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Silver-Sulfur Deposits on Fuel Quantity Indication System and Attendant Wiring

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Final Report

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16. Abstract

This report describes the results of a 3-year program to explain potential problems in aircraft fuel tanks caused by the presence of electrically conductive deposits containing sulfur and metal. A significant conclusion of the work described herein is that the active and harmful inorganic component of the deposits is silver oxide; the roles of copper and sulfur both appear to be secondary and to suppress conductivity. The electrical properties of deposits formed naturally in fuel tanks, or grown under representative laboratory conditions, can cause misreading in presently employed electrical fuel quantification systems. The chemical and electrochemical properties of silver oxide-derived deposits can contribute a potential ignition hazard by two mechanisms studied and analyzed in this report.

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EXECUTIVE SUMMARY

This report describes results obtained from a 3-year program to elucidate potential problems in aircraft fuel tanks caused by the presence of electrically conductive deposits containing sulfur and metal. A team comprising staff members from SRI International, The University of Dayton Research Institute, Arizona State University, Boeing, Goodrich, and Smiths Aerospace was assembled to investigate the characteristics of these deposits and their effects on aircraft components.

The Federal Aviation Administration (FAA) directed research on the following eight objectives:

1. Investigate the characteristics of copper and silver sulfide deposits on probes and wiring, with emphasis on the chemical composition and electrical properties of these deposits.

2. Investigate the mechanism that creates the copper and silver sulfide deposits on probes and wiring in fuel tanks. Emphasis should be placed on factors that contribute to the mechanism, estimated normal growth rates, factors affecting the growth rate, etc.

3. Attempt to grow the deposits under laboratory conditions.

4. Examine the effects of the conductivity of the deposits on the accuracy of the fuel quantity measurements made by fuel quantity indication sensors (FQIS).

5. Determine if there are any potential ignition threats from the copper and silver sulfide deposits during potential FQIS electrical system failures (including shorts to the FQIS wiring).

6. Investigate methods to mitigate the formation of the deposits on FQIS components.

7. Investigate the potential for interaction between Jet A fuel and nickel-plated FQIS wiring and the formation of similar type deposits on such wiring.

8. Analyze FAA-provided Jet A fuel samples for sulfur, natural antioxidant, and trace metal concentrations and attempt to determine what effect these concentrations have on the formation of the sulfides.

Analyses were performed of the chemical and electrical characteristics of naturally formed fuel tanks deposits, the chemical and corrosive properties of aviation fuels in service, and the relationships between these two sets of properties. An electrochemical mechanism was deduced for deposit growth, and chemical, electrical, electrochemical, and ignition tests were performed on laboratory grown deposits.

A significant conclusion of the work described herein is that the active and deleterious inorganic component of the deposits is silver oxide; the roles of copper and sulfur both appear to be secondary and to suppress conductivity. The electrical properties of deposits formed naturally in fuel tanks, or grown under representative laboratory conditions, can cause misreading in presently employed electrical FQIS systems. The chemical and electrochemical properties of

silver oxide-derived deposits can contribute a potential ignition hazard by the two following mechanisms studied and analyzed in this report:

1. Hot-surface ignition of flammable fuel-vapor/air mixtures, induced by electrical power flowing through bridging conductive deposits at power levels greater than those normally employed in electrical fuel quantity determination.

2. Electrochemical or electrothermal initiation of reactions between deposit silver oxide and surface-adsorbed liquid fuel.

1. INTRODUCTION.

This report describes results obtained from a 3-year program to elucidate potential problems in aircraft fuel tanks caused by the presence of electrically conductive deposits containing sulfur and metal. The work and thinking described in this report are largely the effort of a team that was assembled for this purpose and comprises the following members:

- SRI International (SRI) was responsible for devising strategy, coordinating and supervising the team effort, and performing electrochemical, electrical, and some analytical testing.

- The University of Dayton Research Institute (UDRI) was responsible for fuel chemistry and electrochemical studies as well as deposit growth and analytical characterization.

- The Arizona State University (ASU) was responsible for fuel ignition testing and for proposing and interpreting ignition mechanisms.

- Boeing contributed understanding and experience with aircraft fuel and electrical systems and made Boeing experts and data available as needed and where appropriate

- Goodrich contributed understanding and experience with aircraft fuel quantity indication systems (FQIS) and attendant electrical systems and provided samples for group testing.

- Smiths Aerospace was added to the team after the first phase of effort concluded in May 2000. They contributed expertise and experience with electrical systems associated with fuel quantification and made available samples for group testing

The team worked in close cooperation with the Air Force Research Laboratory (AFRL) at Wright-Patterson Air Force Base (WPAFB). The AFRL group had previously been tasked by the National Transportation Safety Board (NTSB) to examine the properties and potential problems associated with the presence of sulfide deposits retrieved from the TWA flight 800 crash sight.

This report summarizes work performed primarily at SRI, ASU, and UDRI that resulted in a number of reports and publications detailing individual experimental activities.

- A report of work performed at UDRI in the first phase of funding [1].

- A report of work performed at ASU in the first phase of funding [2].

- An interim report of the overall results of the first phase [3].

- An ASU Combustion Laboratory report—a Ph.D. dissertation [4].

- A paper presented at the Third Triennial International Aircraft Fire and Cabin Safety Research Conference (October 22-25, 2001), discussing the mechanism of formation of conductive residues in aircraft fuel tanks [5].

- A paper presented at the Third Triennial International Aircraft Fire and Cabin Safety Research Conference (October 22-25, 2001), discussing a mechanism of ignition of Jet A by silver oxide deposits [6].

- The final technical report submitted by ASU to SRI [7].

- The final technical report submitted by UDRI to SRI [8].

2. FUEL TANK DEPOSITS.

2.1 BACKGROUND.

Experience with black residues or deposits in fuel tanks extends back several decades and encompasses many technologies in addition to aircraft. These deposits are known to contain sulfur and have often been referred to as sulfides. The phrase "sulfide deposits" is used in this report, sometimes referred to as "copper-sulfur deposits." It should be made clear, however, that a significant conclusion of the work described herein is that the active and deleterious inorganic component of the deposits is silver oxide; the roles of copper and sulfur both appear to be secondary and to suppress conductivity.

Until 1996, the attention paid to aircraft fuel tank sulfide deposits focused on the reliability of in-tank fuel monitoring equipment, known as fuel quantity indication systems or FQIS. This problem has been recognized and studied, particularly by the U.S. Air Force [9-12], because it can result in underfueling or errors in estimating range capability. The problem is thought to derive from partial or intermittent conductive bridging of contacts electrically in parallel with the FQIS capacitive sensing elements. Adjusting or recalibrating the sensing system can correct the problem, at least temporarily, if the bridging is partial but stable. If bridging is intermittent or transient, the problem is less easily solved. Association of FQIS electrical reading errors with the presence of sulfide deposits is the first tentative or hypothesized indication that such deposits are capable of conducting either electrically or ionically.

More urgent attention was directed to the presence and properties of sulfide deposits when they were found on and in association with FQIS components retrieved from the TWA flight 800 accident site. Although the cause of this accident is still undetermined, what is known with reasonable certainty is that an explosion occurred in the center wing tank and that the explosion probably resulted from the ignition of fuel vapors. Aircraft designers have always assumed that the fuel-vapor/air mixture in the fuel tank ullage can be explosive and have sought to ensure safety by eliminating ignition sources in their electrical systems. Ignition sources are eliminated by preventing short circuits between FQIS and high-voltage, current-carrying wiring and by designing FQIS circuitry to limit the electrical energy entering the fuel tanks.

It is natural to inquire whether the proximity of electrically conductive sulfide deposits to FQIS elements or wiring may facilitate ignition or circumvent preventative electrical safeguards. As a result of the TWA flight 800 inquiry, the NTSB became concerned that sulfide deposits or residues may play a role in creating a hazardous condition within the fuel tanks of aircraft. On April 7, 1998, the NTSB recommended the FAA *"Require research into copper-sulfide deposits on fuel quantity indication system parts in fuel tanks to determine the levels of deposits that may*

be hazardous, how to inspect and clean the deposits, and when to replace the components" (A-98-37).

In its response, the FAA directed research on the following eight objectives:

1. Investigate the characteristics of copper and silver sulfide deposits on probes and wiring, with emphasis on the chemical composition and electrical properties of these deposits.

2. Investigate the mechanism that creates the copper and silver sulfide deposits on probes and wiring in fuel tanks. Emphasis should be placed on factors that contribute to the mechanism, estimated normal growth rates, factors affecting the growth rate, etc.

3. Attempt to grow the deposits under laboratory conditions.

4. Examine the effects of the conductivity of the deposits on the accuracy of the fuel quantity measurements of fuel quantity indication sensors (FQIS).

5. Determine if there are any potential ignition threats from the copper and silver sulfide deposits during potential FQIS electrical system failures (including shorts to the FQIS wiring).

6. Investigate methods to mitigate the formation of the deposits on FQIS components.

7. Investigate the potential for interaction between Jet A fuel and nickel-plated FQIS wiring and the formation of similar type deposits on such wiring.

8. Analyze FAA-provided Jet A fuel samples for sulfur, natural antioxidant, and trace metal concentrations and attempt to determine what effect these concentrations have on the formation of the sulfides.

2.2 DEPOSIT OVERVIEW.

Potential problems caused by the growth of unintended, unanticipated, and historically incompletely specified deposits on the FQIS electronic contacts can be ranked approximately in the following order of increasing concern:

1. Deposits significantly more conductive than Jet A fuel might compromise the electrical isolation at points critical to fuel quantity measurement. If the bridging is stable or slowly changing, this can result either in over- or undermeasurement of fuel level.

2. If bridging by deposits is intermittent or environment sensitive, then resulting mismeasurement will be reported as instrument errors that may be difficult to trace or rectify.

3. If deposits form at sufficient levels of conductivity and conductive stability, it may be possible for them to couple high power from an inadvertent short circuit outside the tank sufficient to ignite fuel vapor within the tank. This scenario, identified by the NTSB [13-

26] and AFRL [27-33] as a possible cause of fuel tank ignition in the loss of TWA flight 800, requires several circumstances to occur simultaneously:

a. A deposit having resistance within a relatively narrow range, bridging contacts in the vapor phase (ullage) of a fuel tank.

b. Wires communicating from the bridged contacts outside the fuel tank boundary, without intervening current or power-limiting circuitry.

c. An accidental hot short to power circuitry* external to the tank.

d. A fuel vapor of ignitable stoichiometry (fuel-to-air ratio) above its flash point.

The scenario described in 3 above is predicated on classical ignition methods and mechanisms: hot surface or plasma arc (spark) ignition. The role of the deposit in this scenario is simply to provide an appropriate level of conductive bridging, with possibly some geometric constraints. No need or role is proposed for special chemical, electrochemical, or catalytic involvement of the deposit in the ignition process.

Aircraft in-tank electrical systems are designed to limit electrical input to levels lower than those believed to be necessary to cause ignition of fuel and air vapors at any attainable stoichiometry and temperature. The initial phase of investigation [1 and 3] revealed the possibility that, as suggested by earlier work [34-37], the deposits that form on silver and silver/copper contacts may be specifically involved in the ignition or preignition process. This report discusses the possibility and evidence that silver-containing fuel tank deposits react spontaneously and exothermically (giving heat with fuel reaction by either chemical or electrochemical means), lowering the effective minimum energy of ignition and the hot-surface ignition temperature. Also discussed is the possibility and consequences of silver and silver oxide deposits playing a catalytic role in fuel vapor/air ignition.

Because new reaction mechanisms and pathways are suggested that may tend to reduce the electrical energetic requirement for fuel vapor/air ignition, it is appropriate to reconsider the strategy for ensuring that the intentional electrical inputs to aircraft fuel tanks are unconditionally safe.

The possibility that deposits can form on copper, silver, and other metallic surfaces in contact with liquid fuel, humid air, and fuel vapors within fuel tanks is well known but incompletely understood. The extent and means by which deposits conduct electricity, the influence on conductivity of such environmental variables as temperature and humidity, and the geometry of deposition relative to metallic contacts at dissimilar potentials determines whether stable or intermittent electrical problems will occur. In general, three classes of deposits are expected and are observed to occur simultaneously:

* As discussed in detail in this report, ac sources are more effective in growing deposits to conductively compromise electrical terminal isolation, but dc sources offer a higher potential for fuel vapor ignition.

- Corrosion products primarily from the reaction of copper and silver with sulfur-containing constituents of Jet A fuel.

- The results of fuel oxidation, primarily by thermally stimulated chemical reaction with oxygen in air, resulting in the deposition of particulates, tars and gums. The role of sulfur species in these reactions and the possibility of electrochemical oxidation are discussed later in this report.

- Electrochemical oxidation of metal surfaces, primarily copper and silver during water bridging of electrical contacts at dissimilar potentials.

For simplicity, three classes of deposits are discussed separately. At this point it should be noted, however, that simultaneous or sequential reactions of these three types most probably determine the composite structure of deposits formed in service and govern their potentially deleterious electrical properties.

2.3 SULFUR CORROSION OF COPPER AND SILVER IN FUEL SYSTEMS.

The predominance of wiring in fuel tanks of aircraft manufactured before 1996 is silver-coated copper. Due to an imperfect or incomplete coating, or as a result of mechanical damage or corrosion, both silver and copper can be freely exposed to fuel that contains sulfur species.

Because sulfur has such a high and known affinity for silver (and, to a lesser extent, copper), these interactions have been studied extensively, and industry standards have been adopted to control the recognized problem of corrosion. Thousands of papers, review articles, books, and patents have been written on this phenomenon. In general, when inorganic sulfur species chemically attack or electrochemically corrode silver and copper surfaces, the result is visible tarnish and buildup of inorganic silver and copper sulfides. The chemical composition and stoichiometry of this form of sulfide deposit can be defined fairly precisely. Depending on the oxidation potential or oxygen partial pressure in a corroding system, copper and silver may both form two sulfides with the metal in oxidation state 1 or 2 and the sulfur in oxidation state -2 (i.e., Cu_2S, CuS, Ag_2S, and AgS). In their pure crystalline forms these ionic materials are far too resistive to be responsible for the FQIS faults or electrical ignition of fuel vapors. When deposited with other impurity elements or present in mixed oxidation states, both silver and copper sulfides have a semiconducting character that may be relevant in some fault or hazard mechanisms.

In a series of laboratory tests performed at Boeing [38 and 39], 20-mil (0.5-mm-diameter) wires of silver and silver-coated copper wire were subjected to corrosion rate testing in Jet A fuel with various levels of sulfur added in elemental form. Wires were submerged in air-saturated fuel, then stirred and heated on a hot plate. Corrosion rates were inferred from the measured resistance rise as a conductive metal was lost from the wire diameter.

An extraordinarily rapid rate of corrosion was observed. For both pure silver and silver-coated copper, the rate of corrosion was approximately linear with concentration of elemental sulfur (up to a level of 1000 ppm), with an apparently Arrhenius dependence on temperature (corrosion rate proportional to $e^{E_a/RT}$, where E_a is an activation energy, T is the temperature, and R is a

constant). With 400 ppm of elemental sulfur added to Jet A at 170ºF (77ºC), the measured rate of corrosion of silvered copper wires was ~2.6 mils per hour (1 mil = 0.001 inch = 25 μm) or sufficient to corrode 10% of the wire in less than 1 hour.

This measured rate is so large it obviously does not typically occur in aircraft fuel tanks or the damage would be obvious. Nevertheless, these data highlight the highly aggressive nature of sulfur with respect to the corrosion of silver and copper, separately or together.

Corrosion of silver and copper by sulfur species found naturally in aviation fuels has also been studied [40 and 41], but is substantially more complex than corrosion initiated by inorganic sulfides. This added complexity is due to the normal presence in fuels of sulfur in both inorganic and organic form, having sulfur in a wide range of oxidation states (potentially from -2 to +6). Of the various types of sulfur found to be present in aviation fuels, only hydrogen sulfide and elemental sulfur were found to be corrosive to copper and silver at very low dosages. What complicates this problem greatly is that other sulfur species or non-sulfur-containing species can have synergistic or antagonistic effects (inhibition) on corrosion or be relatively neutral with respect to their tendencies to corrode copper and silver in fuel systems. Furthermore, these roles may change with concentration.

The known roles of sulfur species in fuels with respect to silver and copper corrosion can be summarized as follows:

- Sulfur-Containing Species Known to be Corrosive:
  - Hydrogen sulfide. A linear relationship exists between the initial hydrogen sulfide concentration and the square of the sulfur deposited on a test coupon.
  - Elemental sulfur. A linear relationship exists between the initial sulfur concentration and the rate of metal loss (i.e., sulfide formed).
  - Hydrogen sulfide/elemental sulfur mixtures. As for hydrogen sulfide alone, but with a synergistic increase in corrosion rate.
- Sulfur and Non-Sulfur-Containing Species Known to Inhibit Corrosion:
  - Sulfur containing mercaptans, monosulfides, disulfides, and thiophenes, and non-sulfur-containing phenols and amines can inhibit corrosivity under some circumstances. Mixtures of these species can nullify their inhibitory effect.

All other sulfur species (of which there are many) either have a negligible effect on corrosion or have not been individually tested.

The important conclusions of the proceeding discussion are twofold:

1. The corrosion susceptibility of copper and silver and, therefore, the rates of sulfide accretion in sulfur-containing fuel systems are not easily predicted on the basis of total

soluble sulfur measurement. To understand this problem, one must measure the chemical and oxidation states of the sulfur or additional parameters.

2. Because some sulfur and non-sulfur-containing species inhibit the corrosion effects of others, corrosion rate and sulfide deposition are not expected to increase monotonically, or at all, with total sulfur content in a fuel. Thus, low-sulfur fuels may be more corrosive than fuels that have a high content of inhibitory species.

2.4 CHEMICAL CHARACTERISTICS OF AIRCRAFT SULFIDE DEPOSITS.

The variability of metal sulfide formation and/or deposition with the content and type of sulfur in fuel (second conclusion above) may be particularly important in understanding the genesis of fuel tank deposits and has been closely investigated at UDRI in the present project [1 and 3] and previously [42]. Of particularly concern is the determination of the role of fuels in sulfide deposit formation.

Based primarily on Fourier transform infrared (FTIR) spectroscopy, but also on scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), x-ray photoelectron spectroscopy (XPS), and depth-profiling Auger electron spectroscopy (AES), it is clear that the electrically conductive deposits that form on or near metal surfaces by the action of sulfur in fuel tanks are largely organic in character, and are not primarily copper or silver sulfide. These deposits have various forms, colors, growth habits, morphologies, and degrees of adherence and conductivity.

The materials do not appear to be homogeneous and can be layered or form discrete islands. Chemical analyses are complicated by the fact that different techniques are sensitive to different material depths. One might expect the outside surface to be more organic, since it is normally bathed in hydrocarbon fuel, and the base of the deposit in contact with a metal substrate to have more inorganic character (as in a metal oxide or sulfide). This expectation is found to hold generally, but it is crucial to apply an arsenal of techniques to the chemical analysis of fuel tank deposits.

The deposits that occur naturally in fuel tanks are very different in composition (and therefore mechanism of growth) from the inorganic sulfides that form as a result of the corrosive attack of silver and copper by hydrogen sulfide and elemental sulfur. Based on analysis and experiments, it appears that five processes contribute to the formation of aircraft fuel tank deposits:

1. Fuel oxidation and deposition of gums and tars

2. Sulfur-induced metal corrosion following direct adsorption of sulfide compounds to Cu or Ag surfaces

3. Reaction between deposition and corrosion products

4. Oxidative corrosion or electrolytically induced oxidation of metals to form oxides

5. Partial chemical conversion of oxides by reaction with the sulfur constituents of fuels

Processes 2 and 4 are completely electrochemical, and processes 3 and 5 require an electrochemical step. Only process 1 is wholly chemical, and this reaction may also be achieved by electrochemical means. Furthermore, process 1 is insufficient to explain the phenomena under investigation. The electrical and surface properties of fuel oxidation deposits are unlikely to support directly any of the mechanisms so far considered to contribute to electrical faults, reading errors, or fuel tank ignition.

The role of process 1, if not sufficient to induce malfunction or hazard, is still considered to be necessary, either as the precursor to more deleterious products (e.g., via process 3) or to bind potential harmful species (produced for example by processes 2, 4, or 5) to the surface. Previous research at UDRI [42] and by other researchers [43-45] has shown that oxidation and deposition of jet engine fuels are strongly affected by the concentration of natural antioxidants present in the fuel. The natural antioxidants are phenol- and amine-containing compounds that act as free radical-trapping antioxidants, and sulfur-containing compounds that act as peroxide decomposing antioxidants. As the natural antioxidants inhibit the oxidation of the fuel, they polymerize, forming surface deposits and suspended particles with high (2%-20%) concentrations of sulfur, oxygen (phenol polymers), and nitrogen (amine polymers). In the absence of natural antioxidants, the fuel oxidizes, rapidly producing high levels of fuel-soluble hydroperoxides, carboxylic acids, and insoluble gums (polymers of carboxylic acids) with low levels of sulfur and nitrogen. A detailed mechanism is given in reference 20.

Consequently, fuels with high sulfur levels (>1000 ppm) would be expected to oxidize slowly, producing deposits and particles high in sulfur, oxygen, and nitrogen and to react with silver and copper surfaces to produce sulfides, whereas low-sulfur fuels (<400 ppm) would be expected to oxidize rapidly, producing hydroperoxides, acids, and gums, which have been found [1 and 3] to react with copper surfaces, but not silver surfaces, to form carboxylates.

To appreciate how fuel oxidation and deposition may occur with the fuels now in aircraft service, initial tests were performed on 32 fuels from the Federal Aviation Administration (FAA) inventory of samples drawn from commercial service jets from April 20 to June 23, 1998 [1]. Fuel samples were obtained from fuel tanks of aircraft after landing and before refueling. Laboratory experiments were performed to determine the characteristics of silver corrosion, fuel oxidation, and deposition at elevated temperatures for each of the 32 fuels chosen to represent the range of total dissolved sulfur levels [1 and 3]. Initial results suggested that Jet A fuels exhibit a wide range of fuel chemistries, particularly with respect to sulfur, and that these fuels support a wide range of corrosion and oxidation characteristics.

An additional 32 fuels were selected and analyzed at UDRI during the current phase of investigation to determine their range of oxidation and corrosion characteristics. These fuel samples were obtained from airports worldwide by the FAA between September 1998 and July 1999, as described by Kauffman [8]. Consistent with the worldwide trend to lower-sulfur fuels, the 32 fuels from the more recent sampling generally contained much lower levels of sulfur and other naturally occurring antioxidants. That is, the fuels did not visibly tarnish (corrode) silver or copper but were much more likely to undergo rapid oxidation, forming high levels of hydroperoxides and, ultimately, the brown gummy deposits characteristic of low-sulfur fuels.

2.5 AQUEOUS ELECTROCHEMICAL DEPOSITS.

During the initial phase of research [1 and 3] attempts to produce conductive residues by chemically or thermally induced reactions of silver, copper, silver-coated copper, and other metal surfaces contacted by sulfur-containing fuels were not successful. Corrosion clearly occurs with high-sulfur fuels. Fuel deposits both brown and gummy (low sulfur) and black particulate (high sulfur) clearly were formed. Nevertheless, in every case the residues produced were determined to have resistivities above 10^8 Ω cm, and, therefore, above the range of present concern [1 and 3].

Similarly, the application of voltages and waveforms characteristic of aircraft fuel gauging [24] to wires suspended in both natural and degraded (oxidized) jet fuel resulted in insignificant increases in interelectrode conduction, independent of fuel sulfur content, so long as the fuel did not contain water.

When water bridged electrode pairs, either as droplets in the presence or absence of fuel or as a continuous moisture film in high humidity and condensing environments, the results were quite different. Copious deposits were easily produced with the passage of current between adjacent copper, silver, or silvered copper wires. Since these deposits are produced by the passage of current, they are naturally and necessarily conductive. Because of the potential importance of this point, it is worth reviewing, for the nonspecialist reader, the basic principles of electrochemistry as distinguished from chemistry.

Electrochemistry occurs at the interface between an electron-conductive medium, typically a metal electrode and an ion-conductive medium called an electrolyte. The elementary reaction involves charge transfer in which an electron is given up by one electrode, while simultaneously, another electron is accepted by a second electrode connected electrically in series and in contact with the same electrolyte. With this paired act of charge transfer, one solution or electrode species is oxidized (the loss of electrons to make more positive) and another is reduced. In a battery, these reactions occur spontaneously to yield power (the product of the rate of electron flow and the potential difference between the electrodes).

Corrosion is a process in which the spontaneous reduction of an oxidized species (typically oxygen) on an electrode drives the oxidation of the metal of the same electrode, at different sites, but at the same potential. In electrochemical synthesis, whether deliberate or accidental, a voltage difference must be supplied to make a current flow. In all cases, electrical continuity between the electrodes or sites of reactions occurs by the conduction of ions in the intervening electrolytic gap.

The rates of electrochemical reactions are influenced by the usual considerations of reaction order, and reactant and product concentration. In addition, two other factors play controlling roles: (1) the rates of diffusion of reactants and products to and from the reaction sites in the electrolyte and (2) the potential difference (voltage) between the sites of the coupled reactions.

This rate dependence can be expressed in simplified form as follows:

$$I = Ai^0 \exp\left[k\left(V - V^0\right)\right] \tag{1}$$

where I is current, A is the area available for reaction, i^o specifies the intrinsic rate in terms of species concentration, etc., the exponential constant k reflects detailed mechanisms and temperature, V is voltage, and V^o is a threshold or overvoltage that contains both kinetic and thermodynamic components. Thus, current is expected to increase exponentially with voltage above some threshold value until it reaches a limit determined by the ability of reactant and products to transport to and from the electrode surface.

These characteristics of electrochemical reactions give rise to several features significant in the present investigation:

- Because of the nonlinearity of equation 1, the resistance of an electrochemically conductive bridge is a strong function of the applied dc voltage and of the amplitude of any ac perturbation signal.

- Due to the presence of capacitive and diffusional impedance elements, the ac frequency dependence of electrochemical conduction is complex, making it difficult to predict a priori, but useful in characterizing the various reaction and transport processes.

- In general, the forward (anodic) and reverse (cathodic) reactions on an electrode surface vary considerably in rate. When ac voltages or currents are applied, this gives rise to a phenomenon called Faradaic rectification, in which dc currents flow in response to an ac perturbation; that is, net electrochemical processes are expected to result from a voltage perturbation that is symmetric about zero (has no dc component).

From an electrochemical standpoint, there is nothing unexpected about the electrochemical reaction of silver (or copper) electrodes in aqueous electrolytes at large (by electrochemical standards) voltages. The thermodynamic stability of water is only 1.23 V. Allowing for the exponential voltage dependence of electrochemical rates, at any voltage above 2 to 2.5 V, H_2O undergoes electrolysis, liberating H_2 at the negative electrode (cathode) and O_2 on the positive electrode (anode). Accompanying these two reactions are the formation of hydroxyl ions (OH^-) and hydrogen ions (H^+) that diffuse away from the respective electrodes. These ions increase the conductivity of the bridging water from its relatively low value (~10^{-6} S cm^{-1}) in distilled or deionized water, and increase the current flow that reflects the net rate of the electrochemical processes. Once ionic continuity is established, silver can be oxidized to Ag^+ and Ag^{++} ions in one or two steps. These silver ions will react with the OH^- ions to produce silver hydroxides (AgOH and $Ag(OH)_2$), with O_2 to produce silver oxides (Ag_2O and AgO) and/or oxyhydroxides, or be reduced at the cathode by reaction with H_2 to produce finely divided elemental silver. The electronic conductivities of these various species deposited in the electrode gap further increase the wire-wire conductivity, which enhances the rate of the electrochemical process. Similar reactions are known to occur with copper.

During the initial phase of research, experiments were performed at UDRI [1] and SRI [3] to measure the rates of accumulation of conductive deposits on copper, silver-coated copper, and silver wire surfaces and to develop kinetic and mechanistic understandings of this deposition process [3]. Deposition occurs very rapidly under ideal or laboratory conditions with the application of modest dc voltages (5 to 9 V) to electrodes coupled by liquid water in the presence or absence of fuel. Deposition has been demonstrated [1 and 3] to occur on the timescale of hours to an extent sufficient to compromise the electronic isolation between adjacent, exposed, silver-coated wires. All that is necessary is a droplet of water to bridge the intervening gap. It is not difficult to imagine that this condition may occur in fuel tanks, either under liquid water at the bottom of the tank or in the ullage as a result of water vapor condensation. The timescale of hours to form a conductive residue obviously is shorter than the time of an average flight or the age of operational aircraft.

Four factors contribute to extending the time of deposit growth and reducing the severity (and frequency) of induced problems in FQIS electrical systems.

1. Most silver surfaces in fuel tanks are intimately connected to copper. As demonstrated at UDRI [1], the products of electrochemical attack on copper are markedly less conductive than those of silver. Copper is oxidized in preference to silver so that, when both elements are present and equally accessible, the products are derived preferentially from copper. Despite the greater tendency of copper to oxidize, the rate of reaction is governed by conduction of oxidation products deposited in the electrode gap, which is less for copper than for silver.

2. The rate of an electrochemical reaction is proportional to the net charge passed, and is therefore far greater for a dc stimulus than ac. Although a variety of waveforms are used for electrical fuel gauging [46], the majority employ ac without a significant intentional dc component. The gross rate of deposit accretion* is limited by two closely related effects for excitation waveforms customarily used in FQIS electronics: (1) the degree of irreversibility of electrochemical oxidation and reduction and (2) the presence of parasitic-rectified current components. These effects are discussed further in appendix A.

3. For simplicity and efficiency, most testing to date was performed by bridging electrified contacts with droplets of bulk phase liquid water (i.e., water). This situation might occur if a sufficient level of water accumulated in the bilge of a fuel tank. Alternatively, such bridging can occur from the impact of a falling droplet of condensed water vapor on a critical contact. In the normal configuration of FQIS wiring, however, it is far more likely that bridging occurs progressively by means of a condensed water film. Because of their thinness and partial discontinuity, the conductance of such a condensation bridge will be many orders of magnitude less than that of bulk water.

4. In the initial phases of conductive residue formation, deposits are flocculent and loosely adherent. In this stage they are easily dislodged by the action of dropping water or sloshing fuel. Adherence and surface binding is provided by the co-deposition of gums

* The effectiveness with which deposit growth compromised isolation increased with increasing frequency as deposits tended to prefer a linear growth habit directly connecting the electrical contacts.

formed by the oxidation of low-sulfur fuels. Thus, the sequencing of water additions, filling the tanks, and the nature of the fuel will determine the net rate of adherent deposit accretion.

Experiments performed at SRI (see appendix D) demonstrated that the role of condensed water might be important in affecting the formation and conductivity of deposits. The normal rates of deposit growth and conductivity compromise are reduced, however, such processes occurring on the timescale of hours under water droplets may require years under humidity films.

2.6 COMPARISON OF LABORATORY AND FIELD DEPOSITS.

The majority of the literature concerned with copper-silver-sulfur deposits on fuel components is in the form of reports on the TWA flight 800 accident [13-33 and 47] or on fuel system components removed from other commercial aircraft due to loss of electrical isolation between electrical contacts. In these early reports, the copper-silver-sulfur residues were described as organic material containing varying amounts of copper sulfide and silver sulfide or sulfates [1]. The residues were colored (brown-black), brittle, and conductive. In one conspicuous and heavily examined example (a terminal block removed from the tank of a civilian B747 aircraft), the terminal-terminal resistance was reduced by the presence of sulfide material from its specified and nominal value of multiple meg-ohms, to roughly 10,000 ohms. The resistances of the conductive films appeared to increase with residue thickness. The organic portions of the deposits were assigned to mixtures of carboxylic acids, carboxylate, and/or degraded polyurethanes. These deposits were found to occur on a wide range of surfaces inside fuel tanks, notably on insulated wires, metal and polymer surfaces, and on a wide range of tank component (FQIS, terminal blocks and bundled wires).

The focus of primary concern is with conductive deposits on FQIS, terminal blocks and associated hardware, and the reduction in accuracy of fuel gauging and potential for fuel vapor/air ignition that they present. For this work, the deposits present on ten FQIS elements and ten terminal blocks with and without associated hardware were analyzed with a variety of analytical techniques at UDRI (see appendix C). On the basis of these analyses, it is possible to classify these deposits into four basic types:

- The first type of deposit was yellow, nonconductive (greater than 10 MΩ at 1 mm spacing) and wiped off easily with a paper towel. The yellow deposit was identified as CdS, most likely produced by the interaction of Cd-plated nuts with the sulfur compounds present in Jet A fuels.

- The second type of deposit was black, nonconductive, and wiped off easily with a paper towel. The black deposit was identified as Ag_2S, most likely produced by the interaction of Ag-plated wires and nuts with corrosive sulfur compounds in Jet A fuels. The black deposits were found primarily on wire insulation abrasions and near wire terminations at connectors and other wire clamps. The majority of the deposits present on the FQIS and terminal block surfaces were nonconductive and analyzed as CdS or Ag_2S.

- The third type of deposit, a brown, gum-like, nonconductive material, was found on the end surfaces of two terminal blocks. These deposits dissolved in solvents, but were

adhesive (could not be wiped off with a paper towel). The FTIR spectra of the brown gum matched the FTIR spectra of fuel oxidation gums [1] and fuel tank deposits in the TWA flight 800 accident reports [48]. The brown gum contained minimal concentrations (less than 1%) of Cu and Ag but contained significant levels of C, O, and S.

- The fourth type of deposit was found on three terminal blocks located on the connectors, on the polymeric surfaces between the nuts and on the polymeric posts where the connectors rest. These deposits were shiny, brown or black in appearance, conductive (below 10 KΩ at 5 mm) and could not be removed by wiping with a paper towel. Solvents were able to extract a gum-like material similar to the third type of deposit from the shiny, conductive deposits. Portions of the deposits were scraped off for analysis. The FTIR spectra of the conductive deposits were similar to the FTIR spectra of gum-like deposits (third type of deposits) and the fuel tank deposits in the TWA flight 800 accident report [9-11].

The surface analysis (XPS, SEM/EDS) results of the conductive residues indicated that the deposits contained primarily C and O (these techniques are not capable of detecting H) with varying amounts of Ag, Cu, and S, depending on the sampling location of the terminal block. The deposits on the nuts (Ag-plated steel) had high (greater than 10%) levels of Ag and S, while the deposits on the connectors (Sn-plated Cu) had high levels of Ag, Cu, and S. The deposits on the polymer surfaces contained low (~5%) levels of Ag, Cu, and S. These surface analyses by location are in agreement with analyses previously reported by AFRL [27] for a terminal block with conductive deposits that had been removed from a commercial airline experiencing refueling problems.

Although the XPS and SEM/EDS detected similar elements in the conductive deposits, the relative amounts of the detected elements differed greatly. The SEM/EDS analyses (1-micron analysis depth) detected high levels of Ag and S on the polymeric surfaces of the terminal blocks, while the XPS analyses (0.008-micron analysis depth) detected low levels of Ag and S. These differences indicated that the conductive deposits were heterogeneous with regard to deposit thickness. Therefore, AES analyses with elemental depth profiling were performed and determined that the conductive deposits basically comprised three layers. The outer layer (farthest from the polymeric surface) was primarily C, O, and S (fuel gums) with minimal Ag or Cu content. The middle layer contained C, O, and S at significant levels but contained a high concentration (20%-40%) of Ag and minimal Cu (below 5%). The results also indicated that the Ag was most likely present as Ag metal or Ag_2O particles instead of Ag_2S. The innermost layer also contained significant levels of C, O, and S but contained a high level of Cu (10%-20%) and minimal Ag (below 5%). The analyses suggest that Cu was present as CuS.

The analytical results, therefore, indicate that only the deposits containing fuel gums and distinct Ag/Ag_2O and CuS layers were conductive. The Ag/Ag_2O layer was postulated to be responsible for the conductivity of the deposit. Another observation was that the conductive deposits only occurred on terminal blocks with Ag-plated nuts. Ag-plated nuts were also shown in reference 48 to be associated with conductive residues, further indicating that the Ag/Ag_2O layer was responsible for the deposit's conductivity. The fact that the Ag-containing deposits were present on the polymeric surfaces and metal connectors of the terminal block indicated that the quantity of Ag particles needed for conductive deposits were created at the Ag-plated nuts, then

transported to the adjacent surfaces and coated with fuel gums, providing adherence to the surfaces.

2.7 ELECTRODE STRUCTURES.

Five methods were explored in the laboratory to recreate the chemistry, structure, and conductivity of the deposits found in service.

1. Pairs of silver-coated copper wires 0.2 mm in diameter and 4 cm in length were affixed in parallel to a glass microscope slide with 1 mm spacing. These wires were connected to a dc power supply or battery supplying between 5 and 9 Vdc. When a 100-microliter (100 µL) drop of water was dispensed between the wires so that the water made contact with each wire, a black deposit initiated at the positive wire and spread across the water to the negative wire. Simultaneously with the black deposit formation, bubbling was observed at the negative wire due to the evolution of H_2 gas. A digital multimeter and an analog strip chart were placed in series with the parallel wires to monitor the current flow through the water drop/deposit. Drops (100 µL) of various fuels were added between the parallel wires so that the fuel was in contact with the wires and water drop. The black deposits with and without fuel present were isolated and analyzed using SEM/EDS.

   This configuration was used to mimic the situation of two closely parallel silvered copper wires, either near their terminations or with proximate defects in the polymeric insulation. This structure was clearly and easily capable of producing conductive deposits similar in form and property to those present in fuel tanks [1 and 3]. A significant limitation of this structure was its fragility and susceptibility of deposit electrical continuity to irreversible mechanical interruption.

2. A mechanically more robust structure was developed at UDRI [1] using a two-hole ceramic insulator as electrode support. Two solid 1 mm diameter wires were placed in parallel in 1 mm holes, with 1 mm spacing, so that 3-5 mm of wire protruded from the ceramic to form the working electrode structure. These wires were sealed at the opposite end in the ceramic holder, and electrical connections made to the metal wires extending from the sealed bores.

   This structure produced a very sturdy idealization of the parallel wire configuration described in 1 above. Numerous experiments were performed at UDRI, ASU, and SRI in this geometry, varying the nature of the metal wires, the excitation waveform and voltage, the sequencing of water additions, and the presence and nature of fuel. Electrical measurements at SRI and UDRI and compositional analyses at UDRI and ASU revealed that structures and conductivities comparable with conductive field deposits were produced only when (1) silver was present at the positive electrode (or either electrode if ac stimulation was used), (2) more than 5 V potential difference was applied (ac or dc), (3) bulk water bridged the conduction gap (even transiently), and (4) fuel was present during the growth and consolidation process.

3. The UDRI ceramic structure described in 2 above was used at ASU in initial ignition testing [2 and 3]. A thermal analysis was applied to this configuration by Colwell [4], and a slightly more elaborate electrode configuration was developed at ASU to allow for temperature measurements in the plane of the deposit [6 and 7]. The ASU modification of structure 2 employed a four-hole ceramic insulator with electrode wires in diametrically opposed holes and a thermocouple in one adjacent hole [6]. This enabled the temperature to be measured slightly off the axis of deposit growth to be compared with the Colwell model of hot-surface ignition [4].

   It is important to note that, while initially similar, the procedure to produce deposits for ignition testing and the structures produced at ASU were progressively different from those employed and characterized at UDRI and SRI. As described above, the conductive structure that forms initially due to the electrochemical reaction of silver and water in the presence of (low sulfur) fuels is predominantly an organic (hydrocarbon) fuel gum with electronic conductivity provided by thin layers of silver and silver oxide (both of which are good conductors of electrons). The procedure employed at ASU [6 and 7] was initially to form a silver/silver oxide conductive structure by electrolysis in the absence of fuel, and to allow this structure to transform with successive additions of fuel followed by the application of relatively high dc voltages (up to 35 V) and sometimes high currents (several amps) in an attempt to promote fuel-vapor/air ignition in closely monitored experiments. Both successful and unsuccessful ignition attempts transform the deposit, by means described by Colwell, et al. [6 and 7], into a robust, electronically conductive deposit capable of withstanding high electrical power dissipation.

   The mechanism and significance of this transformation will be discussed subsequently in this report (see also reference 7). At present, it is important to note only that the structure, conductivity, and composition of the deposits produced by the ASU method are significantly different from the deposit produced by method 2 above. As shown by ASU, repetitive high-power electrical stimulation of an initially silver oxide deposit in the presence of aviation fuel produces a structure that is largely carbon and silver. This carbon is present not primarily in the form of hydrocarbons, which are electronically nonconductive, but as elemental carbon, potentially capable of conducting electrons at relatively high power densities. Structures of this form were measured [7] with resistances as low as 3 ohms.

4. Structures 1-3 above were developed to simulate the condition of two bare, closely proximate, parallel wires within a fuel tank. During the course of this investigation, it became clear [5 and 8] that the presence of silver nuts on terminal strips situated at least transiently above the tank fuel level represented a potentially favorable site for deposit buildup. There are three reasons for potential concern:

   a. Thick silver plating on nuts represents a considerable inventory of reactable metal situated at the point of greatest potential difference.

   b. The situation and geometry of terminal strips may facilitate the formation of condensed moisture films or the inadvertent interception of condensation droplets.

c. The greater spacing of the terminal posts and the polymeric surface of the terminal blocks may increase the probability and stability of conductive hot spots.

These possibilities encouraged the development of two further deposit geometries at UDRI and SRI, using new terminal strips as well as terminal strips removed from service.

At UDRI, either paired silver wires or paired silver-plated nuts were affixed to the back surface of a terminal strip similar to that present in B747 fuel tanks. The back was selected as a conveniently flat surface for accelerated deposit growth tests. The paired electrode spacing was 10-15 mm (the spacing of nuts on the terminal strip).

To make deposits, a large water drop (250 μL) was dispensed with a plastic pipette onto the surface between the Ag wires or Ag-plated nuts. The plastic tip of the pipette was then used to engulf the ends of the Ag wires in the water drop. A glass tube pipette was then used to dispense small drops (2-5 μL) of fuel onto the upper surface of the water drop. Although a portion of the dispensed fuel flowed off the water drop onto the terminal block surface, the majority of the fuel remained supported on top of the water drop due to its lower density.

Deposits were grown with both dc and ac electrochemical stimulus. With dc stimulation [5], bubbles of hydrogen were observed at the negative electrode as a reflective silver layer grew from the positive electrode at the fuel/water interface. With an ac power supply, no bubbles were observed at either electrode, and the silver layer formed at the fuel/water boundary, regardless of its location with respect to the Ag wires. SEM/EDS and XPS analyses of the initially formed shiny silver layer revealed it to be metallic silver with a dendritic morphology [8].

It should be noted that the structure defined in 4 above is simpler than that employed in B747 fuel tanks in service. Boeing specifies this part to include a tin-plated copper terminal lug and a stainless steel washer. The presence of such dissimilar metals would change the galvanic environment affecting the tendency of these parts to corrode in the absence of an externally applied voltage difference (i.e., with the FQIS system inoperative). The additional spacing imposed by the thickness of both the lug and the nut would reduce the likelihood of formation of interterminal bridging water films.

5. For the idealized structures described in 1-4 above, the accumulated electrolysis time necessary to produce significantly conductive deposits is only on the order of minutes or hours. It is unlikely that such optimal conditions occur in fuel tanks. The deposit growth processes described above require the conjunction of four critical conditions: (a) electrically contacted silver surfaces at dissimilar potentials, (b) flow of electrical charge, (c) water, and (d) fuel. Of these, only water is in limited supply in most fuel tanks containing silver plated wire or nuts. It is plausible, therefore, that the rate of deposit growth in field service situations is limited by the presence and conductivity of bulk phase water.

Water enters the fuel tank either dissolved or suspended in the fuel or by humid ambient air. Humid air is capable of promoting interelectrode conduction by one of two means: (a) the accidental interception of a falling (or flowing) condensed water droplet or (b) the formation of a contiguous condensed water film. The latter is essentially inevitable when aircraft fly to altitude from warm, humid environments or when they descend into humid air with an unburned volume of cooled fuel. This condition is not simulated in the idealized electrode structures described in 1-4 above.

An apparatus was established at SRI (see appendix D) to simulate the conditions that would occur in the ullage of a fuel tank in an aircraft flying from or down into tropical or humid summer conditions. Terminal strips both intended for use and removed from B747 fuel tanks were mounted in varying geometries in a humidity test chamber, either with silver nuts attached to the terminal posts or with silver wires connected to reduce the interelectrode gap. Electrical connections were made to adjacent terminals in pairs, and electrical potentials applied to simulate a range of FQIS fuel gauging excitation signals. The current flowing in each electrode (terminal) pair was measured and recorded continuously by computer so that the rate of resistance decrease and charge buildup (deposit formation) could be monitored and extrapolated forwards in time.

To precipitate condensed water bridges between electrode pairs, the humidity test chamber was set to cycle between a high-temperature, nearly moisture-saturated condition (35°-40°C, 90%-95% relative humidity) to ambient temperature (variable and monitored but normally 20° ±3°C). This high temperature (corresponding to 95°-104°F) represents a relatively modest tropical or summer condition for an aircraft standing on a tarmac in full sun. For a center wing tank with fuel adjacent to the air pack, the temperature at takeoff may be considerably higher [49]. The low temperature set point obviously reflects neither the air temperature nor pressure at cruising altitude (ambient temperature below freezing, altitude 30-40,000 ft, pressure 0.2-0.3 atm). Also, in the laboratory humidity cycle tests, the test article and the chamber walls are at effectively the same temperature and, thus, experience similar condensation fluxes. When an aircraft flies rapidly to altitude from warm humid conditions, the walls of the tank, and therefore terminal strips, will experience more rapid cooling and preferential water condensation. Thus, the conditions selected for experimental cycling were relatively conservative. Each laboratory temperature cycle is expected to condense less than half of the mass of water present in the hot humid air, with a very small fraction of this depositing on the specimen surfaces.

In initial tests, cycling was performed once per day, 12 hours at high temperature and 12 hours at low temperature, simulating an aircraft flying one mission per day. In later testing, the cycling rate was doubled. Appendix D contains a complete description of the humidity cycling experiments, as well as a discussion of the results and the limitations imposed by the simplified cycling scheme. At this point, a salient conclusion of this testing was that electrochemical reactions that proceed at mA or tens of mA rates with silver electrodes bridged by bulk water, occur at μA to tens of μA rates in condensation films. That is, deposit-forming reactions occurring on exposed fuel tank surfaces proceed at least 1000 times more slowly than the accelerated testing performed at UDRI, ASU,

and SRI using electrode geometries 1-4. It should be noted, however, that any and all of the electrode geometries described above, and tested, including the humidity test configuration, were demonstrated to produce deposits sufficiently conductive to compromise fuel quantity gauging accuracy.

2.8 MECHANISMS OF DEPOSIT GROWTH.

The electrode studies and analyses summarized above, and described in appendices A and D, can be used to form the basis for a model of the deposit growth mechanisms and their means of conductivity. Residues are present in two basic forms, conductive and nonconductive, each of which are a mixture of reaction products, both inorganic and organic. The inorganic constituents result from the electrochemical oxidation (and possible partial re-reduction), primarily of silver and copper components, and are largely responsible for conduction.

Oxidation of fuels occurs by the action of heat and air and possibly also by electrochemical means, either directly or indirectly, in the presence of oxygen derived from the electrolysis of water or by reaction with electrochemically produced oxides. Aircraft fuels exhibit a wide range of compositions, total sulfur levels, and specific sulfur species concentrations. The oxidation of fuels can nevertheless be characterized into two limiting categories according to their total sulfur concentrations. The oxidized products of high-sulfur fuels tend to occur as discrete particles with limited adherence and low conductivity. Low-sulfur fuels with low concentrations of natural antioxidants oxidize to produce tenacious gums that are light brown if formed on Ag and black if formed on Cu. Potentially, these gums may incorporate cations made available by electrochemical oxidation, typically of Ag and Cu, but also of Zn, Sn, and Cd where these metals are present.

Despite metal ion incorporation at the few percent level, the intrinsic conductivity of these gums also appears to be low, as dictated by their essentially organic nature. The role of gums in the formation of conductive bridging structures, both in laboratory-produced deposits and in conductive residues retrieved from aircraft fuel tanks, resides first in their ability to bond electronically conductive residues to a surface. A secondary role for gums is to provide a source of ions for aqueous phase conduction. A tertiary role is to provide electrochemical and ionic continuity between electronically conductive deposit fragments. Gums may also protect conductive silver and silver oxide particles from sulfidation (and consequent loss of conductivity).

When examined in the laboratory, the electrochemical impedance response of well-developed conductive deposits has the form of a heterogeneous, or porous, multidimensional electrode. Microscopic examination and spatially resolved chemical analyses of the resulting structures reveals the heterogeneous nature and, in highly conductive samples, the presence of conductive layers or bands. From electrochemical impedance analyses discussed in appendix B, it is concluded that the mechanism of growth of conductive deposits involves the dissolution, transportation, nucleation, and growth of inorganic metallic oxide, hydroxide, and sulfide structures that are held to the surface by the codeposition of organic gums formed by the oxidation of low-sulfur fuels. EDS and XPS analyses suggest that some components of silver deposits can be re-reduced to metallic silver, obviously enhancing electronic conduction [5]. Evidence for the re-reduction of silver ions by fuel to produce a bright, highly conductive

metallic silver filament can be obtained directly when a silver electrode is oxidized in water with an overlying layer of fuel [5 and 8].

A similar process of re-reduction has not been observed for copper, although to date, relatively little work has been performed with pure copper electrodes. Since copper corrodes (generally) in preference to silver, the deposits formed between copper- or silver-coated copper contacts with imperfect coatings tend to conduct far less than those formed from pure silver.

The results of ignition studies at ASU [6 and 7] revealed that repetitive large electrochemical power densities in attempted or successful ignitions, in the presence of jet fuels, could transform a largely silver/silver oxide/hydrocarbon gum deposit into a robust structure through which conductivity occurred via elemental silver and carbon. Although not tested, it is likely that conductivity in this case was largely electronic, not ionic.

Figures 1 and 2 present in highly simplified form the elementary processes that can occur in the formation of conductive deposits. Starting initially with adjacent exposed wires at different potentials, bridged by condensed water, the conduction process is entirely ionic. As electrodes corrode and deposits form in the electrode gap, mixed conduction begins to occur, involving both ionic and electronic motion. This process finally ends with a continuous conduction path through solid deposit in the intervening gap, with the current carried wholly by electrons. These processes can be separated into various steps as described in sections 2.8.1 through 2.8.6.

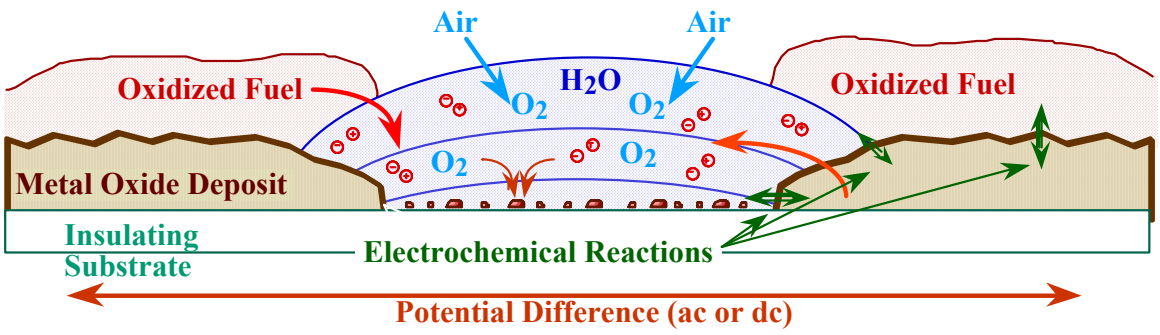


FIGURE 1. INITIAL STAGES OF DEPOSITION AND GROWTH

2.8.1 Aqueous Film Formation.

As a highly polar molecule, water has a strong affinity for ionic surfaces. Water vapor in the ullage will adsorb on surfaces containing cations such as Cu^+ and Ag^+ with a sufficiently strong tendency to displace hydrocarbon films derived from fuel immersion or fuel vapor condensation. The proposed first step in the genesis of bridging conduction is, therefore, the development of an essentially two-dimensional adsorbed water film conforming to the surfaces of metal compounds and pre-existing inorganic ionic deposits. This surface provides a nucleus for further water adsorption, thickening of the aqueous film, and its lateral extension to form a water bridge between two electrified metallic contacts.

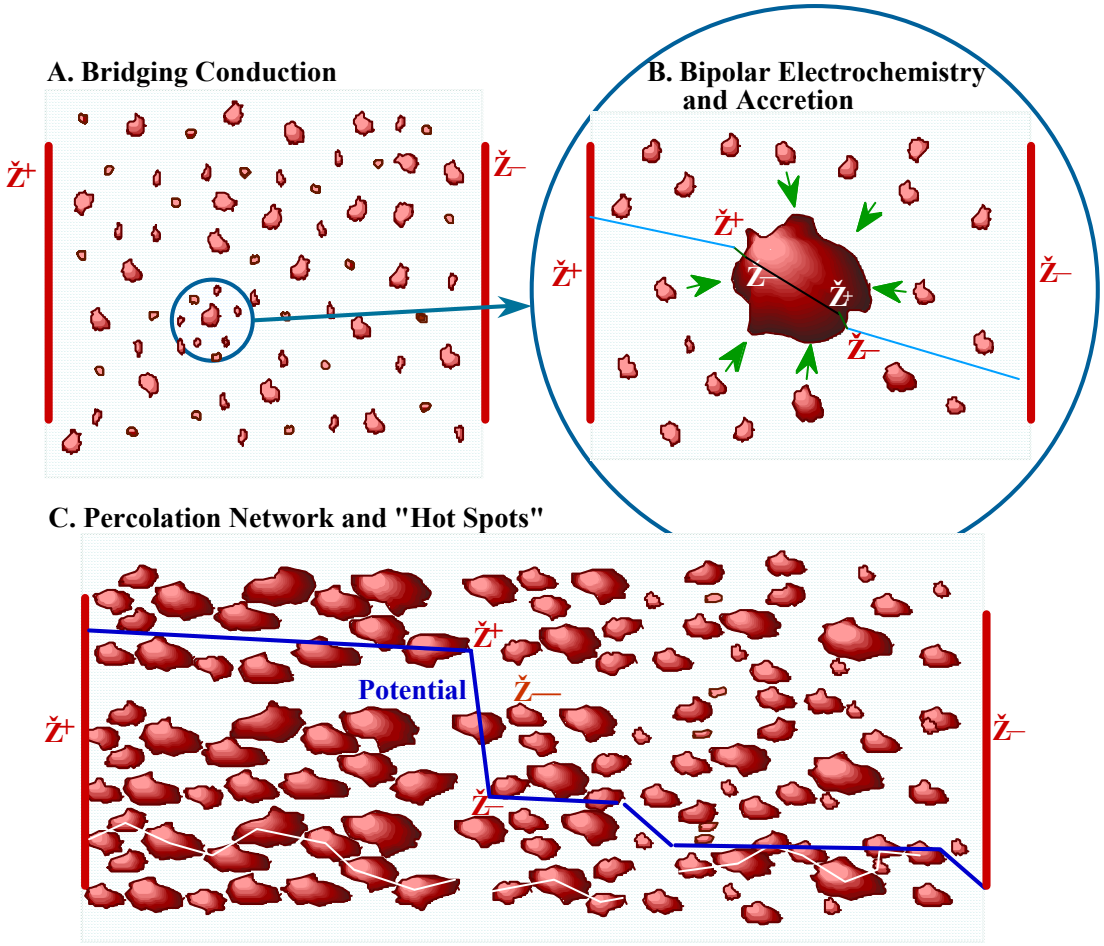


FIGURE 2. DETAILS OF ACCRETION AND CONDUCTION MECHANISMS

2.8.2 Solution Concentration.

Ions dissolve in the formed condensed bridging water film, through contact with fuel, residual oxidized fuel, or previously formed deposits. Proximity to salt sprays will also tend to increase conductivity.

Oxygen from air dissolves in the water, further oxidizing and ionizing soluble species and corroding exposed metals to produce ionic charge carriers.

With ac or dc potential differences of 2.5 V or more, net electrolysis occurs, yielding hydroxyl (OH^-) and hydrogen (H^+) ions as highly mobile conductive species and further concentrating the electrolyte by decreasing the water volume. The direct products of electrolysis are O_2 and H_2 gases. Electrolysis with silver positive electrodes produces Ag_2O and H_2.

2.8.3 Film Growth.

With sufficient ionic conductivity, metal ions are produced on the positive electrode and diffuse toward the counter electrode. Dissolved oxygen, hydroxide, or sulfide species precipitate metal

ions at nucleated points with the electrode gap. Metal ions at or in the vicinity of the negative electrode are re-reduced to metals directly or by reaction with electrolytically produced hydrogen.

Either dissolved or at the water margin, components of degraded (partially oxidized) low-sulfur fuels are further oxidized by O_2 (from air or electrolysis) or electrochemistry (at the positive electrode or both electrodes in an ac system) or by direct reaction with silver oxides, to produce organic gums that bind the nucleated deposits to the surface of the electrode gap. These bound deposits form nucleation sites for further metal deposition.

This cycle of water condensation, ionic conduction, metal corrosion and deposition, and formation of organic binder may repeat many times to increase the volume of adherent deposit, its thickness, conductivity, and conductance.

2.8.4 Bridging Conduction.

The appearance of significant volume fractions of electron conductive materials (metals, metal oxides, hydroxides, and sulfides) in the electrode gap can markedly decrease the electrode-electrode resistance and modify the electrochemical process. When the deposits are more conductive than the electrolyte, the potential gradient across the gap is partially shorted by the particle. A favored conduction path therefore involves electrochemical reduction on one side of a particle, electronic conduction through the particle, and oxidation on the opposite surface in what effectively is a bipolar electrode array. In this way, and with continued net electrochemical reaction, particles move, grow, and accrete into larger, more conductive structures.

As the deposits mature and grow, the density and size of particles approaches or reaches the two-dimensional percolation threshold. At this point, large strings of particles are in electronic contact, forming an effective short circuit of much of the electrode gap. In this state, one of two things can happen:

- Electrochemical accretion occurs predominantly at the end of percolation strings of particles, producing a dendritic conductive network, as shown in figure 3, for a deposit grown in a water bridge between two silver electrodes with a 30 Vac stimulus at 7400 Hz limited to 14 mA [8]. Conduction and the electrochemical reaction rate will then increase rapidly until such time as the electrode gap is completely bridged by electron conductive material. At this point, the electrochemical process stops. Since current is conducted wholly by electrons, there is no charge transfer and no further electrochemical reactions can occur.

- If the percolation strings are narrow, but long in the direction of net current flow, then the current density in this favored path may exceed the electron-carrying capability of the material. Hot spots will form, the solid phase will be dispersed or volatilized, and the deposit conduction path will be disrupted. This may also result in additional chemical reaction, possibly fuel oxidation or partial oxidation to produce carbon capable of contributing to electronic conduction.

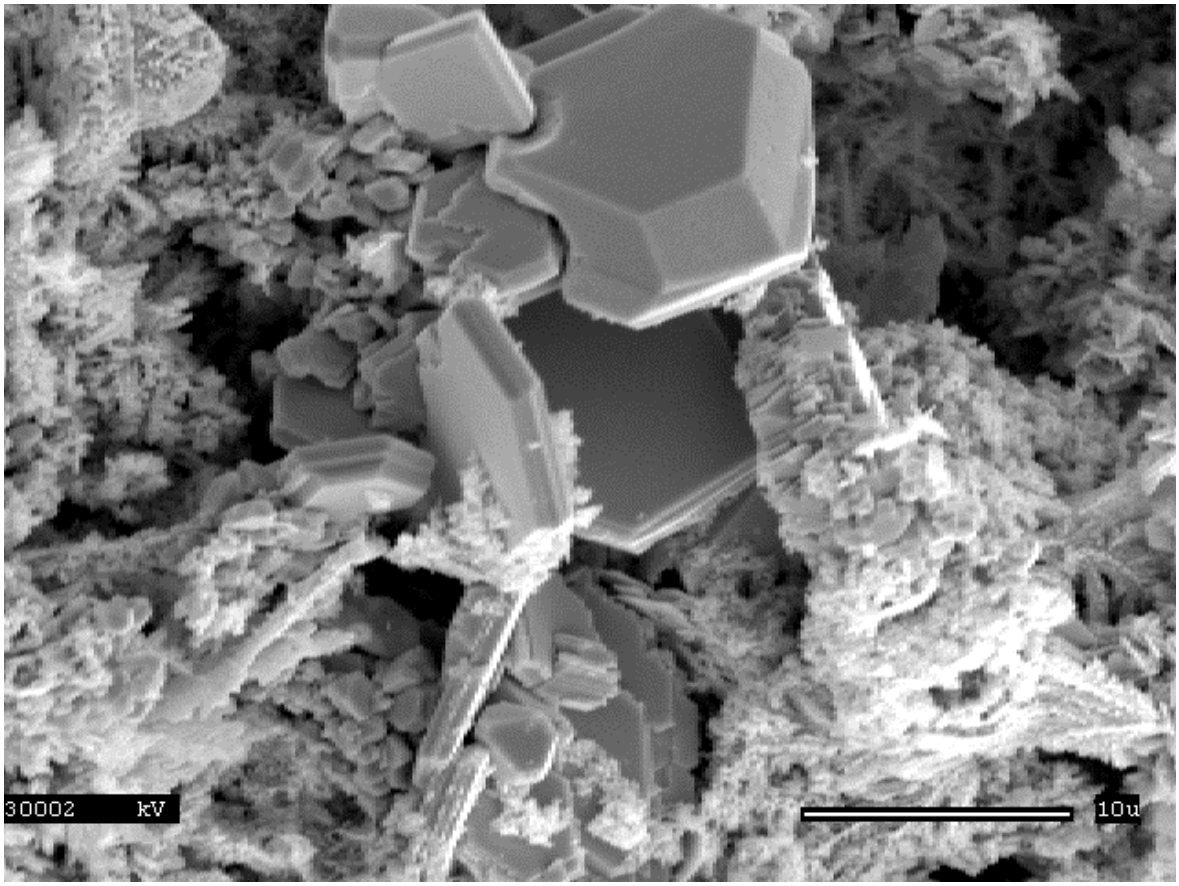


FIGURE 3. DENDRITIC DEPOSIT FORMED BY THE ELECTROCHEMICAL DISSOLUTION AND DEPOSITION OF SILVER ELECTRODES WITH 7400 Hz AC-IMPOSED VOLTAGE

2.8.5 Direct Silver Film Formation.

The process described in section 2.8.4 involves the electrochemically-assisted coalescence of small electronically conductive zones to produce a contiguous conductor. Under special circumstances Kauffman has observed [5 and 8] the rapid formation of continuous (dendritic) silver conductors. This phenomenon occurs in two steps. First, silver is electrochemically oxidized to produce silver ions (presumably Ag^{+}) that dissolve in the bulk water volume bridging two electrodes (at least one of which is silver or silver coated; the positive electrode if dc). Second, these ions diffuse into contact when a layer of fuel adjacent to or overlying the water is present. The silver ions react chemically to oxidize the fuel and are themselves reduced back to form a silver mirror that is very thin but highly conductive.

Silver layers have been observed in analyses of tank fuel deposits taken from service [1 and 5]. It is not clear whether these layers form by chemical silver formation or by the mechanism described in section 2.8.4.

2.8.6 Partial Oxidation.

Under oxidant-starved conditions (see appendix E), the hydrocarbon component of deposit films and surface-adsorbed fuel will partially oxidize to produce H_2O and carbon but not completely to CO_2. That this happens under ignition test conditions has been clearly demonstrated at ASU [6 and 7]. At present, there is no direct evidence from analysis of field samples that this partially oxidative film conversion occurs before (at least localized) ignition, or without significant electrical breakdown. That is, it is not yet clear whether the silver/carbon films formed and studied at ASU are a cause or consequence of fuel vapor/air ignition. This important point will be discussed more fully in the following section.

3. FUEL TANK IGNITION STUDIES.

3.1 INTRODUCTION.

Arguments presented in section 2, referenced reports, and appendices demonstrate that metals and metal coatings currently found in aircraft fuel tanks are capable of forming electronically conductive deposits. These deposits are formed by electrochemical reactions involving electrified metal surfaces, condensed or suspended water, and fuel. When formed by reaction of metallic silver and bound in place by the products of oxidized low-sulfur fuels, these deposits may be capable of conducting sufficient power to cause hot surface or electrochemically assisted fuel vapor/air ignition. Conductive deposits were also observed that contain copper and cadmium, but only when these deposits were wet with water and not with fuel.

The literature contains reports of two studies in which burning of aircraft or spacecraft wires were found to have electrochemical aspects. Elliot [34] reported that water bridging copper wires pairs with damaged polyvinyl insulation and a 28 Vdc voltage difference could cause the insulation to decompose and ignite. It was essential that the insulation be damaged such that the metal conductor was exposed and water bridged both metal conductors. When voltage was applied, electrochemical reactions produced a conductive copper oxide, and copper metal sludge was formed between the two copper wires. This process was accompanied by steam and scintillations. Heat produced by conduction or reactions in the sludge caused spots of incandescent temperature that acted as an igniter of the insulation.

The ignition mechanism suggested by Elliot [34] postulated a feedback process involving the decomposition of the insulation as a result of high temperatures to yield additional ions, carbonaceous material, and hydrocarbon gases. All of these substances then feed the reaction by increasing current flow and heat until ignition of hydrogen or hydrocarbon gases occurs as a result of contact with the scintillations. The reaction could be stopped by the removal of either voltage or water.

In January 1967, an accidental fire in the manned Apollo I command module occurred when a defectively insulated spacecraft coaxial silver-coated copper cable carrying 28 Vdc caught fire in a pure oxygen environment. Ignition occurred when antifreeze (glycol/water) fluids dripped onto the conductive cables. Numerous studies conducted by or through NASA investigated the ignition process and potential hazard mitigation strategies [35-37].

Boies and Northan [36] conducted experiments using both bare wires and coaxial cables that had been intentionally damaged to expose the wires. The bare wires were placed 1 mm apart with 28 Vdc potential difference impressed on the wires, and a mixture of ethylene glycol and water was dripped onto the wires such that the fluid would create a bridge between the wires. Typically, a new drop would be added every 7 minutes. When silver wires were used, a black deposit would grow between the wires. An ammeter showed that the current was initially less than 100 mA, but after the second drop of glycol/water was added at about 7 minutes into the process, the current increased rapidly to blow a 0.5 amp fuse. This rapid increase in the current was accompanied by smoke and scintillations. These current spikes were only observed when silver was the positive wire. When the positive wire was copper, tinned copper, or nickel-covered copper, no current spikes occurred. In summarizing this work, Downs [35] reports that these tests did result in ignition. Although it is possible that Downs was referring to the observed bright scintillations and smoke, this mechanism was proposed to account for the Apollo I command module fire.

Tests with damaged silver-coated copper coaxial cables were also conducted in a similar manner. When placed in an oxygen environment, the tests produced ignition after about 5 hours of exposure to dripping glycol/water. The drip rate was set to one drop every 5 minutes, so approximately 60 drops were added before ignition occurred. Ignition caused a fire and burning of the insulating material around the wires. When tested in an air atmosphere, scintillations were observed but not ignition.

Downs [35] repeated many of the same experiments performed by Boies and Northan [36]. When using damaged silver-covered copper coaxial cables, Downs [35] achieved ignition and subsequent fire in a pure oxygen environment just as Boies and Northan (1967) had. Downs [35] also conducted bare wire experiments using the same configuration as Boies and Northan [36]. When using silver wires, Downs [35] reports that ignition occurred in air just after the second drop of glycol/water was added at about 7 minutes.

Setty [37] performed chemical analysis on deposits formed after several drops of glycol/water had been added between two silver wires and found that the deposit was composed of silver oxide that was likely in the first oxidation state, Ag_2O. Setty [37] refers to the scintillations as sparks, which may be a blue flame [7].

Because of their potential relevance to the present investigation, the work of Elliot, Boies, and Downs [34-37] was reproduced at UDRI using jet fuels [1], and ASU using glycol/water mixtures [2] and summarized in the Phase I report [3]. The basic conclusions from this preliminary phase of testing were that electrical potential differences greater than ~5 V applied to either stranded silver-coated copper or solid silver wire pairs bridged either by ethylene glycol/water solution or Jet A/water admixtures produce flashes of light or scintillations accompanied by audible detonation, puffs of smoke, and radio frequency electrical emissions [1 and 3].

SEM/EDS analyses of surfaces after flashes had occurred [1] revealed chemistries and morphologies that were dependent on the fuel used in the experiments. Regardless of the fuel, silver spheres up to 100 μm in diameter were observed by SEM on the surfaces of the cylindrical

alumina electrode mount after light emission, indicating that the surface temperature had exceeded the melting point of silver (960°C). Both the energy and, temperature, needed to melt silver, and the fact that new and, therefore, clean finely divided silver surfaces are made available for catalytic reaction, suggest that the reaction that gives rise to this product might also facilitate fuel vapor ignition.

In most of the experiments performed in the initial phase of work, the potential driving force for electrochemical reaction, and whatever reaction triggered the scintillations, was a simple 9-V battery. When fresh, such a battery is capable of delivering more than 10 W (or >10 J/s), at least transiently. Nevertheless, from a record of the current obtained with a digital meter and analog strip chart recorder, it is evident that some of the flashes initiated at currents less than 10 mA (< 0.1 W). This current is of similar amplitude to those expected to flow in aircraft FQIS systems [46]. Nevertheless, it is not obvious that this power (or, more accurately, energy density) is sufficient to cause the observed surface damage and melting. The possibility must be considered that, as was shown to be the case for glycol and wet wire fires, a considerable component of the observed exothermic energy release derives from a catalyzed reaction between silver oxide and the fuel.

Two possibilities present themselves for discussion and evaluation:

1. Hot-surface ignition, in which the role of the deposit is simply to provide a somewhat stable electrically conductive bridge between two current-carrying contacts. The resulting current flow heats the deposit to the point sufficient to ignite a proximate fuel-vapor/air mixture. This model presumes no special chemical or catalytic significance for the deposit. Similarly, no special characteristics are required for the current flow, except power (or power density) that are obvious functions of the potential difference across and resistance of the deposit. At this point it is worth remembering that aircraft electrical systems were designed in full cognizance of the conditions for hot-surface ignition and are limited in power precisely to prevent such a possibility. For this mechanism to be relevant for fuel ignition would require power to be accidentally present in the fuel tank at greater than intended levels (see discussion in section 2.2).

2. Electrochemically assisted ignition, in which the deposit may participate as a chemical or electrochemical reactant or as a catalyst. This mechanism was proposed by Elliot [34], Downs [35], and Boies [36] to account for ignition events in situations somewhat similar to aircraft fuel tanks. It is, nevertheless, a relatively unexplored and complex concept, the probability and consequences of which are strongly dependent on the chemical and conductive characteristics of the deposit and on the electrical characteristics of the potential difference.

3.2 HOT-SURFACE IGNITION TESTS.

Combustion of hydrocarbon fuels involves a sequence of elementary chemical reactions leading to products (C, CO, CO_2, H_2O) with accompanying heat release. This process is usually initiated by heating the reactants to a critical temperature such that the reactions are self-sustaining. Heat can be supplied by electrical sparks, friction sparks, hot surfaces, and pilot flames [7].

Hot-surface ignition requires heating a small volume of flammable gas adjacent to the surface to the flame temperature. If the accompanying heat release exceeds the heat loss to the surroundings, the reaction becomes self-sustaining and the system runs away or explodes. The surface temperature required for ignition depends on the surface material, orientation and area, and exposure time (ignition delay time); as well as properties of the flammable gas such as fuel type, equivalence ratio, bulk temperature, pressure, and velocity [50]. In cases when a flammable liquid comes in contact with the hot surface, the liquid must first be evaporated, which consumes additional heat and requires an even hotter surface to achieve ignition. The influence of hot-surface material type has been observed in numerous studies and is not well understood [7].

The defining criterion for this ignition mechanism is the hot-surface ignition temperature (HSIT). HSIT data for aircraft applications are scarce. Tests conducted by Myronuk [51] at Wright-Patterson AFB found a HSIT of 650°C for Jet A sprayed onto stainless steel and 550°C on titanium. Smyth and Bryner [52] at Tyndall AFB found a HSIT of 540°C for both JP4 and JP8 fuels. Measurements of HSIT are subject to wide variability, depending on the experimental determination. HSIT differences between materials have been attributed to surface reactivity effects [53]. Catalytic materials could support surface reactions causing local heating to the hot surface [7] and, thus, greatly reducing the need for surface heating.

Hot-surface ignition can also be achieved by passing electric current through a thin wire [54] or foil [55]. The heat generated due to resistive heating can lead to ignition of nearly flammable vapors [7].

Testing was performed at ASU [3, 4, 5, and 7] to determine whether bulk phase gas-vapor/air ignition could be initiated by passing controlled electrical power through laboratory-grown deposits. The electrode structures selected for deposit growth and ignition testing are those described as in items 2 and 3 in section 2.7. Experiments were performed using a computer-controlled power supply (Agilent 6543 A, 35 V, 6 A) and data acquisition system to control and monitor the power delivered to a deposit pregrown on the ceramic electrode holder and mounted in a Tag open cup flash point tester [7]. The electrode (potential ignition source) was mounted 6.4 mm (0.25 in.) above the fuel level. The Jet A fuel was maintained at a nominal 60°C (140°F), well above the measured flash point of the Jet A used, 55°C (131°F).

These control settings were designed to be extreme, both in terms of stoichiometry (fuel-vapor/air ratio) and temperature above flash point, leading to a high-ignition probability. Such field conditions can and do occur, particularly in nearly empty center wing tanks with operating attached environmental control system, in aircraft subjected to long, hot, runway delays [49].

Deposits were grown at controlled dc voltage (typically 6-20 V) using one or more drops of deionized water to bridge silver electrodes in the ceramic electrode holder [7]. For an unlimited 35-V, 6-A power supply, the resistance of maximum power is 35 V/6 A or ~6 Ω. Deposits were grown to a somewhat higher resistance (~100 Ω) to initiate a test sequence. At this point the electrode was wetted with Jet A by dipping in the flash point test cup, mounted appropriately, and subjected to electrical stimulation and measurements [7]. A controlled voltage ramp was applied to the electrode, increasing from zero at the rate of 1 V/s, terminating at the point of

deposit disruption, fuel ignition, or power supply maximum (35 V). ASU made a series of repeat measurements using the same electrode, measuring resistance before and after the test, and current and voltage during the test.

References 4 and 7 provide a complete description of these experiments and considerably more elaboration on the issues of hot-surface ignition. In addition to correlating ignition test results with electrical power measurements, ASU also developed a thermal model of the ceramic insulator electrode structure [4], the predictions of which were compared with temperature changes measured during ignition tests with a thermocouple mounted in the plane of the deposit (see reference 7 and section 2.7).

A systematic experimental procedure was developed and employed at ASU to characterize the evolution of the electrical, mechanical, and ignition characteristics of initially silver oxide deposits as they were subjected to repeated electrical power ramps in failed and successful ignition attempts. Initially deposits exhibit high conductance, which is easily disrupted. The maximum power passed during the voltage ramp is, therefore, low, and the measured posttest resistance is much greater than its initial value.

As the number of ignition attempts increased, however, the deposit developed a more robust electrical character better able to withstand the imposed electrical power. The resistance before and after the tests remained relatively low, and maximum power input of many watts or tens of watts could be caused to flow through the deposits. These tests were often accompanied by relatively long periods of several seconds or more, where bright orange, red, and white flashes of light were observed [7]. Such effects frequently resulted in ignition of the vapor above the heated pool surface of the flash point tester.

3.3 HOT-SURFACE IGNITION RESULTS.

ASU attempted by statistical means to associate an electrical cause with the vapor ignition effect. Of the parameters measured and tested, the maximum test power appeared to be the best predictor of ignition [7]. ASU performed a total of 221 ignition tests with three identically prepared starting electrodes; approximately 10% of these attempts resulted in vapor phase ignition. From these data, ASU developed a logistic regression of ignition probability versus maximum test power. A formal statistical analysis is presented in reference 7.

While relatively simple and referring to only one electrode configuration, this statistical analysis allows one to draw some qualified conclusions about the role of electrical power in promoting hot surface ignition at an electrochemically formed fuel deposit of the type studied at ASU (reference 7 and section 2.7). Results of the ASU regression fit predict that there is a 95% probability that current flowing through such a deposit will cause hot-surface ignition if the deposit is capable of supporting ~60 ±20 W of electrical power dissipation. Similarly, ignition is predicted to occur on approximately half the attempts at a maximum input power of ~40 ±15 W. Both of these numbers are much larger (by factors of between 100 and 1000) than the power deliberately or intentionally supplied inside aircraft fuel tanks for the purpose of fuel quantity indication. It is clear, however, by the method developed at ASU [7], that deposits capable of

causing hot-surface ignition can plausibly be grown in the electrical and electrochemical environment of fuel tanks.

Nevertheless, a statistically meaningful probability of ignition by hot-surface ignition at such a deposit requires an accidental hot short to high-power circuitry external to the tank to impart high currents and/or voltages to wires communicating with the bridged contacts inside the tank, without intervening current or power-limiting circuitry. This scenario was identified by the NTSB as a possible cause of the fuel tank ignition that occurred in the loss of TWA flight 800 [13-26]. The work performed at ASU [2, 4, 6, and 7] and summarized in this section shows that deposits with sufficiently robust conduction can form in fuel tank environments, and are capable of igniting fuel vapor/air mixtures given sufficient input of electrical power and energy.

Four comments or qualifications should be applied to the preceding conclusions:

1. The form of the logistic regression applied to the ASU ignition test data is incapable of defining a minimum power for ignition, and the predicted ignition probability is finite for all values of maximum input power, including zero. At zero input power the predicted ignition probability is ~0.8 ±0.5%.

2. In his Ph.D. thesis Colwell [4] developed a thermal model of the ceramic holder with which the ASU ignition tests were conducted for two basic purposes:

    a. To determine if the measured electrical power could be correlated with the measured surface temperatures and whether these temperatures were sufficient to induce a hot surface ignition;

    b. To predict a minimum power condition for hot surface ignition.

    Although the agreements between prediction and measurement were not exact, the model does appear to capture essential elements of the thermal physics of the problem [7]. With relatively large electrical energy inputs (several hundred joules), predicted and measured surface temperatures are in approximate agreement and can exceed the Jet A hot-surface ignition temperatures on titanium and stainless steel surfaces [7 and 51]. This suggests that the electrical energy input alone may induce temperatures sufficient for hot-surface ignition.

    An effort was made at ASU [4 and 7] to explore mathematically the effect of deposit dimension on the electric power input needed for hot-surface ignition. Because both the surface temperature that results from an applied heat flux and the required surface temperature to achieve ignition depend on the area of the hot surface, a minimum ignition power may exist. Insufficient data are available from the literature or developed in this present study to quantify the minimum power or energy needed to achieve hot surface ignition. It is clear from the ASU model, however, that as the deposit area decreases, so does the electrical power requirement for ignition. A minimum area and minimum power for ignition might be calculated, although these numbers will be strongly dependent on the electrical nature of the deposit, the thermal characteristics of the support and environment, and the proximity and geometry of the contacting wires or other heat sinks.

3. One of the features of the ASU model is its insensitivity to the form of the electrical input waveform. The only effect ascribed to electrical input is its heating power, and the thermal time constants of the deposit/ceramic structure are long compared with those of ac sources of FQIS or main aircraft power. As such, no distinction needs to be made between dc and ac power sources, or between ac sources of different frequencies within the range of those present on the aircraft. This caveat does not apply to the formation of deposits, just to their capacity to induce hot-surface ignition.

4. The ignition events observed and quantified at ASU appear to be consistent with hot-surface ignition and the thermal model developed in all cases except two. In these instances, ignition of the fuel-vapor/air mixture occurred coincidently with a current spike (at constant voltage) of very brief duration. In one case, an input power of 2.4 W [7] was measured on a single data point at a data acquisition rate of 30 samples per second. This event and another similar event are of concern for several reasons:

    a. Although potentially undermeasured by the paucity of data points, the input power at the time of ignition corresponds to an ignition probability of only ~1% in the ASU logistic regression fit to all data. Furthermore, maximum input powers of 20 W, 23 W, and 32 W, were measured in this same, the preceding, and subsequent voltage ramps, without initiating ignition.

    b. Of more concern than the low power is the very brief time, and therefore, low energy associated with the power pulse. The maximum duration of the power pulse accompanying ignition is 67 ms (=2/30 s), and the maximum accompanying energy between 80 and 160 mJ.

    c. There is both insufficient time and insufficient energy to raise the temperature of the deposit to the point where hot-surface ignition can occur. It is necessary to conclude, therefore, that ignition in this instance occurred by a mechanism different from the studied and analyzed hot-surface ignition.

3.4 ELECTROCHEMICALLY ASSISTED IGNITION.

The discussion of hot-surface ignition in the preceding sections considers the role of electrochemistry in deposit formation, conductivity, and durability, but not in bulk phase fuel-vapor/air ignition. Electrochemically produced deposits have the potential to involve themselves directly in surface reaction with fuels or fuel vapor combustion in several ways:

- Finely divided silver metal is observed to be the product of an electrochemical reaction between silver wires (or nuts) and water. Such a material is capable of catalyzing the air oxidation of fuel vapor, possibly causing ignition at energies less than the supposed minimum energy of ignition.

- In a relatively short time, it is possible to produce milligram quantities of conductive deposit between silver electrodes bridged by water and held at voltages and currents within the range of those present in aircraft fuel tanks. This material contains silver

oxide, shown by NASA and Lockheed to facilitate or initiate ignition of organic solids, liquids, and vapors [34-37].

- The mechanisms by which conductive particulate bridging of the electrode gaps is observed to occur can result in conductive hot spots at which electrical power density and temperature may intensify, possibly initiating or facilitating fuel vapor ignition.

These three processes are chaotic or stochastic by nature and, thus, hard to reproduce and study in the laboratory. As such, the evidence that direct electrochemical involvement of fuel tank deposits plays a significant role in fuel vapor ignition is limited, and the following discussion should be reviewed with this caveat in mind.

The evidence of direct interactions of deposits with films has two possibly related forms:

1. Deposits containing relatively little liquid fuel frequently exhibit flashes of blue or white light (scintillation) accompanied by an audible detonation or popping sound, smoke, and very brief current spikes causing radio frequency (RF) interference [1 and 3]. Because of their very brief duration, the energies associated with these scintillations are as little as millijoules (mJ) or even microjoules (μJ). As argued in section 3.5 below, the chemical consequence of scintillations might be silver metal spheres that appear as the result of local melting.

   The current spikes that cause or result from scintillations can result in ignition of Jet A fuel vapor at low measured power levels, with ignition not closely predicted by measured input power [7]. Two current spikes accompanied the event described in item 4 in section 3.3. The first spike occurred at about 19 seconds into the test and resulted in the maximum recorded power level of 19.5 W. However, ignition of the fuel vapor resulted from the second current spike that occurred at approximately 23 seconds and measured only about 2.4 W [7].

2. Under similar deposit conditions and possibly triggered by the scintillations or the processes that give rise to them, deposits sometimes exhibit prolonged (for several seconds) glowing two-dimensional hot spots. This red-orange glow is similar in intensity to those observed at ASU to cause full vapor ignition with relatively high probability [7]. Such events are of concern because the accompanying electrical power into and apparently sustaining the glow can be very small (30 mW or less [8]). An alternative growth process developed at UDRI to more closely resemble the configuration of deposit growth on terminals strips present in fuel tanks (electrode structure, item 4 in section 2.7) facilitates the initiation of low-current glows. Deposits grown in this manner have not been tested for their ignition characteristics at ASU or elsewhere; quantitative statements about ignition thresholds or probabilities therefore cannot be made. Although the measured electrical power input to cause the glow may be small, the possibility exists for the local heating effect to be augmented by catalyzed surface combustion of residual fuel. Whether or not this conjecture is confirmed, the extended duration of the glowing hot spots integrates energy in the form of conductive and radiant heat loss amply sufficient to

exceed the minimum energy of ignition of fuel vapor/air mixtures. Evidence of such ignitions was observed at UDRI.

The next two sections discuss these two phenomena, explore evidence for their existence, and speculate about their origins and significance with respect to fuel tank ignition.

3.5 SCINTILLATIONS.

Evidence of scintillations was first observed and reported by Downs during electrolysis using silver electrodes in the presence of ethylene glycol [35]. The authors also showed that adding a chemical compound to inhibit silver oxidation also prevented the scintillations [36]. Kauffman [1, 5, and 8] demonstrated that similar scintillations occurred with deposits produced when water was electrolyzed with a silver positive electrode (or ac) in the presence of Jet A. Provided that deposits are produced in this way, then all fuel residue reactions produce scintillations with certain low-sulfur fuels,* regardless of the polarity of a silver/metal electrode pairing in the ignition test [8]. That is, scintillations are the result of a reaction between fuel (or other organic liquid or solids) and the products of oxidized silver (silver oxide or hydroxide). Scintillations are not produced at or by the electrodes. They are triggered by electrical stimulation of silver oxides impregnated (but not saturated) with fuel or other oxidizable liquid. SEM analyses of deposits after scintillations have been observed reveal the presence of distinct spheres of silver metal of diameter less than 2 μm.

Without fully understanding the demands or requirements for electrical triggering (see section 2.8), the simplest chemical reaction can be expressed in general form:

$$n\ Ag_2O + C_xH_y \Rightarrow 2n\ Ag + x\ CO_2 + y/2\ H_2O \qquad (2)$$

Where for balance $n = 2x + y/2$

For a reaction of this type to occur, the overall Gibbs free energy change must be negative. Because of the instability of Ag_2O (weak Ag-O bonds) and the high stability of CO_2 and H_2O (strong O-H and C-O bonds), essentially all reactions of the sort described in equation 2 are strongly exothermic (react spontaneously to produce heat).

Jet A is a multicomponent fuel with a wide range of components and compositions. Nevertheless, with little loss of generality Jet A can be represented in the following exercise by one compound, undecane, with chemical formula $C_{11}H_{24}$. Appendix E presents a thermodynamic analysis of the results of the reaction of this and similar compounds with Ag_2O, AgO, and O_2, in the temperature range 100°-200°C (212°-392°F). Also included in this analysis are the reactions of ethylene glycol with Ag_2O and O_2.

Figure 4 summarizes the results of three such calculations [56] of the free energy of reaction (ΔG) and the heat produced by reaction (ΔH), showing the effect of carbon chain length (11, 12,

* The most extensively studied of these was FAA123 sampled in Madrid with 100-ppm sulfur (see reference 8). High-sulfur fuels suppress reactions and prevent scintillations at low electrical input power. At high power and current (>300 mA), all fuels produce scintillations in the described condition.

and 13) for straight-chain, saturated hydrocarbons (alkanes), and temperature of reaction, in reactions with Ag_2O to produce CO_2, H_2O, and Ag, as described in equation 2. Units on both vertical axes are kJ (thousands of joules) per mole of Ag produced. A negative sign means a spontaneous reaction (ΔG) and heat release (ΔH). These numbers are large on the scale of normal chemical reactions since they result from the combustion of useful fuels. It should be noted, however, that one mole of silver weighs 108 g, occupies a volume of ~10 cm^3, and requires ~10^5 coulombs (amp seconds) to form electrochemically.

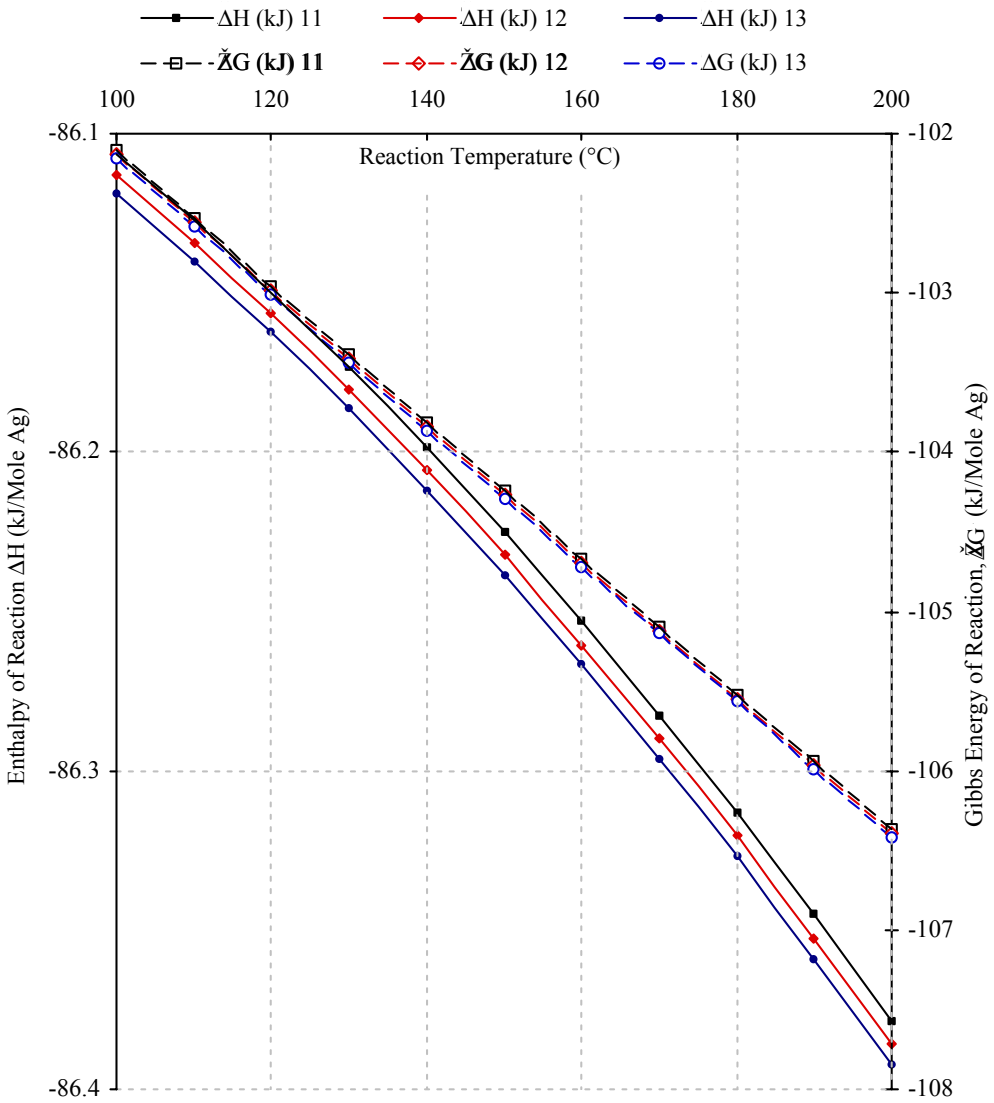


FIGURE 4. ENTHALPY (ΔH) AND GIBBS FREE ENERGY (ΔG) OF REACTION OF ALKANES OF CHAIN LENGTH 11, 12, AND 13, WITH Ag_2O TO PRODUCE CO_2, H_2O, AND Ag

The first things to note in figure 4 is that the reactions posed occur spontaneously at all temperatures tested, and that the amount of heat produced per mole of Ag is essentially independent of carbon chain length and temperature. A single number of ~86 kJ/mole Ag (or ~800 J/g Ag) can, therefore, be used to calculate the expected heat release of reaction (equation 2). As shown in appendix E, this number is essentially the same as the heat release (~91 kJ/mole Ag) from the reaction of ethylene glycol with Ag_2O that is believed to have been a cause of fire in the Apollo command module [35-37].

The reactions under consideration therefore have considerable heat energy density. Even when reaction (equation 2) does not proceed to completion, and produces CO or C plus H_2O and Ag as final products, the heat release is still appreciable (~67 and ~48 kJ/mole Ag, respectively, see appendix E). These numbers can be used to calculate the consequences of an electrically, electrochemically, or thermally triggered reaction between electrochemically produced Ag_2O present in the fuel deposit and fuel (or oxidized fuel products) in the surrounding deposit matrix.

Apart from the scintillations, silver spheres formed as a result of melting provide evidence of reaction. These spheres are typically not more than 2 μm (2×10^{-4} cm) in diameter. Each such sphere formed by reaction (equation 2) would be accompanied by only 3.5×10^{-8} J (35 nJ) of heat release. This is clearly too small an amount of heat to cause bulk phase fuel vapor/air ignition, being 7000 times less than the accepted minimum energy of ignition of Jet A fuel vapor (~0.25 mJ [54]).

In studies at UDRI [1], silver spheres up to 100 μm in diameter were observed by SEM on the surfaces of electrodes after scintillations (an example is shown in figure 52 of reference 1). These earlier studies were performed using a 9-V battery with current relatively uncontrolled. It is, therefore, not certain what power or energy were delivered to the electrode at the time of silver formation. If produced solely by reaction (equation 2), the deposition of a 100-μm silver sphere would be accompanied by an energy release of approximately 4.4 mJ, approximately 18 times greater than the minimum energy of ignition of Jet A fuel vapor.

Using more rapid data acquisition techniques than were employed at ASU [3 and 7], Kauffman [8] was able to capture the electrical signals associated with scintillations. These electrical events are of very brief duration, typically 1-4 μs, and occur at relatively low currents (less than 20 mA). Figure 5 presents one relatively large and well characterized event. The current was measured [8] using a recording oscilloscope triggered to record following a stepped increase of current. The experimental circuit was a 40 Vdc power supply in series with a 200 Ω resister and a ceramic electrode containing two silver wires in the structure described in item 2 in section 2.7. As can clearly be seen in figure 5, the current through the deposit was initially stable at ~10 mA. It then stepped spontaneously and abruptly to ~20 mA for ~3.7 μs before returning, again spontaneously and abruptly, to the pre-established value of 10 mA. There is some structure in the current response, possibly due to multiple stimulations or scintillations. The maximum power presented in figure 5 is ~0.77 W, and the integrated energy above the 10 mA baseline ~1.3 μJ.

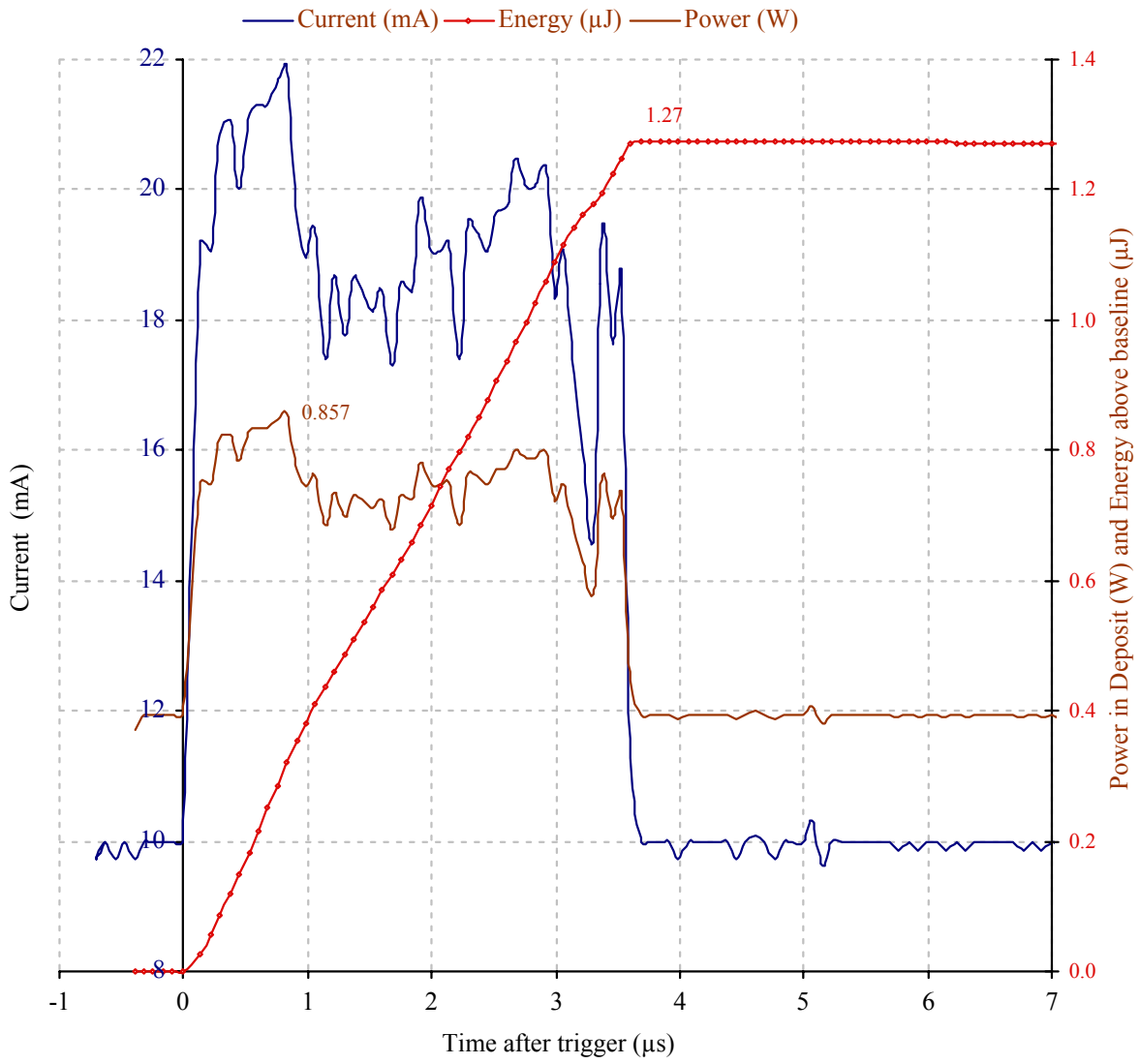


FIGURE 5. TRANSIENT RECORDING OF SPONTANEOUS CURRENT PULSE (1)

Although more than a hundred times less than the accepted minimum energy of ignition of Jet A fuel vapor (~0.25 mJ [54]), this energy is approximately 40 times larger than would accompany the formation of a 2-µm silver sphere from reaction (equation 2). A much smaller current burst event is shown in figure 6. Measured with the same electrode structure and electrical circuit, here the baseline current is ~6 mA and the maximum current and power are ~17 mA and 0.6 W, respectively. The energy under each of the two power spikes in figure 6 is, however, only on the order of 60-70 nJ, essentially the same as the 35 nJ required to produce 2-µm silver spheres by reaction (equation 2).

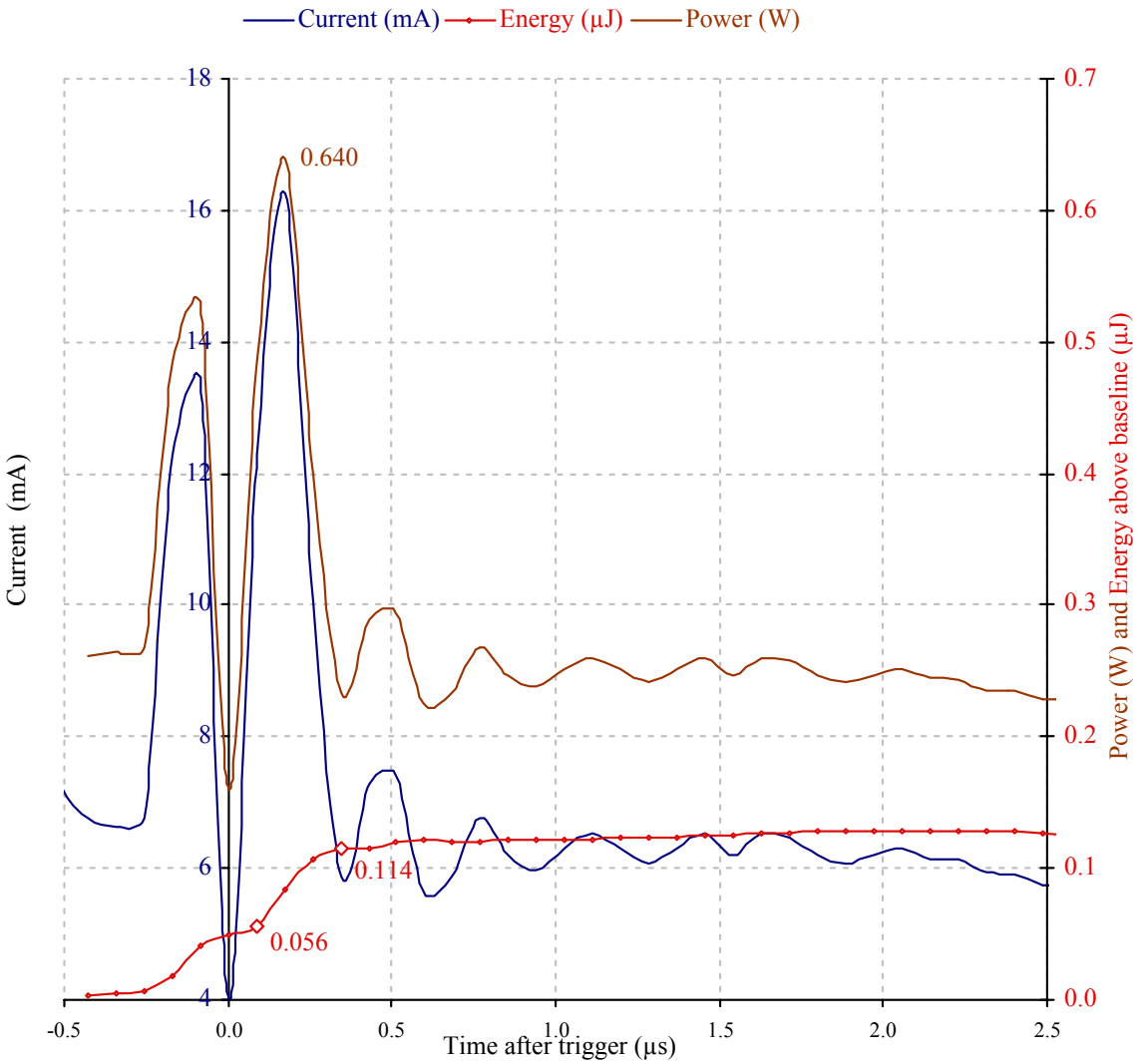


FIGURE 6. TRANSIENT RECORDING OF SPONTANEOUS CURRENT PULSE (2)

From the preceding it is clear that the scintillations are accompanied by current and power spikes, but these are of too small energy and duration to directly initiate bulk vapor phase fuel/air ignition. Apart from their sometimes spectacular pyrotechnic nature, scintillations are of concern for several reasons:

1. The scintillations result in molten silver. The adiabatic temperature resulting from reaction (equation 2) can be calculated assuming only an initial reaction temperature and that sufficient fuel or organic matter is present in the deposit to react fully with the electrochemically produced oxide. With reactants at 150°C (~300°F) the adiabatic final temperature at which liquid silver is produced by reaction (equation 2) is 1728°C (~3140°F). This temperature is the temperature that would be achieved if all of the heat produced by reaction (equation 2) went to produce CO_2 and H_2O gas and Ag liquid, with none of this heat being lost by radiation or conduction. Because of the very brief nature of the scintillations (µs time scale), it is likely that the adiabatic condition is closely

approached. The melting point of silver is 962°C (1763°F). Thus, there is both expectation and evidence that molten silver is present in the vicinity of liquid fuel, albeit momentarily, at nearly 1000°C above its melt temperature in laboratory-grown deposits that closely resemble those found to occur in aircraft fuel tanks.*

2. On cooling, this silver will form a fresh, clean, high-area surface immediately capable of catalyzing further or new chemical reactions. Silver is a modest or good catalyst for some classes of organic reactions [57]. The fact that these catalyzed reactions do not or are not expected to occur normally on the silver coatings present in fuel tanks is largely due to the chemical adherence of sulfur to old surfaces as a result of exposure to (particularly high sulfur) fuels.

3. The presence of reacted silver metal in deposits in both laboratory and field samples, the observation of scintillations in the laboratory, and the association of these observations with a reaction of the type described in equation 2 lead directly to the conclusion that fuels, or products of reacted fuels, are capable of reacting directly with the deposit matrix that results from electrochemical silver oxidation in water. The implications of this finding are potentially profound. Since fuel is generally present in abundance (in fuel tanks), the extent to which reaction (equation 2) can occur, and thus, the total amount of heat energy potentially available to cause hot surface (or catalyzed) ignition is limited only by the amount of Ag2O (or AgO) in the deposit matrix.

   The techniques currently employed limit the amount of energy available to cause bulk phase vapor ignition by controlling the current and the instantaneous electrical power supplied to a fuel tank. As clearly shown in this report, the attached appendices, and in the primary references 1-8, silver oxides can and will grow in situations where silver-plated contacts at dissimilar electrical potentials are bridged by bulk water or humidity films. Retrospective analysis of parts removed from service indicates that this phenomenon does occur in fuel tanks. The rate of deposit growth is affected by the thickness and conductivity of the water layer, the potential difference, and whether the impressed current is ac or dc. The degree of adherence of the deposit is governed by the nature of codeposited fuel oxidation products that is strongly controlled by the sulfur constituents of fuels.

   Nevertheless, silver oxide deposit growth and accretion can occur and does occur with the passage of currents many times lower than those employed for fuel quantification. What is of concern is not the current but the net charge passed. The amount of net charge necessary to form Ag_2O sufficient if reacted to produce energies comparable with fuel vapor ignition energies is very small. Table E-1 in appendix E shows that producing sufficient Ag_2O to yield 0.25 mJ of heat energy when reacted with residual fuel requires only 280 seconds at a net current of 1 μA. Storing chemical energy of 250 J (one million times more than the accepted minimum energy of ignition of bulk fuel vapor) would require nearly 9 years of operation with 1-μA net current, but little more than 3 days at 1 mA.

* The occurrence of silver spheres in field samples could not be confirmed or refuted due to the high organic content covering Ag particles and the susceptibility of silver surfaces to chemical sulfidation.

4. The discussion and calculations above suggest that the scintillations' duration are too brief, and the observed spherical silver products correspond to the release of energy too small to trigger bulk-phase fuel-vapor/air ignition. Nevertheless, the buildup of Ag_2O to vastly greater potential energy levels is inevitable where water bridges silver-plated contacts at dissimilar potentials. This process can occur quite rapidly in fuel tanks at the levels of current control employed for fuel quantification [46]. It is not yet clear why the chemical reactions that give rise to scintillations occur with such brevity and limited energy. In some instances observed at UDRI [8] and ASU [7], it appears that the scintillations cause a transition to, or initiate the condition of, semistable surface glows that can cause ignition of an adjacent volume of fuel vapor and air. It is plausible, therefore, that an ignition reaction sequence follows the following pathway:

   a. Water reacts electrochemically with silver to produce silver oxide at electrified, silver-plated contacts.

   b. The reaction between silver oxide and adsorbed liquid fuel is triggered electrically, electrochemically, or thermally by current flow between partially bridged contacts to produce scintillations, heat, and fine silver particles.

   c. By unknown mechanism the direct reaction of silver oxide and surface-adsorbed fuel undergoes transition from explosive scintillation (time scale of microseconds) to a stable surface glow (time scale of seconds) characteristic of surface catalytic combustion.

   d. Sufficient heat energy (and energy density) is released from surface catalyzed combustion of residual adsorbed liquid fuel (or oxidized fuel products) in the deposit matrix to initiate volumetric fuel vapor/air ignition.

5. Although it is difficult to reproduce the morphological and electrical conditions of deposits, experiments were conducted at UDRI [8] to examine the dependence of scintillations on the sulfur content of fuels. When electrified deposits were treated with low-sulfur fuels (in particular, one sample designated as FAA123 in reference 8), the baseline current increased, then scintillations occurred regularly and were repeatedly accompanied by current spikes. Tests with high-sulfur fuel (e.g. FAA148 in reference 8) decreased the baseline current, did not produce scintillations, and did not produce any current spikes that triggered the recording oscilloscope [8]. Low-sulfur fuel added to an already formed water/fuel deposit caused the current to increase at constant voltage (i.e., decreased resistance). The current decreased when FAA148 fuel was added to the electrolysis residue, by as much as a factor of 10 [8].

   Because sulfur has such a strong affinity for silver, the likely explanation for these observations is that one or more of the sulfur components of high-sulfur fuel reacts chemically at the surface of electrochemically produced silver oxide particles, thereby

   a. increasing the particle surface resistance and decreasing particle-particle contact conduction and

b. preventing, or greatly reducing the rate of, the direct silver-oxide/fuel reaction that results in scintillations.

These observations and conclusions are of possible immediate concern because the trend in modern fuels is to lower sulfur content. Reduction in total sulfur content may result in new or aggravated problems of deposit conductivity and consequent problems for accurate fuel gauging. As repeated washings with low-sulfur fuel gradually remove the protective layers of silver sulfide from existing oxide deposits and new deposits form in low-sulfur environments, the probability of scintillations occurring in fuel tanks by the mechanism described here will increase.

3.6 GLOWS.

The researchers at ASU [7] and UDRI [8] have captured photographic chronologies of the transition in four stages from (1) deposit growth to (2) smoke and flashes to (3) constant glow and (4) ignition. In the testing performed with the ceramic two-wire electrode structures (see items 2 and 3 in section 2.7), considerable electrical current and power input are required to initiate and sustain the combustion processes. In part, this large input power is required to balance the heat lost from the deposit by conduction through two heavy gauge (1 mm diameter) silver wires separated by less than 2 mm. This structure was designed to simulate the condition of two silver-coated wires, closely separated in a region of missing or damaged insulation.

UDRI developed an electrode structure (see item 4 in section 2.7) more representative of the configuration of silver-plated nuts on a Boeing 747 fuel tank terminal strip [8]. By increasing the separation between electrode contacts (to 10-15 mm) and using the flat surfaces on a polymeric terminal strip (instead of a ceramic support), it was discovered [8] that the electrical power input necessary to initiate the glowing surface precursor to ignition could be greatly reduced. Glowing hot spots tend to develop near the center of deposits because reduced lateral conduction of heat decreases the electrical power and power density needed to sustain a zone at significantly elevated temperature. Other factors also may play a role, particularly if a significant fraction of the heat needed to maintain the elevated temperature glow can be derived from fuel or fuel product combustion either as a surface catalytic reaction or by direct reactions with Ag_2O, as discussed in section 3.5.

In a series of experiments recently performed with electrode structure (see item 4 in section 2.7), Kauffman [8] was able to produce low-current scintillations and glows with current-limited dc (40 V, 74 and 30 mA limit) and ac (40 V, 25 mA limit, 400, 2000, and 7400 Hz) power sources. Deposits were grown with silver electrodes contacting the back of polymeric aviation terminal strips in the copresence of water and low-sulfur Jet A (FAA123 in reference 8). Both dc and ac electrolysis resulted in a metallic silver residue that is a mixture of hexagonal platelets, spheres, and dendrites ranging in size up to 10 μm [8].

The silver residues produced by dc electrolysis were studied at UDRI for fuel reactivity. A large drop (100 μL) of low-sulfur (FAA123) fuel was dispensed onto the dried Ag residue, while power from the 40-Vdc power supply (limited to 74 mA) was applied to the Ag wires in contact with the Ag residue. The initial residue resistance was 150 Ω, and the current flow measured in series with the residue was 74 mA (at the current limit of the power supply). Scintillations

comprising flashes of light and smoke occurred within 10 seconds of applying the 40-Vdc power as the current flow decreased from 40 to 6 mA. At 6 mA several scintillations occurred and the current increased to ~17 mA, at which point a hot spot initiated near the middle of the Ag residue [8]. In contrast to the scintillations which lasted for microseconds and caused current spikes [1 and 8], the hot spot lasted for several seconds and produced no spikes, only slow changes in the current. When the hot spot decreased in intensity, a second drop of fuel was added and a new hot spot initiated within 1 mm of the first and lasted for several seconds. FTIR analyses of the resulting residue products indicated the presence of oxidized fuel/gums not present in fresh FAA123 fuel [8].

This experiment was conducted five more times with Ag residues formed by electrolysis at 40 Vdc and allowed to react with FAA123 Jet A [8]. Glowing hot spots were created each time with the addition of the fuel drop to the Ag residue. During the last two experiments, water drops were added to the negative Ag electrode wire to improve the electrical connection, thus achieving current levels above 10 mA and maintaining the activity of the hot spot. The water drop at the negative electrode also provided H_2 to the hot spot that may have contributed to the apparent fuel ignitions (vapor above hot spot bright) that occurred at the hot spot on the edge of the water drop. Four separate fuel ignitions were observed during the last two tests with water drops present [8].

After each Ag residue formation and fuel reaction, the cleaned terminal block surface was inspected for damage caused by the heat of the hot spot. Several small pits (less than 1 mm in diameter) were observed in the polymeric terminal block surface in the area of the hot spots after the first three tests. After the last two tests, a large, irregular crater that provided further evidence that fuel ignitions occurred in the final two Ag residue/fuel reactions replaced the small pits in the terminal block surface. The crater also facilitated the hot spot by acting as a fuel reserve for the Ag residue/fuel reaction, increasing the lifetime and brightness (i.e., temperature) of the hot spots [8].

A similar series of experiments was performed at UDRI to study the fuel reactivity of Ag residues produced by ac electrolysis (more typical of aircraft fuel quantity gauging systems). Three different frequencies (60, 400, and 7400 Hz) and two different waveforms (square and sine) were applied using the 40-Vac modified waveform generator to create six different Ag residues. A drop (100 µL) of FAA123 fuel was dispensed onto each dried Ag residue and power from the 40-Vac generator with selected cycle/waveform combination was applied to the Ag wires in contact with the Ag residue. In every experiment flashes/smoke occurred within 10 s of applying the 40-Vac power. In contrast to the 40-Vdc experiments, no glowing hot spots were created with the 40-Vac power. After the six 40-Vac experiments, no surface damage was observed on the cleaned terminal block, further indicating that hot spots were not created by the ac experiments [8].

Before concluding that glowing hot spots and fuel ignition at low input electrical power are a consequence of direct but not alternating current, it is necessary to make further examination of the expected effect of different electrical circuits. The first point of significant difference is that the dc power supply used in the experiments described above was capable of a maximum power output of 0.74 W, while the ac supply was limited to 0.42 W [8]. Attempts to explore the

reactivity of Ag electrolysis residues and Jet A under dc conditions with current limited similarly to the ac resulted in a changed mode of behavior for scintillations and glows, suggesting a strong influence of the power supply circuit. After the Ag residue was created by electrolysis of the fuel/water drops on the terminal block, a drop (100 μL) of FAA123 was dispensed on the dried Ag residue. When power from a 40-Vdc supply (in this case limited to 30 mA) was applied to the Ag wires, flashes/smoke occurred as the current flow decreased from 30 to 15 mA. As opposed to the 40-Vdc, 74-mA experiments, no hot spots were created with the 30-mA power with the first drop of fuel [8].

As additional fuel drops were dispensed onto the Ag residue, the current remained around 15 to 20 mA and flashes/smoke were observed together with spikes in recorded current. The current then dropped dramatically to 2 mA and a small glowing hot spot was observed. When the hot spot ended after 2-5 seconds, the current returned immediately to the 15-20 mA range. Each time a hot spot was observed, the current decreased to 2 mA, and each time the hot spot ended, the current returned to 15-20 mA. Consequently, the hot spots were occurring at very low measured input power (0.08 W). While of relatively small area, the low-power hot spots were white in color, appeared to ignite fuel vapor, and produced small craters in the terminal block, all indicative of temperatures equal to the glowing hot spots produced with higher measured input powers [8].

Since the hot spots were occurring at low current (high resistance), the burning of fuel may have provided a significant portion of the heat produced by the hot spot. The occurrence of light and heat initiated upon the addition of fuel ended with the evaporation of the fuel, and was extended by using a glass vial to capture the fuel vapor above the hot spot, facts further indicating that burning of fuel was providing energy to the hot spot [8].

The experiment described above was repeated with the silver wires replaced by silver-plated nuts similar to those found in service on terminal strips in fuel tanks. These resulted in scintillations at currents below 5 mA. Glowing hot spots were not seen, possibly because the much larger heat capacity of silver nuts did not allow for a rapid temperature rise or because of poor contact between the silver-plated nuts and the formed residues on the surface. Vapor phase fuel/air ignition did not occur.

3.7 ELECTRICAL CIRCUIT CONSIDERATIONS.

The significant conclusions of the preceding section are:

- Separating the electrical contacts results in a substantial reduction in the electrical input power necessary to promote sustained glowing hot spots.
- Limiting the current delivered to the deposit from a fixed voltage supply decreases the electrical input power necessary to cause hot spots.
- The heat to sustain the glows is supplied in part by the surface combustion of adsorbed liquid fuel.
- Sustained surface glows can result in bulk phase fuel vapor/air ignition.

The first two of these points are somewhat contrary to immediate expectation. All else being equal, increasing the distance between electrodes (and thus the resistance) and decreasing the maximum current should reduce the maximum input power and, thus, decrease the severity and likelihood of any effects caused by this power.

To resolve this apparent discrepancy, a model was developed for the formation of glowing hot spots with the following features:

1. For geometric reasons, possibly introduced during initial deposit formation, a very large fraction of the current that flows between contacts is constrained to flow through a small region.

2. This region may have similar or even smaller resistivity than the surrounding deposit matrix, but has high specific resistance (R) because of its small cross section in the direction of current flow.

3. The electrical power (I^2R) in this region is a large fraction of the total electrical input power; the very high-power density (W/cm^2) heats the high resistance region, raising the local temperature.

4. High local temperature ignites a glowing hot spot either thermally or by thermally induced chemical reaction.

The role of heat dissipation, primarily by conduction and radiation, increases rapidly with temperature, and therefore, does the requirement for input power. The condition of a stable glowing hot spot can occur only if special conditions are met in the electrical circuit comprising the deposit and power source. Let us examine four cases.

1. Voltage Control. This is the manner in which most electrochemical experiments and many laboratory studies are performed (including the ignition testing at ASU) and imposes a controlled, fixed voltage across the sample under test. The power supply is capable of supplying any current (up to some defined limit) without reduction in specimen voltage. This mode of power control is very unlikely to produce a stable hot spot. As the temperature increases, so does the resistivity (typical of metallic conduction). With resistance rise the input power ($\approx V^2/R$) decreases and the system is stable.

2. Current Control. Alternatively, one can specify and control the current at fixed value, allowing the power supply to vary the voltage as the specimen resistance changes. This mode of control is unstable. As the resistance increases with temperature, so do the input power ($\approx I^2R$) and the heating effect, and the system acts like a thermal fuse. Very probably this is what occurs to produce scintillations.

3. Power Governed by Series Resistance. This circuit was used at UDRI [8] to produce low-current glows. By placing a constant voltage supply in series with a fixed external resistance (R_s), the current and voltage in the specimen can be somewhat controlled. In this situation, maximum power is delivered to the specimen under test when its resistance

is equal to the external series resistance. If the chosen value of R_s is much smaller than the specimen resistance (to the right of the power maximum; see figure 7) then voltage control is approximately held. Current control is approached when R_s is much larger than the deposit resistance. Producing a stable glow thus requires a deposit resistance initially lower than the external series resistance (unstable), which increases with heating past the power maximum. Provided the deposit survives without fusing at the maximum input power density and this power density is sufficient to cause a glowing hot spot, then the resistance enters the stable region (figure 5). Under this metastable condition the glow will persist until affected by some other input.

Figure 7 highlights one case observed by Kauffman (see figure 54 in reference 8), where stable glowing hot spots were produced by the reaction of low-sulfur fuel (FAA123) and electrochemically produced silver residues. In this case a 40-Vdc supply was limited with a 1205 Ω series resistance (maximum current 33 mA, maximum power 332 mW).

The point marked initial in figure 7 reflects a period of stable (~20 mA) current flow without scintillations or current spikes prior to the development of a glowing hot spot lasting ~3 seconds. The cause of this transition apparently is the passage of relatively high current and power (20.5 mA and 314 mW) for several seconds without deposit disruption and scintillation. Transition occurs with increasing temperature and increasing resistance (~750 to ~19,000 Ω) into the stable region, accompanied by a significant decrease in electrical input power (~300 to ~75 mW).

In this case, the initial and maximum power points were not greatly different (314 and 332 mW), and the degree of electrical robustness necessary to sustain the preglow current flow clearly was sufficient to permit the deposit to undergo transition through the power maximum without fusing. With a different chosen value of R_s this might not have been the case. With a value of R_s = 800 Ω and maximum power of 500 mW, the deposit might not survive the transition from initial to stable glow condition. With a value of R_s = 8000 Ω and maximum power of 50 mW, it is unlikely that sufficient electrical heating could occur to force the resistance transition. Clearly, the properties of the external circuit are as important as those of the deposit in determining whether glows, scintillations, or no ignition effects occur.

4. Additional Power Input. Neglected in the preceding discussion of electrical effects is the energy necessary to sustain the deposit hot spot. The glowing condition clearly is at higher temperature, dissipating more heat power than in the initial state, and yet the measured electrical input power is less. This additional energy can come only from the consumption of fuel either as vapor, adsorbed liquid or solid oxidized fuel products (gums), with the oxidant being oxygen from air or electrochemically produced silver oxide.

An approximate but definitely lower limit can be placed on the power and energy of this inferred combustion process. For the same surface area, the power supplied by the putative combustion source to maintain the deposit at the temperature of the initial state is 314 - 75 = 238 mW (times 3 seconds equals ~715 mJ). Based on its color, the

temperature of the glowing surface is several hundred ºC higher than the state that precedes it. The estimate of 238 mW and 715 mJ may therefore be substantially low.

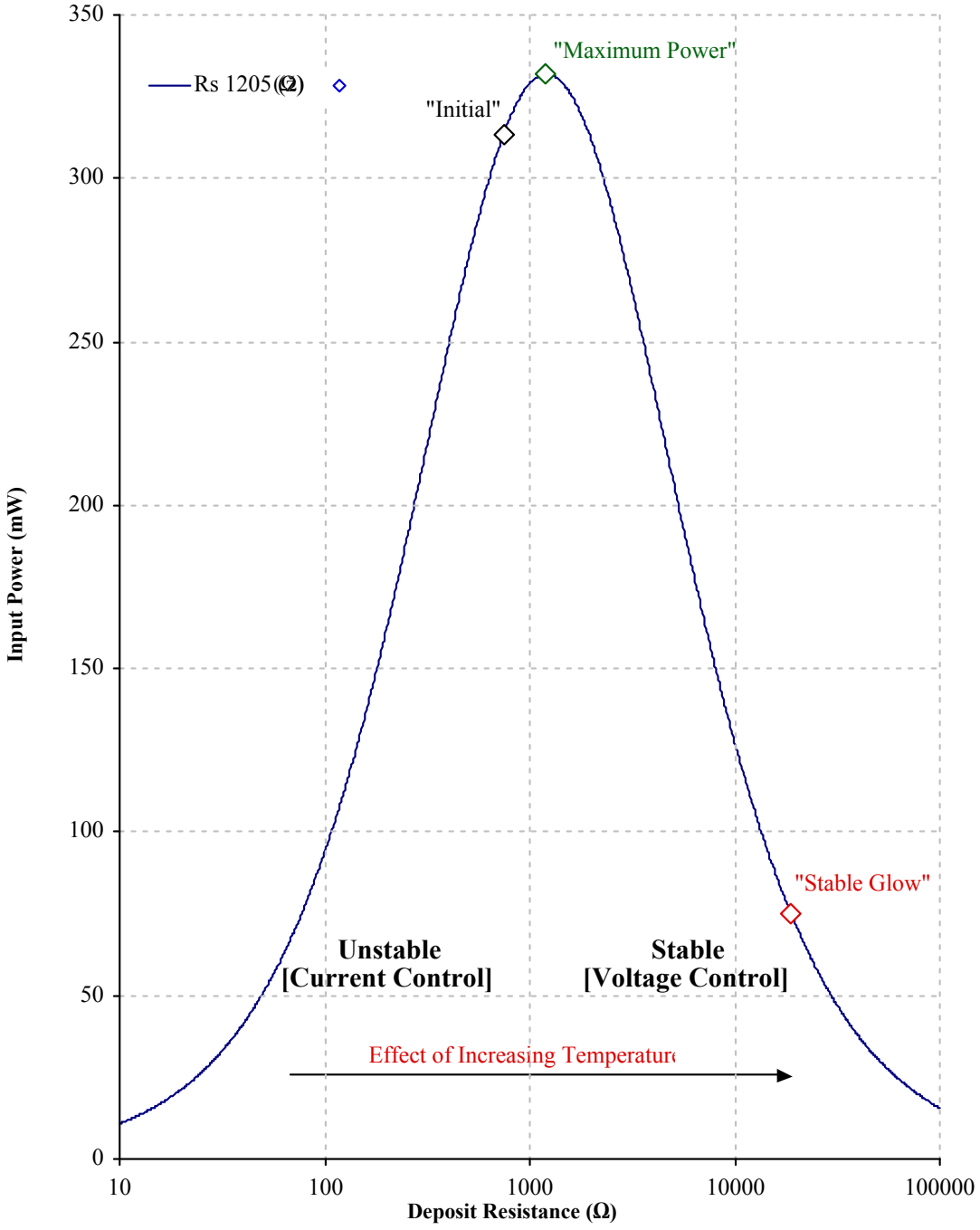


FIGURE 7. ELECTRICAL POWER IN DEPOSIT AS A FUNCTION OF DEPOSIT RESISTANCE, DEMONSTRATING REGIONS OF STABILITY AND INSTABILITY AND THE EFFECT OF INCREASING DEPOSIT TEMPERATURES

4. CONCLUSIONS AND RECOMMENDATIONS.

The research described in this report was directed to the following eight objectives established by the Federal Aviation Administration (FAA) in response to National Transportation Safety Board recommendation A-98-37:

1. Investigate the characteristics of copper and silver sulfide deposits on probes and wiring, with emphasis on the chemical composition and electrical properties of these deposits.

2. Investigate the mechanism that creates the copper and silver sulfide deposits on probes and wiring in fuel tanks. Emphasis should be placed on factors that contribute to the mechanism, estimated normal growth rates, factors affecting the growth rate, etc.

3. Attempt to grow the deposits under laboratory conditions.

4. Examine the effects of the conductivity of the deposits on the accuracy of the fuel quantity measurements of fuel quantity indication sensors (FQIS).

5. Determine if there are any potential ignition threats from the copper and silver sulfide deposits during potential FQIS electrical system failures (including shorts to the FQIS wiring).

6. Investigate methods to mitigate the formation of the deposits on FQIS components.

7. Investigate the potential for interaction between Jet A fuel and nickel-plated FQIS wiring and the formation of similar type deposits on such wiring.

8. Analyze FAA-provided Jet A fuel samples for sulfur, natural antioxidant, and trace metal concentrations and attempt to determine what effect these concentrations have on the formation of the sulfides.

Progress toward achieving these objectives and significant conclusions are summarized below.

4.1 STUDY CHEMICAL AND ELECTRICAL CHARACTERISTICS OF DEPOSITS.

Naturally occurring fuel deposits and similar deposits grown electrochemically in the laboratory are heterogeneous and multilayered mixtures of organic and inorganic materials. The conductive portions of the residues contain a mixture of organic material and silver/silver oxide species providing both ionic and electronic conductivity. The organic portion of conductive deposits has the form of fuel gums resulting from oxidation of low-sulfur fuels.

Copper sulfide and sulfur species that are present in deposits do not contribute significantly to conduction. Addition of high-sulfur fuels causes a decrease in residue conductivity. Addition of certain low-sulfur fuels causes an increase in residue conductivity.

To date, conductive deposits have only been found on terminal blocks with silver-plated nuts. Residues with similar appearance have been reported on silver-plated fuses and fuse-holders, but no samples were analyzed during this work. Conductive deposits have been grown in the

laboratory in the presence of electricity (ac or dc), fuel, water, and silver or silver-plated wires and nuts.

4.2 INVESTIGATE MECHANISMS OF DEPOSIT FORMATION.

Under normal operating conditions, conductive residues form at ac-powered silver surfaces exposed to water in aircraft fuel tanks. Electrochemical reactions of water at silver surfaces produce silver and silver oxide particles that are electronically conductive and thus electrochemically reactive. Certain low-sulfur fuels then react with adsorbed films of water and conductive silver species to form protective layers of oxidized fuel gums. In addition to providing ions for conductivity and electrical continuity, these gums protect the fragile conductive structure against mechanical disruption by liquid fuel and against passive film formation by reaction with high-sulfur fuels.

Necessary and sufficient conditions for the formation of conductive fuel residues are (1) the presence of water; (2) electrical power (at voltages $\geq$ 5 V either ac or dc); (3) exposed silver surfaces; and (4) the presence of low-sulfur fuels that oxidize easily to produce hydroperoxides and gums. Aircraft factors that (1) tend to form and stabilize continuous liquid water and fuel films between polarized, silver-coated electrical contacts; (2) stabilize the layer of produced silver particles; (3) add dc imbalance to the applied ac power; or (4) increase the fuel temperature, all would be expected to increase the rate of deposit growth. Environmental factors such as high humidity, increased air temperature, decreased levels of sulfur in fuels, and fuel aging during storage or between fuelings would also contribute to deposit growth.

4.3 GROW DEPOSITS UNDER LABORATORY CONDITIONS.

Conductive residues were grown under laboratory conditions using silver-plated nuts, silver-plated copper wires, and silver wires in geometries similar to those found in aircraft tanks. The elemental composition and electrical properties of the laboratory-grown conductive residues are similar to those of the conductive residues removed from the field.

The rates of the electrochemical reactions that cause deposit accretion are strongly influenced by the conductivity of the water bridge between the electrified silver contacts. Bulk water droplets were used in the laboratory to facilitate deposits grown in minutes or hours. This condition may be different from that occurring in the ullage of aircraft fuel tanks, where aqueous bridging initially will occur through condensed water films formed when aircraft fly to altitude from warm, humid environments or when descending into humid air with an unburned volume of cooled fuel. Electrochemical reactions that proceed at mA or tens of mA rates with silver electrodes bridged by bulk water occur at µA to tens of µA rates in condensation films. That is, deposit-forming reactions occurring on exposed fuel tank surfaces proceed approximately 1000 times more slowly than the accelerated rates of laboratory-grown deposits.

4.4 EXAMINE EFFECT OF DEPOSITS ON FUEL QUANTITY GAUGING.

Quantitative analyses were not made of the effect of conductive deposit growth on the accuracy of capacitative fuel quantity gauging by the various means extant. Qualitatively it is clear that the initial formation of highly conductive silver residues will exhibit a sporadic (intermittent)

fault condition in electrical gauging systems. Fully stabilized deposits will produce a consistent error of either sign (over- or under-measurement) that may or may not fall within the range of calibration compensation. Because of the characteristic electrochemical impedance of the heterogeneous deposit conduction, its presence can, in principle, be detected by measuring the frequency response of contact-contact conduction external to the tank.

Deposits of sufficient conductivity to cause error in some (possibly all) electrical fuel gauging systems were observed that contained copper or cadmium, and not silver. A characteristic of these deposits is that they conduct only when wet with water, not when dry or wet with fuel, and they do not produce scintillations when electrically powered. Testing in an environment of cycled high temperature and humidity (40ºC and 95% relative humidity) of B747 terminal strips supporting cadmium-containing deposits revealed an extreme moisture sensitivity to conduction that clearly could result in transient fuel gauging errors.

4.5 IDENTIFY POTENTIAL IGNITION THREATS.

Potential threats exist at three levels, summarized below in order of decreasing certainty and increasing sensitivity:

1. Deposits grown in the laboratory by the electrochemical reactions of water and fuel at silver electrodes were shown to ignite fuel vapors above a heated Jet A surface. These ignitions conform to models of hot surface ignition and require the sustained input of electrical power much larger (by factors of between 100 and 1000) than the power deliberately or intentionally supplied inside aircraft fuel tanks for the purpose of fuel quantity indication.

   No special chemical or catalytic role is ascribed to the deposit in hot-surface ignition except to conduct electricity and support an energy-induced temperature rise. Chemical and electrical changes do occur, however, as a consequence of failed, partial, or full vapor phase ignition events. Carbon forms on surfaces subjected to repeated electrical stimulation as a consequence of the incomplete oxidation of surface-adsorbed fuel in the absence of sufficient oxidant (oxygen in silver oxide or air). The presence of carbon appears to be crucial in transforming electrochemically formed deposits into structures sufficiently robust to withstand the high electrical power densities necessary to support hot-surface ignition.

   The role of electricity in this ignition mechanism is simply to sufficiently heat a small area of deposit, and the time constant of heat transfer is long compared with the period of waveforms used for fuel quantification. As such, ac and dc sources will yield similar results.

   The possibility of hot-surface ignition has been considered and anticipated in the design of aircraft fuel tank electrical systems. For this to occur, as a consequence of deposit formation, would require the inadvertent contact of wires with compromised isolation inside the fuel tank to high-power circuits (either ac or dc) outside the fuel tank. Because of the initial fragility of electroformed deposits, it is highly probable that this unintentional contact must be made repeatedly to convert the electrochemically formed

deposit into a structure adequately robust to support electrical heating sufficient for hot surface ignition of flammable fuel-vapor/air mixtures in fuel tanks.

2. A second mechanism was demonstrated to ignite fuel/air mixtures with electrical input levels more closely matched to those in use for fuel quantification. When stimulated electrically or electrochemically, the silver oxide content of deposits formed at silver surfaces can be made to react with surface-adsorbed liquid fuel. This reaction produces heat, molten silver, and can sustain glowing hot spots on electrode surfaces. In hot-surface ignition, these glows are precursors to ignition. Simple calculations show that the energy required to sustain the electrochemically assisted glows is amply sufficient to exceed the minimum energy of ignition of fuel-vapor/air mixtures. Stable glows were observed at current inputs as low as 2 mA and dc power inputs as low as ~75 mW.

   The electrochemically assisted fuel ignition mechanism is far more susceptible to dc power, and the level of dc power shown to be capable of causing fuel ignition is at least an order of magnitude lower than for ac. Most aircraft electrical fuel quantification systems operate with ac (in the range 400 to 7400 Hz). In addition to the waveform dependence, the electrical properties of the external circuit are as important as those of the deposit in determining whether stable glows can and will occur.

   There are, nevertheless, several factors of possible concern:

   a. Some FQIS systems employ diodes, therefore converting ac to dc inside the tank.

   b. Nonlinearity in electrochemical systems can result in significant dc current components from ac voltage inputs greater than ~5 V.

   c. Once a glow is initiated in a deposit (at currents 2 mA dc or less), the output energy is limited only by the masses of pre-existing silver oxide and adsorbed liquid fuel capable of wicking to the reaction site. Thus, potential chemical energy can be stored over very long periods, at unnoticed current levels, to be released with electrochemical stimulus.

   d. The instantaneous temperature reached by reaction of fuel and silver oxide is over 1700°C, capable of melting silver and forming small droplets of clean, catalytically active silver surface.

3. Fuel added to deposits forming or formed by water electrolysis with a silver positive electrode (either electrode if ac) reacts to produce bright spark-like scintillations, audible detonations, smoke, transients in electrical current, and the generation of radio frequency noise. These scintillations occur most readily with easily oxidized low-sulfur fuels. At higher current levels (>300 mA) all fuels scintillate with deposits formed as described. There is considerable historical evidence and literature report of this phenomenon, which is not limited to aviation fuels.

   A mechanism is described in this report that ascribes these scintillations to the explosive exothermic reaction of small volumes of electrochemically formed silver oxide with

intimately contacted liquid fuel or partially oxidized fuel solid products (e.g., gums). Silver spheres up to 2 μm in diameter formed as a result of melting provide evidence of this reaction and permit calculation of the heat released. A 2-μm-diameter sphere formed by reaction of silver oxide and a typical constituent of jet fuel would be accompanied by the release of only 3.5×10^{-8} J (35 nJ). This is clearly too small an amount of heat to cause bulk phase fuel-vapor/air ignition. Furthermore, the durations of the scintillations (fractions of a microsecond) are far too brief to spark fuel vapor ignition.

These scintillations are, however, easily produced and essentially ubiquitous in the presence of deposits containing silver, jet fuel (particularly low sulfur), and small current flows. They apparently evidence ignition and are observed as precursors to both hot surface ignition of fuel vapor and sustained surface glows.

4.6 INVESTIGATE METHODS TO MITIGATE DEPOSIT FORMATION.

No direct methods of mitigation or remediation of the deleterious effects of fuel deposits were studied. Primary effort was directed to understanding their growth mechanism, chemical, mechanical and electrical properties, and potential roles of deposits in electrical fault or ignition hazard. This derived knowledge is used here to prescribe methods to avoid the occurrence of faults and the development of unnecessary potential hazards.

The growth of deposits from nucleation to hazard involves several steps:

1. Initiation
2. Oxide deposition
3. Surface adherence
4. Connective conduction
5. Catalysis and ignition

Different methods can be used to interrupt each of these steps.

1. Deposits initiate with the electrolytic action of water on coupled, exposed metal surfaces maintained at dissimilar potentials. All that is required is exposed electrochemically active metal, bridging water, and current flow (either ac or dc). To prevent this step, metal terminals or wires need either to be fully covered by insulator (a difficult task) or coated with metals not subject to electrochemical attack (these tend to be expensive or difficult to work with). The currents that flow at this stage may be very low (nA to μA). If water is to be prevented from forming an ionically conductive electrolyte bridge, then it must be excluded completely, for example, by fully encapsulating the terminal block and coated wire termination. Alternatively, by maintaining the maximum potential difference between terminals below about 2 to 3 V (ac or dc), water electrolysis and electrolysis-induced deposit initiation can be effectively avoided.

2. When sufficient metal has dissolved by electrochemical action it transports in the bridging electrolyte (water and fuel) and precipitates deposits that form nucleation sites for further growth. Conductive deposits such as silver and silver oxide decrease the terminal-terminal resistance and accelerate the corrosion and deposition rates. At this

stage the current will increase approximately exponentially until limited by material transport or other system resistance. Configuring terminal strips with long paths, or dams, between electrified terminals can slow this process. The ultimate growth rate is governed by the thickness of the bridging water layer (and its conductivity). Minimizing the rate and degree of humidity cycling and condensation can minimize the rate of accumulation and thickening of water films. The geometry of contacts, whether vertical, horizontal, facing up or down, also will affect the rate and maximum extent of water accumulation.

3. At this stage, the oxide deposits from copper and silver are flimsy, flocculent, and poorly adherent. Simple rinsing with water or fuel is sufficient to dislodge them from the surface and remove them from sites that increase conductivity. Although untested, it is likely that a normal flight with an initially full tank would subject deposits to mechanical washing sufficient to dislodge deposits and restart the clock at the initiation step. Conversely, fuel also plays a role in promoting adherence. Oxidation of certain classes of low-sulfur fuels produces tenacious brown gums capable of binding the inorganic protodeposits to the surface. Preventing this requires avoidance of low-sulfur fuels capable of oxidizing to form hydroperoxides and gums. Tests for this condition have been developed and additive antioxidants can be used to prevent it. If this condition is not prevented, the rates and likelihood of oxidation to gums can be reduced by avoiding long storage of fuel and maintaining low fuel temperatures, both in the tank and on the ground. Although also untested, it seems plausible that the adherence of gums can be controlled by appropriately modifying the surfaces of terminal blocks.

4. The conductivity of fully formed deposits is controlled by the conductance of the particles themselves. This conductance has three parts: (1) the intrinsic particle conductivity; (2) particle-particle contact resistance in connected (percolation) strings; and (3) the spacing, thickness, and ionic conductivity of the medium bridging disconnected particles. For the first, metals with highly conductive oxides should be avoided. The oxides of silver are highly conductive, much more so than the sulfides. Washing partially or fully formed deposits with high-sulfur fuel results in an increase in deposit resistance, probably because of the chemical formation of a partially passivating and insulating surface sulfide or oxy-sulfide. Another important role of the oxidized fuel gums may be to prevent this passivation. These observations and analyses clearly support the conclusion that Jet A with high sulfur content (>300 ppm) may be beneficial in preventing the growth of electrochemically derived conductive deposits in fuel tanks.

5. This report discusses in detail two ignition mechanisms of potential concern in fuel tanks: hot-surface ignition and electrochemically assisted ignition. Both have been observed to occur only with deposits derived from silver-coated electrical contacts. The most obvious first step in any strategy to avoid potential ignition hazard is to remove silver-plated nuts from existing fuel tanks, and repair or replace silver-plated wires and other fuel tank components with exposed silver surfaces.

   In addition to silver-formed conductive deposits, both ignition mechanisms require electrical stimulation. For hot-surface ignition, the purpose of this stimulation is to heat a portion of the deposit surface to a point sufficient to ignite a proximate fuel-vapor/air

mixture. The power requirement has been quantified statistically for one electrode configuration and is greater than the power levels intended to be present in commercial fuel quantity gauging systems. The needed power densities are, apparently, greater than can be supported in fully formed silver oxide/gum deposits. To ignite fuel vapors, deposits must be modified by the partial oxidation of surface-adsorbed fuel or solid fuel deposits to form a reinforcing carbon framework. This modified structure is sufficiently robust electronically and mechanically to withstand the high electrical power densities, and high temperatures, necessary to initiate hot-surface ignition. Of significance here is that more power is needed in transformation and ignition than is intended to flow in FQIS wiring, and the power is probably required to flow multiple times. This obviously can be prevented by appropriately decoupling main power wiring outside the tank and FQIS wiring inside. Of primary concern here is limiting the power and energy needed to cause surface heating. A model of hot surface ignition was developed to allow quantitative constraints to be applied.

Less easily quantified is the phenomenon of electrochemically assisted ignition. Glowing hot spots apparently consuming surface-adsorbed fuel in reaction with surface-formed silver oxide have been observed at currents as low as 2 mA and electrical power as low as 75 mW. This phenomenon has been observed to occur only with dc power, and an obvious second step to its prevention (after removal of electrochemically active silver surfaces) is to prevent dc power from flowing in FQIS wiring.

4.7 STUDY INTERACTIONS BETWEEN JET A AND NICKEL-PLATED WIRING.

Silver is the only metal present on aircraft that is capable of producing durable conductive residues in the presence of fuel. While a comprehensive study was not performed, initial results indicate that electrified nickel-plated surfaces and wires do not produce conductive residues in the presence of water and fuel at rates measurable in experiments lasting minutes or hours. Cadmium and copper undergo electrochemical reactions with water to produce residues with intermediate conductivity, which become relatively more nonconductive when exposed to fuel. Humidity testing of B747 terminal strips supporting cadmium-containing deposits revealed an extreme moisture sensitivity to conduction that clearly could result in transient fuel gauging errors.

4.8 ANALYZE JET A FUEL SAMPLES.

The fuels studied during this research have a wide range of sulfur concentrations and oxidation/deposition characteristics. The fuels that have the lowest levels of sulfur species and of naturally occurring phenol and amine antioxidants (fuels obtained from Asian and European regions) and that undergo rapid thermal oxidation to produce hydroperoxides and gums appear to be essential for the rapid formation of conductive deposits. Fuels containing elemental sulfur, hydrogen sulfide, and disulfide-type sulfur compounds that tarnish silver surfaces appear to inhibit formation of conductive residues. There is some indication that the percentage of low-sulfur fuels (capable of supporting the production of conductive residues) is increasing, especially in Europe and Asia. Considering only the phenomena studied and detailed in this report, this trend to lower sulfur should be viewed with some concern.

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APPENDIX A—ELECTROCHEMICAL IMPEDANCE MEASUREMENTS OF LABORATORY-GROWN SULFIDE DEPOSITS

A.1 INTRODUCTION.

A series of experiments was performed using electrochemical impedance spectroscopy to examine the rates and mechanisms of conduction and electrochemical reaction in laboratory-grown deposits and films. Samples were prepared using the cylindrical ceramic holder, described in item 2 in section 2.7, with two 1-mm-diameter Ag wires separated by a 1-mm gap, mounted facing vertically downward with the wire electrodes contacting the bottom of a small, shallow, flat-bottomed disposable plastic weighing dish. In this way, both deionized water and fuel could be added to bridge the electrode gap, quantitatively, and without the need for continuous replenishment.

Experiments were performed to examine the effect of controlled current ac and dc voltage on the growth and conduction of bridging deposits. Various compositions of fuel and water were used, including an intentionally aggressive mixture of 50% deionized water, and 50% degraded (oxidized) fuel.

A.2 CONTROLLED CURRENT AC.

Ten experiments were performed with controlled current ac perturbations of amplitude up to 10 mA, stepped successively in frequency from 1 Hz to 50 kHz in 50 logarithmically spaced steps. The time for each measurement cycle was approximately 6.6 minutes. The results of experiments of this sort are commonly plotted in what is called the complex plane, as shown in figure A-1. The horizontal axis is the real component of resistance (or just the resistance), designated R. The vertical axis is the imaginary component of the impedance (called reactance), designated X. Reactance measures the presence of components that change the phase of the ac response. Negative values of X are caused by capacitive or diffusional impedance elements, both of which are normally present in electrochemical systems. Positive values of X are attributed to inductance or such esoteric things as negative capacitance occasionally found in electrochemistry. Frequency is not plotted explicitly in a complex plane plot.

The blue circles (DI H_2O) in figure A-1 were obtained with deionized water alone, before the addition of oxidized fuel. In this case, due to the high resistance, the current perturbation was 100 μA. Later data sets were obtained with a current perturbation of 200 μA, 500 μA, and the remainder at 1 mA. These changes were made necessary by the decreasing resistance of the system. Because of some time variation in the system, the resistance values measured in deionized water trend toward increasing values, with the lowest frequency points falling near the resistance axis (X = 0). The dashed line continued from the highest frequency point extrapolates the curve expected for a resistance of the specified value, in parallel with a capacitance; the form of this curve is a semicircle centered on the real axis. These data show that, with small ac current perturbation (100 μA) all that was observed is the (relatively high) resistivity of deionized water in parallel with the geometric capacitance of the two wire electrodes bathed in deionized water; there is no evidence of electrochemical process.

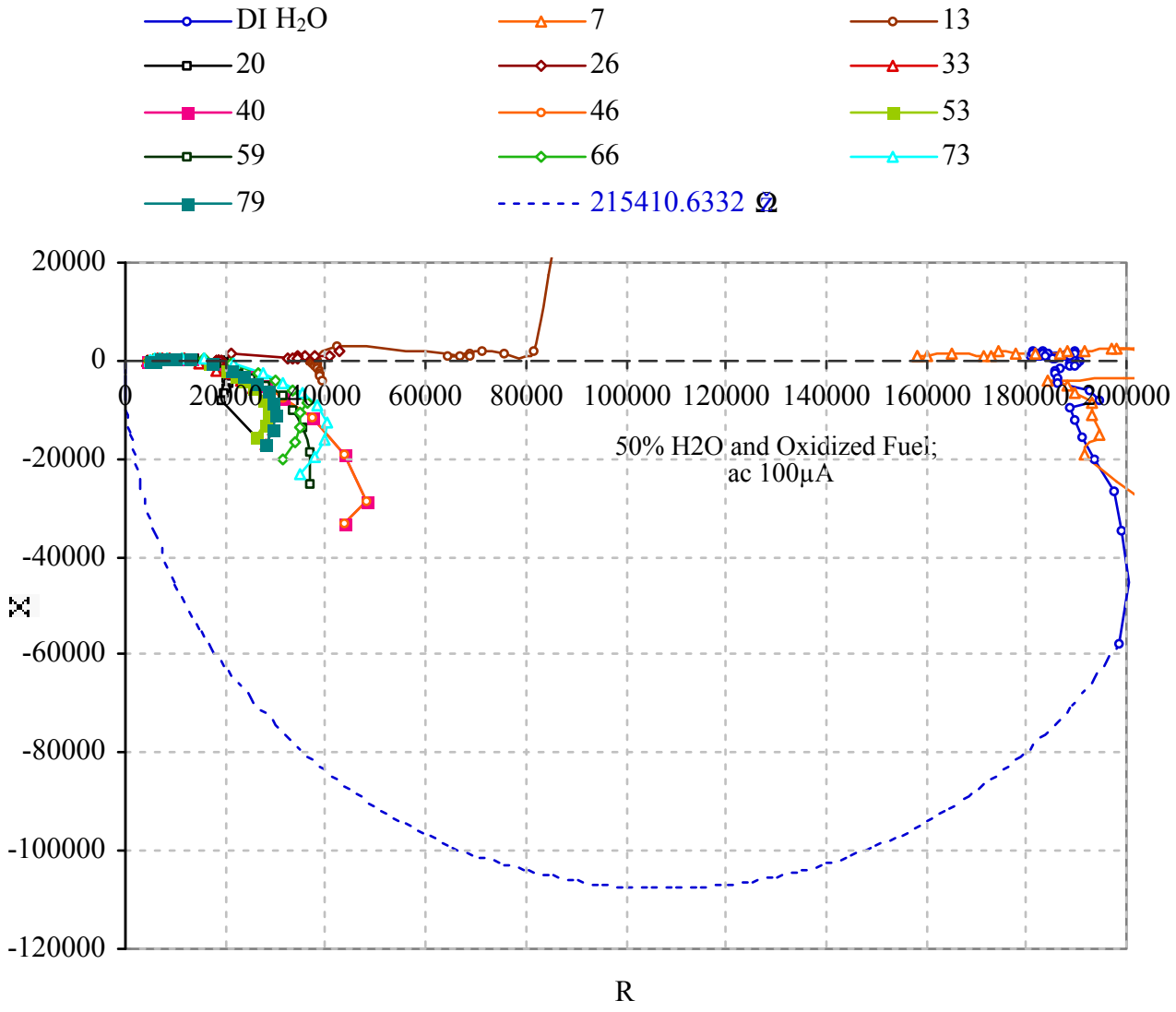


FIGURE A-1. RESULTS OF EXPERIMENTS WITH CONTROLLED CURRENT AC

With the addition of degraded fuel and the increase of current up to 1 mA, this situation begins to change, and a family of curves having completely different shape appears at much lower resistance values. Interpretation of these data is complicated by the presence of time variance, but the various data sets measured at the times specified (in minutes) begin to exhibit characteristics of a heterogeneous mixture of electronically conductive and ionically conductive (diffusional) paths.

Selecting two frequencies from the 50 plotted in figure A-1, one can appreciate more clearly the change in resistance that has occurred by electrochemical means, with the addition of degraded fuel. Figure A-2 plots the resistance measured at 5 Hz (close to the low frequency or dc limit) and 400 Hz (characteristic of aircraft electrical systems) as a function of time after the addition of 50% oxidized fuel. At 400 Hz, the resistance, drops progressively from its initial value of

210 kΩ in deionized water to a constant value of approximately 5 kΩ after only 33 minutes of ac electrolysis. The reason for this invariance is clear from figure A-3, which plots the ac voltage between the two electrodes, calculated as the product of the current perturbation and the resistance measured at the specified frequency. At less than 5 Vac, the cell is apparently incapable of producing further conductive deposits. There is simply insufficient voltage to promote net electrochemical processes, and the decrease in resistance stops.

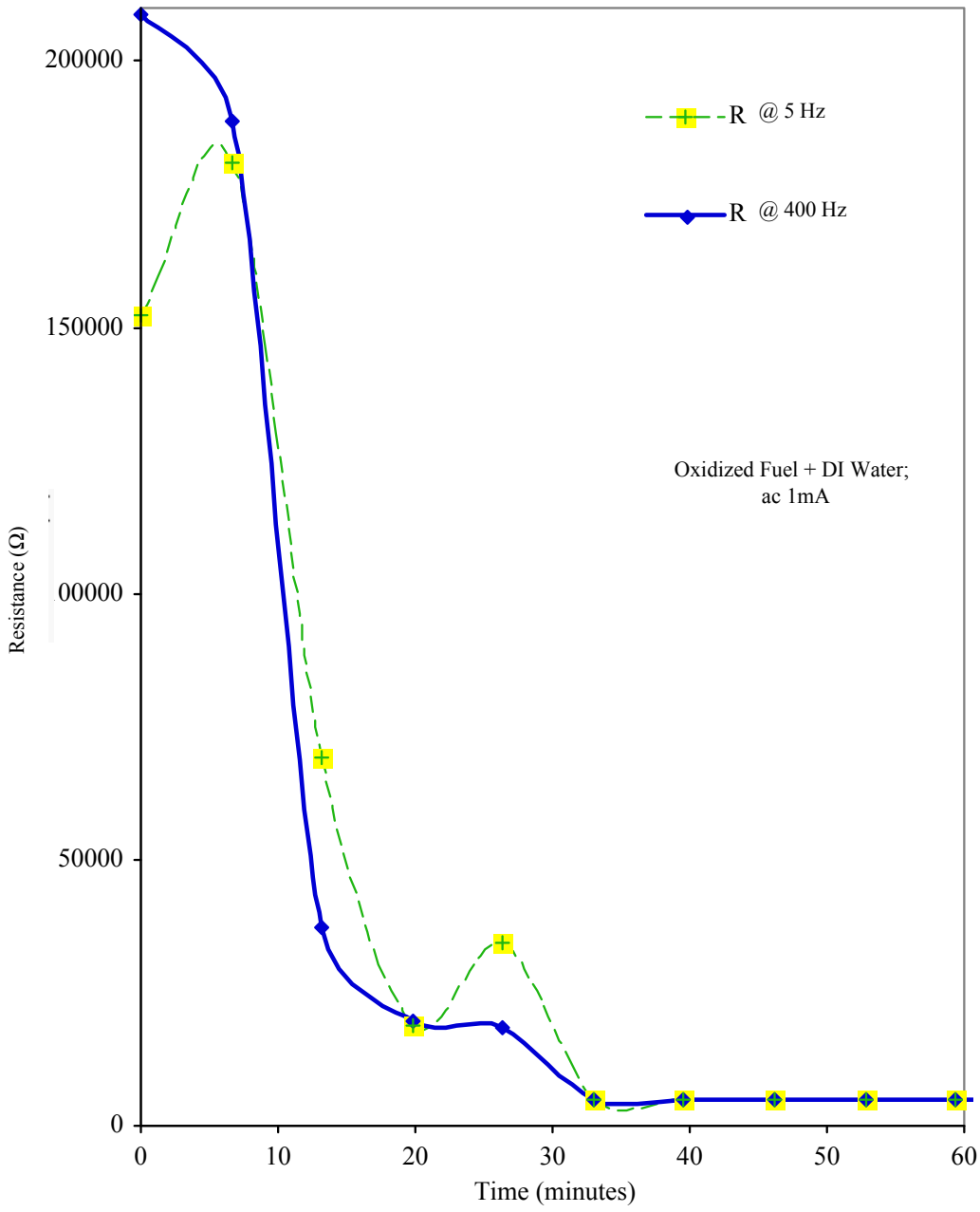


FIGURE A-2. RESISTANCE MEASURED AT 5 Hz AND 400 Hz FOR CONTROLLED CURRENT AC

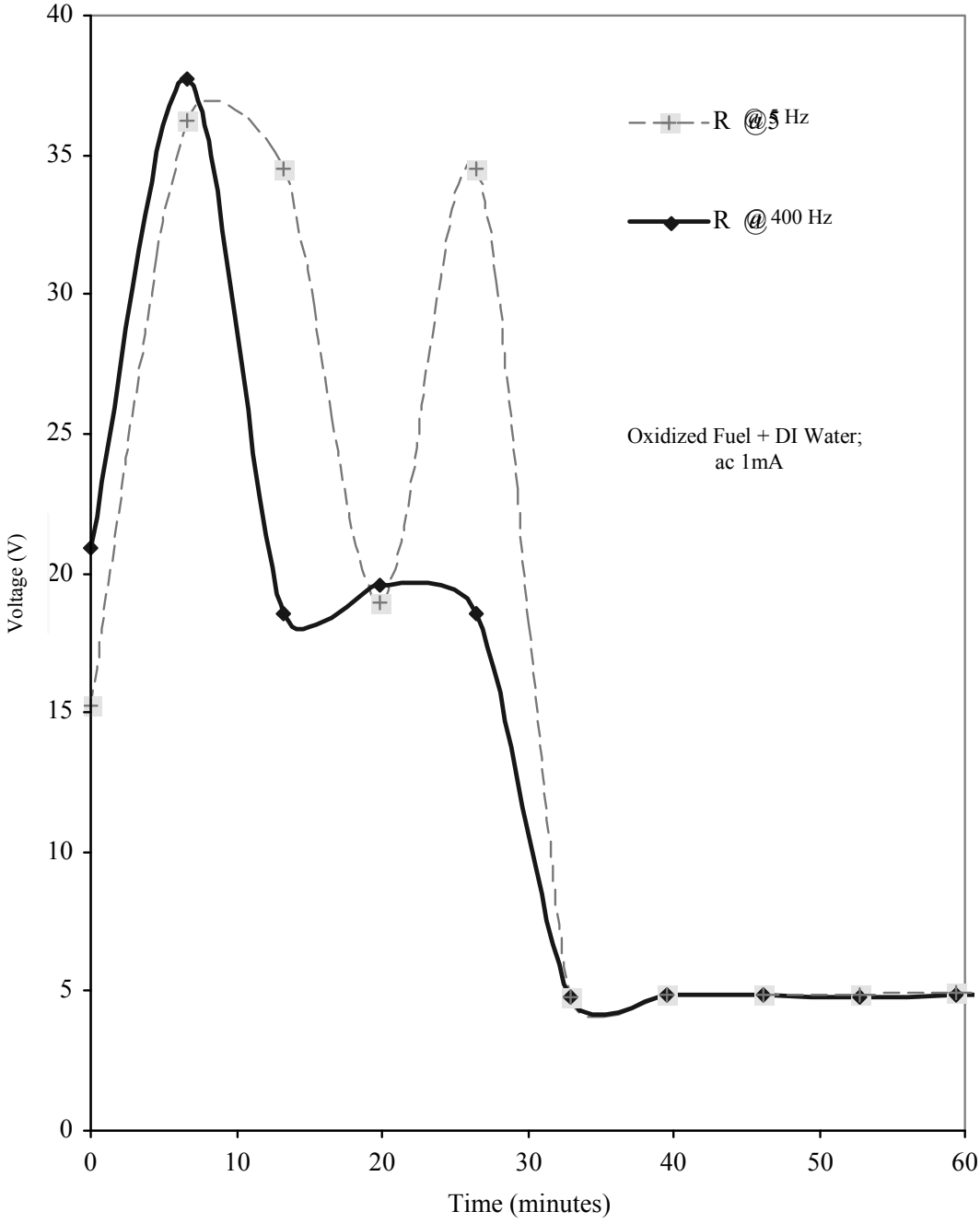


FIGURE A-3. PLOTS OF AC VOLTAGE BETWEEN TWO ELECTRODES FOR CONTROLLED CURRENT AC

After 79 minutes of ac cycling at 1 mA, the current was increased to 10 mA to restart the electrochemical corrosion process. Figure A-4 shows the resulting change in resistance at 5 and 400 Hz. Both resistances fall over a period of nearly 2 hours from approximately 5 kΩ to less than 2 kΩ, at which time the resistance appears to increase slightly. At this point, both silver electrodes were severely corroded with a loss of approximately 20% metal mass. This metal was

converted to a black, particulate, conductive oxide, hydroxide, or sulfide species that is quite firmly adherent. Binding to the surface is apparently provided by the deposition of gums as the result of reaction of the oxidized fuel.

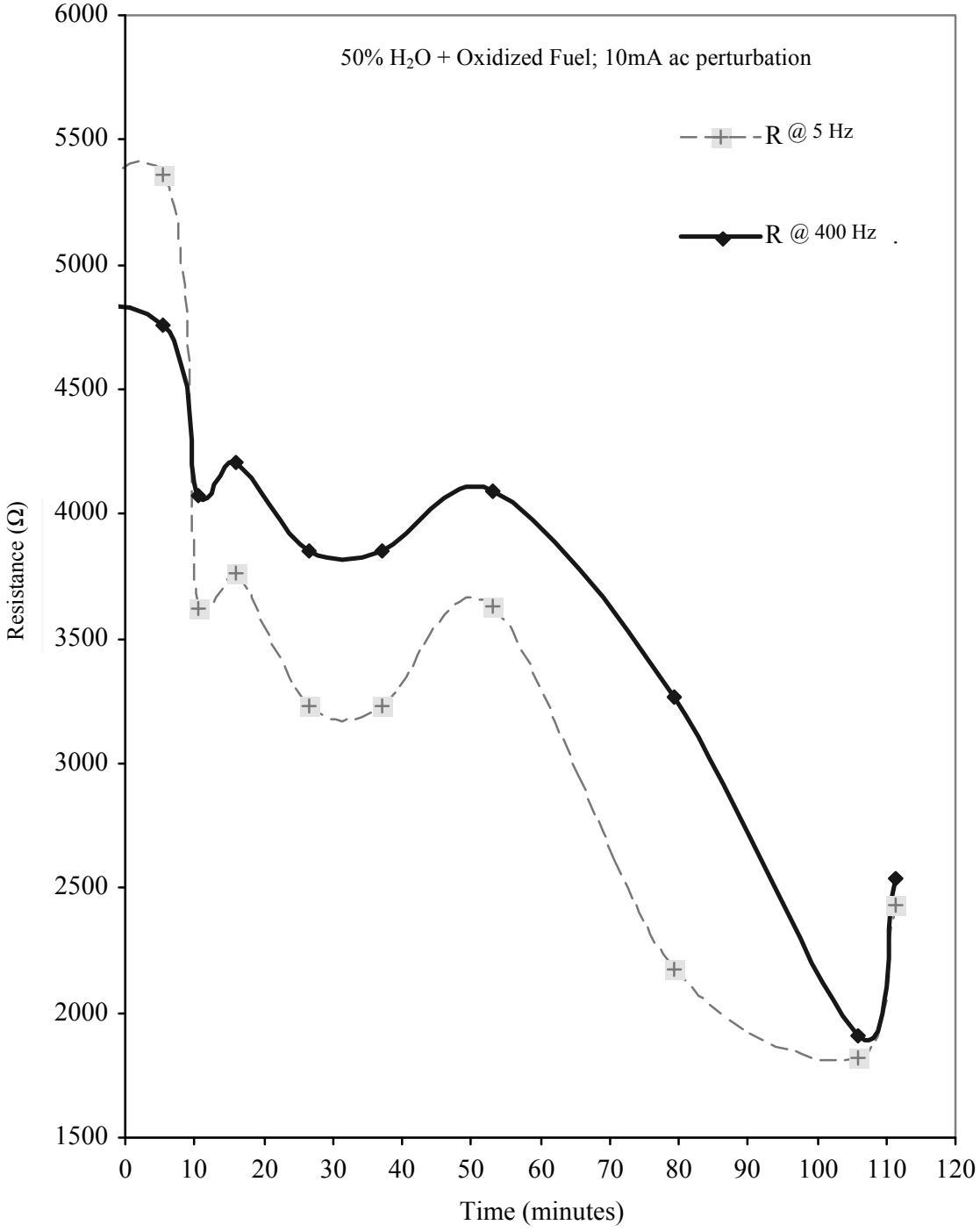


FIGURE A-4. RESULTING CHANGE IN RESISTANCE AT 5 AND 400 Hz FOR CONTROLLED CURRENT AC

A.3 THE EFFECTS OF DC VOLTAGE.

As well as having a characteristic dependence of resistance on ac frequency, electrochemical systems exhibit a characteristic dc voltage response that can be used to obtain information about mechanisms and rates. A second series of experiments in the geometry described in the previous section was performed, in which the dc voltage was stepped progressively from 0 to 5 V, at constant ac perturbation of 100 mV. Figure A-5 shows the resulting complex plane plots. The data represented by the + sign were obtained at zero volts dc with an ac perturbation of 100 mV in the frequency range $1 \leq f \leq 20{,}000$ Hz, before the addition of deionized water and degraded fuel to the experiment. The resulting semicircular arc is that expected for a resistor in parallel with a capacitor; in this case, the capacitance is the geometric effect of the two parallel silver wires, and the resistance is that of an absorbed moisture layer on the ceramic electrode holder. The red dashed line shows the best fit of these data to this model, with values C = 12 pF and R = 812 kΩ.

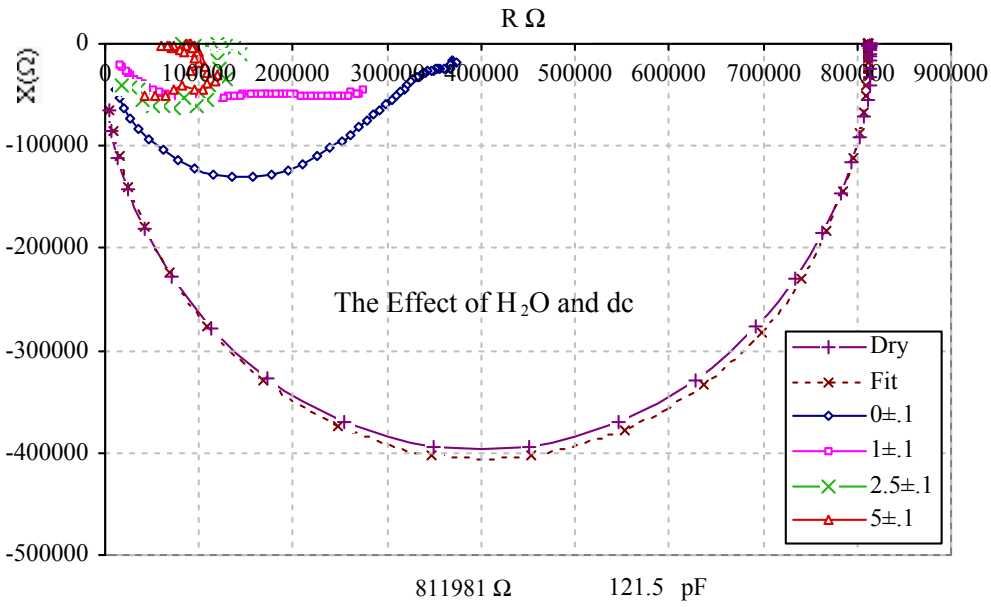


FIGURE A-5. COMPLEX PLANE PLOTS FOR PROGRESSIVELY STEPPED DC VOLTAGE

When water and oxidized fuel are added to bridge the electrodes, the impedance response transforms to that of the blue diamonds (0±.1) in figure A-5. In the absence of a dc voltage component, 100 mVac is insufficient to cause any significant degree of net electrochemical process. Instead, the blue curve describes the potential for electrochemical charge transfer to occur and the capacity of the system to support ionic transfer by diffusion. Close inspection of the blue curve in figure A-5 reveals the presence of two somewhat flattened arcs, completely characteristic of electrochemical processes. The higher frequency arc (larger radius at smaller resistances) can be attributed to electrochemical charge transfer. The smaller somewhat distorted arc at large resistance values is due to ionic diffusion to and from the surfaces of the potentially reactive silver wires.

At 1 Vdc with 100 mVac perturbation (magenta squares 1±.1), the charge transfer arc becomes smaller (higher rates) and the diffusional arc becomes slightly better resolved. Diffusion to a planar electrode in an electrochemical system is characterized by an $f^{-1/2}$ dependence. Normally, this is presented in a plot of the imaginary component of the admittance, B, versus the square root of the angular frequency ($\omega = 2\pi f$), as shown in figure A-5. Data for the dry electrode are curved because no diffusible species are present. For the data obtained in the presence of deionized water and degraded fuel, at 0 and 1 Vdc, there are clearly significant regions of $f^{-1/2}$ dependence as shown by the regression lines plotted in figure A-6. The slopes of these lines measure the diffusional coefficients, and their intercepts are proportional to the rates of electrochemical process.

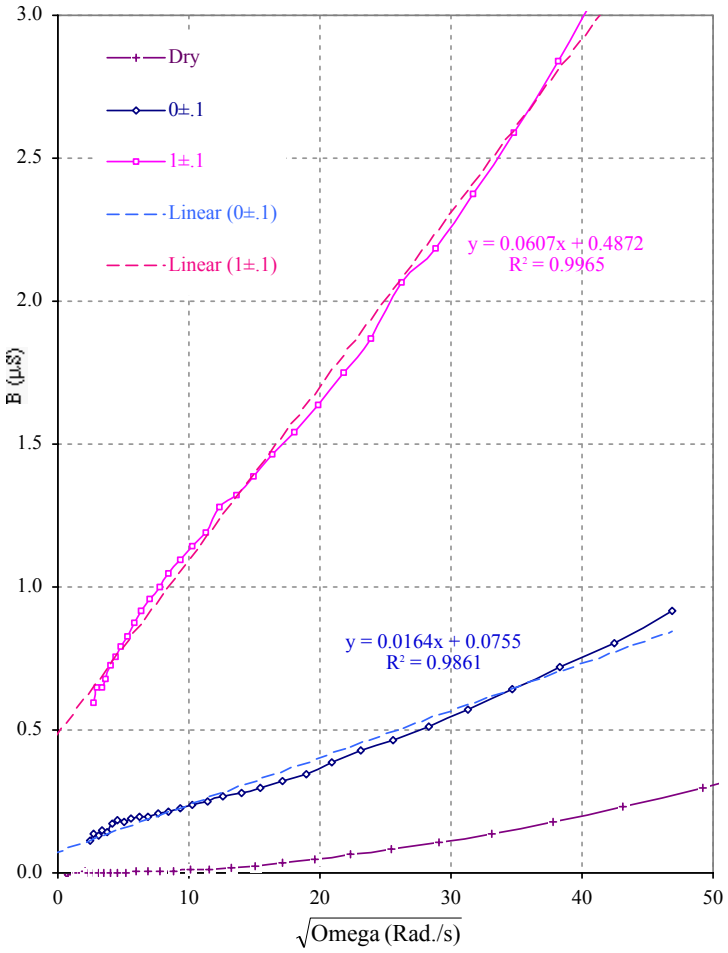


FIGURE A-6. ADMITTANCE VERSUS SQUARE ROOT OF FREQUENCY

Based on these two measured rates and the known exponential dependence of electrochemical rates on dc voltage, we can estimate the intrinsic charge transfer rates at high voltages. Figure A-7 plots the rates determined from the low-frequency regression limits in figure A-6, versus dc voltage, together with an exponential fit extrapolated out to 5 V. In this voltage interval, one can predict a 10,000-fold increase in the intrinsic rate of charge transfer.

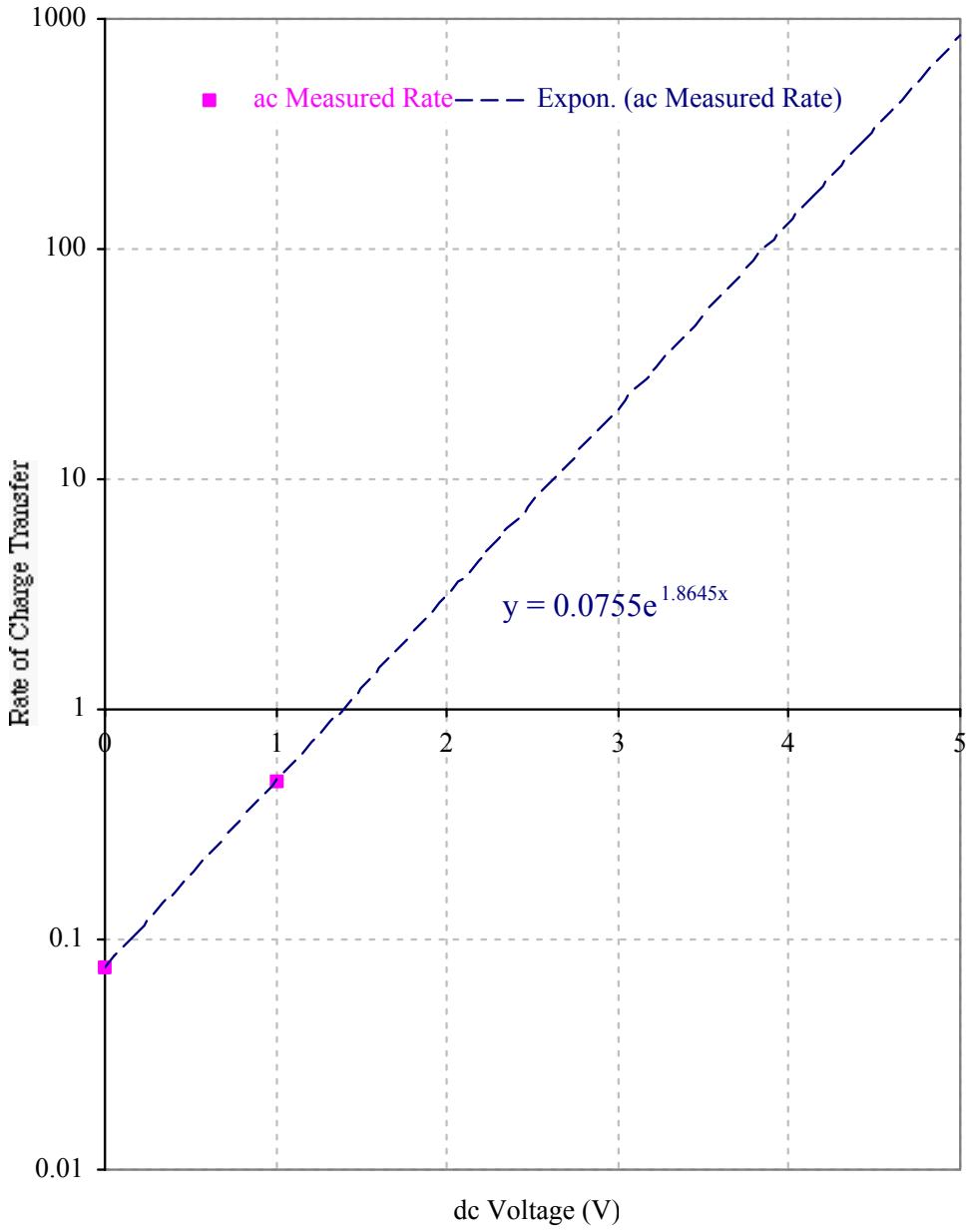


FIGURE A-7. RATES DETERMINED FROM THE LOW FREQUENCY REGRESSION LIMITS IN FIGURE A-6

The exercise in the preceding paragraph is intended to be illustrative, not quantitative. Returning to figure A-5, one can see that the dimensions of the complex plane plots do not decrease 10,000-fold as the dc voltage is increased from 0 to 5 V. These arcs do get smaller, indicating a much more conductive system, but at 2.5 and 5 V, the impedance locus plots change shape. What happens is that the reaction is no longer limited by the rate of charge transfer: the mechanisms change, diffusional effects become more significant, and the system is changing with time as deposits form and grow.

A.3 LONG-TERM TESTS AT LOW AC CURRENT.

An attempt was made to determine the lower limit of ac currents at which meaningful deposit formation and conductive bridging might occur. The same two-wire geometry was used as described above, this time using only two drops of degraded fuel placed at the margin of a pool of deionized water into which the silver wires were immersed. Tests were performed with a 50 µA ac current perturbation covering the range of frequencies between 20 mHz and 10 kHz. The results plotted in figure A-8 reveal a complex, but clearly electrochemical impedance response.

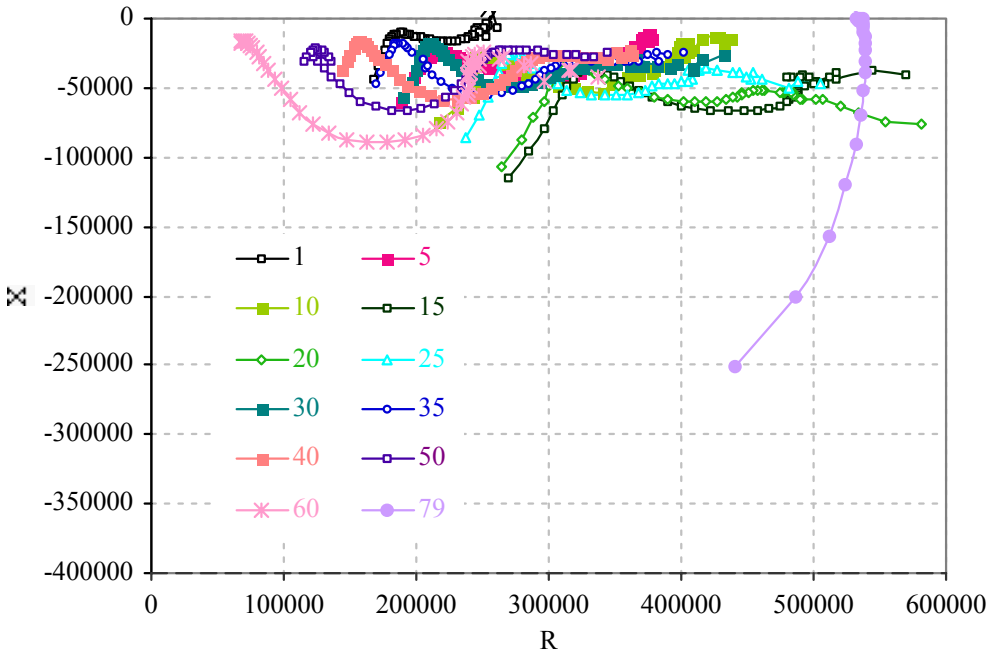


FIGURE A-8. RESULTS OF LONG-TERM TESTS AT LOW AC CURRENT

The data sets plotted in figure A-8 were observed at the following times after initiation of the 50 µA current perturbation:

Series	Time	Series	Time
1	8	30	248
5	42	35	289
10	83	40	330
15	124	50	413
20	165	60	495
25	206	79	652

As described in sections A.1 and A.2, the impedance loci display two arcs, characteristic of charge transfer and diffusional impedances. The lower frequency arc is severely flattened,

suggesting the presence of a heterogeneous multidimensional electrode structure created by the deposition of conductive particles.

A close inspection of the data in figure A-8 reveals that the impedance loci first tend to increase and then decrease with increasing time. This may be due to initial depletion of aggressive and conductive ionic species followed by the increase in deposit conduction. The trend is shown more clearly in figure A-9 in which the resistance measured at various frequencies is plotted versus time of electrolysis. The resistances all reach a maximum after approximately 2 hours and then decline monotonically. It is not clear how long this resistance decrease would continue. In the presence of water and degraded fuel, there appears to be no reason why deposits should not continue to form and grow, reducing the resistance and increasing the corrosion susceptibility. What in fact occurred in this experiment was that all the available water was consumed by electrolysis, and the electrode registered the dry response shown by data set 79 (see figure A-8).

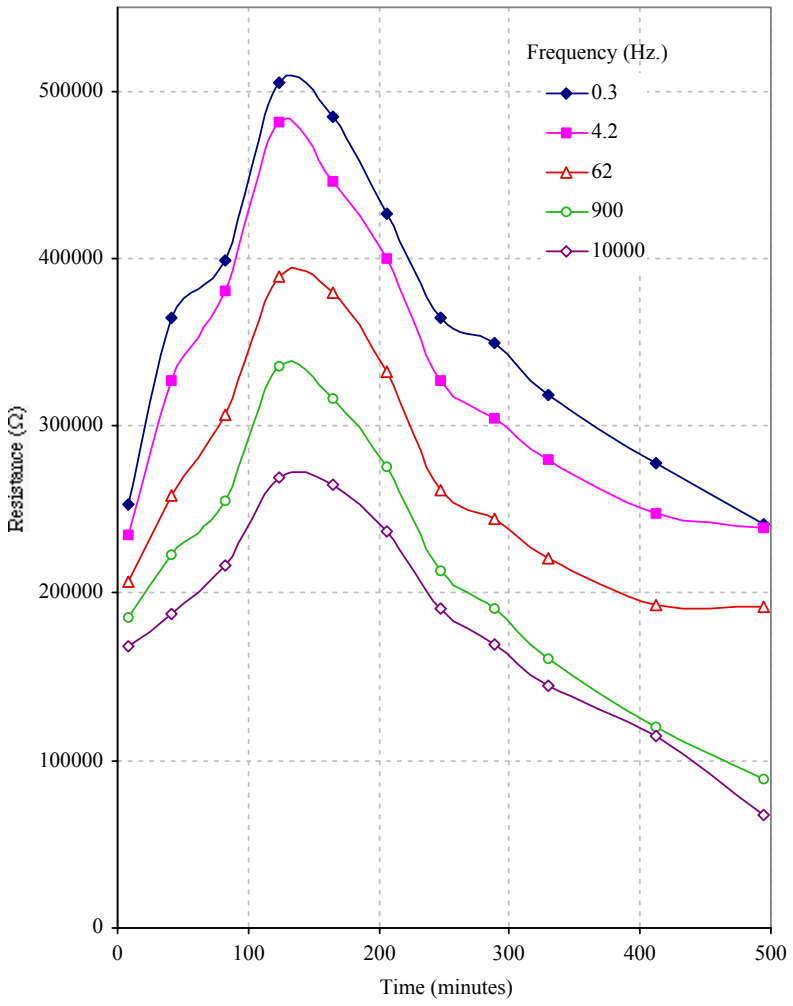


FIGURE A-9. RESISTANCE PLOTTED AS A FUNCTION OF TIME OF ELECTROLYSIS IN LONG-TERM TESTS AT LOW AC CURRENT

APPENDIX B—FARADAIC RECTIFICATION

B.1 INTRODUCTION.

When a nonlinear resistance or impedance is perturbed with a single frequency sinusoidal voltage or current, the response contains a dc component as well as higher frequency components not present in the input. These output sinusoids occur at integral multiples of the input frequency (harmonics) with gradually diminishing intensity. Electrochemical systems are sufficiently nonlinear for this effect to become significant at voltage perturbations much above 50-100 mV. The analysis of the harmonic response of a system to a sinusoidal current or voltage perturbation has received periodic attention in the electrochemical literature since the pioneering work of Warburg [B-1] in 1899 and Kruger [B-2] in 1903. This effect has been studied as Faradaic rectification [B-3-B-6] and Faradaic distortion [B-7]. More recently, Bertocci [B-8 and B-9] and others [B-10] investigated the effect of large-amplitude perturbations on increasing the corrosion rates of electrical conduit materials. This methodology also has been developed as a means of measuring corrosion rates [B-11-B-14].

Nonlinearity, and therefore harmonic distortion and induced dc polarization, can occur in electrochemical systems by a variety of means. Here, one is concerned with estimating the extent that ac voltages presented across wiring bridged by water can result in dc corrosion processes and products. One is then interested to know how the presence of conductive deposits in the compromised gap can influence the Faradaic rectification process. The second of these effects is complex and requires further study before one can achieve a satisfactory understanding.

Neglecting at this point, the irreversible oxidation of metal, the electrochemical reactions of significance occurring in a bridging drop of pure water are just electrolysis:

Anodic: $H_2O = {}_{1/2}O_2 + 2e^- + 2H^+$

Cathode: $2H_2O + 2e^- = H_2 + 2OH^-$

The cell voltage is the sum of six terms:

Anode charge transfer: $V_a = \mathrm{Ln}[I/i^\circ A_a]/\alpha B$

Cathode charge transfer: $V_c = \mathrm{Ln}[I/i^\circ A_c]/(1-\alpha)B$

Anode diffusion: $V_{a,d} = \mathrm{Ln}[1 + I/i_L A_a]/B$

Cathode diffusion: $V_{c,d} = \mathrm{Ln}[1 + I/i_L A_c]/B$

Electrolyte resistance: $V_{IR} = IR_s$

Thermodynamic potential: $V^\circ = 1.229\ V$

where I is the current that flows, i° is the kinetic exchange current density, A the effective area of each electrode with subscripts a and c referring to anode and cathode, α is the reaction symmetry factor, B is a constant dependent on temperature, i_L is the maximum current density that can be sustained by diffusion, and R_s is the resistance of the water in the electrode gap.

For a sinusoidal voltage applied between anode and cathode,

$$V = V_a + V_c + V_{a,d} + V_{c,d} + IR_s + V^\circ = |V| \sin(\omega t)$$

where $|V|$ is the amplitude of the sinusoidal voltage perturbation and ω is the frequency.

One needs to know the current that flows as a consequence of this voltage. This current will, in general, contain a dc component (Faradaic rectification) and a Fourier series of harmonic responses. Thus

$$I = \sum I_h \sin(h\omega t + \emptyset)$$

For the present, one is concerned only about the dc component $I_{dc} = I_0$. Frequency domain analysis of the harmonic components ($h > 1$) may reveal a means of testing fuel tank wiring for the possibility of electrochemical activity.

In a completely symmetric situation, with $A_a = A_c$ and $\alpha = 0.5$, no Faradaic rectification occurs. The harmonic distortion on the positive going half cycle of the sinusoid is completely balanced by the distortion on the negative going half cycle, and no net dc current results. The symmetry can be removed if the two electrodes (arbitrarily called anode and cathode) have different areas and when the electrochemical symmetry factor, λ, is different from 0.5.

Figure B-1 shows the effect of varying α from 0.1 to 0.5 with an electrode-wetted area ratio A_a/A_c of 100. The other parameters are selected to be representative of the electrochemical and mass transport processes expected for water electrolysis and measured in the laboratory. The solid black line shows a single cycle of the input voltage sine wave, in this case with amplitude 6 *V*. The colored curves are the current responses predicted from the model described above, with the parameter values given, with $\alpha = 0.5$, 0.2, and 0.1. It is clear from figure B-1 that, even for a highly asymmetric areas ($A_a/A_c = 100$), no net dc results with $\alpha = 0.5$. The current response shown by the green line, while distorted due to the exponential nonlinearity of the charge transfer reactions, exhibits symmetric areas on either side of zero dc current. As α is reduced (the orange and red lines), so too is the amplitude of the current response, and the responses on either side of zero display unequal areas. Thus, the time-averaged or root mean square (rms) value of the current is not zero, it has a dc component. The values given for the dc effect (0% at $\alpha = 0.5$, 8% at $\alpha = 0.2$, and 31% at $\alpha = 0.1$) are calculated as the ratio of the average current to the rms current (i.e., the dc compared to the ac current). It is quite clear that, for a situation as asymmetric as that used to calculate the red curve ($A_a/A_c = 100$, $\alpha = 0.1$), a very significant dc current can flow to perform net electrochemical reaction or contribute to electrochemically induced fuel ignition.

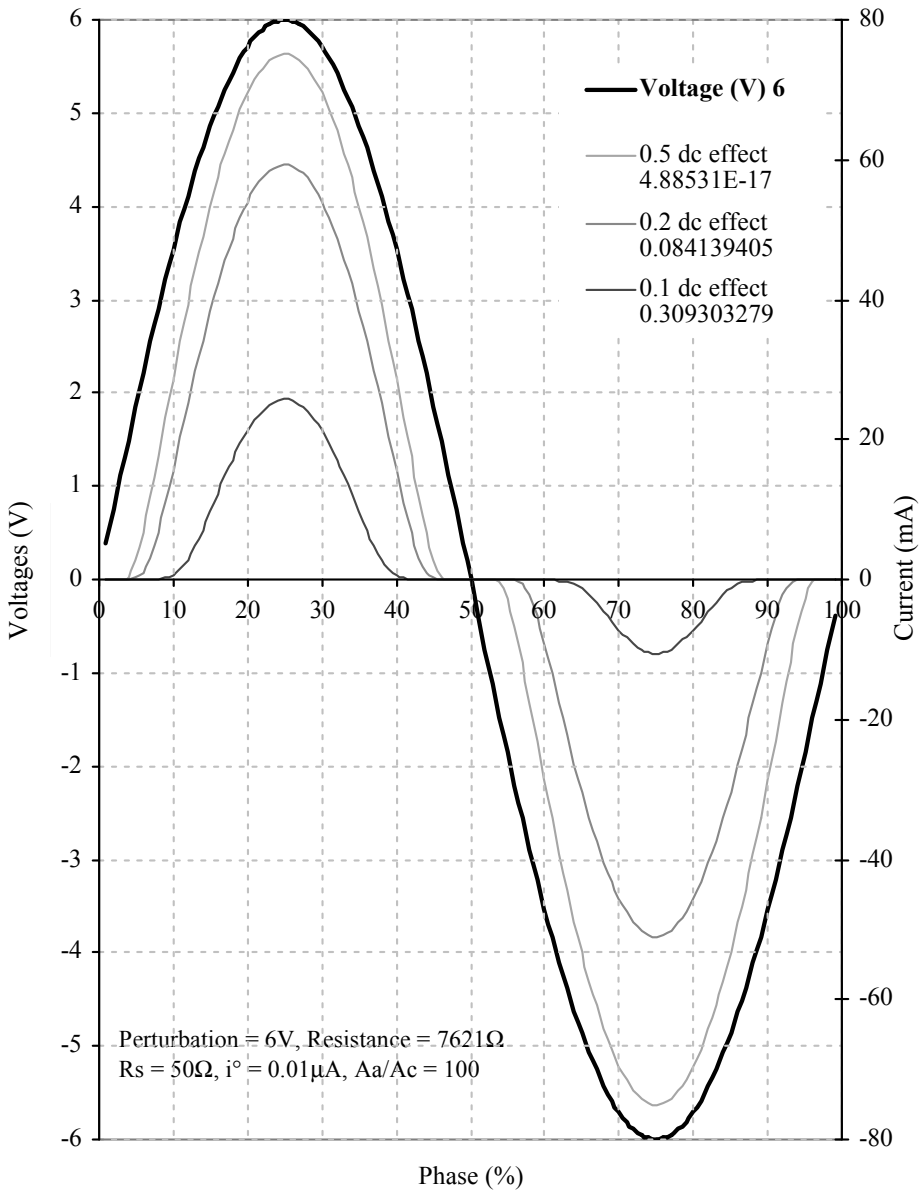


FIGURE B-1. EFFECT OF VARYING ALPHA FROM 0.1 TO 0.5 WITH ASYMMETRICALLY WETTED ELECTRODES

To quantify this effect, calculations were done on the effect of changing key input variables on the expected dc effect in a highly asymmetric situation. Table B-1 presents the results of two parametric calculations, one considering the effect of changing the electrolyte series resistance, R_s, at constant input ac voltage (6 V), the other examining the effect of varying the ac voltage amplitude at constant R_s (50 Ω). The largest dc effect (as a ratio or percentage of ac) occurs with small values of ac perturbation and series resistance and achieves a value of 58% at V_{ac} = 2V and Rs = 50 Ω.

TABLE B-1. CALCULATIONS OF FARADAIC RECITIFICATION

n	α	T (°C)	$i°$ µA /cm^2	$i_{d,l}$ µA /cm^2	A_a cm^2	A_a/A_c	V_{ac} (V)	V rms (V)	I rms (mA)	i_{dc} (mA)	dc Effect	R_{cell} (Ω)	R_s (Ω)
1	0.1	30	0.01	100	1	100	6	4.5	4.3	1.64	39%	1,066	10
1	0.1	30	0.01	100	1	100	6	4.5	3.5	1.35	39%	1,312	20
1	0.1	30	0.01	100	1	100	6	4.5	2.4	0.94	39%	1,902	50
1	0.1	30	0.01	100	1	100	6	4.5	1.7	0.66	39%	2,690	100
1	0.1	30	0.01	100	1	100	6	4.5	1.1	0.44	38%	3,983	200
1	0.1	30	0.01	100	1	100	6	4.5	0.6	0.24	37%	7,071	500
1	0.1	30	0.01	100	1	100	6	4.5	0.4	0.14	35%	11,281	1000
1	0.1	30	0.01	100	1	100	6	4.5	0.2	0.08	34%	18,419	2000
1	0.1	30	0.01	100	1	100	6	4.5	0.1	0.04	31%	36,285	5000
1	0.1	30	0.01	100	1	100	6	4.5	0.1	0.02	30%	61,800	10000
1	0.1	30	0.01	100	1	100	2	1.7	0.0	0.00	58%	4.6E+07	50
1	0.1	30	0.01	100	1	100	4	3.1	0.0	0.01	43%	1.7E+05	50
1	0.1	30	0.01	100	1	100	6	4.5	2.4	0.94	39%	1,902	50
1	0.1	30	0.01	100	1	100	8	5.9	15.3	3.89	26%	389	50
1	0.1	30	0.01	100	1	100	10	7.4	35.7	5.60	16%	206	50
1	0.1	30	0.01	100	1	100	12	8.8	59.2	6.60	11%	148	50
1	0.1	30	0.01	100	1	100	16	11.6	110.1	7.74	7%	106	50
1	0.1	30	0.01	100	1	100	20	14.5	163.2	8.38	5%	89	50
1	0.1	30	0.01	100	1	100	24	17.3	217.5	8.79	4%	80	50
1	0.1	30	0.01	100	1	100	28	20.1	272.4	9.09	3%	74	50

In estimating the likely effect of ac voltage in causing electrochemical corrosion or contributing to fuel ignition, there is less concern with the percentage effect than with the induced average dc currents and charge. As shown in table B-1, the induced dc current is maximized at low values of R_s and large values of V_{ac}. Figure B-2 graphically shows the effect on the induced dc current and the percentage effect of increasing the series resistance. Figure B-3 shows the effect of increasing the ac perturbation voltage.

Figure B-2 shows that the Faradaic rectification likely to result from ac voltages present in aircraft fuel tanks can, under conditions of extreme electrochemical asymmetry, result in dc currents capable of

- inducing electrochemical attack and further compromising insulation and
- potentially playing a role in an electrochemical catalytic fuel ignition process.

Until further testing is performed with laboratory and naturally grown deposits, however, one cannot be certain that the electrochemical processes that occur in fuel tanks are capable of sustaining a high level of reaction asymmetry.

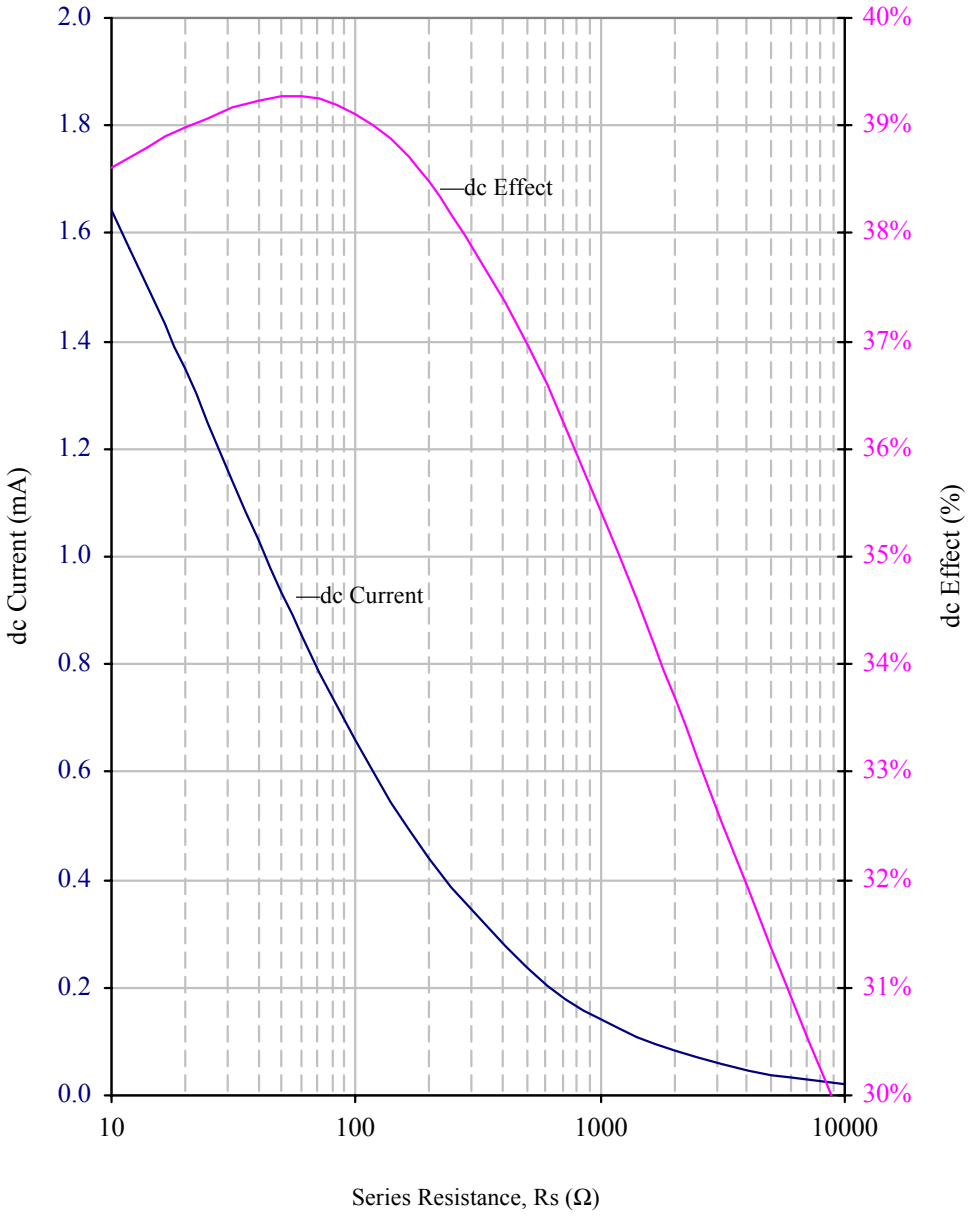


FIGURE B-2. EFFECT OF INCREASING SERIES RESISTANCE ON THE DC CURRENT (BLUE) AND ON THE DC EFFECT (MAGENTA)

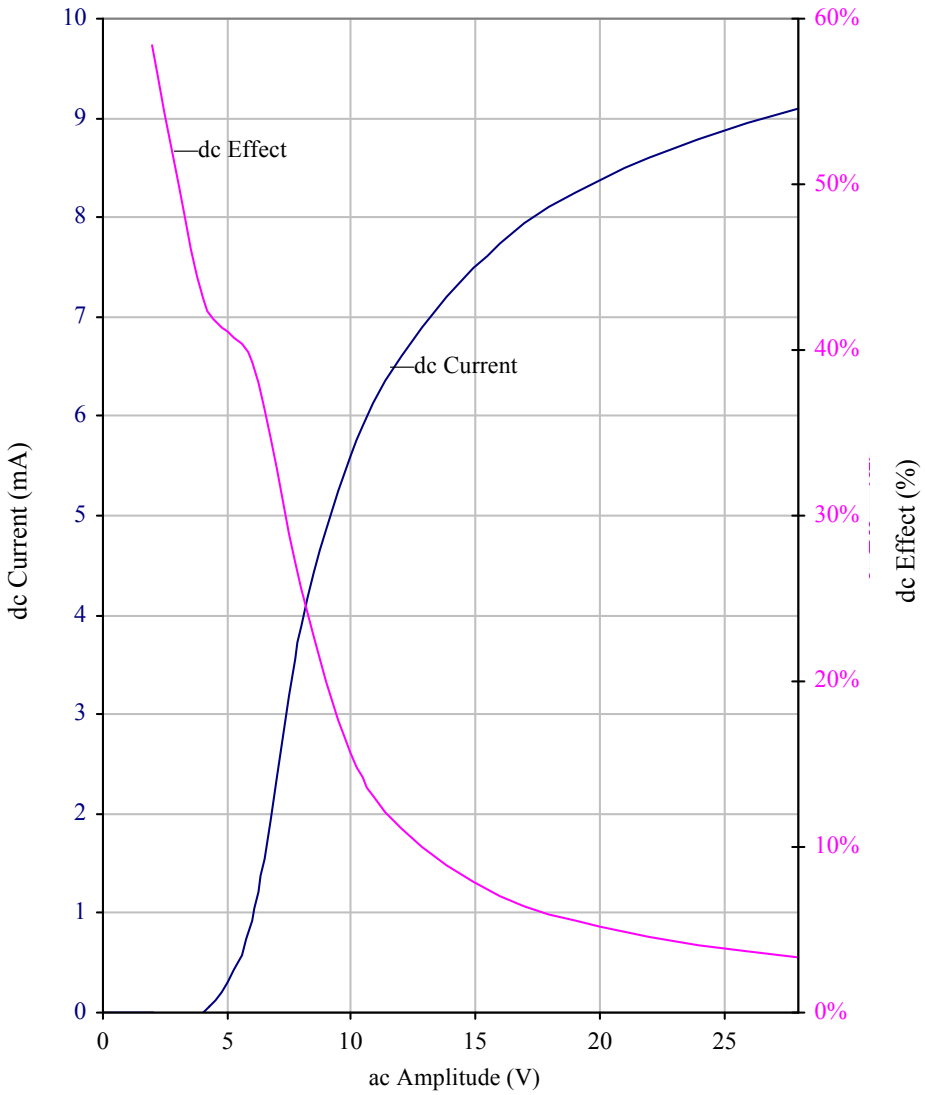


FIGURE B-3. EFFECT OF INCREASING THE AC PERTURBATION VOLTAGE ON THE DC CURRENT (BLUE) AND ON THE DC EFFECT (MAGENTA)

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APPENDIX C—UNIVERSITY OF DAYTON RESEARCH INSTITUTE EXPERIMENTAL METHODS

C.1 SUPPLIES.

C.1.1 Terminal Blocks.

The ten terminal blocks and associated wiring, connectors and nuts (figure C-1) analyzed during this research were supplied by the National Transportation Safety Board (NTSB) and the U.S. Air Force Research Laboratory (AFRL). The terminal blocks were removed from either retired B747 aircraft or from B747 aircraft experiencing FQIS malfunctions.



FIGURE C-1. B747 TERMINAL BLOCK

C.1.2 Jet A Fuels.

The Jet A fuels analyzed during this research were supplied by the FAA, an aerospace company and the AFRL. The 64 fuels supplied by the FAA were obtained at U.S. airports from the fuel tanks of commercial airliners after landing.

Three of the four fuels supplied by the aerospace company were obtained from fuel line components of commercial airliners operating in Asia and experiencing clogged fuel lines/fuel oil coolers. The fourth fuel supplied by the aerospace company was obtained from a fuel farm located in Arizona. The two fuels supplied by the AFRL were obtained from the fuel reserves of local airports.

C.1.3 Metal Wires and Nuts.

The metal wires (1 mm diameter) used in this study to produce residues were obtained from Aldrich Chemical Company and had purity levels greater than 99.99%. The following metals were studied as wires: Ag (silver), Al (aluminum), Au (gold), Cd (cadmium), Cu (copper), Ni (nickel), and Ti (titanium). 316 stainless steel wire was also used.

In addition to the metal wires, new and used Ag- and Cd-plated nuts, supplied by the FAA and NTSB, respectively, were also used in this study to produce residues.

C.1.4 Water.

Three types of water were used in this study: deionized, distilled, and condensed water removed from the plastic pan of a room dehumidifier. In every case, drops (1 cm in diameter) of the different waters had measured resistances of greater than 2.3 MΩ using the needle tip probes of a digital multimeter.

C.1.5 Ceramic Rods.

The ceramic rods used in this research were 3 mm in diameter and contained two bores running the length of the rod. The bores were 1 mm in diameter and were spaced 1 mm apart. The ceramic rods were alumina in composition with a porcelain coating.

C.2 ANALYTICAL TECHNIQUES.

The following analytical tests were used to analyze the as-received (fuel tanks, fuel line components, fuel reserves) and stressed Jet A fuels and to characterize the deposits present on the terminal blocks and associated wires, nuts, and connectors.

C.2.1 Voltammetric Instruments

The RULER™ instrument was used to determine the concentrations of the phenol compounds (naturally occurring and produced by stressing) present in the as-received and stressed fuels. The PERFECT™ instrument was used to determine the hydroperoxide concentrations in the as-received and stressed fuels using ASTM Method D6447-99.

C.2.2 Thermogravimetric Analysis (TGA).

TGA was used to determine the gum contents of as-received and stressed fuels. 10 μL of fuel was weighed in a platinum pan and heated from room temperature to 400°C in a nitrogen atmosphere. The percent remaining weight versus temperature was plotted. The weight remaining at 300°C was considered gum content of the tested fuel.

C.2.3 X-Ray Photoelectron Spectroscopy (XPS).

XPS was used to determine the elemental (Ag, C, Cu, N, O, and S (H not detected)) composition and to differentiate between the oxidation states of Ag, Cu, and S present in particles and residues. The XPS was performed in an evacuated chamber with a magnesium x-ray source and analyzed the top (outer) 3 nanometers of the residue or particle.

C.2.4 Auger Electron Spectroscopy (AES).

AES was used to perform elemental (Ag, C, Cu, N, O, and S (H not detected)) depth profiles of the deposits present on terminal block and associated hardware surfaces. An argon ion beam was used to sputter the deposits at a rate of 2 nm min^{-1} to perform the AES elemental depth profiles in an evacuated chamber.

C.2.5 Scanning Electron Microscopy/Energy Dispersive Spectrometer (SEM/EDS).

SEM was used to obtain magnified (4-nm resolution) photographs of the particles and residues. The EDS analyses were used to perform elemental (Ag, Cu, O, and S (H not detected, C and N poor detection)) analyses of the deposits on the terminal block and associated hardware surfaces. The SEM/EDS analyses were performed in an evacuated chamber.

C.2.6 Fourier Transform Infrared Spectrophotometry (FTIR).

FTIR was used to determine bulk bonding differences (C-H, C=O, C-OH, C=C) among as-received fuel, stressed fuel and residues. The FTIR analyses were performed at atmospheric pressure in the forms of solid flakes, liquid drops, liquid film between two potassium bromide (KBR) plates, or plates formed by compressing a mixture of KBR powder and residue particles.

C.3 EXPERIMENTAL PROCEDURES.

C.3.1 Fuel Oxidation/Vapor Deposition.

To evaluate the oxidative stabilities of the fuels and the tendencies of heated fuels to produce deposits in the vapor phase (terminal block in vapors above fuel), 10 mL of each fuel was dispensed into a 25-mL glass Erlenmeyer flask. Cu wires (0.2 mm diameter) with Ag coating (similar to fuel tank wiring) were also placed into each flask. The wires were positioned so that one end of the wire was submerged in fuel and other end extended out of the open mouth of the flask. The glass flasks containing the fuels were heated at 350°F for 1 hour (with the wire) and at 290°F for 4 hours (without the wires) on top of a hot plate. After 1 hour at 350°F and 4 hours at 290°F, the remaining liquid fuel was analyzed for oxidation (increased levels of hydroperoxides and phenol compounds) and for particles or dissolved gums. The Ag-coated Cu wires heated at 350°F were visually examined for deposits and analyzed by FTIR to characterize the deposits.

C.3.2 Conductive Deposit Formation.

Glass Slide with Parallel Ag Coated Cu Wires—Two Ag-coated Cu wires (0.2 mm diameter, 4 cm length) were placed parallel on a glass microscope slide and the ends of the wires were glued to the glass slide. The wires were spaced 1 mm apart. Electrical connections were made to one end of each Ag-plated Cu wire, and a 9-Vdc battery was used to supply power to the system. When a drop 100 µL of water was dispensed between the wires so that the water made contact with each wire, a black deposit initiated at the positive wire and spread across the water to the negative wire. Simultaneous with the black deposit formation, bubbling was observed at the negative wire. A digital multimeter and an analog strip chart were placed in series with the parallel wires to monitor the current flow through the water drop/deposit. Drops (100 µL) of various fuels were added between the parallel wires so that the fuel was in contact with the wires and water drop. The black deposits with and without fuel present were isolated and analyzed using SEM/EDS.

C.3.3 Conductive Residue Formation.

Ceramic Rod with Parallel Metal Wires—A metal wire (1 mm diameter, 3 cm length) was pushed through each bore in the ceramic rod (2 cm length) so that 0.5 cm of wire extended from each end of the rod. A drop of glue (RTV, super glue, etc.) was placed on one end of the ceramic rod to seal the metal wires extending from the bores. Once the glue had hardened, electrical leads were connected (alligator clips) to the metal wires extending from the sealed bores. The electrical leads were then placed in a polymer-coated adjustable clamp and situated so that the ceramic rod was held vertical when the clamp was tightened. The ceramic rod was positioned so that the end of the ceramic rod with the glue/electrical connections was on the bottom as shown in figure C-2. The digital multimeter was placed in series with the electrical connections of the ceramic rod to measure the current flowing in the circuit.

For each experiment, the power supply was selected and connected to the electrical leads of the ceramic rod. A drop of water (50 µL) was dispensed using a plastic pipette onto the upper surface of the ceramic rod between the two metal wires extending above the surface (figure C-2). Due to its surface tension, the water drop formed a bead engulfing the metal wires and ceramic surface. The selected power supply was then turned ON, causing the water drop to undergo electrolysis (black deposit forms). A radio tuned to a local AM radio station was positioned 3 ft from the ceramic rod. If radio frequencies (RF) were produced during the electrolysis of the water drop, the AM radio station program would be replaced by static.



FIGURE C-2. CONDUCTIVE RESIDUE PRODUCED ON CERAMIC ROD SURFACE BETWEEN SILVER WIRES AFTER DISPENSING FIRST SET OF WATER: LOW SULFUR FUEL DROPS USING 40 Vac (440 Hz), 20 mA (Limited). (Set consists of (1) dispensing water drop (50 µL) onto surface of ceramic rod between silver wires; (2) applying electricity to silver wires to cause complete electrolysis of water drop to produce residue (residue resistance 0.5-5 kΩ); and (3) dispensing fuel drop (50 µL) onto surface of ceramic rod between silver wires with electricity being applied. Current decreases to below 1mA/no flashes when high-sulfur fuel used in place of low-sulfur fuel. Display reads 7.88 mA.)

Once the water drop was no longer visible (1-60 minutes depending on power supplied) and a deposit was visible on the ceramic surface (figure C-2), the resistance of the residue was measured with a digital multimeter. If the resistance of the residue was above 10 kΩ, another drop of water was dispensed onto the surface of the ceramic rod between the metal wires and the power reapplied. The process of adding water drops and applying power was repeated until the resistance of the resulting residue was below 10 kΩ. If the resulting residue had a resistance below 50 Ω, the residue was washed away with a stream of water or wiped away with a paper towel. The process of adding water drops and applying power was then repeated with the cleaned ceramic rod until a residue with a resistance below 10 kΩ was produced.

Once a residue with a resistance between 50 Ω and 10 kΩ was produced (only occurred with Ag wires), a drop of fuel (50 μL) was dispensed onto the Ag deposit with a plastic pipette (figure C-2). Due to its lower surface tension, the fuel drop wetted the Ag residue and formed a thin layer of liquid on the surface of the ceramic rod. The selected power supply was then turned ON, causing smoke with flashes of light. Once the Ag residue appeared dry (fuel evaporated), another drop of fuel was added to the residue, causing additional smoke and flashes of light.

The process of adding drops of fuel to the Ag residue was repeated until the flashes of light caused the resistance of the residue to increase to above 10 kΩ. Once the resistance increased above 10 kΩ, the process of adding water drops and applying power was repeated until the resistance of the produced residue was between 50 Ω and 10 kΩ. The process of adding fuel drops and applying power to produce flashes of light was then repeated with the lower resistance residue. In some cases, inverted glass vials were used to capture the smoke produced by the flashes of light and to affect the air:fuel (smoke = fuel vapor) ratio above the flashes of light. After 20-40 drops of fuel, the flashes of light were replaced by a constant glow upon the addition of a fuel drop to the residue. The residence times of fuel drops decreased from minutes to seconds in the presence of the constant glow. Once the Ag residue exhibited the constant glow in place of the flashes, each additional drop of fuel produced the glow and did not further affect the characteristics of the Ag residue. In some cases the addition of successive fuel drops (spaced approximately 2 seconds apart) resulted in ignition of the fuel residing on the ceramic rod and clamp.

C.3.4 Conductive Residue Formation.

Terminal Block with Ag Wires or Ag-Plated Nuts—As illustrated in figure C-3, the back of the terminal block in figure C-3 is flat with equally spaced holes (15 mm apart). For experiments with Ag wires, the ends of the Ag wires were secured to two adjacent steel studs on the front of the terminal block with steel nuts. The unattached ends of the Ag wires were then guided through adjacent holes in the terminal block and arched so that the end of each Ag wire pressed against the surface of the terminal block (figure C-3). The ends of the Ag wires were spaced 10-15 mm apart (spacing of nuts in figure C-1). Electrical connections were then made to the steel posts to supply power to the moveable Ag wires.

In the case of the Ag-plated nuts, steel wood screws were guided through two nuts and into two adjacent holes to secure the nuts to the surface of the terminal block. Alligator clips were then used to make electrical connections to the Ag-plated nuts.

The terminal block was then placed in a polymer-coated adjustable clamp with the backside of the terminal block on top and the electrical connections and steel studs on the bottom. Once the clamp was tightened to hold the block horizontal, a large water drop (250 µL) was dispensed with a plastic pipette onto the surface between the Ag wires or Ag-plated nuts. The plastic tip of the pipette was then used to engulf the ends of the Ag wires in the water drop by touching the edges of the water drop with the tip and dragging the water to the outer side of each Ag wire. In the case of the Ag-plated nuts, the tip of the pipette was used to drag the edges of the water drop against at least two edges of each nut. A glass tube pipette was then used to dispense small drops (2-5 µL) of fuel onto the upper surface of the water drop (figure C-3). Although a portion of the dispensed fuel flowed off of the water drop onto the terminal block surface, the majority of the fuel remained suspended on top of the water drop due to its lower density.

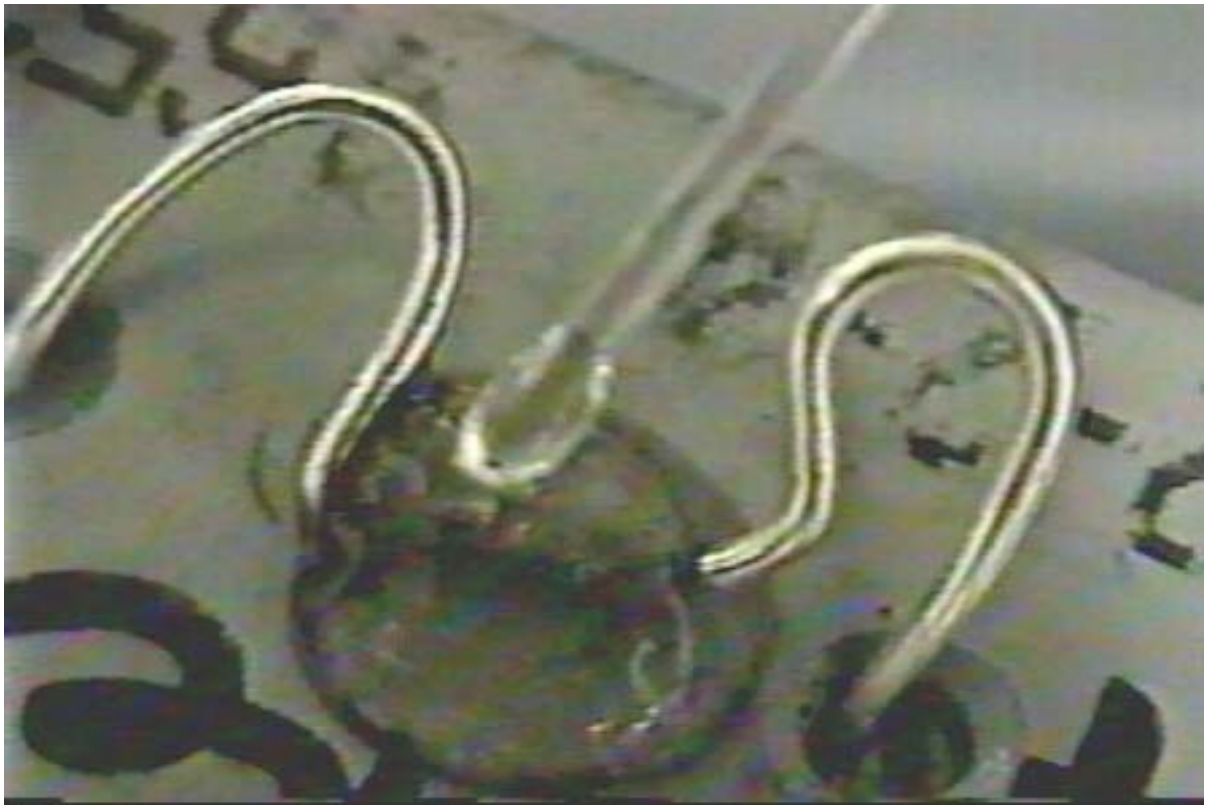


FIGURE C-2. TEST 1: 5 µL OF LOW-SULFUR FUEL ADDED TO WATER DROP BETWEEN TWO SILVER WIRES ON BACK OF TERMINAL STRIP. Silver wires attached to steel posts of terminal strip and pushed through holes in terminal block. (40 Vac (440 Hz), 20 mA applied to silver wires)

Within minutes of turning ON the selected 40-V power supply, a film with a shiny silver appearance formed between the fuel and water surface. If the 40-V power supply was dc voltage based, bubbles (H_2) were observed at the negatively charged Ag wire as the shiny Ag layer formed at the positively charged Ag wire. If the selected 40-V power supply was ac voltage-based, no bubbles were observed at either Ag wire, and the shiny Ag layer formed at the fuel:water interface regardless of its location with respect to the Ag wires. As the shiny Ag grew in size, the measured current increased until it reached the current limitation of the power supply.

In most cases, the power was applied until the water drop was no longer observed, leaving behind a shiny Ag coating on the terminal block surface. In some cases the power supply was turned OFF when the measured current reached the current limitation of the power supply and the water drop was allowed to evaporate (several hours), leaving behind a shiny Ag coating. If the measured current (digital multimeter) was below 1 mA, the water:fuel drop process was repeated with applied power until a current above 1 mA was measured with the dried residue. A fuel drop was then dispensed onto the dry Ag residue and the selected 40-V power supply turned ON. Flashes of light and smoke were produced regardless of the 40-V power supply selected when the measured current (digital multimeter) was between 2 mA and 80% of the current limitation of the power supply. Above 80% of the current limitation of the power supply, the voltage measured at the Ag residue fell to below 10 V and the flashes diminished. In the case of the 40-Vdc power supplies (described in later section), the flashes of light were replaced by constant glows (lasting up to 20 seconds) after only the first or second drop of fuel. Apparent ignitions of fuel vapor above the constant glows were observed for all of the 40-Vdc power supplies.

Inverted glass vials were used to affect the air:fuel (majority of smoke = fuel vapor) ratio above the flashes of light and constant glow. Small drops of water (50 μL) were sometimes dispensed at the Ag wires and Ag-plated nuts to improve the electrical contact (increase current) between the wires and nuts with the dry Ag residue.

C.4 POWER SUPPLIES.

C.4.1 Direct Current Power Supplies.

Two types of dc power supplies were used in this work: 9-Vdc battery and 40-Vdc power supply. The 9-Vdc batteries were connected in series to obtain dc voltages of approximately 9, 18, 27, 36, and 45 Vdc. The measured voltages of the 9-Vdc batteries varied between 8.5 and 9.5 V prior to use and decreased to below 7 V during use. Consequently, each Ag residue was produced with a new battery supply, single or combined. When necessary, an adjustable resistor was placed in series with the battery and residue to limit the current to below 500 mA. Unrestricted, the batteries supplied up to 3 A of current.

The 40-Vdc power supplies were produced by combining a constant output 40-Vdc power modular supply (115-Vac power input) with an internal resistance of 540, 816, or 1333 Ω to limit the supply's maximum current to 74, 49, or 30 mA, respectively. Although the power supplies were termed 40 Vdc, the measured voltage (in parallel with the residue) and current (in series with residue) were totally dependent on the resistance of the Ag residue. As the resistance of the Ag residue decreased and the current in the circuit increased, the voltage measured at the residue decreased for the different 40-Vdc power supplies in a linear fashion. Consequently, the maximum power supplied by the 40-Vdc power supplies were well below the 1 to 3 watts (W) calculated from the supplies' current limitations of 30 to 74 mA, respectively. The actual power maximum of the 40-Vdc power supplies ranged from 0.3 to 0.8 W and occurred when the resistance of the residue equaled the internal resistance of the 40-Vdc power supply.

C.4.2 Alternating Current Power Supplies.

Two types of ac power supplies were also used in this work: 60 Hz ac power supply and modified function generator. The 60 Hz ac power supply was produced by combining a constant output 50-Vac power module (115-Vac power input) with an internal power resistor to limit the current to 300 mA. When the current exceeded 300 mA, the power supply automatically turned OFF. An adjustable resistor was placed in series with the produced residue and power supply to limit the current to below 250 mA to avoid the power supply from turning OFF.

The output (6 V maximum) of the function generator was amplified using a voltage divider with a 1:10 (input:output) ratio. The output of the function generator was adjusted to 4 V to obtain 40 V from the voltage divider. The function generator was capable of producing an ac voltage with cycle rates of 1 Hz up to 100 kHz (400, 2000, and 7400 Hz used by commercial FQIS) in three different waveforms: triangular, square and sine. Although the maximum current of the modified function generator was 30 mA (limited by internal resistance), the current was limited to 20 mA during actual practice due to effects of temperature (generated during use) on the electrical components used to amplify the voltage. As was the case with the 4-Vdc power supplies, the measured voltage (in parallel to residue) and current (in series with residue) of the 40-Vac tests were totally dependent on the Ag residue. In contrast to the dc power supplies, the voltage decreased nonlinearly as the resistance of the residue decreased and the current increased. The maximum power of the 40-Vac function generator was 0.45 W (not 0.8 W = 4 V x 20 mA) and occurred at a residue resistance of 1600Ω.

C.5 ELECTRICAL MEASUREMENTS.

The voltage and current measurements were made with digital multimeters, analog strip chart recorders, and a recording oscilloscope. The digital multimeters were placed in parallel with the residue to directly measure the voltage drop at the residue. The digital multimeter was placed in series with the residue to directly measure the current flow in the circuit and residue. To trend the current flow of the residue, a 1Ω resistor was placed in series with the residue, and the inputs of a strip chart (100 mV full-scale) were connected in parallel with the 1Ω resistor. Consequently, the voltage drop across the 1Ω resistor measured by the strip chart was equal to the current flow in the circuit and residue (V = IR = I when R = 1Ω).

Although the multimeter and strip chart measurements responded to each puff of smoke or flash of light, the maximum current could not be measured due to the short (less than 1 ms) duration of the events. Therefore, a recording oscilloscope with a 10^8 Hz sampling rate was used to obtain an accurate current measurement during each flash of light and puff of smoke. Due to the high acquisition rate of the oscilloscope and the sporadic nature of the flashes of light/smoke, the parameters of the oscilloscope were set so that the oscilloscope recorded the current whenever a 5 mA rise in the current was detected. With this setup, the oscilloscope recorded the current of each flash of light or puff of smoke observed during testing.

APPENDIX D—HUMIDITY TESTS

D.1 INTRODUCTION.

The first step in the formation of silver and silver sulfide deposits in fuel tanks is electrochemical oxidation of silver plating on electrified contacts, forming silver ions (Ag^{+} and Ag^{++}) and silver oxide (Ag_2O and AgO). This process is greatly accelerated when bulk liquid-phase water bridges electrical contacts with potential differences greater than ~5 V (dc or ac). Such droplets were carefully placed by experimenters to accelerate testing in the bulk of the experimentation described in this report and its primary references (1-8). It is unlikely that such optimal conditions occur in fuel tanks where bridging water contact may be limited to the presence of condensed moisture films or the inadvertent interception of falling or flowing condensation droplets.

The deposit growth processes described above require the conjunction of four critical conditions: electrically contacted silver surfaces at dissimilar potentials, flow of electrical charge, water for reaction and conduction, fuel for reaction. Of these, only water is in limited supply in most aviation fuel tanks. It is plausible, therefore, that the rate of deposit growth in field service situations is limited by the presence and conductivity of bulk phase water.

Water enters fuel tanks either dissolved or suspended in fuel or via humid ambient air. Humid air is capable of promoting interelectrode conduction by one of two means: the accidental interception of a falling (or flowing) condensed water droplet or the formation of a contiguous condensed water film. The latter is essentially inevitable when aircraft fly to altitude from warm, humid environments or land in highly humid air with cold unburned fuel.

D.2 EXPERIMENTAL.

A measurement capability was established at SRI to simulate the conditions that produce water vapor condensation in the ullage of fuel tanks. Electrical connections were made to allow the testing of multiple electrode pairs inside a Blue-M Vapor Temp® controlled relative humidity chamber. A Solartron 1254 frequency response analyzer was used in conjunction with a Kepco BOP 50-2M bipolar operational power supply to deliver controlled current, voltage, and frequency signals to as many as nine electrode pairs on test. The Solartron was also used to conduct electrochemical impedance tests of growing deposits. Current and voltage measurements, both ac and dc, were made using a Keithley 706 scanner and a Keithley 195A digital multimeter. Measurements were sequenced, multiplexed and data recorded using a MacIntosh IISI computer controlling an IoTech MacSCSI488 GPIB interface. In some measurements of single-test electrodes, the multichannel power supply was replaced with a Princeton Applied Research Model 173 Potentiostat/Galvanostat with PAR Model 276 interface.

Electrodes on test were mounted inside the controlled humidity chamber (~40 cm diameter and height with working volume ~50 liters), with each electrode pair held at a controlled voltage. Measurements were taken of the imposed voltage (both ac and dc components) and the current passed (ac and dc) every minute and a 1-hour average recorded. In this way one could calculate

the effective resistance (= $|V_{ac}|/|I_{ac}|$) the total charge passed (= $\int I_{ac}\, \partial t$) and the net or Faradaic rectification charge (= $\int I_{dc}\, \partial t$).

In general, tests were performed at a single, fixed ac frequency and voltage (typically 400 Hz, 28 V. Occasionally, single electrode pairs were subjected to frequency scans from ~0.1 to 10,000 Hz to probe the electrochemical processes of deposit growth and conduction.

To precipitate a condensed water bridge between electrode pairs, the humidity test chamber was set to cycle between high-temperature, nearly moisture-saturated conditions (35°-40°C, 90%-95% relative humidity) and ambient temperature (variable and monitored but normally 20° ±3°C). A drip shield was positioned to prevent moisture droplets from directly striking the specimens so that a percolation bridge of communicating surface droplets is necessary to provide continuous ionic conduction.

The high-temperature set (corresponding to 95°-104°F) represents a relatively modest tropical or summer condition for an aircraft standing on tarmac in full sun. For a center tank with fuel adjacent to the air pack, the temperature at takeoff may be considerably higher [D-1]. The low-temperature set point obviously reflects neither the air temperature nor pressure at aircraft cruising altitude (ambient temperature below freezing, altitude 30-40,000 ft, pressure 0.2-0.3 atm).

Figure D-1 plots the mass of water contained in air at 100% relative humidity (r.h.) as a function of temperature from 0° to 40°C (32°-104°F). The volume of the test chamber was 0.05 m^3 so the full content of water is 2.57 g (or ~2.6 cm^3). The total area of specimens is ~10 cm^2, so that preferential deposition of condensed phase water would result in a moisture film of considerable depth and conductivity. This did not occur for three reasons:

1. The high-temperature condition was not completely saturated (~95% r.h.), and the condensing point (~20°C) still had a considerable water-bearing capability. The magenta line referenced to the right axis in figure D-1 plots the approximate percentage of humidity condensation as the temperature is reduced from 40°C, 95% r.h. At 20°C, ~64% of the water is condensed (~1.6 g) in the 0.05 m^3 chamber.

2. As can clearly be seen in the humidity chamber, condensation occurs preferentially on the walls that are the first to cool. For the cylindrical test chamber, the wall area was ~ 0.75 m^3. If uniformly distributed, one would expect a moisture film of ~2 μm thickness to nucleate and grow on each condensation cycle.

3. Films of this thickness tend not to be continuous on surfaces that are not easily wetted. Condensed films on the inner surface of the humidity chamber and on the specimens during early stages of deposit growth appeared as small, hemispherical, disconnected water “islands” with very limited surface tension-driven coalescence. At this stage the conductivity of such moisture films is low because the condensed water is relatively pure, the thickness of the film small, and the degree of connectivity low.

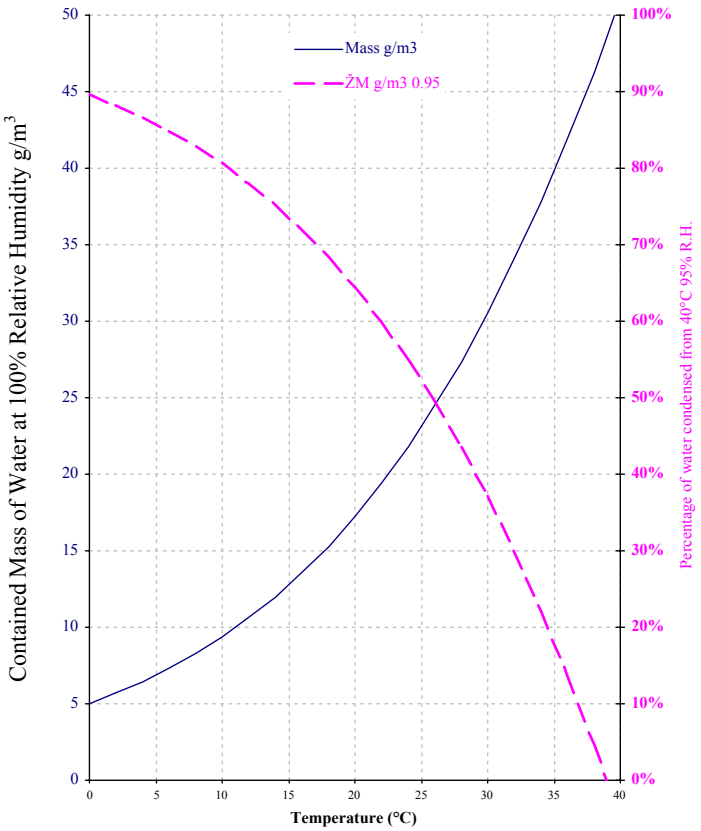


FIGURE D-1. MASS OF WATER CONTAINED IN AIR AT 100% RELATIVE HUMIDITY

D.3 TERMINAL STRIPS—HUMIDITY ONLY.

The first tests were performed with 1-mm Ag wire electrode pairs mounted in two-hole ceramic holders (item 2 in section 2.7). Initially, the humidity chamber was set to cycle once per day, 12 hours at high temperature and 12 hours at low temperature, simulating an aircraft flying once per day. The cycling rate was doubled 12 days into the test to accelerate the deposit growth process.

Each of six electrode pairs was connected to an ac 400 Hz 28-V supply and the current in each circuit measured with a sensitive microammeter. Before the start of the test the dry current was measured for each pair at 20°C. This leakage current (I°) was subtracted from the measured current to calculate the net increased current due to conductance of the growing electrode deposit.

Figure D-2 presents data for six nominally identical Ag electrode pairs during the first 12 days of 12-hour humidity cycling. As can clearly be seen in this logarithmic plot of I-I°, initial currents are very low (10-100 μA), corresponding to interelectrode resistances of 300-3000 MΩ, characteristic of dry, separated contacts. Missing data in figure D-2 are points where $I \leq I°$. The black line connecting the + point plots the temperature measured with a thermocouple probe on the plane versus the approximate position of the electrode pairs.

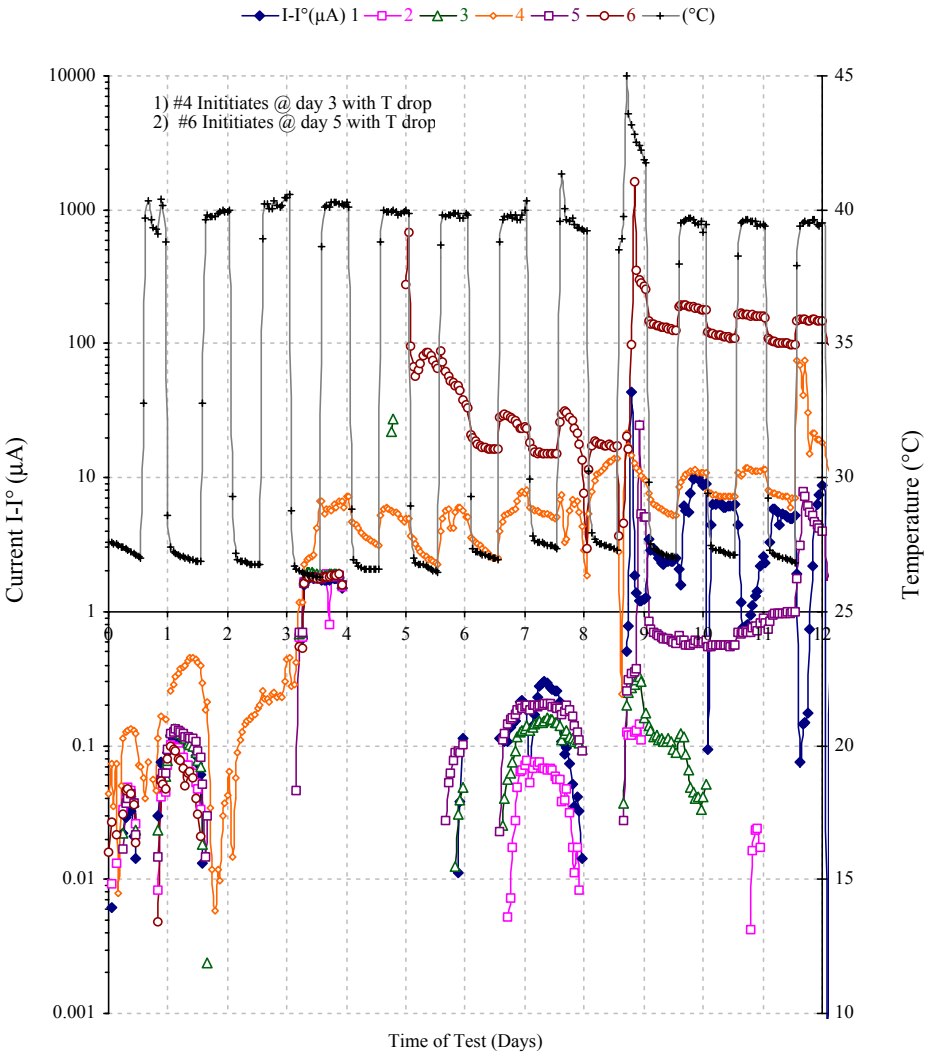


FIGURE D-2. TEST STRIP CHART, DAYS 1 THROUGH 12

Electrode pair no. 4 exhibited a sudden increase in current (conductance) on day three, coincident with reduction in temperature and, thus, onset of condensation. This increase occurs in two steps, each approximately a factor of 10. Although remaining at this high value, the current (conductance) then established a pattern in phase with the temperature, high when the temperature is high and vice versa. This suggests a process of thermally activated conduction such as an electrochemical reaction or ionic conduction, since the degree of water coverage is anticipated to be higher when the temperature is lowered from 40°C. Electrode pair no. 6 initiated a bridging conductive path on day six, also with temperature drop in the humidity chamber, and then exhibited the same characteristics as pair no. 4. The conductivity rise for pair no. 6 is by a factor of nearly 10,000 times. Electrodes nos. 1 and 5 exhibited increased conductivity on day nine, but to a much lesser extent than nos. 4 and 6. The remaining two pairs (nos. 2 and 3) show no measurable current or conductance increase on this timescale. Figure D-3 presents data for all electrode pairs from days 12-28 of the humidity tests with 6-hour cycling. Note the factor of 100 increase in the minimum current axis value compared with figure D-2.

On day 12, electrode pair nos. 1, 2, 3, and 4 all displayed an abrupt increase in current (conductance). The current in pair no. 5 stayed low until day 14 of the test. The current in electrode pair no. 6 remained high. For ease of display, the data in figure D-3 are averaged over a 6-hour period (i.e., over the high- and low-temperature states of the humidity chamber). With this averaging, the trend for electrode no. 1 is most easily seen. Until day nine, the current was 0.01-0.1 µA (300-3000 MΩ). From days 9-13, the current was 1-10 µA (3-28 MΩ), and henceforth the current was fairly stable at 1000-10000 µA (1-10 mA and 3-30 kΩ). In all, this electrode pair demonstrated an increase in conductance by a factor of more than 1 million in approximately 2 weeks. This dynamic increase was exhibited by electrode pair nos. 4 and 5 in approximately 3 weeks of humidity cycling in the absence of fuel or ionic additives.

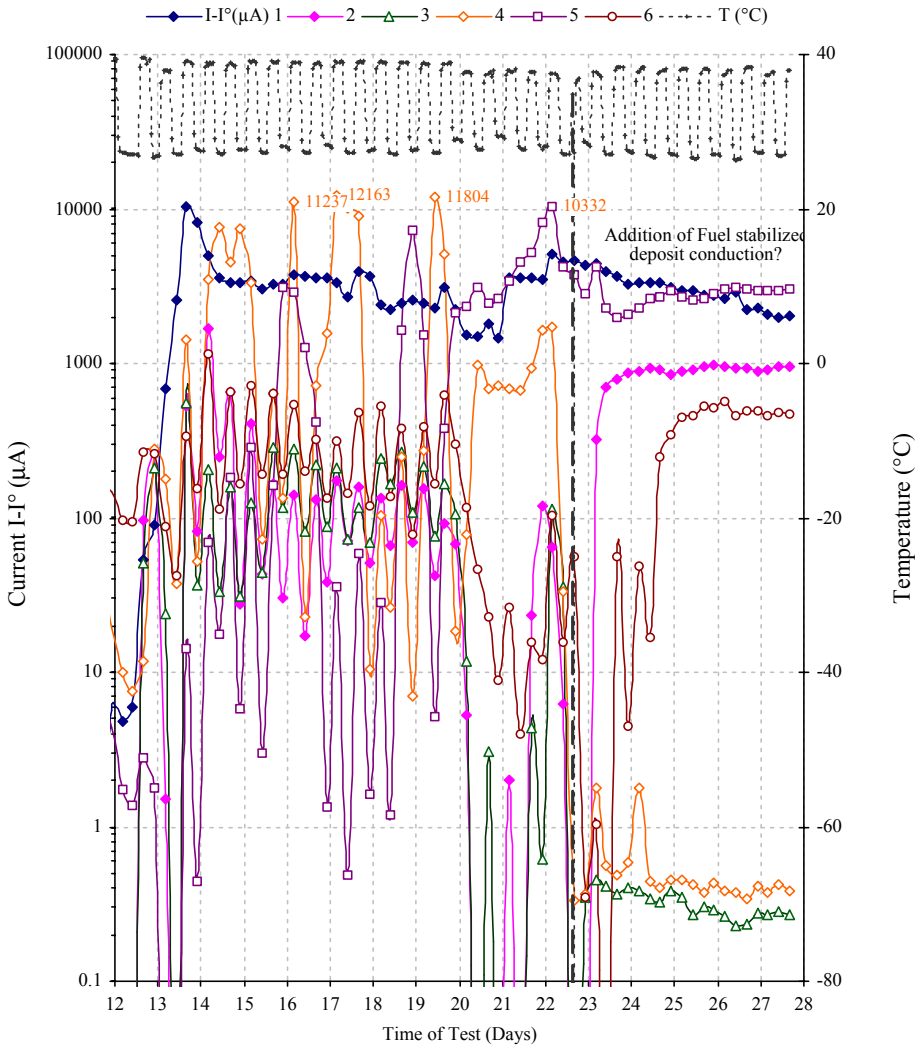


FIGURE D-3. TEST STRIP CHART, DAYS 12 THROUGH 28

The trend for the other electrodes is unclear in figure D-2 because of the oscillating trend of conductance with temperature cycling. These data have been replotted in figures D-4 and D-5, which separate the high- and low-temperature data and allow the evolution of conductance to be examined. Note the change in current scale from µA to mA. Although there is considerable

dispersion of data in both plots, a heavy black line has been added to show the (linear) average effect. On average, the electrode currents increase from 0.028 μA (figure D-2) to 2.2 mA in the high-temperature state (figure D-4) and 1.7 mA in the low-temperature state (figure D-5). This represents an average increase in current and conductance of nearly five orders of magnitude accomplished in only 2 weeks of humidity cycling. The maximum currents (1-10 mA) and corresponding interelectrode resistances (3-30 kΩ) are slightly larger but of similar range to those measured with similar electrodes formed by direct water immersion at UDRI and ASU. It is clear, therefore, that structures of similar conductivity to those produced in seconds or minutes with the addition of bulk water droplets to electrified silver electrodes require some weeks to produce in humidity films formed in environments containing only water vapor.

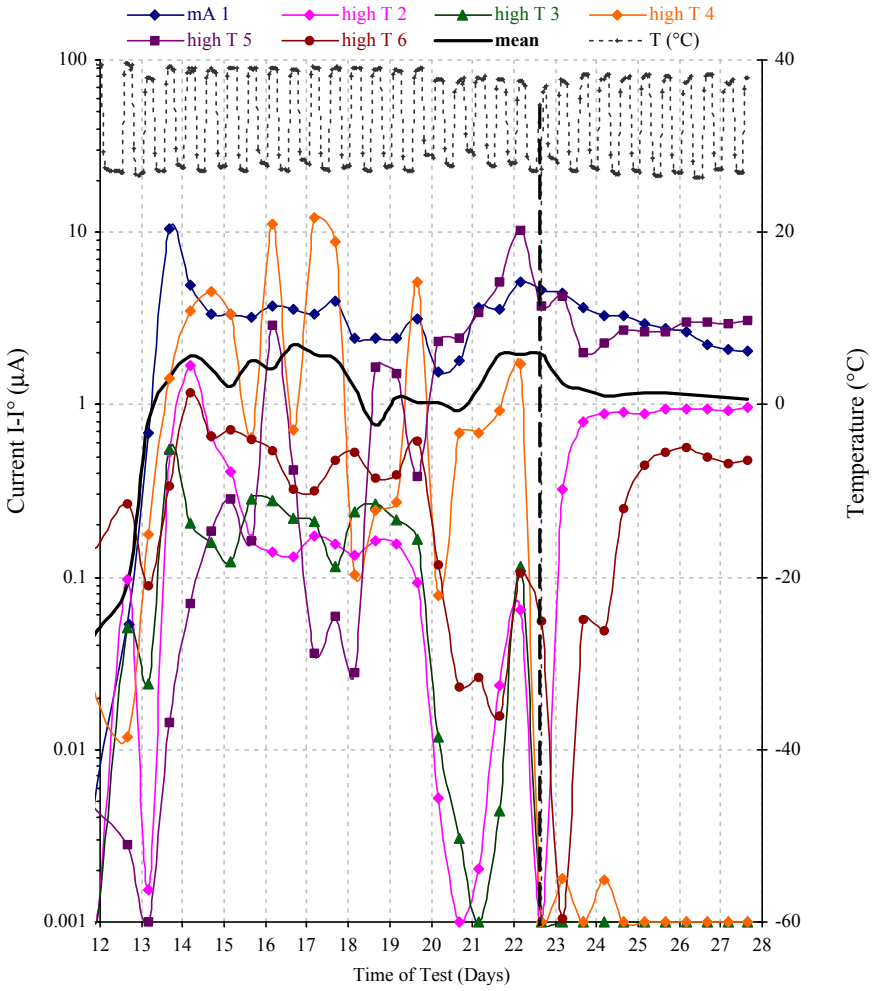


FIGURE D-4. ELECTRODE CURRENT AT HIGH-TEMPERATURE STATE

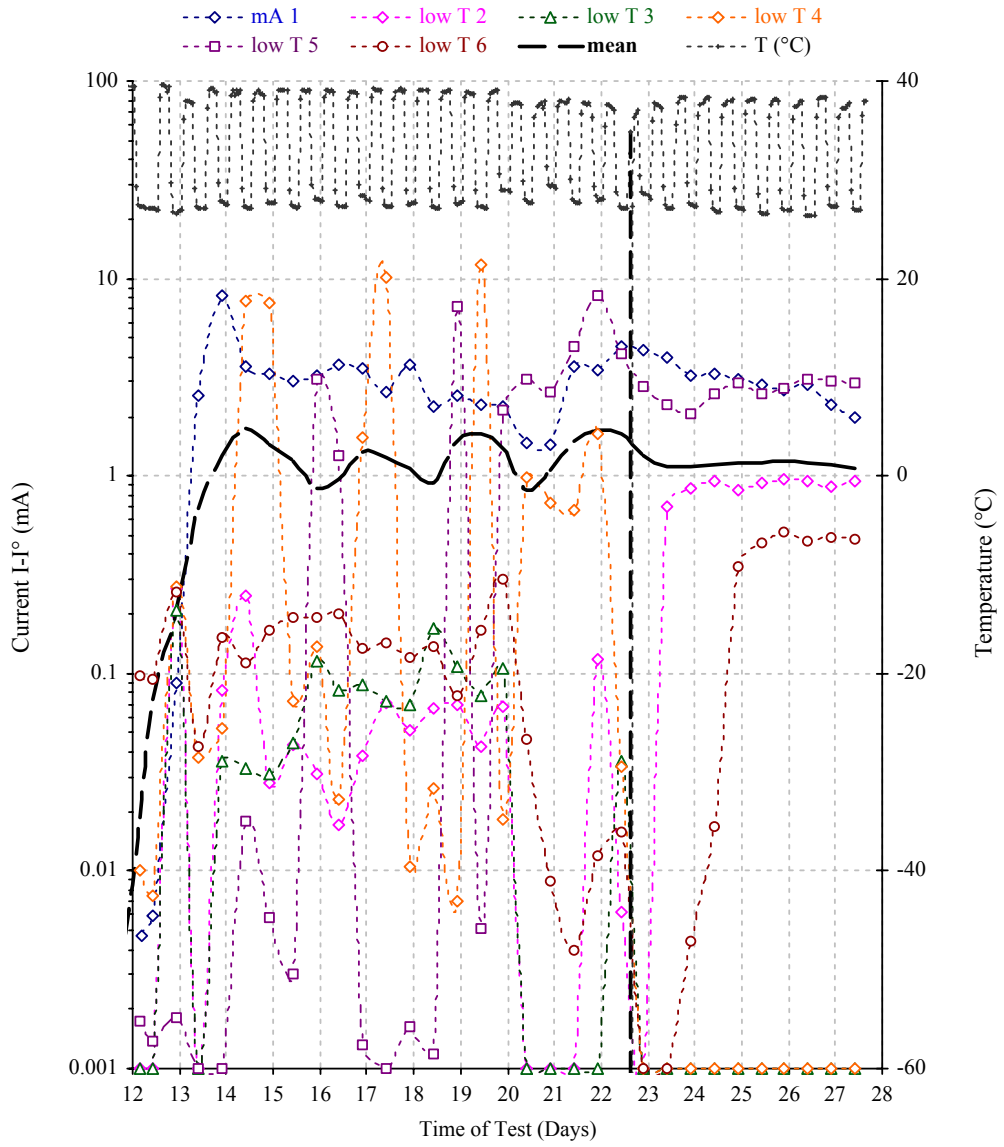


FIGURE D-5. ELECTRODE CURRENT AT LOW-TEMPERATURE STATE

D.4 THE EFFECT OF MOISTURE DEPRIVATION AND FUEL ADDITION.

On day 20, the humidity chamber become inadvertently depleted of water so that temperature cycling continued without causing condensation. On day 21 the chamber was rehydrated. The result (most clearly seen in figure D-4) for the least conductive electrode pairs, nos. 2 and 3, is a dramatic decrease in current with dehydration and increase with rehydration, suggesting that liquid water plays an important role in the conduction of these deposits. For the most conductive pairs, nos. 1 and 5, the presence or absence of water appears to have little effect on conduction, suggesting direct ionic and electronic connectivity of the deposit film between the electrodes. This film is called fully formed. Electrode nos. 4 and 6, with intermediate conductivities, exhibit an intermediate result. The conclusion is that liquid phase water is needed to produce the conductive deposits, but is not needed to sustain conductivity once fully formed.

On day 22 the temperature cycling was interrupted and drops of first fresh and then oxidized FAA123 low-sulfur fuel (see table 1 in reference D-2) were added to each of the electrode pairs in succession, while voltage control was maintained. Contrary to the effect of adding water, adding fuel to fully formed conductive deposits produced a pronounced response, while adding fuel to partially formed, poorly conductive deposits produced no measurable electrical effect.

Figure D-6 shows detail of figure D-4 for a 2 1/2-hour window at 22.6 days into the test. The decrease in recorded temperature at 0.12 h corresponds to the cover being removed from the humidity chamber for access to the specimens. Possibly because of mechanical effects (forming or breaking contacts between electrodes and deposit), this event resulted in a stepped increase in current for electrode pair no. 5, and a spiked increase and decay in current for pair no. 6. After allowing time to re-establish a steady state, two drops of fresh FAA123 Jet A were dispensed onto the deposit covering the ceramic surface between electrode pair no. 6, at the point noted in figure D-6. This addition produced no obvious effect.

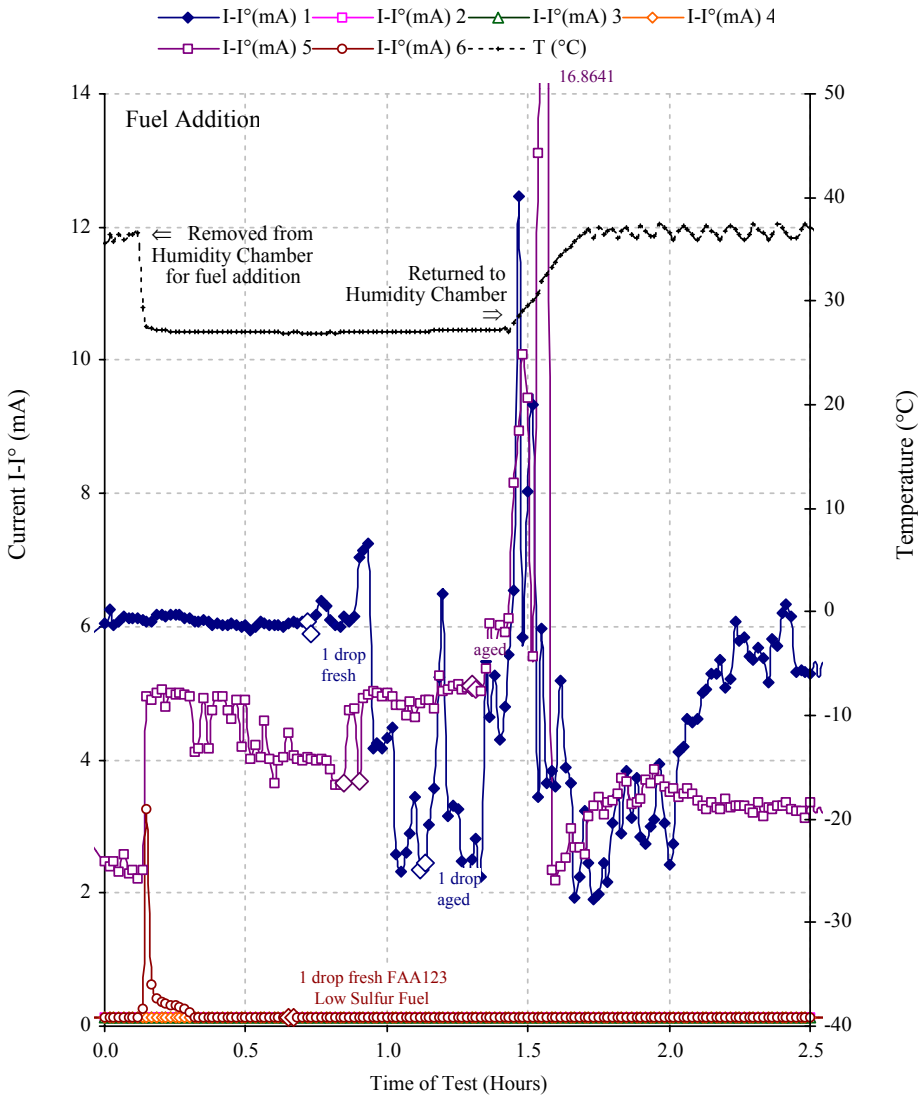


FIGURE D-6. EFFECT OF FUEL ADDITION ON DEPOSIT CONDUCTION

Some 4 minutes later, one drop of fresh fuel was added to the deposit on electrode no. 1, (points marked by open diamonds in figure D-6). This resulted in a small transient increase in current from ~6 to ~7 mA, and then declined. A second drop resulted in a current increase and possible scintillation. Either as a result of structural disruption caused by this scintillation, another unnoticed scintillation, or some other effect, the current in electrode pair no. 1 rapidly declined from ~7.5 to ~4.3 and then ~2.3 mA in two steps. It is important to note the greatly expanded dynamic range of the current response of this electrode following the first fuel addition.

Two drops of fresh fuel were added successively to electrode nos. 2 through 5; for none, except the last, was any response observed. Addition of the first drop of fresh fuel to the deposit of electrode pair no. 5 resulted in a current increase from 3.6 to 4.8 mA, and then decline. Addition of the second drop resulted in a more stable current increase to ~5 mA.

The first point to note is that the conductivity of the highly conductive (well-connected) deposits was not affected by the addition of water but was affected by the addition of jet fuel. Since the effect of fuel addition is to displace (conductive) water from the deposit pore structure with (nonconductive) fuel one can first conclude that fully formed deposits do not require these pores in order to conduct. The conductivity goes up with the addition of fuel suggests that components of the fuel (possibly ionic in nature) are incorporated rapidly into the deposit, allowing it to conduct better.

Fuel additions were repeated in sequence (no. 6 and nos. 1-5), this time using FAA123 that had been aged at elevated temperature to produce aggressive electroactive species (see references D-2, D-3, and D-4). No effect was observed for the poorly conductive deposits (nos. 2, 3, 4, and 6). For the fully formed films (nos. 1 and 5), the result of adding two drops of oxidized fuel was much more dramatic. For pair no. 1, the current immediately doubled, declined, and then increased more than six-fold within 20 minutes of fuel addition. Electrode pair no. 5 increased from a higher base current (~5 mA), but increased more than three-fold to a maximum current of ~17 mA. It is clear that the oxidized fuel has greater capacity than fresh fuel to cause increased current flow in already conductive fully formed deposit films and increased dynamic current range. Although not observed, possibly due to excessive light and inattention, it is possible that the disruptions in connectivity and conductivity that cause precipitous current decreases are coincident with or related to scintillations (see section 3.4).

Figure D-6 shows the short-term effects of fuel additions on deposit conduction. Figures D-3, D-4, and D-5 show the long-term effects. For highly conductive deposits no. 1 and particularly no. 5, the effect of fuel addition appears to be to stabilize the deposit, making conductivity even less sensitive to effects of moisture and temperature. As noted in figure D-4, the effect of fuel addition to electrode pairs nos. 2 and 6 may have been to activate or reactivate a conduction mechanism that had declined or deteriorated when the electrodes were starved of moisture on day 20. For pair no. 3 this reactivation never occurred and conduction was not facilitated by fuel addition. Electrode pair no. 4 is a special case. It was the first to activate (figure D-2) and exhibited the highest current, conductivity (figure D-3), and current dynamic range. Significant conductivity basically ceased 4 hours before the humidity chamber was opened to begin the fuel tests.

D.5 NEW TERMINAL STRIPS.

A new terminal strip intended for use in a B747 aircraft was obtained from the FAA together with ten silver-plated nuts appropriately sized to fit the studs (16) on the terminal strip. The terminal strip was cut into two unequal parts: one with ten studs, the other with six. Silver-plated nuts were attached to adjacent studs, leaving two studs bare between pairs. In this way, one terminal strip had three pairs of studs with nuts separated by two empty pairs. This was mounted in the humidity chamber with the studs pointing vertically upwards. The other strip with two adjacent pairs of studs with nuts was mounted in the humidity chamber with the studs pointing horizontally and in the same horizontal plane. The three vertical pairs were considered to be a worst case, since condensed water can pool and bridge by means of the horizontal surface between nuts. The two horizontal pairs were considered to be the best case, since water droplets, if formed, can flow down off the terminal strip without bridging the nuts.

The five electrode pairs were connected (initially) to a 400 Hz ac 28-V power supply and current monitoring resumed. Figures D-7 and D-8 summarize results of the first 70 days of testing with 6-hour humidity cycling before fuel addition. The gap in the data record was an acquisition problem; the test continued during this time.

Figure D-7 shows the increase in amplitude of the ac current. A current of 0.0001 mA (0.1 μA) corresponds to a resistance of 280 MΩ. The initial resistance of all contact pairs was >300 MΩ, which is considered to be a "minimum acceptable resistance for this part under any conditions." With the commencement of humidity cycling it is clear in figure D-7 that there is a disparity in conductance for the five contacts (which is not correlated with orientation) and that the current (and conductance) increases slowly with time.

Figure D-8 plots the measured dc current that results from the imposition of an ac driving voltage. The rectification current results from nonlinear circuit elements, primarily electrochemical (see appendix B), and measures the net rather than total current passed. The dc currents in figure D-8 represent an average of only 25%-60% of the ac currents. This is, however, a very significant degree of rectification, indicating the presence of highly nonlinear and irreversible circuit elements. The total net charge passed ($\int i_{dc}\, \partial t$) varies from 0.19 coulombs for electrode pair no. 3V to 0.31 coulombs for electrode pair no. 2H (contrary to worst and best case expectations). This corresponds to between 19,000 and 31,000 moles of net electrochemical process. Most of this charge must have gone into the formation of gaseous reaction products (H_2 and O_2) since 19,000 moles of silver oxidation would yield more than 80 g of Ag_2O.

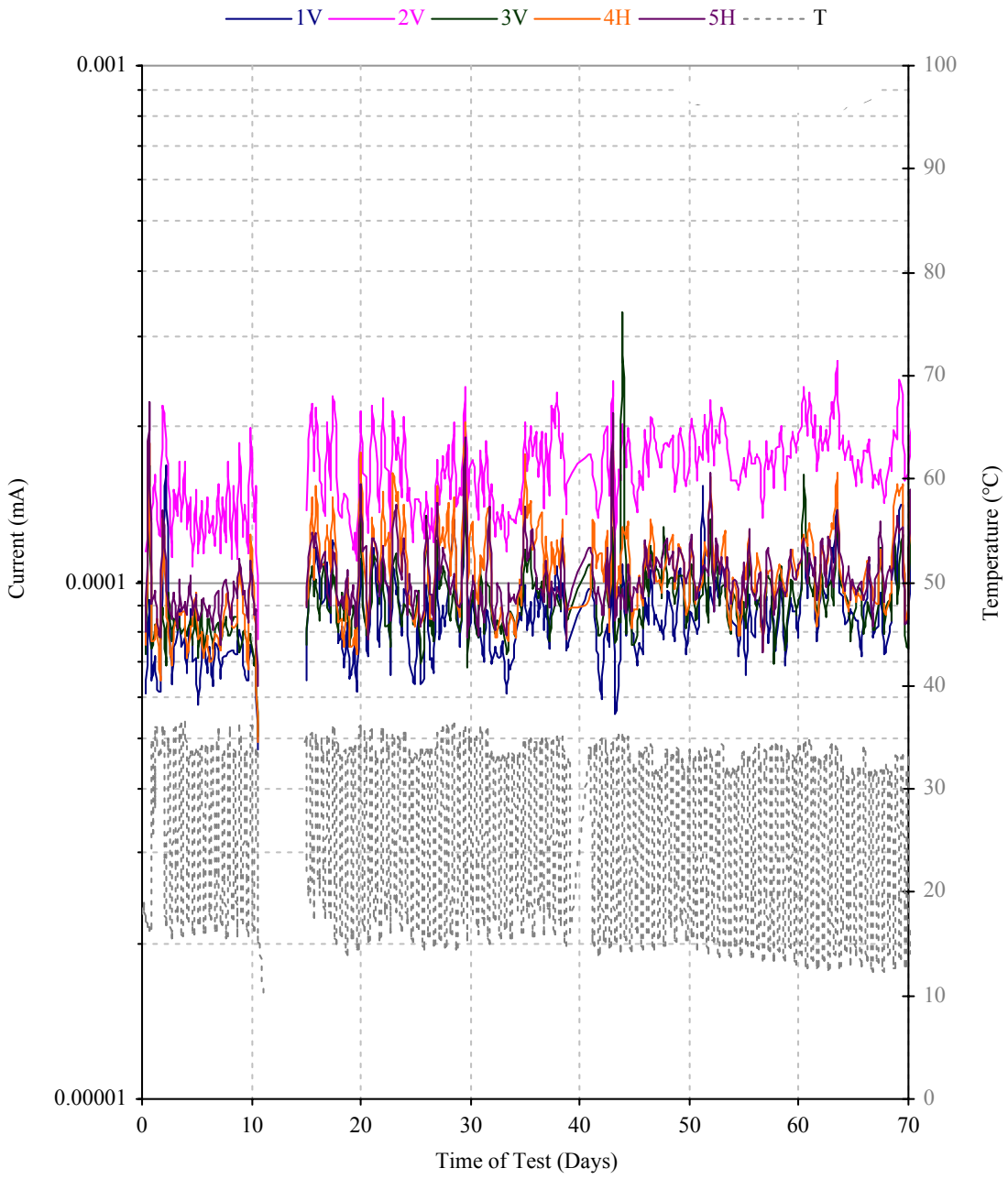


FIGURE D-7. AMPLITUDE OF AC CURRENT

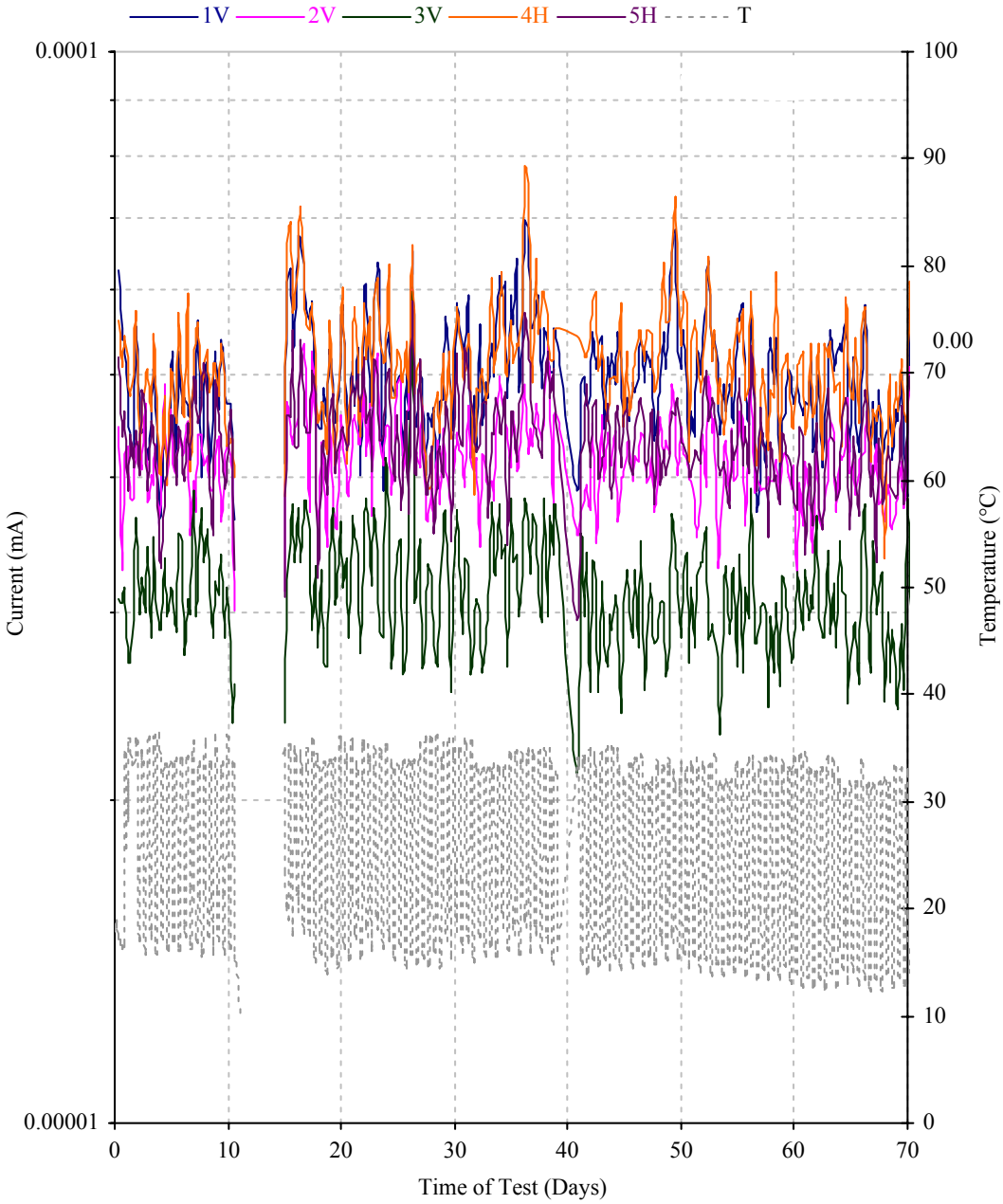


FIGURE D-8. MEASURED DC CURRENT

It is clear from the above that, while the currents are small, the integrated net charge in 70 days is certainly sufficient to form bridging deposit sufficient to severely compromise the isolation of silver nuts on terminal studs experiencing 28-Vac polarization. The extent to which this did happen is difficult to assess in figure D-7 because of the high degree of scatter of the data and very slow increasing trend. The expected trend is an approximately exponential increase in current as the accumulated deposit increasingly improves conductivity. Figure D-9 replots the data of figure D-7 as Log[$i_{dc}/\mu A$] versus time of testing. The calculated regression lines have the characteristic listed in table D-1.

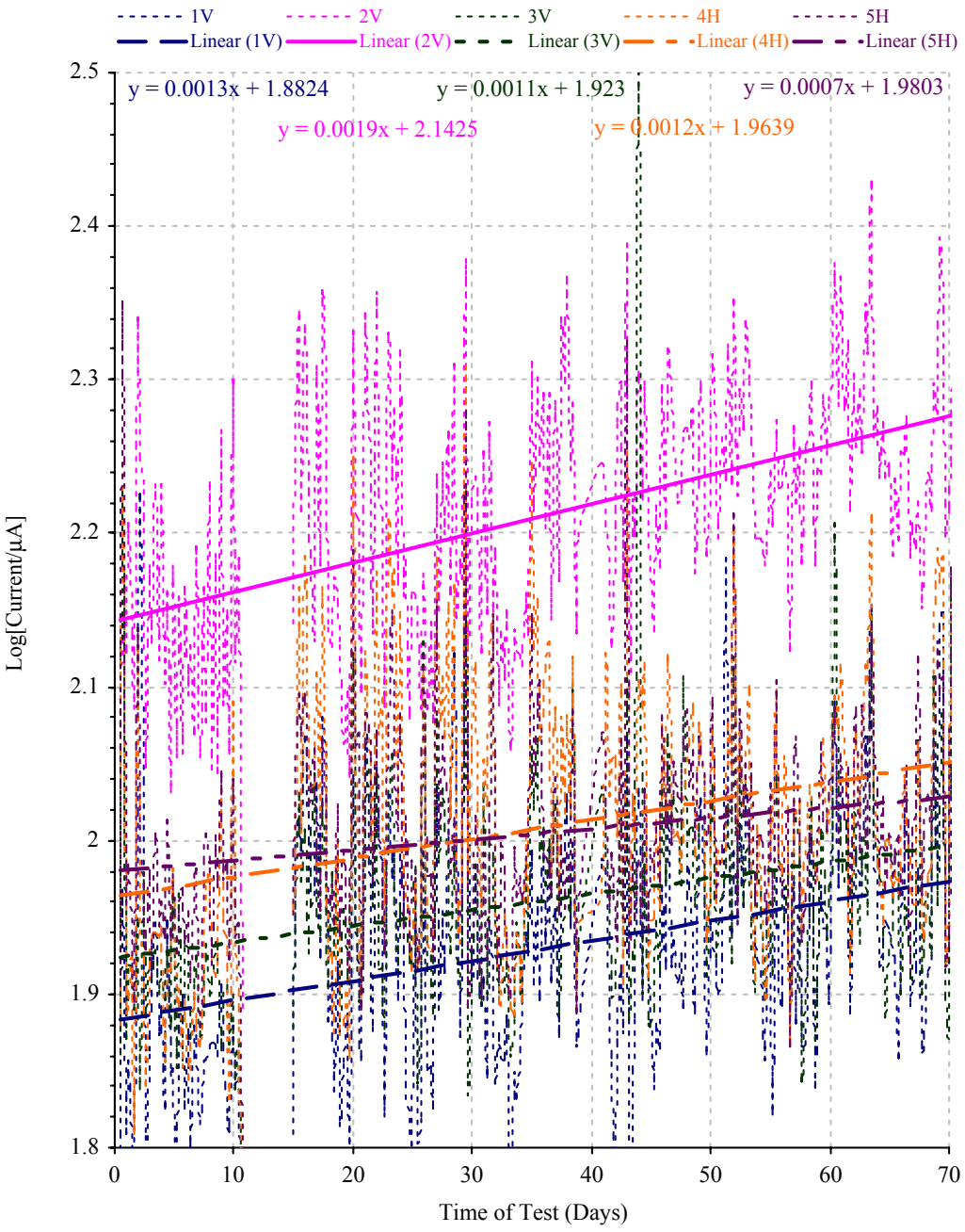


FIGURE D-9. LOG[i_{dc}/µA] VS TIME OF TESTING

TABLE D-1. LINEAR REGRESSION OF DEPOSIT RESPONSE

Electrode Pair	Regression Line		$I_{ac}°$ (nA)	Years to Reach	
	Slope	Intercept		1 MΩ	1 kΩ
1V	0.00131	1.88	76	5.4	11.6
2V	0.00192	2.14	138	3.3	7.6
3V	0.00106	1.92	83	6.5	14.3
4H	0.00124	1.96	91	5.5	12.1
5H	0.00069	1.98	95	9.8	21.7

V = vertical
H = horizontal

The last two columns in table D-1 are the calculated times (years) to reach an intercontact resistance of 1 MΩ and 1 kΩ, assuming that the log-linear trend of current increase continues. One MΩ is taken to represent the degree of isolation compromise that could clearly cause fuel quantity indication errors. Under the circumstances of the test, this would take 3 to 10 years to occur. One kΩ is the value at which scintillation, glowing hot spots and the potential for bulk fuel ignition begins to be of concern. The numbers calculated are well within the range of expected service life of aircraft despite the very low values of initial leakage currents. Before drawing any general conclusions, however, several factors should be taken into consideration:

1. A very small sample of specimens has been tested, all prepared from a single terminal strip and single lot of silver-plated nuts. It is not known how representative these nuts are or how prevalent they are in service.

2. The time to failure calculated in table D-1 assumes that the 28-V 400-Hz ac power is applied 24 hours per day (as in the humidity tests). These times need to be divided by a use factor that may be substantially less than unity.

3. Although the humidification and condensation conditions in the tests were less extreme than might occur in the field, they nevertheless are more severe than the condition of the average flyout and descent.

4. There is a very significant danger in extrapolating the results of a 70-day accelerated test to timescales of many years. The assumption of exponential increase may not hold, or the mechanism of conductivity increase may change, become limited, or even reverse.

5. Table D-1 relates only to the effect of water condensation and electrolysis. The fuel (in fuel tanks) is known to affect the growth and conduction of deposits. High-sulfur fuel will terminate growing silver oxide deposits and will tend to displace water from the porous deposit matrix. Both effects will slow the rate of conductance increase. Some low-sulfur fuels have been shown [D-5] to increase the rate of conductance increase.

D.6 TERMINAL STRIPS—AGED LOW-SULFUR FUEL.

On day 70 of the test described above, ~0.1 cm^3 of aged and highly oxidized Jet A fuel was added to each of the three vertical electrode pairs, leaving the horizontal pairs as reference. To facilitate intra-electrode communication, the droplet of fuel on the end of a hypodermic needle was touched to each nut, wetting the nut and its contact with the terminal strip. The remaining fuel (from the 0.1 cm^3 aliquot) was spread in a fine layer across the upper surface of the intervening terminal block.

This fuel addition to pair nos. 1V-3V did not result in a noticeable current increase, although contact pair 5H (the slowest corroding in table D-1) began to exhibit spontaneous current increases of one or two orders of magnitude. On day 84 the test was modified to increase the rate of deposit growth by decreasing the effective distance between terminal posts. Two cm of 1-mm-diameter Engelhard Ag wire (99.99% purity) was connected under the Ag-plated nut of each of the six posts used for the three vertical electrode pairs. These wires were dressed flat on the surface of the terminal strip to produce a ~1 mm gap with overlap of ~0.5 mm. This new electrode geometry was similar to that employed by Kauffman when working with terminal strips [D-6]. This configuration might also be likened to that of two silver-plated wire pairs with missing insulation draped on the terminal block. Two further drops of fuel were added to each of the three modified vertical electrode pairs.

Figures D-10 and D-11 presents the ac and dc currents measured for the three vertical electrode pairs during the final 52 days of humidity testing. From day 70 to day 84, the presence of fuel on the terminals strip produced little if any change in the measured currents. When reconfigured on day 84 with the addition of silver wires and added fuel, all three electrode pairs show an immediate increase in current followed by a slow decline. For electrode pair no. 1V, the current increases only by a factor of ~2. For pair no. 2V, the reduced electrode spacing and fuel addition results in the current increasing by a factor of ~300, and for no. 3V the current increased more than 10,000 times. A maximum current of 10.8 mA was recorded for electrode no. 3V, some 10 days after reconfiguration of the electrodes. This value corresponds to a resistance of ~2.5 kΩ, typical of values produced by electrolysis of bulk water droplets at ASU [D-6] and UDRI [D-3].

The appearance of the direct (net, rectified) current in figure D-11 is conspicuously different from the alternating current record in figure D-10. The timing is such that it is difficult to identify cause and effect, but one interpretation of the current spikes in figure D-11 is that these mark times when net electrochemical reactions occur to produce conductive deposits. The increase in ac conductance thus follows the accumulation of dc charge.

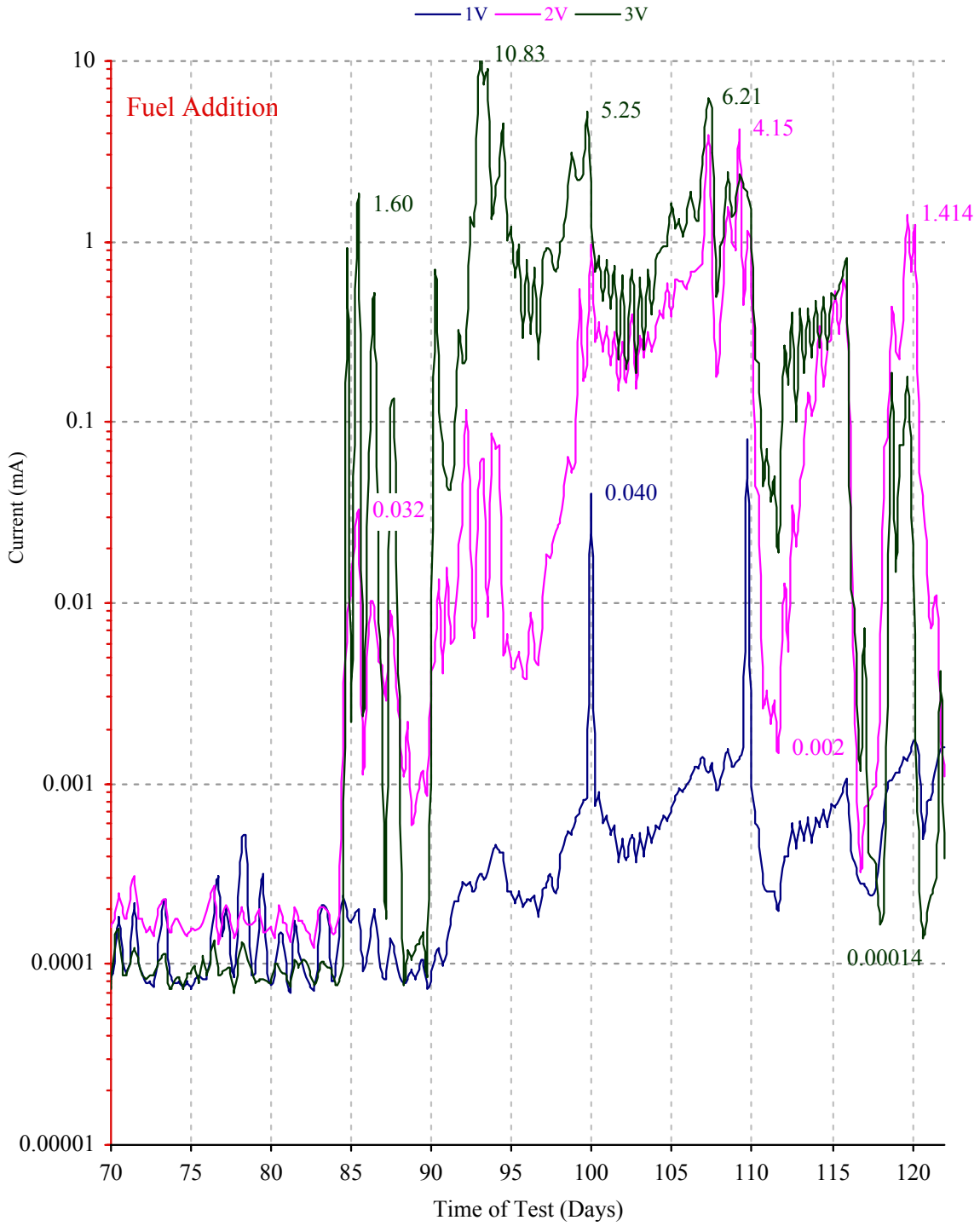


FIGURE D-10. MEASURED AC CURRENT FOR THREE VERTICAL ELECTRODE PAIRS

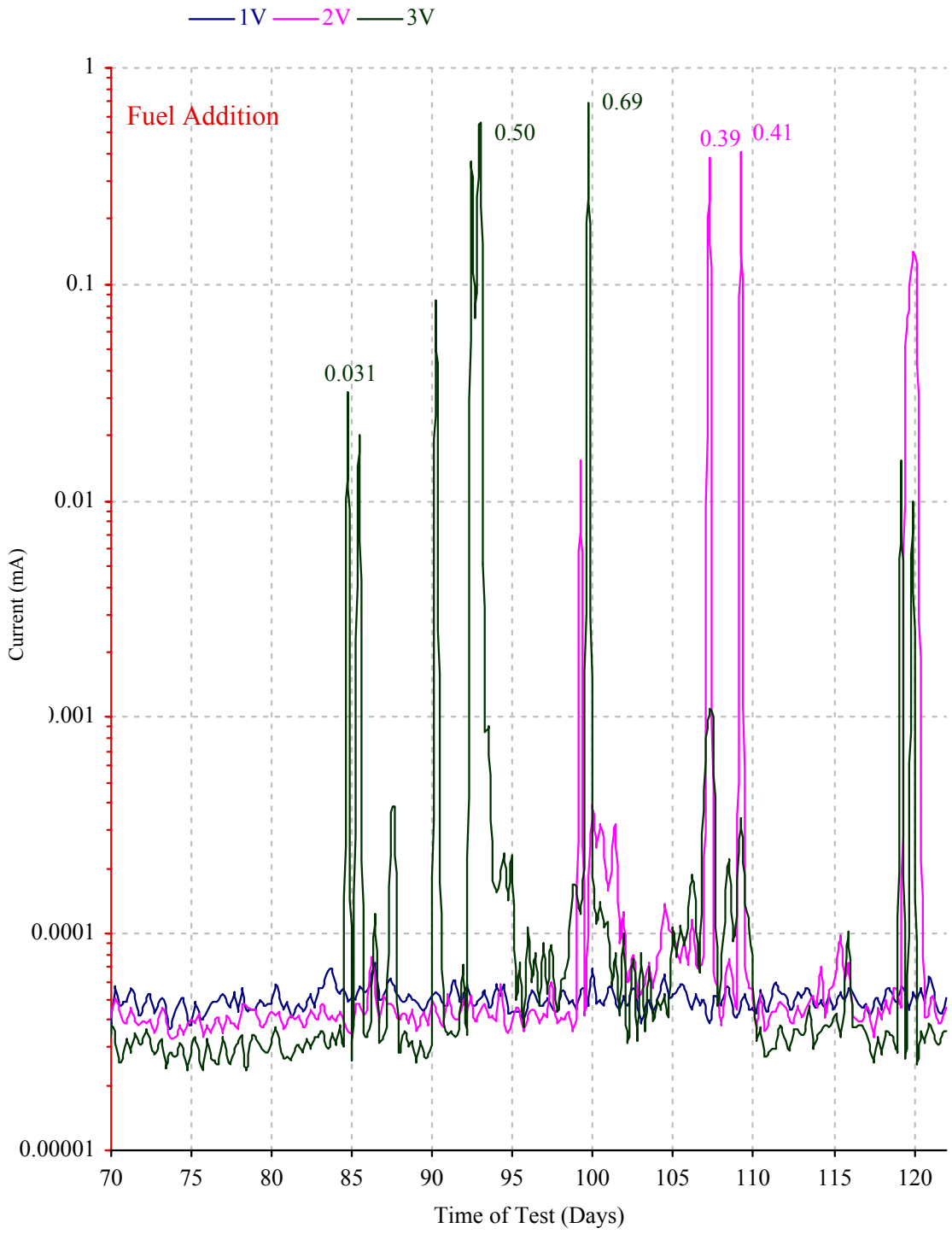


FIGURE D-11. MEASURED DC CURRENT FOR THREE VERTICAL ELECTRODE PAIRS

In retrospect, it is not surprising that narrowing the electrode gap and adding aggressive fuel caused growth of conductive deposit similar to that observed with test electrode structures, items 1-3 in section 2.7, in the presence of bulk liquid water. It is significant that this growth of

deposit required ~10 days with cyclic humidity condensation, but occurs on the timescale of 1-10 minutes with bridging water drops. From this, it is clear that the effects created and studied in the laboratories can occur in the condensing environment of fuel tanks, but may take 1,000-10,000 times longer to evolve.

D.7 AIRCRAFT TERMINAL STRIP NO. 1.

A terminal block was removed from the no. 4 reserve tank on a B747 airplane. This part was removed for cause, having exhibited unusual and out of tolerance electrical properties. This part was tested by the airline and then sent to an FQIS manufacturer and, thence, to SRI for testing.

Initial inspection revealed that this five-terminal block complete with nuts, but not lugs, was largely covered with a light brown patina of deposit. No black deposit characteristic of silver oxide deposits was observed. This part was included in the humidity cycle test substituting for the two horizontal electrode pair nos. 4H and 5H. After testing, the terminal block was examined at UDRI [D-5]. The deposit patina was found to contain cadmium in an organic matrix. Silver was not observed in the deposit, although samples of deposit were taken from creviced regions remote from the nuts and studs. All five nuts were found to be silver-plated.

The terminal strip was put on test in the humidity chamber with imposed 28-V 400-Hz ac connected between both of the two outer pairs, leaving the center stud of the five-terminal strip free. All studs had what are believed to be their original nuts attached. The terminal strip was oriented for testing with studs pointing vertically upwards.

Figure D-12 shows the results of 3 days of testing. The initial ac current at 28 V was ~0.1 μA, corresponding to a resistance of ~300 MΩ. When placed in the humidity chamber at high humidity but room temperature, the current in both pairs immediately began to rise. After a 6-hour soak at room temperature, the conductance of one pair had risen by a factor of ~6 with resistance decreased to ~30 MΩ. On the first humidification cycle, with increasing temperature and moisture content, the conductance of both contact pairs rose markedly, in each case by a factor of ~100. Six subsequent humidity cycles caused a further progressive rise of current to an approximately steady value of ~0.2 mA, corresponding to a resistance of ~140 kΩ.

This extreme moisture sensitivity causing dramatic increase in conductance and, thus, current is not characteristic of a clean, new terminal strip. One can only conclude that it is a property of the thin surface coating, either as a surface tension effect to promote easy wetting and thus spreading of water condensate or as a bulk property of conduction in the deposit, which required rehydration to facilitate ionic motion.

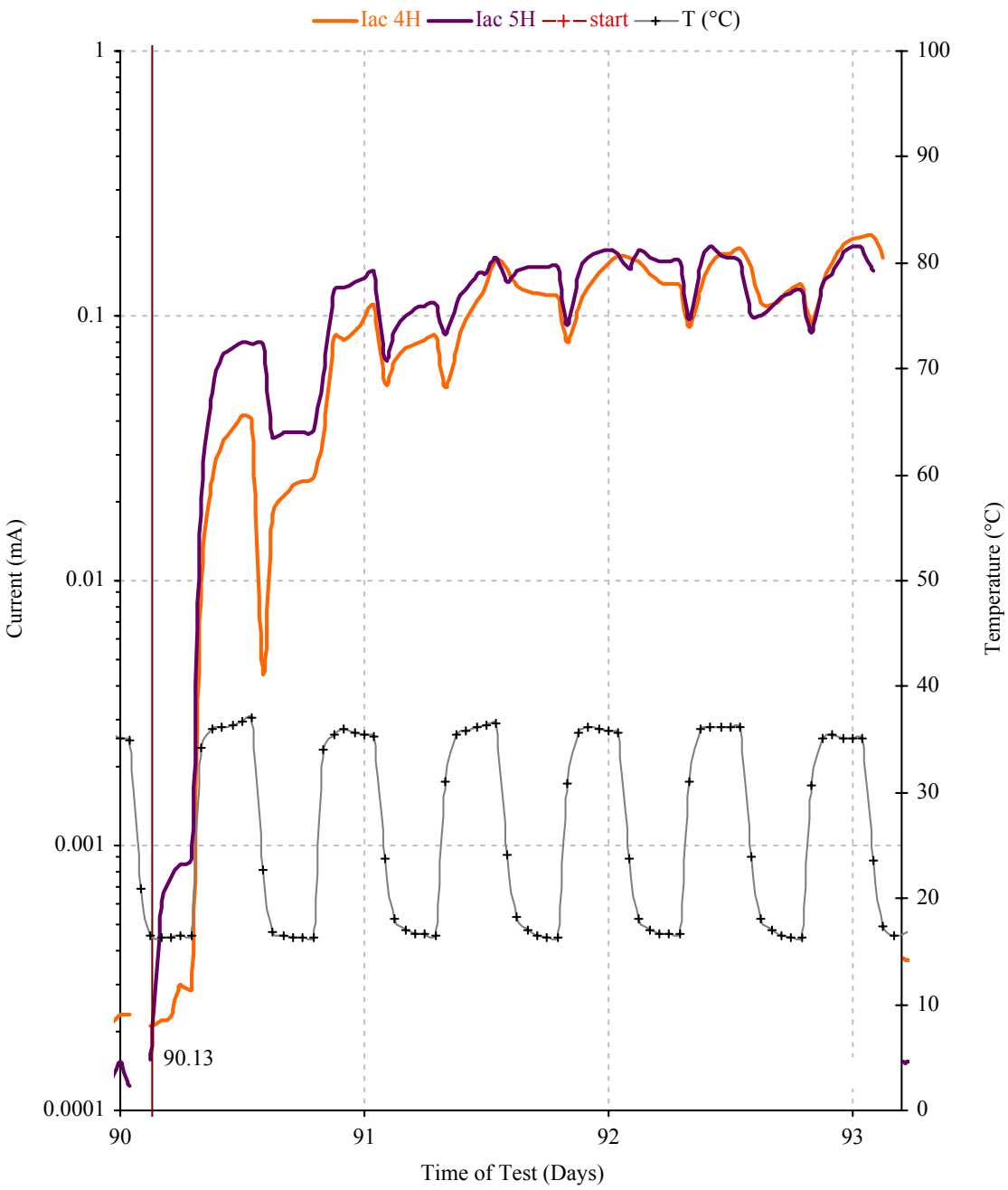


FIGURE D-12. THREE DAYS OF TESTING OF HORIZONTAL ELECTRODE PAIRS

The limiting conduction observed in this case is less by nearly 2 orders of magnitude than the value observed to be associated with fuel scintillations, glowing hot spots, and possible fuel vapor ignition. This deposit also did not have measurable amounts of silver, which is believed to be associated with low-power ignition events. However, the conductivities obtained relatively quickly were quite sufficient to cause fuel quantification errors, and this part was removed for this cause. Of comparable or potentially greater concern is the extreme moisture sensitivity of the conductance change. This phenomenon could make fault conditions difficult to diagnose.

D.8 SECOND USED AIRCRAFT PARTS TEST.

A shipment of FQIS parts from a B747 aircraft was obtained from the airline for analysis. These parts had been removed from aircraft undergoing refit of the fuel quantity gauging electronics package. It is believed that at least some of these parts were associated with low resistance problems. A complete test of parts received is listed in table D-2.

TABLE D-2. USED FQIS PARTS

Item	Line No.	Tank No.	Nuts			
			S	M	L	
1	610	1 Reserve				Compensator Probe (FG7C4)
2	610	R/H Wing				FQIS Main Harness
3	610	1 Main	8	8	8	FQIS Probe Nuts
4	602	1 Main	4	2	4	FQIS Probe Nuts
5	610	4 Main			2	4-Terminal Strip
6	602	1 Main		3	4	4-Terminal Strip
7	602	2 Main		2	4	4-Terminal Strip
8	602	3 Main		3	4	4-Terminal Strip
9	602	4 Main		3	4	4-Terminal Strip
10	610	4 Reserve				5-Terminal Strip
11	602	CWT		2	5	5-Terminal Strip
12	602	1 Reserve	3			5-Terminal Strip
13	602	4 Reserve	2		5	5-Terminal Strip
14	610	R/H Wing				FQIS Main harness

The nuts, specified in the table as small (S), medium (M), and large (L) all are associated with probe and terminal strip mounting and electrical hardware. The large nuts affix to the electrified studs of the terminal strips and therefore are of potential concern in our study of deposit formation. The 34 unattached nuts (items 3 and 4 in table D-2) were analyzed at UDRI. Without exception and irrespective of size, all these nuts were silver-plated.

Three terminal strips (items 6-8 in table D-2) were put on test in the humidity chamber with their original nuts (but no lugs) attached. All three were four-terminal strips, and two independent pairs of contacts were tested for each.

Part no. 6 was mounted with studs horizontal and in a horizontal plane; part nos. 7 and 8 were mounted with studs facing vertically up. Initial testing was made at 28-V 400-Hz ac.

Figure D-13 presents data from the first week of humidity cycling for three main tank B747 terminal strips as-received. Note that data for probe no. 6H are not plotted due to a recording error. The phenomenon described in the preceding section is repeated in each case, with rapid increase of conductance (and thus current) on the first humidification cycle, and then slow increase thereafter. This increase on the first day (I_{max}/I_{min}) ranges from 15 to 150; over 7 days the increase is between 100-250 times. Clearly there is a strong susceptibility of interelectrode

conductance to wetting or rehydration effects for parts with fuel tank experience. There is no obvious specificity of this effect toward particular terminal strips or orientation.

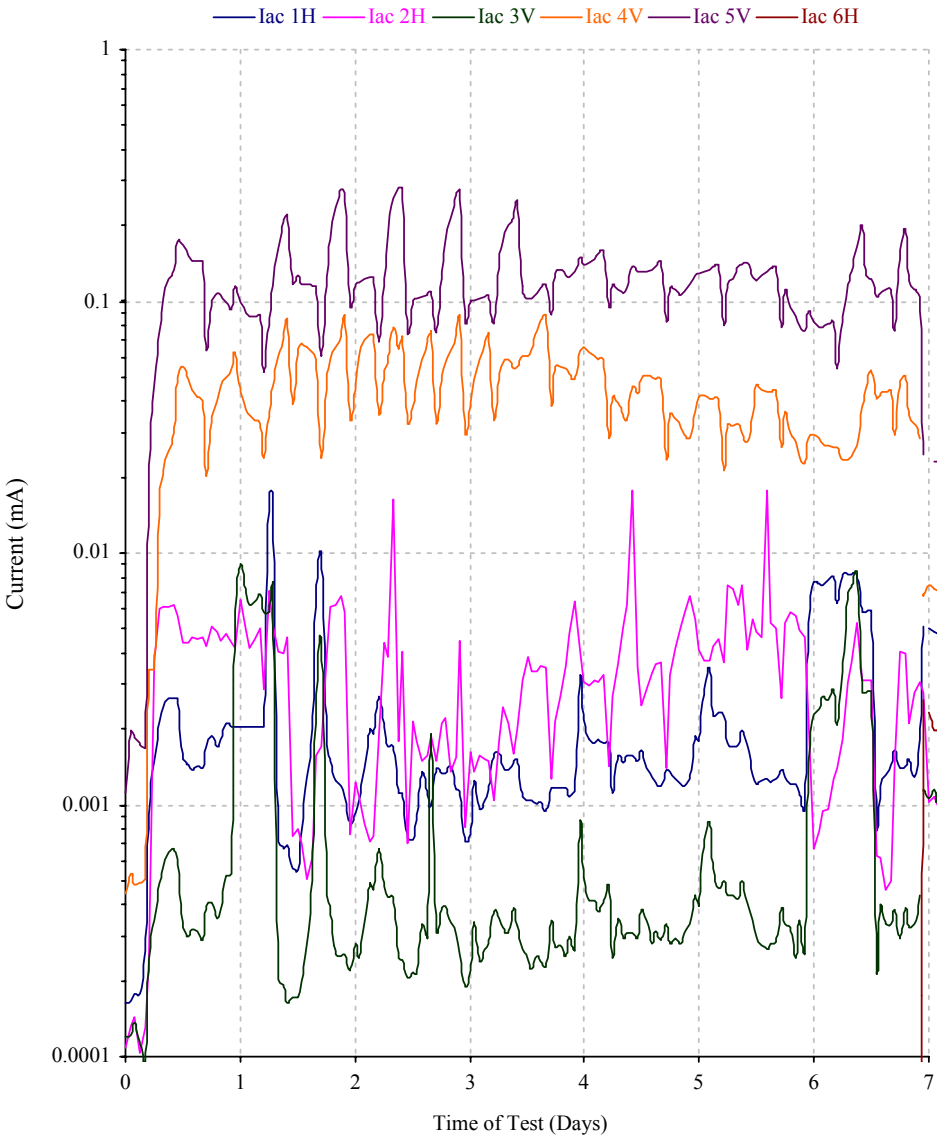


FIGURE D-13. TEST STRIP CHART 1

There was some interest to study the effect of probe signal amplitude and frequency on the deposit conductance. On day 7 the power supply was reprogrammed to deliver 7.07 V rms (10 V peak-to-peak) 7400-Hz ac. The resulting change in current and impedance was complex and puzzling. Figure D-14 extends the data of figure D-13. For the better conducting deposits (nos. 4V and 5V), the current drops with decreasing voltage, but by an amount far larger than the factor of 4 decrease in voltage (for no. 4V, the drop is ~34; for no. 5V ~44 times). For electrode pair nos. 1H and 3V, the current clearly rises with decreasing voltage (and increasing frequency). For no. 2H, the effect is what one would expect from an Ohms Law resistor (V=IR).

The effect of increasing current with decreasing voltage but increasing frequency is relatively easily explained as the result of capacitive impedance elements in the interelectrode conduction process. Presumably, the deposit is not fully formed (hence low current and conductance), containing gaps that can be bridged capacitively. That this phenomenon exists at all suggests that switching from a high-voltage, low-frequency system to a low-voltage, high-frequency signal may exacerbate pre-existing problems and display faults where none were noted before.

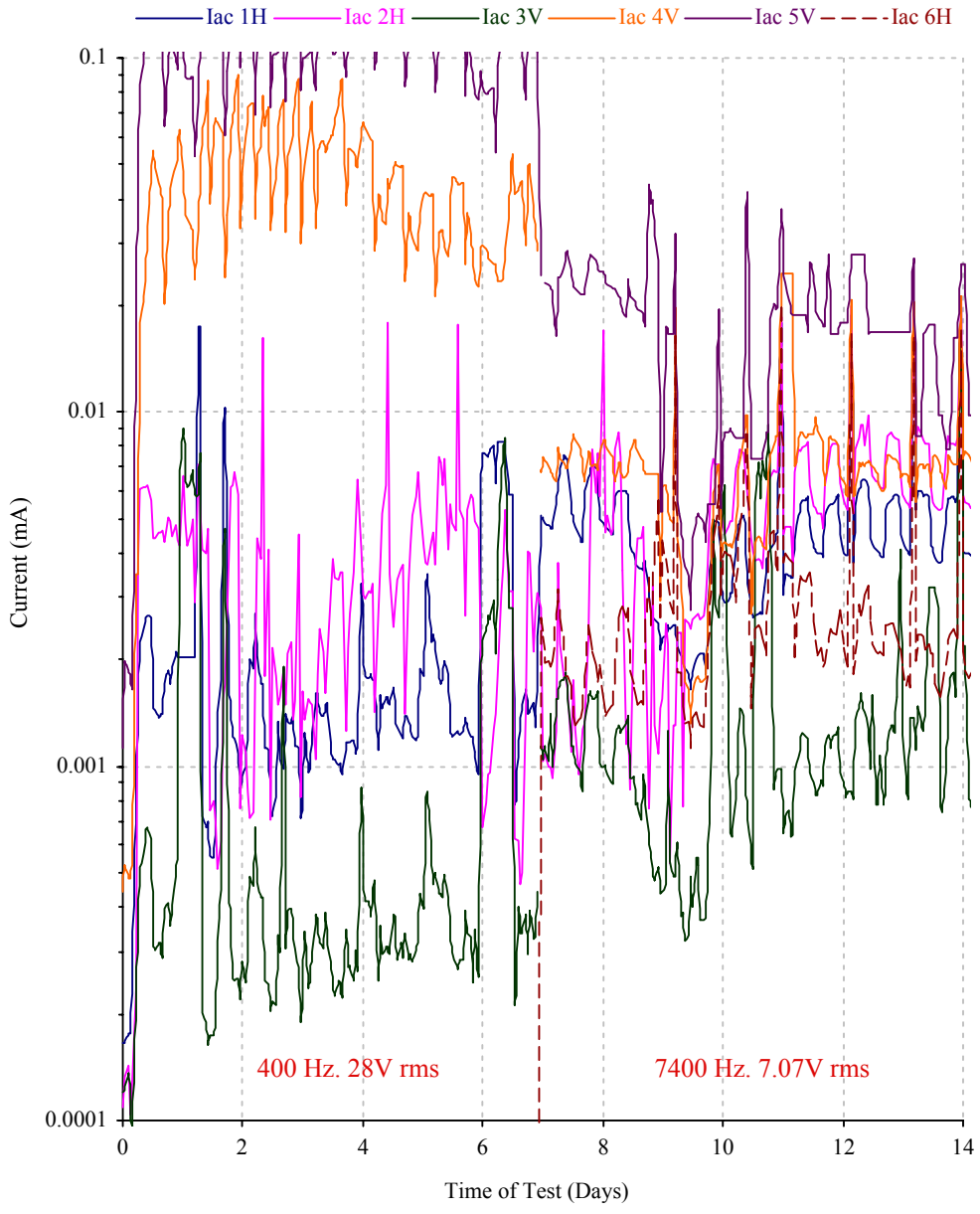


FIGURE D-14. TEST STRIP CHART 2

The effect of increasing frequency on the higher-conducting deposits is far more difficult to explain. In strictly electrical terms this might argue for the presence of inductive impedance elements. Such processes, however, have no physical significance for the conduction (and reaction) processes expected to occur in fuel deposits. Electrochemical impedance measurements covering the relevant frequency range did reveal the presence of inductive terms.

Figure D-15 plots the measured impedance ($|Z| = |V_{ac}|/I_{ac}|$) for the six electrode pairs for the entire duration of the 63-day test. If there is a trend here, it is not obvious, and although starting from values separated by nearly 3 orders of magnitude, the electrode pairs all settle into a range between ~2 and ~20 MΩ at 7400 Hz. Excluding electrode no. 3V, this range is only ~2 to ~5 MΩ.

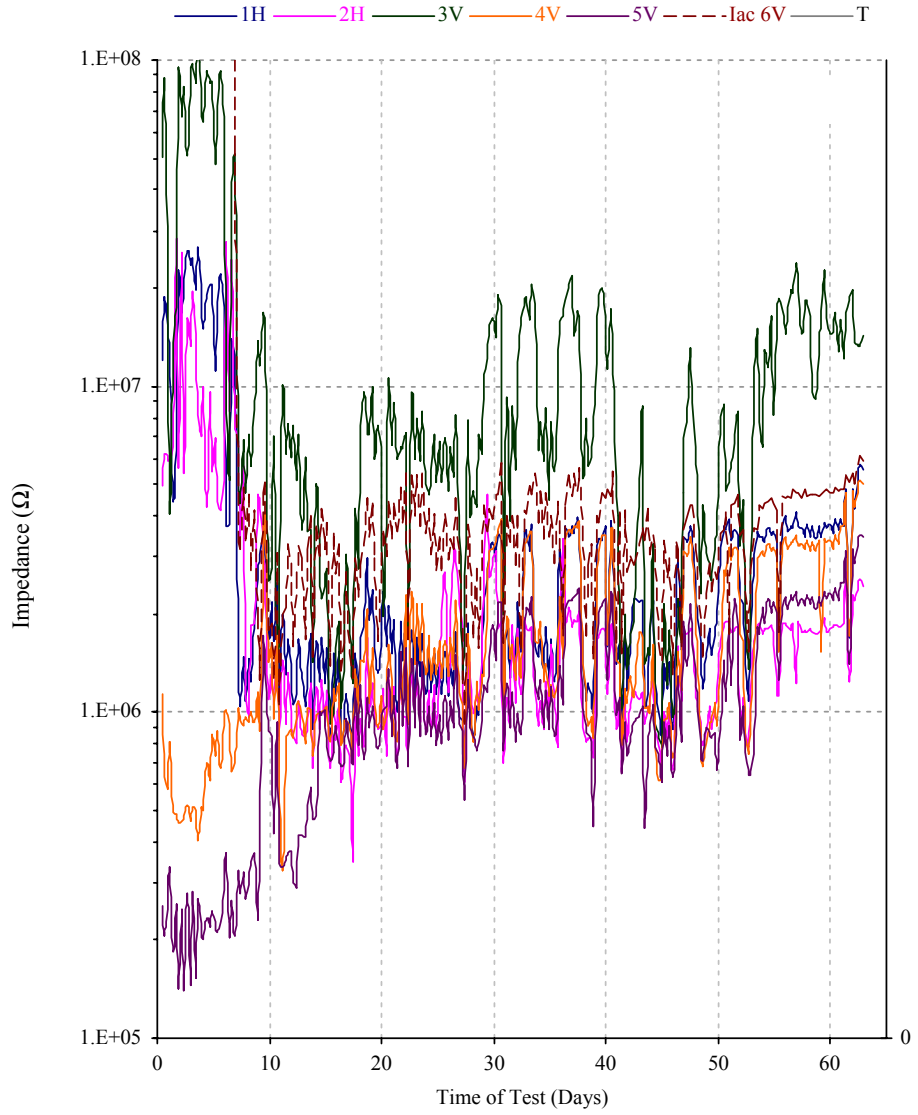


FIGURE D-15. PLOT OF THE MEASURED IMPEDANCE ($|Z| = |V_{ac}|/i_{ac}|$) FOR THE SIX ELECTRODE PAIRS

Some further information can be obtained from the integrated current. Figure D-16 plots the total charge ($\int i_{ac}\,\partial t$) passed during the test. The electrode pairs clearly separate into 3 groups: low conductive (nos. 3V and 6V), intermediate (nos. 1H and 2H), and conductive (nos. 4V and 5V). This last group, alone, underwent much more dramatic change with 28-V 400-Hz input during the first 7 days of testing.

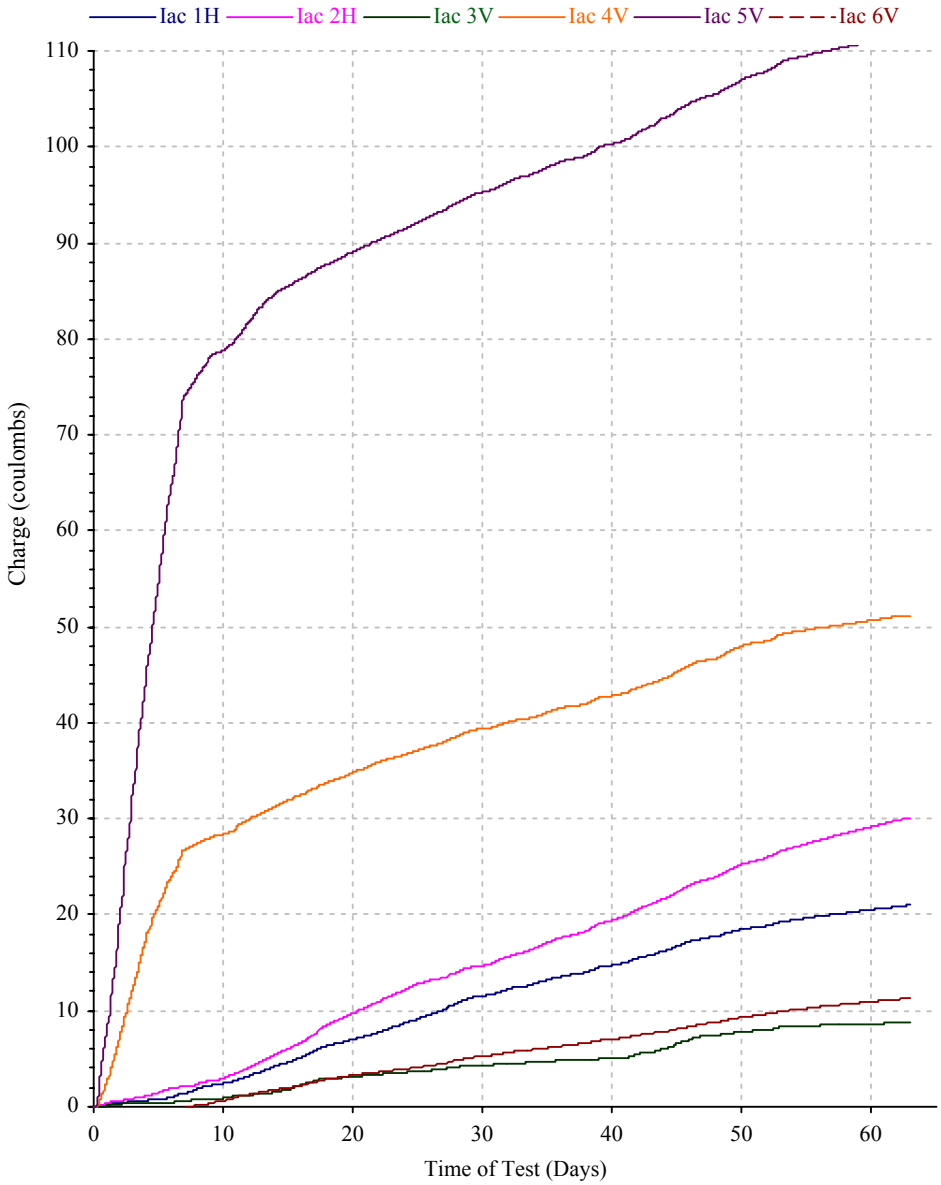


FIGURE D-16. PLOT OF THE TOTAL CHARGE ($\int i_{ac}\,\partial t$) PASSED

Figure D-17 plots the net charge (($\int i_{dc}\,\partial t$) accumulated during the test. Here the data separate very precisely into two groups with electrode pair nos. 4V and 5V accumulating on average 5.35 ±0.07 mC/day, and the other four electrodes averaging 3.94 ±0.16 mC/day. Even this smaller number is sufficient to accumulate a large (relative to the available surface) amount of

electrochemical product (1 mC = 1 g of Ag_2O). It is clear from figure D-15 and posttest examination that this did not occur.

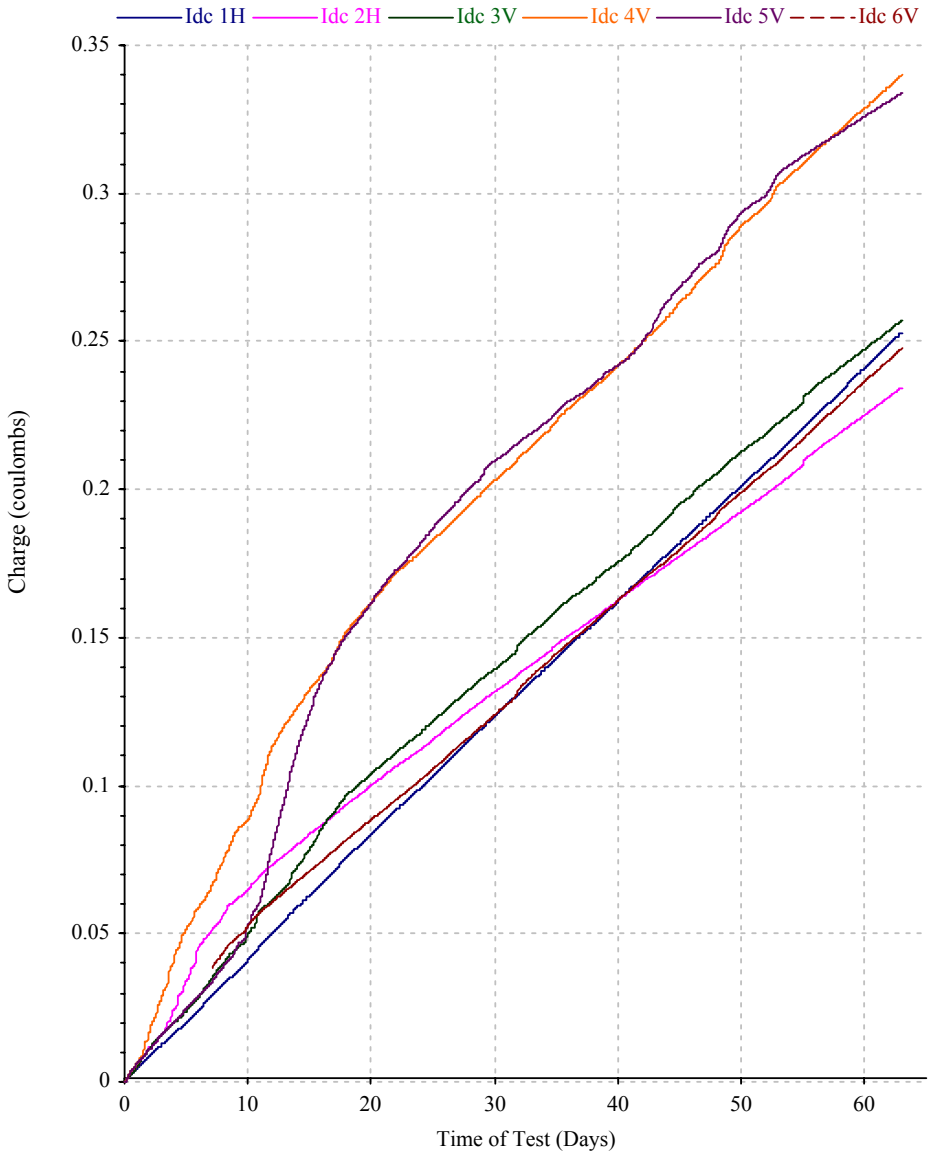


FIGURE D-17. PLOT OF THE TOTAL CHARGE ($\int i_{ac}\,\partial t$) PASSED

D.9 REFERENCES.

D-1. Slenski G., "Surface Analysis of 747 Aircraft Fuel Probe and Wiring (Materials Analysis)," report no. AFRL/MLSA 99-2, 26 January 1999.

D-2. R.E. Kauffman, "Final Technical Report, September 1999-October 2001," SRI P10950-3, November 2001.

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D-4. M.C.H. McKubre, “Copper-Sulfur Deposits on Fuel Quantity Indication System and Attendant Wiring,” SRI P10950-2, May 2000.

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APPENDIX E—THERMODYNAMICS OF FUEL OXIDATION

E.1 INTRODUCTION.

Chemical reactions occur spontaneously if the overall change in Gibbs free energy (ΔG) is negative. In most reactions this energy appears primarily in the form of heat (enthalpy, ΔH) that also is negative. These two thermodynamic properties are related by the temperature of the reaction, T, and the change of overall system entropy, ΔS,

$$\Delta G = \Delta H - T\Delta S \tag{E-1}$$

Hydrocarbons are used as fuels because their reactions with oxygen are spontaneous (ΔG negative) and highly exothermic (ΔH strongly negative). A generic reaction of hydrocarbons with oxygen can be written as

$$(x + y/4)\ O_2 + C_xH_y \rightarrow x\ CO_2 + y/2\ H_2O \tag{E-2}$$

This reaction yields energy because the net energy of the bonds C-O and O-H is greater than C-H and O-O. Reaction E-2 can proceed with any oxidant so long as this condition holds. Thus

$$n\ Ag_2O + C_xH_y \rightarrow 2n\ Ag + x\ CO_2 + y/2\ H_2O \tag{E-3}$$

proceeds spontaneously and exothermically (with $n = 2x + y/2$). This reaction is unusually exothermic because Ag_2O (and even more AgO) is relatively unstable.

Jet A is a multicomponent fuel with a wide range of compositions and possible components, not all of which are straight chain alkanes. Nevertheless, with little loss of generality one can represent Jet A in the following exercise by one compound, Undecane, with chemical formula $C_{11}H_{24}$. Presented here is an analysis of the results of reaction of this and similar compounds with Ag_2O, AgO, and O_2 in the range of reaction temperatures 100°-200°C (212°-392°F). Also included in this analysis are the reactions of ethylene glycol with Ag_2O and O_2.

E.2 REACTIONS AND THERMODYNAMIC RESULTS.

The following reactions were evaluated in the temperature interval 100°-200°C.

A. $$C_{11}H_{24} + 34Ag_2O \rightarrow 68Ag + 11CO_2 + 12H_2O \tag{E-4}$$

B. $$C_{11}H_{24} + 34AgO \rightarrow 34Ag + 11CO_2 + 12H_2O \tag{E-5}$$

C. $$C_{11}H_{24} + 17O_2 \rightarrow 11CO_2 + 12H_2O \tag{E-6}$$

D. $$C_{11}H_{24} + 23AgO \rightarrow 23Ag + 11CO + 12H_2O \tag{E-7}$$

D'. $$C_{11}H_{24} + 23Ag_2O \rightarrow 46Ag + 11CO + 12H_2O \tag{E-8}$$

E. $$C_{11}H_{24} + 12Ag_2O \rightarrow 24Ag + 11C + 12H_2O \quad \text{(E-9)}$$

F. $$C_{12}H_{26} + 37Ag_2O \rightarrow 74Ag + 12CO_2 + 13H_2O \quad \text{(E-10)}$$

G. $$C_{13}H_{28} + 40Ag_2O \rightarrow 80Ag + 13CO_2 + 14H_2O \quad \text{(E-11)}$$

H. $$C_2H_6O_2 + 5Ag_2O \rightarrow 10Ag + 2CO_2 + 3H_2O \quad \text{(E-12)}$$

I. $$C_2H_6O_2 + 2.5O_2 \rightarrow 2CO_2 + 3H_2O \quad \text{(E-13)}$$

Table E-1 presents the results of thermodynamic calculations for this set of reactions using a reaction data base and software developed for this purpose by Outokumpu Research [E-1].

The first thing to note in table E-1 is that large negative values are calculated for ΔG for all reactions considered. That is, all reactions will proceed spontaneously, given either a suitable catalyst to reduce the activation energy barrier or added energy to surmount it. Once initiated, these reactions also all release very significant amounts of heat energy so that once started, it is likely that these reactions will proceed at increasing rate until limited by the availability of either fuel (hydrocarbon) or oxidant (oxygen or silver oxide).

E.3 EFFECT OF TEMPERATURE.

The temperature interval selected was chosen to reflect the lowest range accessible in fuel tanks where reaction initiation might plausibly occur. The formation of silver oxides and silver metal that facilitate the establishment of conditions favorable to ignition, result from electrolysis of liquid water. The minimum temperature in the calculations was set to 100°C with the idea that liquid water would need to evaporate from the ignition site before ignition could occur. A temperature interval of 100°C was selected to provide a convenient base for extrapolating predictions to higher (or lower) temperatures.

Figure E-1 plots the calculated reaction enthalpy (ΔH) versus temperature for all nine reactions considered. The slopes of these lines are all negative (increasingly exothermic with increasing temperature), but on the scale presented, only slightly so. This scale is slightly deceptive as it is normalized by the number of moles of fuel. The reactions with least energy release are H and I which consume ethylene glycol (2 C atoms) as fuel. The next most exothermic are those with incomplete combustion to form carbon (E) and carbon monoxide (D).

The slopes of the free energy changes (ΔG) plotted in figure E-2 are slightly more negative because of the increasing effect of $T\Delta S$. To first order, however, all reactions studied are insensitive to temperature in the range studied.

TABLE E-1. CALCULATED VALUES OF ΔH AND ΔG FOR REACTIONS A-I
REACTION ENTHALPY (ΔH) AND ENERGY (ΔG) PER MOLE OF C_xH_y REACTED

Reaction	A	A	B	B	C	C	
T (°C)	ΔH (kJ)	ΔG (kJ)	ΔH (kJ)	ΔG (kJ)	ΔH (kJ)	ΔG (kJ)	T (°F)
100	-5855	-6943	-6523	-7869	-6905	-7154	212
110	-5857	-6972	-6524	-7905	-6905	-7161	230
120	-5858	-7002	-6525	-7941	-6905	-7168	248
130	-5860	-7031	-6527	-7977	-6905	-7174	266
140	-5862	-7060	-6528	-8013	-6905	-7181	284
150	-5863	-7089	-6529	-8049	-6905	-7188	302
160	-5865	-7118	-6530	-8084	-6905	-7194	320
170	-5867	-7146	-6531	-8120	-6904	-7201	338
180	-5869	-7175	-6532	-8156	-6904	-7208	356
190	-5871	-7204	-6533	-8192	-6904	-7214	374
200	-5874	-7233	-6533	-8228	-6904	-7221	392

Reaction	D	D	E	E	F	F	
T (°C)	ΔH (kJ)	ΔG (kJ)	ΔH (kJ)	ΔG (kJ)	ΔH (kJ)	ΔG (kJ)	
100	-3078	-4254	-2205	-2739	-6372	-7558	212
110	-3079	-4286	-2206	-2754	-6374	-7589	230
120	-3079	-4317	-2206	-2768	-6376	-7621	248
130	-3080	-4349	-2207	-2782	-6377	-7653	266
140	-3081	-4380	-2207	-2797	-6379	-7684	284
150	-3082	-4412	-2208	-2811	-6381	-7716	302
160	-3083	-4443	-2208	-2825	-6383	-7747	320
170	-3084	-4475	-2209	-2839	-6385	-7779	338
180	-3085	-4506	-2209	-2854	-6388	-7810	356
190	-3087	-4537	-2210	-2868	-6390	-7842	374
200	-3088	-4569	-2211	-2882	-6393	-7873	392

Reaction	G	G	H	H	I	I	
T (°C)	ΔH (kJ)	ΔG (kJ)	ΔH (kJ)	ΔG (kJ)	ΔH (kJ)	ΔG (kJ)	
100	-6890	-8172	-907	-1149	-1062	-1180	212
110	-6891	-8206	-908	-1155	-1062	-1183	230
120	-6893	-8241	-909	-1162	-1063	-1186	248
130	-6895	-8275	-909	-1168	-1063	-1189	266
140	-6897	-8309	-910	-1175	-1064	-1192	284
150	-6899	-8343	-911	-1181	-1064	-1196	302
160	-6901	-8377	-912	-1187	-1065	-1199	320
170	-6904	-8411	-912	-1194	-1065	-1202	338
180	-6906	-8445	-913	-1200	-1065	-1205	356
190	-6909	-8479	-914	-1206	-1066	-1208	374
200	-6911	-8513	-915	-1213	-1066	-1211	392

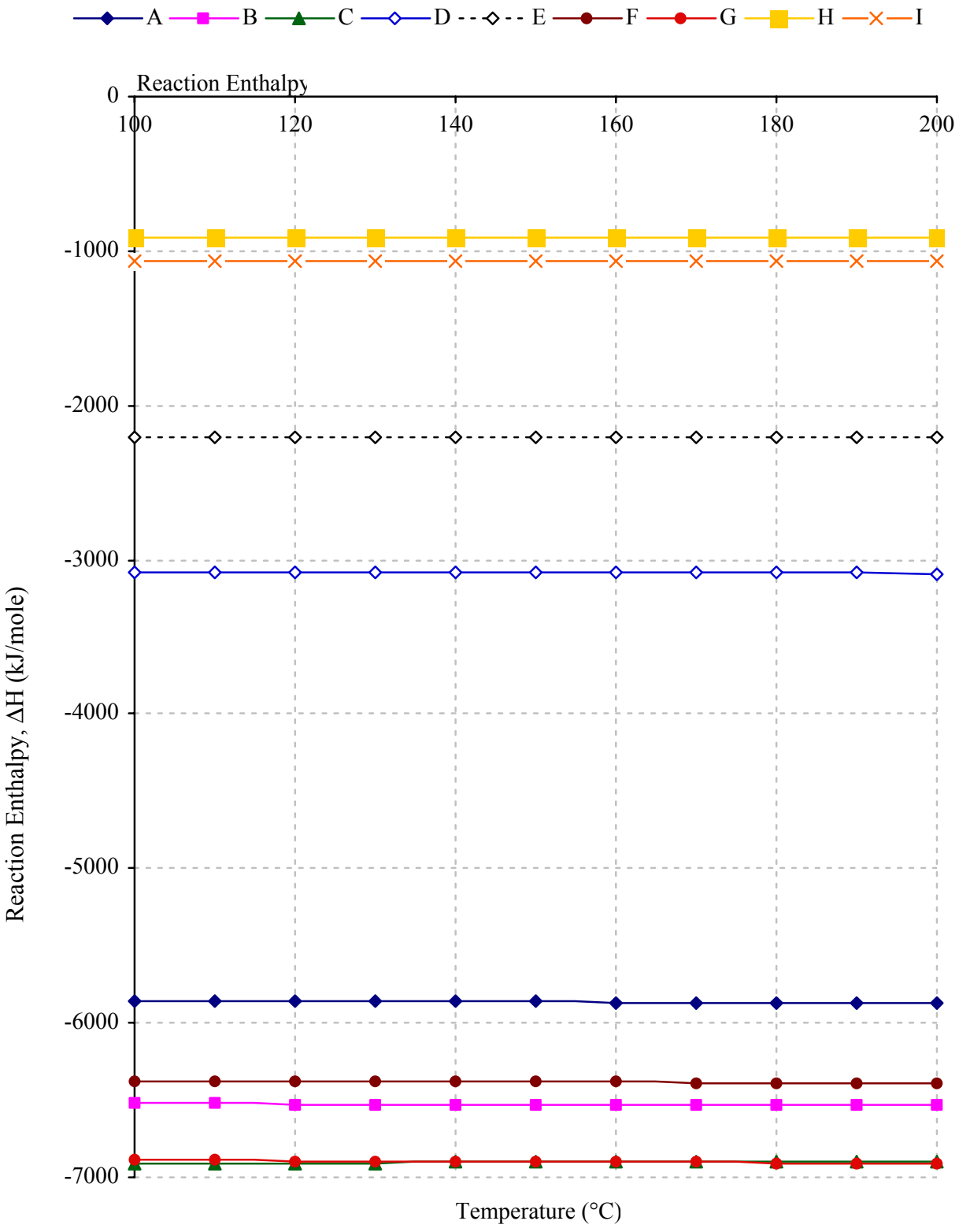


FIGURE E-1. REACTION ENTHALPY VS TEMPERATURE

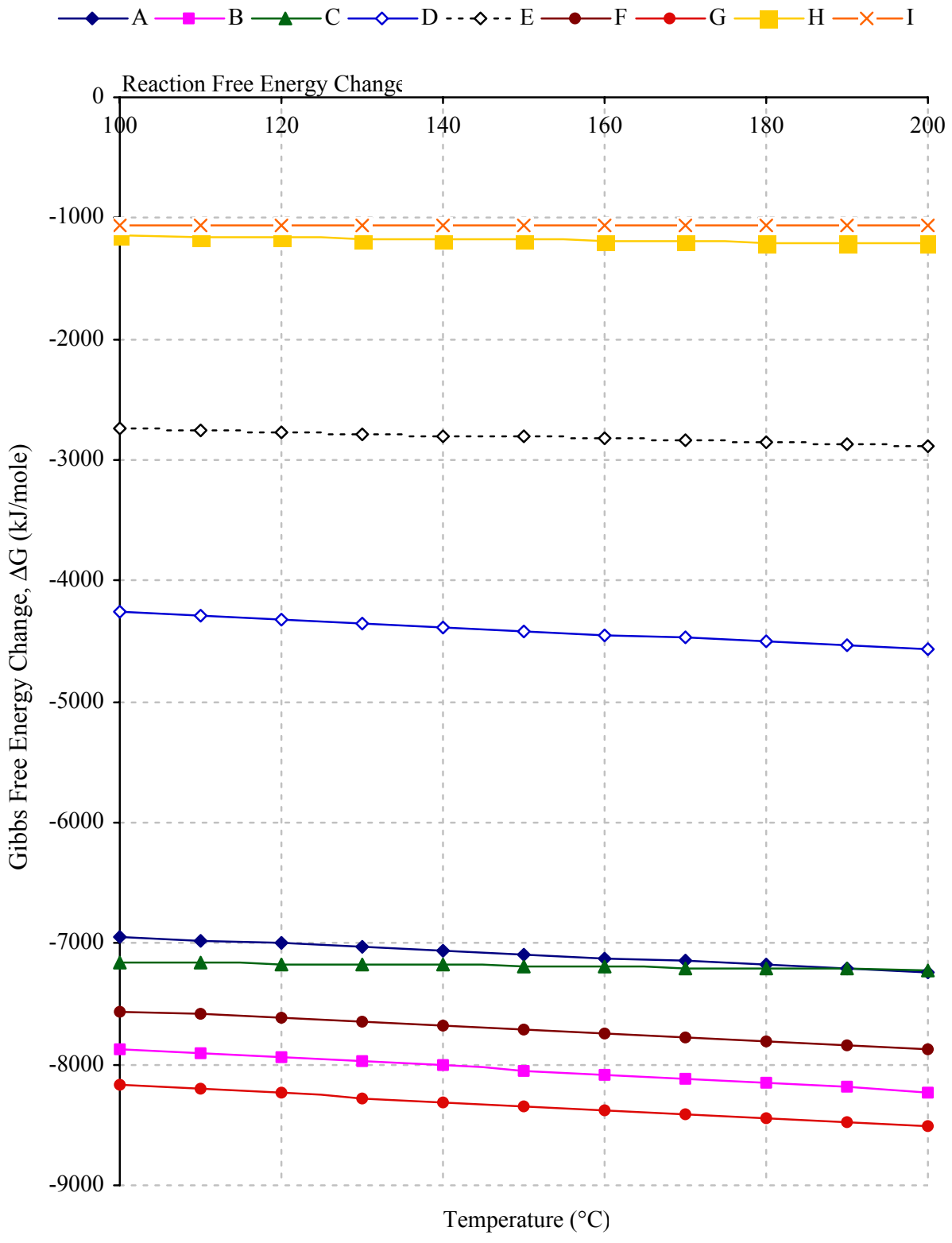


FIGURE E-2. GIBBS FREE ENERGY VS TEMPERATURE

E.4 THE EFFECT OF CARBON CHAIN LENGTH.

We are primarily concerned with the reaction of Jet A with Ag_2O. Undecane (C_{11}) was selected as most representative, but additional calculations were made for C_{12} and C_{13}. Figure E-3 plots ΔH and ΔG per mole of Ag reacted. This normalization in terms of the oxidant shows that, thermodynamically, the carbon chain length of the fuel is of little energetic importance. For the purposes of this discussion, Jet A can be conveniently represented by Undecane with a reaction enthalpy of ~86 kJ per mole of Ag(I) (i.e., in oxidation state 1) reacted.

E.5 THE EFFECT OF OXIDANT.

If the oxidant is not Ag(I), then the thermodynamics change a little. Figure E-4 plots the reaction enthalpy and free energy for the combustion of Undecane per mole of O reacted, with the source of O being Ag_2O (reaction A), AgO (reaction B), and O_2 (reaction C). The greater the oxidation state of the oxygen reacted (O_2 > AgO > Ag_2O), the greater the heat and energy released by combustion. This effect, however, only results in a ~18% difference between O_2 and Ag_2O, and an ~11% difference between A_2O and Ag_2O.

E.6 THE EFFECT OF EXTENT OF REACTION.

The complete reaction of hydrocarbons to H_2O and CO_2 occurs only under favorable conditions and with excess of oxidant. For surface reactions of fuel with solid oxide deposits, neither condition may hold, resulting in an incomplete burn to form CO as gaseous product or C as a solid coke. Evidence that this latter reaction does in fact occur can be found in the analyses performed by ASU after repetitive unsuccessful and successful attempt to ignite Jet A at silver electrodes bridged by electrolysis products [E-2]. EDX, Raman, and FTIR analyses of postignition deposits revealed the presence of C and Ag, presumably formed from the partial ignition of hydrocarbons by reaction with Ag_2O (or AgO). Incomplete reaction results from a stoichiometric excess of fuel (i.e., the reaction was starved of silver oxide).

Figure E-5 plots the results of reacting Undecane with Ag_2O to produce CO_2 (reaction A), CO (reaction D'), and C (reaction E) as products together with Ag and H_2O. The reaction free energies do not differ significantly for the production of carbon in three different oxidation states. Of significance, however, is that the line for the formation of C is the most negative in the temperature range plotted. This means that under conditions where insufficient oxidant (oxygen, AgO or Ag_2O) is available for complete oxidation, the reaction of Undecane (or any similar hydrocarbon) proceeds to form water vapor and carbon. Water forms as the first product of reaction, and then CO_2 forms with any further available oxygen source. From the thermodynamics of figure E-5, formation of CO is not energetically favored. If Ag_2O is present in molar concentrations greater than needed to react with the surface available fuel, then the reaction products are Ag metal and H_2O and CO_2 gases, with enthalpy release 86 kJ/mole of Ag produced. If Ag_2O is present in lesser molar concentration than the available surface adsorbed fuel, the reaction products are Ag metal, H_2O gas, and carbon solid, with enthalpy release 48 kJ/mole of Ag produced.

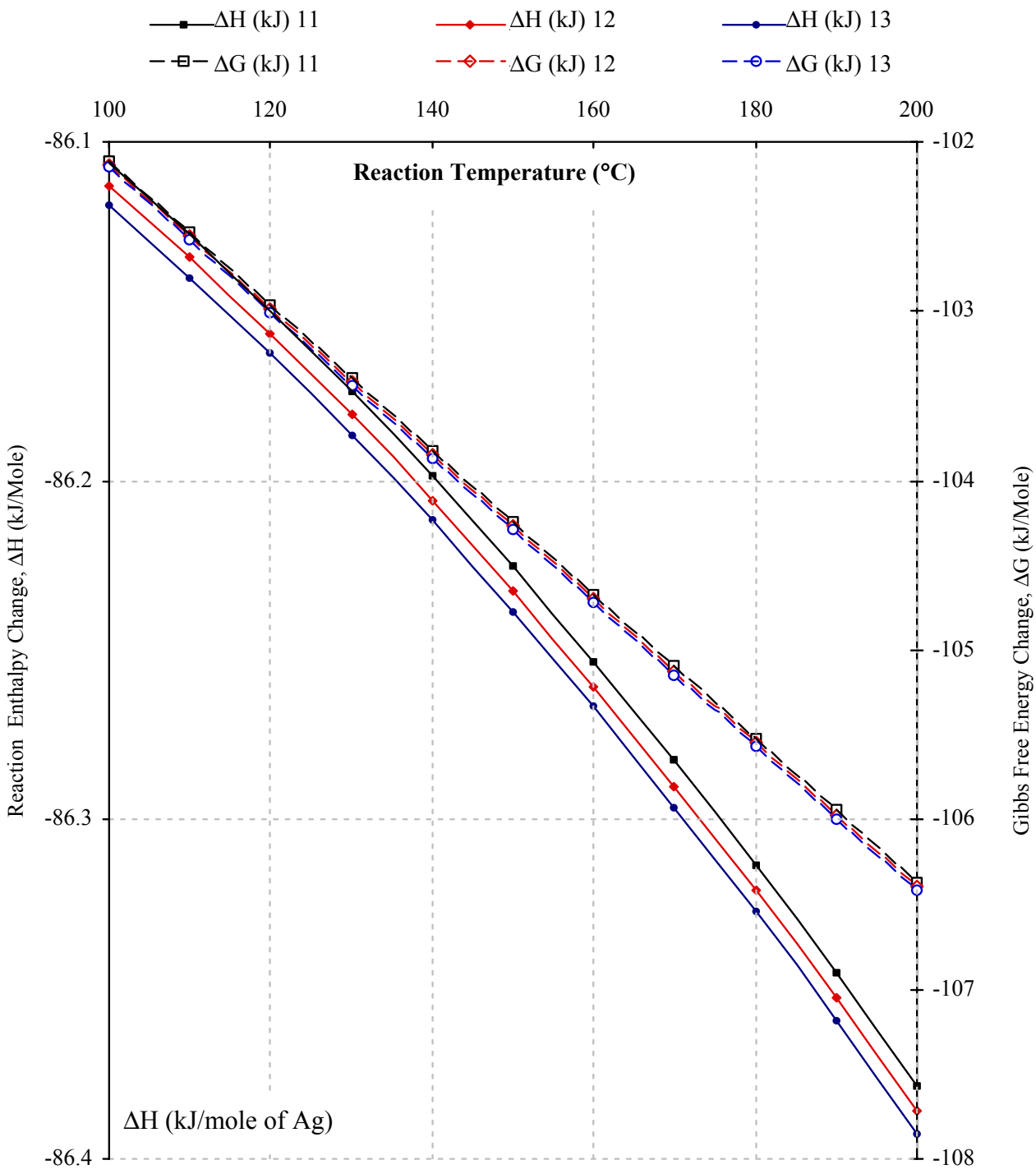


FIGURE E-3. ΔH AND ΔG PER MOLE OF Ag REACTED

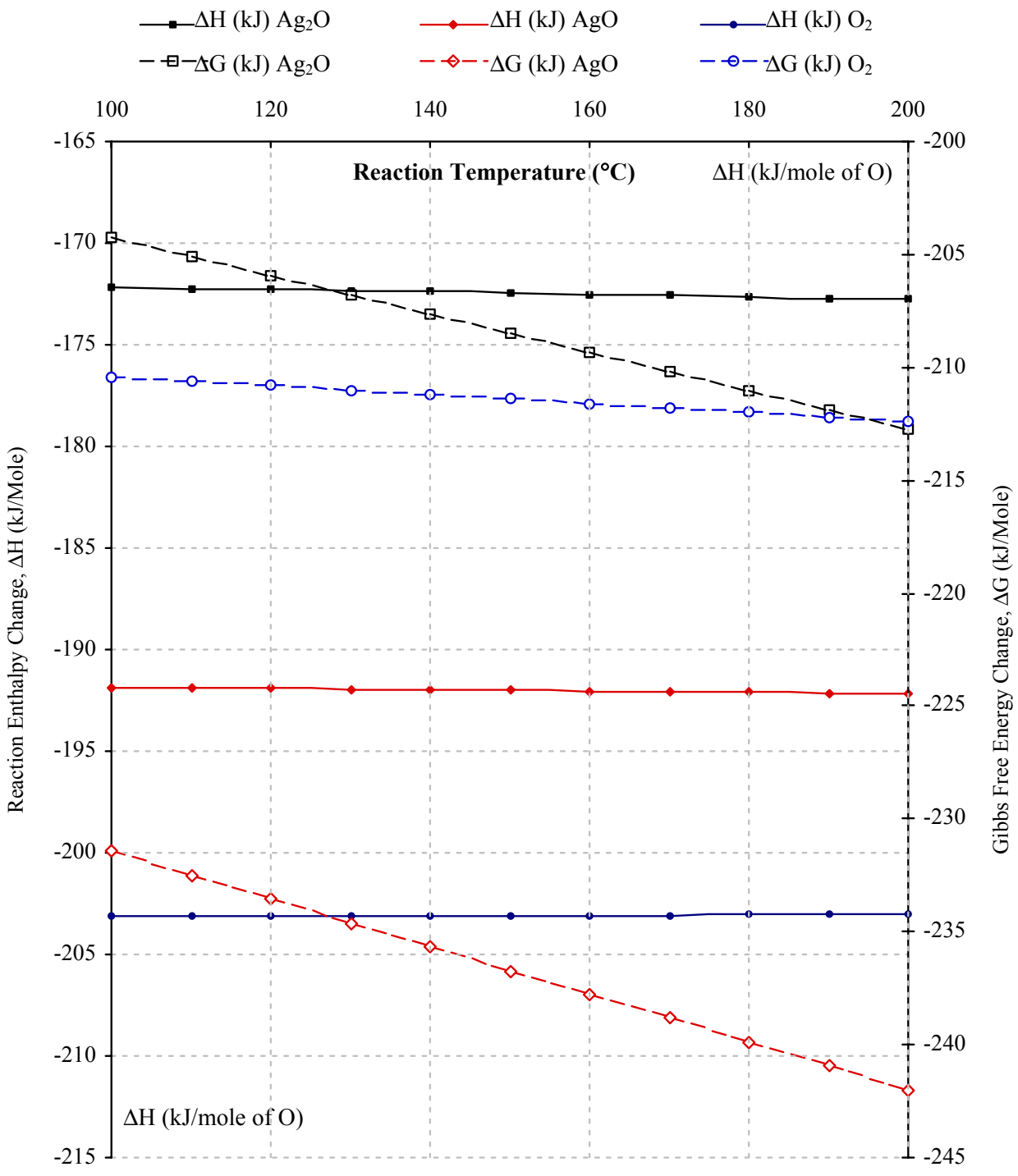


FIGURE E-4. REACTION ENTHALPY AND FREE ENERGY FOR UNDECANE COMBUSTION PER MOLE OF O_2 REACTED

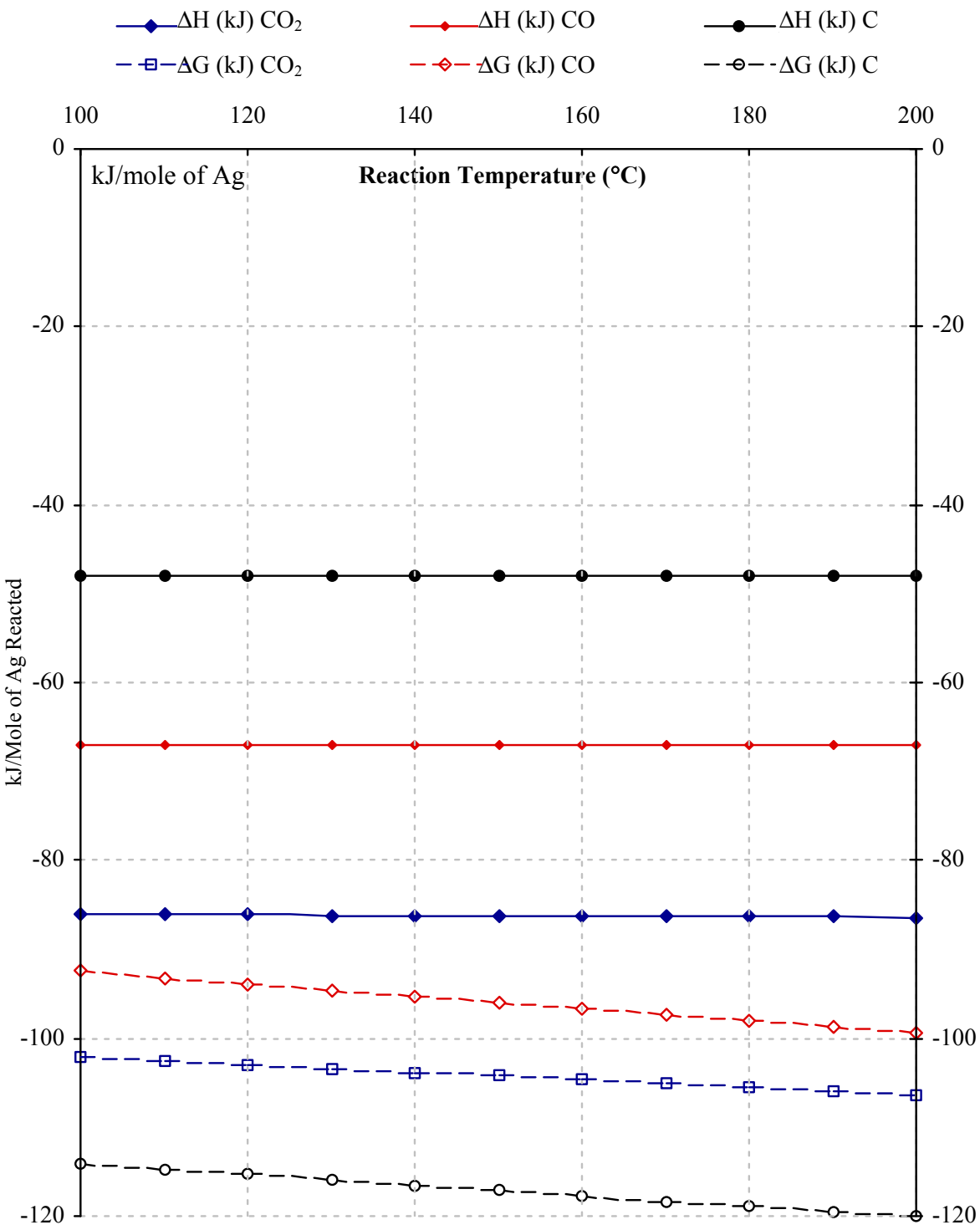


FIGURE E-5. RESULTS OF REACTING UNDECANE WITH AgO_2 TO PRODUCE CO_2, CO, AND AS PRODUCTS WITH Ag AND H_2O

E.7 ADIABATIC TEMPERATURE.

From the reaction energetics listed in table E-1, and knowledge of the heat capacities and thermodynamic properties of the compounds and phases of reactants and products, one can estimate the final product temperatures. The adiabatic temperature is the temperature achieved if a reaction occurs without loss of heat (i.e., adiabatically) to its surroundings. This is a hypothetical value because conductive, convective, and radiative heat loss will occur when the product temperature is elevated above ambient. The adiabatic temperature, therefore, is the limit at short time. It is useful to determine what phases products form in.

With reactants at 150°C (~300°F) the adiabatic temperature of reaction of Undecane and Ag_2O to produce CO_2, H_2O and Ag (reaction A) is 1728°C (~3140°F). The melting point of Ag is 962°C (1763°F) and its boiling point 2212°C (~4014°F). Thus, silver is produced by reaction A as a liquid, which exists, albeit momentarily, at nearly 1000°C above its melt temperature.

E.8 REFERENCES.

E-1. Outokumpu, "Chemical Reaction and Equilibrium Software With Extensive Thermochemical Database," Outokumpu Research Oy, 1997.

E-2. T. M. Korb, J. D. Colwell, and R. E. Peck, "Conductive Coating Assisted Ignition of Jet Fuel," ASU Combustion Laboratory Report ASU-CL-01-04, January 2002.