INFLUENCE OF THE ACIDITY ON THE UNSTABLENESS AND
THE CORROSIVENESS AT HIGH TEMPERATURE OF MOLten
NITRATES AND NITRATE-NITRITE MIXTURES.
A DEMONSTRATIVE EXAMPLE SHOWING THE INTEREST OF
CONTROLLING THE ACIDITY IN MOLten SALTS.

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ABSTRACT

Research objectives which fit into the prospect of promoting the
applications of molten nitrates are to reduce their thermic
unstableness and define conditions which favor the passivation of
metallic materials at their contact. Quantitative considerations
about the decomposition reactions of the nitrate melts lead to
establish that two essential conditions must be fulfilled in order to
obtain an optimal stability allowing the utilization of these melts at
temperature up to about 500-550°C: i) The addition of a certain
percentage of nitrite; ii) The control of the melt acidity (pO2) by
means of a proper pO2+ buffer system (OH–/H2O). Concerning the
corrosion of metallic materials, the acidity has also to be
controlled, generally, in order to achieve the formation of oxidized
layers (due to the strong oxidizing power of the nitrate anion)
showing the best passivating properties. In the case of iron (and
steel) considered in this study, the formation of ferrate NaFeO2,
which occurs in an intermediate pO2 range corresponding again to
the OH–/H2O buffer system, leads to a maximal passivation
effect.

1. INTRODUCTION

It is likely that no other melt has been concerned by so many fundamental works
as the alkaline nitrates, in spite of their small number of applications. The latter may be
explained on one hand by the thermic unstableness of these melts and on the other hand by
their corrosive power towards metals and alloys, related to the strong oxidizing
character of the NO3– ion. Therefore, reducing the thermic unstableness and defining
conditions which favor the passivation of metallic materials are research objectives
which fit into the prospect of promoting the applications of melted nitrates.
In our laboratory, we were led to work towards these objectives some years ago, within the framework of a research to adjust the use of the so-called "HITEC" mixture (KNO\textsubscript{3} 53%, NaNO\textsubscript{3} 40%, NaNO\textsubscript{2} 7% w/w) as a heat transfer liquid in the experimental solar power station "Themis" built by Electricité de France. As a matter of fact, the normal working of this power station supposed the possibility that the temperature of the melt rises to over 500°C, which required an optimisation of the stability conditions of the melted mixture. The corrosion effects on the iron alloy containers and tubing in contact with the 500 tons of molten salts at temperatures varying between about 250 and 500°C was at the same time an important matter of concern which justified a thorough study.

The work realized to reach these objectives consisted in making a serie of experimental determinations by electrochemical methods whose results, in combination with thermodynamical data, allowed to predict the reactions which may occur, using an analytical reasoning.

I shall here describe the principal results we obtained -- without insisting on technical aspects of the study which have already been described elsewhere \cite{8,21} --, mainly with the purpose of pointing out the successive steps of the reasoning.

At this point, some general characteristics of molten nitrates must be redefined in order to make the whole description clear.

2. REACTIONS OF DECOMPOSITION

Because the anion NO\textsubscript{3}\textsuperscript{-} can be considered theoretically as an oxobase (donor of O\textsuperscript{2-}), the first explanations of the behavior of the molten alkaline nitrates postulated the intervention of the following autodissociation system \cite{1}:

\[ \text{NO}_3^- \rightleftharpoons \text{NO}_2^+ + \text{O}_2^- \quad (1) \]

considering the nitronium cation NO\textsubscript{2}\textsuperscript{+} as the strongest oxoacid existing in solution in these media. But two facts came to invalidate this assumption:

(i) The cation NO\textsubscript{2}\textsuperscript{+} (and nitrogen hemipentoxide N\textsubscript{2}O\textsubscript{5}, originated by NO\textsubscript{2}\textsuperscript{+} + NO\textsubscript{3}\textsuperscript{-}) is unstable and undergoes a decomposition if set in the conditions leading to its formation (acidificating the melt). As this decomposition produces nitrogen oxide and oxygen, it corresponds to a redox reaction which follows the dissociation of NO\textsubscript{3}\textsuperscript{-}.

(ii) The anion O\textsubscript{2}\textsuperscript{2-} cannot stay in a free state at an appreciable concentration (in NaNO\textsubscript{3}•KNO\textsubscript{3}) because of the oxidizing power of the NO\textsubscript{3}\textsuperscript{-} ion: peroxide ions O\textsubscript{2}\textsuperscript{2-} and superoxide ions O\textsubscript{2}\textsuperscript{-} (already observed in NaOH-KOH \cite{2}, are formed as well as nitrite ions NO\textsubscript{2}\textsuperscript{-} (as the product of the reduction of NO\textsubscript{3}\textsuperscript{-}) \cite{3}.

Hence, in order to specify the "oxoacidobasic" characteristics and especially the size of the acidobasicity range actually accessible in molten nitrates, it is convenient to start examining these chemical unstabilities, related to the redox properties of the nitrate ion.

Independently of the above-mentioned decompositions, which correspond to acidity or basicity effects, the decomposition of the nitrate ion according to the following reaction (independant of the acidity) also occurs \cite{4}:

\[ \text{NO}_3^- \rightarrow \text{NO}_2^+ + \text{O}_2 \]
NO₃⁻ ⇌ NO₂⁻ + 1/2 O₂(g)  

This redox reaction corresponds to both systems that fix the limits of the electrochemical stability of the solvent.

As a matter of fact the two limits are caused by oxidation and reduction of the NO₃⁻ ion. The reduction leads to the formation of nitrite NO₂⁻, with the liberation of an oxide ion O²⁻. The oxidation leads to the formation of oxygen (as the nitrogen of NO₃⁻ is already in its maximal oxidation state), the initial step being the liberation of the cation NO₂⁺ that decomposes into NO₂ and oxygen. So, the whole electrochemical reaction is:

2NO₃⁻ - 2e⁻ → O₂(g) + 2NO₂(g)  

But the formation of NO₂ doesn’t take place any longer if the melt is kept at a sufficient basicity level (by the presence of an oxobase); a simple release of oxygen is then observable, corresponding to the system:

O(-II) - 2e⁻ → O₂(g)  

In a strongly basic melt, the free O²⁻ ion becomes oxidizable to peroxide O₂²⁻ or superoxide O₂⁻, before O₂ is formed (in NaNO₃, KNO₃ and their mixtures).

Thermochemical calculations, completed by experimental results, allow to establish the equilibrium potential-acidity diagram E-pO₂⁻ that corresponds to the stability area (from the thermodynamical point of view) limited by these different reactions. As an example, figure 1 presents this diagram, in the case of equimolar NaNO₃-KNO₃ at 230°C and NaNO₃ at 470°C.

With respect to the straight line giving the variation of the equilibrium potential of the oxygen electrode (system O(-II)/O₂ (g)), it is possible to place the line that represents the variation of the equilibrium potential of the system NO₃⁻/NO₂⁻, which has the same slope 2.3RT/2F, by calculating the e.m.f. that corresponds to the reaction:

MNO₂(l) + 1/2 O₂(g) → MNO₃(l) :  ΔE⁺ = ΔG⁺/2F  

As it has been shown that the nitrate-nitrite mixtures behave ideally [5], the equilibrium potential difference between the systems O(-II)/O₂ (1 atm) and NO₃⁻/NO₂⁻ (dissolved in NO₃⁻) is then obtained from the simple relation:

ΔE = ΔE⁺ + 2.3RT/2F log N(NO₂⁻)  
= ΔE⁺ + 2.3RT/2F [log m(NO₂⁻) - 1.026]  

(N : molar fraction ; m : molality). Thus one predicts that the thermodynamical stability range only corresponds to a very small potential interval (only 120 mV at 470°C with m(NO₂⁻) = 1 mol.kg⁻¹) and that the molten nitrate cannot be free from nitrite: according to the calculation, the equilibrium concentration under
\( P(0_2) = 0.2 \text{ atm} \) must be about \( 6.10^{-2} \text{ mol.kg}^{-1} \) at \( 470^\circ \text{C} \) (a value the experience appreciably confirms).

A similar calculation leads to the variation of the equilibrium potential corresponding to the system \( \text{NO}_3^-/\text{NO}_2(\text{g}) \) \{i.e. \( \text{NO}_3^- + e^- = \text{NO}_2(\text{g}) + \text{O}^{2-} \}, (7) \} as well as to the system \( \text{NO}_3^-/\text{NO}(\text{g}) \) \{i.e. \( \text{NO}_3^- + 3e^- = \text{NO}(\text{g}) + 2 \text{O}^{2-} \}, (8) \}, for it is known that \( \text{NO}_2 \) is unstable (which is confirmed by the respective positions, in the E-\( \text{pO}_2^- \) diagram, of the achieved straight lines : the reduction of \( \text{NO}_3^- \) into \( \text{NO} \) appears to be thermodynamically easier that the one into \( \text{NO}_2 \)).

Then, to complete the stability diagram, it is possible to process experimental data from electrochemical studies :

(a) The unstableness of the free \( \text{O}^{2-} \) ion is demonstrated by the voltammogram (2) of figure 2 A, given by a diluted solution of \( \text{Na}_2\text{O} \) (in \( \text{NaNO}_3\text{-KNO}_3 \) at \( 230^\circ \text{C} \)) : in fact the solution contains a mixture of peroxide \( \text{O}_2^{2-} \) (oxidizable into \( \text{O}_2^- \) and further into \( \text{O}_2 \)) and superoxide \( \text{O}_2^- \) (reducible into \( \text{O}_2^{2-} \) and oxidizable into \( \text{O}_2 \)) that comes from the reactions :

\[
\text{O}_2^- + \text{NO}_3^- \iff \text{O}_2^{2-} + \text{NO}_2^- \tag{9}
\]

\[
\text{O}_2^- + 3\text{NO}_3^- \iff 2\text{O}_2^- + 3\text{NO}_2^- \tag{10}
\]

The voltammogram also shows the presence of \( \text{NO}_2^- \) through the appearance of an anodic wave that corresponds to the oxidation \( \text{NO}_2^- + e^- \to \text{NO}_2 \) [notice that, in the absence of a donor of \( \text{O}^{2-} \), the oxidation of the nitrite can only occur by this reaction. But due to the presence of an oxobase this oxidation may produce again \( \text{NO}_3^- \) ions : see for example voltammogram (5) of figure 2 B, that corresponds to the oxidization reaction in presence of the oxobase \( \text{OH}^- \) :

\[
\text{NO}_2^- + 2\text{OH}^- - 2e^- \to \text{NO}_3^- + \text{H}_2\text{O} \tag{11}
\]

This reaction occurs at a lower potential than the reaction \( \text{NO}_2^- + e^- \to \text{NO}_2 \), voltammogram (4)).

Owing to the determination (from voltammetric measurements) of values of standard potentials and equilibrium constants for the disproportionation reactions of superoxide and peroxide ions into oxide and oxygen, the E-\( \text{pO}_2^- \) diagram can be completed for basic media as shown in figure 1.

(b) Further, to complete it on the acidic side, it is sufficient to obtain the coordinates of a point like \( P \) that corresponds to the chemical equilibrium :

\[
2\text{NO}_3^- \iff 1/2 \text{O}_2(\text{g}, 1 \text{ atm}) + 2\text{NO}_2(\text{g}, 1 \text{ atm}) + \text{O}^{2-} \tag{12}
\]

Such a point is located on the straight line that gives the variation of the equilibrium potential of the system \( \text{O}(-II)/\text{O}_2 \) (g, 1 atm) and consequently it is only necessary to measure its potential (potential of a platinum electrode in molten nitrate)
under bubbling of a gaseous mixture NO\textsubscript{2} + O\textsubscript{2}, as it has been done at about 230°C [6] (see figure 1 A). It is also possible to use the point P' (see figure 1 B) that corresponds to the chemical equilibrium:

\[
\text{NO}_3^- + 2\text{NO(g, 1 atm)} + \text{O}^{2-} \rightleftharpoons 3\text{NO}_2^- \quad (13)
\]

and whose pO\textsubscript{2}^- value has been experimentally measured with a stabilized zirconia membrane indicator electrode [8] (**).

**Electrochemical decomposition**

From the point of view of electrochemical decomposition, some important observations have to be made.

1) The oxidation of O(-II) into oxygen and that of NO\textsubscript{2}^- into NO\textsubscript{3}^- depend, as far as the potentials at which they occur are concerned, on the presence of an oxobase and on its strength (O\textsuperscript{2-} donor power). On the opposite, the reduction of NO\textsubscript{3}^- into NO\textsubscript{2}^- depends on the presence of an oxoacid (acceptor of O\textsuperscript{2-}) and on its strength. As a matter of fact, such an oxoacid as H\textsubscript{2}O fixes the O\textsuperscript{2-} ion liberated by the reduction of NO\textsubscript{3}^- and this reduction turns easier: thus on the voltammogram (curve (6), figure 2 B), a cathodic wave whose current is limited by the diffusion of H\textsubscript{2}O (**) appears before the reduction of the pure nitrate. The same thing happens in presence of the oxoacid CO\textsubscript{2}, and the difference in half-wave potentials E\textsubscript{1/2}, with respect to the diffusion wave of H\textsubscript{2}O, corresponds to a greater oxoacidic power for CO\textsubscript{2} than for water (curve (7), figure 2 B).

Other oxoacids act in the same way: they are metallic cations. With the exception of Ag\textsuperscript{+} which is cathodically reduced into metal [11], most of the metallic ions lead to a cathodic reduction wave which has been shown (for example for Ca\textsuperscript{2+} and Ba\textsuperscript{2+} [12], as well as Cd\textsuperscript{2+}, In\textsuperscript{3+}, Pb\textsuperscript{2+}, Ti\textsuperscript{4+}, Zn\textsuperscript{2+} [13]) not to correspond to the formation of a metal but to the reduction of NO\textsubscript{3}^- into NO\textsubscript{2}^- in the presence of the oxoacid (acceptor of O\textsuperscript{2-}) M\textsuperscript{2+}:

\[
\text{NO}_3^- + \text{M}^{2+} + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{MO} \quad (15)
\]

(*) At 230-250°C the decomposition of NO\textsubscript{2} into NO + 1/2 O\textsubscript{2} is slow enough for equilibrium (12) to be realized. This no longer occurs at 470°C, in that case the possible equilibrium is: 2NO\textsubscript{3}^- \rightleftharpoons 3/2 O\textsubscript{2}(g) + 2NO(g) + O\textsuperscript{2-}, (14).

The use of the stabilized zirconia membrane pO\textsubscript{2}^- -indicator electrode (ZME) in molten nitrate has been described in previous papers [9].

(**) Though the limiting current corresponds to the diffusion of water, here this one plays the role of an oxoacid and not that of a reducible substance, because no production of hydrogen is observed [10].
This interpretation is consistent in so far as only cations of high oxidizing power (Ag⁺, Hg²⁺...) can lead to metal formation, for the reduction of a metallic ion can only be observed if it is easier than that of the anion NO₃⁻.

2) In a mixture of pure molten nitrates, the potential range between the two limits due to reduction and oxidation of NO₃⁻ (non-electroactivity range of the pure solvent) has an extent of over 2.5 Volts at 230°C, which the E-pO₂⁻ diagram can explain. As the oxidation produces oxygen and NO₂, it takes place in medium conditions, near the electrode, that correspond to point P. On the contrary, the reduction produces oxygen and NO₂, it takes place in medium conditions, near the electrode, that correspond to point P. On the contrary, the reduction produces nitrite and O₂²⁻ ions (and O₂⁻ or O₂⁻) and thus occurs in the conditions of the strongest basic medium next to the cathode. According to the E-pO₂⁻ diagram, this leads to a difference of over 2 V between the anodic and cathodic potentials (plus the overpotentials related to the kinetics of both electrochemical processes).

On the other hand, if in the molten nitrate there is a pO₂⁻ buffer system that forces anode and cathode to work in the same medium conditions, the non-electroactivity range of the NO₃⁻ ions reduces to the potential difference between the two (parallel) lines limiting the stability diagram (lines which correspond to the formation of oxygen and nitrite), that is (including overpotentials) less than 1 Volt. This change appears on figure 2 C where curve (8) corresponds to the presence of the buffer system H₂O/OH⁻ (in this case, the formation of NO₂ at the anode and that of O₂⁻ or O₂⁻ at the cathode are suppressed).

3. CONDITIONS FOR OPTIMAL STABILITY

Starting from the foregoing thermodynamic considerations, it is now possible to discuss the optimal stability conditions of molten nitrates.

The previously established E-pO₂⁻ diagrams point out that the pO₂⁻ scale in molten nitrates is limited at both ends by the intervention of the described decomposition reactions. Quantitative data concerning these reactions allow to define these limits precisely. Thus, in the case of the equimolar mixture NaN₂O₃-KNO₃ at 230°C in equilibrium with air [P(O₂) = 0.2 atm], if one wishes to limit the formation, on one side, of O₂⁻ at a maximal molality of 10⁻² mol.kg⁻¹ and, on the other side, of NO₂ at a maximal pressure of 10⁻² atm, it is foreseen that pO₂⁻ must remain in the range :

6.6 < pO₂⁻ < 34

(the maximal value is even lowered to 27 if the formation of NO instead of NO₂ is contemplated, with the same partial pressure limit of 10⁻² atm). At 470°C, the data connected with the diagram in figure 2 B point out that the limits are only about 2.5 and 12.

In fact, adding a strong oxoacid which has a tendency to rise the pO₂⁻ over the
maximal value defined in this way produces decomposition of the nitrate into NO₂ or NO. This happens for example with dichromate (at 470°C) [9]:

\[
\text{Cr}_2\text{O}_7^{2-} + 2\text{NO}_3^- \rightarrow 2\text{CrO}_4^{2-} + 3/2 \text{O}_2(g) + 2\text{NO}(g)
\]  

(16)

Therefore, two actions favor the stability of molten nitrate:

1*) The addition of a certain proportion of nitrite, which by shift of equilibrium (2) lowers the equilibrium oxygen pressure and thus slows down the progressive thermic decomposition by oxygen release.

From the values of equilibrium constants given in ref. [14], in the case of the melt NaNO₃ + NaNO₂ 1 mol.kg⁻¹ (nitrite proportion very close to that of the HITEC mixture) the equilibrium oxygen pressure remains under 10⁻² atm until a temperature of about 500°C is reached (with the equimolar mixture NaNO₃-NaNO₂, this temperature would rise up to 630°C).

Through lowering of the redox potential of the melt, the presence of nitrite also reduces the formation of O₂²⁻ and O₂⁻ and permits to reach the most oxobasic media (lowest values of pO₂⁻). Per contra, the upper limit of pO₂⁻ is lowered by the intervention, at high pO₂⁻, of the disproportionation of NO₂⁻ according to the reaction:

\[
3\text{NO}_2^- \rightleftharpoons \text{NO}_3^- + 2\text{NO}(g) + \text{O}_2^-
\]  

(17)

In the case of the melt NaNO₃ + NaNO₂ 1 mol.kg⁻¹, figure 3 A (curve 1) shows how this upper limit varies with the temperature (according to ref. [14]) so that the partial pressure of NO should remain under 10⁻² atm.

2*) By means of a proper pO₂⁻ buffer system, pO₂⁻ is kept in the stability range previously defined. As it is practically very difficult to avoid the presence of moisture, the oxoacid/oxobase system which one can most naturally think about is the system H₂O/OH⁻. The measured values [14] of the constant (K₁) of the equilibrium 2OH⁻ \rightleftharpoons H₂O(g) + O²⁻ show that this system is quite convenient for the required buffer effect: according to the values of P(H₂O) and m(OH⁻), the value of pO₂⁻ fixed by the buffer varies within 2 units around pK₁, which varies according to the temperature from 4.4 at 310°C to 2.3 at 500°C. Curves 3, 3’, 3” in figure 3 A show that the addition of 1% (w/w) soda to the melt NaNO₃ + NaNO₂ 1 mol.kg⁻¹ is convenient to avoid an appreciable decomposition of the melt up to T = 500°C, taking in account a partial pressure of steam above 10⁻² atm.

In the absence of OH⁻, the single oxoacid H₂O imposes high pO₂⁻ values that produce, when temperature rises, the decomposition of NO₂⁻ with release of nitrogen oxide vapors, as indicated by curve 4 of figure 3 A.

Concluding, to stabilize nitrate melts in order to heat them to temperatures as high as possible (about 500-550°C), it is necessary, on
one hand to add a certain proportion of nitrite (\(^*\)), and on the other hand to add a small proportion of soda (about 1% w/w) and to keep a sufficient percentage of moisture so as to realize the buffering of \(pO_2^-\) at a convenient level.

4. CORROSIVE ACTION. THE CASE OF IRON

It has been shown experimentally that the strong oxidant nitrate ion attacks metals, with the exception of the noblest among them (Ag, Au, Hg, Pt). Generally, an insoluble oxide forms in the neutral melt (the end of the attack on the metal depends on the passivating power of this oxide). It is easy to predict this property by means of the E-pO\(_2^-\) diagrams, as on these diagrams the position of the variations of the equilibrium potentials \(E_{eq}\) of the systems M(s)/metal oxide (s) can be established by thermochemical calculations which connect this position to that of the straight line corresponding to the system O\(_2^-\)/O\(_2\). Thus, for example, at 230°C, the system Ni(s)/NiO(s) gives an \(E_{eq}\) variation located 0.1 Volt under the straight line corresponding to the reduction system of NO\(_3^-\) into NO\(_2^-\) (1 mol.kg\(^{-1}\)), which implicates the oxidizability of nickel by NO\(_3^-\).

This oxidizability of metals corresponds to the previously mentioned irreducibility of metallic cations in nitrate melts.

This does happen in the case of iron which will be detailed now.

The attack of iron and its alloys by nitrate melts and nitrate + nitrite mixtures, with the formation of a superficial iron oxide layer, has already been observed and pointed out several times [15-18]. Generally the formation of Fe\(_2\)O\(_3\) (hematite \(\alpha\)-Fe\(_2\)O\(_3\)) is considered; but other compounds may also play a role, according to the acidobasicity level of the melt, especially the ferrate Fe\(_5\)O\(_7^-\) whose formation has already been demonstrated for other melts (hydroxides [19], alkali chlorides [20]). Hence an experimental study proved to be necessary to clear up the nature of the (stable) oxidation products of iron in molten nitrates as a function of \(pO_2^-\). This study, quite recently published [21], led to the following main results.

It has been observed that the addition of ferric nitrate to the neutral melt leads to the precipitation of Fe\(_2\)O\(_3\) [22,23], which can be identified by X-ray diffraction. Besides, the simultaneous apparition of nitrogen oxide induces to assign the formation of Fe\(_2\)O\(_3\) to the decomposition of the nitrate caused by the oxoacidic character of the Fe\(^{3+}\) ion:

\(^*\) Diagram 3 B points out that in order to keep both partial pressures of the gaseous decomposition products \(O_2\) and \(NO\) smaller than 10\(^{-2}\) atm it is necessary to choose a mixture of optimal composition close to NaN\(_3\) + NaN\(_2\) \(2.5\) mol. kg\(^{-1}\) (about 15% w/w) to be able to reach the maximal temperature of 550°C, buffering \(pO_2^-\) at a lower value than 1.5. A mixture containing more nitrite involves a decomposition of the latter at lower temperature.
On the other hand, the addition of ferric nitrate to a melt which has been made basic by a previous addition of OH⁻ (and dissociation 2OH⁻ → O²⁻ + H₂O through bubbling of dry nitrogen) gives a reaction between the O²⁻ and Fe³⁺ ions without the decomposition of NO₃⁻ (except after the total consumption of the O²⁻ ions). This reaction has been studied quantitatively realizing the titration of O²⁻ through progressive addition of Fe³⁺ and following the variations of pO²⁻ during the titration with a ZME. Typical curves are represented in figure 4.

One can observe on these curves that a steep rise in pO²⁻ occurs, which corresponds to an end point α₁ = 0.4. The reaction that corresponds to this value is:

$$5O^{2-} + 2Fe^{3+} \rightarrow Fe_2O_5^{4+} \text{ (or Na}_4\text{Fe}_2\text{O}_5)$$

This reaction occurs during the first step of the titration, between α = 0 and α = α₁.

Notice that, if the decomposition (18) occurred before the consumption of O²⁻ ions and the latter combined further with the Fe₂O₃ formed, the end point would correspond, for the same compound Fe₂O₅⁴⁺, to the value α = 1, very far from the observed one.

In the second place, pO²⁻ remains invariable from α₂ > 0.5 on. This invariance must correspond to an equilibrium between two precipitated forms of iron (III): α - Fe₂O₃, which appears (by decomposition of NO₃⁻) at the end of the reaction due to the initial free O²⁻, and a form of scarcely soluble ferrate obtained from the reaction of Fe³⁺ on Fe₂O₅⁴⁺. Identified by X-ray diffraction, this ferrate is NaFeO₂ (allotropic form β, although the stable form at the temperatures of the experiments is the α one; but it has been shown previously that at T > 300°C the reaction between Fe₂O₃ and NaOH gives the β form whose allotropic transformation β → α is very slow [24]). It can be deduced that, in the range [α₁ = 0.4 ; α₂ = 0.5], the following reaction must occur:

$$2Na_4Fe_2O_5↓ + Fe^{3+} \rightarrow 5NaFeO_2↓ + 3Na^+$$

The value α₂ = 0.5 corresponds indeed to the end point of the global reaction:

$$2O^{2-} + Fe^{3+} + Na^+ \rightarrow NaFeO_2↓$$

As a matter of fact, the mathematical analysis of the variation of pO²⁻ in the interval [α₁ ; α₂] induces to admit that both the identified ferrates have non negligible solubilities whose orders of magnitude, in the range of temperature 420-520°C, are 0.02 mol.kg⁻¹ for Na₄Fe₂O₅ and 0.03 mol.kg⁻¹ for NaFeO₂ [21].

Thus it appears possible to form three compounds of iron (III) by a contact with
molten nitrate, each being stable in a different acidity range: \( \text{Fe}_2\text{O}_3 \) in an acidic melt, \( \text{Na}_4\text{Fe}_2\text{O}_5 \) in a strongly basic one, \( \text{NaFeO}_2 \) at middle basicity. The \( pO^{2-} \) values corresponding to the successive equilibria between two solid forms (\( \text{Fe}_2\text{O}_3/\text{NaFeO}_2 \) and \( \text{NaFeO}_2/\text{Na}_4\text{Fe}_2\text{O}_5 \)) which have been deduced from this experimental study, in combination with the standard potential values of the redox systems formed by iron and its solid oxides, calculated with respect to the system of oxygen by means of the values of the Gibbs energies of formation given in the literature \([25]\), allow to establish the \( E-pO^{2-} \) diagram of iron, shown on figure 5. Through the superposition of the variations of the potentials imposed by the systems of the melt (\( \text{NO}_3^-/\text{NO}_2^- \) or \( \text{NO}_3^-/\text{NO(g)} \), according to the \( pO^{2-} \) range), thus it is confirmed that the only stable species of iron in contact with molten nitrates can be those of iron(III).

But from the point of view of the corrosion of the metal, besides the existence of insoluble oxidation products forming a well-adhesive layer at the surface of the metal, the important point is the passivating power of this layer which fixes the velocity of corrosion. As it is possible to postulate that the part of the oxidized layer which is in contact with the melt is made out of the compound in equilibrium with the latter, whose nature depends on the acidity, and as a priori the passivating power of different insoluble compounds must be different, one can expect that the velocity of corrosion varies with the acidity of the melt. Hence, for the applications, it is convenient to fix the acidity (by means of a proper \( pO^{2-} \) buffer system, as in the case of the stabilization of the melt) at a level that corresponds to the formation of the oxidized compound which has the greatest passivating power. The results of the experimental works of EL HOSARY et al. \([15]\) and SPITERI \([18]\) agree with this hypothesis: they show that the corrosion velocity is the lowest in a moderately basic medium and that in these conditions sodium ferrate \( \text{NaFeO}_2 \) forms as the corrosion product of iron. Our quite recent electrochemical study with impedance measurements, described by G. PICARD in another paper presented at this meeting, corroborates this conclusion: it appears that the layers formed in the conditions of acidity corresponding to the stability area of \( \text{NaFeO}_2 \) (that is \( pO^{2-} \) about 4.5 to 5 at 420°C) present the greatest resistance to charge transfer, which allows to assign the lowest porosity and further the lowest corrosion velocities to this compound.

Hence, in conclusion, the best protection layer of iron (and in all probability of its alloys) is obtained fixing the \( pO^{2-} \) of the melt, for which the use of the buffer system \( \text{OH}^-/\text{H}_2\text{O} \) is again the easiest way. The positioning of the stability area of \( \text{NaFeO}_2(s) \) on the diagram in figure 3 A shows that, in the case of the melt \( \text{NaNO}_3 + \text{NaNO}_2 \) 1 mol.kg\(^{-1}\), the choice of the conditions \( m(\text{OH}^-) = 0.06 \text{ mol.kg}^{-1} \) (that is 0.25% of \( \text{NaOH} \) w/w) and \( P(\text{H}_2\text{O}) = 0.1 \text{ atm} \) would be consistent with the seek for both an optimal stabilizing effect of the melt and the best protection of the steel elements in contact with the melt.

Note. Experimentally, it has been possible to put in evidence a nitration of the steels in contact with a nitrate melt. As a matter of fact the formation of compounds like \( \text{Fe}_4\text{N} \) may be originated by the presence of nitrogen oxide (NO) coming from the decomposition of \( \text{NO}_2^- \) or from the reduction of \( \text{NO}_3^- \) (in a very acidic medium), or from that of \( \text{NO}_2^- \).
Yet a thermodynamical diagram, $\log P(O_2)/\log P(NO)$, in which the stability areas of the different iron oxides and nitrides, as well as the area corresponding to the molten mixtures NaNO$_3$-NaNO$_2$ could be represented (figure 6), shows that no nitride may have a stable existence in contact with these mixtures. Hence it appears that the effective formation of such a compound must be interpreted putting forward the diffusion of nitrogen oxide into the lower layers of the oxidized film, next to the metal, where a tiny partial pressure of oxygen holds.

5. CONCLUSION

To conclude, at the end at this talk, I think I showed the importance of controlling the acidity (or basicity) level of a melt to achieve the optimal conditions of use of this medium (for the same reason that it is important to control the pH when working on aqueous solutions). This appears to be quite important in the case of molten nitrates at relatively high temperature because of the decomposition reactions that they undergo, whose effects nevertheless can be minimized by a sensible control of the pO$_2$ with the buffer system OH$^-$/H$_2$O.

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Table I. Constants $K$ of chemical equilibria

| Equilibrium | Mass action law expression | $pK = A + B1000/T$ |
|-------------|----------------------------|-------------------|
| $2 \text{OH}^- = \text{H}_2\text{O(g)} + \text{O}^{2-}$ | $K = P(\text{H}_2\text{O}) m(\text{O}^{2-}) m(\text{OH}^-)^{-1}$ | $A = -6.00, B = 5.48$ |
| $3\text{NO}_2^- = \text{NO}_3^- + 2\text{NO}(g)$ | $K = P(\text{NO})^2 m(\text{NO}_3^-) N(\text{NO}_2^-)^{-1}$ | $A = -15.8, B = 15.75$ |
| $\text{NO}_3^- = \text{NO}_2^- + \frac{1}{2} \text{O}_2(g)$ | $K = P(\text{NO})^2 N(\text{NO}_2^-)^{-1}$ | $A = -5.47, B = 5.88$ |
| $2\text{NO}_2^- = 2\text{NO}(g) + \frac{1}{2} \text{O}_2(g)$ | $K = P(\text{NO})^2 P(\text{NO}_3^-)^{-1}$ | $A = -21.4, B = 21.5$ |
| $\text{NO}(g) + \frac{1}{2} \text{O}_2(g) = \text{NO}_2(g)$ | $K = P(\text{NO}) P(\text{NO}_3^-)^{-1}$ | $A = -32.3, B = 33.4$ |
| $2\text{NO}_2^- + \frac{1}{2} \text{O}_2(g) = 2\text{NO}_2(g) + \text{O}^{2-}$ | $K = P(\text{NO})^2 m(\text{NO}_2^-)^{-1}$ | $A = -13.4, B = 15.5$ |
| $2\text{NO}_3^- = 2\text{NO}_2(g) + \frac{1}{2} \text{O}_2(g) + \text{O}^{2-}$ | $K = m(\text{NO}_3^-)^{-1}$ | $A = -24.3, B = 27.3$ |
| $3\text{NO}_2(g) + \text{O}^{2-} = 2\text{NO}_3^- + \text{NO}(g)$ | $K = N(\text{NO}_3^-)^{-1} P(\text{NO}) m(\text{O}^{2-})^{-1}$ | $A = 20.3, B = -24.2$ |

Table II. Redox equilibria and standard potentials $E^*$ ($\lambda = 2.3RT/F$)

| Electrochemical system | Equilibrium potential | $E^* = A + B \cdot 10^{-\frac{E^*}{298}}$ |
|------------------------|-----------------------|----------------------------------------|
| $\text{NO}_2^- + 2e^- = \text{NO}_4^- + \text{O}^{2-}$ | $E = E^* + \frac{1}{2} \log \frac{N(\text{NO}_4^-)}{N(\text{NO}_2^-)} + \frac{1}{2} p\text{O}^{2-}$ | $A = -1.317, B = 0.50$ |
| $\text{NO}_2^- + e^- = \text{NO(g)} + \text{O}^{2-}$ | $E = E^* + \frac{1}{2} \log \frac{N(\text{NO}_2^-)}{P(\text{NO})} + \lambda p\text{O}^{2-}$ | $A = -2.887, B = 2.08$ |
| $\text{NO}_2^- + 3e^- = \text{NO(g)} + 2\text{O}^{2-}$ | $E = E^* + \frac{1}{3} \log \frac{N(\text{NO}_2^-)}{P(\text{NO})} + \frac{2}{3} p\text{O}^{2-}$ | $A = -1.840, B = 1.03$ |
| $\text{O}_2(g) + 4e^- = 2\text{O}^{2-}$ | $E = E^* + \frac{1}{4} \log P(\text{O}_2) + \frac{1}{2} p\text{O}^{2-}$ | $A = -0.731, B = -0.045$ |
| $\text{NO}_2^- + e^- = \text{NO(g)} + \text{O}^{2-}$ | $E = E^* + \frac{1}{2} \log \frac{P(\text{NO}_2^-)}{P(\text{NO})} + \lambda p\text{O}^{2-}$ | $A = -3.453, B = 2.38$ |
| $\text{NO}_2(g) + 2e^- = \text{NO(g)} + \text{O}^{2-}$ | $E = E^* + \frac{1}{2} \log \frac{P(\text{NO}_2)}{P(\text{NO})} + \frac{1}{2} p\text{O}^{2-}$ | $A = -1.036, B = 0.353$ |
Fig. 1. Equilibrium potential–pO$_2^-$ diagrams corresponding to the decomposition of molten alkaline nitrates.

(A) For equimolar NaNO$_3$–KNO$_3$ at 230°C, from thermochemical data, ref. (25), and experimental results, ref. (3) (concerning the oxygen systems) and ref. (6) (concerning the potential value of point P); cf also ref. (7).

(B) For NaNO$_3$ at 470°C, from results of ref. (8).
Fig. 2. Voltammograms in molten NaNO$_3$-KNO$_3$
(as solvent) at 240-265°C, using a rotating platinum microelectrode.

1. pure solvent;
2. addition of Na$_2$O 1 mmole/kg;
3. oxidation of OH$^-$ ions;
4. oxidation of NO$_2^-$ in the pure solvent;
5. oxidation of NO$_2^-$ in the presence of OH$^-$;
6. reduction of NO$_3^-$ in the presence of H$_2$O;
7. reduction of NO$_3^-$ in the presence of CO$_2$ (1 atm);
8. oxidation and reduction in the presence of H$_2$O/OH$^-$ buffer.

[from ref. (3) and (10)]
Fig. 3. Diagrams showing the variation of the values of $pO_2^-$ which correspond to different limiting or buffering conditions, in molten NaNO$_3$ + NaN$_2$O$_2$ (under an inert atmosphere: $P(O_2) < 0.01$ atm), as a function of temperature.

A - NaN$_3$ + 1 mol kg$^{-1}$ NaN$_2$O$_2$

B - a. NaN$_3$ + 1 mol kg$^{-1}$ NaN$_2$O$_2$
   b. NaN$_3$ + 2.5 mol kg$^{-1}$ NaN$_2$O$_2$
   c. NaN$_3$ - NaN$_2$O$_2$ 50-50 mol %

Fig. 4. Titration curves of sodium oxide (initial concentration: 0.21 mol kg$^{-1}$, under N$_2$) by iron(III) nitrate, in NaNO$_3$ - NaN$_2$O$_2$ (99 - 1)
Fig. 5. Potential-pO$_2$ and potential-log [P(H$_2$O)·m(OH$^-$)$^{-2}$/atm kg$^2$ mol$^2$] diagrams:

--- iron systems

--- NaNO$_3$-NaNO$_2$-NO system and --- O$_2$/O$_2^-$ system.
Fig. 6. log $P(O_2)$-log $P(\text{NO})$ diagram for iron oxides and iron nitrides. $T = 693$ K. Stability area of the sodium nitrate-nitrite mixtures.