Chlorine-Induced High Temperature Corrosion:
II. The Tedmon Equation as a Theoretical Approach of the Kinetics

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ABSTRACT

A model for the corrosion rate of metals and alloys induced by the presence of chlorine is discussed. The overall kinetics are described by the Tedmon equation which describes simultaneous reactions, one leading to an increase in mass of specimens by solid state diffusion and vapour phase transport of the reactants obeying a parabolic rate equation and one resulting in a decrease of mass due to scale evaporation, following a linear rate equation with rate constant k_v. This model can only be used if the overall kinetics are determined by the diffusion of ions through the solid or molecules through the gas phase (pores) and not by the chemical reaction rate or gas phase transport through a diffusion boundary layer.

KEYWORDS

Tedmon equation, chlorine, high temperature corrosion, oxidation, mechanisms, scale growth, evaporation

1. INTRODUCTION

The corrosion behaviour of metals and alloys under purely oxidizing or oxidizing/sulphidizing circumstances changes significantly after the addition of small amounts of hydrogen chloride or chlorine. In the past, research on corrosion of materials used in coal gasification systems was primarily focussed on the attack by oxygen and sulphur. This means that much effort was spent on finding materials with a good corrosion resistance to environments with relatively low oxygen and high sulphur partial pressures. Various materials and protective coatings have been developed with adequate mechanical and chemical properties in atmospheres without chlorine.

Due to the increased tendency to use coals contaminated with significant amounts of chlorine, to the incineration of municipal waste and to heat recovery from waste and chemical or metallurgical processes involving chlorine, additional problems occur associated with the high concentration of chlorine in these atmospheres /1/.

The interest in corrosion in chlorine-containing environments is growing /2-7/. Next to oxygen and sulphur, chlorine can have a considerable effect on the long term performance of the used materials. In order to calculate the thermodynamically most stable phases it is necessary to know the pCl_2 or the ratio HCl/H_2.

The major part of recent studies is concerned with the effect of chlorine or hydrogen chloride in oxidizing atmospheres on metals and commercially available alloys. For example, Bramhoff et al /2/ investigated the oxidation of 10CrMo9.10 at 500 °C in He-O_2-HCl atmospheres. The addition of hydrogen chloride leads to accelerated oxidation. Chlorides are formed below the porous and cracked oxide scales. "Active oxidation" determines the corrosion process at low hydrogen chloride pressures (0-1000 ppm). At higher hydrogen chloride contents (1000-3000 ppm), corrosion behaviour becomes paralinear, indicative of a simultaneous parabolic oxide growth and a linear mass loss by chloride evaporation.

In this paper, the modeling of the kinetics of corrosion accelerated by hydrogen chloride or chlorine is discussed. The proposed mechanism for accelerated corrosion is based on 1) solid state diffusion of cations and vapour phase transport of molecules through pores (parallel transport mechanisms) and 2) formation of volatile products.

2. MODELING OF THE KINETICS OF CHLORINE-INDUCED CORROSION

2.1. *Corrosion Mechanism of Metals and Alloys in HCl/Cl_2 Containing Atmospheres*

Bramhoff et al /7/ studied the effect of hydrogen chloride on the oxidation of Fe-20Cr at 900 °C in atmospheres with low oxygen pressures. According to Bramhoff /2,3,7/ HCl-induced oxidation can be described by two simultaneous reactions. The first reaction is that of the common parabolic corrosion which is ascribed to the oxidation of the alloy or metal by:

$$2M + O_2 \rightarrow 2MO \qquad (1)$$

The second reaction is that between the formed protective oxide scale and chlorine in the gas mixture at the oxide-gas interface. For example /7/, the formation of chromia leads to a stable condensed phase and thus to an increase of the sample mass. Consumption of chromia by the reaction with hydrogen chloride can be described by the following equation:

$$Cr_2O_3 + 2Cl_2(g) \rightarrow 2CrCl_2(g) + 1\tfrac{1}{2}O_2(g) \qquad (2)$$

Due to the high volatility of chromium chloride, it does not remain in or on the scale but evaporates and condenses on the cooler parts of the test system.

If a dense, pore-free and intact chromia layer cannot be obtained, additional processes are necessary to describe the overall corrosion attack. The porosity of the oxide scale enables the transport of chlorine or hydrogen chloride through the scale, most likely by gaseous diffusion along the pores, to the base metal. Hydrogen chloride or chlorine can subsequently react with the metallic matrix to form metal chlorides /8-10/:

$$M(s) + Cl_2 \rightarrow MCl_2(s) \qquad (3)$$

Higher partial pressures of metal chlorides are produced if the chlorine penetrates the oxide scale to regions of low oxygen pressures near the scale-metal interface. Due to the high vapour pressure of some metal chlorides, for example, iron chloride, these evaporate, according to:

$$MCl_2(s) \rightarrow MCl_2(g) \qquad (4)$$

If the oxidation process is controlled by transport through the oxide scale, regardless of whether the transport is by cation diffusion through the solid scale or chloride molecules through pores in the scale, the diffusion of iron can be described by a flux of iron cations through the solid and by a flux of iron atoms transported as iron chloride through pores /10/.

During the diffusion of gaseous metal chloride through the oxide scale, from the metal-oxide interface (low oxygen partial pressure) to the scale-gas interface (higher partial oxygen pressure), the equilibrium partial pressure of the metal chloride decreases. Since the equilibrium partial pressure of the gaseous metal chlorides decreases with increasing pressure of oxygen, there is a driving force for the outward diffusion of the metal chlorides towards the scale-gas interface (where the partial pressure of the volatiles is considered to be zero). But as the chloride vapour diffuses into regions of higher oxygen pressures, the chlorides react with oxygen-forming oxide deposits and chlorine. The chlorine can diffuse again to the scale-metal interface and the whole process can start again. This process is called "active oxidation".

The addition of hydrogen chloride to the oxidizing/sulphidizing atmosphere also leads to a thicker, more porous and less adherent scale on the substrate /1,11-16/. This means that there is a similarity between the corrosion mechanism of metals and alloys under pure oxidizing and under oxidizing/sulphidizing circumstances when small amounts of hydrogen chloride or chlorine are added

It has been proposed /17/ that metal chlorides and oxides or sulphides form simultaneously in the initial stage of the corrosion process. Depending on process parameters such as temperature and partial pressures of the aggressive components, a scale is formed after some time. Eventually the chlorides are overgrown by the oxide or sulphide, and a steady state corrosion attack is obtained. The overall steady state corrosion process of "active" corrosion is believed to consist of the following steps:

1) transport of chlorine or hydrogen chloride through a laminar diffusion boundary layer,
2a) reaction at the scale surface between the oxide or sulphide and HCl or Cl_2 which forms volatile metal chlorides followed by diffusion through a laminar diffusion boundary layer,
2b) (in case of a porous scale) diffusion of the reactants through the oxide or sulphide scale,
3) reaction of the chlorine with the metal,
4) formation of the volatile chloride,
5) diffusion of the volatile chlorides through pores in the scale,

6a) formation of chlorine and MO from MCl_2 and oxygen,
6b) (in case of a porous scale) transport of part of the volatile metal chlorides to the scale/gas interface and subsequently through a laminar diffusion boundary layer, and
7) diffusion of the reformed chlorine to the metal-scale interface.

2.2. *Kinetics of Chlorine-Induced Corrosion*

The kinetics of hydrogen chloride or chlorine induced accelerated corrosion have been described by Bramhoff et al /2,3,7/, Ihara et al /9/ and Kim and McNallan /19/ among others using the Tedmon equation /23/. This equation describes the simultaneous formation and sublimation of the scale by:

$$\frac{dx}{dt} = \frac{k_p}{x} - k_v \qquad (5)$$

where
x = thickness of the scale,
t = time,
k_p = parabolic rate constant, and
k_v = rate constant of linear evaporation.

It has been reported /2,3,7,9,10/ that the decrease in mass, a time-independent evaporation loss, follows a linear rate equation and depends, e.g., on the partial pressures of the aggressive components. In many cases, the parabolic rate constant was determined and calculated from pure oxidizing atmospheres without the addition of gas components such as sulphur and chlorine. Lee and McNallan /4/ reported that k_p for the oxide formation can be measured from the results of experiments performed under conditions where no chlorine was present.

This means that in this case the overall k_p (calculated) is based on solid state diffusion. Since /2,3,7,10/ the vapour phase transport through pores and voids play a role in the total corrosion rate and the specific surface area or contact area between the metal or alloy and the scale is also reduced, the overall k_p-value changes.

This means that the overall k_p used in the Tedmon equation must not only be based on solid state diffusion but also on the transport of reactants by gas phase diffusion through pores in the scale. Another aspect is that the diffusion coefficient for the ionic transport through the scale probably changes if, for example, chloride-ions are incorporated in the oxide or in the sulphide lattice. The kinetics of HCl or Cl_2-induced oxidation is very complex for many reasons: changes of morphology, pores, cracking of such scales also must be considered.

2.3. *Oxide Growth by Solid State Diffusion*

In the following theory, a simplified model is used which describes corrosion where the diffusion of ions is rate-determined (thus not the chemical reaction rate of gas phase transport of the reactants through a diffusion boundary layer) under the restriction of ideal conditions. It is assumed that:

- solid state diffusion is based on ionic transport across the growing oxide layer,
- thermodynamic equilibrium is established at each interface,
- activities are set equal to mole fractions, concentrations or partial pressures, and
- the total process is based upon steady state conditions.

The flux of cations by diffusion through a solid and based on the Nernst-Einstein relation is given by:

$$J_i = -\left(\frac{D_i c_i}{RT}\right) \frac{d\mu_i}{dx} \qquad (6)$$

where
J_i = flux of cations (mole.cm^{-2}.s^{-1}),
D_i = diffusion coefficient of component i in the layer (cm^2.s^{-1}),
c_i = concentration of component i in the layer (mole.cm^{-3}),
T = absolute temperature (K),
R = gas constant (82.05 cm^3.atm.mol^{-1}.K^{-1}),
μ_i = chemical potential of component i (J.mole^{-1}),

and
x = thickness of the scale (cm).

The chemical potential of particles of type i is related to the activity of component i through:

$$\mu_i = \mu_i^o + RT\ \ln(a_i) \qquad (7)$$

where
μ_i^o = standard chemical potential of component i (J.mole^{-1}), and
a_i = activity of component i.

If ideal conditions are assumed, the activity of component i can be put as equal to the mole fraction or concentration of i. Hence, the chemical potential gradient is given by:

$$\frac{d\mu_i}{dx} = RT\frac{dlnc_i}{dx} = \left(\frac{RT}{c_i}\right)\frac{dc_i}{dx} \qquad (8)$$

Substituting this expression for the chemical potential gradient in the equation for the particle flux (Eq. 2) of i leads to:

$$J_i = -D_i\frac{dc_i}{dx} \qquad (9)$$

The scale growth is described by dx/dt, following:

$$\left(\frac{dx}{dt}\right)_s = n.V_m J_i \qquad (10)$$

where
$(dx/dt)_s$ = the contribution to the scale growth by solid state diffusion,
n = amount of moles of products, formed from 1 mole of reactant, and
V_m = molar volume of the product (cm^3.mole^{-1}).

From these equations which describe the flux of i and scale growth (6), J_i can be eliminated resulting in:

$$\left(\frac{dx}{dt}\right)_s = -\ n.V_m.D_i\left(\frac{dc_i}{dx}\right) = \frac{k_p}{x} \qquad (11)$$

The parabolic rate constant can thus be written as:

$$k_p = -n.V_m\, D_i\, \Delta c_i \qquad (12)$$

where
Δc_i = concentration gradient of component i in the layer (mole.cm^{-3}).

Eq. 11 can only be used when a dense and adherent scale is formed on the substrate, for example, under purely oxidizing circumstances. Incorporation of elements such as chlorine in the oxide scale (lattice) lead to a change of D_i.

It is known /2,3,4,7,10/ that the presence of hydrogen chloride or chlorine increases the oxidation rate as well as the void fraction in the oxide, especially at the metal/oxide interface. Due to the increase of the void fraction, the oxide growth diminishes by a factor $(1-\epsilon)$ where ϵ is the void fraction of the oxide scale. The equation describing the oxide growth by solid state diffusion and also taking into account the void fraction can be written as:

$$\left(\frac{dx}{dt}\right)_s = \frac{k_p(1-\epsilon)}{x} = \frac{k_p^{\prime}}{x} \qquad (13)$$

2.4. *Oxide Growth by Vapour Phase Transport*

If one only observed an increased void fraction and considered only solid state diffusion, a decreased corrosion rate should be obtained. However, according to many authors /2-4,7,10,18-20/, the corrosion rate increases if hydrogen chloride or chlorine is added to the gas mixture. This means that other mechanisms also play a role in the total corrosion rate. It is assumed that the volatile chloride compounds are transported by diffusion through pores by vapour phase transport. The equation describing the scale growth by vapour phase transport of M and based on the transport of M by MCl_x is:

$$j_{MCl_x} = -\left(\frac{D_{MCl_x} c_{MCl_x}}{RT}\right)\frac{d\mu_{MCl_x}}{dx} \qquad (14)$$

where

J_{MClx} = flux of MCl_x (mole-cm^{-2}.s^{-1}),
D_{MClx} = diffusion ocefficient of MCl_x in the vapour phase (cm^2.s^{-1}),
c_{MClx} = concentration of MCl_x in the vapour phase (mole.cm^{-3}),
T = absolute temperature (K),
R = gas constant (82.05 cm^3.atm.mole^{-1}.K^{-1}),
μ_{MClx} = chemical potential of the volatile chloride compound MCl_x (J.mole^{-1}), and
x = thickness of the oxide scale (cm).

Whereas M is transported by MCl_x(g), the scale growth should be considered in terms of MCl_x for the vapour phase transport. The chemical potential μ_{MClx} can be expressed as:

$$\mu_{MCl_x} = \mu^o_{MCl_x} + RT\ \ln(a_{MCl_x}) \qquad (15)$$

Since ideal conditions are assumed to be present, the activity of MCl_x can be set equal to the partial pressure of MCl_x (P_{MClx}) at the scale-metal interface, which appears to be a reasonable simplification. The chemical potential gradient is given by:

$$\frac{d\mu_{MCl_x}}{dx} = \left(\frac{RT}{P_{MCl_x}}\right)\frac{dP_{MCl_x}}{dx} \qquad (16)$$

Using this for expressing the flux of MCl_x molecules, which is equal to the flux of M molecules (mole.cm^{-2}.s^{-1}), Eq. 12 leads to a scale growth expression, following:

$$\left(\frac{dx}{dt}\right)_v = n.V_m.J_{MCl_x} \qquad (17)$$

where $(dx/dt)_v$ is the contribution to the scale growth by the vapour phase transport of M and with J_{MClx}, considering that $P_{MClx} = 0$ at the scale-gas interface, equal to:

$$J_{MCl_x} = -D_{MCl_x}\frac{P_{MCl_x}}{x} \qquad (18)$$

Based on Fick's first law, the equation describing the scale growth and adjusted for the void fraction (ϵ) is obtained by eliminating J_{MClx}, following:

$$\left(\frac{dx}{dt}\right)_v = -n.V_m.D_{MCl_x}.\epsilon.\frac{P_{MCl_x}}{x} = \frac{k_p''}{x} \qquad (19)$$

where

n = amount of moles of products, formed from 1 mole of reactant,
D_{MClx} = diffusion coefficient of MCl_x in vapour phase,
V_m = molar volume of the product,
P_{MClx} = partial pressure of metal chloride at the scale metal interface,
ϵ = void fraction in the scale, and
x = thickness of the scale.

The k_p'', which corresponds with the scale growth accelerated by the vapour phase transport of chlorides, can be written as:

$$k_p'' = -n.V_m.D_{MCl_x}.\epsilon.P_{MCl_x} \qquad (20)$$

2.5. *The Tedmon Equation modified for HCl/Cl_2-Induced Accelerated Corrosion*

The total scale growth can be explained by two parallel mechanisms, one based on solid state diffusion and the other on gas phase transport of the volatile chloride compounds through the pores. The amount of pores (void fraction) may also be a function of the concentration of chlorine or hydrogen chloride.

The decrease in mass is due to the time-independent evaporation loss. This loss is expressed by the rate constant of linear evaporation k_v, which implies the reaction between the blank metal (unoxidized) and/or scale and the chlorine or hydrogen chloride-forming volatile metal chlorides. k_v is a function of among others the temperature, saturated vapour pressure of the chloride compounds and the relative activities of the aggressive gas components.

The Tedmon equation can now be written as:

$$\left[\frac{dx}{dt}\right]_{total} = \left[\frac{dx}{dt}\right]_s + \left[\frac{dx}{dt}\right]_v - k_v \qquad (21)$$

or:

$$\left[\frac{dx}{dt}\right]_{total} = \frac{(k_p' + k_p'')}{x} - k_v \qquad (22)$$

The overall k_p is thus equal to:

$$k_p = k_p' + k_p'' = -n.Vm[((1-\epsilon).D_i.\Delta c_i) + (\epsilon.D_{MCl_x}.P_{MCl_x})] \qquad (23)$$

2.6. *The Overall Tedmon Equation*

As mentioned in Section 2.2, the Tedmon equation describes simultaneously the kinetics of parabolic growth of a layer and the evaporation of some corrosion products. In this section, k_p from Eq. 23 includes both the solid state transport of ions and the diffusive transport of the metal chlorides. This gives the differential equation for the layer as shown in Eq. 5.

Using the initial condition of x=0 at t=0, integration of this equation gives:

$$-k_v x - k_p \ln\left[1 - \left(\frac{k_v}{k_p}\right)x\right] = k_v^2 t \qquad (24)$$

Eq. 24, which gives the scale thickness as function of k_p and k_v, cannot be solved in closed form for x, but it can be solved using Lagrange's theorem /21,22/ as a series expansion. This leads to the following expression for the coating thickness as a function of k_p, k_v and t:

$$x(t) = \frac{k_p}{k_v}\left[1 - \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!} \exp\left[-n\left(\frac{k_v^2}{k_p}t + 1\right)\right]\right] \qquad (25)$$

and for the metal loss cq. sublimation of the scale as function of time:

$$m(t) = K\frac{k_p}{k_v}\left[\left(\frac{k_v^2}{k_p}t + 1\right) - \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!}\left[-n\left(\frac{k_v^2}{k_p}t + 1\right)\right]\right] \qquad (26)$$

where

K = D.F/100,

D = density of the layer, and

F = metal content in weight %.

An approximate solution can be obtained by rewriting Eq. 24 in the form:

$$\frac{\exp\left[-\left(\frac{k_v}{k_p}\right)x\right]}{1 - \left(\frac{k_v}{k_p}\right)x} = \exp\left[\left(\frac{k_v^2}{k_p}\right)t\right] \qquad (27)$$

For not too large values of $(k_v/k_p).x$, the exponentials can be expanded:

$$\frac{1 - \left[\frac{k_v}{k_p}\right]x + \frac{1}{2}\left[\frac{k_v}{k_p}\right]^2 x^2}{1 - \left[\frac{k_v}{k_p}\right]x} \approx 1 + \left[\frac{k_v^2}{k_p}\right]t \qquad (28)$$

Rearranging and solving the resulting quadratic Eq. 28 in x then gives:

$$x(t) \approx -k_v t + (k_v^2 t^2 + 2k_p t)^{\frac{1}{2}} \qquad (29)$$

At short times or for small k_v, the metal loss approximates to a parabolic law because then $k_v^2 t^2$ can be neglected with respect to $k_p t$:

$$x(t) \approx (2k_p t)^{\frac{1}{2}} \qquad (30)$$

It can be seen from Eq. 25 that for t→∞ a constant layer thickness is reached given by:

$$x_{(t\to\infty)} = \frac{k_p}{k_v} \qquad (31)$$

A schematic view is given in Fig. 1. It is seen from this figure that during the initial stage the mass gain follows parabolic kinetics due to the fact that then $k_p/x >> k_v$. But with increasing thickness, the influence of k_v increases and at t→∞ the layer thickness versus time corresponds with $dx/dt = 0$, or $k_p = x.k_v$ (steady state conditions).

The total metal loss when considering only scale formation and scale evaporation is given by Eq. 26. A more simplified equation can be given by the following formula:

Total metal-loss = metal in layer + metal evaporated.

$$m(t) \simeq \frac{DF}{100}\left[x(t) + \int_0^t k_v dt\right] \qquad (32)$$

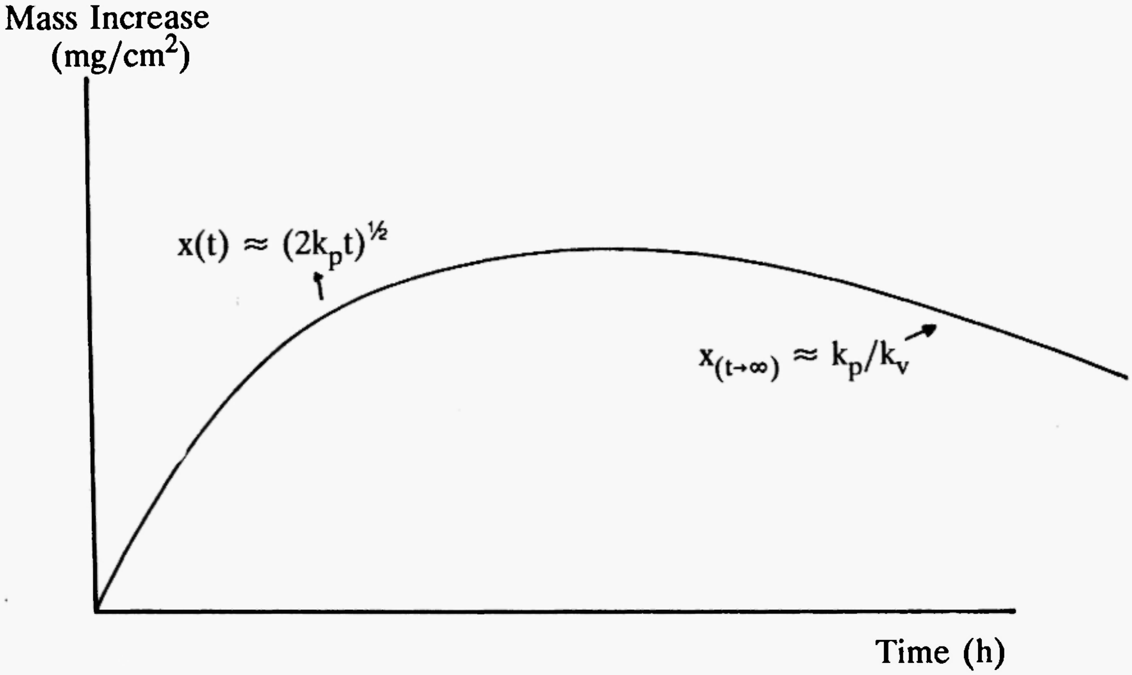

Fig. 1: Schematic view of the mass increase as function of time.

Substituting Eq. 29 for x and performing integration gives:

$$m(t) \approx \frac{D.F}{100}(k_v{}^2t^2 + 2k_pt)^{\frac{1}{2}} \qquad (33)$$

3. EVALUATION

Considering that the rate determining step is the diffusion of ions through the solid or vapour phase (thus not the chemical reaction rate or the gas phase transport through a diffusion boundary layer), a Tedmon equation with modified parameters is discussed. In this simplified model, it is assumed that solid state diffusion of cations and vapour phase transport of MCl_x in the pores are parallel transport mechanisms.

The sublimation rate was calculated from the difference between the measured weight gain and the calculated mass increase if only oxidation was performed.

The overall k_p for the vapour phase induced corrosion is probably higher than calculated under purely oxidizing circumstances. According to Eq. 23, the overall k_p is now also a function of the partial pressures of the volatile metal chlorides. Therefore, it is necessary to study both the kinetics of scale formation and that of sublimation in order to discuss the scale growth by solid state diffusion and vapour phase transport.

To investigate whether vapour phase transport is rate-controlling, a quantification of the transport phenomena should be performed. Additional experiments are needed to obtain more detailed information about chlorine-induced corrosion.

Of course, the kinetics of the chlorine-induced oxidation can also be changed by factors such as differences in morphology, pore structure, etc. which in particular will influence the diffusion transport of the metal chlorides expressed by k_p'' (Eq. 23).

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