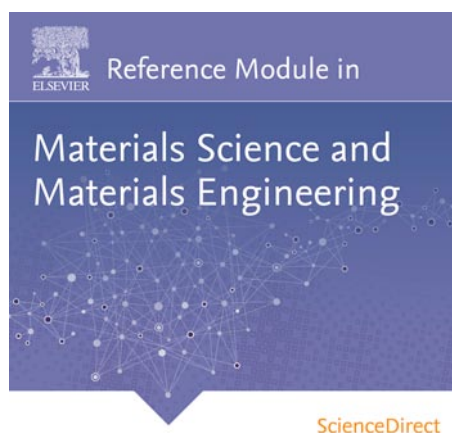


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Corrosion in Nitric Acid ☆

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Abbreviations

AISI American Iron and Steel Institute

AR As-received

Gy Grays (unit of absorbed radiation dose;

1 Gy = 1 J kg⁻¹)

mpy Thousandths of an inch per year

M Molar or metal

NAG Nitric acid grade

SCC Stress corrosion cracking

ss Stainless steel

☆*Change History:* December 2015. A.A. Abdullahi added Abstract, Keywords; incorporated 'Introduction' section featuring recent literature on corrosion, and updated the list of references.

Symbols E Electrode potential i Current density V_{SCE} Electrode potential, volts with respect to the Standard calomel electrode $X(\text{Y})$ Element X present in valency state Y; for example, Cr(VI) is $\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-} **Glossary****18/13/1** A niobium-stabilized stainless steel used in UK nuclear reprocessing plant, conforming approximately to the top end of the AISI 347 specification range.**20Cr25Ni1Nb** A proprietary stainless steel used in UK advanced gas-cooled reactor fuel.**End grain** The cross-section perpendicular to the hot-working direction of a fabricated component.**Grain drooping** Dislodgement of metal grains as they are undermined by intergranular corrosion.

Dropped stainless steel grains have the appearance of fine soot.

Magnox A magnesium alloy containing 0.8% aluminum, used to clad uranium metal fuel for CO_2 -cooled Magnox reactors.**NAG 18/10L** A proprietary stainless steel used in UK nuclear reprocessing plant, similar to AISI 304L but with tighter control of residuals.**Radiolysis** Chemical change resulting from the absorption of ionizing radiation.**R-SUS 304ULC** A proprietary stainless steel used in Japanese nuclear reprocessing plant. Similar to NAG 18/10L.**Uranus 65** A proprietary stainless steel, conforming approximately to AISI 310L, but with added niobium. Used in UK and French nuclear reprocessing plant.**1 Introduction**

The term corrosion is the breakdown of materials, namely metals, through electrochemical reactions within a given environment. The phenomenon occurs in virtually all engineering materials' applications.

Liu *et al.*¹ studied the corrosion behavior of Q235 carbon steel in the presence of *Chlorella vulgaris* was investigated by surface analysis. Likewise, the use of anticorrosion² and inhibitors are explored. The effect of acetohydroxamic acid (AHA) on the corrosion behavior of stainless steels is studied by Wilbraham and Boxall.³ In addition, Zhang⁴ investigated behavior and mechanism of galvanic corrosion with special consideration of materials and environmental factors. Although many environments have been identified to be highly corrosive, but this study focused on corrosion in nitric acid.

Therefore, this article presents corrosion processes affecting industrially-significant metals in nitric acid solutions and attendant vapors are reviewed. Consideration is given to the various corrosion mechanisms that operate and the major factors that exert an effect on corrosion rates, including welding, cold work, NO_x gases, dissolved species, radiation, solution boiling, heat transfer, and liquor-lines. Corrosion test methods are discussed. However, the study begins from the uses and application of nitric acid.

2 Uses of Nitric Acid

Nitric acid is used in salt formation, preparation of organic nitrates and nitro compounds, and oxidation of organic compounds.⁵ Major applications include the production of agricultural fertilizers and reprocessing of nuclear fuels.

3 Chemical Attack by Nitric Acid**3.1 Pure Nitric Acid**

At greater than about 96–97% concentration, HNO_3 chemistry is dominated by the NO_2^+ ion. The acid undergoes no proton transfer to water molecules and it cannot be considered as an acid in the protionic sense at this concentration.⁶ The initial electron transfer reaction with a metal, M:



leads to the overall reaction



with nitrates produced at the metal surface.⁶ The reaction of some metals with pure HNO_3 is given in [Table 1](#).

Table 1 Reaction of pure HNO₃ with metals

Solution complete within			Evidence of inhibition by film	No evidence of reaction
1 day	1 week	1 month		
Mg	Cr powder	Fe	Ca	Be
Sc		Mn	Cu	Al
V	Ni		Ag	Ti
Co	Cd		Bi	Pt
Zn	U			Sn
Hg				

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There is no correlation between apparent reactivity and position of the metal in the periodic table. In some instances, there is evidence of cohesive film formation (e.g., Ca) while some metals are either inert (e.g., Pt) or form protective oxide films (e.g., Al).

3.2 Aqueous Nitric Acid

In practice, most nitric acid corrosion occurs in aqueous mixtures of <96% concentration.

3.2.1 Base metals in aqueous nitric acid

These generally dissolve extremely rapidly to form nitrates, cathodically discharging hydrogen, which reacts with the nitric acid to give compounds such as ammonia, ammonium nitrate, hydroxylamine nitrate, nitrogen, and nitrous oxide.⁷

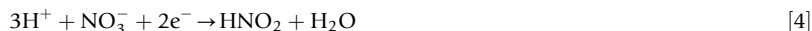
3.2.2 Noble metals in aqueous nitric acid

The dominant cathodic reaction in this case is the reduction of the nitrate ion. This is a complex process, proceeding via an autocatalytic mechanism involving a charge transfer reaction and various chemical reactions leading to the regeneration of the active species (nitrous acid). The autocatalytic nature of the reaction can readily be demonstrated by simple observation of the corrosion rate of copper, for example, in nitric acid solutions: the rate, as evinced by NO_x evolution, is initially low, but accelerates rapidly if the copper is placed in contact with a surface, thus forming a crevice, which traps the nitrous acid generated, or if a little nitrite is added to the solution; conversely, the rate is retarded by agitation or stirring of the acid, which displaces the nitrous acid generated, or by the addition of a chemical such as urea, which impedes the autocatalytic reaction by destroying nitrous acid.⁷

Two basic mechanisms have been proposed: one heterogeneous⁸ leading to NO₂ formation and one homogeneous⁹ leading to NO. Both mechanisms have been shown to be consistent with experimental data collected over different potential ranges.¹⁰ More recently, a modified mechanism has been suggested, which results in two limiting cases, one applicable for low nitric acid concentrations (<8 M) leading to NO formation, the other for high nitric acid concentrations (>8 M) leading to NO₂.¹¹ According to this scheme, the major species involved in the reduction of nitric acid at low overvoltages are nitrous acid (HNO₂), NO, and NO₂, and the charge transfer reaction is the reduction of HNO₂:



The product of the overall cathodic reaction is HNO₂, thus giving rise to autocatalysis:



Whatever the precise mechanism, the important point is that nitrate reduction is autocatalytic, being strongly affected by HNO₂, NO, and NO₂.

Reactions [3] and [4] indicate that H⁺ is required, but in all but the most dilute solutions it is the nitrate concentration that is important; thus, the addition of neutral nitrate salts to nitric acid generally increases the liquor corrosivity.

Iron can show both base and noble metal characteristics in its corrosion reactions. It is attacked at an increased rate in crevices, but its corrosion products include nitrous oxide, ammonia, and nitrogen as well as nitrogen dioxide and nitric oxide. In concentrated acids of >~40%, after an initial reaction, iron becomes passive (although this can be disrupted relatively easily, e.g., by agitation), whereas in dilute acids, reactions are rapid.¹²

3.2.3 Passive metals

Highly reactive metals such as chromium, titanium, hafnium, niobium, and zirconium rapidly form thin insoluble surface oxides in air. These films may grow slightly on immersion in oxidizing acids, but then prevent further corrosion or reduce it to negligible rates in a wide range of nitric acid conditions. These metals or their alloys, as in the case of stainless steels, where alloying of iron with chromium confers much greater passivity, are the most important class of metals for the industrial handling of nitric acid.

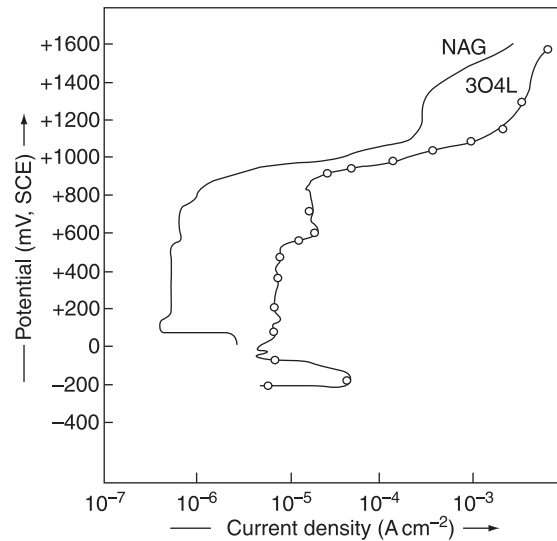


Figure 1 Anodic polarization of stainless steel in 1M nitric acid at room temperature. Reproduced from Kain, V., Shinde, S., Gadiyar, H.J., 1994. Mater. Eng. Perform. 3, 699–705, with permission from ASM International.

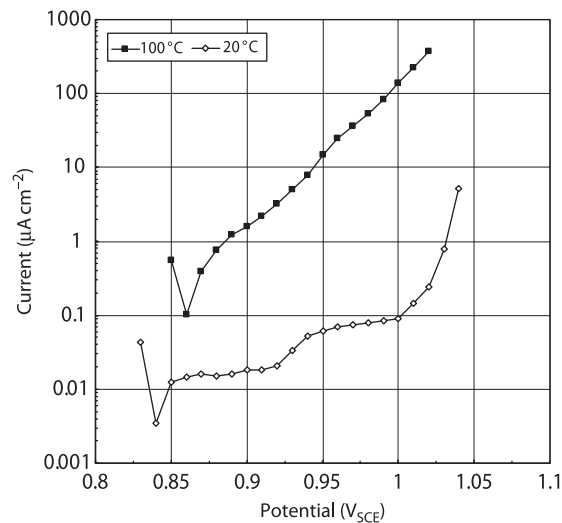


Figure 2 Effect of temperature on polarization behavior of NAG 18/10L stainless steel in 8M nitric acid (measured by step-wise potentiostatic polarization, 10 mV steps each of 1 h duration). Takeuchi, M., Whillock, G.O.H., BNFL unpublished work.

This behavior is illustrated for stainless steels in [Figure 1](#).¹³ The polarization curve shows three distinct regions of active, passive, and transpassive corrosion. The effect of temperature on the anodic reaction is important, as demonstrated in [Figure 2](#). Although increasing the temperature of stainless steel in nitric acid produces only a small increase in corrosion potential (due to augmentation of the cathodic reaction), the anodic polarization curve changes significantly; the passive region is effectively lost, and therefore, a small increase in potential leads to significantly increased corrosion. This is pertinent when considering the effect of oxidizing species or galvanic effects, which will therefore be more pronounced at high temperatures (see Sections 5.7 and 6.4.1).

4 Materials for Nitric Acid Containment

The primary materials used for nitric acid environments are stainless steels, titanium, and zirconium. Aluminum can also be used in some circumstances. The austenitic stainless steel, AISI 304L, and its variants are now the most commonly used, although much early plant has been made from stabilized austenitic steels such as AISI 321, AISI 347, and 18/13/1. In more oxidizing conditions, higher alloy steels such as AISI 310L or possibly high Si stainless may be preferred. In the most aggressively oxidizing conditions, titanium, zirconium, niobium, hafnium, or tantalum may be used. In the past, titanium has been the most widely used, but the

use of zirconium in preference has increased in recent years. The others find only occasional use, despite their excellent corrosion resistance, because of high cost and fabrication difficulties. **Table 2** provides indicative corrosion rates for some of these metals.

4.1 Stainless Steels

The industrial use of stainless steel for nitric acid containment seeks to ensure that it operates in the passive regime where corrosion rates are typically $<0.01 \text{ mm year}^{-1}$. However, it is also possible to operate stainless steel plant successfully for extended periods in the potential regime between passivity and full transpassivity where intergranular corrosion occurs and the corrosion rate is significant (see Section 5.1). In practice, all stainless steel plant handling hot nitric acid operates in the intergranular corrosion regime.

Corrosion rates show Arrhenius behavior over a large range of acid concentrations and temperatures, as illustrated in **Figure 3**, indicating that electron transfer is the rate-determining step in the corrosion mechanism.

Austenitic stainless steels are the most widely used for nitric acid containment. Reasonable or good nitric acid resistance can be achieved with ferritic, super ferritic, and ferritic–austenitic (duplex) steels, but they are generally less resistant than the austenitics, and factors such as compositional variation, heat treatment, and welding can lead to reduction in corrosion resistance.¹⁴ Ferritic

Table 2 Indicative corrosion rates of various metals subject to testing in boiling 65% nitric acid

Metal	Corrosion rate (mm year^{-1})
18/13/1 stainless steel ^a	0.2–0.5
NAG 18/10L stainless steel ^b	0.1–0.2
NAG 18/10L stainless steel ^c	0.1–0.3
310L stainless steel	0.05–0.1
Ti ^d	0.7
Zr	<0.001
Ta	<0.001

^aSimilar to AISI 347.

^bAs-received.

^cSensitized.

^dThe high corrosion rate is due to the test conditions employed (see Section 4.2).

Source: Quayle, B.E., BNFL unpublished work.

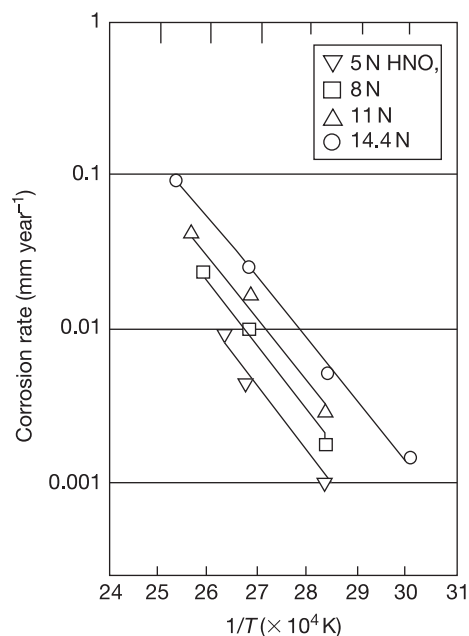


Figure 3 Corrosion rate of stainless steel (R-SUS 304ULC) as functions of temperature and nitric acid molarity. Reproduced from Onoyama, M., Nakata, M., Hirose, Y., Nakagawa, Y., 1991. In: Proceedings of the RECOD'91, vol. II, Japan Atomic Industrial Forum, Tokyo, pp. 1066–1071.

stainless steels with > 14% Cr resist corrosion in nitric acid at room temperature, and high Cr/Mo ferritics such as 26Cr1Mo, and 29Cr4Mo resist nitric acid up to 65% boiling. Duplex stainless steels have similar resistance to ferritics, but the ferritic phase can be preferentially attacked.¹⁴

AISI 300 series stainless steels (i.e., austenitic) are adequate for a wide range of applications up to about 70% acid concentration. AISI 304L is now commonly used and improvements in its performance can be achieved by improved manufacturing processes to reduce elements such as Si, P, S, and C, as illustrated in **Figure 1**. Here, a nitric acid grade version of 304L shows improved corrosion resistance in the passive and lower transpassive region. However, it is doubtful whether significant corrosion differences persist under more aggressive oxidizing conditions where higher chromium steels such as 310L may be required.¹⁵ Alternatively, in extremely oxidizing conditions stainless steels containing Si at > ~4% (e.g., Uranus S1N) may find application, although such steels are more problematic to join because some ferrite needs to be maintained in the welds to avoid cracking.¹⁶

4.2 Titanium

Titanium has a high corrosion resistance to a range of nitric acid concentrations, provided there is sufficient concentration of dissolved titanium or other oxidizing ions present.^{17,18}

In the absence of such dissolved ions, corrosion rates can reach or exceed 1 mm year⁻¹. Hence, corrosion rates in the vapor regions of operating plant handling condensing nitric acid, where continuous washing prevents the accumulation of dissolved titanium, can be significant even though the metal below liquor is unaffected. Titanium is accordingly no longer recommended for use in condensing nitric acid. Owing to the sensitivity of titanium corrosion rates to the presence of dissolved titanium, account must be taken of the suppressing effect of corrosion product accumulation when assessing corrosion rate data. The susceptibility of titanium to corrosion in pure acid can be mitigated by alloying with tantalum; at > 5% Ta, corrosion is significantly reduced.¹⁷ These effects are illustrated by the corrosion data in **Table 3**.

Titanium can also be susceptible to enhanced corrosion in both weld metal and heat-affected zones. This has generally been attributed to the redistribution of iron impurities during the welding operation so that the iron originally present in discrete stringers or well-distributed particles is deposited on grain boundaries either as iron–titanium intermetallic compounds or as β -phase. The formation of a continuous grain boundary network can lead to intergranular corrosion and grain dropping in certain conditions. This is likely to become more significant in marginally passive environments where these iron-rich phases may become soluble. To avoid this problem, it is now recommended that iron levels in titanium are specified to be < 0.05%.¹⁹

4.3 Zirconium, Niobium, Hafnium, and Tantalum

These materials are generally highly resistant to nitric acid corrosion (see **Table 2**), although operating experience of these materials is less extensive than that of titanium. There are no reported materials issues affecting corrosion performance, although stress corrosion cracking (SCC) of zirconium cannot be entirely discounted in extremely oxidizing conditions (see Section 5.4). In addition, zirconium is very susceptible to trace levels of fluoride ions (see Section 6.5). There have been no reported instances of enhanced vapor phase corrosion and they do not require the presence of dissolved ions to achieve passivity.

4.4 Aluminum

The corrosion rate of aluminum and its alloys is appreciable in all but very concentrated nitric acid, reaching 3–5 mm year⁻¹ at room temperature in 30% acid, whereas rates of < 0.1 mm year⁻¹ can be achieved in > 85% acid. This is illustrated in **Figure 4**.²⁰

Table 3 Effect of test conditions on the corrosion rate of titanium and titanium–tantalum alloys

<i>Metal</i>	<i>Nitric acid concentration plus additions</i>	<i>Liquor renewal (h)</i>	<i>Corrosion rate (mm year⁻¹)</i>	<i>Source</i>
Ti	6 M	14	0.6	<i>a</i>
	6 M	65	0.43	<i>b</i>
	6 M	280	0.15	<i>a</i>
	6 M + 0.1% Fe ³⁺	65	0.14	<i>b</i>
	6 M + 0.1% Ce ⁴⁺	65	< 0.01	<i>b</i>
	40%	24	0.75	<i>c</i>
	40% + 40 mg l ⁻¹ Ti	24	0.05	<i>c</i>
	Condensing acid	24	0.33	<i>c</i>
	40%	4	0.74	<i>c</i>
Ti–6.1%Ta	40%	4	0.02	<i>c</i>

^aQuayle, B.E. BNFL unpublished work.

^bShimogori, K., Satoh, H., Kamikubo, F., 1984. Titanium Science and Technology. In: Luthering, G. (Ed.) Proceedings of the 5th International Conference on Titanium, Munich, Germany, September 10–14, vol. 4, pp. 1111–1114.

^cTakamura, A., Arakawa, K., Moriguchi, Y., 1970. In: Jafee, R.I., Promisel, N.E., (Eds.) The Science Technology and Application of Titanium, Oxford: Pergamon Press, pp. 209–216.

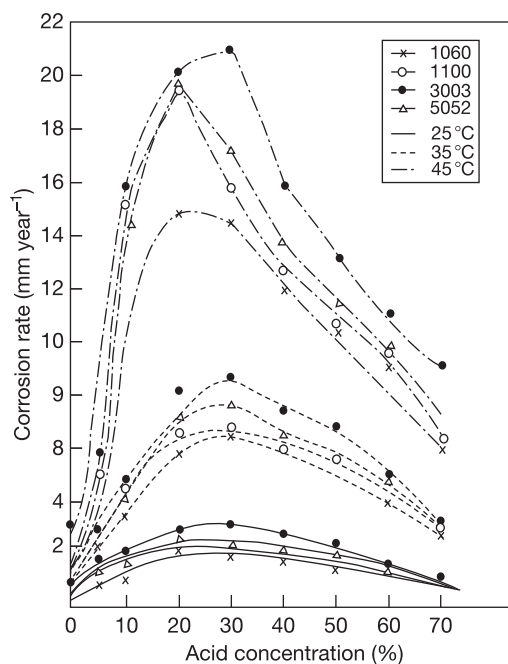


Figure 4 Corrosion rate of various aluminum alloys as a function of nitric acid concentration and temperature. Reproduced from Singh, D.D.N., Chaudhary, R.S., Agarwal, C.V., 1982. *J. Electrochem. Soc.* 129, 1869–1874, with permission from The Electrochemical Society.

The corrosion rate is strongly temperature dependent and increases with the level of copper impurity. However, a number of aluminum alloys containing magnesium silicon or manganese have corrosion rates comparable with those of pure aluminum in 98.5% acid.²¹ As would be expected from its decreased corrosion resistance in dilute acids, aluminum corrodes more quickly where dilute acid condensates are formed above concentrated acids.²² Hence, although aluminum can be suitable for room temperature storage of concentrated nitric acid, the vapor regions of storage vessels may undergo increased corrosion.

5 Corrosion Mechanisms of Passive Metals in Nitric Acid

5.1 General Corrosion and Intergranular Corrosion

For stainless steels, full transpassivity occurs when the Cr_2O_3 -based passive film becomes unstable in extremely oxidizing conditions, allowing corrosion to proceed by the formation of soluble CrO_3 ; this occurs at $\sim 1.0 V_{\text{SCE}}$.²³ However, grain boundaries are more vulnerable to corrosion. This is largely due to impurities in the metal, with the segregation of silicon and phosphorus being particularly implicated.^{24,25} The transpassive corrosion process therefore proceeds primarily by grain boundary dissolution, but is manifest as general corrosion owing to grain dropping. Owing to the high corrosion rates encountered, stainless steels are unsuitable for use in extremely oxidizing conditions where transpassive corrosion occurs.

In the potential band between full passivity and transpassivity (i.e., between ~ 0.9 and $\sim 1.0 V_{\text{SCE}}$), intergranular corrosion occurs. This is the principal mechanism affecting stainless steels handling nitric acid solutions which are too oxidizing for the maintenance of passivity. Intergranular attack increases significantly if the steel has become sensitized by heat treatment,²⁶ but sensitization is not a prerequisite, intergranular corrosion occurring in the fully solution-annealed condition even in very clean stainless steels providing potentials in excess of $\sim 0.9 V_{\text{SCE}}$ are achieved in hot solutions. The intergranular corrosion rate can be strongly anisotropic, depending on the orientation of the exposed face to the underlying microstructure (see also Section 5.2). **Figure 5** illustrates this. The effects tend to be less pronounced in modern ultraclean stainless steels, but are still evident.

General corrosion curves derived for stainless steels from weight loss are broadly characterized by two regions, as illustrated in **Figure 6**.²⁷ In the early stages, grain boundaries are etched, but no grains are lost, and weight loss is by chemical dissolution only. The apparent corrosion rate rises as the grain boundaries are penetrated more deeply because a greater area of metal is opened to corrosion. As time progresses, grains begin to drop out of the metal surface as their boundaries are completely corroded. Eventually, a relatively stable corrosion rate is reached, which is a combination of chemical dissolution and grain dropping. For AISI 304L stainless steel and related steels, grain dropping accounts for only $\sim 25\%$ of the total metal loss, chemical dissolution of the grain boundary regions accounting for the rest.²⁸ It is therefore important in deriving corrosion rates from analysis of dissolved species to allow for grain dropping.

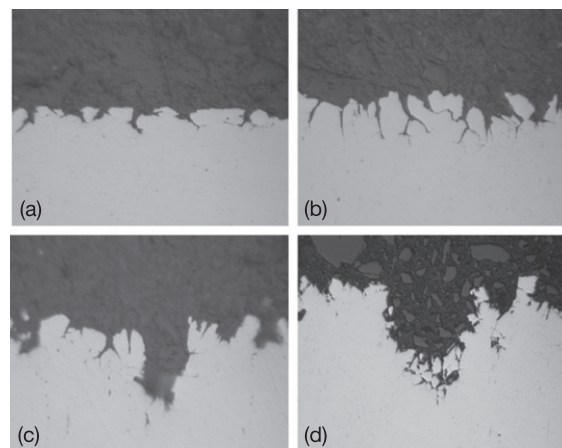


Figure 5 Morphology of intergranular corrosion of 18/13/1 stainless steel exposed to 8 M nitric acid containing 25 g l^{-1} Fe(III) at 100°C . The sections show penetration into (a) plate, (b) side and (c) end surfaces after 340 h exposure. (d) Shows end grain pitting after 1000 h exposure. Magnification: (a)–(c) $\times 360$; (d) $\times 150$. Dunnnett, B.F., BNFL unpublished work.

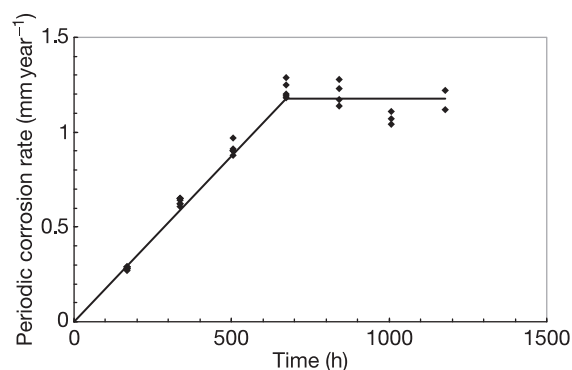


Figure 6 Effect of immersion time on the corrosion rate of 18/13/1 stainless steel in 8 M nitric acid containing 25 g l^{-1} Fe(III) at a solution temperature of 100°C . Reproduced from Dunnnett, B.F., Whillock, G.O.H., 2003. *Corrosion* 59, 274–283, with permission from NACE International.

Corrosion rates derived from weight loss averaged over the specimen area will tend to be underestimated in the early stages of corrosion. In practice, the corrosion curve is an artifact of the measurement process; if measurements of penetration are made, then it is found that the rate of penetration is constant and corresponds to the corrosion rate derived from weight loss once steady grain dropping is established.²⁷ The time to reach this state depends on the corrosion resistance of the steel, its grain size, and the corrosivity of the medium.

This problem can be addressed either by numerical models to predict the long-term rate from short-term data^{29,30} or by pre-corroding test samples in aggressive media to establish grain dropping before reverting to the required test media.^{27,31} The validity of numerical models is still to be fully established. Pre-corrosion appears to be a valid method, although it appears that care needs to be taken in selecting the pre-corrosion conditions, otherwise reasonably prolonged testing in the liquor of interest may be required in order to establish the true corrosion rate. In practice, it is found that the overall metal loss by intergranular corrosion is fairly uniform even in plants operating with relatively aggressive environments. Hence, extrapolation of the steady-state corrosion rate to predict plant life is valid, provided there are no localized mechanisms acting, such as crevice/underdeposit corrosion (see Section 5.3).

Intergranular corrosion in stainless steels can be suppressed by alloying with silicon.¹⁶ At $> \sim 4\%$ Si, intergranular corrosion is suppressed, but general corrosion rates at most nitric acid concentrations are higher at least in the early stages of corrosion compared with the equivalent AISI 300 series stainless steel. In particular, high Si stainless steels show a significant improvement in corrosion resistance in super-azeotropic solutions. However, welding of these alloys can be problematical; ferrite needs to be maintained in the welds to avoid cracking, and welds can be susceptible to enhanced corrosion.¹⁶

Intergranular corrosion of other passive metals such as zirconium and tantalum has not been reported. Of these metals, only titanium shows a transpassive breakdown in normal operating conditions, although a form of transpassivity (breakaway oxidation) can be induced in zirconium and its alloys under extreme conditions (in excess of $\sim 2 V_{\text{SCE}}$).³² Titanium can also exhibit intergranular corrosion at welds; this propensity tending to be associated with the presence of β -phase (see Section 4.2).

5.2 End Grain Corrosion

The rate of intergranular penetration depends on the orientation of the exposed face to the underlying microstructure. In general, the corrosion rate increases in the order: plate < side < end (see Figure 5). The effects of end grain corrosion are clearly seen in boiling nitric acid testing (the Huey test, see Section 5.6) if specimens are cut so as to vary the percentage of exposed end grain in a susceptible material. Figure 7 shows an example, clearly demonstrating a significant effect for end grain fractions exceeding ~10%.

In addition to this pronounced effect of end grain on the general corrosion rate, localized pitting-like attack can develop parallel to the hot-working direction. This is known as 'end grain' or 'tunneling' corrosion. Figure 8 shows an example. Older stabilized steels appear to be most vulnerable, and the phenomenon is extremely variable even within the same grade of steel. However, extremely clean stainless steels such as R-SUS 304ULC and Uranus 65 also exhibit end grain pitting.^{33,34} In such steels, the mechanism is considered to be a consequence of the exposure of segregated material in the original ingot, which has been distributed, producing bands with more susceptible grain boundaries.³⁴ In stabilized steels, stringers of magnesium sulfide and precipitates of niobium or titanium carbide mark out the regions of maximum segregation as they solidify late from the melt. The outer regions of the ingots solidify first, and hence contain little impurity segregation conferring superior corrosion resistance to the as-formed plate surface.

In practice, end grain corrosion of stainless steels is usually more of a problem for corrosion testing (see Section 7) than for operating plant where most end grain is welded over in pipe or plate joints, although issues can arise, for instance, with forgings where outcropping end grain can be present.

End grain corrosion of other passive metals has not generally been reported, although at least one instance on titanium is known.

5.3 Crevice Corrosion

Although crevice corrosion is not widely reported in nitric acid, austenitic stainless steels are known to be susceptible to this mechanism in certain circumstances. One such example is corrosion testing of heat transfer surfaces, where corrosion focuses at the

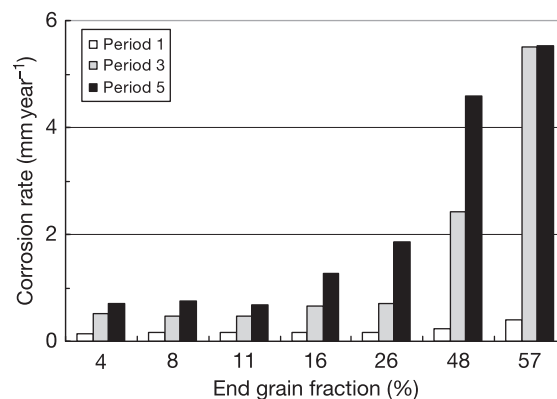


Figure 7 Effect of end grain fraction on the corrosion rate obtained from successive 48 h test periods of 18/13/1 stainless steel in boiling 65% nitric acid. Quayle, B.E., BNFL unpublished work.

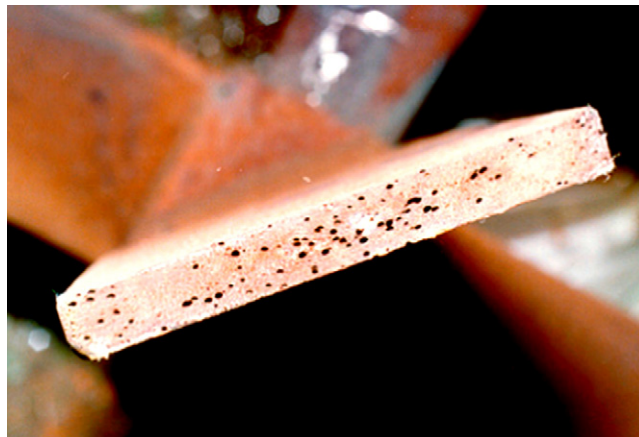


Figure 8 End grain corrosion pits: 18/13/1 stainless steel stirrer paddle in nitric acid media. Green, D.S. BNFL unpublished work.

mouth of the crevice on the external surface; for instance, under nucleate boiling at a heat flux of 50 kW m^{-2} , the depth of attack was twice that on the free surface.³⁵ Crevice corrosion appears to be possible only in more aggressive conditions, although indications of it have been found in isothermal tests at temperatures as low as 90°C ,³⁶ and in a nitric acid reboiler where corrosion rates increased from ~ 0.02 to 0.1 mm year^{-1} on a heat transfer surface at $\sim 90^\circ\text{C}$ in 12 M nitric acid. The mechanism may have several origins depending on the circumstances. For heat-transfer surfaces, the inhomogeneity provided by the crevice may simply lead to increased local surface temperatures, and hence increased local corrosion rate. The entrapment of stainless steel corrosion products is also possible (see Section 6.4.1), as is entrapment of NO_x species (see Section 6.3). The mechanism is oxidative rather than reductive in contrast to crevice corrosion brought about by chloride ions in water systems. The operation of a crevice in nitric acid systems is capable of adversely affecting the potential outside the crevice and increases the external corrosion rate. Care is therefore required in interpreting corrosion test data where the operation of a crevice is suspected.

Crevice corrosion has not been found on zirconium, titanium, or niobium under similar heat-transfer conditions in nitric acid. However, it has been recorded on zirconium in laboratory trials in acid contaminated by fluoride ions (see also Section 6.5) and also under cathodic polarization. It is probable that here the phenomenon is one of active corrosion in localized reducing conditions in the crevice. Crevice corrosion has not been reported for these metals in operating plant.

5.4 Stress Corrosion Cracking

Despite the intergranular nature of nitric acid attack of stainless steels, SCC of stainless steels in nitric acid is almost unknown. This is not due to a simple absence of stress, as postfabrication stresses at welds in austenitic stainless steels invariably approach yield. SCC is known to occur in weak nitric acid solutions and is facilitated by severe sensitization, the only known example in practice being intergranular SCC of irradiated stainless steel nuclear fuel cladding exposed to moist air, the corrosive agent being generated by nitrogen radiolysis (see Section 6.6). Slow strain rate testing reveals a link between the oxidizing power of the acid (i.e., the repassivation rate) and the metal rupturing rate (i.e., the strain rate). SCC can occur in a critical regime where repassivation kinetics are such that the crack tip remains active; otherwise, crack blunting occurs at one extreme, with the absence of sufficient crack advancement at the other. The absence of SCC of stainless steel in stronger nitric acid solutions is accordingly attributed to too rapid repassivation rates relative to practically achievable strain rates.

SCC has also been induced in zirconium by slow strain rate testing.³⁷ However, this only occurs above the azeotrope and is therefore unlikely to be relevant other than in extremely oxidizing conditions. SSC of zirconium has not been reported in plant operating in nitric acid media.

5.5 Corrosion Fatigue

Normal air fatigue processes can be exacerbated in the presence of corrosive media, leading to corrosion fatigue. As in SCC, the process is complex, requiring conditions where a crack tip is continuously formed by fatigue and its propagation is accelerated by corrosion of the exposed metal. However, in passivating media, crack blunting is also possible.³⁸ Test rig data indicate that corrosion fatigue of stainless steel in nitric acid solutions is feasible in some circumstances, indicating that careful assessment may be required. However, corrosion fatigue in nitric acid plant appears not to have been encountered in practice.

There is no indication that zirconium or similar passive metals are susceptible to corrosion fatigue in nitric acid.

5.6 Erosion Corrosion and Fretting Corrosion

These mechanisms proceed in passive metals by removing the protective oxide film, leading to oxidation of the underlying reactive metal. Erosion corrosion requires the surface oxide to be scoured by a slurry of abrasive particles. The erosion corrosion rate depends on a variety of factors, including particle weight and sharpness, but is especially sensitive to particle velocity, with attrition rates typically increasing as $(\text{velocity})^n$ where n is ~ 4 .³⁹ A dynamic process ensues in which oxide is continuously removed and regrown. In metal–environment combinations where transient metal dissolution rather than simple repassivation of the scoured surface is possible, considerable enhancement of metal loss can occur.⁴⁰ For stainless steel abraded in water and in dilute nitric acid, the attrition rates have been found to be similar. Although repassivation kinetics will differ for the two media, they will be rapid in both cases, and therefore, unless the erosion rate approached the repassivation rate, it is probable that full repassivation occurs at any given point before it is re-eroded, and therefore, no difference between the attrition rates in the two media is apparent.

It is, however, anticipated that a corrosive element will be more significant in erosion corrosion at transpassive potentials or where nitric acid is contaminated with halides (see Section 6.5) or other species, which lead to active dissolution of bared metal.

Fretting corrosion is possible when loaded surfaces move against each other in a corrodant. The process depends on loading, displacement, and cycling frequency and tends to be exacerbated if debris remains between the moving faces. Some studies in nitric acid show high attrition rates, but the relative contribution of wear and corrosion was not established and it is likely that similar processes and considerations to erosion corrosion apply.

5.7 Galvanic Corrosion

Galvanic corrosion effects can occur in nitric acid in much the same way as other media. The consequence depends on the strength and direction of the resulting potential shift and may thus be beneficial, neutral, or deleterious to the half-couple of interest. Coupling with an actively corroding base metal, such as Magnox or uranium, tends to reduce the corrosion rate of stainless steels in hot nitric acid solutions. The behavior of aluminum is more complex, ranging from slight reduction in the corrosion rate of stainless steel in concentrated nitric acid solutions,⁴¹ to marked enhancement in the stainless steel corrosion rate if the potential shift is sufficient to move stainless steel into its active region.⁴² Caution is therefore needed in predicting the effect of coupling with base metals. Deleterious effects on stainless steel arise from coupling with lead⁴³ and noble metals, such as, for example, platinum catalyst fragments (fertilizer plant) or fission product solids rich in platinum metals (nuclear reprocessing plant). Less obvious is the effect of coupling stainless steels with markedly different chromium contents; coupling 18% and 25% Cr stainless steels (i.e., 304L and 310L) results in significant increase in corrosion rate of the former and decrease in corrosion rate of the latter in hot nitric acid solution. This arises because the corrosion potential of 25% Cr stainless steel is ~ 20 mV higher than that of 18% Cr stainless steel in hot nitric acid, illustrating the extreme sensitivity of corrosion rate to potential close to the onset of full transpassivity. In less oxidizing liquors, the effects of coupling noble metals to stainless steel are much less pronounced.⁴⁴

Connections between other passive metals tend not to be problematic. For example, connections between stainless steel and zirconium plant have minimal effects on the corrosion of the junction below transpassivity; similarly, measurements on titanium/stainless steel couples show no enhanced corrosion.⁴⁵

6 Factors Affecting Corrosion Processes in Nitric Acid

6.1 Welding

Sensitization can occur during welding of stainless steels even if they are stabilized or low carbon grades, although the effects are much less pronounced than is the case for nonstabilized or high carbon steels. The formation of chromium-rich carbides at grain boundaries leaves chromium-depleted steel in their vicinity, creating a band of corrosion susceptible material running parallel to the weld but displaced a few millimeters from it. Such zones are more susceptible to intergranular corrosion in hot nitric acid, leading to heat-affected zone corrosion (weld decay). In niobium-stabilized stainless steels, the enhancement appears to be modest, amounting to at most $\sim 10\%$ of the parent metal corrosion rate. [Figure 9](#) shows an example.

Knife-line corrosion is also possible in some circumstances. This is manifest as a sharp band of corrosion penetrating along the weld–parent metal interface where temperatures exceed 1150°C during the welding process. In most nitric acid solutions, this is an issue primarily for stabilized stainless steels such as AISI 321, since titanium carbides are susceptible to dissolution releasing carbon into solid solution, which then reacts with chromium, resulting in a chromium-deficient narrow band at the weld interface. Niobium-stabilized stainless steels such as AISI 347 and 18/13/1 do not exhibit knife-line corrosion in most nitric acid solutions, but are susceptible in mixed acid systems such as nitric acid/fluoride.

In general, welds in austenitic stainless steels are at least as corrosion resistant in nitric acid as the parent metal (see [Figure 9](#)). Their coarse-grained structure may delay the onset of grain dropping relative to the parent material, but overall penetration rates are similar. Occasionally preferential attack of weld roots may be seen.

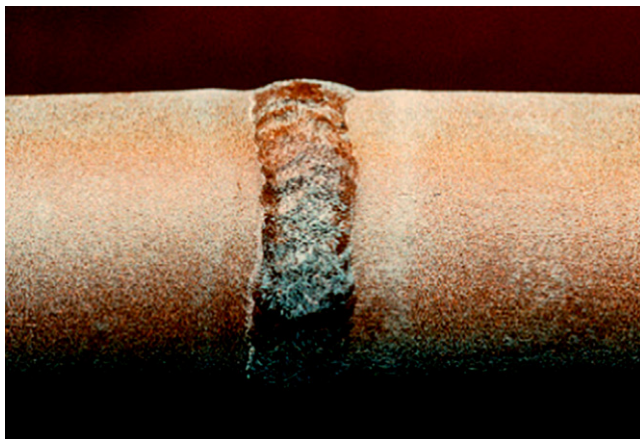


Figure 9. Weld metal and heat affected zone corrosion: 18/13/1 stainless steel tube (steam-heated) in nitric acid media. Green, D.S., BNFL unpublished work.

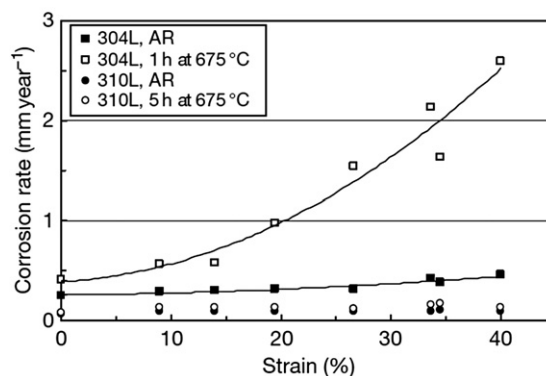


Figure 10 Effect of cold work and subsequent thermal treatment on the corrosion resistance of austenitic stainless steels in boiling 65% nitric acid. Quayle, B.E., BNFL unpublished work.

Titanium welds can be susceptible to enhanced corrosion, both the weld metal and the heat-affected zone, in hot nitric acid solutions (see Section 4.2).

6.2 Cold Work

Most information on the effects of cold work on corrosion in nitric acid relates to austenitic stainless steels. The effect of cold work is intimately linked to the thermal and mechanical history of the steel and can lead to an increase or reduction in corrosion rate depending on the circumstances. Data can appear to be contradictory, and the mechanisms by which cold work affects corrosion are not fully explained, although processes such as carbon diffusion, precipitation, and martensite formation appear to be involved.^{46,47} The relevance of the process by which cold work is achieved appears not to have been assessed and both compression by cold rolling, and tension by tensometer have been used in studying the phenomenon.

Cold work on the as-received material has generally been found to produce little effect or a marginal decrease in corrosion resistance; steels with an intrinsically lower corrosion resistance (including high Si stainless steels) and greater susceptibility to sensitization tending to fall into the latter category.^{46,48–50} Figure 10 illustrates this.

The order of cold working and thermal treatments seems to be important. Austenitic stainless steels, either sensitized⁴⁹ or partly sensitized as a result of cooling after prolonged solution treatment,^{47,51} have been found to exhibit improved corrosion resistance when subsequently cold worked, although at very high levels of cold work the corrosion resistance can begin to decrease again due to martensite formation.⁴⁷ Conversely, if austenitic stainless steels are first cold worked and then sensitized, those steels having a susceptibility to sensitization show decreased corrosion resistance with increasing levels of cold work (see Figure 10), although the effect can reach a peak at relatively low deformation for some stainless steels.⁴⁶

In practice, cold work is only likely to be problematical, at least for austenitic stainless steels, if they are in fact subsequently sensitized, for instance, by welding or by operation for prolonged periods at temperatures exceeding ~ 300 °C.⁴⁶

6.3 NO_x Gases

NO_x gases dissolve in aqueous nitric acid producing nitrous acid. The resulting concentration of nitrous acid depends on temperature and it has been shown that steady state is established relatively quickly owing to solution saturation.⁵² In the absence of other dissolved species, the redox potential of a given aqueous nitric acid solution is determined by its nitrous acid content and is amenable to calculation over a wide temperature range for a wide range of nitric acid concentrations.⁵³ Increasing nitrous acid concentration leads to an essentially perfect Nernstian decrease in solution redox potential. Nitrous acid is thus more reducing in nature than nitric acid. Metals such as zirconium exhibit the same behavior as platinum, the corrosion potential decreasing upon NO_x addition. However, because nitrous acid catalyzes nitrate reduction (see Section 3.2.2), the effect on stainless steels is a significant rise in the metal's corrosion potential (see Figure 11). These opposing effects on solution redox potential and stainless steel corrosion potential are explained in Figure 12.

Because NO_x addition increases the corrosion potential of stainless steels in pure aqueous nitric acid solutions, the corrosion rate rises.⁵² However, in the presence of more powerful oxidants, such as Cr(VI) or Ce(IV), NO_x purging significantly lowers the corrosion rate of stainless steel by reducing these strong accelerators to innocuous valency states. A similar effect was observed by Truman,⁵⁴ indicating the importance of considering the effect of NO_x gases in experimental design (see Section 7). In addition, the operating pressure and state of solution boiling could be of significance in some circumstances (see Section 6.7); lowering the partial pressure of NO_x gases would favor solution oxidation reactions, which would have the potential to exert a significant effect in solutions containing dissolved species such as chromium and cerium, particularly when the conditions were otherwise just insufficiently oxidizing to give significant equilibrium concentrations of Cr(VI) and Ce(IV) (see Sections 6.4.1 and 6.6).

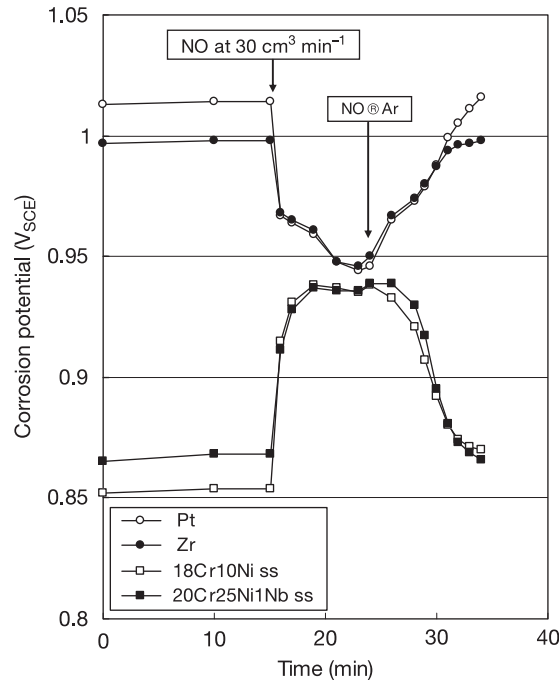


Figure 11 Effect of NO_x purging on the corrosion potential of the indicated metals in 8 M nitric acid at 100 °C. Takeuchi, M., Whillock, G.O.H., BNFL unpublished work.

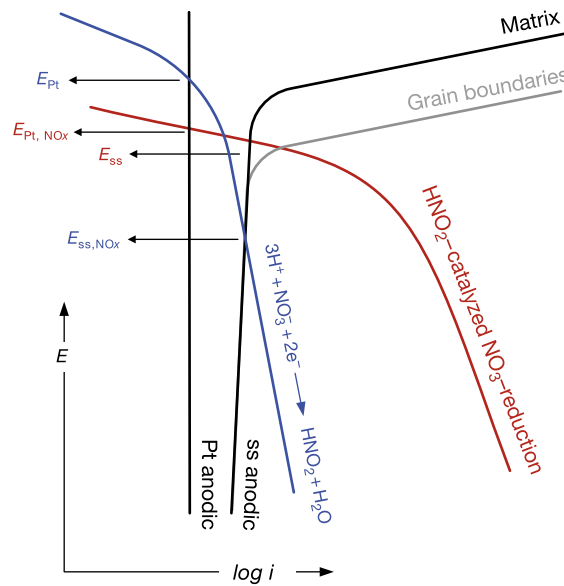


Figure 12 Evans diagram accounting schematically for the observed effect of NO_x purging on corrosion processes occurring in nitric acid. Adapted from Takeuchi, M., Whillock, G.O.H., 2002. Br. Corros. J. 37, 199–205, with permission from Maney Publishing.

6.4 Dissolved Oxidizing Species and Corrosion Products

6.4.1 Stainless steel

Many dissolved species capable of existing in more than one valency state can increase the corrosion rate of stainless steel in nitric acid; for instance in boiling 12 M nitric acid, Cr(VI), Ce(IV), Au(III), V(V), Ru(VIII), and I(VII) are strong corrosion accelerators.⁵⁵ The effect of oxidizing species like these is to provide a facile cathodic reaction, essentially replacing nitrate reduction, which is capable of polarizing stainless steel to a potential where breakdown of the passivating film occurs (specifically, Cr₂O₃ to CrO₃

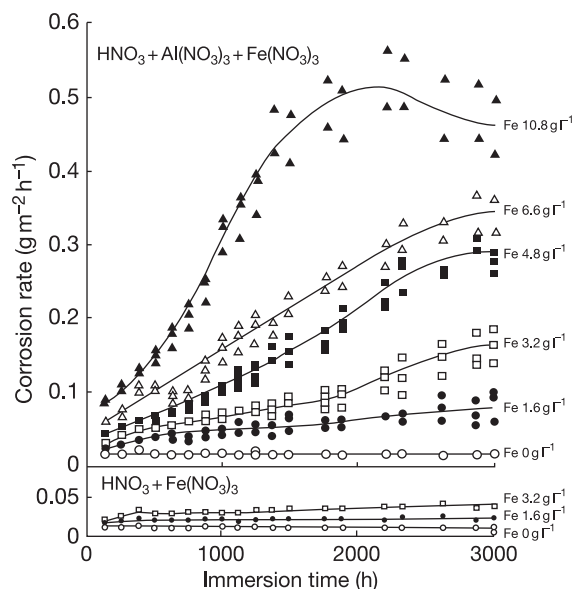


Figure 13 Effect of dissolved iron on the corrosion rate of R-SUS 304ULC stainless steel in (i) 8 M nitric acid containing 1.53 M (Al + Fe) and (ii) 9 M nitric acid, both at 100 °C. Reproduced from Hirose, Y., Suzuoki, A., Sukekawa, M., 1994. Fall Meeting of Atomic Energy Society of Japan, Japan Atomic Energy Society, Kyoto, p. 70, with permission from Atomic Energy Society of Japan.

conversion). It was proposed that any species that forms a redox couple lying in the range 1.05–1.30 V_{SCE} will produce the same effect, and hence would act as a strong accelerator.⁵⁵ This appears to provide a means of assessing the likely effect of species that cannot be tested easily (e.g., Pu, Np, Tc, etc).

However, this theory is incomplete in that it fails to predict the accelerating effect of a number of dissolved species, notably Fe (III) (see **Figure 13**),⁵⁶ Np(VI), Ru(III), and Pu(VI), the redox potentials of which are all too low to induce transpassivity, ranging between 0.53 V_{SCE} (Fe(II)/(III)) and 0.89 V_{SCE} (Np(V)/Np(VI)). The failure of Evans's approach⁵⁵ is due in part to oversimplification of the anodic metal dissolution reaction: commercial stainless steels do not remain passive until Cr_2O_3 to CrO_3 conversion occurs; instead, grain boundary attack sets in at significantly lower potential (see **Figure 12**). Thus, corrosion accelerators can be considered to fall into two classes:

- species capable of polarizing stainless steel to very high potential, sufficient to promote Cr_2O_3 to CrO_3 conversion (i.e., Cr(VI), Ce(IV), Au(III), Ru(VIII) and I(VII));
- species capable of polarizing stainless steel to slightly lower potential where intergranular attack occurs (i.e., Fe(III), V(V), Ru(III), Np(VI), and Pu(VI)), but Cr_2O_3 to CrO_3 conversion does not (except perhaps at very high concentrations).

The mechanism whereby species belonging to the latter type act to elevate the corrosion potential of stainless steel has not been rigorously established. However, it is probably due to catalysis of nitrate reduction. This has previously been suggested to account for the action of dissolved iron⁵⁷ and neptunium,⁵⁸ but kinetic studies demonstrating this unequivocally have not been reported. The catalysis mechanism, if this is correct, is obscure, as Fe(II) should be unobtainable even transiently in hot nitric acid; it may be the case that the thermodynamic properties of the transitional complex have not been properly considered.

An important feature of species such as dissolved iron is that they will produce a persistent effect, because, in nitric acid solutions of sufficient strength and temperatures to pose a corrosion threat, they will be ever-present in their highest oxidation state. Conversely, deliberate additions of species such as Cr(VI) and Ce(IV) would not be capable of creating a persistent effect (provided the solution volume to metal surface area ratio was sufficient to preclude a complicating effect from released iron corrosion product) except in extremely oxidizing conditions where the oxidation of the reduced species proceeds reasonably quickly, because the reduced forms (i.e., Cr(III) and Ce(III)) are not corrosion accelerators *per se*, but can be converted to their oxidized forms by reaction with nitric acid if the conditions are sufficiently oxidizing. **Figure 14** illustrates this effect for dissolved cerium (added as Ce(III)), indicating that cerium accelerates corrosion in boiling nitric acid stronger than ~7 M. However, at lower temperature (100 °C), 8 M nitric acid can be tolerated without significant effect of dissolved cerium, since these conditions are just insufficiently oxidizing for the production of Ce(IV) in solution. But at still lower temperature (70 °C), significant production of Ce(IV) occurs in 10 M nitric acid, but Cr(III) does not act as an accelerator under these conditions because the oxidation of Cr(III) is more difficult than the oxidation of Ce(III) owing to the more complicated chemical rearrangements required. These examples demonstrate the complex effect of temperature, nitric acid (i.e., nitrate) concentration, and dissolved species on solution oxidizing power, and hence the corrosive effect on stainless steels.

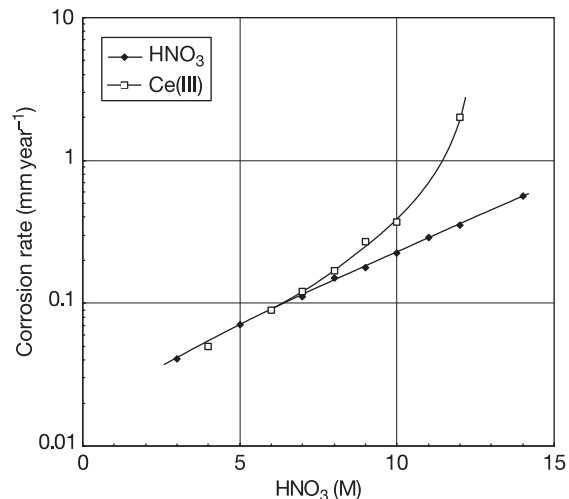


Figure 14 Effect of 0.01 M Ce (added as Ce(III)) on the corrosion rate of 18/13/1 stainless steel in boiling nitric acid solutions. Jones, F., BNFL unpublished work.

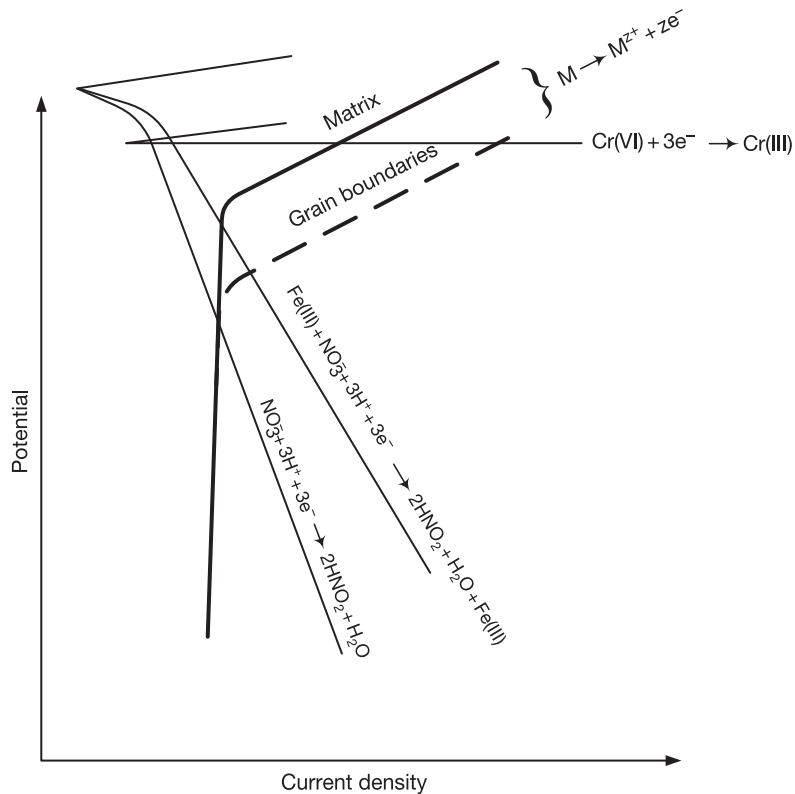


Figure 15 Schematic Evans diagram, showing increased corrosion rate due to Fe(III) and Cr(VI).

Although in hot, concentrated solutions, nitric acid is usually the most powerful oxidant present, it is not capable of polarizing stainless steel to as high a potential as can be achieved in the presence of species such as Fe(III), Cr(VI), etc.; this must be due to the kinetics of the various reduction reactions, as illustrated in Figure 15. Redox potentials alone therefore provide no certain guide to the corrosive effect of dissolved species in nitric acid solutions. The valency state of potential corrosion accelerators is of critical importance (i.e., the equilibrium concentration of the most oxidized form) and this is governed by the balance between the solution oxidation rate and the reduction rate by reaction with stainless steel. It is therefore a prerequisite of successful corrosion testing that the valency states that would be present in an operating plant liquor are maintained during the course of testing.

6.4.2 Other passive metals

Similar considerations can be applied to other metals as to stainless steels in terms of the effect of dissolved species on polarization behavior. The need for oxidants to be present for titanium to achieve passivity has already been noted (Section 4.2). Although the very passive metals such as zirconium and tantalum will be polarized by the presence of dissolved species, the absence of a low breakdown potential in nitric acid ensures that this is of little consequence for corrosion in most circumstances. Hence, these materials are generally suitable for use in oxidizing plant conditions where stainless steel would suffer an unacceptably high corrosion rate.

6.5 Dissolved Reducing Species

Dissolved ions such as chloride and fluoride in sufficient quantity can lead to weakening of passivity in nitric acid. The process is dynamic, depending on the relative concentration of halide to nitrate and appears to occur more readily at lower temperatures as the passivating tendency of the nitric acid decreases. The breakdown in passivity is readily indicated by a fall in the corrosion potential, which is intermittent at low concentrations (i.e., downward spikes are observed, increasing in frequency and duration as the halide concentration increases), but sustained at high concentrations leading to rapid active corrosion. **Figure 16** maps out regions of active corrosion and passivity for AISI 304 stainless steel in nitric acid/chloride mixtures.⁵⁹ On the borderline between activity and passivity, sustained active corrosion can be induced by the application of ultrasound.⁶⁰ Although SCC, corrosion fatigue, and erosion/fretting corrosion appear not to have been reported for nitric acid/halide systems, susceptibility to all such chemicommechanical processes is expected.

An effect of chloride ions on corrosion in nitric acid is not reported for other passive metals such as zirconium and tantalum. However, zirconium, and, to much lesser extent, tantalum are sensitive to attack by fluoride ions in nitric acid. For zirconium, a significant effect is observed as low as $1 \mu\text{g ml}^{-1} \text{F}^-$, as illustrated in **Figure 17**. For tantalum and Ta-40 Nb alloy, an increase in corrosion rate is not seen for fluoride concentrations $< 10 \mu\text{g ml}^{-1}$.⁶¹ The effect of fluoride ions can be reduced by the addition of ions such as Zr^{4+} or Al^{3+} , which form strong fluoride complexes, although in high fluoride concentrations, the effect appears to be difficult to suppress completely. The corrosion of zirconium is thus amenable to self-inhibition to some extent, although this would not be expected in a frequently-washed situation such as condensing vapor regions. **Table 4** illustrates the major effects observed.

6.6 Radiation

An overview of the basic effects of ionizing radiation of all types on corrosion processes is given by Byalobzhevskii.⁶² For nuclear reprocessing plant, the most important result of radiation is the formation of a large number of short-lived radical species, which react to produce stable molecular products. This is known as radiolysis. Radiolysis of the nitrate ion and water produces the following molecular products, although the reaction chains are long and complex involving a great number of intermediate species^{63,64}

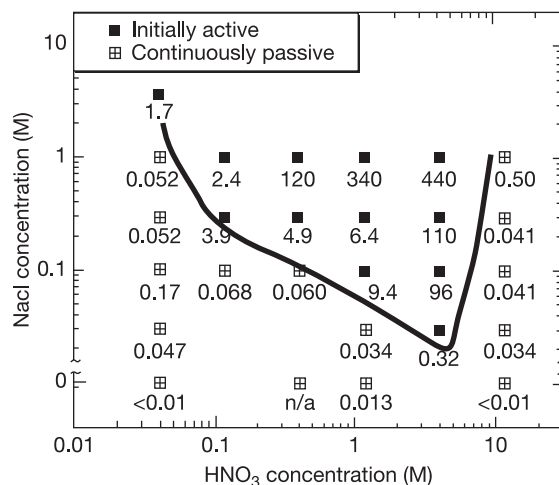


Figure 16 Plot of corrosion state and average corrosion rate (mpy) determined from immersion tests for 1 week of 304 stainless steel in aerated HNO_3/NaCl liquors at 22°C . Reproduced from Kolman, D.G., Ford, D.K., Butt, D.P., Nelson, T.O., 1997. *Corros. Sci.* 39, 2067–2093, with permission from Elsevier.

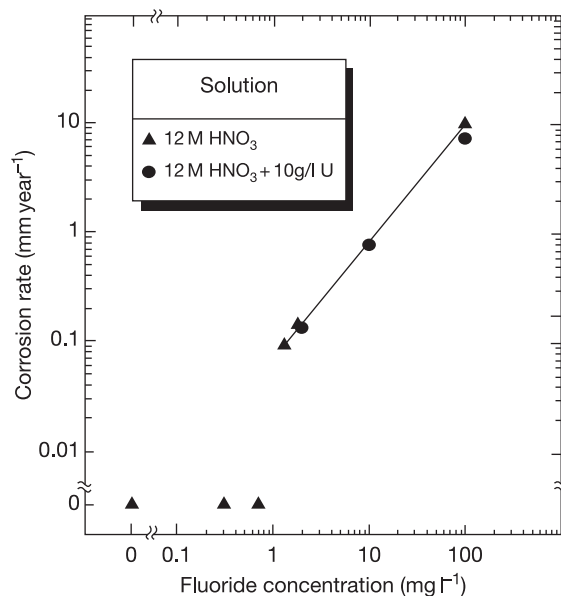


Figure 17 Effect of fluoride ion additions on the corrosion rate of zirconium 702 in boiling nitric acid solutions. Herbert, D., BNFL unpublished work.

Table 4 Effect of fluoride ion concentration and various additions on the corrosion rate of zirconium 702 in boiling nitric acid solutions

Solution			Corrosion rate (mm year ⁻¹)	
HNO ₃ (M)	F ⁻ (mg l ⁻¹)	Additions	Period 1	Period 2
12	0	–	0.001	0.001
	0.1	–	18.9	10.5
	0.1	10 g l ⁻¹ U	13.9	8.0
	0.1	3.5 g l ⁻¹ Bi	12.9	7.3
	0.1	1.1 g l ⁻¹ Al	1.6	1.4
3	1.8	–	29.6	29.6
	1.8	1.8 g l ⁻¹ Zr	19.1	20.1
	0.5	2.4 g l ⁻¹ Zr	1.7	1.4
	0.5	4.8 g l ⁻¹ Zr	0.002	0.001

Note: Two 24 h test periods without solution renewal.

Source: Herbert, D., BNFL unpublished work.

Radiolytic reactions will be affected by the nitrate concentration, dissolved species, temperature and the radiation type. At high dose rates, appreciable levels of nitrous acid (up to $\sim 0.5 \text{ g l}^{-1}$) are formed, though the nitrous acid would be expected to become increasingly unstable at higher temperatures. Although the action of hydrogen peroxide has not been exhaustively assessed, it probably has little direct impact on corrosion in hot nitric acid as it decomposes by reaction with nitric acid, producing nitrous acid.

Although data are sparse, the overall effect of the irradiation of nitric acid on corrosion appears to be similar to that produced by nitrous acid. Analogous to the effect of NO_x purging (Figure 11), in pure nitric acid solutions the corrosion potential of stainless steel is increased and hence the corrosion rate is increased slightly, as illustrated by Figure 18.⁶⁵ The effects of irradiation are more pronounced when nitric acid contains dissolved oxidizing species where reduction of oxidizing species such as Cr(VI) and Ce(IV) can profoundly reduce corrosion rates by maintaining the corrosion potential below transpassivity.⁵⁵ Whether the oxidation by the acid or reduction by irradiation predominates depends on the nitric acid concentration and temperature, increase of either favoring oxidation, and radiation dose rate, increase of which favors reduction. The effect of radiation on the corrosion of stainless steels in nitric acid containing the oxidizing species Cr(VI), Ce(IV) and Ru(III) is demonstrated in Figure 19.⁶⁶ It is notable that in the case of Ru(III) the effect is less than for Cr(VI) and Ce(IV).

By analogy with the behavior of Ce(IV) and Cr(VI), it is expected that other species of the same type (i.e., Ru(VIII), I(VII) and Au(III)⁵⁵) would also be reduced by high radiation fields and thus exert negligible corrosive effect toward stainless steels. Redox

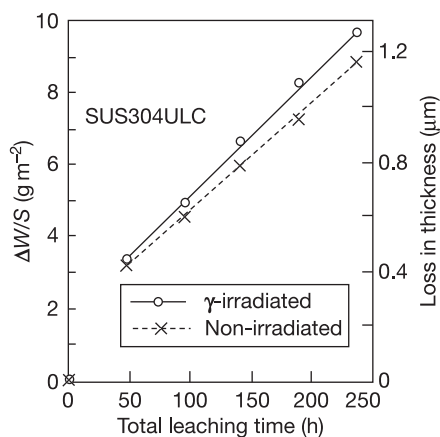


Figure 18 Effect of Co-60 radiation (40 kGy h^{-1}) on the corrosion rate of SUS 304ULC stainless steel in boiling (at atmospheric pressure) 9 M nitric acid. Reproduced from Yamamoto, T., Tsukui, S., Okamoto, S., *et al.*, 1996. *J. Nucl. Mater.* 228, 162–167, with permission from Elsevier.

potential considerations indicate that nitrous acid is incapable of reducing either Fe(III) or V(V); hence, no effect of radiation on their corrosive effect results.

Because the corrosion resistance of metals such as zirconium and tantalum is unaffected by oxidizing species in solution (Section 6.4.2), no effect of radiation is apparent. No effect of radiation on the corrosion resistance of titanium has been reported, although a deleterious effect might be expected if reliance were placed on oxidizing ions, rather than dissolved titanium, for the maintenance of passivity.

6.7 Solution Boiling

The effects, if any, of boiling on corrosion processes on passive metals appear to be minimal in simple nitric acid systems. This is demonstrated by the failure of Arrhenius data to show a marked discontinuity at the boiling point (see, e.g., Figure 3). Other studies found no difference between corrosion rates measured in boiling (under reduced pressure) and nonboiling nitric acid solutions containing dissolved iron.

However, in a more complex nitric acid solution containing many dissolved species a reduction in corrosion rate is apparently found in the boiling solution. Such systems are very corrosive and there are several possible mechanisms which could occur once boiling commences including enhanced mass transport, reduction in dissolved NO_x by mechanical stripping from solution, removal of reactants and corrosion products from the reacting metal surface by agitation, local concentration effects in nucleating bubbles, limitation of corrodant access to the metal surface by gas blanketing and facilitation of interaction between dissolved species. It may be the case that removal of iron and chromium corrosion products from the corrosion surface by agitation reduces corrosion.

In practice, individual systems may need to be tested if the possibility of a boiling effect is of interest.

6.8 Heat Transfer

It would not be expected that the transfer of heat *per se* would affect corrosion processes and to date heat flux has not been demonstrated to have an effect on the corrosion process which cannot be assigned to the metal/liquor interface temperature. However, consequent processes such as changes of interface temperatures, modification of the Helmholtz layer, effects on diffusion/mass transport, solute concentration and gas blanketing under boiling could affect corrosion processes.

Data, which are limited, are principally derived from either heated disc^{35,67,68} or heated tube rigs^{28,69} and can be difficult to interpret. The former suffer from crevice corrosion effects on stainless steel, and the latter from difficulties in maintaining controlled and even heating.

In most simple nitric acid systems, the predominant factor determining the corrosion rate is the effective interface temperature; this will lie between that of the metal heat transfer surface and that of the liquid, but can be difficult to determine with precision. So at a constant metal surface temperature the presence of cooler acid at the metal surface under heat flux reduces the corrosion rate compared to a fully isothermal system.^{35,67}

However, it is plausible that oxidation processes such as Cr(III) to Cr(VI) could proceed on heat transfer surfaces with a consequent increase in corrosion providing the surface is of sufficient temperature even if the liquors are significantly cooler. When boiling occurs on the heat transfer surface, the effects may be further complicated. Although no effect of nucleate boiling on austenitic stainless steel corrosion was found at a heat flux of 9 kW m^{-2} ,³⁵ other workers indicate that boiling improves heat transfer and leads to a reduction in metal surface temperature with a consequent reduction in corrosion rate.⁶⁷ Conversely, other

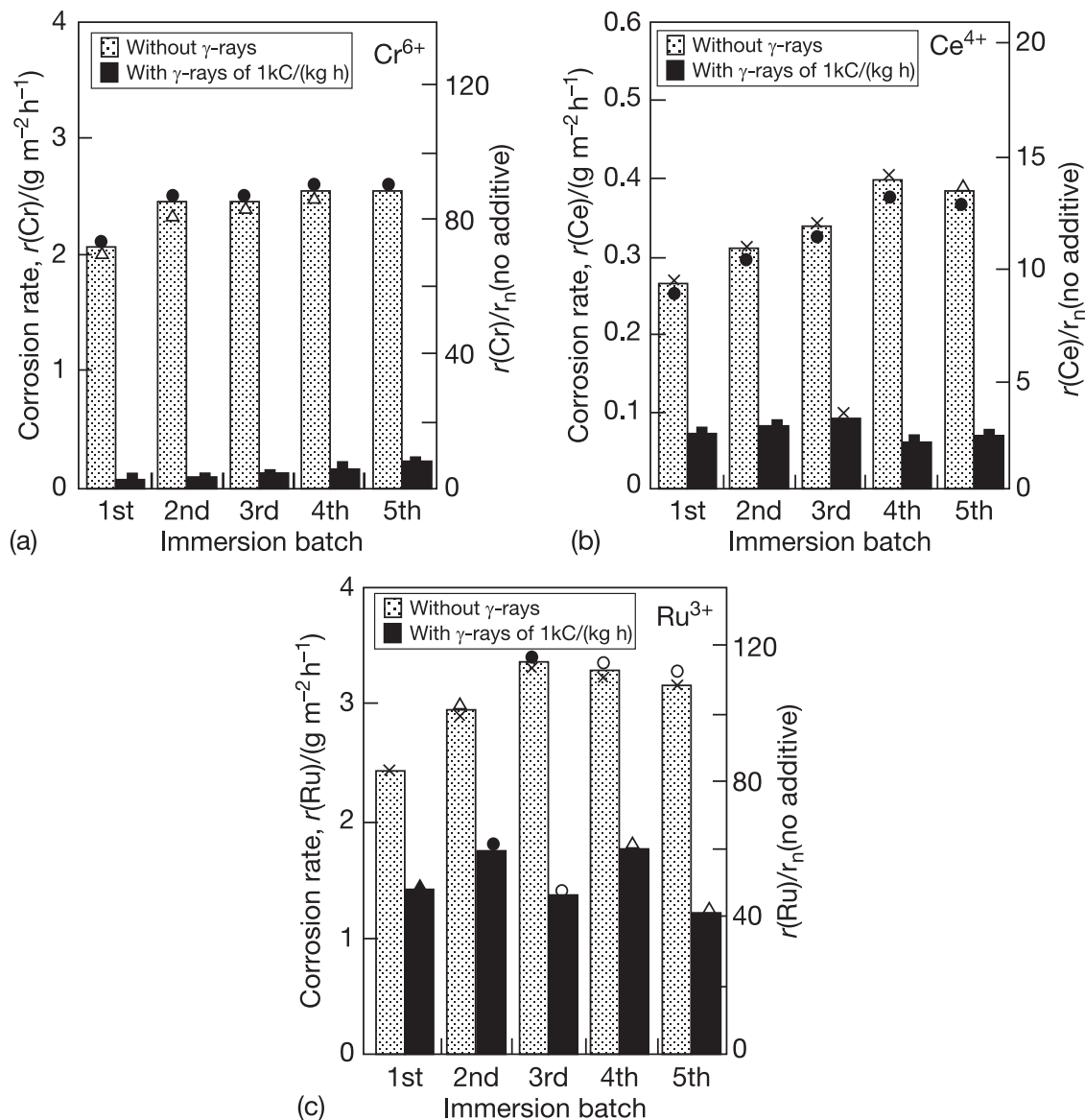


Figure 19 Effect of Co-60 radiation (40 kGy h^{-1}) on the corrosion rate of SUS 304ULC stainless steel in boiling 9 M nitric acid containing: (a) 0.02 M Cr(VI); (b) 0.01 M Ce(IV); (c) 0.004 M Ru(III). Reproduced from Yamamoto, T., Tsukui, S., Okamoto, S. *et al.*, 1998. J. Nucl. Sci. Technol. 35, 353–356, with permission from Atomic Energy Society of Japan.

workers suggest an increased oxidizing effect on heated surfaces, generally consistent with solute rejection from nucleating voids.⁶⁸ It is evident that further, carefully controlled, studies are required to resolve the debate.

Industrial experience tends to support the view that corrosion processes on heated surfaces can be affected relative to isothermal surfaces, but that the effects can vary from increasing the corrosion rate where temperatures are increased at the heat transfer face to decreasing them where heating and boiling are so rapid as to create gas-blanketing effects.

6.9 Liquor-Line and Vapor Regions

No significant liquor-line corrosion effects have been found for stainless steel exposed to nitric acid liquors, either in operating plant or in test conditions.²⁸ Significant effects would not be expected on other passive metals.

Enhanced corrosion effects can occur in vapor–condensate phases, however. This can occur, for instance, where condensing films run onto heated tubes in boiler systems and are reevaporated allowing high solute concentrations to build up. In some circumstances transpassivity can be reached with consequent rapid corrosion. Instances have occurred in situations as diverse as stainless steel nitric acid transport tankers and industrial acid boilers. For stainless steels, such thin liquor film effects are considered largely to be due to corrosion product build-up, since both Fe(III) and Cr(VI) are corrosion accelerators (Section 6.4.1).

Conversely, titanium is prone to corrosion in condensing systems owing to continuous removal of its corrosion products (Section 4.2), as is aluminum (Section 4.4).

In mixed acid systems, enhanced corrosion can occur in vapor regions if preferential partitioning of the active species occurs. For stainless steels in nitric acid/chloride solutions, the formation of volatile nitrosyl chlorides may be implicated.⁷⁰ Preferential partitioning of fluoride to vapor occurs, hence enhanced corrosion of zirconium in vapor regions above nitric acid/fluoride liquors might be expected; however, the absence of reports of any such effect in operating plant points to the presence of fluoride complexants that prevent or limit fluoride partitioning.

7 Corrosion Testing Methods

7.1 Ranking Tests

These are intended to indicate general trends of corrosion resistance for different materials or to show the effect of, for example, different heat treatments. They are also used to screen different batches of material procured for plant construction to ensure consistency of supply.

For stainless steels in nitric acid, the Huey test,⁷¹ which is covered in both ASTM⁷² and European standards,⁷³ is the most frequently used procedure for the assessment of intergranular or general corrosion of stainless steel. It can also form the basis of assessing general corrosion rates of other metals intended for nitric acid service. In this test, a prepared coupon is subjected to five successive 48 h test periods in boiling 65% nitric acid with the solution renewed at each period, the periodic corrosion rate being determined by weight loss. It is noted that the acid specification is more stringently controlled in the ASTM specifications with F⁻ limited to <0.1 ppm as opposed to <3 ppm in the European standard. This could be significant for some passive materials such as zirconium.

Even with such a simple test, care must be taken to ensure consistency of apparatus (e.g., the type of condenser used affects the results obtained⁵⁴) and the selection of a consistent ratio of liquor volume to metal surface area, since this affects the rate of corrosion product build-up. Maintenance of a constant end, to side, to face grain ratio is essential in materials that have any susceptibility to end grain corrosion; in particular, care is needed in the selection of a consistent coupon design which avoids the exposure of excessive or varying end grain fraction (see [Figure 7](#)). Although not recommended in the test procedures, some assessment and recording of the attack on the end grain is usually worthwhile. Additional periods of testing may be required to discriminate between similar materials.

7.2 Prediction of In-Service Corrosion Rates

Owing to the dependence of the corrosion rate of stainless steels in nitric acid on microstructural orientation (see Section 5.1), corrosion rates derived from periodic weighing of immersed coupons can significantly overestimate in-service corrosion rates and can also be subject to considerable variability if different coupon designs are used; the latter in particular prevents meaningful comparison of test data in a great many instances. Conversely, owing to the progressive nature of intergranular attack, short-term tests can lead to significant underestimation of in-service corrosion rates. These problems can be overcome in a number of ways:

- direct measurement of the corrosion rate by metallurgical sectioning transverse to the surface of interest (this works only for relatively short test times otherwise grain dropping removes the initial surface)³³;
- short-term weight loss measurements made on specially-prepared coupons where the surface of interest has been corroded to the grain dropping stage, but all other surfaces are freshly-ground²⁷;
- weight loss measurements made on a series of coupons specially prepared to have very different ratios of plate, side and end surfaces, all these previously having been corroded to the grain-dropping stage.³³

In addition, it is possible to seal exposed end grain by overlaying it with weld metal,⁷⁴ but this can produce undesirable metallurgical changes and usually requires excessively large coupons unless laser techniques are employed.

All these methods are time consuming, but are necessary where a high confidence of plant life prediction is required. However, none are effective at predicting pit depths where tunneling occurs on the end grain,³³ so prediction of forging life, for instance, is difficult.

Great care must of course be paid to reproducing anticipated plant conditions as closely as possible owing to the many factors which affect the corrosion rate (see Section 6).

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