JOURNAL OF PROPULSION AND POWER
Vol. 12, No. 3, May–June 1996

Laboratory Methodologies for Propellant Corrosion Research

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Storable liquid propellants are stored for extended periods of time in metal tankage prior to usage in rocket engines. Knowing the chemical interaction of the propellant and the tankage material is essential to evaluating the structural integrity of the tankage in service and determining if the propellant remains within specifications at the time of use. Some of this information has been obtained through long duration storage studies for periods of over 20 years in some cases. It is desirable to establish valid methods to obtain quantitative data to project long-term corrosion rates in lieu of real-time storage experimentation. Experimental methods and techniques currently used in obtaining such corrosion data and their theoretical basis are described in this article. These include 1) electrochemical: dc polarization and ac impedance measurements; 2) weight loss; and 3) surface analytical: x-ray photoelectron spectroscopy, auger electron spectroscopy, and optical microscopy. This article presents a description of the fundamental methods used by two research organizations and a comparison of these methods and equipment. These techniques are valid for evaluation of corrosion rates on various fuel and oxidizer propellants. The results of specific research with nitric acid based oxidizers with various aluminum alloys are presented in a companion article.

Nomenclature

a = area exposed to oxidizer, cm^2
B = $b_a(-b_c)/2.303(b_a - b_c)$, V
b_a = anodic Tafel constant, V $decade^{-1}$
b_c = cathodic Tafel constant, V $decade^{-1}$
C_{dl} = double-layer capacitance
E_{corr} = rest potential, mV
F = Faraday, 96,484.6 C/mole
I_{corr} = corrosion current, A
ICR = instantaneous corrosion rate (electrochemistry), $mg/cm^2 \cdot day$
i_{corr} = corrosion current density, $A/m^2 \approx$ corrosion rate, mm/year
R = 8.31441 J K^{-1} mol^{-1}
R_p = polarization resistance, Ω
R_s = resistance of electrolyte solution
r^2 = least-squares-fit value
T = 298.15 K (25°C)
z_a = $3(Al \rightarrow Al^{3+} + 3e^-)$
z_c = $1(NO_2^+ + e^- \rightarrow \frac{1}{2}N_2O_4$ or $NO^+ + e^- \rightarrow NO)$
β = 0.5, symmetry factor or transmission coefficient

Presented in part as Paper 94-3257 at the AIAA/ASME/SAE/ASEE 30th Joint Propulsion Conference and Exhibit, Indianapolis, IN, June 27–29, 1994; received Feb. 22, 1995; revision received Nov. 13, 1995; accepted for publication Nov. 13, 1995.

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Introduction

HISTORICALLY, liquid rocket service life information has been obtained by storage of propellant in tankage of representative materials and construction for extended periods of time. The propellant was sampled periodically to check its composition against specifications and, eventually, completely drained from the tank. The tank was then dissected to determine the extent of corrosion and any deleterious effects on the containment material.

The research described here had the objective of developing laboratory methodologies for the determination of corrosion of storable propellants on tankage materials used in common rocket construction and determining the storage life of systems containing the propellants and tankage materials of interest. The oxidizers selected to evaluate these techniques and procedures were inhibited red fuming nitric acid (IRFNA) liquid (neat) and gelled IRFNA. The tankage materials selected were the aluminum alloys currently in use in typical rocket propulsion system construction.

Methods to measure the process experimentally and effect correlation to real-time storage have been developed for neat liquids (both fuel and oxidizer).[1–5] This research specifically addresses the application of those methods and modifications and improvements to them.

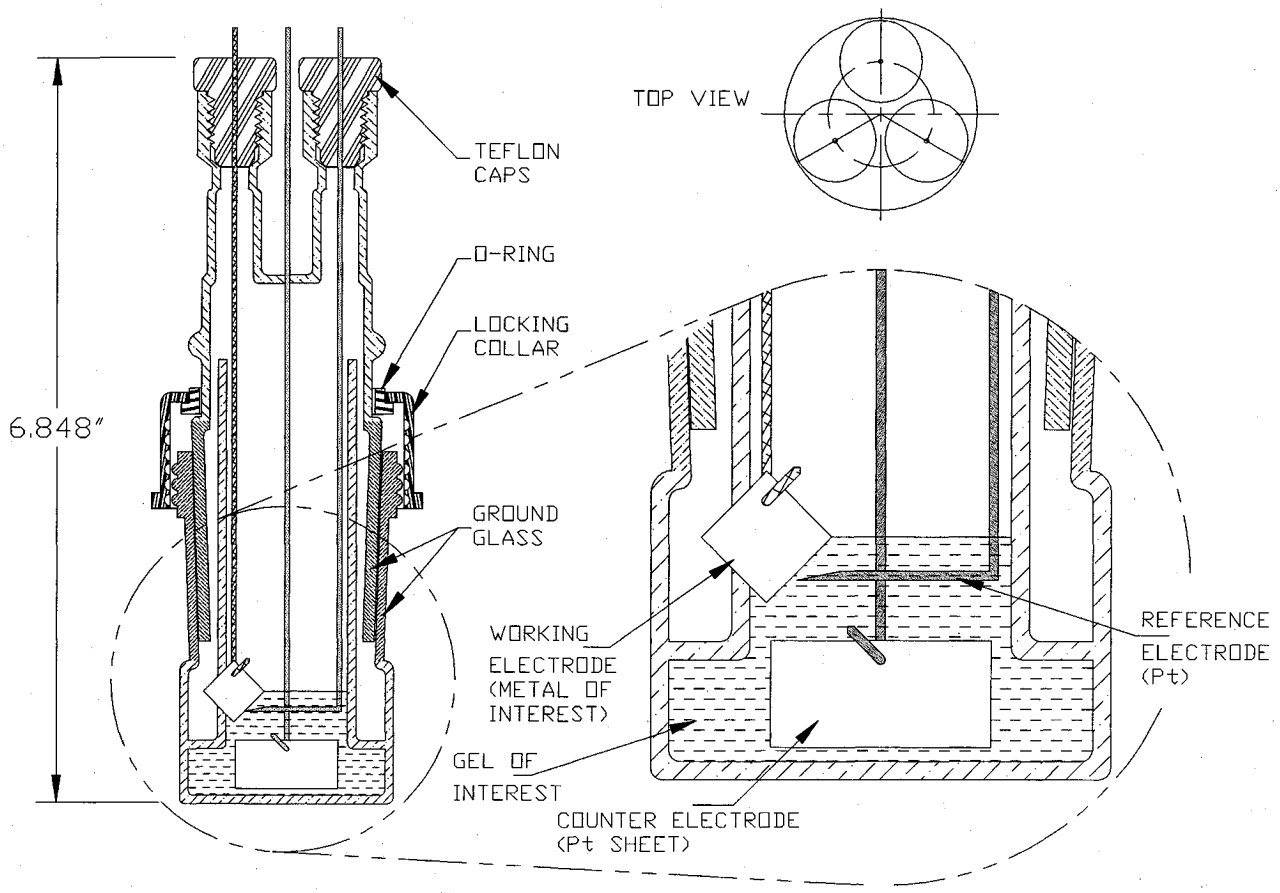

Fig. 1 Glass electrochemical cell and the electrode area enlarged.

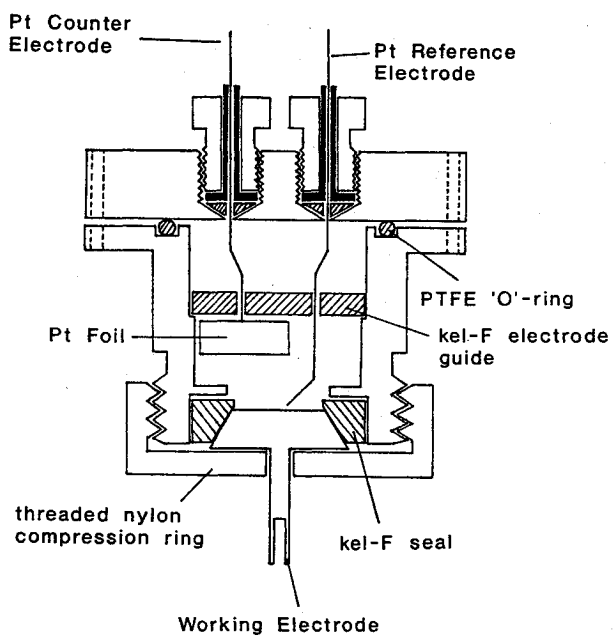

Fig. 2 2014 aluminum alloy cell (BWE type).

Approach

The approach taken has three research aspects:

1) The use of electrochemical cells as a means to obtain corrosion data.

2) The use of a weight loss technique as a means of comparison with and validation of the electrochemical method.

3) Surface studies of the test metals as a means to understand the surface chemistry.

Electrochemical Cell Design and Operation

Two types of electrochemical cells were employed in this research, one of glass construction (Fig. 1) and the other of aluminum alloy (Fig. 2). The intent of conducting research with both types was to assess the applicability of the glass cell by comparing and contrasting the results from each design.

The reference electrode in both cases was a platinum wire that was placed as close as possible to the working electrode. Platinum or rhodium wires were previously validated as suitable reference electrodes for electrochemical studies in red fuming nitric acid oxidizers.[6]

Glass

The glass electrochemical cell uses a coupon (ca. 1.0 × 1.0 × 0.2 cm) as the working electrode. A hole is drilled in one corner (Fig. 1, enlarged inset), enabling the attachment of a suitable wire. The reference electrode was placed as close as possible to the working electrode, without touching it. The platinum sheet counter electrode has a much greater surface area (20 cm^2) than the working electrode and was positioned remotely from the other two electrodes. The electrode wires fit snugly through the Teflon® cap, but could still be manipulated into their relative positions in the cell. There is usually some additional adjustment required after the oxidizer of interest is placed into the cell and assembly of the cell is completed.

Aluminum

The aluminum electrochemical cell (Fig. 2) has a 2014 Al body and a bottom-working electrode (BWE). The working electrode is either polished or finely abraded. The tip of the reference electrode is brought as close as possible to the working electrode, without touching.

Electrochemical Parameters Monitored

The measurements made in both the glass and aluminum electrochemical cells are well established.[7] Their physical interpretation follows:

Corrosion Potential (E_{corr})

This is the potential developed across the electrical double layer at the metal surface in a freely corroding metal/electrolyte system. In practice, it is the potential measured between the reference and working electrodes in an electrochemical cell containing such a system. Its variation with time, or log time, yields important information on surface film modification (thickening or chemical change) processes.

Polarization Resistance

1) DC measurements—the polarization resistance technique: If a small potential increment ΔE is applied to a freely corroding electrode, the current flowing between the working electrode and counterelectrode increases from zero to ΔI. This current increment is directly proportional to the corrosion rate. If a graph is plotted of ΔE vs ΔI close to the corrosion potential E_{corr}, linear behavior is usually seen up to approximately ± 10 mV. The polarization resistance R_p is the ratio $\Delta E/\Delta I$. The relationship between the corrosion current density i_{corr} and R_p is described by the Stern–Geary equation:

$$i_{corr} = \frac{1}{2.303R_p a} \times \frac{b_a(-b_c)}{b_a - b_c} = \frac{B}{R_p a}$$

This equation assumes that the rate-determining step is controlled by the charge–transfer reaction of metal ions crossing the electrical double layer and that E_{corr} is far removed from the reversible potential of cathodic deposition of metal and anodic oxidation of the cathodic species. As seen from the Stern–Geary equation, R_p is inversely proportional to i_{corr}, which is directly proportional to the corrosion rate. The technique is reviewed in detail by Mansfeld.[8] The data acquisition (dc) software calculates R_p from i vs E data subjected to a least-squares line-fit. Only R_p values for which $r^2 \geq 0.9$ were accepted.

2) AC impedance—electrochemical impedance spectroscopy, (EIS): R_p can also be determined from ac impedance measurements. These measurements are customarily presented as Bode (Fig. 3) or Nyquist plots. The resistor–capacitor array shown at the lower part of Fig. 3 is the simplest equivalent circuit model of an electrode/electrolyte interface and would generate the idealized plot of Fig. 3. This figure illustrates how R_p and C_{dl} can be extracted from this type of data presentation.

3) Calculation of the corrosion current density and the instantaneous corrosion rate of aluminum from polarization resistance: Corrosion current density can be calculated from the Stern–Geary relationship. Using the theoretically calculated Tafel constants b_a and b_c such that

$$b_a = \frac{2.303RT}{(z_a F\beta)} \quad \text{and} \quad b_c = -\frac{2.303RT}{[z_c F(1-\beta)]}$$

the Stern–Geary equation becomes

$$i_{corr} = 0.0128/R_p a = B/R_p a$$

where

$$B = \frac{b_a(-b_c)}{(b_a - b_c) \times 2.303}$$

Therefore, the theoretical value of B is 0.0128 at 25°C, assuming $\beta = 0.5$.

The value of i_{corr} in units of Am^{-2}, is approximately equal to the wastage rate (penetration) of the surface of the metal in mm $year^{-1}$. The term B can be determined experimentally using values of b_a and b_c obtained from Tafel polarization measurements. Such measurements for nitric acid based systems, for example, result in the value $B = 0.045$ ($T = 25$°C). The corrosion current density can be converted to the instantaneous corrosion rate (ICR) of aluminum (mg cm^{-2} day^{-1}) for the working electrode of the (BWE) 2014 Al alloy cell ($a = 1.767 \times 10^{-4}$ m^2), by the detailed expression:

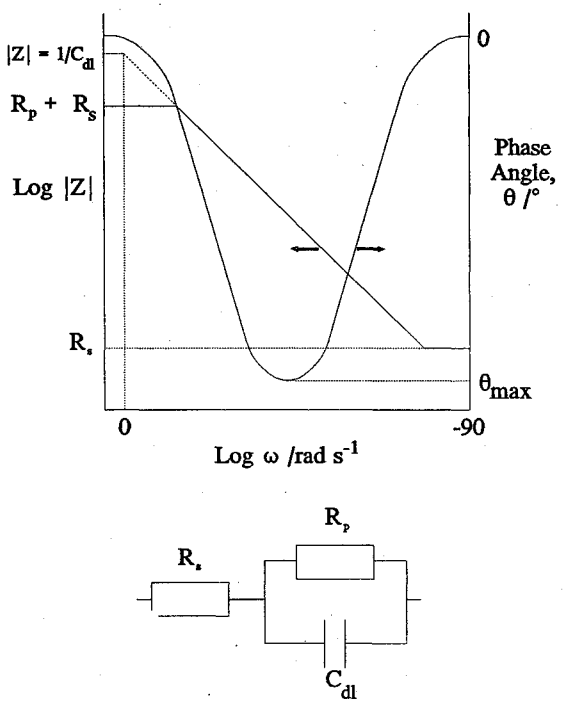

Fig. 3 Bode plot.

$$\text{ICR} = \frac{B \times 10^{-4} \times 60 \times 60 \times 24}{R_p \times 1.767 \times 10^{-4}} \times \frac{9 \times 10^3}{96{,}484.6}$$

$$= \frac{4561.017B}{R_p} = \frac{205.2}{R_p}$$

This conversion factor for the glass cell in the previous equation is

$$\text{ICR} = 362.7/R_p$$

The working electrode area immersed is 1.0×10^{-4} m^2. These conversion factors were used to calculate the instantaneous corrosion rates.

Corrosion Current Density (i_{corr})

A further dc technique for the determination of corrosion rate is the Tafel extrapolation method. In polarization experiments, the potential of the working electrode (the corroding metal electrode) is shifted to values positive (anodic polarization) and negative (cathodic polarization) relative to E_{corr}. The resulting polarization curves, illustrated in Fig. 4, are not linear over the full potential range. At low overpotentials (region 1, Fig. 4), deviations in linearity in the E vs log i plot arise where the limiting form of the Butler–Volmer equation is no longer appropriate. In this region, contributions to the measured current from reverse reactions are no longer negligible. At higher overpotentials (region 2, Fig. 4, the Tafel region), straight-line behavior is observed, with Tafel slopes b_a and b_c dependent upon the transfer coefficient β and the num-

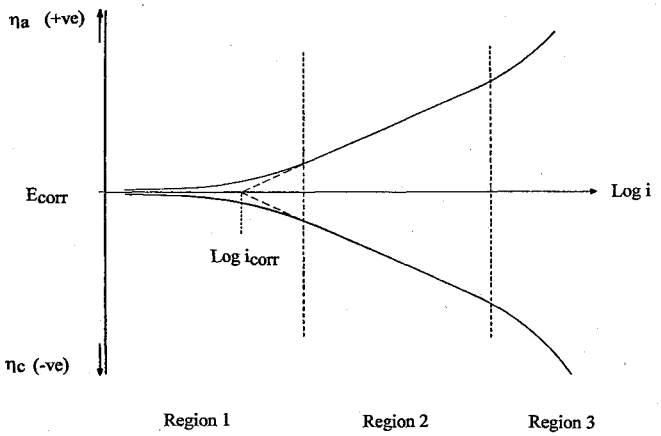

Fig. 4 Anodic and cathodic polarization curves derived from theoretical Tafel slopes.

ber of electrons involved in the transfer process. Extrapolation of the linear anodic and cathodic regions to E_{corr} allows the determination of i_{corr} to be made (Fig. 4). At high overpotentials (region 3, Fig. 4), deviations from linearity arise as a result of mass transfer limitations. In this region, the current density is controlled by the rate of diffusion of species to or from the electrode surface, and is affected by the prevailing solvodynamic conditions.

To determine corrosion current densities from the Tafel extrapolation technique, the application of large polarization voltages (hundreds of millivolts) to the working electrode is necessary, since the linear relationship between applied potential and log current density, from which i_{corr} is obtained by extrapolation, does not appear at lower overpotentials. At the large applied potentials where Tafel behavior is to be expected, the reactions occurring need not be the same as those occurring at the corrosion potential E_{corr}. Furthermore, the application of large overpotentials can result in the production of corrosion products that then affect further polarization sweeps, or polarizing over large potential ranges may result in changes in the electrode surface area.

In contrast to the Tafel extrapolation method, the polarization resistance technique involves the application of only small polarizing voltages, typically ±10 mV, at which potentials the same reactions should occur that occur at E_{corr}. Thus, the measurement process does not interfere with the quantity to be measured; it is for this reason that the polarization resistance technique was used almost exclusively in the work reported in a companion article.

Test Preparation Procedures: Electrochemical Instrumentation

The University of Nottingham electrochemical studies were conducted using EG & G instrumentation (275 potentiostat and 5208 lock-in analyzer). The UAH/MICOM studies used Solartron instrumentation (1286 electrochemical interface, and 1250 frequency response analyzer); they are regarded as complementary.

Cell Preparation

Nottingham

The BWE cells (Fig. 2), constructed from 2014 Al, were used. The working electrodes were polished by first grinding with four grades of silicon carbide paper, polishing on 6- and 1-μm diamond wheels, and finally washing in distilled water and methylated spirit. The cell filling procedure was as follows:

1) The metal components were degreased using 1,1,1-trichloroethane.

2) The cell body and lid were assembled and weighed.

3) The gelled acid was spooned into the cell and packed down using a stainless-steel spatula.

4) The cell was assembled and reweighed, the charge of gelled acid being determined by difference.

Huntsville

The glass cells were carefully washed, rinsed with de-ionized water and dried before use. The working electrode coupon of each glass cell was used, as received, without any special surface treatment other than rinsing with 1,1,1-trichloroethane and drying in ambient air. Gelled acid sufficient to immerse half the working electrode, was transferred into the glass cell from a stock vessel as quickly as possible by means of a ceramic spatula. The gel flowed slowly down the inner glass tube to the bottom of the cell, resulting in an immersed working electrode area of about 1 cm^2. The cell was then sealed and the electrode positions in the gel adjusted by manipulations of the electrode wires.

The BWE cell components and the working electrode were degreased using 1,1,1-trichloroethane and dried in ambient air. The working electrode surface was refinished with 600-grit emery. The cell body was assembled and completely filled with gel. The platinum counter and reference electrodes, carried by the lid, were carefully positioned in the gel and the lid was then bolted to the body.

Both the glass and the BWE cells were maintained at 25°C in a stirred, water-filled thermostat bath. Corrosion potential E_{corr} and polarization resistance R_p were monitored as a function of time.

Conventional Gravimetric Technique

Time-average corrosion rates were obtained from the weight loss of test coupons after immersion for various periods of time in liquid or gelled IRFNA media. This provided a comparison with the instantaneous corrosion rates determined electrochemically from R_p values.

Preparation of Materials: Al Coupon Weight Loss Studies and Optical Microscopy

Two sets of weight loss experiments were undertaken for comparison with the Nottingham electrochemical ICR data. Each of the coupons was engraved with an identifying number, degreased in 1,1,1-trichloroethane, and weighed to five decimal places. Eight coupons were placed in a sealable Teflon bottle, containing 50 g of the appropriate oxidizer. Five such bottles were set up together with a sixth containing 8 coupons (blanks), but no oxidizer. A coupon was periodically removed from each of the bottles containing the oxidizer and water washed to remove all traces of the acid. The procedure was as follows:

1) The coupon was immersed in de-ionized water for 30 s.

2) The coupon was gently rubbed with a rubber teat to remove any loose surface deposits (e.g., gelled acid residues).

3) The coupon was placed in fresh de-ionized water (30 s) and again rubbed with the teat.

4) The coupon was subjected to a final rinse in de-ionized water, placed in a clean glass weighing bottle, and oven dried (110°C) for 10 min.

5) The coupon was identified, reweighed, and the weight difference calculated.

Coincident with the removal of a coupon from the reactant, a blank coupon stored for the same period, but not in reactant, was also subjected to this procedure.

A preliminary, and very limited, weight-loss study was carried out for comparison with ICR results from the Huntsville electrochemical cells and the Nottingham weight-loss studies. The procedures used were identical to those described previously, except that the coupons were immersed in oxidizer in a polypropylene screw-capped vial. The samples were weighed to four decimal places and rubbed with a plastic spatula to remove loose surface deposits. Each of the coupons, one un-

immersed coupon and the electrode removed from a glass cell, was examined using an optical microscope at 100, 200, and 400× magnification.

Coupon Surface Studies

Sets of polished coupons were examined by x-ray photoelectron spectroscopy (XPS) and/or auger electron spectroscopy (AES) before and after treatment with oxidizer for various periods of time.

The (2.0 × 1.0 × 0.2 cm) coupons were polished on 6- and 1-μm diamond wheels. The posttest treatment of the coupons was varied. Some were blown dry in a stream of nitrogen and some were washed in water. Polished blanks were used as a referee.

Summary

The equipment and procedures described in this article provide the foundation upon which to conduct research into the corrosion effects of propellants. The electrochemical cells provide a means by which to conduct short-term experiments that produce data applicable to understanding the long-term corrosion effects in metal tankage. The weight-loss methods provide a means to validate the methodology by comparison and contrast with the electrochemistry results. Surface chemistry studies can be accomplished using optical microscopy and electron spectroscopy.

These methods were applied specifically to propellants of current interest in rocket applications. The results of an oxidizer study are reported in the accompanying article.

Acknowledgments

The authors extend their thanks to the U.S. Army for financial support under Contract DAJA 45-89-C-0022 through its European Research Office; TRW for financial support under Contract FG7372DC3S; Krishnan Chittur, University of Alabama in Huntsville, Department of Chemical Engineering, for his advice and counsel throughout the research; and D. Thompson, U.S. Army Missile Command, for experimental assistance.

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