, R., Stott, F.H. and Elliott, P., *Corr. Sci.*, **29**, 465 (1989).
 73. Pruton, C.F., Turnbull, D. and Dlouhy, G., *Ind. Engng. Chem.*, **37**, 1092 (1945).
 74. Ree, M.H., McNallan, M.J. and Rothman, M.F., in: Proc. Symp. High Temp. Corros. Energy Syst., *Metall. Soc. AIME*, M.F. Rothman (Ed.), 483, Warrendale, Pa. (1985).
 75. Reinhold, K. and Hauffe, K., *J. Electrochem.*, **124**, 875 (1977).
 76. Reinhold, K. and Hauffe, K., *Werkst. Korros.*, **29**, 202 (1978).
 77. Ross, W. and Umland, F., *Werkst. Korros.*, **35**, 47 (1984).
 78. Ruedl, E., De Asmundis, C. and Coen-Porisini, F., *Werkst. Korros.*, **28**, 827 (1977).
 79. Saunders, S.R.J., 2nd Annual Progress Report, Project No. UK2, COST 501 Round II, Work Package WP4 (1990).
 80. Stott, F.H., Prescott, R. and Elliott, P., *Mater. Sci. Technol.*, **6**, 364 (1990).
 81. Stott, F.H., Prescott, R. and Elliott, P., *Werkst. Korros.*, **39**, 401 (1988).
 82. Stott, F.H., Prescott, R. and Elliot, P., Al'Atia, M.H.J.H., *High Temp. Technol.*, **6**, 115 (1988).
 83. Strafford, K.N., Data, P.K. and Forster, G., *Mater. Sci. Eng. A*, **A120-121**, 61 (1989).
 84. Strafford, K.N., Data, P.K. and Forster, G., *Corr. Sci.*, **29**, 703 (1987).
 85. Tedmon, C.S. Jr., *Electrochem. Soc.*, **113**, 766 (1966).
 86. Thongtem, S., Diss. Abstr. Int. B, **49**, 3956 (1989).
 87. Tseitlin, K.L., *J. Appl. Chem. USSR*, **27**, 889 (1954).
 88. Tseitlin, K.L., *J. Appl. Chem. USSR*, **28**, 467 (1955).
 89. Tseitlin, K.L., *J. Appl. Chem. USSR*, **29**, 253 (1956).
 90. Tseitlin, K.L., *J. Appl. Chem. USSR*, **29**, 1182 (1956).
 91. Tseitlin, K.L., Strunkin, V.A., *J. Appl. Chem. USSR*, **29**, 1793 (1956).
 92. Tseitlin, K.L., Strunkin, V.A., *J. Appl. Chem. USSR*, **31**, 1832 (1958).
 93. Turkdogan, E.T., Grieveson, P. and Darken, L.S., *Thermochem. Acta*, **67**, 1647 (1963).

94. Smeggil, J.G. and Bornstein, N.S., in: Proc. International Conference on High Temperature Corrosion (National Association of Corrosion Engineers), Houston, Texas (1983).
95. Viswanath, R.P., Rein, D. and Hauffe, K., *Werkst. Korros.*, **31**, 778 (1980).
96. Daniel, P.L. and Rapp, R.A., *Adv. in Corrosion Science and Technology*, **5**, 55 (1976).
97. Rahmel, A., Private Communications.
98. Haanappel, V.A.C., Haanappel, N.W.J., Fransen, T., van Corbach, H.D. and Gellings, P.J., Paper submitted for publication in *Corrosion*.

