USE OF IMPEDANCE MEASUREMENTS FOR STUDYING
THE EFFECT OF ACIDITY ON THE CORROSION OF IRON
IN THE MOLTEN EQUIMOLAR NaNO₃-NaNO₂ MIXTURE

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ABSTRACT

The iron corrosion process in the molten equimolar NaNO₃-NaNO₂ mixture was studied as a function of melt acidity. A reaction model has been proposed from analysis of impedance spectra and was compared with earlier thermodynamic and kinetic results. This model which accounts for experimental data has allowed us to show the importance of the diffusion phenomena through the various iron oxide layers constituting the corrosion products. Besides, the acidity dependence of impedance spectra and more precisely of charge transfer resistances has revealed the existence of a narrow range of acidity (relative to NaFeO₂ stability) for which iron corrosion is minimized.

INTRODUCTION

Corrosion of iron and iron alloys in molten nitrate-nitrite mixtures has been studied primarily because of the application of these salts as both a heat transfer fluid and a thermal energy storage medium. Results in the literature for salts without contaminants indicate the formation of iron oxides (1-11). It has been observed that the corrosion products are Fe₂O₃(s), which forms the external layer in contact with the salt, and Fe₃O₄(s), the internal layer in contact with the metal. For temperatures greater than 600°C, it has been shown that a highly basic species of iron(III), the sodium ferrate, NaFeO₂, appears in the external layer (8). Studies on steel behavior in molten sodium-potassium nitrate-nitrite mixtures at 450°C reported by Spiteri (6) indicate that there

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are different corrosion rates depending on the (oxo)acidity level defined by \( pO^{2-} = -\log m(O^{2-}) \). In particular, a decrease in the corrosion rate has been observed in moderately basic media, jointly with the formation of sodium ferrate as one corrosion product. A similar result has been observed by Baraka et al. (1) in sodium-potassium nitrate for temperatures between 250°C and 400°C.

In previous work (9,10) we have demonstrated the relationship between the nature of iron oxide species and the oxide anion content in the melt. Stability constants of iron oxides have been determined by means of potentiometric titrations and equilibrium potential-pO\(^{2-}\) diagrams have been deduced from them in the temperature range from 420 to 500°C. The main result of this thermodynamic study is that different compounds of iron(III) may be formed according to the acidity of the nitrate-nitrite mixtures. In strongly basic media, \( Fe_2O_5^{4-} \) or \( Na_4Fe_2O_5(s) \) are stable in contact with the melt. In moderately basic media, the stable iron oxide species are \( FeO_2^- \) or \( NaFeO_2(s) \), and in acidic media \( Fe_2O_3(s) \).

From the previously quoted authors' works and ours, we can assert that the iron corrosion in molten nitrate-nitrite mixtures leads to the formation of a multilayered product. The outer layer in contact with the melt is constituted by iron(III) oxides whose surface composition depends on the melt acidity, and the deepest layer consisting of \( Fe_3O_4(s) \) [and perhaps \( FeO(s) \)] in contact with metallic iron. Moreover, knowing after Spiteri (6) that alkali ions are contained in the iron(III) oxide layer, suggests penetration of melt inside the outer layer, we can predict for the latter a structure formed by several secondary layers constituted by iron(III) compounds all the more acidic the deeper they are because of the oxide ion concentration gradient in the layer (Fig. 1).

The purpose of this paper is to study the iron corrosion process in the molten equimolar nitrate-nitrite mixture from a kinetic point of view, thus completing our work on the stability of iron(III) oxides. This was undertaken by using chronopotentiometry and especially A.C. impedance techniques. The latter allow us to obtain in situ information on the mechanism and kinetics of the steps involved. This electrochemical technique has been successfully used in aqueous solutions (12-14). However, relatively few studies have been carried out in media where corrosion leads to the formation of insoluble products adhering to the metal surface (15-17).

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Technical.**

Preparation of the melt, procedure, and apparatus have been described in detail in previous papers (18-20). For each experiment,
100g of an equimolar sodium nitrate-nitrite mixture were introduced into a platinum crucible. $pO^{2-}$ was imposed by using the buffer couple $H_2O(g)/OH^-$ whose acidity constant, given by $K_d = P(H_2O) . m(O^2-)/m(OH^-)^2$, takes the value $10^{-3.1}$ at 420°C (20). [Concentrations m of the dissolved species are given in the molality scale and partial pressure of water $P(H_2O)$ is given in atm].

The working electrode was a high purity iron wire (1 mm diam.) supplied by Johnson-Matthey, with a dipped surface area in the melt of 60mm². The platinum crucible was used as a counter electrode. The reference electrode is described elsewhere (20).

The chronopotentiograms were recorded with the help of a three pen Y/T Servofram SRM recorder (Sefram).

Impedance measurements have been performed over the frequency range 100 kHz-10mHz using the Z computer system (Tacussel) composed of a Tacussel electronic unit and of a Hewlett-Packard 9826 microcomputer. Measurements have been carried out under linear conditions using a small amplitude sine wave signal of 10mV. In order to avoid external perturbations on the electrical measurements, the cell was surrounded with a ground connected Faraday cage, and screened wires were used for connecting electrodes with the electronic unit. Fifteen minutes are necessary to perform measurements over the whole frequency range considered. Data were stored on standard 5 1/4 inch flexible disks and further analyzed by means of the HP 9826 microcomputer and HP 7470 A plotter.

**Chronopotentiometric evidence for a first transient phase followed by a quasi steady-state second phase in iron corrosion.**

The potential of an iron electrode under open circuit conditions was followed as a function of time for different values of $pO^{2-}$ (Fig.2). In all cases, the iron electrode potential increases at the beginning of corrosion, involving the formation of iron oxides. This transient phase was observed until the potential reaches a steady-state value depending on melt acidity, which corresponds to the potential of the $NO_3^-/NO_2^-$ redox couple as indicated by comparison with the potential of an inert platinum electrode (Fig. 2). The stabilization of the iron electrode potential does not exceed 2 hours and is shorter at lower $pO^{2-}$ values. Impedance measurements were performed at the stabilized rest potential of the iron working electrode.

**A.C. Impedance studies of the second phase of the iron corrosion process.**

Variation of impedance spectra as a function of oxide ion bulk concentration at a given immersion time (t = 3.5 h). Fig. 3 gives in the complex plane typical impedance spectra obtained in the
molten equimolar NaNO$_3$-NaNO$_2$ mixture at 420°C, for four pO$_2^-$ values: 1.4 and 2.9 corresponding to basic media where the stable iron(III) oxide is Na$_4$FeO$_2$O$_5$, pO$_2^- = 4.3$ which is the value for which the latter ferrate transforms into NaFeO$_2$ (moderately basic media) and the last, pO$_2^- = 5.2$, which corresponds to the transformation of NaFeO$_2$ into Fe$_2$O$_3$ (acidic media).

These spectra are constituted, whatever the pO$_2^-$ values, by two composite capacitive loops. They show (i) that the different phenomena involved during iron corrosion have time constants close to each other, resulting in a convolution of capacitive loops and (ii) that the effect of pO$_2^-$ is characterized by a frequency shift of the capacitive phenomenon (Fig. 5) and by a maximum of impedance (and so a minimum in the corrosion rate) for a pO$_2^-$ value equal to 4.3, which corresponds to the formation of the ferrate, NaFeO$_2$.

**Variation of impedance spectra as a function of immersion time at a given oxide anion bulk concentration.** Two values of pO$_2^-$ were considered: 1.4 and 4.3 for which a maximum impedance was observed. Analysis of Fig. 4 clearly shows the opposite corrosion behavior of iron for the two media considered. In the first case (pO$_2^- = 1.4$), impedance decreases when immersion time increases, to reach a low value indicating a fairly constant corrosion rate. On the contrary, for pO$_2^- = 4.3$, impedance increases with immersion time indicating the formation of a passivating film. Iron corrosion is then strongly limited.

Somewhat different behavior, depending on melt acidity, is observed for impedance spectra toward the low frequency region. Contrary to that which is observed for a pO$_2^-$ value equal to 4.3, experimental data obtained at pO$_2^- = 1.4$ present a large scattering for frequencies lower than 1 Hz (Fig. 5). This fact suggests that iron corrosion products can flake off the metal for this melt acidity.

**MODELLING OF THE IRON CORROSION PROCESS**

Thermodynamic and kinetic experimental studies have shown that after the transient phase of iron corrosion (during which NO$_3^-$ and/or NO$_2^-$ oxidize the metallic iron which is quickly recovered by an oxide layer), corroded iron can be schematically represented as follows: metallic iron is coated by a layer of magnetite, which is itself covered by a layer of iron(III) oxides (whose surface is in contact with the melt), thus defining four zones and three interfaces as indicated in Fig. 6. It should be noticed here that the sequence Fe/Fe$_3$O$_4$/Fe$_2$O$_3$ has been reported as the thermodynamically most stable system (21) and is often referred as the passive film on iron in aqueous solutions (21,22).
Proposed reaction mechanism.

The iron corrosion process in the molten equimolar NaNO₃-NaNO₂ mixture can be described by the following steps:

(i) diffusion of the oxidizing species (NO₃⁻ and/or NO₂⁻) and O²⁻ anions through the outer iron (III) oxide layer from its interface I melt to the interface II (Fig. 6):

\[
\begin{align*}
\text{NO}_2^- & \quad \text{D}(\text{NO}_2^-) \rightarrow \text{NO}_2^- \quad \text{(Interface I)} \quad \text{(1)} \\
\text{O}_2^- & \quad \text{D}(\text{O}_2^-) \rightarrow \text{O}_2^- \quad \text{(Interface I)} \quad \text{(2)}
\end{align*}
\]

with \( z = 3 \) or 2,

(ii) the occurrence of two electrochemical reactions at the interface II: the NO₂⁻ species, which have diffused, can be reduced when they contact the magnetite [which is known to have excellent semi-conductive properties (23,24)] with the production of oxide ions:

\[
\begin{align*}
\text{NO}_2^- + z\text{e}^- & \quad \text{k}_1 \rightarrow \text{NO} + (z - 1)\text{O}_2^- \quad \text{(3)}
\end{align*}
\]

(diffusion of NO has been assumed to be sufficiently fast so as not to be a limiting step).

The oxidation of Fe₃O₄ to Fe₂O₃, which consumes a part of both O²⁻ produced by reaction [3] and O²⁻ coming from the melt by diffusion [2], according to:

\[
\begin{align*}
2\text{Fe}_3\text{O}_4 + \text{O}_2^- & \quad \text{k}_2 \rightarrow 3\text{Fe}_2\text{O}_3 + 2\text{e}^- \quad \text{(4)}
\end{align*}
\]

(iii) diffusion of the oxide anions not consumed by reaction [4] through the magnetite layer:

\[
\begin{align*}
\text{O}_2^- & \quad \text{D}(\text{O}_2^-) \rightarrow \text{O}_2^- \quad \text{(Interface II)} \quad \text{(5)}
\end{align*}
\]

and finally,

(iv) oxidation of metallic iron into magnetite (Interface III):

\[
\begin{align*}
0.75\text{Fe} + \text{O}_2^- & \quad \text{k}_3 \rightarrow 0.25\text{Fe}_3\text{O}_4 + 2\text{e}^- \quad \text{(6)}
\end{align*}
\]

We can state here that nitriding is a result of isolating the surface of the metallic iron from the melt by oxide layers. Metallic iron is in fact in contact with nitrogen monoxide under a very low partial pressure of oxygen; conditions are favorable for further nitriding (10,11).
Determination of the faradaic impedance.

In order to test the reaction model, we have calculated the corresponding impedance $Z_f$ by the classical method. The details of the calculation of $Z_f$ have been given elsewhere (25). The following expression for the faradaic impedance was obtained:

$$Z_f = \frac{R_1 R_2 R_3 (1+a)(1+b)(1+c)}{R_1 R_2 (1+a) + R_1 R_3 (1+a)(1+c) + R_2 R_3 (1-0.33b)(1+c)}$$

where:  
$R_i$ = charge transfer resistance of the $i$th electrochemical reaction.

$R_1 = [3FS k_1 b_1 m_{II(NO_3^-)}]^{-1}$ for [3],
$R_2 = [2FS k_2 b_2 m_{II(O_2^-)}]^{-1}$ for [4], and
$R_3 = [2FS k_3 b_3 m_{III(O_2^-)}]^{-1}$ for [6]

$F = 9.6487 \times 10^4 \text{ C mol}^{-1}$
$S = \text{surface area of the iron electrode (0.6 cm}^2\text{)}$

$k_i^\circ = \text{rate constant for the } i\text{th electrochemical reaction} = k_i^\circ \exp(-b_i \eta)$

($k_i^\circ = \text{intrinsic rate constant}; b_i = \text{Tafel slope}; \eta = \text{overpotential}$).

$m_{II(NO_3^-)}$ and $m_{II(O_2^-)}$ are the concentrations of $NO_3^-$ and $O_2^-$ at the interface II, respectively.

$$a = k_1 \text{th} \left[ \delta_2 \sqrt{\frac{j\omega}{D_2(NO_3^-)}} \right] / \sqrt{j\omega D_2(NO_3^-)}$$
$$b = k_2 \text{th} \left[ \delta_2 \sqrt{\frac{j\omega}{D_2(O_2^-)}} \right] / \sqrt{j\omega D_2(O_2^-)}$$
$$c = k_3 \text{th} \left[ \delta_3 \sqrt{\frac{j\omega}{D_3(O_2^-)}} \right] / \sqrt{j\omega D_3(O_2^-)}$$

where: $\delta_2$ and $\delta_3$ are the thicknesses of the iron(III) oxide layer and that of the magnetite layer, respectively; $D_2(NO_3^-)$ and $D_2(O_2^-)$ are the diffusion coefficients of $NO_3^-$ and $O_2^-$ in the iron(III) oxide layer, respectively, and $D_3(O_2^-)$ is the diffusion coefficient of $O_2^-$ in the magnetite layer.

The overall impedance was obtained by taking into account the contribution of electrolyte resistance $R_e$ and double layer capacitance $C_d$, as well as, the resistance $R$ and the capacitance $C$ of the iron(III) oxide layer, which appears as indicated in the equivalent electrical circuit represented in Fig. 7. Such a circuit has been successfully used in aqueous solution to describe the corrosion of iron(26) and mild steel(27) coated with organic compounds. The overall impedance $Z$ is given by the following expression:
\[ Z = \text{Re} + z [1 + j\omega Cz]^{-1} \]  

with:
\[ z = R + Z_f [1 + j\omega C_d Z_f]^{-1} \]

**Testing of the proposed reaction mechanism**

Impedance spectra have been simulated from the expression of the overall impedance (Eq.[8]). A good fit has been observed (Fig. 8) with the values of the considered parameters collected in Tables 1 and 2. This confirms that the proposed reaction model accounts well for all the experimental data.

Moreover, information about the electrical properties of the iron(III) oxide layer and the charge transfer resistances were also obtained. In particular, the charge transfer resistances determined at \( pO_2^- = 4.3 \) are quite obviously higher (low corrosion rate) than those determined at \( pO_2^- = 1.4 \). This is consistent with the fact that the product RC has a constant value for \( pO_2^- = 4.3 \) (Table 2) thus indicating a poor porous film, which is not the case for \( pO_2^- = 1.4 \) (Table 1).

**CONCLUSION**

Iron corrosion in the molten equimolar NaNO\(_3\)-NaNO\(_2\) mixture involves complex processes in which diffusion phenomena play an important role. A reaction model accounting for impedance measurements has been proposed and has led to the acquisition of electrical parameters characterizing the outer iron(III) oxide layer, which is one of the corrosion products. The composition of this layer depends on melt acidity. Only NaFeO\(_2\), formed in the very narrow domain ranging from \( pO_2^- = 4.3 \) to 5.2 has passivating properties.

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Figure 1: Predicted compositions of iron corrosion products as a function of the bulk oxide ion activity in the molten equimolar NaNO₃-NaNO₂ mixture.

Figure 2: Chronopotentiometric study of iron corrosion in the molten equimolar NaNO₃-NaNO₂ mixture at 420°C for given values of pO²⁻, cologarithm of the bulk oxide ion activity [(iron electrode; platinum electrode)]
Figure 3: Potential-acidity diagram of iron and Nyquist plots obtained at given $pO_2$-values in the molten equimolar NaNO$_3$-NaNO$_2$ mixture at 420°C.
Figure 4: Immersion time dependence of impedance spectra for two values of melt acidity: $pO_2^- = 1.4$ and $pO_2^- = 4.3$ [equimolar NaNO$_3$-NaNO$_2$ mixture at 420°C].
Figure 5: Bode phase plots and Bode amplitude plots for iron corrosion in the molten equimolar NaNO₃-NaNO₂ mixture at 420°C, obtained with an iron electrode immersion time of 20 hours at two given pO²⁻ values: showing experimental data scattering for frequencies lower than 1 Hz when pO²⁻ = 1.4 (strongly basic medium).

Figure 6: Schematic representation of the proposed reaction mechanism for iron corrosion in the molten equimolar NaNO₃-NaNO₂ mixture.

Figure 7: Equivalent circuit of the overall impedance relative to iron corrosion in the molten equimolar NaNO₃-NaNO₂ mixture.
Figure 8: Comparison of the Bode phase plots and Bode amplitude plots calculated from Eq [8] (solid lines) and experimental data (points) for iron corrosion in the molten equimolar NaNO₃-NaNO₂ mixture at 420°C and for an immersion time equal to 3.5 h showing the consistency of the reaction mechanism proposed.
Table 1: Immersion time dependence of impedance model parameters for iron corrosion in the molten equimolar NaNO₃-NaNO₂ mixture at pO₂ = 1.4 and T = 420°C.

| t  | 1.25 | 3.5  | 23   | 69   |
|----|------|------|------|------|
| R₀ | 1.1  | 1    | 0.7  | 0.5  |
| R  | 1.8  | 3    | 0.2  | 0.8  |
| C  | 25   | 50   | 66   | 16   |
| Cₓ | 30   | 60   | 100  | 55   |
| R₁ | 200  | 280  | 100  | 100  |
| R₂ | 400  | 200  | 3    | 3    |

\[
k₂\sqrt{2D₂} (O_2^-) = 2
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 1
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 1
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 400
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 0.4
\]

[k In Table 1 and Table 2, all parameters have their usual units.]

Table 2: Immersion time dependence of impedance model parameters for iron corrosion in the molten equimolar NaNO₃-NaNO₂ mixture at pO₂ = 4.3 and T = 420°C.

| t  | 1    | 3.5  | 20.5 | 44   | 69   |
|----|------|------|------|------|------|
| R₀ | 1    | 0.4  | 0.4  | 0.4  | 0.4  |
| R  | 9    | 11   | 17   | 18   | 20   |
| C  | 27   | 13   | 9    | 8.5  | 7.5  |
| Cₓ | 15   | 4.5  | 2    | 3    | 2.5  |
| R₁ | 350  | 700  | 750  | 750  | 780  |
| R₂ | 2000 | 3000 | 4000 | 4000 | 5000 |

\[
k₂\sqrt{2D₂} (O_2^-) = 0.4
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 1.7
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 5
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 160
\]
\[
k₂\sqrt{2D₂} (O_2^-) = 1
\]

[k In Table 1 and Table 2, all parameters have their usual units].