



Short communication

The effect of acetohydroxamic acid on stainless steel corrosion in nitric acid



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ABSTRACT

We present the first study of the effect of acetohydroxamic acid (AHA) on the corrosion behaviour of stainless steels. Particularly, studies have been performed using steels and physico-chemical conditions equivalent to those proposed for use in advanced nuclear reprocessing platforms. In these, AHA has been shown to have little effect on either steel passivation or reductive dissolution of both SS304L and SS316L. However, under transpassive dissolution conditions, AHA while in part electrochemically oxidised to acetic acid and nitroxyl/hydroxylamine, also complexes with Fe^{3+} , inhibiting secondary passivation and driving transpassive dissolution of both steels.

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1. Introduction

The PUREX (Plutonium and URanium EXtraction) separation process is used worldwide to recover uranium and plutonium from dissolved spent nuclear fuel (SNF). It is based on the selective liquid/liquid extraction and separation of uranium and plutonium from nitric acid solutions of dissolved SNF by use of a tri-*n*-butylphosphate (TBP) extractant in odourless kerosene (OK) [1].

As part of an Advanced PUREX process (Adv-PUREX), the use of acetohydroxamic acid (AHA) has been proposed as a means to hold back Pu and Np in the aqueous phase, thus allowing U(VI) to be extracted into the TBP without Pu/Np contamination [2–6]. This has led to the development of a variety of advanced fuel cycle concepts that incorporate AHA, such as URanium EXtraction Plus (UREX+) [7,8] and Grouped ActiNide EXtraction (GANEX) [9,10], which do not extract pure plutonium but rather a mix of Pu, Am, and Np, providing a non-proliferation advantage over the traditional PUREX process [11].

Importantly, with regards to safety, little is known about the influence of AHA on the corrosion behaviour of the steels that typically make up process pipework, tanks, and centrifugal contactors in each extraction step. It has been reported that di- and long-chain mono-hydroxamic acids at concentrations $\leq 5 \text{ mmol dm}^{-3}$ may act as corrosion inhibitors through self-assembled monolayer formation [12,13]. However, hydroxamic acids have seen no study at concentrations higher than 0.1 mol dm^{-3} , typical of those suggested in UREX, GANEX, and Adv-PUREX flowsheets. Further, hydroxamic acids themselves, while known

to have high affinities for e.g. Fe^{3+} (present in all steels) [14,15], have not specifically been studied in a corrosion context.

Thus, here we present preliminary electrochemical corrosion studies that have been performed on the nuclear process steels, 304 L and 316 L stainless (SS) in the presence of AHA concentrations up to 0.5 mol dm^{-3} in the presence of HNO_3 concentrations typical of those expected in the aqueous phase of a UREX+/GANEX/Adv-PUREX process.

2. Experimental section

2.1. Materials

All chemicals were of AnalaR grade or better and supplied by Sigma Aldrich (Gillingham, Dorset, UK). All H_2O used was Ultrapure from a Direct-Q 3 UV Millipore water purification system (Millipore, Watford, UK) to a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$.

2.2. AHA preparation

A 20 ml stock solution of 0.54 mol dm^{-3} AHA was prepared in deionised H_2O and used for both LSV and EQCM studies. The stock solution was kept refrigerated up to a maximum of 5 days and colourmetrically checked daily for AHA degradation using UV-vis spectrophotometry [14].

2.3. Linear sweep voltammetry (LSV) studies of SS304L and SS316L in the presence of AHA

All LSV experiments were conducted in a small volume ($200 \mu\text{l}$) electrochemical cell in order to achieve high AHA concentrations while minimising teratogenic risk [16]. LSV measurements were performed

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using a PGSTAT120N potentiostat (Metrohm Autolab B.V., Utrecht). Working electrodes were constructed using 1 mm diameter SS316L (wt.-%: C-0.015%, Si-0.38%, Mn-1.5%, P-0.035%, S-0.002%, Cr-17.0%, Mo-2.5%, Ni-10.0%, and the remainder Fe) and SS304L (wt.-%: C-0.03%, Si-0.75%, Mn-2.0%, P-0.04%, S-0.015%, Cr-18.0%, Ni-10.0%, and the remainder Fe) wire (Advent, Oxford, UK) in glass Pasteur pipettes, backfilled with epoxy resin and polished using decreasing SiC paper grades and 6, 3, and 1 μm diamond polishing pastes. To complete the three-electrode cell, a Ag/AgCl reference (RE-5B, Bioanalytical Systems Inc., USA) and coiled platinum wire counter electrodes were inserted via a simple PTFE manifold.

Aliquots of the AHA stock were taken and diluted to the desired concentration before being acidified using concentrated HNO_3 to a concentration of 1.13 mol dm^{-3} (5% wt.). Current measurements were then recorded from 0.5 to 1.5 V at a scan rate of 10 mV s^{-1} .

2.4. Electrochemical quartz crystal microbalance (EQCM) studies of SS2343 in the presence of AHA

EQCM experiments were conducted using a RQCM frequency counter (Inficon Ltd, Blackburn UK) and Q-sense open module (Biolin Scientific, Cheshire, UK) connected to a PGSTAT20 potentiostat (Metrohm Autolab B.V.). QCM piezoelectrodes were comprised of polished SS2343 (wt.-%: C-0.020%, Si-0.38%, Mn-1.5%, P-0.041%, S-0.025%, Cr-16.5%, Mo-2.5%, Ni-10.5%, and the remainder Fe) and were supplied from Biolin Scientific. SS2343 is a compositional analogue of SS316L with almost identical electrochemical/potentiodynamic properties as SS316L [17].

QCM crystal substrates were AT-cut quartz with a nominal resonant frequency of 5 MHz. Piezoelectrodes were created using physical vapour deposition (PVD) of SS2343 onto a thin Ti/Au adhesion layer (front and rear). The thickness of the steel layer is 100 nm with a surface roughness

of 1.4 nm ($\pm 0.2 \text{ nm}$) with little reduction in the fundamental frequency of 5 MHz. Frequency change to mass conversion was conducted assuming the applicability of the Sauerbrey equation [18] and a conversion factor of $0.0557 \text{ Hz/ng/cm}^2$. This conversion factor was determined by the standard Cu deposition and stripping method [19,20].

Experimentally, 2 ml aliquots of the AHA solution were prepared as above. Simultaneous LSVs and voltamassograms were then recorded from 0.5 to 1.5 V at a scan rate of 10 mV s^{-1} using a platinum wire counter and Ag/AgCl reference electrode. *Ex situ* SEM images and roughness measurements using a Phenom desktop SEM (Phenom-world, Eindhoven) were taken before and after each electrochemical experiment to assess any associated changes in surface morphology.

3. Results and discussion

3.1. Linear sweep voltammetry studies of SS304L and SS316L in the presence of AHA

Linear sweep voltammograms and associated polarisation curves for SS304L and SS316L in AHA concentrations from 0.1 to 0.5 mol dm^{-3} are shown in Fig. 1.

Considering first the polarisation curves of Fig. 1b and d, it can be seen that there is little change in E_{corr} , i_{corr} , and the range of passivity with increasing AHA concentration for both steels. The primary difference in the polarisation curves is an increase in transpassive current with increasing AHA concentration.

From the LSVs of Fig. 1a and c, it can be seen that AHA at concentrations from 0.1 to 0.5 mol dm^{-3} significantly increases the oxidation current in the transpassive region for both steels. A larger transpassive current is observed for SS316L compared to SS304L, presumably due to the decreased silica content in SS316L which protects against intergranular corrosion in oxidative acidic environments [21,22]. However,

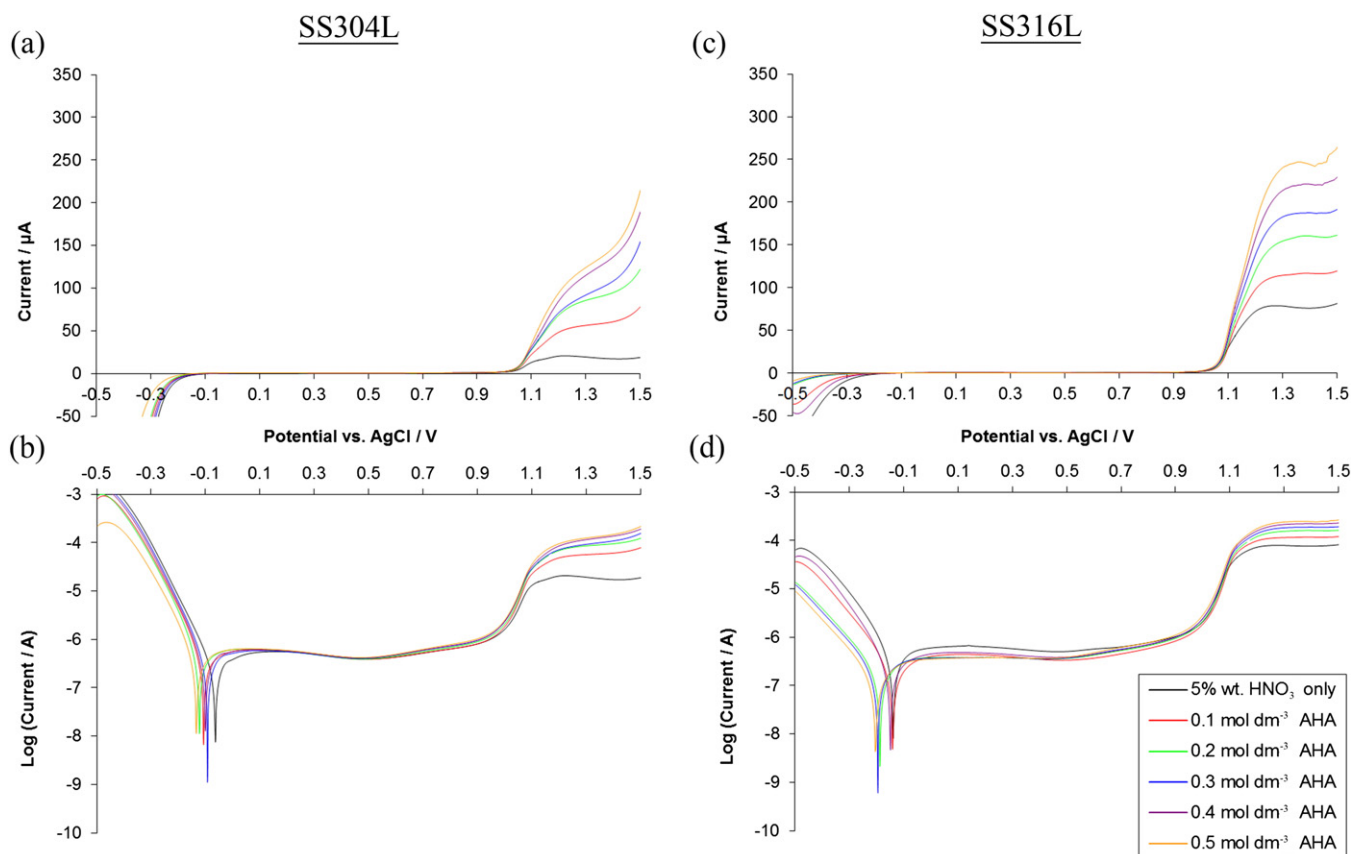


Fig. 1. Linear sweep voltammograms (a and c) and polarisation curves (b and d) for SS304L and SS316L in 5% wt. HNO_3 and AHA concentrations from 0.1 to 0.5 mol dm^{-3} .

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