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Corrosion mechanisms of austenitic stainless steels in nitric media used in reprocessing plants

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Abstract

Austenitic stainless steels type 304L, 316L and 310Nb are largely used as structural materials for equipments handling nitric acid media in reprocessing plants. In almost all nitric media, these materials, protected by a chromium(III) oxide rich layer, remain in their passive state. However, in some particular nitric media, their corrosion potential may be shifted towards their transpassive domain. In this domain, they can suffer intergranular corrosion, even though they are not sensitized owing to their very low carbon content. The corrosion potential of the steel depends greatly on the cathodic reaction involved in the oxido-reduction process between the elements Fe, Cr, Ni of the steel and the oxidizing species of the medium. Three cases of an increase in the corrosion potential can be found in reprocessing media: pure nitric acid–water solutions, in which the cathodic reaction is the reduction reaction of HNO_3; nitric acid media containing oxidizing species, in which the cathodic reaction is the reaction of reduction of the oxidizing species into the reduced one; nitric media containing metallic elements electrochemically more noble than the steels, causing galvanic coupling. In each case, the mechanism and the relevant situations we experimentally studied are described.

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1. Introduction

In France, the treatment of spent fuel is carried out in La Hague plants using the Purex process. This process uses nitric acid to dissolve spent fuel. Thus, along the all process line, nitric media that contain dissolved species such as oxidizing ions as well as undissolved solid species are found at various concentrations (up to the azeotropic one) and at temperatures up to and slightly higher than their boiling point. In order to properly contain these very acidic and very oxidizing media, metallic materials have been chosen according to their corrosion limits, optimized and qualified before the building of the plants. These materials are mainly:

- zirconium, chosen for the construction of the most critical equipments in term of corrosion, such as fuel dissolvers and nitric acid recovery concentrators [1–4];
- very low carbon austenitic stainless steels (type AISI 304L, 316L and 310Nb) for the major part of the equipments [5–9];
- a special stainless steel with 4% silicon, for the fission products evaporators.

All these materials are protected by a stable passive layer in nitric acid. However, each condition which promotes the deterioration of this passive layer may lead to severe corrosion phenomena.

For zirconium, three types of phenomena can lower the protective effect of the passive layer which is constituted of ZrO_2:

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- the presence of a stress: in this case, stress corrosion cracking essentially requires an electrochemical depassivation of the material to occur. As a matter of fact, in the passive conditions, which are those of the process equipments, the behaviour of zirconium submitted to a stress or a strain is only very slightly modified by nitric acid [4,7–9], and no SCC occurs;
- a mechanical degradation, for instance by friction or erosion [10];
- the presence of complexing agents in the nitric media, particularly of fluorides. The dissolution rate of zirconium increases with their concentration, even at a very low level (1 mg/L) [8].

Except for the special stainless steel with 4% Si, all stainless steels, although they are protected by a passive layer rich in chromium (III) oxide, can suffer an intergranular corrosion when their corrosion potential is shifted towards the transpassive domain. This type of corrosion is characterized by a selective attack of the grain boundaries up to grain losses for the most severe conditions. It can occur even with a no sensitized and optimized (with regard to carbon, silicon and phosphorus content) steel.

In this paper, after a recall on the corrosion behaviour of austenitic stainless steels in nitric media, we will present and discuss the situations which promote a shift of the corrosion potential towards the transpassive or the active domains and thus to an increase of the steel corrosion. Three situations can be found in reprocessing media:

- nitric media in which an autocatalytic mechanism of nitric acid reduction can occur;
- nitric media containing oxidizing ions;
- nitric media containing metallic elements allowing galvanic coupling with the steel.

2. Austenitic stainless steels used in French spent fuel treatment plants

Table 1 summarizes the general composition of the four stainless steels used in French spent fuel treatment plants to contain nitric media [6,7].

Since corrosion resistance is essentially determined by the chromium content (Fig. 1), the most widely used steels are unstabilized low carbon steels type AISI 304L (AFNOR Z2 CN 18.10) or Uranus 65 (AFNOR Z2 CN 25.20) similar to an extra low carbon (ELC) type AISI 310 steel.

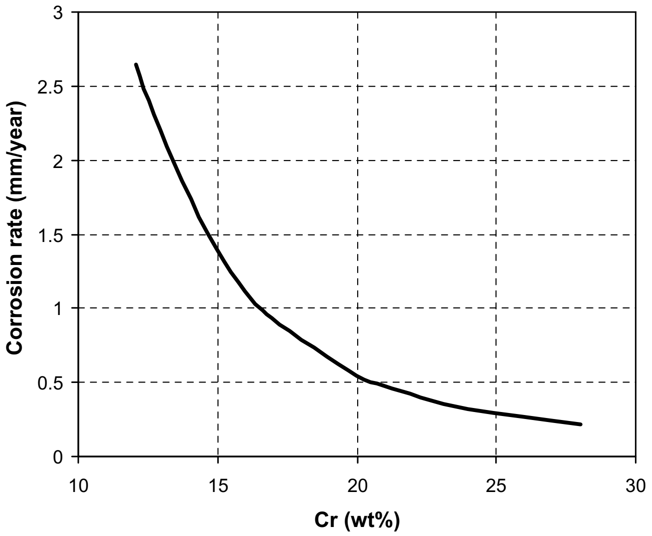

Fig. 1. Effect of the chromium content on the behaviour of austenitic stainless steels in nitric acid (65 wt%, boiling temperature) [7].

A carbon content below 0.03% or better below 0.02%, and optimized quench annealing temperatures and heating times [7] prevent from intergranular corrosion resulting from the chromium depleted zones due to a steel sensitization after a thermal treatment or by welding. The effect of carbon on the behaviour of AISI 304L steel is, for instance, illustrated by the answer of the material using the double loop EPR test (Fig. 2) [11]. Moreover, in order to detect the possible carbon local enrichments due to a surface contamination susceptible to occur during the transformation steps, the products are submitted to reception tests based on Strauss or Huey procedures with drastic limits of acceptance.

In order to increase the resistance to intergranular corrosion, the content of S and P minor elements, which preferentially segregate at the grain boundaries [12], are reduced. Moreover, non-metallic inclusions (such as sulphides) with heterogeneous shapes, sizes and distribution can induce end-grain attack. This phenomenon largely depends on the steel transformations such as working, forging and rolling [14–16]. The Uranus 65 and Uranus S1N steels are refined under vacuum in order to fulfil the cleanliness required to meet specifications for welded vessels operating with nitric media [7].

Addition of molybdenum is detrimental to the behaviour of the austenitic stainless steels in hot nitric acid.

Table 1
Chemical composition of the austenitic stainless steels used in French spent fuel treatment plants (wt%) [6,7]

Grades		C	Cr	Ni	Si	S	P	Mo	Mn	N	Nb
AFNOR	Commercial										
Z2 CN 18.10	AISI 304L	⩽0.03	18	10	⩽1.0	⩽0.02	⩽0.03	–	–	–	–
Z2 CN 25.20	Uranus 65, AISI 310	⩽0.015	24–26	19–22	⩽0.25	⩽0.005	⩽0.025	⩽0.5	⩽2	–	Addition
Z2 CND 17.13	AISI 316L	⩽0.03	17	13	⩽1.0	⩽0.02	⩽0.03	2.5–3	–	–	–
Z1 CNS 17.15	Uranus S1N	⩽0.015	16.5–18.5	13.5–15	3.8–4.5	⩽0.005	⩽0.025	⩽0.5	⩽2	⩽0.035	Addition

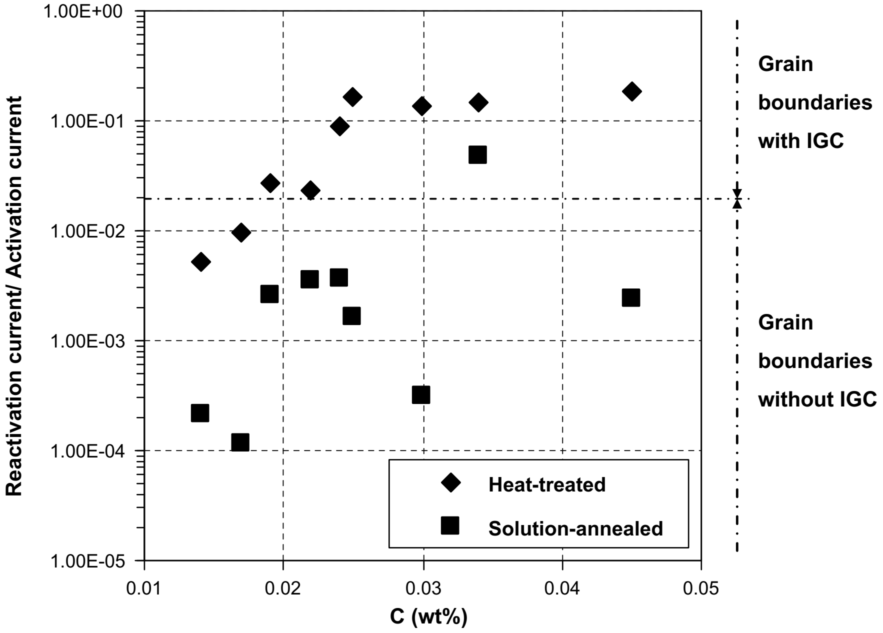

Fig. 2. Effect of the carbon content on the behaviour of 304 stainless steel in nitric acid, as revealed by the double loop EPR technique [11].

However, an addition of 2–3% molybdenum makes the steel more resistant to pitting corrosion in the event of an accidental chloride contamination, of the presence of deposits or of iodine condensates [17] (Fig. 3). In these potential conditions, AFNOR Z2 CND 17.13 steel (AISI 316L) is used.

Whereas a maximum intergranular corrosion is observed for about 1% Si content, the absence of intergranular corrosion is observed for Si values higher than 3% in boiling nitric acid containing oxidizing species (Fig. 4) [7,12]. By contrast, in pure boiling nitric acid, the uniform corrosion rate increases continuously as the Si-content of steel increases [13]. Therefore, when immunity to intergranular attack and thus corrosion resistance predictability in strongly oxidizing media is required and that a relatively high general corrosion rate can be tolerated, the use of high purity grades containing at least 4% silicon such as Uranus S1N steel (AFNOR Z1 CNS 17.15) offers a safe choice.

Based on these general metallurgical considerations, the limits of use of these different steels can be summarized in Fig. 5, as a function of the concentration in nitric acid, of the temperature (up to boiling), and of the presence or absence of oxidizing species.

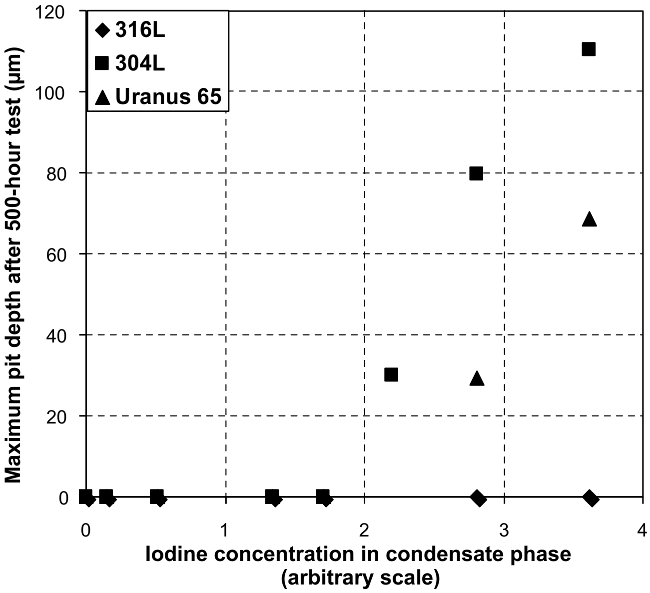

Fig. 3. Effect of the molybdenum content (see Table 1) on the pitting corrosion of austenitic stainless steels in the presence of iodine condensates [17].

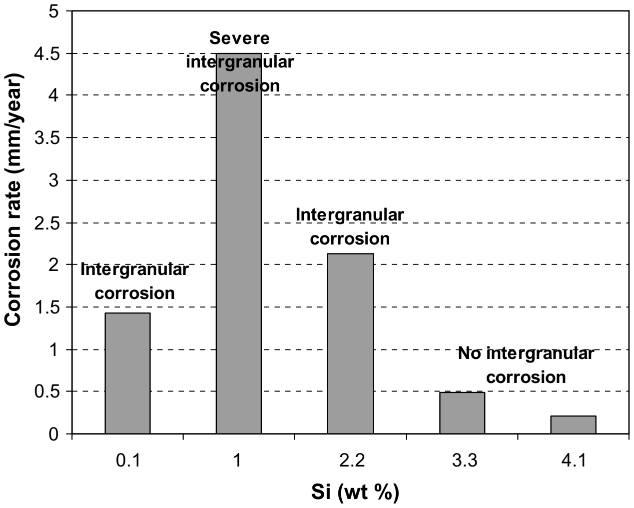

Fig. 4. Effect of the silicon content on the behaviour of austenitic stainless steels in boiling 5 mol/L nitric acid + 1 g/L Cr(VI) [7].

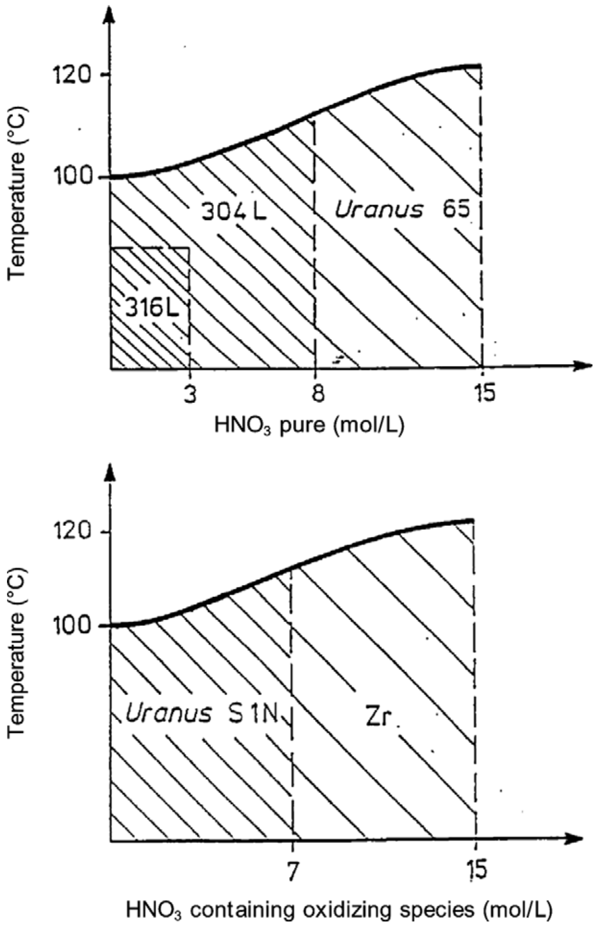

Fig. 5. Typical limits of use of the steels in nitric media.

3. General electrochemical behaviour of austenitic stainless steels in nitric media

Fig. 6 shows a diagram which illustrates the behaviour of an austenitic stainless steel in acidic media as a function of its potential [7].

The partial anodic process, which relates to the oxidation of the elements (mainly Fe, Cr and Ni) of the steel, includes four domains:

- an active domain where the uniform dissolution rate of the stainless steel is high, if the medium conditions are sufficiently reducing;
- for moderately oxidizing medium conditions, austenitic stainless steels are in their passive state characterized by a uniform and low-rate dissolution. As revealed by XPS analyses of specimens treated in nitric acid [18], steels are then protected by a passive layer. For AISI 304L type steel, this passive layer, a few nm thick, is mainly composed of Cr_2O_3. For a 4% Si type steel, the presence of silicon in the steel does not affect the chromium or iron oxidation degree, nor the iron/chromium ratio in the passive layer. Silicon is present in the passive layer in an important content: the passive layer of a 4% Si type steel is composed of 35 at.% silicon whereas the matrix contains only 7 at.%. Thus it decreases the content of each other element of the passive layer: after passivation in nitric acid, the Cr content is 80 and 50 at.%, respectively for 304L and 4% Si stainless steels. The 4% Si steel exhibits a less protective passive layer and thus its corrosion rate is higher than the one of a 304L type steel in the same medium conditions;
- if the medium becomes excessively oxidizing, passive film dissolution occurs, specially by oxidation of Cr(III) (as insoluble Cr_2O_3) to Cr(VI) (as soluble $Cr_2O_7^{2-}$). This results in a fast and accelerating transpassive corrosion. This form of attack is preferentially intergranular, even if the steel is not sensitized or has been optimized in Si and P (for AISI 304L type) in order to reduce the risk for this type of corrosion. In the less severe conditions (transition domain), only intergranular indentations are observed. In the most severe oxidizing conditions, grain losses occur and successive rows of material get lost. The rate of this phenomenon based on morphological considerations has been recently modeled [19].

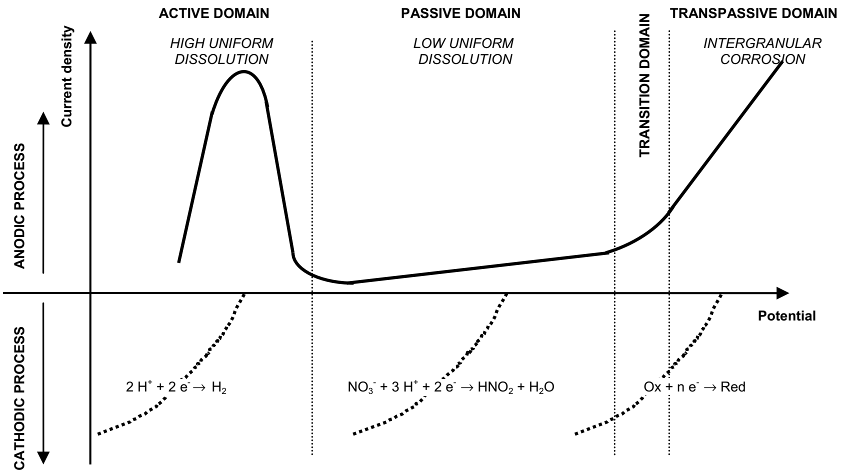

Fig. 6. General electrochemical behaviour of austenitic stainless steels in acidic media as a function of the potential [7].

In the following of this paper, we are going to examine different kinds of partial cathodic processes specific to the nitric acid media found in reprocessing plants. These partial cathodic processes mainly determine the corrosion potential of the steel and thus, impose the type and the rate of corrosion of the steel according to the previous diagram.

4. Pure nitric acid solutions

4.1. Corrosion mechanism: autocatalytic reduction of nitric acid

In most of nitric media, the electrochemical reaction which imposes the redox potential of the solutions is the global reduction reaction of nitric acid HNO_3 in nitrous acid HNO_2

$$NO_3^- + 3H^+ + 2e^- \leftrightarrow HNO_2 + H_2O \quad E^\circ_{25\,^\circ C} = 934\ \mathrm{mV/SHE} \tag{1}$$

From this reaction, the redox potential increases with concentrations in NO_3^- and H^+ and with temperature and decreases when HNO_2 concentration increases [20–22].

However, in order to conclude on the modifications in the corrosion potential induced by these different species, it is necessary to detail the specific reduction mechanism of nitric acid, which has been analysed in many studies [23–25].

A thermodynamic study of the equilibrium between gas and liquid phases for concentrated aqueous solutions of nitric acid allowed to identify the predominant species involved in the process of reduction of nitric acid: these are two gaseous species (NO, NO_2) and an aqueous species (HNO_2) (Fig. 7) [24].

The study of the influence of the nitric acid concentration on the nature of the species limiting the stability area of nitric acid in reduction shows that the final reduction product is nitrogen monoxide NO for concentrations lower than 8 mol/L and nitrogen dioxide NO_2 for concentrations higher than 8 mol/L.

The electrochemical study of the reduction process of nitric acid was carried out on a platinum electrode then on a stainless steel electrode. Similar results were obtained. It allowed to confirm the predictions of thermodynamics and led to a better understanding of the mechanism [25].

Nitric acid is indirectly reduced by an autocatalytic mechanism including a charge transfer step and a chemical reaction which regenerates the electro-active species.

The electro-active species is nitrous acid which is reduced into nitrogen monoxide

$$(HNO_2)_{el} + H^+ + e^- + s \leftrightarrow (NO)_{ads} + H_2O \quad \text{(s is a site on the electrode)} \tag{2}$$

Nitrous acid is then regenerated by a heterogeneous chemical reaction between nitric acid and nitrogen monoxide

$$HNO_3 + (NO)_{ads} \leftrightarrow (HNO_2)_{ads} + (NO_2)_{ads} \tag{3}$$

A third reaction occurs between nitric acid and nitrous acid:

$$HNO_3 + (HNO_2)_{el} + 2s \leftrightarrow 2(NO_2)_{ads} + H_2O \tag{4}$$

Reactions (2)–(4) are the elementary reactions of the reduction mechanism of nitric acid. They are valid on the whole concentration area.

For low to moderate (<6 mol/L) nitric acid concentrations, the reaction of regeneration of nitrous acid (3) is slow. The nitrogen monoxide formed during the charge

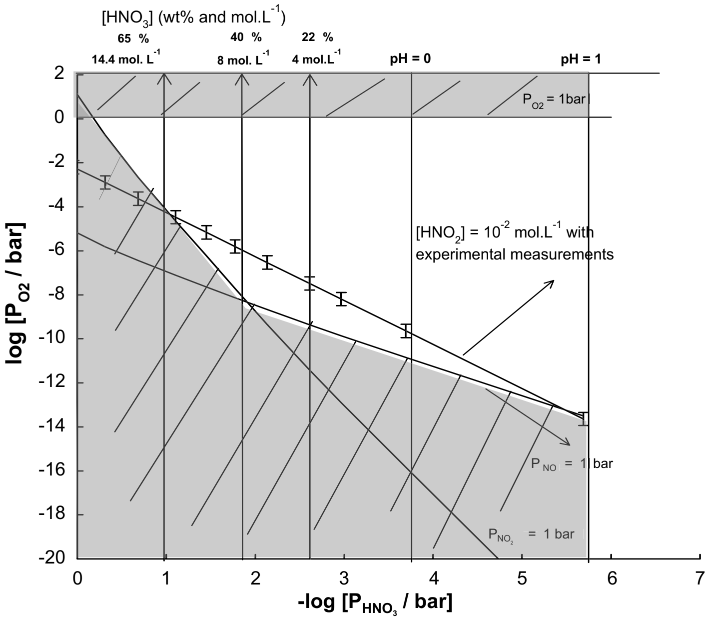

Fig. 7. Stability area of nitric acid at 100 °C (white part of the diagram) [24].

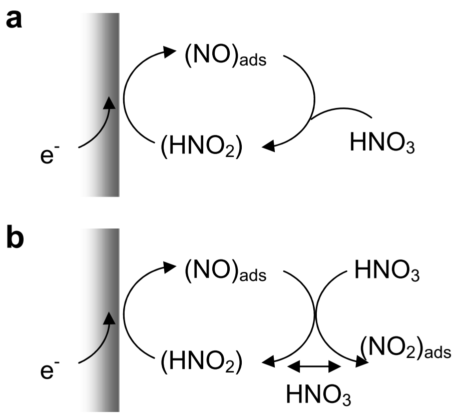

Fig. 8. Sketch of the mechanism of reduction of nitric acid [25]. (a) Low to moderate concentrations (<6 mol/L) and (b) high concentrations (>8 mol/L).

transfert step (2) may accumulate. Reaction (4) is also drawn back towards HNO_2 formation, because NO_2 is not thermodynamically stable for concentrations lower than 8 mol/L. So, for low to moderate HNO_3 concentrations, the mechanism of reduction of nitric acid is (Fig. 8(a))

$$(HNO_2)_{el} + H^+ + e^- + s \leftrightarrow (NO)_{ads} + H_2O \qquad (2)$$

$$HNO_3 + 2(NO)_{ads} + H_2O \leftrightarrow 3(HNO_2)_{el} + 2s \qquad (5)$$

For more concentrated media (>8 mol/L), the reaction of regeneration of nitrous acid (3) is fast, because it is enhanced by the high HNO_3 concentration. This reaction leads to a gaseous evolution of NO_2 which is stable at these HNO_3 concentrations. The mechanism of HNO_3 reduction is then (Fig. 8(b))

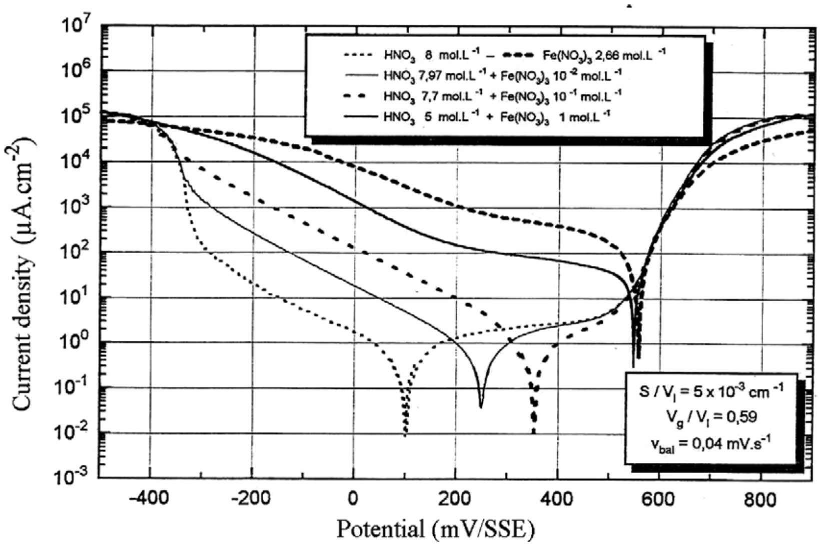

Fig. 9. Influence of the ferric ions on the cathodic reduction of nitric acid on AISI 304L steel in HNO_3 8 mol/L at 100 °C [26,27].

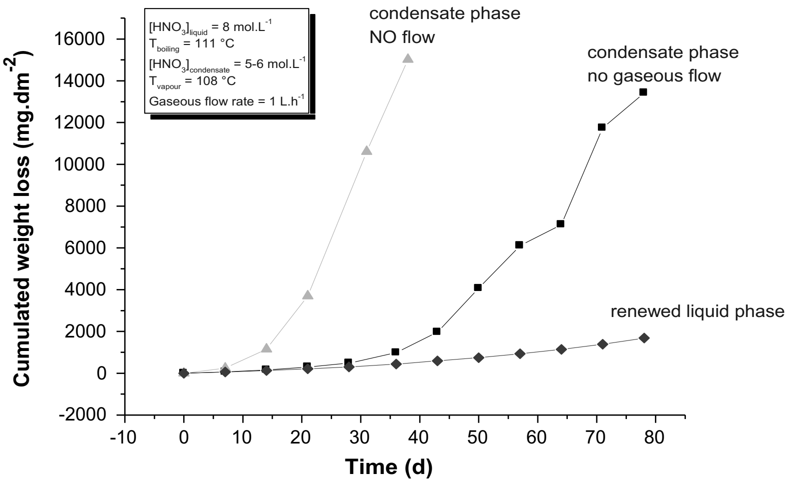

Fig. 10. Comparison between the corrosion of AISI 304L steel in the presence of nitric acid condensate and in the presence of a renewed liquid phase [23,28].

$$(HNO_2)_{el} + H^+ + e^- + s \leftrightarrow (NO)_{ads} + H_2O \quad (2)$$

$$HNO_3 + (NO)_{ads} \leftrightarrow (HNO_2)_{el} + (NO_2)_{ads} \quad (3)$$

and Reaction (4) which is supposed to be at equilibrium

$$HNO_3 + (HNO_2)_{el} + 2s \leftrightarrow 2(NO_2)_{ads} + H_2O \quad (4)$$

The kinetics of HNO_3 reduction can be modified by:

- products resulting from the corrosion of the steels themselves (Fe(III) ions and to a less extend Cr(III) ions) which catalyze this reduction reaction;
- dissolved oxygen, which slows it down.

As a conclusion, it can be said that nitrous acid (and nitrogen mono- and di-oxides) plays an ambivalent role in nitric media:

- from a thermodynamic point of view, it is the reduced species of nitric acid (Reaction (1)), so that the higher the HNO_2 concentration, the more reducing the medium is; the redox potential of the medium is imposed by the $[HNO_2]/[HNO_3]$ ratio;
- from a kinetic point of view, it increases the reduction rate of nitric acid by the autocatalytic mechanism described above; consequently, the corrosion potential and the corrosion rate of the steel increase, although the medium is more reducing. In extreme cases, the corrosion potential may be shifted in the transpassive domain, and an intergranular corrosion may occur.

4.2. Application to non-renewed nitric media and nitric acid condensates

Most of nitric acid media used in spent fuel treatment plants are sufficiently renewed to prevent that HNO_2 concentrates sufficiently to start the autocatalytic HNO_3 reduction mechanism, so that the corrosion potential of steel remains in its passive domain.

However, two practical cases may be relevant to this autocatalytic mechanism. The first one concerns nitric media which are confined and weakly renewed [26,27]. In this case, the reduction products of the nitric acid (nitrous acid, nitrogen dioxide), and the cations Fe(III) and Cr(III) coming from the steel corrosion itself, catalyze the HNO_3 reduction reaction. This autocatalytic phenomenon moves the corrosion potential of the steel towards its transpassive domain, and thus leads to intergranular corrosion. Fig. 9 illustrates this phenomenon with ferric ions: AISI 304L steel is still in its passive domain for 0.1 mol/L Fe(III), whereas it is in its transpassive domain for 1 mol/L Fe(III).

The second case concerns nitric condensates [23,28,4]. It is, in fact, very similar to the previous case regarding the causes of intergranular corrosion. The very large metallic surface to solution volume ratio and the slow condensate renewing rate lead to a fast increase of the corrosion potential of the steel, as soon as the oxidation products of the metal and the reduction products of HNO_3 are accumulated in the condensate film.

Fig. 10 shows that a condensate phase is much more corrosive (grain losses) than a renewed liquid phase of a similar HNO_3 concentration (uniform dissolution) [23,28]. A NO flow shortens the induction time and enhances the corrosion rate under condensates. This illustrates the autocatalytic effect of this species as explained in the previous paragraph for nitric acid concentrations low to moderate.

5. Nitric acid media containing oxidizing species

5.1. Corrosion mechanism

As explained in the previous paragraph, spent fuel treatment media are generally nitric media. Their redox potential depends on the standard potential of the NO_3^-/HNO_2 couple

$$NO_3^- + 3H^+ + 2e^- \leftrightarrow HNO_2 + H_2O$$
$$E^\circ_{25\,^\circ C} = 934\ \mathrm{mV/SHE} \quad (1)$$

However, reprocessing media can contain metallic ions coming from oxido-reduction couples the standard potential of which is higher than the value of the NO_3^-/HNO_2 couple. Data concerning these so-called ‘oxidizing’ ions susceptible to be present in spent fuel treatment media are summarized in Table 2, together with relevant data.

In nitric media containing oxidizing ions, the reaction of reduction of the medium is not any more Reaction (1), but the reduction reaction of the oxidizing ion by the metallic elements of the steel

$$Ox + ne^- \leftrightarrow Red \quad (14)$$

From a thermodynamic point of view, the standard potentials of Table 2 allow to classify the relative aggressiveness of the different oxidizing ions. However, the corrosion potential taken by the stainless steel, and thus the dissolution rate of the material, depends on the kinetics of Reaction (14). In a closed medium without any external addition of oxidizing ion, the stationary concentration of the oxidizing ion results from the difference between its rate of formation by re-oxidation of the reduced species by the nitric media and its rate of consumption by oxidizing the elements of the steel. The ability of the nitric media to re-oxidize the reduced species depends on the real potential achieved by Reaction (1). So, it is enhanced by high nitric acid concentration and temperature and by low nitrous acid concentration. For instance, boiling high concentrated nitric acid solutions from which nitrous acid escapes by evaporation favour re-oxidation of the reduced species.

On the contrary, NO_2 (or N_2O_4) generated or introduced in the medium acts as a reducing species according to the reaction

$$2NO_3^- + 4H^+ + 2e^- \leftrightarrow N_2O_4 + 2H_2O$$
$$E^\circ_{25\,^\circ C} = 803\ \mathrm{mV/SHE} \quad (15)$$

Thus, many oxidizing species can be reduced and the corrosion of stainless steels be lowered in their presence

Table 2
Data concerning ‘oxidizing’ ions susceptible to be present in spent fuel treatment media

Element	Origin	Oxido-reduction couple	Oxido-reduction reaction		Standard potential $E^{\circ}_{25\,^{\circ}\mathrm{C}}$ mV/SHE	
Nitrogen	Nitric acid	N(V)/N(III)	$NO_3^- + 3H^+ + 2e^- \leftrightarrow HNO_2 + H_2O$	(1)	934	[29]
Plutonium	Fuel	Pu(IV)/Pu(III)	$Pu^{4+} + e^- \leftrightarrow Pu^{3+}$	(6)	970	[30]
	Fuel	Pu(VI)/Pu(IV)	$PuO_2^{2+} + 4H^+ + 2e^- \leftrightarrow Pu^{4+} + 2H_2O$	(7)	1040	[30]
Neptunium	Fuel	Np(VI)/Np(V)	$NpO_2^{2+} + e^- \leftrightarrow NpO_2^+$	(8)	1150	[30]
Vanadium	Pu and Np corrosion simulation	V(V)/V(IV)	$V(OH)_4^+ + H^+ + e^- \leftrightarrow VO^{2+} + 3H_2O$	(9)	1000	[29]
Chromium	Corrosion	Cr(VI)/Cr(III)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$	(10)	1232	[29]
Cerium	Fission product	Ce(IV)/Ce(III)	$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$	(11)	1610	[29]
Manganese	Reagent	Mn(VI)/Mn(IV)	$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2 + 2H_2O$	(12)	1679	[29]
Silver	Reagent (electro-generated)	Ag(II)/Ag(I)	$Ag^{2+} + e^- \leftrightarrow Ag^+$	(13)	1980	[29]

[31,32]. Similarly, gamma-ray irradiation produces nitrous acid or nitrogen dioxide by radiolysis of nitric acid. This explains that oxidizing ions such as Ce(IV), Cr(VI), Ru(VIII) can be reduced to their lower valences [33], so that the corrosion rate of 304L stainless steel is lowered compared to non-irradiated conditions [34].

The kinetics of oxidation–reduction of many couples of interest for spent fuel treatment have been determined in nitric media: Cr(VI)/Cr(III) [35,37]; Np(VI)/Np(V) [36,38,40]; Pu(VI)/Pu(IV) [38,39]. In particular, it was demonstrated that the kinetics of the oxidation reaction of Np(V) into Np(VI) increases with the nitrous acid concentration for nitrous acid concentrations significantly lower than Np(V) concentrations, whereas the reaction is first order versus the Np(V) concentration for other cases [40]. Thus a complete thermodynamic and kinetic knowledge of Reaction (14) in the nitric medium is required to better understand the consequence of a given oxidizing species from a corrosion point of view.

5.2. Examples of stainless steel behaviour in nitric media containing oxidizing ions

Many studies have been carried out on the behaviour of stainless steels in the presence of nitric media containing oxidizing ions of direct interest for spent fuel treatment processes: Np(VI) [41,42] and Pu(VI) [43–45]. They confirm the aggressiveness of these ions according to the standard potentials in Table 2: intergranular corrosion occurs on 304L stainless steel for a few tens of mg/L of Np(VI) and for some g/L of Pu(VI) in boiling nitric acid solutions.

Two studies carried out with a lot of oxidizing ions show that, either for 310Nb stainless steel [31] or for 304L stainless steel [32], the corrosion rate of the steel depends mainly on the corrosion potential it takes in the solution, whatever the nature or the concentration of the oxidizing ion are. Evidently, the shape of the curve representing the corrosion rate versus the corrosion potential (Fig. 11 [32]) is the same as the oxidation curve of the steel in the transition and transpassive domains.

By using the same hypothesis on the relation between the corrosion rate and the corrosion potential, the corrosivity of V(V) and Pu(VI) have been compared for 304L stainless steel in boiling HNO_3 8 mol/L. This comparison is of practical interest for the simulation of the corrosion role of Pu(VI) by V(V) in inactive experiments. V(V)/V(IV) has been chosen for two reasons: its standard potential (1000 mV/SHE) is close to this one of Pu(VI)/Pu(IV) (1040 mV/SHE) and VO_2^+ and PuO_2^{2+} are cationic forms with similar structure.

The results reported in Fig. 12 show that the corrosion rate of the steel depends only on its corrosion potential, and not on the nature of the oxidizing ion, although the corrosion potentials are not well stable for low oxidizing ion concentrations. Whatever the oxidizing ion is, 304L steel is in its passive domain for corrosion potentials from

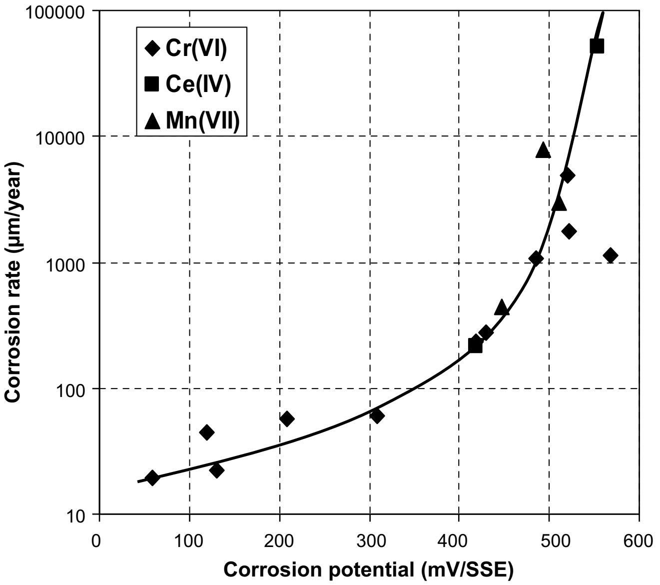

Fig. 11. Relation between the corrosion rate and the corrosion potential of 304L stainless steel in the presence of different oxidizing ions [Cr(VI), Ce(IV), Mn(VII)] in boiling HNO_3 5 mol/L [32].

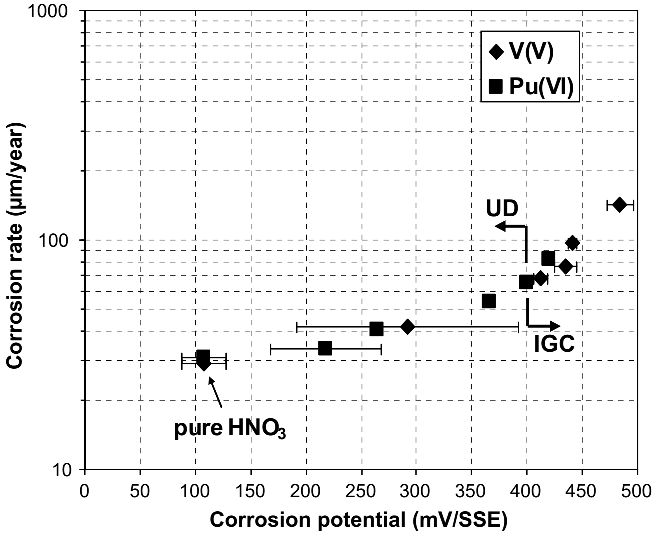

Fig. 12. Relation between the corrosion rate and the corrosion potential of 304L stainless steel in the presence of V(V) and Pu(VI) in boiling HNO_3 8 mol/L (UD: uniform dissolution; IGC: intergranular corrosion).

100 to approximately 400 mV/SSE (760–1060 mV/SHE) and then it is subject to a uniform dissolution. For corrosion potentials above 400 mV/SSE, the transition domain (as defined in Fig. 6) is reached and the steel begins to suffer intergranular corrosion.

A same corrosion potential is obtained with a molar concentration much higher (1–2 orders of magnitude) with Pu(VI) than with V(V), although the standard potential of Pu(VI)/Pu(IV) is higher than the one of V(V)/V(IV). In other words, at a same molar concentration, V(V) is more corrosive than Pu(VI). This can be surely related to the kinetics of the re-oxidation reaction of the reduced species. Though no specific study has been carried out on this subject, it can be said that visually V(IV) is 'instantaneously' oxidized into V(V) when the nitric acid solution boils (change in colour from blue to yellow). On the contrary, the oxidation of Pu(IV) results from the dismutation of Pu(IV) into Pu(III) and Pu(VI) and then from the oxidation of Pu(III) in Pu(IV) by the couple NO_3^-/HNO_2 according to the reactions [38]

$$3Pu^{4+} + 2H_2O \leftrightarrow PuO_2^{2+} + 2Pu^{3+} + 4H^+ \tag{16}$$

$$2Pu^{3+} + NO_3^- + 3H^+ \leftrightarrow 2Pu^{4+} + HNO_2 + H_2O \tag{17}$$

Reaction (17) is fast but Reaction (16) is rather slow, since the acidity of the solution is high. These kinetic aspects can explain the difference in corrosivity of the two ions V(V) and Pu(VI).

Nevertheless, V(V) appears to properly simulate Pu(VI) from a corrosion point of view, provided that the comparison is made at the same corrosion potential.

6. Nitric acid media with metallic elements

6.1. Corrosion mechanism

In the framework of the spent fuel treatment process, metallic elements can be in contact either with stainless steels and nitric acid media acting as an electrolyte. If the corrosion potentials of the steel and of the metallic elements are different in the nitric acid medium, a corrosion cell forms and galvanic corrosion occurs.

The metallic elements which can be in contact with stainless steels and might be responsible of galvanic corrosion can have several origins:

- structural materials of some specific nuclear fuels (Al, graphite);
- fission products from irradiated fuels, and especially platinoïds (Pd, Rh, Ru, Tc);
- other structural materials of equipments in the plants (Zr, Ti); these equipments are connected to stainless steel equipments by explosion-bonded junctions which are composed of Zr (or Ti)/Ta sheet/stainless steel [46].

Experience in nitric acid allows at least, if not to establish a galvanic series, to classify the metallic elements in comparison with the corrosion potentials of type 304L and 316L steels in their passive state. Table 3 summarizes this classification in hot and concentrated nitric acid: qualitatively, the trends are the same as the galvanic series in flowing seawater [50].

The corrosion mechanism of galvanic corrosion in nitric acid is the same as in other aqueous electrolytes. It is explained by a classical Evans diagram. However, the cathodic reaction occurring on the more noble material is the reduction reaction of nitric acid (1). An example of

Table 3
Metallic elements susceptible to induce a galvanic corrosion of stainless steels in hot and concentrated nitric media

Metallic elements less noble than 304L and 316L stainless steels (passive state) (acting as anode in the galvanic coupling with steel)		Metallic elements more noble than 304L and 316L stainless steels (passive state) (acting as cathode in the galvanic coupling with steel)	
Al	[47]	Platinoïds (Pd, Rh, Ru)	[48]
Ti	[46]	Pt	[48]
Zr	[46]	Graphite	[49]
Ta		Au	[49]
		Zircaloy (passivated)	

mechanism is shown on Fig. 13 for the aluminium–stainless steel couple.

Without coupling, aluminium is not passive in nitric acid; it dissolves at a high rate according to the anodic reaction

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^- \tag{18}$$

whereas the cathodic reaction is Reaction (1). Without coupling and in not too highly concentrated ($\leqslant 8$ mol/L) nitric acid, stainless steel (for instance of 304L type) is in its passive domain, with a low corrosion rate; the anodic reactions are the oxidation reactions of the elements of the steel, and the cathodic reaction is Reaction (1). The corrosion potential of aluminium is much lower than the one of stainless steel. When the two materials are coupled, the coupling potential is such that the anodic current on aluminium equilibrates the cathodic current on stainless steel. On aluminium, it results from this a higher dissolution rate compared to the situation without coupling. For stainless steel, it results from this that the coupling potential may be in the active domain, so that the cathodic current is the sum of the reduction current due to Reaction (1) and of the current due to anodic dissolution of the elements of the steel; for stainless steel also, the dissolution rate is enhanced by the coupling, as it will be shown in the following paragraph.

6.2. Examples of stainless steel behaviour under galvanic coupling

6.2.1. Cathodic polarization

The galvanic coupling of stainless steels with aluminium in hot concentrated nitric acid is the most spectacular case of cathodic polarization [47]. In that case, the potentials of stainless steels (type 304L or Uranus 65) are shifted in their active domain. Consequently, their corrosion rates are considerably enhanced. Fig. 14 summarizes results obtained by

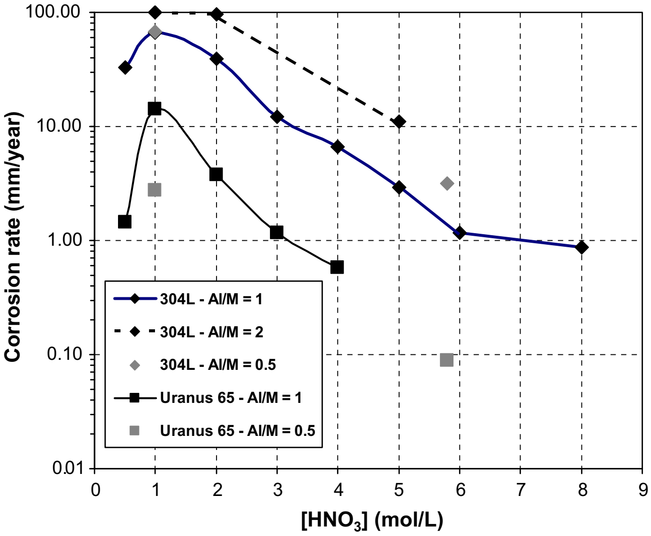

Fig. 14. Corrosion rates of stainless steels obtained by galvanic coupling with aluminium (Al/M is the ratio of the areas; nitric acid is at its boiling temperature) [47].

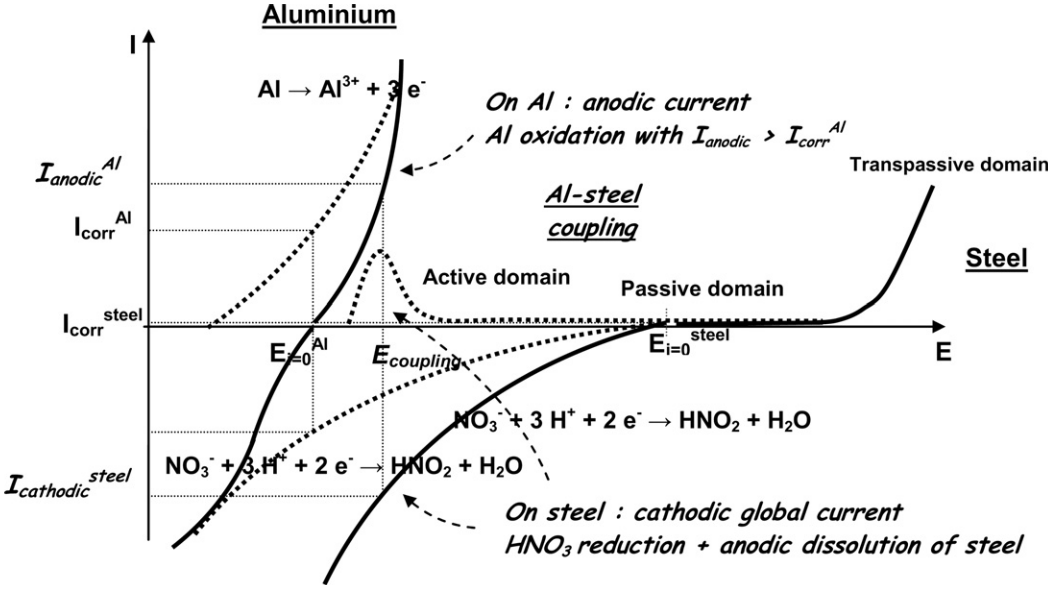

Fig. 13. Electrochemical explanation of galvanic corrosion between stainless steel and aluminium in nitric acid.

coupling externally the two materials in boiling nitric acid. Corrosion rates can reach some mm per year to some tens of mm per year. They depend on many parameters such as the nitric acid concentration (maximum around 1 mol/L), the ratio of the areas of the two coupled materials (Al/M), and the chromium content of stainless steel (25% Cr steel being more resistant than 18% Cr steel). Steels suffer a uniform dissolution, although the interfaces present deep transgranular indentations [47].

The galvanic coupling effect between zirconium and stainless steel is of high practical interest for the behaviour of Zr–SS junctions in nitric media. Electrochemical studies in boiling HNO_3 5 mol/L without or with 1 g/L Cr(VI) show that passivated Zircaloy (used for simulating pure Zr) acts as a cathode and 304L stainless steel acts as an anode, but the coupling current is negligible ($\leqslant 0.1\ \mu A\ cm^{-2}$). From the study [46], pure Zr acts as an anode and 304L stainless steel acts as a cathode. This discrepancy may be due to a slight difference in corrosion potentials between Zircaloy and pure Zr. Nevertheless, a negligible galvanic corrosion is confirmed on stainless steel by immersion tests on coupled and no-coupled specimens, and on real Zr–SS junctions.

6.2.2. Anodic polarization

The galvanic coupling of stainless steels with graphite in hot concentrated nitric acid is the most spectacular case of anodic polarization [49]. In that case, the potentials of stainless steels are shifted in their transpassive domain, and intergranular corrosion may occur. This study emphasizes that the effects of galvanic coupling are considerably enhanced by the nitric acid temperature and concentration: for example, from 80 °C to 106 °C in HNO_3 5 mol/L, the corrosion rate of 304L stainless steel is multiplied by a factor 30 and the morphology goes from uniform dissolution to deep intergranular corrosion; from 1 mol/L to 8 mol/L at 100 °C, the corrosion rate is multiplied by a factor 8 and the morphology goes from intergranular indentations to deep intergranular corrosion. These tendencies are also confirmed by other cases of anodic polarization of stainless steels, in particular with ruthenium.

Another situation conducting to anodic polarization of stainless steels by galvanic coupling occurs when stainless steels are in contact with platinoïds (Ru, Rh, Pd) which are fission products weakly soluble in nitric acid [48]. The comparison of the anodic polarization curve (for AISI 316L stainless steel) and of the cathodic polarization curves for each platinoïd allows to predict the galvanic effect (Fig. 15). It involves an increase of the corrosion potential of steel towards its transpassive domain. The galvanic effect of platinoïds decreases in the order: Ru > Pt > Rh > Pd. This ranking may be explained by the kinetics of the cathodic reaction (reduction of nitric acid), which appears to be slower on Rh and Pd than on Ru and Pt.

Direct coupling of 316L stainless steel with powder of each platinoïd during long-term immersion experiments confirms that the corrosion of the steel increases by galvanic coupling (Fig. 16). The increasing factor is of 8–10 whatever the platinoïd is. However, a corrosion rate below 6 μm/year and only slight intergranular indentations show that the potential of the steel does not reach its transpassive domain and that the corrosion risk remains low. During the test with the Pd powder, Pd(0) is oxidized to Pd(II) ions by nitric acid, then Pd(II) ions are reduced by stainless steel; so it forms a Pd deposit on the grain boundaries of steel which are slightly less noble than the grains. Consequently, stainless steel which was not initially in contact with the Pd powder, is corroded first by the Pd(II) 'oxidizing' ions and then by galvanic coupling with Pd(0) formed.

Finally, it was verified that a mixture of real radioactive platinoïds does not cause additional coupling effect for 316L steel, showing no specific effect of irradiation nor the presence of elements (for instance Tc) more corrosive than Ru, Rh and Pd [48].

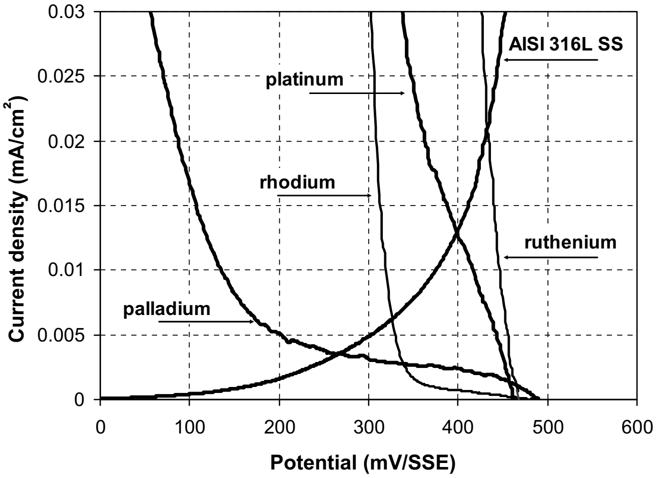

Fig. 15. Superposition of polarization curves for AISI 316L stainless steel (anodic curve) and platinoïds (cathodic curves) in HNO_3 1 mol/L at 80 °C (area ratio 1:1) [48].

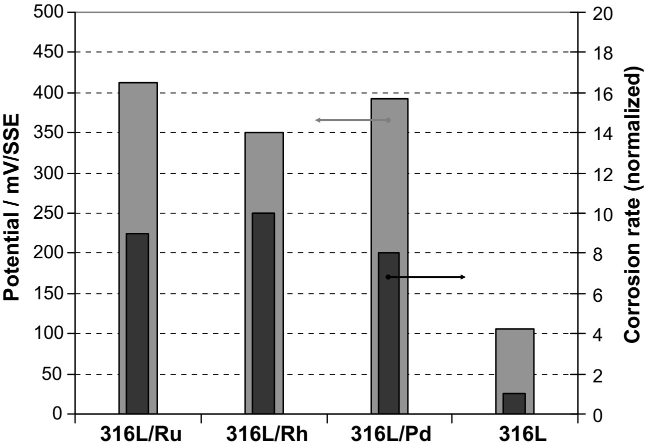

Fig. 16. Corrosion rate and potential of AISI 316L stainless steel coupled or not coupled with platinoïd powder in HNO_3 1 mol/L at 80 °C during 90 days [48].

7. Conclusion

The different conditions promoting a corrosion potential shift from the passive domain, and thus an enhancement of the corrosion of stainless steels in nitric media used in spent fuel treatment plants have been reviewed and illustrated by examples. These conditions are:

- nitric media where an autocatalytic mechanism of nitric acid reduction can occur;
- nitric media containing oxidizing ions;
- nitric media containing metallic elements allowing galvanic coupling with the steel.

Each of these conditions may shift the corrosion potential of stainless steels in their transpassive domain and thus cause intergranular corrosion. One case, the galvanic coupling with metallic elements less noble than the steels, may shift the corrosion potential in their active domain and thus cause enhanced dissolution.

The examples presented show the complexity of nitric acid itself and of the different nitric media found in the spent fuel treatment process.

An optimal initial choice of the steel grades according to the process conditions and drastic metallurgical controls during the building of the spent fuel treatment plants ensure that stainless steels work at present in their passive domain and suffer only uniform and low-rate dissolution.

The knowledge of the mechanisms susceptible to move away stainless steels from their passive domain, and the determination of convenient corrosion data, allow to prevent any unexpected situation for example due to the evolution of the process conditions, and work towards ensuring the durability of the French spent fuel treatment plants.

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