

# Effect of dissolved chromium species on the corrosion of stainless steel in nitric acid

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The effect of Cr(vi) species in HNO<sub>3</sub> (concentrations 15–3 M) on the corrosion rate of stainless steel has been investigated. The gaseous phase over the HNO<sub>3</sub> was carefully controlled using Ar, NO, NO<sub>2</sub> or N<sub>2</sub> purging. With Ar purging the corrosion rate increased when the Cr(vi) concentrations were above 0.05 M. There was evidence that the reduction of Cr(vi) leads to insoluble Cr reduction products on the surface of the steel. Sparging of nitric acid by NO and/or NO<sub>2</sub> caused the reduction of any Cr(vi) species present in the solution, to Cr(III) in a few minutes. However, with no Cr(vi) present, the effect of continuous purging with NO and/or NO<sub>2</sub> was to increase the steel corrosion rate when compared with Ar purged solutions, due to catalysis of nitrate reduction by the NO<sub>x</sub>. The conversion of Cr(III) to Cr(vi) by nitric acid was shown to require high concentrations of nitric acid, high temperatures and low partial pressures of NO<sub>2</sub> over the liquid phase.

Keywords: *stainless steel, nitric acid, corrosion, chromium(vi), nitrogen oxides*

## 1. Introduction

Stainless steels are generally passive in contact with nitric acid and hence exhibit good corrosion resistance [1–3]. The passivity is due to the formation of Cr<sub>2</sub>O<sub>3</sub> (containing some Fe<sup>3+</sup>, Ni<sup>2+</sup> etc.) on the electrode surface. Cr(III), Fe(III) and Ni(II) species are slowly generated in the solution when the steel is in the passive region. If strong oxidizing agents [4] are added to the nitric acid the corrosion potential sometimes lies in the transpassive region with consequent rapid corrosion and the production of Cr(vi) species.

The effect of Cr(vi) additions on the corrosion rate of 18–30% Cr steel in boiling nitric acid has been investigated previously [5–9]. Early work by Truman [5] and McIntosh and Evans [6, 7] showed that the rate of steel corrosion is approximately linearly related to the Cr(vi) concentration in the nitric acid and that whilst trivalent chromium has no accelerating effect itself, it can be oxidised by boiling nitric acid to Cr(vi). Thus an autocatalytic process leading to steel breakdown is possible involving the oxidation of Cr(III) by the boiling nitric acid and the reduction of Cr(vi) on the corroding steel. It was also found that [5–7] higher corrosion rates are obtained with open Allihn condensers than with sealed flasks containing cold finger condensers. This was attributed to the fact that cold finger condensers in sealed vessels retain reducing gases from the nitric acid and prevent oxidation of Cr(III) to Cr(vi). Later work by Maness [8]

and by Smith and Purdy [9] showed that oxidation of Cr(III) in boiling nitric acid solutions is often a much slower process than Cr(vi) reduction on steel. This means that the rate determining step in the steel corrosion could be the oxidation of Cr(III). Maness [8] also found that Cr(vi) in nitric acid could be reduced to Cr(III) by bubbling NO<sub>2</sub>(g) through the solution, which could be important in relation to corrosion product build up in long term stainless steel storage tanks. Kolman *et al.* [10] in a study of the effect of HNO<sub>3</sub> and Cl<sup>-</sup> on the corrosion of stainless steel found that the surface area to volume ratio was important. They attributed this effect to the build up of reduction products from the nitric acid in the solution and the autocatalytic nature of the nitric acid reduction process.

Unfortunately, in most of the previous work in this area, the composition of the gaseous phase over the nitric acid was not well defined, since the experiments were carried out using boiling nitric acid with a variety of condenser systems. Also, since the addition of salts to nitric acid generally increases the boiling point of the solution, there is in this earlier work a problem in that measurements have sometimes been compared at different solution compositions and at different temperatures. In the present work the gas phase above the acid was carefully controlled by bubbling Ar, NO, NO<sub>2</sub> or N<sub>2</sub> through the acid and the nitric acid solutions were always at temperatures below their boiling points.

## 2. Experimental details

All electrochemical measurements were made using a three electrode glass cell connected to a Solartron 1286 potentiostat controlled by a PC. The software package used was Corrware (Scribner Associates, Charlottesville, VA). The cell sat in an oil bath with the saturated calomel reference electrode (SCE) kept at room temperature and connected to the Luggin capillary of the cell via a three way tap. This allowed the solution containing the working and counter electrodes to be heated without affecting the reference electrode. All potentials quoted in this paper are referred to the SCE at room temperature. A platinum counter electrode was used throughout and the working electrode consisted of a 3 cm long (6 mm dia.) piece of 304L stainless steel (C, 0.019%; Si, 0.74%; Mn, 1.38%; Ni, 9.38%; Cr, 18.21%; P, 0.002%; S, 0.023%; Fe, bal.) rod sealed in PTFE by a screw thread. The electrodes were pretreated by sweeping the potential of the electrode from an active to a passive potential ( $-0.4$  to  $+0.5$  V) at a sweep rate of  $1 \text{ mV s}^{-1}$  in a solution of  $3 \text{ M}$  nitric acid at room temperature (r.t.),  $(20 \pm 2)^\circ\text{C}$ , to provide a consistent surface for the measurements. However, when the steel showed visible signs of corrosion either a new electrode was used or a fresh surface was generated by turning it down on a lathe. The electrode was left on open circuit until the potential (OCP) came to a steady value (typically 30 min). Linear sweep measurements were then made at sweep rates of  $1.0$  and  $0.1 \text{ mV s}^{-1}$ , always starting at cathodic potentials. In most experiments there was little difference between the  $i/E$  data for the two different sweep speeds, making it reasonable to assume that 'steady state' measurements were being made. Analysis of the data was carried out using the 'Fit Auto-Tafel' option of the software package, which fitted Tafel lines within  $250 \text{ mV}$  of the open circuit potential, yielding the values of corrosion current, corrosion potential and the Tafel slopes. All corrosion rates quoted in this paper are in units of  $\mu\text{A cm}^{-2}$  ( $1 \mu\text{A cm}^{-2} \equiv 7.9 \mu\text{m y}^{-1}$  for this steel).

The effect of nitric acid concentration and temperature on the corrosion current and corrosion potential of 304L stainless steel was studied using  $3$ ,  $12$  and  $15.8 \text{ M}$  nitric acids (AnalaR). Measurements were made at r.t.,  $60$  and  $100^\circ\text{C}$ , at a sweep rate of  $1 \text{ mV s}^{-1}$  and with  $\text{Ar(g)}$  purging.

The effect of various concentrations of  $\text{Cr(vi)}$  in  $3$  and  $12 \text{ M}$  nitric acid on the corrosion rate of the steel was also investigated. All these measurements were made with  $\text{Ar(g)}$  purging and at sweep rates of  $1.0$  and  $0.1 \text{ mV s}^{-1}$ . Some electrochemical estimates of corrosion rates were compared with those obtained by weight loss measurements in similar solutions. The effect on the corrosion rate of purging by  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{N}_2$  rather than argon was also explored.

Polarization curves on gold were carried out on the same equipment as above, using a gold sheet working electrode, a platinum counter electrode and

a SCE reference electrode. All sweeps on gold were made at  $0.1 \text{ mV s}^{-1}$ .

Conversion of  $\text{Cr(III)}$  to  $\text{Cr(vi)}$  was carried out starting with  $0.01 \text{ M}$   $\text{Cr(III)}$ . Various concentrations of nitric acid and three different temperatures were explored, using a heating mantle and  $250 \text{ ml}$  round bottom flasks, containing  $150 \text{ ml}$  of solution. Long condensers were fitted to avoid any loss of solution during the experiment. Samples were taken out periodically and analysed using a u.v./vis. spectrophotometer (Unicam 5675 spectrometer).

## 3. Results and discussion

### 3.1. Comparison of nitric and sulphuric acids

Figure 1 shows typical linear sweep measurements and compares results for stainless steel in nitric and sulphuric acids. For sulphuric acid the cathodic reaction is hydrogen ion reduction while in nitric acid it is clear that the cathodic reaction must be largely nitrate reduction, since the cathodic reaction is occurring at potentials which are positive to the  $\text{H}_2/\text{H}^+$  reversible potential. The anodic reactions are similar and involve the dissolution of the stainless steel. The sweep in sulphuric acid shows only a small active/passive transition and an open circuit potential of  $-0.33 \text{ V}$ . This compares with an open circuit potential of  $+0.42 \text{ V}$  in nitric acid, a difference of about  $0.75 \text{ V}$ .

### 3.2. Effect of nitric acid concentration and temperature on the corrosion rate

Corrosion rate measurement results for 304L stainless steel in three concentrations of nitric acid ( $3$ ,  $12$  and  $15.8 \text{ M}$ ) at three different temperatures (r.t.,  $60$  and  $100^\circ\text{C}$ ) are shown in Table 1. It is clear from the  $\log i$  against  $E$  measurements (not shown) which lie

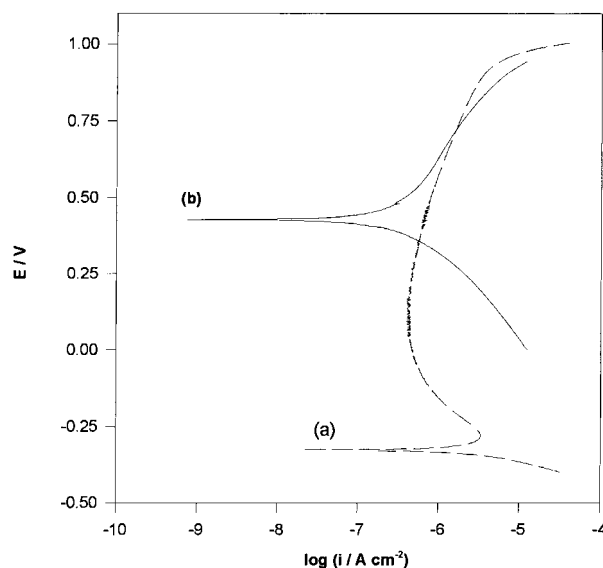


Fig. 1. Linear sweep measurements for 304L stainless steel in (a)  $1.5 \text{ M}$   $\text{H}_2\text{SO}_4$  and (b)  $3 \text{ M}$   $\text{HNO}_3$ . In both cases the sweep rate was  $1 \text{ mV s}^{-1}$  and solutions were  $\text{Ar(g)}$  purged.

Table 1. Corrosion currents and corrosion potentials of 304L stainless steel in 3, 12 and 15.8 M nitric acids at r.t., 60 °C and 100 °C

Sweep rate, 1 mV s<sup>-1</sup> and under Ar(g) bubbling

Acid strength	Corrosion potential/mV			Corrosion current/ $\mu\text{A cm}^{-2}$		
	20 °C	60 °C	100 °C	20 °C	60 °C	100 °C
3 M HNO <sub>3</sub>	380	512	515	0.10	0.57	0.88
12 M HNO <sub>3</sub>	753	934	896	0.58	4.54	8.91
15.8 M HNO <sub>3</sub>	822	929	948	0.88	4.89	10.10

behind Table 1 that the effect of temperature is to increase both the currents due to nitric acid reduction and the currents due to passive/transpassive metal dissolution. Hence the corrosion current increases with increasing temperature. Increasing the acid concentration causes the currents due to nitric acid reduction to increase considerably, whilst only slightly increasing those due to passive/transpassive metal dissolution. The overall effect is to increase the corrosion current with increasing acid concentration.

### 3.3. Electrochemistry of nitric acid

Figure 2 shows linear sweep measurements on gold working electrodes in solutions of 3 M nitric acid at 100 °C under Ar(g), NO(g) and NO<sub>2</sub>(g) purging, at a sweep rate of 0.1 mV s<sup>-1</sup>. From the polarisation curves it can be seen that NO(g) and NO<sub>2</sub>(g) are oxidized (to nitrate ion) at electrode potentials positive to 0.844 and 0.860 V, respectively, in reactions which are diffusion controlled. These potentials are the open circuit potentials which a gold electrode would take up if it were in contact with 3 M HNO<sub>3</sub> saturated with NO or NO<sub>2</sub>. The mass balance equations for these oxidations are as follows:

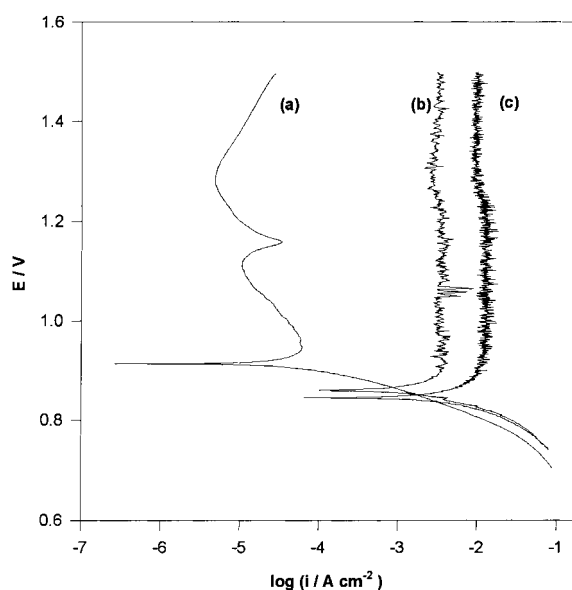
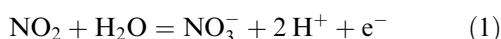
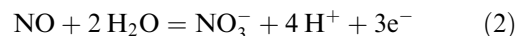
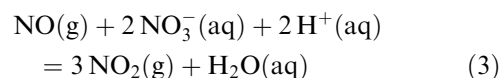


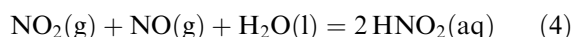
Fig. 2. Gold polarisation curves in (a) 3 M HNO<sub>3</sub> + Ar(g), (b) 3 M HNO<sub>3</sub> + NO<sub>2</sub>(g) and (c) 3 M HNO<sub>3</sub> + NO(g). All sweeps done at 0.1 mV s<sup>-1</sup> and at 100 °C.



The cathodic reaction for all three plots shown in Fig. 2 is nitrate reduction, since the currents are identical in all three cases and, in the case of argon, the current can only be due to nitrate reduction. Substitution of N<sub>2</sub> or N<sub>2</sub>O for argon showed that N<sub>2</sub> and N<sub>2</sub>O are electrochemically inert over the potential range used. Previous work [11] has shown that reduction of nitric acid on an inert electrode leads to a mixture of species, including both NO and NO<sub>2</sub> in the gas phase. This is expected from thermodynamic considerations. Thus for the reaction



using data from standard tables [12] the standard free energy change at 100 °C can be estimated as 27 kJ mol<sup>-1</sup>. This gives the equilibrium constant for Reaction 3 as 2 × 10<sup>-4</sup> (in terms of the partial pressures/atm for the gaseous reactants and concentration/M for NO<sub>3</sub><sup>-</sup>(aq) and H<sup>+</sup>(aq)). Thus, if the partial pressure of NO above the liquid is maintained at 1 atm and the system is allowed to come to equilibrium the partial pressure of NO<sub>2</sub> will be 0.25 atm for 3 M HNO<sub>3</sub> at 100 °C. Likewise, if the total pressure of NO and NO<sub>2</sub> above the liquid is maintained at 1 atm and the system is allowed to come to equilibrium the partial pressure of NO<sub>2</sub> will be 0.24 atm and that of NO 0.76 atm for 3 M HNO<sub>3</sub> at 100 °C. This means that if the initial product of nitric acid reduction were NO some NO<sub>2</sub> would be generated via Reaction 3 and, conversely, if the initial reduction product were NO<sub>2</sub> some NO would be generated via Reaction 3. This calculation also means that when NO<sub>2</sub> is bubbled through the nitric acid NO will be formed. A similar calculation shows that in the presence of NO and NO<sub>2</sub>, HNO<sub>2</sub> will be formed via



Thus, if the partial pressure of NO<sub>2</sub> is 0.24 atm and that of NO 0.76 atm, then [HNO<sub>2</sub>] = 0.21 M in 3 M acid at 100 °C, since the equilibrium constant for Reaction 4 is 0.26 at 100 °C (using standard thermodynamic data). In any real system where nitric acid is being reduced electrochemically, the concentrations of the reduction products NO, NO<sub>2</sub> and HNO<sub>2</sub> in the nitric acid at any time, will of course depend on the particular circumstances. For example

argon purging of the nitric acid will mean that the reduction product concentrations will be very low at all times. Because the reduction species are present as a mixture, then the experimentally measured zero current potentials i.e. 0.844 and 0.860 V will only approximate to the thermodynamic reversible potentials for Reactions 1 and 2, respectively. The calculated thermodynamic reversible potentials for Reactions 1 and 2 (using standard data and our own measurements of the potential of a reversible hydrogen electrode against SCE) are 0.763 and 0.809 V, respectively. The difference between the measured and experimentally observed potentials is probably due to the uncertainty in the extrapolations from room temperature to 100 °C involved in the calculations.

Figure 3 shows the linear sweeps obtained for stainless steel under different purge gases. It is clear that the open circuit potential of the stainless steel is brought to more positive values by both NO and NO<sub>2</sub>. In fact the values are close to the values for Reactions 1 and 2 found on gold, i.e. stainless steel is behaving like an inert electrode in relation to Reactions 1 and 2. In the presence of NO and NO<sub>2</sub> the current for nitrate reduction is always higher than in the presence of argon. This must mean that the nitrate reduction is catalysed/autocatalysed by the NO and NO<sub>2</sub>, thus leading to higher corrosion potentials and corrosion currents than in the presence of argon. Those for NO<sub>2</sub> are shown in Table 2 (Note that in the presence of NO<sub>x</sub> the corrosion current was estimated by finding the current flowing in the absence of NO<sub>x</sub> at the open circuit potential in the presence of NO<sub>x</sub>.) Hence in nitric acid, which has reduction products (NO, NO<sub>2</sub>) dissolved in it the corrosion rate of the stainless steel will be higher than in fresh nitric acid. Therefore, the presence of high concentration NO<sub>x</sub> in a solution of nitric acid may result in a maximum

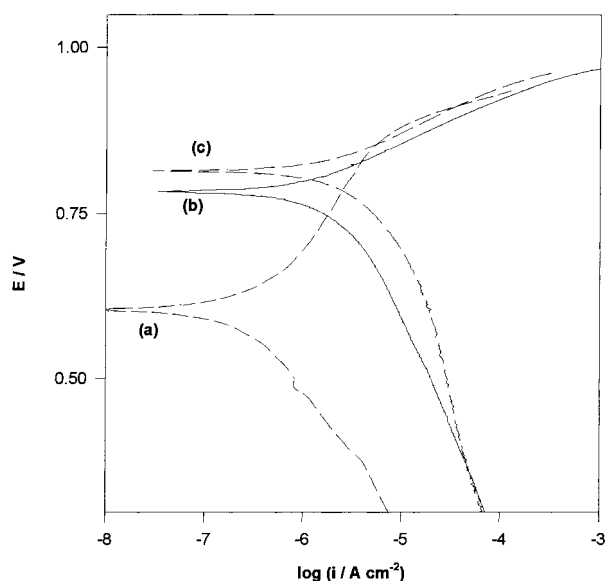


Fig. 3. Linear sweep measurements for 304L stainless steel in 3 M HNO<sub>3</sub> under (a) Ar(g), (b) NO(g), and (c) NO<sub>2</sub>(g). All sweeps done at 0.1 mV s<sup>-1</sup> and at 100 °C.

Table 2. Corrosion currents and corrosion potentials of 304L stainless steel in solutions of 3, 12 and 15.8 M nitric acid at 100 °C under Ar(g) and NO<sub>2</sub>(g) purging

Sweep rate, 0.1 mV s<sup>-1</sup>

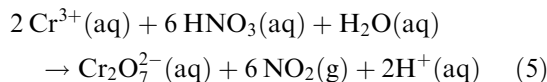
Solution	Corrosion potential/mV		Corrosion rate/μA cm <sup>-2</sup>	
	Ar(g)	NO <sub>2</sub> (g)	Ar(g)	NO <sub>2</sub> (g)
3 M HNO <sub>3</sub>	608	783	0.27	1.17
12 M HNO <sub>3</sub>	847	941	4.27	55.94
15.8 M HNO <sub>3</sub>	944	1000	6.41	63.66

potential being imposed on the stainless steel, which may prevent transpassive corrosion being reached but will result in faster corrosion.

In other experiments we found that Cr(vi) is rapidly reduced by NO<sub>2</sub> and NO to Cr(III), so that it was not possible to study the effect of Cr(vi) on the steel in the presence of NO<sub>2</sub> and NO purge gases. This means that whilst NO and NO<sub>2</sub> cause an increase in the corrosion rate of the steel when permanently bubbled, they could be useful gases to use for short sparges to prevent the acceleration which is due to Cr(vi) by reducing it to Cr(III).

### 3.4. Chemistry of Cr(vi) and Cr(III) in nitric acid

Since the presence of Cr(vi) in nitric acid is known to increase the corrosion rate of stainless steel, it is important to understand the conditions under which Cr(III) (which is generated by the steel corrosion in the passive condition) can be converted to Cr(vi) in nitric acid. The reaction for the conversion of Cr(III) to Cr(vi) in nitric acid is



Equilibrium constants were calculated for Reaction 5 from standard thermodynamic data and used to calculate the  $[\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr(III)}]^2$  for a series of different acid concentrations, partial pressures of NO<sub>2</sub> and temperatures. The data are shown in Fig. 4. It can be seen that for appreciable conversion to occur the following are required: (i) a high temperature, (ii) a high concentration of nitric acid and (iii) a low partial pressure of NO<sub>2</sub>(g) above the solution.

Two simple ways in which the partial pressure of NO<sub>2</sub>(g) can be reduced are purging the solution with an inert gas and rapidly boiling the solution. It should be noted that Fig. 4 provides information as to which conditions are required for the reaction to become thermodynamically feasible and that it does not give any information on the rate of conversion. (It should also be noted that for closed systems there is no prospect of lowering the partial pressure of NO<sub>2</sub>(g) above the solution since an equilibrium will be set up that cannot readily be changed without large changes in solution composition.)

Figures 5 and 6 show experimental data for the conversion of Cr(III) to Cr(vi) in 12 and 15.8 M

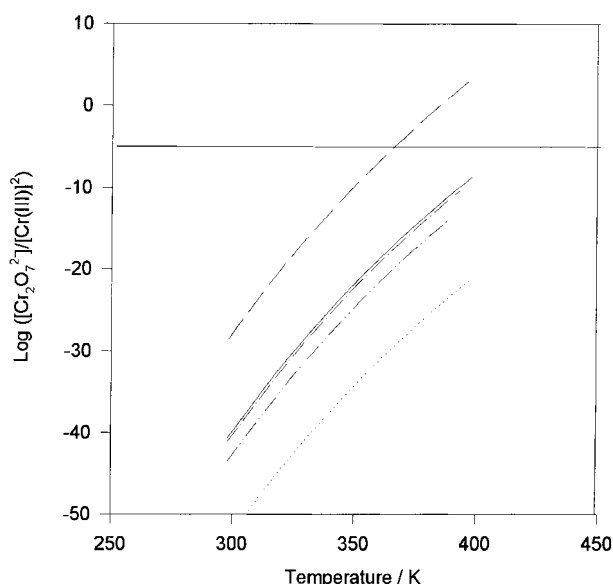


Fig. 4. Theoretical equilibrium ratios for Cr(III) and Cr(VI) as functions of nitric acid concentration, temperature and partial pressure of  $\text{NO}_2(\text{g})$ . Key: (.....)  $\log ([\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}(\text{III})]^2)$  against temp. (in 12 M  $\text{HNO}_3$  at 1 atm  $\text{NO}_2$ ); (---)  $\log ([\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}(\text{III})]^2)$  against temp. (in 3 M  $\text{HNO}_3$  at  $10^{-2}$  atm  $\text{NO}_2$ ); (-.-.-)  $\log ([\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}(\text{III})]^2)$  against temp. (in 12 M  $\text{HNO}_3$  at  $10^{-2}$  atm  $\text{NO}_2$ ); (—)  $\log ([\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}(\text{III})]^2)$  against temp. (in 15.8 M  $\text{HNO}_3$  at  $10^{-2}$  atm  $\text{NO}_2$ ); (- -)  $\log ([\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}(\text{III})]^2)$  against temp. (in 15.8 M at  $10^{-4}$  atm  $\text{NO}_2$ ).

$\text{HNO}_3$  respectively at temperatures of 100, 110 °C and boiling point (b.p. for 12 M ~ 116 °C and for 15.8 M ~ 120 °C). Thus 50% conversion of 0.01 M Cr(III) in boiling 12 M  $\text{HNO}_3$  takes about 45 h whereas in boiling 15.8 M  $\text{HNO}_3$  it takes about 6 h. No conversion was observed after five days of rapid boiling of a solution of 3 M  $\text{HNO}_3$  + 0.01 M Cr(III), indicating that the low acid strength (together with the associated lower boiling point of about 105 °C) make any conversion impossible on the timescale

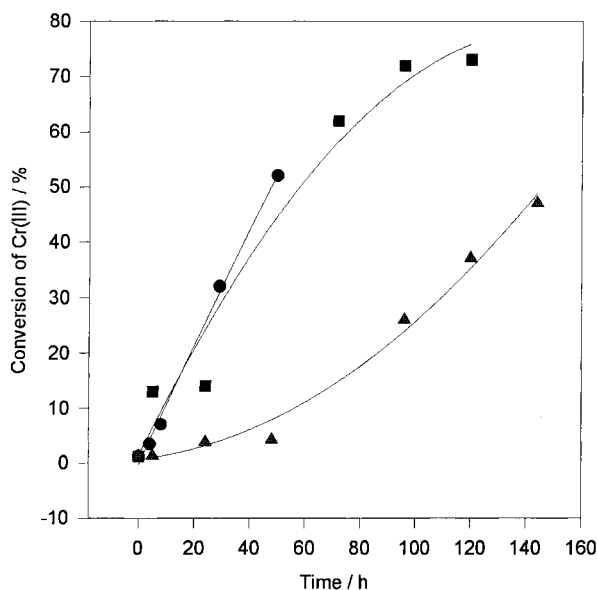


Fig. 5. Conversion of Cr(III) to Cr(VI) by 12 M nitric acid at 100 °C, 110 °C and b.p. All under  $\text{Ar}(\text{g})$  purging. Key: (●) b.p.; (■) 110 °C; (▲) 100 °C; (—) regressions.

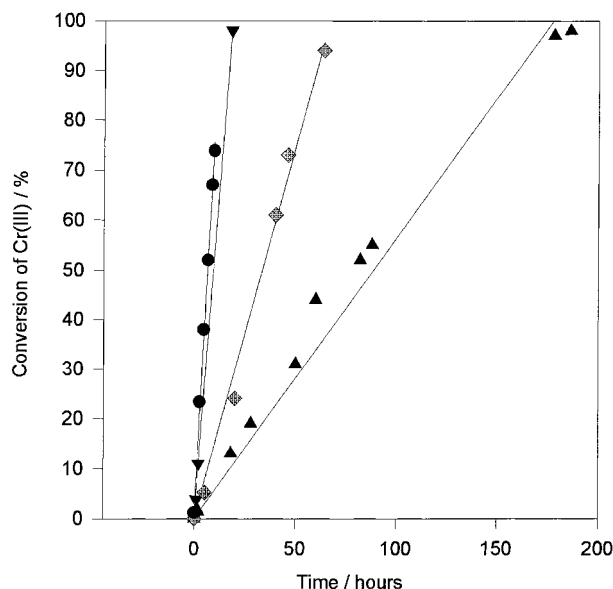


Fig. 6. Conversion of Cr(III) to Cr(VI) by 15.8 M nitric acid at 100 °C, 110 °C and b.p. All under  $\text{Ar}(\text{g})$  purging. Key: (▲) 100 °C; (▼) b.p.; (◆) 110 °C; (●) b.p. (repeated).

involved. These results are similar to those obtained by Maness [8] and Smith and Purdy [9]. Thus Smith and Purdy [9] showed that a boiling solution of 7.7 M  $\text{HNO}_3$  was unable to oxidize Cr(III). Therefore when Cr species are involved in accelerating the rate of corrosion of stainless steel the rate determining step for the steel corrosion could well be the rate of oxidation of the Cr(III) by the nitric acid. Only at high temperatures in strong nitric acid solutions is the rate of reduction of Cr(VI) on the steel likely to be rate determining. Of course in any specific case the ratio of steel surface exposed to the solution volume will also be important in determining the slow step in the corrosion process, since the Cr(III) oxidation is a bulk solution process and corrosion is a surface process.

### 3.5. Influence of Cr(VI) on corrosion of stainless steel under an argon atmosphere

Table 3 shows electrochemically obtained corrosion potentials and corrosion currents for 304L stainless steel in 12 M  $\text{HNO}_3$  containing various concentrations of Cr(VI). Cr(VI) causes an increase in the corrosion rate when it is at a concentration of 0.1 M or higher. At concentrations of 0.01 M and less the corrosion rate is very similar to that in Cr(VI) free solutions. However corrosion potentials are significantly increased by Cr(VI) concentrations of 0.01 M and higher. Since electrochemical measurements give the 'instantaneous' corrosion rate, the rates of corrosion were determined over a period of seven days to see if the rate changed with time. Figure 7 shows the steady state  $i/E$  curves for a solution of 3 M  $\text{HNO}_3$  + 0.1 M Cr(VI) at room temperature, where it can be seen that very little change was evident over the seven day period.

The fact that low concentrations of Cr(VI) increase the corrosion potential without increasing the cor-

Table 3. Corrosion currents and corrosion potentials of 304L stainless steel in 12 M nitric acid containing 0.001, 0.01 and 0.1 M Cr(vi) at r.t., 60°C and 100°C

Sweep rate 1 mV s<sup>-1</sup> and under Ar(g) bubbling

Solution and conditions	Corrosion potential/mV				Corrosion current/ $\mu\text{A cm}^{-2}$			
	No	0.001 M	0.01 M	0.1 M	No	0.001 M	0.01 M	0.1 M
	Cr(vi)	Cr(vi)	Cr(vi)	Cr(vi)	Cr(vi)	Cr(vi)	Cr(vi)	Cr(vi)
12 M HNO <sub>3</sub> at 20°C	753	857	943	1002	0.58	0.27	0.40	0.87
12 M HNO <sub>3</sub> at 60°C	934	926	999	1097	4.89	2.06	2.22	223.3
12 M HNO <sub>3</sub> at 100°C	896	973	1030	1081	8.91	5.54	6.65	1742

rosion current is probably related to the complexity of the Cr(vi)/Cr(III) reduction mechanism. Thus Burke *et al.* [13] found evidence that in the reduction of Cr(vi) on gold and platinum electrodes there is a complex pattern of behaviour. Our own measurements of Cr(vi) reduction on a gold electrode are shown in Fig. 8, where all sweep measurements start at cathodic potentials. The *i/E* curves for solutions containing Cr(vi) show, at anodic potentials, an initial cathodic current due to Cr(vi) reduction which reaches a maximum before sharply decreasing. A section of 'passivity' then follows in which the currents for both Cr(vi) and nitrate reduction are very low before further reduction is seen at more cathodic potentials. This low current section where reduction is inhibited is possibly due to the formation of insoluble Cr(vi) reduction products on the gold electrode. Similar species may be present on the stainless steel in the presence of Cr(vi), thus lowering the rates of all the electrochemical reactions on the steel surface and leading to the observed anomalously low corrosion rates which are much lower than would be expected at the observed corrosion potentials.

In the previous work by Truman [5] and McIntosh and Evans [6, 7] an approximately linear dependence

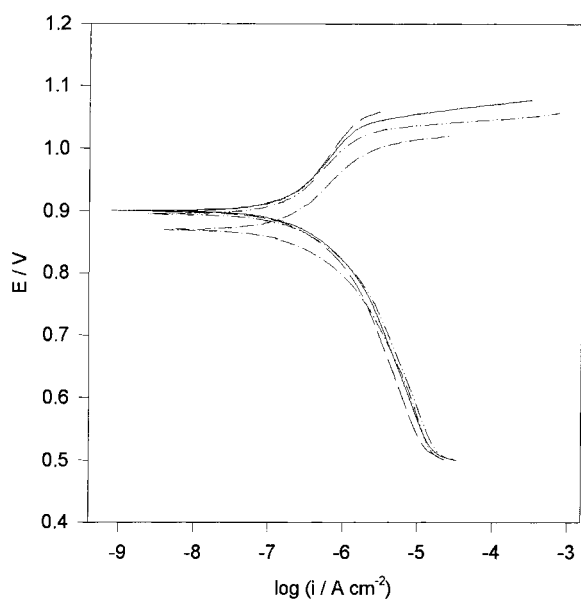


Fig. 7. Stainless steel polarization curves obtained over one week in a solution of 3 M HNO<sub>3</sub> + 0.1 M Cr(vi) at room temperature and at a sweep rate of 0.1 mV s<sup>-1</sup>. Key: (---) original sweep; (-.-) sweep after 24 h; (—) sweep after 72 h; (- -) sweep after 168 h.

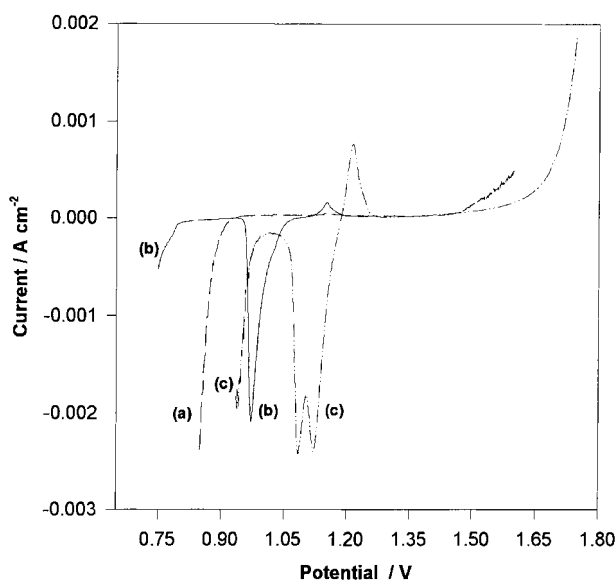


Fig. 8. Gold polarization curves in solutions of (a) 3 M HNO<sub>3</sub> alone, (b) 3 M HNO<sub>3</sub> + 0.1 M Cr(vi) and (c) 12 M HNO<sub>3</sub> + 0.1 M Cr(vi). Sweeps started at cathodic potentials and done at 100°C and at 0.1 mV s<sup>-1</sup>.

of the corrosion rate was found on Cr(vi) concentration, which extended down to lower Cr(vi) concentrations than found here, i.e. acceleration of the corrosion rate was found at Cr(vi) concentrations where no acceleration was found in the present work. This is probably because the earlier measurements [5–7] were restricted to boiling nitric acid, where the higher temperatures are likely both to increase the acceleration factor and to extend the acceleration effect to lower Cr(vi) concentrations. There is also the difference with the previous work that the methods used in this paper are electrochemical and give the 'instantaneous' rate of corrosion whereas the earlier results were based on weight loss [5–7]. There is also the possibility that Cr(III) corrosion products are converted by the boiling acid to Cr(vi) thus making a significant difference to the corrosion rate when the initial Cr(vi) concentration is as low as 10<sup>-4</sup> M. The acceleration factor found by Smith and Purdy [9] of 75 for 7.7 M HNO<sub>3</sub> + 0.03 M Cr(vi) at 80°C is comparable with those reported here.

#### 4. Conclusions

- (i) In the absence of Cr species the presence of dissolved NO and/or dissolved NO<sub>2</sub> in nitric acid

- cause the corrosion rate of stainless steel to increase by a factor which may be as high as 10.
- (ii) The effect of Cr(vi) on the corrosion rate of stainless steel is complex. At high concentrations the rate of corrosion is increased. At low concentrations the corrosion potential is increased whilst the corrosion rate is anomalously low, probably as a result of the formation of Cr(vi) reduction products on the electrode surface. The concentration at which the switch in behaviour occurs is a function of temperature and acid strength.
- (iii) Where Cr(vi) species are present, periodic sparging of NO and or NO<sub>2</sub> will generally be beneficial since the gases will reduce Cr(vi) to Cr(III) with, in most cases, a reduction in the corrosion rate. This is because the acceleration factor for high concentration Cr(vi) is likely to be greater than that for NO/NO<sub>2</sub>. It must be stressed that continuous bubbling of NO/NO<sub>2</sub> would not be beneficial due to the catalysis, by these gases, of nitric acid reduction. This can result in an increase in the steel corrosion rate by a factor of 10.
- (iv) Thermodynamics shows that Cr(III), which does not accelerate the corrosion of stainless steel in nitric acid, can only be converted to Cr(vi) under extreme conditions i.e. high temperatures, high nitric acid concentrations and low partial pressures of NO<sub>2</sub>. Even where the conversion is thermodynamically feasible the slow kinetics of the process means that the conversion time may be many hours.
- (v) Under certain circumstances it is possible to have a situation where the corrosion of stainless steel in the presence of nitric acid containing Cr(III) will be controlled by the rate of conver-

- sion of Cr(III) to Cr(vi). Factors which favour this are a rate of conversion of Cr(III) which is slow, but not so slow that the level of Cr(vi) at the metal surface falls below approx 0.01 M.
- (vi) The measurement of the corrosion rate of stainless steel in nitric acid requires that all the relevant variables are controlled, particularly the atmosphere above the liquid.

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