CHAPTER 4 (Addendum re Corrosion Kinetics)

Corrosion Kinetics, WTE Emissions and the Effects of HCl and SO$_2$ to Corrosion

4.1 Introduction

In this chapter the kinetics of high temperature corrosion are discussed. Three different kinetic models are discussed in detail to understand the growth of the oxide scale with time. This section on kinetics is aimed to provide an understanding how to control the rate-determining step in order to minimize corrosion. This chapter also examines the concentrations of HCl and SO$_2$ encountered in the combustion gases of WTE and coal-fired power plants as well as the respective emissions of these two types of plants. The purpose of the comparison is to see the relative differences between emissions of modern WTE technology to that of the dominant technology for electricity generation. The impact of MACT (Maximum Achievable Control Technology) to emissions from WTE is also examined.

4.2 Corrosion Kinetics

4.2.1 Basic Kinetics Principles [10]

Three basic kinetic laws have been used to characterize the oxidation rates of pure metals namely: 1) the parabolic rate law, 2) logarithmic rate law and 3) linear rate law and catastrophic oxidation.

The parabolic rate law (equation 48) assumes that the diffusion of metal cations or oxygen anions is the rate-controlling step and is derived from Fick's first law of diffusion. The concentrations of diffusing species at the oxide-metal and oxide-gas interfaces are assumed to be constant. The diffusivity of the oxide layer is also assumed to be invariant. This assumption implies that the oxide layer has to be uniform, continuous and of the single phase type. The diffusion rate constant, k_p, changes with temperature according to an Arrhenius type relationship:

$$x^2 = k_p t + x_0 \qquad (48)$$

where   x = oxide film thickness (or mass gain due to oxidation, which is proportional to oxide film thickness)

t = time

k_p= diffusion rate constant (directly proportional to diffusivity of ionic species that is the rate controlling step)

x_o=constant

The logarithmic rate law (equation 49) is an empirical relationship, that has no fundamental underlying mechanism. This law is mainly applicable to thin oxide layers formed at relatively low temperatures and therefore is rarely applicable to high temperature engineering problems.

$$x = k_p \log(ct + b) \qquad (49)$$

where: k_p =rate constant, and c and b are constants

The linear rate law (equation 50) is also an empirical relationship that is applicable to the formation and build-up of a non-protective oxide layer:

$$x = k_L t \qquad (50)$$

where k_L = constant

In general, high temperature oxidation rate decreases with time (parabolic behavior), due to an increasing oxide thickness acting as a stronger diffusion barrier. However, due to the formation of highly porous, poorly adherent or cracked non-protective oxide layers, corrosion rates may remain linear. Metals with linear oxidation kinetics at a certain temperature have a tendency to undergo so-called catastrophic oxidation (also referred to as breakaway corrosion) at higher temperatures. In this case, a rapid exothermic reaction occurs on the surface, which increases the surface temperature and the reaction rate even further. Metals that may undergo extremely rapid catastrophic oxidation include molybdenum, tungsten, osmium, rhenium and vanadium, associated with volatile oxide formation. In the case of magnesium, ignition of the metal may even occur. The formation of low-melting point oxidation products (eutectics) on the surface has also been associated with catastrophic oxidation. The presence of vanadium and lead oxide contamination in gases deserves special mention, as they pose a risk to inducing extremely high oxidation rates.

4.3 Reaction Kinetics Models

4.3.1 Tedmon Equation

Analysis of paralinear kinetic behavior caused by a parabolic rate weight gain and a linear weight loss that occur at the same time can be carried out using the Tedmon equation [40], devised for growth of Cr_2O_3 from the outer surface of the scale:

$$\frac{dx}{dt} = \frac{K_p}{x} - K_V \qquad (51)$$

where: *x is the scale thickness*

K_p is the parabolic rate constant for scale growth

K_v is the linear rate constant for loss of scale by volatilization.

Equation (51) can also be rewritten as [2] provided that K_v/K_p <1:

$$x = K_v t + (K_V^2 t^2 + 2K_p t)^{1/2} \qquad (52)$$

The process involved scale growth following diffusion of metal species through the scale and loss of metal following formation of $FeCl_2$ at the scale/metal interface. As discussed previously, the chloride has a high vapor pressure especially at higher temperatures [above $500^{\circ}C$], and some it diffuses away as vapor which may be lost in the environment or will react with oxygen to form oxide within the scale or at the scale gas interface, resulting in weight loss or weight gain respectively. Hence, it can be appropriate to consider the kinetics in terms of weight changes than scale thickness changes, such as equation (53) [42]:

$$w = -K_v t + (K_v^2 t^2 + 2K_p t)^{1/2} \qquad (53)$$

The measured weight gain versus time curve should follow this equation, if the reaction gives a paralinear behavior.

Attempts can also be made to determine the values of K_v and K_p independently and compare the measured kinetics with those calculated from equation 53. By metallography, the extent of metal loss and scale thickness can be determined. The measured weight change *(w)* represents the sum of the weight increase due to growth of the oxide scale or solid chloride deposits plus deposition of the oxide following chloride-to-oxide reactions and the weight decrease due to evaporation and complete loss from the scale of volatile reaction products (equation 56).

$$\frac{w}{A_o} = \frac{w_g}{A_o} - \frac{w_1}{A_o} \qquad (54)$$

where: w is the measured weight gain after time, t

w_g is the total weight of the scale

w_1 is the total weight of metal lost from the specimen core

A_o is the original specimen area.

W_1 can be determined by measuring the dimensions of the original specimen and of the metal core after time, t and converting it to weight. Since w_1 can be assumed to be the total weight of the metal in the scale plus the weight of metal lost as vapor *($w_1=w_s+w_v$)*. Thus, w_v can be calculated from estimations of the weight of the metal in the scale. It should also be noted that the surface area of the metal core decreases with time. For reactions involving scale growth only, this can be accommodated by assuming that all of the metal lost from the specimen is incorporated into the scale. For simplicity, it is necessary to assume that the surface area (A_o) remain constant, otherwise interpretation of data can be difficult [39].

Using metallography, the scale and the residual metal thickness can be determined. Thus, values of w_g, w_1, w_s and w_v can be calculated. From these metallographic measurements, rate constants could be calculated for the growth of the scale assuming parabolic behavior, and for metal loss assuming linear behavior, as can be seen in equations 55 and 56.

$$\frac{w_g - w_s}{A_o} = \left(K_{pe} * t\right)^{1/2} \qquad (55)$$

$$\frac{w_v}{A_o} = -K_{ve} * t \qquad (56)$$

where:

K_{pe} = the empirical parabolic rate constant for scale growth

K_{ve} = the empirical linear rate constant for metal loss by vaporization

A numerical calculation can also be used to determine the K_p values from the measured weight-change data. This involves substituting the value of K_{ve} in equation (53) and calculating K_p value for the best fitting curve. The difference between the numerical K_p (K_{pn}) and the empirical K_p (K_{pe}) may arise in the variations in scale thickness for a given specimen, the porosity in the scale and in particular, K_{pe} is calculated based on the assumption that the scale thickens according to a simple parabolic rate law, which can be unlikely for a situation

where scale growth results from both solid-state diffusion of cations and vapor-phase transport of molecules through the scale.

4.3.2 Gas Kinetic Theory

The linear rate constant for metal loss by evaporation may also be estimated from the gas kinetic theory. At steady state, the flux of $FeCl_2$ is given by [42]:

$$J = \frac{h}{RT}(P_s - P_b) \qquad (57)$$

and the metal loss due to evaporation at time, t is:

$$\frac{w_v}{A_o} = \frac{Mh}{RT}(P_s - P_b)t = K_{v,kin}t \qquad (58)$$

$$K_{v,kin} = \frac{M}{RT}h(P_s - P_b) \qquad (59)$$

where:

M = the atomic mass of iron

h = the mass transfer coefficient of FeCl₂

P_s = partial pressure of FeCl₂ at the metal/scale interface

P_b = partial pressure of FeCl₂ in the bulk gas

R = the gas constant

T = temperature

The mass transfer coefficient can be approximated for laminar flow over a flat plate [42]:

$$h = 0.664D^{2/3}v^{-1/6}(V/L)^{1/2} \qquad (60)$$

where:

v = the kinematic viscosity of the gas

D = is the diffusivity of the volatile species

V = is the superficial velocity of the gas flow passing the specimen

L = length of the specimen

The values of V and L are empirical data, v can be taken as the viscosity of oxygen at specific temperature (T), and the diffusivity of the volatile species can be estimated via the kinetic theory of gases using the Chapman-Enskog equation [43], and assuming suitable values for the collision diameter of $FeCl_2$ molecules.

As $FeCl_2$ is formed at the metal surface in contact with Fe_3O_4 or FeO, the values of P_s can be determined from the partial pressures of $FeCl_2$ in thermodynamic equilibrium with these oxides, while P_b is assumed to be negligibly small. Thus, $K_{vkin,}$ can be determined in equation (59).

4.3.3 Modification to the Tedmon Equation

The value of K_p in Tedmon's original equation is set equal to the parabolic growth rate for simple oxidation. However, K_p can be considered to consist of a combination of oxide growth by conventional solid-state diffusion and oxide growth by conversion of volatile species to solid oxide (equation 61) [39]:

$$\frac{dw}{dt} = \frac{\beta(K_{po})}{w} + \frac{K_{con}}{w} - K_v \qquad (61)$$

where:

β = is a constant (less than 1)

K_{po} = the parabolic rate constant for simple oxidation

K_{con} = the parabolic rate constant for conversion of chloride to oxide

The value of K_v and K_{po} can be determined from experimental measurements and numerical treatment of the kinetics curve, as discussed previously. As discussed in the section on active oxidation, the rate of $FeCl_2$ (g) outward diffusion through the scale is the rate controlling for the overall process of active oxidation. The rate would correspond to the outward diffusion flow of $FeCl_2$ (g) through the open spaces in the oxide scales, pores, fissures, and or cracks. The diffusion flow is given by [18]:

$$J(FeCl_2) = \varepsilon * \frac{D(FeCl_2)}{x} \left(P_s(FeCl_2) - P_b(FeCl_2) \right) \qquad (62)$$

where ε is the labyrinth factor, resulting from the open space free for outward $FeCl_2$ diffusion, $D(FeCl_2)$ is the diffusivity of $FeCl_2$(g), $P_s(FeCl_2)$ is the partial pressure of $FeCl_2$ at the interior interface and $P_b(FeCl_2)$ is the partial pressure at the surface. As the partial pressure at the surface is virtually zero then, the rate of Fe_2O_3 formation per unit area is given by the outward flux of $FeCl_2$ as:

$$2\frac{dn(Fe_2O_3)}{Adt} = J(FeCl_2) = \varepsilon \frac{D(FeCl_2)}{x} \left(P_s(FeCl_2) \right) \qquad (63)$$

The diffusion flow is temperature dependent, which mainly results from the temperature dependence of P_s ($FeCl_2$) which is the vapor pressure of $FeCl_2$(s). The temperature dependence of diffusivity of $FeCl_2$ (g), i.e. volatile phases in the gas phase, is negligible ($\approx T^{1/2}$). The value of ε can be assessed using experimental data for the formation rate of Fe_2O_3 in the active oxidation for certain oxide thickness and approximate values for the diffusivity and saturation pressure of $FeCl_2$ (g).

Similarly, the diffusion flow can be written as:

$$\frac{dx}{dt} = Z(V_{ox}) \frac{\varepsilon D}{RT} \left(\frac{P_s - P_b}{x} \right) \qquad (64)$$

where V_{ox} is the molar volume of the relevant oxide, and Z is 1/3 for Fe_3O_4 and at higher temperature FeO is formed (based on thermodynamic stability diagram) then Z is 1.

In order to determine $K_{con,}$ equation (64) can be written as:

$$\frac{dw}{dt} = Z(M_{ox})(\sigma_{ox})\left(\frac{\varepsilon D}{RT}\right)\left(\frac{P_s - P_b}{w}\right) \qquad (65a)$$

Thus:

$$K_{con} = Z(M_{ox})(\sigma_{ox})\left(\frac{\varepsilon D}{RT}\right)(P_s) \qquad (65b)$$

where: M_{ox} = the molar mass of the oxide

σ_{ox} = density of the oxide

4.3.4 Kinetics Summary

The basic principles of chemical kinetics are discussed, and 3 different models are presented, the Tedmon equation, the Kinetic gas theory and the modified Tedmon equation. The main objectives of these models are to predict the weight changes over time by determining the rate constants for scale growth and loss of scale by volatilization. In the Tedmon model, only the parabolic growth rate for simple oxidation is considered, while in the case of the modified Tedmon Model, the parabolic rate constant for scale growth included the oxide growth by conversion of the volatile species to solid oxides. By presentation of these models, it is hoped that this will help link laboratory metallography results, i.e. the degree of correlation between the measured weight-gain curve and curves obtained from K_v and K_p values, to the actual corrosion problems in the industry.