



Evaluation of Nitrate and Nitrite Reduction Kinetics Related to Liquid-Air-Interface Corrosion



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ABSTRACT

Liquid-air interface (LAI) corrosion has been a concern for causing leaks in the carbon steel tanks used for holding high-level radioactive liquid waste. To assist in understanding the mechanism of LAI corrosion, the kinetics of nitrate and nitrite reduction reactions were investigated electrochemically. Cyclic voltammetry and cathodic polarization measurements indicated that the nitrite reduction reaction exhibited faster kinetics than the nitrate reduction reaction at higher cathodic overpotential. However, the primary reduction reaction at the open circuit potential under aerated conditions was the oxygen reduction reaction. The reduction of residual oxygen was also the dominant cathodic reaction at open circuit potential in deaerated conditions. Moreover, the kinetics of oxygen reduction on steel electrodes were significantly influenced by the sample immersion conditions (partial vs. full) for aerated liquid nuclear waste simulants, but not for deaerated conditions. Lastly, the gaseous products formed during LAI corrosion were analyzed using the gas detector tube method and gas chromatography-mass spectrometry and found to contain NH_3 , NO_2 and NO . However, the results suggested that these products were caused by the local acidification generated by the hydrolysis of cations after LAI corrosion underwent extensive propagation, instead of being directly reduced in alkaline conditions. Thus, the results in this work showed that the kinetics of nitrate and nitrite reduction could not generate a salt concentration cell in the meniscus region to cause LAI corrosion.

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1. Introduction

In the United States, millions of gallons of high-level radioactive liquid waste, byproducts of producing nuclear weapons that used plutonium, are still awaiting vitrification for permanent geological disposal [1–6]. In the meantime, they are being stored in temporary large underground carbon steel tanks ever since being produced. However, the corrosive chemistries in the complex wastes, namely, chloride ions and highly concentrated nitrate ions, have resulted in various corrosion-induced integrity issues for the steel tanks [3,4,7], especially leaking. Among the various corrosion issues, liquid-air-interface (LAI) corrosion has been a concern for initiating cracks or penetrating through the tank wall in the long term. The mechanism of LAI corrosion is still not well understood [8,9].

LAI corrosion of nuclear waste storage tanks is the phenomenon of corrosion at the LAI region on a partially-immersed steel surface in solutions that normally do not corrode a fully-submerged steel surface [10]. In several waste tanks, maximum wall thinning or notable localized pitting was found at regions that were at one time the location of the LAI by *in-situ* ultrasonic testing inspections [7,11]. Although no leaks have been reported to result from LAI corrosion, more severe LAI corrosion damage sites are likely to develop in the tanks as they are forced to operate beyond their design life

due to delays in the waste vitrification facility [7,12–14]. Improving the understanding of the mechanism of LAI corrosion could be beneficial for tank integrity management. For example, it is important to understand the effects of any future modifications of the waste chemistry specifications on LAI corrosion.

Previous work has shown that LAI corrosion is not the typical ‘waterline corrosion’ that is caused by an oxygen concentration cell [8,10,15–18]. One obvious evidence is the difference between their initiation locations, with LAI corrosion at the very top of the meniscus and waterline corrosion forming at sites below the waterline [8,15]. In addition, LAI corrosion of carbon steel in simulated nuclear waste liquids still initiates under deaerated conditions, where oxygen should be at a very low level, if not totally absent [10,15].

Several other explanations for LAI corrosion have been considered, including the CO_2 -induced local hydroxide depletion theory, the ohmic potential drop theory and the salt concentration cell theory (nitrate enhancement or nitrite depletion) [9,10,19,20]. A salt concentration cell was suggested to form if nitrite was actively involved in the cathodic reduction reactions [9,10,19–21]. If nitrite was reduced in the liquid nuclear waste simulants, a depletion of nitrite ion could occur in the meniscus region given that the crevice-like geometry of the meniscus region could limit the replenishment

of nitrite from the nearby bulk solution [22–25]. Considering its powerful inhibiting nature, the local depletion of nitrite ion at the meniscus could result in an inferior passive film relative to that elsewhere and thus increase the local dissolution rate of the carbon steel surface exposed to the meniscus solution. As a result, a preferential attack would initiate at the meniscus region leading to LAI corrosion. Conversely, a similar depletion of aggressive nitrate ion in the meniscus region would decrease the local dissolution rate of steel in the meniscus region. This would prevent the intensified corrosion in the meniscus region and some other mechanism would then be required to counteract this effect and initiate corrosion first in the meniscus region.

In another part of this work, *in situ* Raman spectroscopy was used to analyze the concentration change of nitrate and nitrite with time in the meniscus region as LAI corrosion formed [9]. However, neither nitrate enhancement nor nitrite depletion was confirmed in the meniscus before LAI corrosion initiated [9].

In this study, a different approach was used to examine the hypothesized salt concentration cell theory; the kinetics of nitrate and nitrite reduction reactions in the liquid nuclear waste simulants were studied. This study is critical for understanding the mechanism of LAI corrosion, because the cathodic partial reaction could be the rate-determining step for the overall corrosion rate. It is also important to identify other cathodic partial reactions that could support LAI corrosion of steel in liquid nuclear waste simulants, especially in the absence of oxygen. Apart from common reduction reactions of O_2 and H_2O in alkaline aqueous solutions, the reduction reactions of nitrate and nitrite ions might be an integral part of cathodic reactions in the liquid nuclear waste simulants [26] and play an important role in the LAI corrosion mechanism. The reduction of nitrate and nitrite to gaseous products has been reported in the literature for various materials [27–29].

It is also of interest to understand the nature of the gas bubbles that were often observed to collect on the corrosion products during LAI corrosion [15]. The formation of gaseous products on the working electrode was clearly revealed by submerging the entire working electrode into the bulk solution after LAI corrosion had propagated for a period of time [8,15]. The gas bubbles continuously evolved and rose up from the previous initiation location of LAI corrosion while the sample remained under potentiostatic polarization. This phenomenon was unexpected given that the sample was under anodic polarization at 0.1 V/SCE (saturated calomel electrode). This potential was not high enough to oxidize water into oxygen. For example, the oxygen reduction reaction (ORR) has an equilibrium potential of 0.22 V/SCE at pH 13 according to Nernst equation. Furthermore, normally, the cathodic reaction will mainly occur on the counter electrode for anodic potentiostatic polarization. Therefore, it is important to determine the composition of the gaseous products on the working electrode to provide insight to the reduction reaction mechanism of LAI corrosion. It was postulated that the gas bubbles were not hydrogen and could result from the reduction of nitrate or nitrite ions during LAI corrosion even at an applied anodic potential.

This work studied the kinetics of cathodic partial reactions of carbon steel in the primary components of liquid nuclear waste solutions under both aerated and deaerated conditions. Cyclic voltammetry (CV) was first carried out to investigate the redox behavior of nitrate and nitrite ions. Then, the cathodic polarization behavior of fully immersed steel electrodes was investigated using the potentiodynamic polarization method. In addition to these measurements on static electrodes, cathodic polarization was also performed with rotating disk electrodes (RDEs). Moreover, the effects of partial and full immersion conditions on the kinetics of cathodic reactions were also investigated. Lastly, an analysis of the gaseous products formed during LAI corrosion was performed to assist in the verification of nitrate or nitrite reduction reactions

during LAI corrosion using two different methods: gas detector tube method and gas chromatography–mass spectrometry (GC-MS).

2. Materials and Experimental Methods

Materials. The electrodes were made of AISI 1018 (0.15–0.20 C, 0.60–0.90 Mn, <0.04 P, <0.05 S all in wt%) and AISI 1010 (0.08–0.13 C, 0.30–0.60 Mn, <0.04 P, <0.05 S all in wt%) steels [30]. The electrodes were used in varied geometries depending on the purposes of the tests, including cylinder (Metal Samples, Inc.), disk (Metal Samples, Inc.), plate (McMASTER-CARR Supply Company) mounted in epoxy and polyimide coated wire (California Fine Wire Company) mounted in epoxy. The cylindrical carbon steel electrodes were ground using 400, 600, and 800 grit silicon carbide abrasive papers before being rinsed with deionized (DI) water and dried with compressed air, while the other electrodes were further polished with 6 μm , 3 μm and 1 μm diamond pastes.

Electrolyte. The test solution was based on simplified solutions of sodium nitrate, sodium nitrite and sodium hydroxide, instead of using a complex liquid nuclear waste simulant containing all of the waste components. The solution details are provided below when presenting the relevant experimental results. All the solutions were prepared with reagent grade chemicals and DI water with a resistivity of 18.2 M Ω cm. The solution pH was adjusted using sodium hydroxide immediately before each test at room temperature (RT). The tests were conducted at either RT or 50 °C as indicated. A water bath was used to control the solution temperature at 50 °C in certain tests. N_2 or Ar was used to deaerate certain test solutions as indicated.

Cyclic Voltammetry. A Bio-Logic VMP-300 multipotentiostat was used to perform cyclic voltammetry on a 2.0 mm diameter platinum disk electrode (Pine Instruments) or a 2.0 mm diameter 1010 carbon steel disk electrode. The counter electrode was a coil of platinum wire, and the reference electrode was a silver–silver chloride electrode (Ag/AgCl), which has a potential of –49 mV vs. SCE. An SCE reference electrode was not used because one small enough to fit the voltammetry cell (VC-3, ALS Co., Ltd) is not available. For each test, 10 cycles of scanning were performed at 250 mV/s at RT from the open circuit potential (OCP) to –1.0 V vs. Ag/AgCl and then back to OCP.

Cathodic Potentiodynamic Polarization. A Gamry Reference 600TM potentiostat or a Gamry PC4 potentiostat was used to perform cathodic potentiodynamic polarization. After a period of OCP immersion, the potential was scanned at 0.167 mV/s at RT from the OCP to at least –1.0 V/SCE. The three-electrode system used for this measurement consisted of an SCE reference electrode, a platinum counter electrode, and a carbon steel working electrode.

Rotating Disk Electrode Experiments. Cathodic polarization was also performed on RDEs using an EG&G PAR model 636 rotator and a Bio-Logic VMP-300 multipotentiostat. A 1010 carbon steel disk with 1 cm² surface area was used as working electrode while an SCE was the reference electrode and a coil of platinum wire was the counter electrode. The potential was scanned at 0.167 mV/s at RT from OCP to at least –1.0 V/SCE.

Potentiostatic Polarization. Potentiostatic polarization was employed to accelerate the initiation of LAI corrosion in the laboratory, facilitating gas analysis over short periods. The experiments were performed with a Gamry Reference 600TM potentiostat or a Gamry PC4 potentiostat. The three-electrode electrochemical system consisted of an SCE reference electrode, a platinum counter electrode, and a cylindrical carbon steel working electrode. The potentiostatic polarization measurements were preceded by 1 h of OCP measurement before applying a potential of 0.1 V/SCE, which is in the passive potential region according to the potentiodynamic polarization results.

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