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U.S. Navy Halon 1211 Replacement Program: Assessment of Aircraft Collateral Damage From Dry Chemical Fire Extinguishing Agents

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A literature survey and analysis (qualitative analysis) was performed of the potential collateral damage of typical aircraft materials caused by bicarbonate-based fire extinguishing agents. Very little data were found in the open literature assessing the corrosion, materials compatibility or other potential collateral damage effects caused by these agents. These data mainly address the typical storage and distribution system materials and do not address the necessary range of issues required to assess all potential aircraft exposures. In order to project the potential collateral damage, the general corrosion behavior and data for typical aviation alloys were used to supplement the limited specific data available. The general analysis indicated that significant collateral damage potential exists for airframes, structures and engines. While it is more likely that significant damage would result from a long-term exposure, potentially catastrophic short-term corrosion issues are also indicated. Increased corrosion rates are indicated for aluminum and magnesium based on the pH of bicarbonate agents and their breakdown products. The potential for turbine component damage is indicated from high temperature corrosion and through overheating caused by physical clogging of cooling holes.

14. SUBJECT TERMS

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PKP	Sodium bicarbonate	Extinguishing agent
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U.S. NAVY HALON 1211 REPLACEMENT PROGRAM: ASSESSMENT OF AIRCRAFT COLLATERAL DAMAGE FROM DRY CHEMICAL FIRE EXTINGUISHING AGENTS

1.0 INTRODUCTION

Previous efforts under the U.S. Navy Halon 1211 (CF_2Br) Replacement Program developed operational requirements for flight deck and hangar deck (and flight line) fire fighting systems [1]. The operational requirements for fire extinguishing systems on the flight deck and hangar deck may be defined into two main cases. The first case is for engine and electrical fires where the need to minimize collateral damage caused by the firefighting agent is high. These fires are termed small fires and are defined by the collateral damage requirements. The second case is for engine, electrical and catastrophic event (i.e., crash) fires where the need to extinguish the fire quickly outweighs any concerns of collateral damage caused by the agent. These fires are termed large fires and are defined by the lack of collateral damage concerns. For general aviation firefighting needs, the requirements may be summarized as follows.

- Small Class A fires
- Small Class B 2-dimensional, 3-dimensional and hidden, deep-seated fires
- Small Class C fires with Class A and/or Class B fuels.
- Large Class B 2-dimensional, 3-dimensional and hidden, deep-seated fires.

The two main firefighting requirements that need to be assessed for potential Halon 1211 replacements are fire extinguishing effectiveness and collateral damage. It is expected that the currently fielded systems utilizing the primary agents Aqueous Film Forming Foam (AFFF) and water meet the requirements for large 2-dimensional Class B fires from both a fire extinguishment and collateral damage stand-point (i.e., lack of collateral damage requirements). Currently, Halon 1211 is used to meet the remaining firefighting requirements. It is the small engine and electrical fires (including their attendant collateral damage requirements) and the 3-dimensional and hidden, deep-seated portions of the large fires that require Halon 1211 replacement systems.

The optimum solution to the replacement of Halon 1211 systems is to determine if currently fielded systems meet these requirements. Three different secondary agents are currently fielded in shipboard hand-held extinguishers. The Naval Air Training and Operating Procedures Standardization (NATOPS) Aircraft Firefighting and Rescue Manual allows for either (1) a 15-pound CO_2 (MIL-E-24269B) and a 18-pound potassium bicarbonate, PKP (MIL-E-24091C) hand-held extinguisher or (2) a single 20-pound Halon 1211 hand-held extinguisher (MIL-E-

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24715) to be located at the AFFF hose stations [2]. While the NATOPS manual provides for this option, it is much more likely for the CO_2/PKP option to be encountered [3]. These ships were commissioned with the CO_2 and PKP extinguishers. When the P-25 Mobile Firefighting Vehicle is fielded, three additional extinguishers will be provided on that vehicle. These extinguishers are currently planned to be the 20-pound Halon 1211 unit.

From a fire extinguishing point of view, existing systems using more traditional agents such as dry chemicals and carbon dioxide (CO_2) may meet these fire fighting requirements for small engine and electrical fires. The traditional agents/systems pre-date the use of Halon 1211 and their firefighting efficacy is well established. Systems exist with adequate UL ratings to meet the firefighting requirements in most commercial and residential applications where Halon 1211 had been used. In addition to the existing fielded systems, other commercially available systems are being evaluated to determine if they meet the flight deck firefighting requirements. The new so called "clean agents," e.g., C_3F_7H (HFC-227ea) and $C_3F_6H_2$ (HFC-236fa) do not perform as well as Halon 1211 based on the cup burner test, however it is possible that commercially available systems using these agents perform well enough to combat the small engine and electrical fires encountered on the flight deck (with potential application on the flight line as well). As is true for the traditional agents, systems using these agents are being commercialized in hand held extinguishers with adequate UL ratings to replace Halon 1211 extinguishers in most commercial and residential applications. It is recognized that there is no direct correlation between UL ratings and firefighting effectiveness on the flight deck (and flight line). It is necessary to test these systems against the specific, representative fire threats encountered on the flight deck. This work is currently being performed by the Naval Research Laboratory (NRL) and the Naval Aviation Warfare Center Aviation Division, China Lake and will be reported separately.

For collateral damage requirements, the "clean agents" HFC-227ea and HFC-236fa are expected to meet the requirements. For the UL rated BC dry chemical agent systems, i.e., sodium bicarbonate and potassium bicarbonate (PKP), the concern has been the collateral damage caused by the agent and not their ability to extinguish fires. These agents have historically been excluded from the list of potential agents considered to minimize collateral damage based on the perception that the use of these agents requires extensive clean up of the engine and airframe. With the high density of aircraft on the flight deck, the potential exists to expose adjacent uninvolved aircraft that may also require extensive clean up. While this appears to be the general consensus throughout the Navy and other services, no definitive information was found during the previous work to determine the rationale for this "conventional wisdom" [1,4].

2.0 OBJECTIVE

The objective of this work was to assess the potential collateral damage issues of using dry chemical agents for aviation firefighting from data in the available literature. In recognition of the potential use of bicarbonate agents to replace Halon 1211 in portable applications and Halon 1301

(CF_3Br) in fixed applications within aircraft, this work assessed the collateral damage concerns of sodium and potassium bicarbonate-based agents.

To the greatest extent possible this work sought to either corroborate or contest the conventional wisdom that bicarbonate-based agents require extensive clean up immediately after their use. It was not the intent to try to reclassify these agents as "clean agents" for all applications. Throughout the remainder of this report the term "clean agent" will be avoided in recognition of the historical view that these agents have been considered "dirty agents" in most applications. Instead, the intent was to assess whether or not bicarbonate-based agents may be successful in meeting the collateral damage requirements for the small fires defined within the U.S. Navy Halon 1211 Replacement Program [4]. In recognition of the potential use in small engine fires or in engine nacelle fixed systems, this work emphasized the materials in aircraft airframes and engines. Where possible, the potential effects on typical alloys used for electronics/avionics was also assessed.

3.0 APPROACH

It was originally anticipated that the pervasive view that bicarbonate-based agents cause significant collateral damage would be based on data available in the open literature. The initial approach was to perform a literature review to obtain any available data and assess the data to determine their potential suitability in meeting the collateral damage requirements of the small engine and electrical fires. The sources of the literature review were the National Institute of Standards and Technology (NIST) FIREDOC and the National Technical Information Service (NTIS).

While some limited information was found in these literature sources, no reports were identified that provided significant amounts of data or evidence of detailed testing. Due to the lack of data in the open literature, additional sources of information were sought. These sources included engine designers and manufacturers, manufacturers of dry chemical fire extinguishers and extinguishing systems and the Naval Air Systems Command (NAVAIR). As was true of the open literature review, no definitive open-literature reports were identified that provided data to corroborate or contradict the conventional wisdom on the corrosion and collateral damage caused by bicarbonate-based agents.

In order to provide an assessment of the potential suitability of bicarbonate-based agents the initial approach was modified. The limited specific data was supplemented with general corrosion data and principles for the classes of materials typically used in aviation applications, e.g., aluminum alloys, magnesium alloys, titanium alloys, high strength steel and nickel alloys. It is recognized that such an analysis cannot be definitive. The specific alloys in use may not exhibit the general behavior predicted by such an approach. None-the-less it will be useful as an indicator of the potential corrosion and other collateral damage issues that may or may not likely occur.

4.0 CORROSION PRINCIPLES

Corrosion can generally be defined as the destructive attack of materials by chemical or electrochemical reaction with its environment [5]. Some prefer to keep the definition restricted to metals while others prefer to keep the definition broad to include nonmetallic as well. For the purposes of this study the term corrosion will be reserved for metallic materials only and the term materials compatibility will include both the corrosion of metals and deterioration of nonmetallic. The three main fundamental regimes to consider for corrosion are aqueous solutions, gases and non-aqueous solutions [6]. These three corrosion regimes are described below.

4.1 Aqueous Corrosion

The corrosion that occurs in water or aqueous corrosion is the most commonly associated form of corrosion. Water from rain, manmade solutions or atmospheric humidity create the conditions necessary for this type of attack to occur. The process of aqueous corrosion is the same process that occurs in a battery. For a battery to function it requires four items: a material to be oxidized (at the anode), a material to be reduced (at the cathode), an electrolyte to carry ionic charge and electrical connection between the anode and cathode to carry electrical current. The thermodynamics determine which will be oxidized or reduced. In aqueous corrosion the material that is oxidized is the metal, forming positively charged ions and liberating electrons. Typical oxidation half cell reactions are shown below.

$$Fe \text{ ---> } Fe^{2+} + 2e$$
$$Al \text{ ---> } Al^{3+} + 3e$$
$$Cd \text{ ---> } Cd^{2+} + 2e$$

The material that is reduced and gathers the electrons is generally either O_2 gas or H^+ ions, depending upon the pH. In some cases other ions in the solution can be reduced. Typical reduction half cell reactions are provided below.

$$2H^+ + 2e \text{ ---> } H_2(g)$$
$$\tfrac{1}{2}\, 0_2(g) + 2\, e \text{ ---> } O^{2-}$$
$$Ni^{2+} + 2e \text{ ---> } Ni$$

When the two half cell reactions are combined, the result is the product of corrosion as shown below.

$$Fe + 2H^+ \text{ ---> } Fe^{2+} + H_2(g)$$

The iron metal reacts with the hydrogen ions in the solution to produce hydrogen gas and dissolved iron ions. This reaction is an example of acid cleaning where no visible corrosion products are left behind. For atmospheric corrosion, it is more typical that the pH is near neutral or higher where the predominant reduction is for O_2 and not H^+ from acids. Taking into consideration the charges of the species and the predominant reaction products, the two half cell

reactions can be combined to form solid products, the red rust typified in iron and steel corrosion or the white powder found on aluminum corrosion as shown below.

$$2Fe + 3/2O_2 \text{ ---> } Fe_2O_3 \text{ (ferric oxide or hematite)}$$

$$2Al + 3/2O_2 \text{ ---> } Al_2O_3 \text{ (aluminum oxide or alumina)}$$

The final example shown below is a case where metal ions in the water cause corrosion of a base metal. The Cd metal is oxidized to form Cd ions and the Ni ions are reduced to produce Ni metal. The actual composition of a nickel-cadmium (NiCad) battery is somewhat more complex but in the simplest terms this is how a NiCad battery functions. (To recharge the battery the reaction is driven in the opposite direction by use of an electrical charge.)

$$Cd + Ni^{2+} \text{ ---> } Ni + Cd^{2+}$$

It is not necessary to have separate pieces of metals acting as anode and cathode for corrosion to occur. When water is present on a single piece of metal, particularly on an alloy, the four requirements can still be obtained. The surface is not completely homogeneous. Impurities, alloying agents and surface morphologies allow one site on this single piece to serve as an anode and another site to serve as a cathode, allowing corrosion to proceed.

The corrosion products that initially form on the surface may inhibit further corrosion resulting in the protection of the majority of the underlying metal. Aluminum oxide, chromium oxide and nickel oxide are examples of corrosion products that form during aqueous corrosion that result in protecting the surface. Nickel and chromium are added to alloys to increase their corrosion resistance, e.g., stainless steels. While aluminum oxide is an excellent barrier against corrosion in neutral pH environments, it is not very protective in high or low pH environments nor in the presence of chlorides. This illustrates the importance of understanding the environment in which the metal or alloy will function.

4.2 High Temperature Corrosion - Oxidation and Mixed Gas Attack

Corrosion in gases is different than the other two types of corrosion in that the atmosphere is non-conductive. At ambient temperatures the reaction rates of gases of interest with metals are slow so that this type of corrosion only becomes a concern at elevated temperatures 500 - 600°C [7]. When the only oxidant present is oxygen gas, the process is referred to as oxidation or high temperature oxidation. When other species are involved, the process is referred to as mixed gas attack. High temperature oxidation results when O_2 present in air reacts quickly with a hot metal to form metal oxides. In some cases, the resulting metal oxide is uniform over the entire surface and adheres tightly to the surface, protecting the underlying metal from further oxidation. In this case, the rate of corrosion is initially high and is reduced with time. In other circumstances the metal oxide does not form uniformly or does not adhere well to the underlying metal. These oxides do not provide protection to the surface and the rate of oxidation remains relatively

constant with time. As was the case for aqueous corrosion, chromium oxide and aluminum oxide are very effective at protecting the underlying metal surface. Chromium and aluminum are specifically added to alloy compositions to increase the oxidation resistance of alloys.

When more than O_2 is present in the gas phase, the corrosion process gets more complex. In general, the same principles hold for mixed gas attack as for oxidation. The corrosion products, whether they are oxides or other species that form on the metal surface, need to protect the underlying metal to reduce the corrosion rate. Alloying elements are specifically added to increase protection from this form of high temperature corrosion. As was the case for aqueous corrosion, it is important to know the environment to which the alloy will be exposed. Significantly different corrosion resistance can be found in the same alloy with subtle changes in the corrosive environment.

4.3 High Temperature Corrosion - Hot Corrosion

Corrosion in non-aqueous solutions is a less prevalent form of corrosion but important in the evaluation of corrosion of turbine engines. The specific form of non-aqueous corrosion applicable to turbine engines is called sulphidation or hot corrosion. Corrosion can result from the presence of molten salts deposited on metallic parts that form at high temperatures as a result of combustion. Hot corrosion is a specialized case of high temperature corrosion. It occurs when both a gas phase, typically a mixed gas phase, and a liquid phase are present in the environment. In turbine engines, the alloy surfaces can become covered by deposits of molten salts such as sodium sulphate, vanadium oxide or sodium chloride. These species are formed during the combustion process from contaminants in the fuel or air. The presence of the molten salt interferes with the high temperature oxidation/mixed gas processes that form the needed protective oxides. In this instance, the molten salt can be seen as taking the place of the water as an electrolyte. The corrosion products can dissolve or react with the molten salt. Analogous to aqueous corrosion, the process is electrochemical in nature resulting in destructive attack of the metal.

Alloys that may form protective layers under conditions of oxidation, or mixed gas attacks that occur during combustion of jet fuels, may not form protective layers under the conditions of hot corrosion. The change in rate of corrosion versus oxidation or mixed gas attack can be small or quite large.

The alloys typically used in the hot end of turbine engines do not have a high enough natural resistance to hot corrosion. Specialty coatings have been developed to increase the hot corrosion resistance of these alloys. The most common are combinations of cobalt, chromium, aluminum and yttrium (CoCrAlY) and may also contain nickel (NiCoCrAlY). Such coatings are specifically designed to protect against the molten salt deposits and mixed gases expected to be encountered in normal turbine engine operation. Changes to the environment may affect the performance of these coating systems.

4.4 Categories of Corrosion Based in Appearance

Corrosion is generally classified into 8 specific categories based on the appearance of the attack. The eight categories are as follows: (1) General Corrosion or Uniform Attack; (2) Pitting; (3) Galvanic or Two-Metal Corrosion; (4) Crevice Corrosion; (5) Intergranular Corrosion; (6) Selective Leaching or Parting, (7) Erosion Corrosion and (8) Environmentally Induced Stress Corrosion [5, 8].

1. Uniform attack is the most common form of corrosion. It is typified by the characteristic red rust of steels, tarnishing of silver, the blue-green product on exposed copper and the high temperature oxidation of metals. It derives its name from the appearance of being uniform over the entire exposed surface.

2. Pitting corrosion is a localized phenomenon where the corrosion proceeds faster in some areas than in others, forming holes or pits in the metal. Pitting can be very detrimental in that a small amount of localized corrosion can cause a failure with little or no warning. Pitting is generally caused by the specific operating environment, particularly by the presence of chlorides. Examples include pin holes that form in copper pipes due to certain water qualities and cavities or holes that form in aluminum exposed to salt water. Certain metals and alloys are more susceptible than others.

Another corrosion process, fretting corrosion, can also lead to the formation of pits and can be considered a subset of pitting corrosion. Fretting corrosion results when two parts in contact with each other, one or both being metal, experience small movements against each other, as is typically caused by vibrations. Pitting of the metal surface usually results. For example, fretting corrosion has been evidenced at the fayed or overlapping surfaces of the aluminum sheet used for aircraft skin.

3. Galvanic, or two-metal corrosion, results when two different metals or alloys are in direct contact. Each metal or alloy has a different tendency or potential to corrode, based on electromotive series. When the two metals are in contact in an electrolyte, a potential difference (i.e., voltage) is created between the two metals where one will act as the cathode for reduction and the other will act as the anode for oxidation. The metal that will be the anode and corrode will be the less-noble (or more active) of the two materials as determined by the thermodynamics. The metal that serves as the cathode corrodes very little or not at all.

To determine which metal will be the anode and corrode and which will be the cathode under these conditions, the standard Electromotive Force (EMF) Series is used. Table 1 provides the EMF Series for typical metal-metal ion pairs based on oxidation reactions. For reduction reactions, the sign of the voltage changes. When metals are coupled together the metal that is lower in the list, when written as oxidation reactions, will generally be the cathode. The opposite is true when the reactions are written for reductions, the metals that are higher in the list will be the cathode. A few exceptions from this standard list exist for certain alloy pairs in particular environments. In general, the list is accurate for predicting results of galvanic corrosion.

The list is also useful to determine a relative rate of corrosion. Metal pairs that are farthest away from each other on the list will have the greatest potential difference (voltage) or driving force and can be expected to have a faster rate of corrosion that metal pairs closer together on the list with a smaller driving force. While many other factors will also affect rate such as pH and surface areas, this is a useful first-order estimate of the potential corrosion problem.

4. Crevice corrosion is a second form of localized corrosion. It is associated with crevices or other areas where the solution becomes stagnant Examples include areas under bolt and rivet heads, lap joints and as the result of surface deposits such as dirt or other particulate matter.

5. Intergranular corrosion is a third form of localized corrosion. It results when the areas at and near the grains boundaries are preferentially corroded. This type of attack is severe and can lead to catastrophic failure. Intergranular corrosion can result from impurities or excess alloying elements present in the grain boundaries.

6. Selective leaching, or parting, is a corrosion process that preferentially removes one or more of the elements in a solid alloy. It was first encountered with brass alloys where the zinc would be corroded leaving behind a porous copper and corrosion product residue. When this type of attack occurs with brass, it is called dezincification, indicating the origin of this type of corrosion. The selective leaching process may leave the alloy in its original shape with an undamaged appearance when inspected visually, yet the mechanical strength of the alloy has been greatly reduced. Selective leaching is the result of a more noble metal in the alloy, e.g., copper acting as the cathode and the less noble metal in the alloy, e.g., zinc, acting as the anode. This condition essentially provides a galvanic corrosion scenario within the same alloy.

7. Erosion corrosion results from the movement of a corrosive fluid in contact with a metal. The movement of the fluid may remove any protective oxide layer that has formed on the surface that would otherwise provide protection from subsequent corrosion. Most metals and alloys are susceptible to this form of attack. Many types of corrosive environments can cause erosion corrosion, i.e., gases, aqueous

Table 1. Electromotive Force Series [5]

Electrode Reaction	Standard Oxidation Potential, E° (V), 25°C*
$Li = Li^+ + e^-$	3.05
$K = K^+ + e^-$	2.93
$Ca = Ca^{++} + 2e^-$	2.87
$Na = Na^+ + e^-$	2.71
$Mg = Mg^{++} + 2e^-$	2.37
$Be = Be^{++} + 2e^-$	1.85
$U = U^{+3} + 3e^-$	1.80
$Hf = Hf^{+4} + 4e^-$	1.70
$Al = Al^{+3} + 3e^-$	1.66
$Ti = Ti^{++} + 2e^-$	1.63
$Zr = Zr^{+4} + 4e^-$	1.53
$Mn = Mn^{++} + 2e^-$	1.18
$Nb = Nb^{+3} + 3e^-$	ca. 1.1
$Zn = Zn^{++} + 2e^-$	0.763
$Cr = Cr^{+3} + 3e^-$	0.74
$Ga = Ga^{+3} + 3e^-$	0.53
$Fe = Fe^{++} + 2e^-$	0.440
$Cd = Cd^{++} + 2e^-$	0.403
$In = In^{+3} + 3e^-$	0.342
$Tl = Tl^+ + e^-$	0.336
$Co = Co^{++} + 2e^-$	0.277
$Ni = Ni^{++} + 2e^-$	0.250
$Mo = Mo^{+3} + 3e^-$	ca. 0.2
$Sn = Sn^{++} + 2e^-$	0.136
$Pb = Pb^{++} + 2e^-$	0.126
$H_2 = 2H^+ + 2e^-$	0.000
$Cu = Cu^{++} + 2e^-$	−0.337
$Cu = Cu^+ + e^-$	−0.521
$2Hg = Hg_2^{++} + 2e^-$	−0.789
$Ag = Ag^+ + e^-$	−0.800
$Pd = Pd^{++} + 2e^-$	−0.987
$Hg = Hg^{++} + 2e^-$	−0.854
$Pt = Pt^{++} + 2e^-$	ca. −1.2
$Au = Au^{+3} + 3e^-$	−1.50

Standard reduction potentials, ϕ°, have the opposite sign.

solutions and liquid metals. Solids in suspension with a liquid are often very destructive from the erosion corrosion process. An example of erosion corrosion is the accelerated damage and subsequent premature failure caused to pump impellers when this type of corrosion is not accounted for in material selection.

8. Environmentally induced stress cracking is the combination of mechanical stresses and reaction with the environment to cause cracking. When metal is subjected to repeated or alternating tensile stresses in an 'inert' environment, the metal will develop fatigue cracks. When the fatigue cracks develop earlier than would otherwise occur in an 'inert' environment, the phenomenon is known as corrosion fatigue. Examples of fatigue are aircraft structural components that crack or fail after a certain number of in-service hours due to the repeated cyclic tensile stresses induced during flight. The effect of corrosive environments such as salt laden air near marine environments may reduce the fatigue life of aircraft structural components due to corrosion fatigue.

A second form of environmentally induced cracking is Stress Corrosion Cracking (SCC) SCC is the combination of constant stress and exposure to a particular corrosive environment. The stress may be internally induced, such as a hoop stress, or applied externally. Most structural alloys are subject to SCC in some environments. The phenomenon was first encountered in brass parts that would only develop cracks during certain seasons of the year. These failures were eventually linked to the internal hoop stresses of the brass parts coupled with the corrosive environment produced when ammonia or amines were present.

5.0 LITERATURE REVIEW

5.1 Corrosion Control and Cleanup Requirements

In the discussions with Navy personnel and military contractors on the collateral damage issues for dry chemical agents, citation was often made to the NATOPS, Aircraft Weapon Systems Cleaning and Corrosion Control Technical Manual (NAVAIR 01-1A-509) and the Avionic Cleaning and Corrosion Prevention/Control Technical Manual (NAVAIR 16-1-54). The latter two manuals are generally referred to as the Tri-Service Corrosion Control Manuals. All three of these documents were cited as requiring clean up of the aircraft after exposure to dry chemical agents, and were used as justification for the current perception that dry chemical agents cause significant collateral damage. A review of the NATOPS and the Tri-service Corrosion Control Manuals follows.

5.1.1 NATOPS

In Chapter 3, Firefighting Agents and Equipment, a 'caution' is provided with the description of PKP that the maintenance officer must be notified if PKP is ingested into the engine

or accessory section [2]. It states "PKP injected into a jet engine cannot be completely removed without disassembly of the engine to remove deposits that penalize engine performance and restrict cooling air passages."

5.1.2 Aircraft Weapon Systems Cleaning and Corrosion Control Manual (NAVAIR 01-1A-509)

The exposure of aircraft to dry chemical agents is covered in Chapter 9 entitled "Emergency Procedures"[9]. The purpose of Chapter 9 is to provide "the emergency procedures to be followed after aircraft incidents or accidents involving exposure to gross amounts of salt water or fire extinguishing agents. The procedures described are normally used only to prevent further damage and will usually require further treatment at a higher level of maintenance." A 'caution' is provided that "exposure to salt water, purple K powder (potassium bicarbonate or PKP) and protein foam require immediate action to prevent serious corrosion damage." A review of the separate cleaning procedures is provided below for Purple K, AFFF, CO_2 and Halon, protein foam and salt water.

5.1.2.1 Purple K

The procedure for Purple K or other dry chemical agents calls for vacuuming up the excess powder and brushing clean any that may still be present on surfaces. The entire surface is then rinsed with fresh water, dried and covered with a water displacing corrosion preventative compound (CPC). All areas exposed to the dry chemical agent are placed into the corrosion prone areas of the aircraft log book

5.1.2.2 AFFF

The procedures for AFFF depend upon whether the AFFF solution is made from fresh water or salt water. For AFFF from salt water, the procedures call for rinsing the effected areas with fresh water, followed by cleaning using an AFFF solution made from fresh water. The surfaces are then cleaned with aircraft cleaning solution, rinsed, dried and covered with water displacing CPC. The effected areas are entered into the appropriate section of the aircraft logbook. A note is provided that AFFF made from fresh water is not expected to be corrosive. Exposure to fresh water AFFF only needs to be cleaned with aircraft cleaning solution, scrubbed, rinsed, dried and covered with water displacing CPC. It does also require entry into the appropriate section of the aircraft logbook.

5.1.2.3 CO_2 and Halon 1211

The procedures for exposure to CO_2 and Halon 1211 only require clean up in the presence of moisture or high temperature. Under one or both of these conditions, the areas should be purged by use of compressed air, cleaned with aircraft cleaning solution, scrubbed, rinsed, dried and covered with water displacing CPC. The effected areas are entered into the appropriate section of the aircraft logbook.

5.1.2.4 Protein Foam

The procedures for protein foam and soda acid note that the residues from these materials can be very corrosive to aircraft structure and components. The effected area is rinsed with fresh water, cleaned with aircraft cleaning solution, scrubbed, rinsed, dried and covered with water displacing CPC. The effected areas are entered into the appropriate section of the aircraft logbook

5.1.2.5 Saltwater

Contamination by saltwater is essentially treated the same as for the firefighting agents, except for AFFF from fresh water. The effected areas are rinsed with fresh water and drained or dried. The area is cleaned with aircraft cleaning solution, scrubbed, rinsed, dried and covered with water displacing CPC. Two alternate methods are provided for cleaning saltwater contamination when fresh water is not available. While these secondary procedures are only listed for saltwater, it is presumed they also apply to cleanup of firefighting agents when fresh water is not available. The first option is to apply water displacing CPC over the effected surface. It is likely meant to be a stopgap measure until proper cleaning can be achieved. The second method is to directly clean the surface with aircraft cleaning solution to mix the contaminants into the cleaning solution as best as possible. The mixture is wiped off and the effected area coated with water displacing CPC.

5.1.2.6 General Analysis

The initial impression from the title of the chapter and the 'caution' is that most fire extinguishing agents are considered as corrosive as saltwater. The exception is fresh water AFFF. The Technical Manual (TM) states that fresh water AFFF is not expected to be corrosive. While the TM provides the specific cleanup requirements and procedures when an aircraft is exposed to saltwater and firefighting agents, it does not provide or reference any technical data supporting the cleanup requirements. With the exception of AFFF from fresh water, the specific differences in cleaning procedures for the firefighting agents and salt water appear to be based more on the state of the contamination, e.g., solid powder versus a liquid, than on potential differences in their corrosive effects. The procedures are designed to remove or dilute the contaminants as best as possible and treat the surfaces to reduce the potential for future corrosion. For fresh water AFFF, the procedures do not require diluting or removing the AFFF but do require treating the areas to reduce the potential for future corrosion.

The removal of liquids that can act as electrolytes and any solid residues that can trap moisture (i.e., crevice corrosion) are prudent acts to reduce corrosion potential. In both cases the intent is to eliminate one of the four requirements needed for aqueous corrosion to occur, i.e., the electrolyte. The recommended use of a water displacing CPC is just as likely the result of using water to clean up the exposure as it is to combat any potential corrosion that may be caused by these materials. The use of a water-displacing CPC to reduce corrosion is generally prescribed

after any water washing procedure. The implication from these procedures is that all firefighting agents, even protein foam and soda acid that are noted as corrosive to aircraft materials, are not expected to cause an immediate corrosion problem to the airframe. Exposure to these firefighting agents may increase corrosion over the long term. That is not to say that the increase in corrosion would be trivial or of no concern.

5.1.3 Avionic Cleaning and Corrosion Prevention/Control Manual (NAVAIR 16-1-540)

As was the case for the Aircraft Cleaning and Corrosion Control manual, the cleanup procedures for electronics, avionics and wiring exposed to firefighting agents is contained in the same chapter as exposure to saltwater, Chapter 10 "Emergency Action for Serious Corrosion of Avionic Equipment" [10]. This chapter also contains the same 'note' that these procedures are generally intended to reduce further potential damage and that further treatment will typically be required at a higher level of maintenance. Unlike the Aircraft Cleaning and Corrosion Control manual, the clean up and preservation procedures for exposure to firefighting agents are identical to that for salt water. In addition, all of the firefighting agents are treated exactly the same. It is not clear from this manual whether these procedures should also be followed for exposures to Halons.

The general procedure provided in the manual is to rinse the affected area, remove excess water, and if the rinse did not completely remove the salt or fire extinguishing agent, the area is scrubbed with aircraft cleaning compound, rinsed and excess water removed. Avionics-grade water displacing CPC is then applied to the effected areas and the equipment is dried in an oven, heated compartment, with a hot air blower or by hand depending upon the particular component involved. The implication from this TM is that the potential corrosion to electronics, avionics and wiring from firefighting agents is the same as from saltwater which would be considered to be corrosive to such equipment. As was the case for the aircraft procedures, the use of avionics grade water displacing CPC is just as likely the result of using water in the clean up procedures as it is to combat any potential corrosion that may be caused by these materials.

5.1.4 Summary

Both of the Tri-service Corrosion Control manuals require extensive clean up after exposure to firefighting agents. Specific procedures are required for all firefighting agents. For the most part the exposure to firefighting agents is treated the same as exposure to saltwater which is known to cause corrosion, thus supporting the position that these materials would be corrosive to the aircraft. Under some conditions the clean up requirements for Halon 1211 and CO_2 are identical to those required for dry chemical agents, contradicting the position that dry chemical agents are inherently more corrosive than other firefighting agents.

5.2 Open Literature

5.2.1 U.S. Army Corp of Engineers Study

The earliest study identified assessing the dry chemical agents with military equipment was performed in 1949 by the U.S. Army Corp of Engineers (USACE). Interestingly this is the same time period in which USACE was also evaluating gases and vaporizing liquids as potential fire suppressants, which eventually led to the development of the three major Halons 1211, 1301 and 2402 ($C_2F_4Br_2$). At that time dry chemical agent portable extinguishers using primarily sodium bicarbonate had been just recently placed on the commercial market [11]. Comparative tests were run between CO_2 and the newly developed dry chemical extinguishers to determine the types of fires for which the dry chemical agent was best suited and the type of equipment to which the agent could be applied without causing collateral damage.

To assess the collateral damage, non-fire tests were run using 'delicate' machinery and an engine generator [11]. The delicate machinery consisted of a roller bearing driven at high speed by an electrical motor. The dry chemical was expelled directly onto the running equipment. The results indicated that the dry chemical mixed with the lubricating oil and quickly seized the bearing. Two tests were run on an engine generator. In the first scenario the dry chemical was expelled directly on a running generator with no effect on the performance of the equipment. In the second scenario the crankcase oil was preloaded with the dry chemical agent and run in ½ hour intervals for 75 hours. The results indicated a break down of the lubricant with deleterious effects on wear and performance. While corrosion tests were also run in a Tropical Testing Chamber, these tests were restricted to the fire extinguisher itself. From a collateral damage standpoint, USACE concluded that dry chemical agents were not suitable for delicate machinery due to the abrasiveness of the agents.

5.2.2 Tri-Service System Program Office for Aircraft Ground Fire Suppression and Rescue Study

Little if any information appears in the reviewed literature re-evaluating dry chemical agents for potential military use until the early 1970s. The first study identified was sponsored by the Tri-Service System Program Office for Aircraft Ground Fire Suppression and Rescue [12,13]. The two phase study was aimed at reducing the number of different systems used for Crash Fire Rescue (CFR) operations at airports. Phase 1 of the study evaluated a wide range of dry chemical agents, vaporizing liquids, Halon foam and CO_2. Included within the dry chemicals were PKP, PKX - a newly developed form of potassium bicarbonate from ANSUL, and two sodium bicarbonate agents - one with a stearate and one with a silicone treatment. The potential corrosive effects of the dry chemical agents were evaluated on alloys and elastomers commonly used in aircraft structures and agent delivery systems: aluminum, brass, titanium, mild steel, stainless steel, neoprene rubber and nitrite rubber. Two sets of corrosion and materials compatibility tests were performed. The dry test consisted of immersing each material in 10 g of agent stored at 130°F for 20 days. The wet or aqueous test consisted of immersing each material

in a mixture of 5 grams of dry chemical and 5 grams of water stored at 130°F for 20 days. Both of the sodium bicarbonate-based agents were tested. Only the PKP version of the potassium bicarbonate agents and not the PKX version was tested in phase 1.

The results from the dry tests indicated that little if any corrosive effect was found for any of the dry chemical agents [12]. Prior to performing the aqueous corrosion tests, tests were carried out to evaluate the miscibility of the dry chemical agents with water. The three bicarbonate-based agents were fully miscible with water. Both of the sodium bicarbonates produced a thin paste while the potassium bicarbonate produced a thick paste. Results from the aqueous corrosion tests indicated that attack occurred for certain agent and material combinations. For the bicarbonate-based agents, titanium, mild steel and stainless steel were not affected at all. Aluminum was not attacked by the sodium bicarbonates but was slightly attacked by the potassium bicarbonate. The results for brass were more complex. Brass exhibited a mild attack from the potassium bicarbonate and the sodium bicarbonate with silicone treatment, and moderate attach by the sodium bicarbonate with stearate treatment. From a general conclusion the solid agents that were not miscible with water caused more attack than those that were miscible with water.

Phase 2 of the study evaluated the top candidates identified from Phase 1, which included Halon 1211 and PKX [13]. Additional corrosion and materials compatibility tests were performed for the three agents. The materials tested included magnesium, brass, copper, mild steel, stainless steel, titanium, aluminum and neoprene rubber. Two series of tests were performed. The materials were mounted on an inclined plane and exposed to a JP-4 fire with and without agents. The neoprene was exposed to the neat agent and not the fire. The samples were stored in ambient conditions for four months without any removal of the agent or products from the fire. After the four months, half of each sample was cleaned to allow examination of the surface for evidence of attack. Results for the PKX indicated that only brass exhibited a slight surface attack. No other material exhibited evidence of corrosion or deterioration. As a point of reference, it is worth noting the results for Halon 1211. All of the metals tested exhibited slight surface effects such as darkening or blueing of the surface with evidence of black deposits. The researchers concluded that the short-term effects of Halon 1211 did not warrant concern but recognized that these short-term tests could not be used to indicate the potential for long-term stress cracking or pitting, They also concluded that although both of the dry chemicals appeared to perform better than Halon 1211 from a corrosion and materials compatibility stand-point, the dry chemical agents do leave a residue that must be cleaned.

The results of the accelerated testing in phase 1 and the exposure tests in phase 2 were consistent for potassium bicarbonate except for aluminum. The potassium bicarbonate (PKP) caused a slight attack of aluminum under accelerated conditions. The potassium bicarbonate (PKX) did not show any evidence of attack during the short-term exposure tests. The difference between PKP and PKX was not found in the literature. Anecdotal information indicated that the difference between the agents was only the particle size distribution [3]. Under the assumption that PKX and PKP differ only in particle sizes and are equivalent from a materials composition

stand-point, this suggests that potassium bicarbonate agents may cause corrosion problems for aluminum under long-term exposure. These results may also indicate that the four-month exposure test may not adequately predict the corrosion resulting from actual in-use conditions.

5.2.3 Joint Technical Coordinating Group for Aircraft Survivability Studies

The next study evaluating compatibility issues for dry chemical agents occurred in the late 1970s and was sponsored by the Joint Technical Coordinating Group for Aircraft Survivability (JTCG/AS) [14]. Unlike the previous study, the aim of this work was to evaluate dry chemical agents for onboard systems. It must be noted that an initial premise of the study was that Halon 1301 systems would not be suitable for engine nacelle applications because Halon 1301 was not a persistent agent. The goal of the study was to select several candidate agents that would be more suitable than Halon 1301 for that application. The study reviewed more than 150 potential agents including dry chemicals, liquids, gases, gels and slurries. The researchers down-selected to four dry chemicals (potassium bicarbonate, potassium iodide, lithium carbonate and sodium carbonate)and a lithium chloride water solution based on fire tests conducted in a simplified engine nacelle simulator. An assessment of the compatibility of four of the five selected agents was included in the study aimed at evaluating the long-term storage of these materials

Two sets of compatibility tests were performed. The nonmetallic materials neoprene, Teflon, PVC and buna-n-rubber were tested for their compatibility with potassium iodide, lithium carbonate, sodium carbonate and lithium chloride powders. Compatibility tests for potassium bicarbonate were not performed in this study. The powder was placed directly on the entire surface of the 2.5 cm square sample and placed in an oven at 38°C for 33 days. Two sets of reference samples without the dry chemical agent were maintained for purposes of comparison. One set was placed in the oven with the exposed samples and the other set kept at room temperature. Separate compatibility tests were also performed on the lithium chloride solutions at room temperature by completely submerging the nonmetallic samples in the solution for 19 days and partially submerging the samples for 43 days. The researchers concluded that the nonmetallic materials appear to be compatible with the four dry chemicals tested under these test conditions.

The metallic materials Al 5502, Al 6061, brass, copper, nickel, mild steel, 304 stainless steel and titanium were tested in a similar manner except the temperature was controlled at 260°C for one week. Separate corrosion tests were also performed on the lithium chloride solutions using the same procedure as described previously for the nonmetallic samples. The results indicated that the lithium chloride powder resulted in a surface reaction with all metals, the sodium and calcium carbonate with copper and the potassium iodide with brass, copper and mild steel. The aqueous lithium chloride solution reacted with all of the metallic samples except the stainless steel and titanium. No analysis was provided for the potential effects of the observed corrosion on either potential storage systems or the aircraft structure. While materials compatibility and corrosion tests for potassium bicarbonate were not included in the study, they concluded that the dry chemical agents such as potassium bicarbonate may be the best solution for aircraft fire protection.

Testing of dry chemical agents continued into the early 1980s. The U.S. Air Force (USAF) and the JTCG/AS sponsored work with Monnex; sodium dawsonite with silicon dioxide; and potassium dawsonite with potassium iodide and silicon dioxide [15,16]. (MONNEX was produced by ICI, Ltd as a condensation product of potassium bicarbonate and urea. Dawsonite is the aluminum carbonate anion $Al(OH)_2CO_3^-$. The silicon dioxide was added to the dawsonite compounds as a flowing agent.) Small scale experiments were carried out to establish fire extinguishment performance data for these three materials and evaluate any potential corrosion issues that may affect their test facility.

Desmarais reported that after a week of continuous testing, cumulations of Monnex caused corrosion and roughening of the upstream side of the flame holder [15]. The agent and corrosion could be cleaned by scrubbing with a wire brush followed by vacuuming. The sodium dawsonite would also accumulate on the surfaces but did not appear to cause corrosion. It could be removed by scrubbing and vacuuming. The potassium dawsonite was the easiest of the three agents to clean up but it was noted that the surface accumulations were green instead of white. Desmarais concluded that the potential for adhering to the surfaces and for corrosion was present with all three agents. It was suggested that this result was likely due to the repeated exposures from testing and may not be a major disadvantage in actual service. It was noted that the inadvertent release of these materials in an engine nacelle would pose a serious corrosion concern.

In the Executive Summary for the overall JTCG/AS program, Grenich reported that handling of these materials was very similar to the Halons but after repeated exposures they reacted with the test surfaces [16]. It was also reported that the sodium dawsonite was the most difficult of the three to cleanup and unlike Desmarais reported that it was also the most corrosive. Based on the advantages and disadvantages of the dry chemical agents, it was decided that other agents had a higher priority than the dry chemicals for use in engine nacelle fire protection.

5.2.4 National Institute of Standards and Technology Study

Further work evaluating the potential collateral damage concerns for the dry chemical agents did not appear in the literature until the early 1990s. This is the time frame in which alternatives to Halon 1301 were being sought. A study sponsored by the U.S. Military and the FAA was performed by the NIST to determine the best candidate agents to replace Halon 1301 in aviation engine nacelles and dry bays [17,18]. A specific objective of the study was to determine whether or not sodium bicarbonate was a viable option. The study included assessing the potential corrosion caused by the neat candidate agents with the typical alloys used for storage and distribution, and the potential corrosion from neat agent and byproducts with the aircraft structure and component materials. The two main objectives of the study were to 1) rank the corrosiveness of the potential agents with respect to the storage materials to eliminate the most corrosive, and 2) rank the corrosion susceptibility of the potential storage and distribution materials to eliminate the most susceptible. The materials considered were recommended by the

USAF as those typical of storage and distribution systems. Eight alloys were tested: 304 stainless steel, 13-8 Mo PH stainless steel, AM 355 stainless steel, stainless steel alloy 21-6-9 (Nitronic 40), 4130 alloy steel, Inconel 625 (nickel-based alloy), CDA-172 copper/beryllium alloy and 6061 aluminum alloy with a T6 temper.

The NIST researchers developed three different exposure scenarios to assess the aircraft storage and distribution system materials: mass change, weld/crevice attack and environmentally induced fracture (or stress cracking) [17]. These experiments were designed to assess the six forms of corrosion they believed would be of potential concern to this scenario: uniform attack, pitting, crevice corrosion, intergranular attack, environmentally induced stress cracking and selective leaching. Erosion corrosion and galvanic corrosion were not thought to be of particular concern for storage and distribution systems.

The mass change experiments were designed to provide the rate of formation of corrosion scales or the rate of loss of metal during uniform attack [17]. Three samples of each alloy were exposed to each agent for 25 days at 150°C. At the end of the test each specimen was weighed to determine the change in mass. Visual and optical examinations were also performed to evaluate any occurrence of pitting, selective leaching and intergranular corrosion.

The weld/crevice test specimens were designed to evaluate crevice corrosion and intergranular attack [17]. The weld/crevice specimens were tested using the same experiment approach as the mass change experiments. After the test, the weld/crevice coupons were cut open and evaluated for crevice corrosion and intergranular attack, including weld-zone decay.

The environmentally induced stress tests were designed to measure the change in cracking from exposure to the agents versus that in an inert atmosphere [17]. Tensile test specimens were exposed to the agents at the same temperature as for the mass change and weld crevice tests, i.e., 150°C, and tested using the slow strain rate tensile test. Upon fracture, the tensile specimens were examined to determine any changes in ductility caused by exposure to the agents. Select fracture surfaces were examined using a scanning electron microscope to evaluate the crack propagation.

In order to combine the results from the three corrosion scenarios and to rank the agents, each result was rated one to ten based on its performance [17]. A rating of one was used to signify no evidence of corrosive attack, a five to indicate that corrosion may be a concern, and a ten to indicate rapid corrosion. A rating above four indicated more than just superficial corrosion that warrants further investigations. The results of this ranking process indicate that sodium bicarbonate had the worst overall rating of all of the agents evaluated, slightly above four.

The post deployment experiments for the sodium bicarbonate consisted of two different compositions: 1) a 50/50 mixture of sodium bicarbonate and sodium carbonate; and 2) sodium hydroxide [17]. Post deployment experiments for fluorine containing species were also conducted but are not included in this review. The 50-50 bicarbonate/carbonate mixture was used because

sodium bicarbonate is transformed to sodium carbonate upon heating. The sodium hydroxide was used because the sodium bicarbonate may hydrolyze to form sodium hydroxide. When sodium bicarbonate is in aqueous solution or in a moist state, it slowly loses CO_2 even at room temperature leaving behind sodium hydroxide and water. Above 65°C, the reaction can be vigorous. (An analogous reaction also occurs for potassium bicarbonate.) The coatings were produced by spraying the metal surfaces with ASTM artificial seawater and either sprinkling the surface with a 50/50 mixture of sodium bicarbonate and sodium carbonate, or spraying it with a 0.1 M sodium hydroxide solution [17]. The ASTM artificial seawater was used to simulate the conditions in a marine environment, considered to be the worst case.

The post deployment exposure environment was designed to simulate the condition where the agent decomposition products may be allowed to remain on the surface for up to one month [17]. The exposure consisted of placing the samples in humidity controlled environments for 30 days. Three humidity conditions were used, low (20%), moderate (52%) and high (93%). The results of these indicated that the worst corrosion for the Al 6061-T6 was obtained from the 50/50 bicarbonate/carbonate mixture. This was also true for the Cu-Be alloy where the mass change was so high at the 93% humidity that a much larger scale had to be used to plot the data than used for any other alloy. For the bicarbonate/carbonate mixture on the Cu-Be alloy the results were nearly an order of magnitude higher than observed for Al 6061 and 4130 steel, and almost two orders of magnitude above the results found for the other five alloys. They noted that the results with Al were somewhat surprising in that the sodium hydroxide was expected to result in the highest rate of corrosion. This was attributed to the possibility that the quantity of sodium hydroxide used in these experiments may not have been high enough to cause the expected corrosion. It was postulated that the potential quantities of sodium hydroxide that may form in actual service could be significantly higher than tested in these series.

While the results of corrosion experiments for both storage materials and post deployment environments indicated that the corrosion rates obtained with pure sodium bicarbonate, or mixtures of bicarbonate, carbonate and hydroxide did not appear to create any major problems, the researchers believed that it would be very risky to use a fire suppressant that formed mixtures of bicarbonate, carbonate and hydroxide particularly on aluminum [17]. Coupled with the result that sodium bicarbonate exhibited the worst average corrosion during the storage material tests, they concluded that sodium bicarbonate was not a desirable candidate from a corrosion point of view.

The tests performed by NIST were the most comprehensive tests found in the literature. The results provide a good sense of the types of corrosion issues that may affect the storage and distribution systems and a generalized sense of the aqueous corrosion issues that may affect typical alloys used in the aircraft structure. The NIST tests were limited to the same materials initially chosen to represent storage and distribution systems and may not be truly representative of the structural materials in use. While they provide a good general sense, these results, like any other accelerated or simulated corrosion testing, can be difficult to directly correlate to in-service conditions. For example, the researchers expected that aluminum exposed to sodium hydroxide

would have a much higher rate of corrosion based on known interactions between the two materials. The expected result was not obtained. While the researchers proposed an explanation for this unexpected result, it is not possible to determine if this result or the expected result would hold for actual in-service conditions. This is not a unique problem to the NIST study but can be true of corrosion testing in general.

A second difficulty with the NIST tests, and corrosion testing in general, arises from trying to extrapolate longer-term corrosion rates from short-term tests. The 30 day exposure in the NIST test is likely a far shorter time period than actually occurs in practice. For example, in an incident of two F-14 engines exposed to saltwater and/or fire suppressants, it took several months before the engines were cleaned and the repairs performed at the depot [19]. (This incident will be described in further detail in the Engine Corrosion section below). It was reported that this length of time is not inordinate depending upon shipping time and work load. It is typical in short-term tests to try to accelerate the corrosion by creating artificial conditions that far exceed in-service conditions. Without correlating data, the use of short-term data such as 30 days to extrapolate to a longer time period may either underestimate or overestimate the rate of corrosion. It is possible that an initiation time is needed after which the rate of corrosion proceeds faster. It is also possible that the rate of corrosion is initially faster but slows significantly with time as protective oxides are produced or reactive species are depleted.

5.2.5 Federal Aviation Administration Study

Also in the early 1990s, the Federal Aviation Administration (FAA) sponsored a study to determine if there was a correlation between aircraft corrosion and exposure to heat from a fire, fire extinguishing agents or byproducts of the fire extinguishing agents [20]. The study was undertaken based on a finding that a single Boeing 727 aircraft that had experienced a fire 12 years earlier had significantly more corrosion than was expected for its age and operational history. While this study does not appear to be directly related to evaluating the use of dry chemical agents as replacements to halons, the timing of the study does coincide with the worldwide efforts to find suitable Halon alternatives.

To evaluate the potential relationship between fire and fire extinguishing agents on corrosion, aircraft that experienced fires and had more than 25 Service Difficulty Reports (SDRs) were investigated [20]. The location of the corrosion was evaluated on these twenty-two aircraft against the location of the fire, the smoke and the extinguishing agent. No definitive trends were observed. To evaluate further the potential relationship between fires and corrosion, the worldwide corrosion trends of the Boeing 727 fleet and specific corrosion findings from 727s with similar operational histories were evaluated. They reported that the 727s with the greatest amount of corrosion did not have fires and that there did not appear to be any correlation between fires and subsequent corrosion.

The SDRs contained in the report were reviewed to determine the fire extinguishing agents involved. Many of the SDRs do not mention the specific agent involved. The agents

specifically cited were CO_2, water and Halon, presumably Halon 1211 in portable extinguishers and Halon 1301 in the fixed systems. In one case the term "chem" extinguisher was used but it was not possible to determine the exact agent. It is likely that dry chemical agents were not involved in this study.

5.3 Engine Corrosion

Turbine engine components are composed of many different materials including magnesium alloys, aluminum alloys, titanium alloys, steels, stainless steels, copper alloys, nickel alloys and cobalt alloys. A major discriminator in the use of these materials is the operating temperature. Magnesium, aluminum, copper and steels are used in the "low" temperature applications. Stainless steel, titanium, nickel and cobalt alloys are used in the higher temperature applications with the nickel and cobalt alloys used predominantly in the components exposed to the extreme temperatures past the combustor section.

The corrosion of engine components is also separated into two main temperature regimes: cold corrosion occurring below approximately 290 - 315°C and high temperature corrosion occurring over 315°C [21,22]. The term "cold corrosion" is somewhat of a misnomer in that it includes temperatures up to 315°C. From a basic corrosion standpoint, cold corrosion best equates with aqueous corrosion and for the purposes of this report will be evaluated as such. Cold corrosion is used to categorize all corrosion of turbine engines that is not considered high temperature corrosion [22]. Alloys used in low temperature applications exhibit aqueous corrosion (cold corrosion) while alloys used in high temperature applications may exhibit both aqueous corrosion and high temperature corrosion.

The literature data specifically assessing dry chemical firefighting agents mainly address the aqueous corrosion issues for some but not all of the typical materials used in aircraft structures and turbine engines. In order to obtain further information and specific data if possible, two engine manufacturers were contacted, Pratt and Whitney and General Electric.

5.3.1 Pratt and Whitney

A meeting was held with Pratt and Whitney staff to determine what data they may possess on the use of dry chemical agents on their engines [23]. They indicated that the military owns the technical data and is responsible for alloy selection and compatibility issues. They reported that they did not have any internal reports or data covering the use of dry chemical agents for military engines and to the best of their knowledge they had never been asked about this issue in the past. While they are responsible for alloy selection and compatibility for their commercial engines, they did not have any information on corrosion and compatibility issues from dry chemical agents.

On an informal basis they suggested that the use of any dry chemical agent on their engines would not be recommended. This position was based on general corrosion knowledge and principles, particularly on hot corrosion known to occur in military turbine engines. Two

other issues were raised but without any specific reports or data these concerns are recognized as speculative. The first concern related to the potential clogging of cooling channels within the turbine blades. Such clogging may result in overheating the alloy causing a reduction in lifelike or premature failure of the blades. This is the same concern provided in the NATOPS [2]. The second concern cited was the potential abrasiveness of these materials. If the dry chemical agents contaminated the turbine oil, it could cause damage to the bearing and seals leading to a reduced lifetime or premature failure.

5.3.2 General Electric

General Electric was contacted by Navy personnel to determine what if any reports, data or information they could provide on the use of dry chemical agents on their engines [24]. The GE opinion was that dry chemical agents would be detrimental to their engines and other parts of the aircraft. They cited sections of their engine Technical Manuals, and the Tri-service Corrosion Control Manuals. As was the case for Pratt and Whitney, GE did not have any specific reports or data available to support the requirements listed in the TMs.

5.3.3 Navy Jacksonville Detachment, Oklahoma City Air Logistics Center

Through the contacts at GE it was learned that the Navy Jacksonville Detachment located at Oklahoma City Air Logistics Center, had two F-14 engines that were exposed to firefighting agents and had been returned to depot as required. While a full engineering investigation was not required, a request was in place to disassemble the engines and document their condition [25]. Both of the engines had evidence of white residue throughout the engine with a greater quantity of corrosion than expected from normal operations. The engines were exposed to the firefighting agents in August of 1997 and worked on at the depot in the latter fall and early winter [19]. It was initially thought that the white residue was PKP and that the several month exposure to PKP lead to the higher corrosion levels found. A further review of the details of the incident by the Jacksonville Detachment staff led to the premise that the engines were exposed to AFFF/seawater solution from the hose lines on the carrier deck. The white powder was likely the dried salt and AFFF that remained after the water evaporated. No chemical analysis was obtained on the residue. The excessive corrosion found could be explained by a long-term exposure to salt water.

5.3.4 Naval Air Systems Command

A discussion of the potential use of sodium and potassium bicarbonate agents was held with the Team Leader of the NAVAIR Corrosion Group [26]. He was not aware of any specific testing or data available on this issue. From general corrosion principles he offered the following.

- From an aircraft structure standpoint, an immediate concern is for creation of pitting by formation of local corrosion cells (i.e., crevice corrosion) under the dry powder. The major issue is that the material would need to be cleaned up immediately or it could increase the corrosion of typical aircraft structural alloys,

particularly aluminum. A single exposure allowed to remain in contact with the aircraft components could be enough to significantly increase corrosion.

- With respect to the engine, a single exposure in the parts per million (ppm) range could be enough to create a problem. These materials would incorporate themselves into the protective oxides/coatings that develop on the alloys to provide corrosion protection. If the exposure occurred at a particularly critical point in the development of the protective oxides, it could have an immediate detrimental effect. For cases where the exposure occurred outside of any critical points, it would still incorporate itself into the protective oxides and would likely result in reduced life of the engine. On a case-by-case basis, estimates could be made on the potential impacts based on history of the exposed parts. It is reasonable to estimate that the effects may result in a significant reduction in performance and life. In general, any exposure to an engine would likely have detrimental effects.

- In general, any exposure to bicarbonate-based agents would likely be a longer term corrosion issue than a short-term issue, but the short-term effects could also be significant. To be prudent, any exposure should be evaluated. The immediate response should be to completely clean up these materials and not allow for a long term exposure, as is currently required in the Tri-Service Corrosion Control Manuals.

5.4 Literature Review Summary

Only four studies were found in the literature with direct assessment of the corrosion and materials compatibility effects of bicarbonate based dry chemical agents. Far less data was found than expected based on the prevalent view that these materials caused significant collateral damage. For the tests that were run, the data are limited and do not cover the necessary range of corrosion or other damage issues relevant to all potential aircraft exposures. With the exception of the tests performed by the U.S. Army Corps of Engineers in the late 1940s, the studies were aimed at assessing the compatibility of the agents with typical storage and distribution system materials or airframe structure.

No data were identified in the reviewed literature on the corrosive or physical effects caused by dry chemical agents to turbine engines and turbine engine materials. Cobalt alloys were not included in any of the studies. A single nickel alloy was included in the NIST study and a single magnesium alloy was included in phase 2 of the Tri-Service System Program Office for Aircraft Ground Fire Suppression and Rescue study. In addition, the tests did not address the specific high temperature corrosion issues known to cause problems with turbine engines, i.e., hot corrosion or the other physical concerns raised by engine manufacturers, the NATOPS and the Tri-service Corrosion Control Manuals such as clogging of air passages. Anecdotal information was provided that tests had been performed on an operating engine to assess these concerns [27].

The anecdotal information provided indicated that these concerns were valid but a report could not be identified in the literature.

6.0 AQUEOUS CORROSION ASSESSMENT

In order to fill in some of the data gaps, the available data will be supplemented with general corrosion behavior and data from studies with similar materials. It is recognized that the corrosion behavior of a particular aircraft or engine will depend greatly upon the specific alloys used and the physical design. The following assessment can only provide a general outline of the potential issues for material and alloy classes and not for specific aircraft systems. Of particular concern is environmentally induced cracking that may be highly alloy and environment specific.

6.1 Aluminum Alloys

Aluminum is an active metal in the EMF series that quickly forms an oxide through contact with water. The formation of the tightly adhering oxide, Al_2O_3, provides a barrier against further corrosion thus passivating the surface. As a result of this scale formation, aluminum exhibits good atmospheric corrosion resistance. Aluminum is not resistant to either alkalies or acids [5, 28]. The aluminum oxide scale that is responsible for corrosion resistance is not thermodynamically stable in high or low pHs. In general, aluminum will passivate in the pH range 4 to 8.5. This range will vary with temperature and specific constituents in the environment that may form complexes or insoluble products. At 70 to 95°C the pH range for passivation is reduced to 4.5 to 7 [5].

The corrosion behavior of aluminum alloys is dependent upon the alloying elements and heat treatment used to generate the necessary mechanical properties [5]. With the exception of magnesium, the alloying elements are all cathodic to aluminum. In general, aluminum alloys are less corrosion resistant than the pure metal. Aluminum alloys are separated into 8 series, designated 1XXX - 8XXX for wrought alloys and 1XX.X - 8XX.X for cast alloys [29]. The designations follow specific rules with the first digit determined by the main alloying element. Within aircraft uses, the two main alloy groups are the 2XXX (two thousand series) with copper as the main alloying element and the 7XXX (seven thousand series) with zinc as the main alloying element. The 2XXX and 2XX.X series are the least corrosion resistant of all of the aluminum alloys due to the presence of copper [28]. The 7XXX and 7XX.X series are the second least corrosion resistant of the aluminum alloys. The 7XXX series alloys used in aviation applications, e.g., 7075 also contain copper and are the least corrosion resistant of the 7XXX series alloys. The 7XXX series are also among the most susceptible to stress corrosion cracking. In general, stress corrosion cracking can be avoided by proper alloy selection and temper (heat treatment) for the exposure environment.

Aluminum was included in all four studies identified assessing the bicarbonate or carbonate-based agents. In the accelerated corrosion testing in phase 1 of the Tri-service System

Program Office for Aircraft Ground Fire Suppression and Rescue study, the two sodium bicarbonate agents did not attack aluminum while the potassium bicarbonate PKP caused a slight attack [12]. In phase 2 of the testing, the short-term (four month) exposure of PKX and fire products did not cause any corrosion to aluminum [13]. No information was provided on the exact composition or series of the aluminum tested.

In the Joint Technical Coordinating Group for Aircraft Survivability study, the aluminum alloys included were 6061 and 5502 [14]. The potassium bicarbonate agent included within their study was not included in the corrosion tests. The results of the one-week 260°C accelerated corrosion tests indicated that no corrosion was found with sodium and calcium carbonate on the two aluminum alloys tests. In addition to the limitation of these tests previously described, both of the alloys tested are more corrosion resistant than the 7XXX and 2XXX series alloys used in aircraft structures.

The NIST tests included the 6061 aluminum alloy and sodium bicarbonate in their four scenarios [17]. As was the case for the Joint Technical Coordinating Group for Aircraft Survivability study, the aluminum alloy tested is more corrosion resistant than the 2XXX and 7XXX used on airframe structures. The results from the weld/crevice tests indicated evidence of superficial attack. The results of the mass loss rate and the environmentally assisted cracking tests indicated that superficial attack occurred and more study may be required. Of particular concern is the fact that the 7XXX series alloys used in aviation applications would be expected to be more sensitive to stress cracking than the 6061 alloy tested, adding further support to their assessment that further work is warranted. In general, their results showed that the aluminum- sodium bicarbonate pair was ranked with the worst performers in their tests.

In the post deployment tests with aluminum, the worst corrosion resulted at 93% humidity with the saltwater - carbonate - bicarbonate mixture. At the 20% humidity level the NaOH - saltwater mixture caused pitting of the aluminum alloy. The NIST researcher indicated that their results were surprising in that the worst results for aluminum were expected to be with the sodium hydroxide. This was anticipated because the pH of the sodium hydroxide would be expected to be outside of the stability region of Al_2O_3, i.e., greater than 8.5. While their tests did not find this result, they believed that the possible creation of sodium hydroxide with its attendant high pH warranted considerable concern.

The exposure of aluminum to high pH environments is of considerable importance. Sodium and potassium bicarbonate solutions are alkaline. Solutions of their carbonates or hydroxides that may form are more alkaline than the bicarbonates. Depending upon the pH of these solutions, exposures may be a concern for aluminum. In order to evaluate the potential corrosion issues of the bicarbonate agents, it is important to understand both the effect that pH has on the stability of Al_2O_3 and the pH of solutions that may form from the bicarbonate agents.

6.1.1 Effect of pH on Aluminum

Under acidic conditions, pH < 4 and basic conditions, pH > 8.5, Al_2O_3 is not the stable form of the oxidized (corroded) aluminum. The dominate species are the Al^{3+} ion in acidic conditions and the AlO_2^- ion in basic conditions. Both of these species are soluble and do not protect the aluminum metal surface. To illustrate this effect graphically, the potential - pH or Pourbaix diagram (named for Dr. Marcel Pourbaix who first suggested their use) is used. (Information on the use and interpretation of Pourbaix diagrams is provided in Appendix A.)

Figure 1 provides the Pourbaix diagram for aluminum - water at 25°C. In general, solutions with a pH between 4 - 8.5 would not be expected to be corrosive to aluminum. Chloride solutions are a notable exception due to pitting even in the normally passive region. With the exception of phosphates, acids and bases only form soluble products with aluminum so that the aluminum- water Pourbaix diagram will be useful over a wide range of environments [30]. In the case of aluminum it is not so much the potential that is important, aluminum will react directly with H_2O, but the pH of the solution allowing either soluble products to form that do not offer protection or an insoluble product to form that will passivate the aluminum surface. It is important to note that this evaluation cannot account for the onset of pitting from chloride solutions or for the potential of environmentally induced stress cracking. None-the-less it is useful in predicting whether or not the conditions for corrosive attack will be present.

6.1.2 pH of Sodium and Potassium Bicarbonate Agents

According to Merck the pH of newly prepared, 0.1 M aqueous solutions of sodium bicarbonate and potassium bicarbonate is 8.3 and 8.2 respectively [31]. The pH of sodium bicarbonate in aqueous solutions in the range 0.01 to 4% is complex. It goes through a maximum at approximately 0.1% with a pH of approximately 8.6 [32]. The pH of 1%, saturated and ½ saturated solutions of potassium bicarbonate all have a pH of 8.2[1]. These pH ranges are generally within, but very near to the end of, the stability range of Al_2O_3. At these pHs, general corrosion would not be expected to occur.

Sodium bicarbonate will decompose to form sodium carbonate beginning at about 50°C [31]. At 100°C the sodium bicarbonate will be completely converted to sodium carbonate. An analogous reaction occurs for the potassium bicarbonate as well. The pH of sodium carbonate solutions in the range of 0.01 to 4% increases with concentration from 10.5 to 11.5 [32]. A fully saturated solution is 35% and has a pH of 12.5 [31]. If sodium hydroxide forms, the pH would be even higher. The pH of sodium hydroxide solutions in the range 0.01% to 4% is approximately 11-2 - 13-5. The pH ranges for the sodium carbonate, sodium hydroxide and presumably their potassium analogs are outside of the stability of Al_2O_3. At these pHs corrosion is expected to occur.

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[1]Tests performed by Naval Research Laboratory, NRL Code 6181, 1 October 1998.

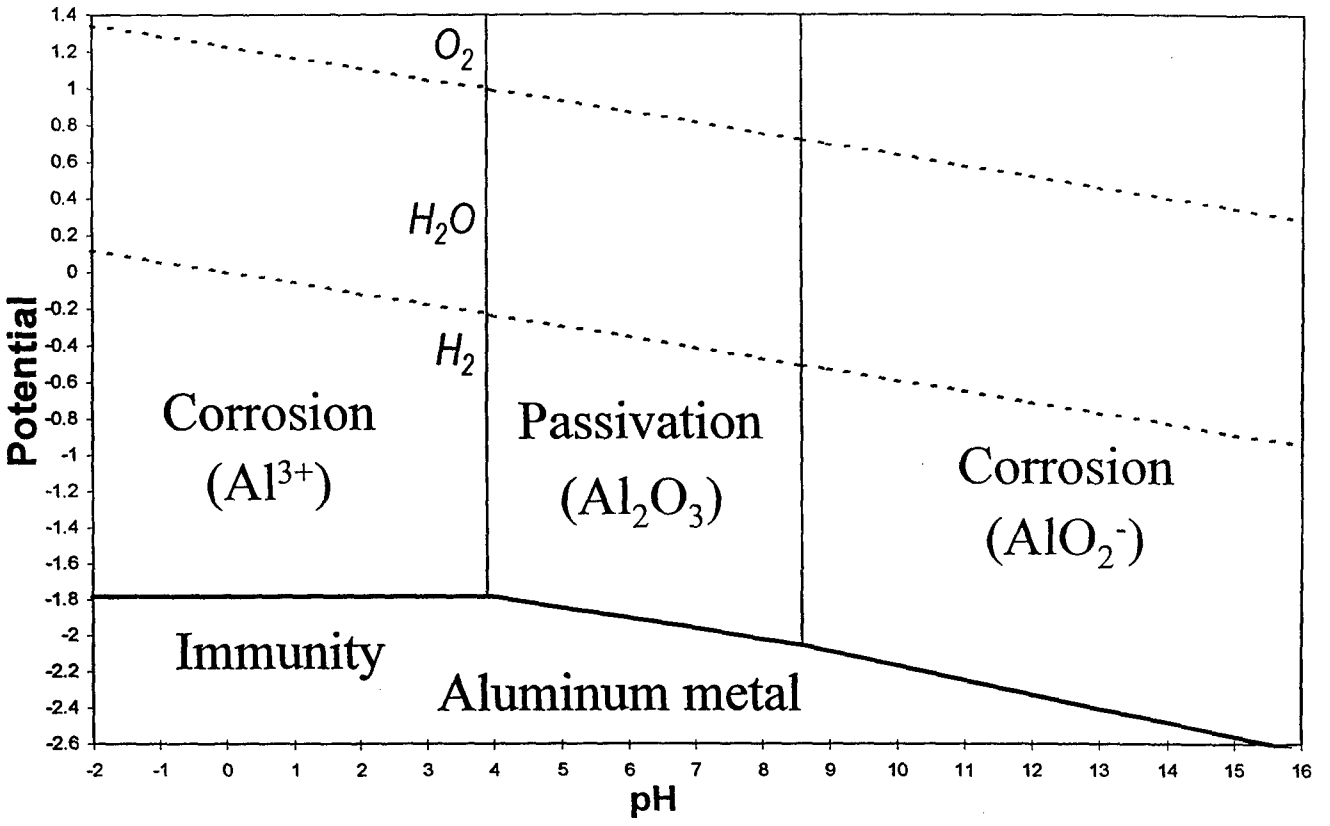

Fig. 1 – Pourbaix diagram for the system aluminum-water, at 25 °C and activities for soluble species at 10^{-6} [30]

While the above analysis indicates that pure sodium and potassium bicarbonates would not be expected to be corrosive to aluminum, the carbonates and hydroxides that form can create a corrosive environment. Further, the bicarbonate based firefighting agents are not pure sodium or potassium bicarbonates. Table 2 lists the ingredients for 7 different manufacturers of PKP or PKP extinguishers derived from their respective Material Safety Data Sheets (MSDSs) [33, 34, 35, 36, 37, 38, 39]. As can be seen, some formulations are complex with many different constituents while others are much less complex. Only one MSDS directly listed a pH. Amerex indicated a pH of between 9 - 10 which would be in the corrosive range for aluminum [33]. A single MILSPEC PKP was tested for pH at 1% and at ½ the saturation level for pure potassium bicarbonate[2]. The pH was 9.0 and 9.2 respectively, agreeing well with the Amerex MSDS.

During the test it was also noted that most of the PKP stayed on the surface of the liquid and was not very soluble in water[2]. As seen in Table 2, significant difference in solubilities exists between the various formulations of PKP. For example, Amerex indicates that their PKP is not soluble while General Fire Extinguisher indicates that their PKP is 94% soluble. The differences in compositions and solubilities may give different pHs affecting the general corrosion behavior. The difference in solubilities may also effect crevice corrosion. Those agents that are soluble would hold in moisture (i.e., the necessary electrolyte) providing a necessary ingredient for corrosion. Agents that are not soluble in water might be less prone to this effect.

6.1.3 Summary of Effect of Bicarbonate Agents on Aluminum

The pH data available from potassium bicarbonate agents, and the literature data on the pH of potassium and sodium carbonates and hydroxides indicate that these materials can be corrosive to aluminum. This finding is generally consistent with the literature data assessing the bicarbonate and carbonate agents. Under some scenarios, attack was evident while under other conditions no attack was observed. Based particularly on the pH data, long-term exposures of the bicarbonate agents and their decomposition products may present corrosion problems for aluminum.

6.2 Magnesium Alloys

Magnesium has the highest oxidation potential of structural materials. The alloying elements that are necessary for obtaining structural properties of magnesium alloys greatly increase the corrosion rates [5]. Magnesium has a high tendency toward galvanic (dissimilar metal) corrosion and much care must be taken to electrically isolate the magnesium or choose carefully the metal pairs. Like aluminum, magnesium can form a protective oxide/hydroxide barrier as a result of the corrosion process [5, 8]. Unlike aluminum, this barrier will only form in

[2]Tests performed by Naval Research Laboratory, NRL Code 6181, 1 October 1998.

Table 2. Constituents

	Company						
Ingredients	**AMEREX Corporation**	**R. C. Industries**	**General Fire**	**ANSUL Fire Protection**	**Buckeye Fire Equipment**	**Flag Fire Equipment**	**Industrial De Fosatos**
Potassium Bicarbonate	x	x	x	x	x	x	x
Calcium Carbonate	x	x					
Mica	x	x		x	x	x	x
Sodium Bicarbonate							x
Magnesium Aluminum Silicate	x	x					
Methyl Hydrogen Polysiloxane	x	x		x			x
Naphthalenecarboxamide	x	x					
Attapulgus Clay							x
Amorphous Silca							x
Red Dye	x						
Violet Dye	x	x	x	x	x	x	x
Black Dye	x	x					
Blue Dye	x						
Carbon Dioxide				x			
Compressed Air						x	
Quartz						x	
Other			x				
Solubility	Not soluble	Water repellant	94% soluble	Slight	Water repellent coated	23% soluble	Limited

high pH and is stable at all pHs above 11.5. As shown in the water - magnesium Pourbaix diagram provided in Figure 2, the stability of magnesium metal is well below the H_2O - H_2 line indicating that, like aluminum, magnesium will react directly with water to produce H_2 [30]. Depending upon the pH, soluble Mg^{2+} ions or solid $Mg(OH)_2$ will be formed. The $Mg(OH)_2$ is a protective scale analogous to Al_2O_3 and will reduce the corrosion. For magnesium ion concentrations of 1 ppm the $Mg(OH)_2$ barrier will form at pHs as low as 11.5. The more magnesium ions in solution the lower the pH for which the protective scale will be stable. At magnesium ion activity of 1 the $Mg(OH)_2$ will begin to become stable at a pH as low as 8.5.

Due to the formation of a protective scale at high pH, magnesium is considered resistant to alkalies. A ten percent caustic solution is typically used for cleaning magnesium up to temperatures of its boiling point [40]. Magnesium alloys can be considered for use with caustics such as potassium hydroxide, sodium hydroxide and sodium carbonate. Magnesium is not acceptable for use with carbonated water, i.e., carbonic acid, due to this pH effect.

Magnesium was only included in one of the four studies identified evaluating the corrosion of bicarbonate/carbonate agents. In phase 2 of the Tri-service System Program Office for Aircraft Ground Fire Suppression and Rescue study, the short-term (four month) exposure of PKX and fire products did not cause any corrosion to magnesium [13]. It is difficult to assess this result due to the lack of specific data provided in the report. The conditions were only described as ambient. They did not provide any details of the environment or the exposure. The magnesium panel was described as exhibiting no change in surface appearance after the four-month exposure. The magnesium control panel also did not show evidence of corrosive attack. An outdoor exposure of untreated magnesium would be expected to exhibit some corrosion based on known experience. This suggests that the environment itself was not conducive to corrosion. In addition, they did not find any corrosion of aluminum in their short-tem exposure study but did find corrosion in their accelerated tests. Their short-term exposure test may not accurately predict the corrosion from long-term exposure.

As with aluminum, the assessment of the corrosion of magnesium will rely heavily upon the pH effects caused by the bicarbonate agents. Using the same pH data described previously, the pH of pure bicarbonates and likely the bicarbonate-based agents with high solubility in water, would be below the stability of the magnesium protective scale even with magnesium ion activities as high as 1. The PKP agents with a pH between 9 to 10 are also below the stability of the magnesium scale unless the magnesium ion activity is raised to 0.1 to 0.001 suggesting that at a minimum some corrosion will occur. Removal of these ions through washing or exposure to rain would allow the corrosion to reoccur. For the carbonates and hydroxides, the pH of more concentrated solutions would be in the pH range where the protective scale was stable. Based on the pH effect of the bicarbonate agents, some corrosion of magnesium would be expected.

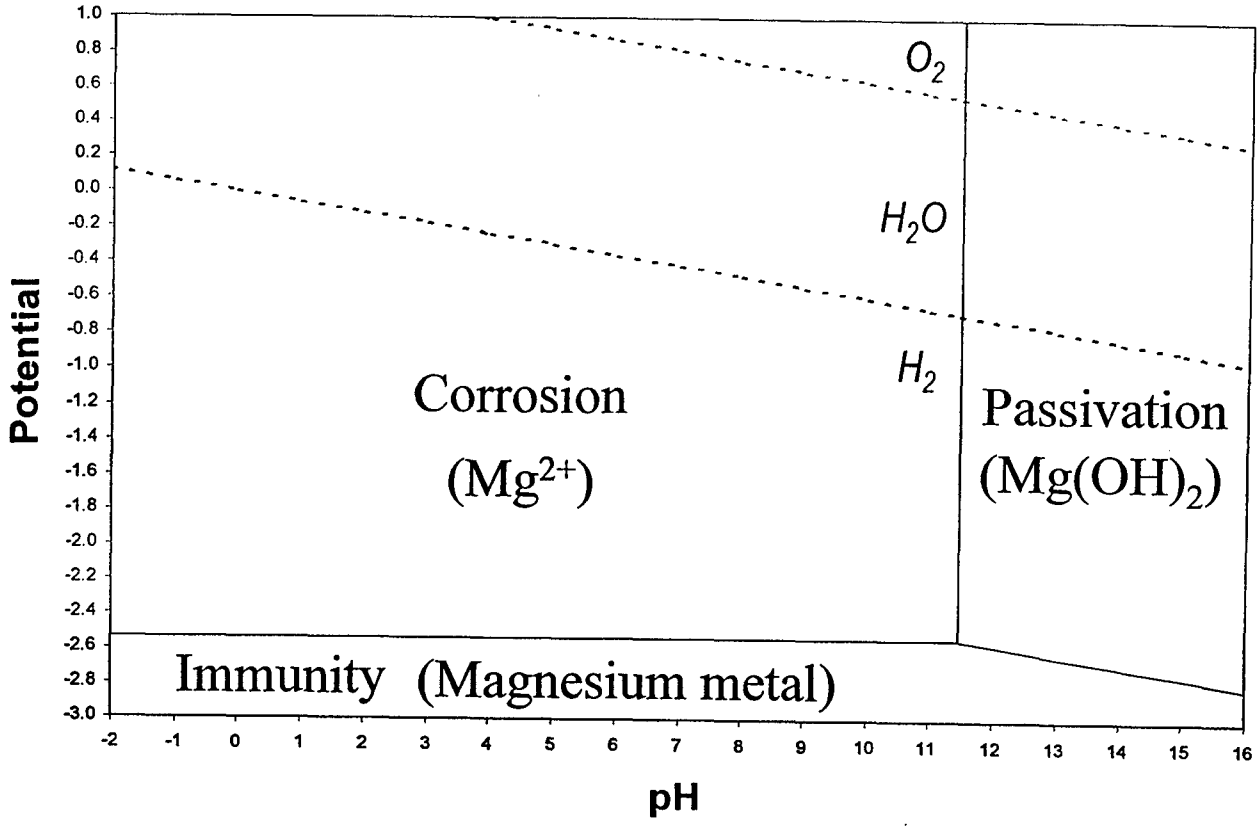

Fig. 2 – Pourbaix diagram for the system magnesium-water at 25°C and activities for soluble species at 10^{-6} [30]

It must also be noted that the limitation of the magnesium - water Pourbaix diagram is that it does not consider the formation of solid species such as magnesium carbonate. Hydrated magnesium carbonates have been found in the corrosion products resulting from atmospheric exposures [40]. It is believed that these species result from reaction of the protective scale with the acidic form of the carbonate, i.e., carbonic acid. This secondary reaction affects the corrosion of magnesium. It is possible that an analogous reaction of the bicarbonates or carbonates occurs with magnesium. Further investigation of the potential corrosion of magnesium exposed to bicarbonate agents would be warranted. The potential for environmentally induced stress cracking or pitting under specific conditions would also need to be studied further.

6.3 Steels

Steel in its simplest form is iron and carbon. Carbon steels generally contain less than 2% alloying agents [41]. At these concentrations the alloying elements do not generally provide any significant increase to corrosion resistance. Alloy steels are a class of steels that exhibit better mechanical properties than carbon steels due to the addition of alloying elements such as chromium, nickel and molybdenum [41]. The total alloy content can be as low as 0.5% up to a maximum just below that of stainless steels. In general, the purpose of the alloying elements in alloys steels is to enhance mechanical properties. In moderately corrosive environments the alloying elements may provide additional corrosion resistance. In severe environments, alloy steels are generally no more corrosion resistant than the carbon steels. Stainless steels are defined as ferrous alloys containing at least 10.5% chromium [42]. With increasing chromium content and/or the addition of other alloying elements, stainless steels can provide a wide range of corrosion resistance.

6.3.1 Carbon (Mild) and Alloy Steels

From a basic corrosion point of view, the corrosion of carbon steels and alloy steels is best understood through the corrosion of iron. It has been demonstrated experimentally that without the presence of O_2, the passive region for iron exists between approximately pH 9.5 to 12.5 [30]. In the presence of O_2 however, the potential is increased such that the passive layer will form at pH 8 and above as indicated in the Iron-Water Pourbaix diagram shown in Figure 3.

Due to this effect, the corrosion rates of iron are different for different pH ranges. For non-oxidizing solutions below pH 4 the rate is governed by the concentration of H^+ ions (pH) producing H_2 [5]. The presence of oxygen or other oxidizers within this pH range will increase the potential but not high enough to support the formation of the passive layer [30]. The corrosion rate will increase. In the relatively neutral pH of 4 to 10 the corrosion rate is not affected by the pH [5]. Instead it is governed by the ability of oxygen to diffuse to the surface. Small changes in alloy composition will not effect the corrosion rate because O_2 diffusion is the rate controlling step. A high or low carbon steel, low alloy steel, wrought iron or cast iron will all have essentially the same corrosion rate in a given environment. Within this pH range the iron-water Pourbaix diagram is applicable to a wide range of carbon and low alloy steels.

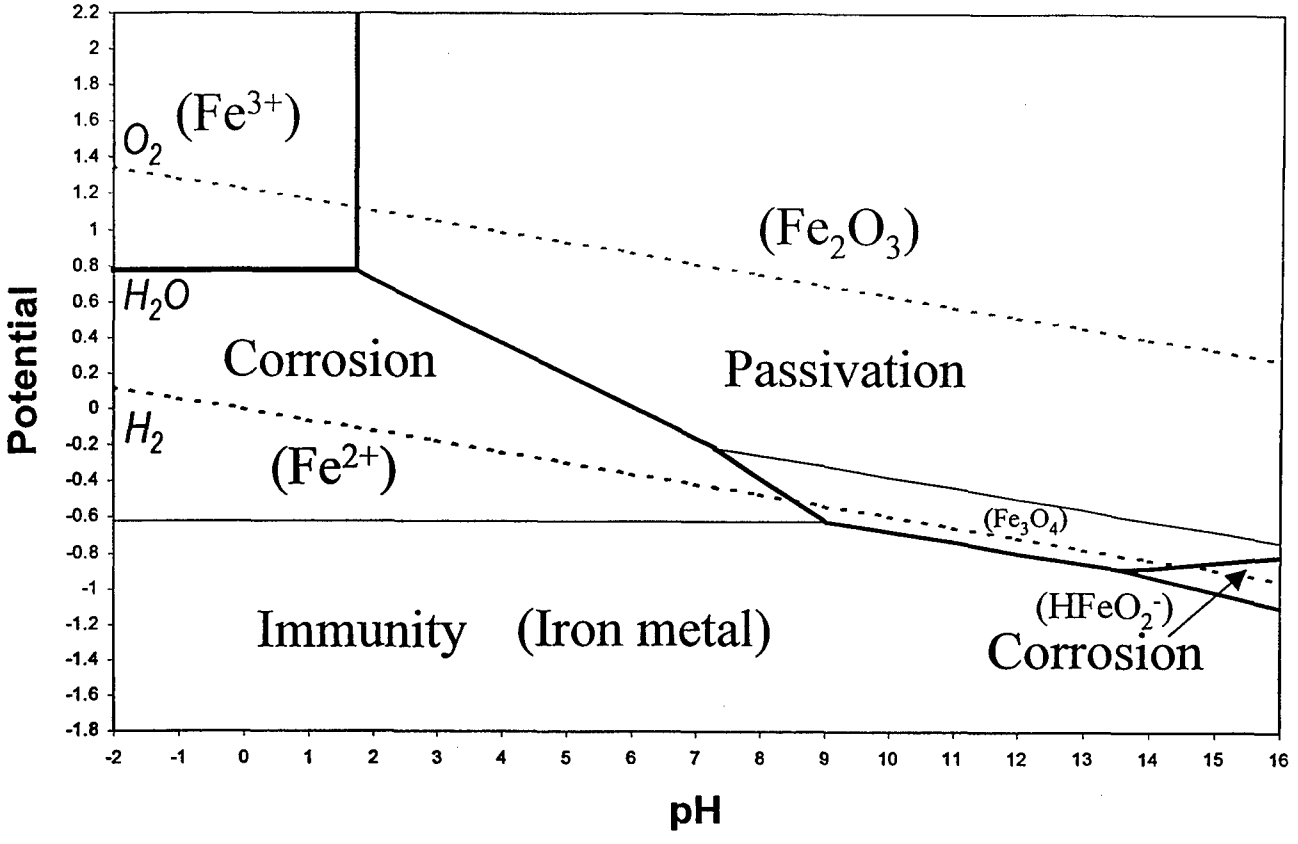

Fig. 3 – Pourbaix diagram for the system iron-water at 25°C and activities for soluble species at 10^{-6} [30]

Steel was included in all four of the studies identified assessing the corrosion of the bicarbonate and carbonate agents. In both phases of the Tri-service System Program Office for Aircraft Ground Fire Suppression and Rescue study mild steel was used [12, 13]. For the accelerated tests no corrosion was found on the steel exposed to both of the sodium bicarbonate agents or the potassium bicarbonate agent PKP. In the short-term (four month) exposure test no corrosion was found from the exposure to potassium bicarbonate PKX.

In the Joint Technical Coordinating Group for Aircraft Survivability study mild steel was also tested [14]. The results of the one-week 260°C accelerated corrosion tests indicated that no corrosion was found with sodium and calcium carbonate on the mild steel.

The NIST tests included the alloy steel 4130 with sodium bicarbonate in their four scenarios [17]. The results of the mass loss rate and the weld/crevice tests indicated superficial attack and that more study may be required. The results from the environmentally assisted cracking tests indicated only a small evidence of attack. In the post deployment tests 4130 steel exposed to both the carbonate - bicarbonate mixture and the sodium hydroxide mixture showed only small mass increases indicating a very small level of corrosion.

The results of the four studies are generally consistent with the corrosion predicted by the Pourbaix diagram based on the pHs of the bicarbonate agents and mixtures used by NIST under the assumption of the presence of O_2. The pH of the pure bicarbonates and the bicarbonate agents is in the regime where corrosion rate is not a function of pH, i.e., 4 to 10. The carbonate - bicarbonate mixture and the sodium hydroxide may be at higher pHs where they would assist in passivating the iron resulting in a decrease in corrosion.

In addition to the effect of pH, iron carbonates (e.g., $FeCO_3$) exist that are only slightly soluble in water [30]. $FeCO_3$ or mixtures of $FeCO_3$ with iron oxides and hydroxides may form at the higher pHs serving to increase the passivity of the iron surface. Further, it has been long known that soft waters are more corrosive to iron and steel than hard waters (i.e., high concentration of calcium and magnesium salts) [5]. This is due to the formation of a solid species comprised mainly of calcium carbonate ($CaCO_3$) that deposits itself on the surface of the iron or steel. This film also acts as a barrier augmenting the passivation offered by the iron oxide/hydroxide resulting in a reduced rate of corrosion. Depending upon the exact conditions, soft waters may be hardened by the addition of alkaline species such as sodium carbonate, sodium hydroxide and presumably their potassium analogs to decrease the corrosiveness of the water. The formation of carbonates and hydroxides from the bicarbonate agents may serve to decrease the corrosion of mild and low alloy steels.

Based on the experimental results and general corrosion principles it does not appear that the uniform corrosion of mild steels and low alloy steels will be adversely affected by exposure to bicarbonate-based agents. As is the case for all of the other materials evaluated, the potential for environmentally induced stress cracking of specific alloys or pitting under specific conditions would need to be studied further in order to provide a definitive analysis.

6.3.2 Stainless Steels

Five main types of stainless steels exist based on their metallurgical structure [43].

- The martensitic stainless steels are named from the analogous martensite iron-carbon phase in carbon alloys. They are essentially iron and chromium alloys containing 10.5 to 18% chromium and are magnetic. Small amounts of nickel may be added to improve corrosion resistance. In general, martensitic stainless steels are only resistant to corrosion in mildly corrosive environments.

- The ferritic stainless steels are also named for the analogous ferrite phase, relatively pure iron, of carbon steels. As the martensitic stainless steels they are essentially iron chromium alloys containing 10.5 to 30% chromium and are also magnetic.

- Austenitic stainless steels are named for the austenite phase of iron. They contain chromium, nickel and manganese. Alloying elements such as aluminum, molybdenum and copper can be added also to improve the pitting or oxidation resistance.

- Duplex stainless steels have a mixed ferrite and austenite structure based principally on iron, chromium and nickel. Addition alloying elements such as molybdenum and copper may be added to increase specific corrosion resistance. The corrosion behavior of duplex stainless steels is similar to their austenitic counterparts with similar alloy contents with the notable exception of increased stress corrosion cracking resistance.

- The precipitation hardened stainless steels are iron-chromium-nickel alloys that are hardened through heat treatment. The corrosion behavior is generally comparable to the other nickel - chromium stainless steels [44].

The mechanism for corrosion resistance of stainless steels is different than for carbon or alloy steels, and other metals and alloys [44]. As previously described, most alloys obtain corrosion resistance through the formation of an oxide or hydroxide on the surface of the metal or alloy. In contrast, stainless steels do not form a true oxide at low temperature. Instead they form a film that provides passivity to the underlying alloy. Passivity of stainless steels can exist under certain environmental conditions that will depend upon the family and composition of the alloy. When passivity is maintained stainless steels corrode very slowly. When passivity is not maintained, stainless steels will corrode very much like carbon and alloy steels. Particular care must be taken when choosing stainless steels. Improper alloy choice may result in corrosion and perforation of the alloy faster than a mild steel would fail through uniform attack.

In general, stainless steels are considered resistant to alkaline solutions [42]. In a 20% solution of boiling sodium hydroxide the austenitic 304 alloy exhibits low rates of corrosion but stress corrosion cracking can occur at 100°C. Other alloys are less susceptible to the problems of stress corrosion cracking under similar conditions.

Stainless steels were included in all four of the studies identified assessing the corrosion of bicarbonate and carbonate agents. In the accelerated corrosion testing and short-term exposure testing in both phases of the Tri-service System Program Office for Aircraft Ground Fire Suppression and Rescue study, the two sodium bicarbonate agents and the two potassium bicarbonate agents, PKP and PKX, did not show any evidence of attack [12, 13]. No information was provided on the exact composition or series of the stainless steel tested.

In the Joint Technical Coordinating Group for Aircraft Survivability study the stainless steel tested was 304 [14]. The potassium bicarbonate agent included in their study was not included in the corrosion tests. The results of the one-week 260°C accelerated corrosion tests indicated that no corrosion was found with sodium and calcium carbonate on stainless steel 304.

The NIST study included 4 stainless steels: Nitronic 40, 304, 13-8MoPH and AM355 [17]. Nitronic 40 and 304 are austenitic stainless steels and 13-8MoPH and AM355 are phase hardened stainless steels [43]. The results of their 25 day, 150°C exposure tests indicated that Nitronic 40 and 13-8MoPH exhibited superficial attack where more study may be warranted, while 304 and AM355 exhibited only superficial attack [17]. The weld/crevice tests indicated superficial attack where more study may be required for 13-8MoPH and AM355, the two phase hardened alloys and only exhibited evidence of superficial attack for Nitronic 40 and 304, the two austenitic alloys. The results for environmentally induced stress cracking indicated that the attack of 13-8MoPH would need to be considered and was the worst rating of any of the alloys tested. Nitronic 40 showed no evidence of attack, AM355 exhibited some evidence of attack and 304 exhibited evidence of superficial attack. In the post deployment tests, all of the stainless steels exhibited very small weight losses with correspondingly low corrosion rates.

In general, the results of the four studies were consistent with the expected behavior of stainless steels based on general corrosion properties. Changes in the pH caused by the presence of bicarbonates, carbonates or hydroxides would not be expected to adversely effect the uniform corrosion of the stainless steels. With respect to cracking, the NIST results indicate that three of the four stainless steels tested would not likely be adversely affected by the bicarbonate agents. The exception is 13-8MoPH where stress cracking may be a concern. The results for stress cracking of 13-8MoPH indicate the need to consider the actual alloy in the actual environment and re-enforces the premise that general corrosion behavior is not always adequate to predict environmentally induced stress cracking. While most stainless steels may be unaffected by long-term exposure to the bicarbonate-based agents, some alloys may have problems.

6.5 Titanium Alloys

Titanium is relatively active in the EMF scale readily passivating in aerated solutions including dilute acids and alkalies [5]. As shown in the Titanium-Water Pourbaix diagram provided in Figure 4, the stability of titanium metal is below the H_2O/H_2 line indicating that it will react directly with water to produce H_2 gas, the non-protective Ti^{2+} ions or the protective TiO_2 depending upon pH and importantly potential [30]. The corrosion behavior of titanium, like iron, is impacted by both the pH and potential. In oxidizing atmospheres and in the absence of any substances with which titanium will form complexes or insoluble products, titanium will passivate over essentially the entire pH range. In non-oxidizing, strong acids, titanium will corrode as predicted by the Pourbaix diagram. Not predictable by the Pourbaix diagram the corrosion rate will be low. Titanium resists alkalies at room temperature but is attacked by hot concentrated sodium hydroxide [5].

Due to the strong behavior of the protective oxide, small changes in the alloying elements typically used in titanium alloys have little effect on the corrosion behavior [45]. In this case the Titanium-Water Pourbaix diagram is useful for predicting the corrosion of titanium alloys in general. Under conditions when titanium is not passive, alloy changes have been shown to effect corrosion rates so that specific alloys must be considered [45]. As the bicarbonate agents do not reduce the oxidizing nature of the solution, this should not be the case for this evaluation. Although titanium forms weak complexes with carbonates, the corrosion rate for a 20% solution of boiling sodium carbonate is nil suggesting that this may not be a significant issue [30, 45].

Titanium was included in three of the four studies identified assessing the corrosion behavior of the bicarbonate and carbonate-based agents. The NIST study did not include titanium so that none of the tests identified evaluated environmentally induced stress cracking. That evaluation will rely solely on the general stress cracking behavior of titanium. For the studies evaluating uniform corrosion, no corrosion was found in both phases of the Tri-service System Program Office for Aircraft Ground Fire Suppression and Rescue study or the Joint Technical Coordinating Group for Aircraft Survivability study [12, 13, 14]. While no information was provided on the exact composition of the titanium alloy tested, these results are expected to be applicable to the family of titanium alloys under the oxidizing conditions of the tests. The results of these three studies are in agreement with the general corrosion behavior of titanium. It is not expected that the bicarbonate's agents will adversely affect the uniform corrosion of titanium.

With respect to environmentally induced stress cracking, it has been found that these phenomena are generally limited to specific conditions and environments [45]. For all titanium alloys, environments containing anhydrous methanol/halide solutions, nitrogen tetroxide, red fuming nitric acid and liquid or solid cadmium has been shown to cause stress cracking. For some alloys aqueous chloride solutions have been shown to also cause stress cracking. These specific environments are well outside of the changes that would be expected by the presence of bicarbonate-based agents. Based on this general stress cracking behavior, environmentally

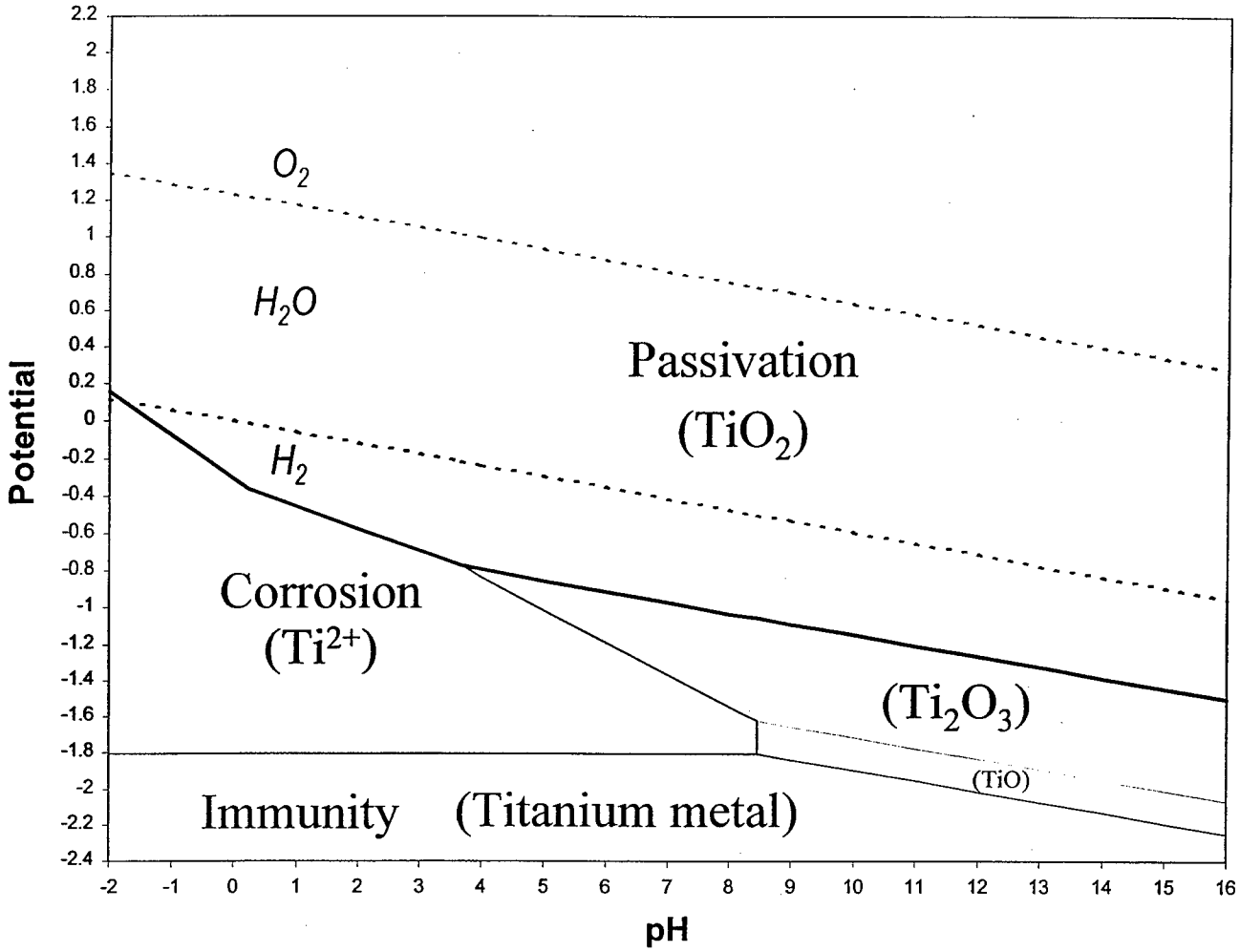

Fig. 4 – Pourbaix diagram for the system titanium-water at 25 °C and activities for soluble species at 10^{-6} [30]

induced stress cracking does not appear to be a likely concern from exposure to the bicarbonate agents. It should be cautioned that as noted previously, general corrosion behavior does not always provide a reliable measure of environmentally induced stress cracking for specific alloys and environments. Additional study for specific alloys of interest would be needed in order to provide a more definitive analysis.

6.6 High Copper Alloys

Copper in the absence of constituents that form complexes is a noble metal. As shown in the Copper-Water Pourbaix diagram provided in Figure 5, copper metal exists above the H_2O-H_2 line but below the H_2O-O_2 line indicating that O_2 must be present for copper to corrode [30]. In completely de-aerated water, copper will not corrode at all. Depending upon the pH, oxygen will react with copper to produce the non-protective ions Cu^{2+}, $HCuO_2^-$ and CuO_2^{2-} and the protective solid Cu_2O. The corrosion behavior of copper is analogous to aluminum in that the stability region for the protective Cu_2O is limited to fairly neutral conditions. For copper ions with an activity of 10^{-6}, the pH for passivity is approximately 7 to 12.5. For copper ion activities of 1, this stability region is expanded to approximately a pH range of 4.75 to 15.25 region. From a general corrosion perspective, copper and all high copper alloys are expected to have similar corrosion resistance due to the formation of this protective scale [46].

Baring the formation of complexes or other solid species that may form, the Pourbaix diagram indicates that within the pH range of the bicarbonate agents and their carbonate analogs, the passivating film would be expected to form. If sufficient hydroxides form the pH may be raised beyond the stability region of the protective barrier. The concentration of the hydroxide would have to be significant in order for this effect to occur. Tests with 1 to 2 N sodium hydroxide at room temperature corroded a high copper alloy at 0.2 mils/yr, a low corrosion rate, suggesting that even higher concentrations of hydroxide would be necessary to raise the pH beyond the stability of the passive film [46].

At room temperature and from a purely pH perspective, it is not anticipated that bicarbonate agents would cause corrosion problems with copper alloys. At elevated temperature, copper alloys can exhibit a significantly higher rate of corrosion. The rate of attack for copper-zinc alloys exposed to most alkalies such as hydroxides is 2 to 20 mils per year at room temperature and 20 to 70 mils/yr in aerated, boiling solutions. (As a general rule of thumb, corrosion rates of less than 1 mil/year are considered outstanding, 1-5 are considered excellent, 5 to 20 are good, 20-50 are fair, 50-200 are poor and over 200 are considered unacceptable [8].)

Copper alloys were assessed in two of the four tests identified assessing the corrosion behavior of bicarbonate agents. It is expected that the two copper alloys tested would be applicable to the broad range of high copper alloys. In phase 2 of the Tri-Service System Program Office for Aircraft Ground Fire Suppression and Rescue study no corrosion was found in the short-term exposure (4 months) of copper to potassium bicarbonate PKX [13]. While this finding is in agreement with general corrosion behavior, it must be noted that none of the alloys

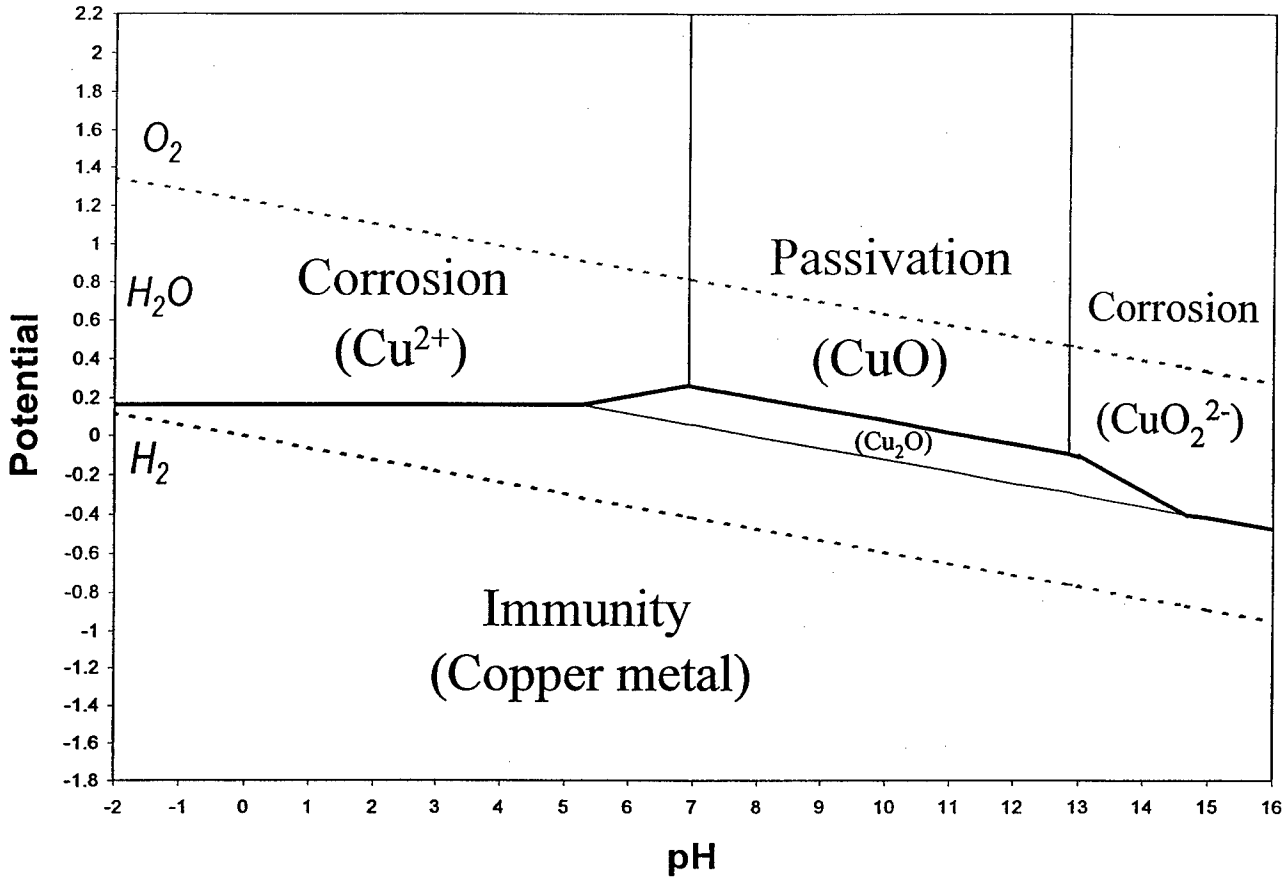

Fig. 5 – Pourbaix diagram for the system copper-water at 25 °C and activities for soluble species at 10^{-6} [30]

tested in this study exhibited any corrosion, including the very reactive magnesium. As indicated previously, this test may not be a good measure of the corrosion potential of in-service conditions.

The NIST 25-day exposure tests indicated that corrosion may be a problem and the crevice/weld corrosion test indicated superficial attack that may need further study to assess the potential severity [17]. The poor performance of this copper alloy in the NIST tests was not limited to the sodium bicarbonate as it was ranked the lowest of the eight alloys tested. These results can also be viewed as in agreement with anticipated corrosion behavior of copper due to the temperature of the tests, 150°C. Copper/ high copper alloys are regarded as having excellent corrosion resistance to both sodium and potassium bicarbonates and good corrosion resistance to sodium and potassium carbonates and hydroxides at ambient temperatures [46]. In general, with temperatures below 150°C corrosion rates are expected to be very low. Above 150°C the corrosion rates are appreciable and will increase substantially with temperature. This temperature phenomenon may account for the relatively poor performance of the copper alloy and the specific results for sodium bicarbonate found in the NIST tests.

The NIST post deployment experiments at ambient temperature found low mass changes at the two lower humidities [17]. An apparent inconsistency existed at the highest humidity, 93%, where the highest mass changes for any agent/alloy combination was found for the bicarbonate/carbonate mixture while the mass change for sodium hydroxide mixture remained low. The results for the bicarbonate/carbonate mixture at the two lower humidities are consistent with the same general corrosion behavior of copper alloys listed above. At the lower humidities, the corrosion of copper from the carbonate/bicarbonate mixture does not appear to be a corrosion concern. The results for sodium hydroxide at all three humidities can be considered consistent assuming the quantity of sodium hydroxide was not great enough to raise the pH above the stability region of the protection oxide. The presence of sodium hydroxide at the concentrations tested does not appear to be corrosive to copper alloys.

The results for the bicarbonate/carbonate mixture at 93% humidity might be explained by the specific behavior of coppers in carbonate/bicarbonate mixtures. Waters that have been softened with resulting high levels of sodium bicarbonate are known to be considerably more corrosive to copper than hard waters [5]. The same water unsoftened was not nearly as corrosive to the copper because analogous to steels, a protective layer of $CaCO_3$ formed acting much like the protective oxide layer. The chemistry of carbonates/bicarbonates can be somewhat complex. It is possible that in the NIST study the particular combination of high humidity and bicarbonate/carbonate mixture was the right chemistry to be corrosive to copper. This suggests that under certain conditions such as high humidity, increased corrosion rates for copper alloys might be obtained as a result of exposure to bicarbonate agents. It is recognized that this is only a possible rationale for the resulting behavior and additional analysis would be better understand this potential effect.

6.7 Nickel Alloys (Superalloys)

Nickel metal can be viewed as both somewhat active and somewhat noble in that it has a small region of stability where is will not react with water to form H_2 [30]. Analogous to stainless steels, the corrosion resistance of nickel alloys is more dependent upon the major alloying elements than the base material so that the Pourbaix diagram is not as applicable for nickel alloys as for other alloys. Nickel alloys can offer a wide degree of corrosion resistance having an advantage over stainless steels in that higher quantities of alloying elements, such as chromium and aluminum, may be used to increase the corrosion resistance of an alloy [47]. As a result, nickel alloys can be used over even a wider range of corrosive atmospheres than stainless steels. They have been used often as a replacement for austenitic stainless steels when stress corrosion cracking has been a concern [48]. Stress corrosion cracking can still occur in high temperature caustics, near 315°C and is highly dependent upon the applied potential.

Of the four studies identified assessing the corrosion caused by bicarbonate and carbonate agents, only the NIST study included a nickel alloy. The results indicated that the nickel alloy exhibited evidence of superficial attack in the 25 day exposure tests, and some evidence of attack in both the environmentally induced stress cracking test and the weld/crevice tests at 150°C [17]. In the post deployment test, the nickel alloy exhibited very small mass losses analogous to those for the stainless steels.

The results for the exposure tests and the post deployment tests were expected from a general corrosion stand-point. From a uniform corrosion perspective, the nickel alloys would be expected to behave at least as well as the stainless steels for the conditions created by the bicarbonate agents. The results for stainless steels in all four studies, and the generally good properties of nickel alloys toward alkalies suggest that with the possible exception of stress cracking, the aqueous corrosion of nickel alloys typical of those used in turbine engines would not be adversely affected by the bicarbonate-based agents. While the NIST results for the stress cracking tests indicate that for at least the one alloy tested, stress cracking does not appear to be a concern, it is important to note that the NIST tests were well below the temperature where stress cracking has been found. Additional evaluation would be needed to fully evaluate the potential for stress cracking.

6.8 Cobalt Alloys (Superalloys)

While less used than Nickel alloys, cobalt alloys may also be present in turbine engines. As cobalt alloys were not assessed in any of the reports found in the literature, the entire assessment of cobalt alloys will rely on general corrosion behavior. From a general or uniform corrosion perspective, cobalt alloys as a group are considered corrosion resistant due to the presence of the typical alloying elements used to obtain mechanical properties, e.g., chromium [49]. Cobalt alloys will undergo uniform attack, pitting, particularly in the presence of chlorides and stress corrosion cracking particularly as a result of pit formation. Contrary to nickel alloys, cobalt alloys are not considered as providing a high level of resistance to caustics [50]. As a

comparison, the corrosion rate of nickel in 50% NaOH at 150°C is 0.5 mils/year (considered excellent) while the corrosion rate of typical cobalt alloys in boiling NaOH range from 17 to 108 mils/yr (considered poor) [32, 50]. Cobalt alloys are susceptible to stress cracking only in a few environments such as strong caustics at elevated temperatures of 150 - 175°C. It is expected that the stress cracking behavior would be similar to nickel alloys.

The general corrosion behavior of cobalt alloys may be expected to be similar to nickel alloys with the important exception of behavior in alkaline environments. The limited general corrosion data in alkaline environments was for boiling concentrated sodium hydroxide solutions, which will likely be a far more aggressive environment than would be actually encountered through exposures to bicarbonate agents. It does point to the possibility that cobalt alloys may experience corrosion problems from exposure to bicarbonate agents under extreme conditions. The limited data available does not support assessing more moderate exposures.

6.9 Specific Turbine Engine Aqueous (Cold) Corrosion Issues

In addition to the general aqueous corrosion of turbine engine alloys provided above, information is also available on known cold corrosion issues of turbine engine components. The two most common forms of cold corrosion (below 315°C) documented on turbine components are pitting and fretting corrosion [22]. The evaluation of pitting was included to some extent within the NIST study while none of the studies identified evaluated the potential for fretting corrosion. Additional evaluation of these forms of corrosion is provided below. Other known cold corrosion problems such as stress corrosion cracking, corrosion fatigue, intergranular corrosion, erosion corrosion and general (uniform) corrosion are less prevalent than pitting and fretting. With the exception of erosion corrosion, these other forms of corrosion were evaluated to some degree within the four studies identified and to the extent possible in the preceding sections. No further evaluation for these forms of corrosion will be provided. It must be noted that a relationship exists between environmentally induced stress cracking and pitting. Pits can act as sites for crack nucleation so that any indication of pitting should also raise cautions on the possibility of stress cracking.

6.9.1 Pitting

Pitting of turbine engine components has been documented with low alloy steels and certain stainless steels [22]. This form of corrosion is very detrimental in that a relatively small amount of corrosion can greatly reduce the mechanical properties of the alloy resulting in failure of the component. It has long been established that pitting is a particular problem for many alloys when chlorides are present in the environment, for example from marine exposures. The presence of chlorides, while a predominant cause of pitting, may not be the only cause. Metal ions and dissolved gases have been shown to result in pitting under certain conditions. Pitting has also been found at higher temperature, 100°C, in more benign environments such as pure water [51]. This phenomenon is highly localized and cannot be predicted through the use of Pourbaix diagrams that describe the equilibrium thermodynamics of the entire system. Within the pit itself,

considerably different pHs and potentials can exist as compared with the bulk environment. For example, pitting is known to occur under conditions when the bulk system predicts passivation of the metal/alloy surface. Due to the complex nature of pitting a complete evaluation is beyond the scope of this report. Some general information is provided below for use as an indicator for the potential of pitting.

The bicarbonates themselves are known to affect pitting of copper alloys [51]. Waters with a lower pH of 5-7 with low levels of bicarbonates have been found to cause pitting. Similar waters with a higher level of bicarbonates for the same pH range do not. No other general information was found on pitting caused by the bicarbonate agents themselves.

A better evaluation of the effect of bicarbonate agents may be with environments that also contain chlorides as was performed in the NIST study. Aircraft will be exposed to marine environments so that chlorides are expected to be present. The NIST study included ASTM salt water in their post deployment tests to account for this fact. The steels and stainless steels typical of those that have been documented as failing from pitting did not show any evidence of pitting in their 30 day exposure test [17]. The NIST results are in agreement with very general pitting behavior under the assumption that the main effect of the bicarbonate agents is pH. For environments containing chlorides, the pH has been shown to be negligible on the effects of pitting of steels, including stainless steels, in moderate pH ranges [51]. This suggests that the pH effect of the bicarbonates and their breakdown products would not be expected to alter pitting behavior of steels and stainless steels.

Although not a direct problem documented with cold corrosion of aircraft, it is important to note that the NIST study did find pitting of aluminum with the sodium hydroxide - salt water exposure at 20% humidity. This finding is somewhat contrary to general pitting information. Pitting of aluminum over the pH range, 4 to 10 has been found to be relatively independent of pH [51]. Many possible factors may account for this finding. It is possible that the aluminum would have been pitted by the ASTM salt water without the sodium hydroxide. The low humidity may allow the chloride concentration to be higher than in the other humidities, i.e., less diluted. Another possible explanation is that the sodium hydroxide - salt water at 20% humidity has a higher pH, again due to a reduced dilution factor, and that the pH may be above the range verified as not affecting pitting. It is not possible to draw any definitive conclusions based on this one test.

6.9.2 Fretting Corrosion

Fretting corrosion has been documented as a particular concern for titanium alloys [22]. Fretting corrosion requires both consistent mechanical vibration of tight fitting surfaces in addition to a 'corrosive' environment. The general mechanism is that the vibrations serve to reduce or remove the protective oxide that naturally forms in the exposure environment allowing uniform corrosion or pitting corrosion to proceed. Changes in the environment that may reduce the ability of the alloy to form the protective oxide may also exacerbate fretting corrosion.

Fretting corrosion was not directly considered in the four studies identified assessing the corrosion of bicarbonate and carbonate agents. As indicated previously, the results from the studies with titanium indicate that the presence of bicarbonates and their breakdown products do not appear to alter the environment to reduce the formation of the protective titanium oxide layer. [12, 13, 17]. This suggests that the bicarbonate agents may not increase the potential for fretting of titanium.

6.10 Physical Effects

The pre-existence of known fretting problems on turbine engines indicates that there are mated surfaces that may be susceptible to the physical abrasiveness of the bicarbonate agents. The abrasive effects of sodium bicarbonate is illustrated in its recent use as an environmentally friendly alternative to remove paint from military aircraft. Analogous to sand blasting, the sodium bicarbonate powder is used to physically remove the paint from the surface. An unaccounted for side effect of this technology was increased wear and corrosion in areas where the sodium bicarbonate would become entrapped in tight fitting and overlapping joints. Due to normal vibrations that occur in flight, the abrasiveness of the sodium bicarbonate was wearing away the coatings used to protect the surfaces, e.g., paints and metal plating and ultimately wearing the metal substrate as well. As found 50 years ago by the U.S. Army Corps of Engineers, dry chemical agents may cause increased physical damage such as galling and/or increased wear of high tolerance engine components.

In addition to the physical wear of the metal surface, the abrasiveness of the bicarbonates may also increase effective corrosion rates. As described previously, metals and most alloys rely on the development of solid corrosion products to reduce or essentially eliminate corrosion. Any mechanism that will reduce or eliminate this protective layer will increase corrosion. In the example described above, the sodium bicarbonate was found to also physically remove the passive aluminum oxide layer that is responsible for reducing the corrosion of aluminum. As a result the corrosion rates were higher than would be expected based on the environment and pH. Such an effect would not be limited to aluminum and would be expected to increase the effective corrosion rate of all of the alloys used on aircraft.

6.11 Summary of Aqueous Corrosion and Physical Effects

The four studies identified in the literature assessing the corrosion potential of the bicarbonate or carbonate agents were mainly aimed at the aqueous corrosion of typical storage and distribution systems. As a result, a limited number of different alloys were tested that may not be fully representative of those used on aircraft. Significantly different corrosion results may be obtained from the alloys in actual use. The four studies also assess different bicarbonate or carbonate agents and use different test methods to evaluate the corrosion leading to differences in results. The NIST study was the most comprehensive of the four in that it included a broader range of alloys and tests, and included analysis of intergranular corrosion, crevice corrosion, environmentally assisted stress cracking and pitting in addition to the uniform corrosion assessed

in the other three studies. The NIST study has the same limitation as the other three studies in that the alloys tested were not fully representative of those used on aircraft. As a result of these limitations, the data assessing the bicarbonate agents is not complete enough to fully evaluate their potential corrosive effects.

In general terms, the results of the four studies can be viewed as consistent with expected corrosion behavior predicted by Pourbaix diagrams and other corrosion principles. With the exception of the environmentally induced cracking results for the 13-8MoPH stainless steel, the majority of the results indicate corrosion will be more a long-term exposure problem than an immediate one. Although this analysis cannot be definitive particularly for pitting and stress cracking, the following general corrosion behavior is suggested through the preceding analysis.

- For the majority of the alloys considered the effect of the bicarbonates appears mainly to be related to pH. A notable exception is copper alloys where bicarbonate/carbonate chemistry may affect corrosive attack. In cases where solid carbonate species may form, they have the tendency to increase corrosion resistance.

- For aluminum alloys it is possible that the pH can be raised above that for the stability of the passive layer through the formation of hydroxides. This is consistent with the experimental data indicating that in some cases corrosion was found and in other cases no significant corrosion was found. These finding suggest that long-term exposures may result in corrosion. While no stress cracking was indicated in the NIST test results, it is important to note that they did not assess the alloys used on aircraft structures. These alloys are the most prone to stress corrosion cracking. Some evidence of pitting was also found but it was not determinable if this was related to the bicarbonate breakdown products (hydroxide) or the presence of sea salt in the NIST test. The known interaction between pitting and stress cracking indicates that further study of potential stress cracking is warranted.

- Magnesium was only included in one of the four tests that assessed mainly uniform corrosion. No evidence of corrosion was found in that test but it is difficult to analyze the exact exposure scenario and the results are discounted. Unlike aluminum, the pH of the bicarbonate agents is in the region where a passive layer does not form unless significant quantities of carbonates or hydroxides form. This suggests that exposures to bicarbonates may be result in corrosion. It is possible that the corrosion might decrease with exposure time if the breakdown products raise the pH high enough.

- From a purely pH perspective, copper would be expected to exhibit acceptable corrosion resistance upon exposure to the bicarbonate agents and their respective carbonates and hydroxides. The experimental data found evidence of corrosion

with the different copper alloys tested, suggesting more than a pH effect. This result might be due to the complex nature of the bicarbonate chemistry under certain conditions or related to the higher temperature of some of the tests. None-the-less, it points to potential corrosion issues with exposures to electronics or other copper components, particularly in long-term scenarios. No evidence of pitting or cracking was found on the single copper alloy included in the NIST tests.

- For mild and alloy steels, stainless steels, titanium alloys and nickel alloys the experimental results agree well with the results predicted through the Pourbaix diagrams and other general corrosion data. While, in most instances, the majority of these materials will likely not be affected by the bicarbonate agents, stress cracking was found for one of the stainless steels so that the effect of the bicarbonate agents might be catastrophic for some alloys. Nickel alloys are generally used to replace stainless steels when cracking is indicated, but nickel alloys are also prone to cracking, albeit at more elevated temperatures. Additional work to assess the particular alloys and exposures would be needed to further quantify this effect.

- Cobalt alloys used in turbine engines were not included in any of the studies. Little specific information is available on these alloys. In general, cobalt alloys are expected to behave similarly to nickel alloys except in alkaline pH, suggesting a potential corrosion issue. Additional study of cobalt alloys would be needed to further quantify the potential effects of exposure to bicarbonate agents and their break down products.

- The bicarbonate agents can have two physical effects both related to their abrasiveness. Physical scratching or galling may occur especially for tight fitting parts. The abrasiveness may also remove the passive scales that form resulting in increased rates of corrosion.

7.0 HIGH TEMPERATURE CORROSION ASSESSMENT

High temperature corrosion occurs above approximately 315°C and primarily includes three specific forms of corrosion: 1) hot-salt stress corrosion cracking, 2) rapid oxidation (combustion/fires) and 3) hot corrosion (sulfidation) [22]. As indicated previously, no specific studies were identified in the literature addressing the high temperature concerns for bicarbonate agents. The following assessment will rely mainly on general corrosion principles and general data and will be supplemented where possible with specific data that can be considered similar in nature.

7.1 Hot-salt Stress Corrosion Cracking and Rapid Oxidation

Hot salt stress cracking is a form of environmentally induced stress cracking. It is the result of the combination of high stress, high temperatures and high concentrations of chloride salts. The bicarbonate agents do not affect these three conditions so it is possible that these agents may not have any effect on this type of corrosion. Due to the lack of data available in the literature it is not possible to assess the effect of the bicarbonate agents to any greater degree.

Rapid oxidation (combustion) is not a prevalent corrosion issue but it has been observed on titanium [22]. Rapid oxidation can be viewed as a specialized form of general or uniform corrosion where the rate of attack (i.e., formation of titanium oxide) is extremely fast. The ignition temperature of titanium in air is 1625°C which is well above the normal operating temperature of turbine engines. In order to cause the onset of rapid oxidation, a significant problem must be present within the engine. Case studies have shown that the interference of loose particles with rotating parts can raise the temperature high enough to cause the combustion of the titanium parts. The bicarbonate agents would not be expected to exist as solids at the temperatures required for titanium combustion so that they would not be expected to contribute to this phenomenon. The melting points for sodium bicarbonate and potassium bicarbonate are 270 and 100-200°C respectively [52]. The bicarbonates break down to form carbonates that may also breakdown into oxides, none of which exist at solids at the temperature for the onset of titanium combustion. The melting point of sodium carbonate is 851°C and the melting point of potassium carbonate is 891°C. Sodium monoxide sublimes at 1275°C and the potassium oxides all decompose at temperatures below 500°C.

7.2 Hot Corrosion

Hot corrosion is a known problem with the nickel and cobalt alloys used in the hot end of turbine engines. Hot corrosion is caused by the condensation of molten salts on engine components. The major constituents of the molten salt are sodium and potassium sulfates that presumably form as a result of interaction between the sulfur and the sodium/potassium from the air and/or fuel. Hot corrosion is temperature dependent and most readily occurs between 700 and 925°C [21]. While sodium sulfate is generally considered the major constituent of the molten salt, the effective range of attack is not defined by the melting point of pure sodium sulfate. Pure sodium sulfate has a melting point of 884°C [52]. Other constituents in the combustion air may mix with the sodium sulfate to reduce the melting point of the effective salt resulting in the lower temperature range found in practice.

For land based or stationary turbine engines such as used in fossil fuel power plants, it has been suggested that below 0.008 ppm sodium by weight in air hot corrosion will not occur [53]. In order to avoid hot corrosion the fuel specifications for stationary turbine engines limit the quantity of sulfur (1%), sodium and potassium (0.2 to 0.6%) and vanadium (0.5 ppm) another contaminant thought to contribute to hot corrosion. For land based turbines, the combination of

fuel quality control and air filtration has proven to be effective in limiting hot corrosion to acceptable levels.

For mobile turbines (aircraft) fuel quality is maintained but it is impractical to install effective air filtration. The maximum total sulfur content of JP-5 and JP-8 is 0.4% and 0.3% by weight, respectively [54]. The specifications for JP-5 and JP-8 do not specifically include limits for vanadium, sodium or potassium. Even with the limited sulfur in the fuel, hot corrosion will occur on aircraft turbine engines and must be managed through the use of alloy selection and specialty coatings designed for hot corrosion resistance.

Based on the mechanism of hot corrosion it is envisioned that there are two ways in which the bicarbonate agents may effect hot corrosion. Just as is presumed in practice, the sodium or potassium may combine with sulfur in the combustion air to form sodium or potassium sulfate that precipitates on the cooler portions of the hot end of the turbine. This would only affect the "normal" creation of the molten sulfate if excess sulfur is available. If more potassium or sodium was available than sulfur, then additional potassium and sodium would not create more of the sulfate salt. In this case, the bicarbonate agents would not have a detrimental effect on hot corrosion. The second manner in which the bicarbonate agents may affect hot corrosion is if the agents themselves can replace the sulfate salt in the corrosion process. The mechanism for hot corrosion requires that the salt be molten, essentially taking the place of the water as an electrolyte in aqueous corrosion. If the carbonates are molten within the effective operating temperatures of the turbine, they may also cause hot corrosion similar to that found with the sulfate salts.

The melting points of the bicarbonate agents and their breakdown products may serve as a preliminary screen in evaluating their potential to cause hot corrosion. As indicated previously the bicarbonate agents will convert to their carbonates upon exposure to moisture or high temperatures, and may be further converted to their oxides on exposure to high temperatures. Corrosion data for carbonates may be predictive of the behavior of the bicarbonate agents for evaluating hot corrosion. The melting points for sodium carbonate and potassium carbonate are 851 and 891°C, respectively [52]. These melting points are nearly the same as for sodium sulfate which is known to cause hot corrosion, suggesting that it is possible that the potassium and sodium carbonates that may form from the bicarbonates can also serve as the molten salt required for hot corrosion to occur.

It is recognized that the assessment based solely on melting points is simplistic in that it does not account for the specific chemistry of the molten salt that will affect its ability to cause hot corrosion. Additional information was found in the literature on the potential corrosive effects of sodium carbonate that while not directly related to the potential for hot corrosion of turbine engines adds further support to the premise that carbonates may be capable of causing such an effect. The Department of Energy sponsored work evaluating the high temperature corrosion of Inconel 690 caused by sodium carbonate, calcium carbonate and sodium meta silicate [55]. Inconel 690 is a nickel-chromium alloy with excellent corrosion resistance in many aqueous

and high temperature atmospheres [47]. It is in the same family of alloys that are used in turbine engines and may be illustrative of the corrosion behavior of other alloys in this class. Samples of Inconel 690 were exposed to the three chemicals for 3 days maintained at 900°C and 1100°C [55]. These temperatures are reasonable compared with the normal operating temperatures of turbine engines.

At 1100°C, the sodium carbonate caused significant attack with evidence of intergranular corrosion [55]. The calcium carbonate did not appear to melt at 1100°C nor did it cause corrosive attack. The melting point for calcium carbonate is 1339°C [52]. Consistent with general hot corrosion behavior the carbonate that did not melt does not cause hot corrosion. On the other hand, the sodium carbonate appeared to melt and caused corrosive attack at the melt line suggestive of a hot corrosion type mechanism. The intergranular corrosion was measured at 0.67 mils/day (245 mils/yr) [55]. A high corrosion rate. Since the potassium bicarbonate has a melting point similar to sodium bicarbonate, it is reasonable to assume that it also would exhibit a hot corrosive attack under these conditions.

At 900°C neither of the carbonates exhibited evidence of significant corrosive attack even though the sodium carbonate appeared to melt [55]. This is also consistent with hot corrosion behavior where longer activation times may be necessary for the attack to occur at the lower temperature. Attack may still occur but it may take longer than three days under these conditions. This finding does not negate the finding of significant corrosion at 1100°C. In addition, the lower temperature range of hot corrosion would not be limited by the melting point of the pure carbonate. Analogous to sodium sulfate, other constituents in the combustion air may serve to reduce the melting point lowering the temperature range for attack that may occur in practice. Both sodium and potassium bicarbonates may cause hot corrosion within the normal operating temperatures of turbine engines.

7.3 Physical Effects

The main high temperature physical effect that has been cited is clogging of cooling holes in the blades and veins. No direct literature was found on the potential of the bicarbonate agents to cause this effect. Anecdotal information was provided that a test was performed to evaluate this effect but a report could not be identified in the literature to verify it [27]. According to the anecdotal information, the test consisted of spraying a dry chemical agent into an engine followed by running the engine. Evidence was reportedly found for clogging of the cooling holes with significant quantities of corrosion. While this information is only anecdotal and could not be verified in the literature it has been well established that ingestion of small particles into a turbine engine can have such an effect. For example, experience with aircraft stationed in the Persian Gulf indicated that ingestion of small dust particles normally present in the air led to severe clogging of cooling holes [56]. As a result, the engine components were found to operate at higher than design temperatures leading to significantly more hot corrosion than expected and premature failure of components. To resolve this problem, a high pressure water wash system was developed to clean the blades on a routine basis or as evidence of excessive clogging was

found. Additional study would be required to determine the actual extent of the problem and the utility of this potential solution for bicarbonate agents.

7.4 Summary of High Temperature Effects

A major high temperature concern for the bicarbonate agents is the potential for causing hot corrosion. Historically, hot corrosion is viewed as the result of prolonged, repeated exposures to low concentrations of ingested salts such as sodium chloride from marine environments. In contrast, the exposure to the bicarbonate firefighting agents would be in relatively high concentrations and in a single exposure. It is not possible to assess the quantitative effects of a single exposure from the data found in the literature. From a qualitative standpoint, it appears that the sodium and/or potassium in the agents may contribute to the creation of the adverse sulfate salts when excess sulfur is present. It also appears that the carbonate forms of the agents themselves may serve as the molten salt creating the conditions necessary for this type of attack to occur.

While no direct information was found documenting that the bicarbonate agents caused clogging of cooling holes, this potential effect cannot be dismissed. Evidence from dusty operation such as the Persian Gulf can be considered illustrative of the potential effects. The fact that exposure to the bicarbonate agents would be expected to occur from a single event may make this effect manageable. The high pressure water wash system may prove effective in reducing or eliminating the clogging problem and potentially the hot corrosion problem as well. This would require additional study to ensure that such as approach would be effective. It would also have the disadvantage that additional equipment would need to be fielded in order to reduce the collateral damage potential of the bicarbonate agents.

8.0 COSTS

In 1992, NRL performed a study for the USAF to address the potential maintenance costs of using bicarbonate agents in lieu of Halon 1211. The study was limited to considering costs from exposure to the engine and assumed that once exposed the engine would need to be returned to the depot. The study estimated that the engine repair costs could be as high as $40.5 million per year, with a per engine average repair cost of $250,000 per incident. In addition to the cost impacts, significant logistics and readiness impacts would also occur.

Based on the assessment that the bicarbonate agents may contribute to or cause by themselves hot corrosion, the premise of the NRL study is valid. It is prudent to completely remove the agent from inside of the engine before it can lead to hot corrosion, clogging of cooling holes and potential premature or catastrophic failure. Currently, the only method available to the field is to return the engine to depot. The high pressure water wash system might offer a solution to this situation. In addition to studies to determine effectiveness of the system for the bicarbonate agents, an economic analysis would need to be performed to determine if fielding

such equipment with the bicarbonate agents would be cost effective compared with fielding an alternative fire suppressant with reduced collateral damage potential.

From a aqueous corrosion standpoint, additional maintenance costs would also be expected. In addition to the clean up requirements, any resulting corrosion must be repaired. This is particularly true for the long-term exposures. Some short-term catastrophic effects are also indicated. The specific alloys that may exhibit catastrophic attack may require additional maintenance or potentially replacement adding significantly to the cost potential.

9.0 CONCLUSIONS

Very little data was found in the literature assessing the corrosion, materials compatibility or other potential collateral damage effects of bicarbonate-based agents. Far less data were found than was anticipated based on the prevalent view that these agents caused significant collateral damage. A single study, performed in the latter 1940s by the U.S. Army Corps of Engineers, was identified that assessed the physical effects of these agents with respect to moving parts. Only four other studies were found in the literature with direct assessment of the corrosion and materials compatibility effects of bicarbonate or carbonate based dry chemical agents. The tests that were run were limited mainly to the materials used for storage and distribution systems and do not cover the necessary range of corrosion or other damage issues relevant to all potential aircraft exposures. In particular was the lack of studies and data on the potential high temperature corrosion problems for turbine engines.

In order to perform a more extensive evaluation, it was necessary to supplement the limited data identified in the literature with general corrosion principles. It is recognized that this results in a qualitative assessment. The actual corrosion behavior of a particular aircraft or engine will depend greatly upon the specific alloys used and the physical design that cannot be evaluated with the data available. Of particular concern are pitting and environmentally induced stress cracking that may be highly alloy and environment specific. With this limitation in mind, the following general conclusions may be drawn.

- From general corrosion principles and the identified experimental data it appears that for most alloys used on aircraft the main aqueous corrosion concern of the bicarbonate agents and their breakdown products is pH. In some cases the pH of the agents or breakdown products is outside of the region where passivation would be expected to occur. Increased corrosion might result for aluminum, magnesium and potentially cobalt alloys particularly in long-term exposures. From a purely pH perspective, mild and alloy steels, stainless steels, titanium alloys and nickel alloys would not be expected to be affected by the bicarbonate agents.

- The one study that assessed environmentally induced stress cracking, i.e., the NIST study, found that one of the four stainless steels tested maybe susceptible to

this effect. Stress cracking is a particularly detrimental form of corrosion that may result in catastrophic failure. This finding suggests that the bicarbonate-based agents should not be considered for use on stainless steels until this potential effect is studied further.

- The NIST study also identified pitting of aluminum for the sodium hydroxide - ASTM salt water post deployment exposure in one of the three test conditions. Pitting is also a detrimental form of corrosion in that a small amount of corrosion can result in greatly reducing the mechanical properties of the alloy and may lead to catastrophic failure.

- The abrasiveness of the bicarbonate agents may cause physical damage such as scratching and galling of tight fitting surfaces. The abrasiveness may also increase corrosion rates through the physical removal of the protective oxides that would normally form on metal and alloy surfaces.

- No information was found in the literature on the potential of the bicarbonate agents in causing hot corrosion of nickel and cobalt turbine engine alloys. From general corrosion principles and similar data, it is suggested that the bicarbonate agents may cause hot corrosion in two possible ways. The sodium and potassium of the bicarbonate agents may be added to the sodium and potassium normally ingested resulting in increased formation of the sulfate salts responsible for hot corrosion. It is also possible that the sodium and potassium carbonates that would form naturally as breakdown products of the bicarbonates agents may also replace the sulfates as the molten salt leading directly to hot corrosion. This finding suggests that the bicarbonates would have a detrimental and potentially catastrophic effect on turbine engines particularly in longer-term exposures. While the limited data available does not allow a quantitative assessment particularly for short-term exposures, it does support the view that it is prudent to completely remove these materials before allowing the engine back into service.

- No direct information was found in the literature on the potential of the bicarbonate agents to cause clogging of cooling holes in the turbine blades. This effect is known to occur in sandy and dusty environments resulting in decreased performance, decreased life or potentially catastrophic failure. High pressure water wash systems have been designed to reduce this effect and may offer an alternative to returning the engine to the depot in the case of bicarbonate agents. An evaluation would be necessary to determine its effectiveness both from performance and economic standpoints.

It appears that the bicarbonate agents can cause collateral damage to typical airframe and engine materials under certain exposure scenarios. The exact extent of the collateral damage could not be determined from the data available in the literature. For the airframe, the data

suggests that for the most part collateral damage in the form of corrosion would more likely result from long-term exposures than short-term ones. Long-term exposures cannot be ruled out even with extensive cleaning. It may not be possible to adequately clean up the agent in tight fitting joints and inaccessible areas. In addition, the potential for catastrophic failure was also indicated for one stainless steel. For the engine it appears that hot corrosion and clogging of cooling blades is possible. The available data suggest that collateral damage would more likely result from long-term exposures, but even more than for the airframe, the potential for short-term effects on the engine cannot be adequately assessed.

10.0 RECOMMENDATIONS

For many years, PKP has been used successfully on the flight deck to combat fires where the need to limit collateral damage is outweighed by the need to extinguish the fire quickly. The acceptability of PKP should continue for applications where collateral damage is not a concern.

The clean up procedures for aircraft exposed to PKP, provided in the NATOPS and the Tri-Service Corrosion Control Manuals, appear to be prudent based on the potential collateral damage identified in this study. While clarification of some of the procedures for particular agents is recommended, the general clean up procedures should continue to be followed. It is also recommended that the proponents for these three documents coordinate and integrate the clean up requirements and exact procedures to provide consistent policy and guidance.

To fully quantify the potential collateral damage indicated in this study, additional evaluations and tests would be needed. In light of the fact that other firefighting agents are available that are expected to have significantly less potential for causing collateral damage, it is recommended that PKP be adopted as the agent of last resort for use on fires where collateral damage is a concern.

If the other potential agents should not prove viable for small fires, it is recommended that a comprehensive test protocol be developed that considers all of the potential materials that will be exposed on the airframe, engine (powerplants) and electrical components. Emphasis should be placed on the alloy and environment-specific corrosion issues, such as environmentally induced stress cracking, raised in this study.

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Appendix A

Use and Interpretation of Pourbaix Diagrams

Pourbaix diagrams are thermodynamic constructs describing the electrochemical and corrosion behavior of metals. These diagrams are used to show the specific conditions of potential (voltage) and pH that result in immunity (no reaction) or corrosion in the forms of soluble ions or solid species. The diagrams can be used to indicate the direction of a reaction, the approximate composition of corrosion products, and the environmental changes that will affect corrosion. Pourbaix diagrams have three main limitations that must be understood to properly interpret their meaning. Firstly, as they are based on thermodynamic data, they do not provide any information on how quickly a reaction may occur, (i.e., they do not provide any information on chemical kinetics or rates), nor give any indication on the protective nature of any solid species that may form. Secondly, they do not account for non-equilibrium species that may form. Lastly, they are only accurate for the species and concentrations considered. Significantly different results can be obtained when different species, concentrations or temperatures are considered.

Figure A-1 provides the Pourbaix diagram for aluminum and water at 25°C. The dotted lines at the top of the diagram represent the thermodynamic stability of water. The top most dotted line represents the H_20 - O_2 stability and the lower dotted line represents the H_2O - H_2 stability. The fact that aluminum metal exists only below the H_2O - H_2 line indicates that aluminum metal will react directly with water (H^+ or OH^-) to form H_2 and depending upon the pH either Al^{3+}, Al_2O_3, or AlO_2^-. The Pourbaix diagram illustrates the potential and pH conditions for each of the stable species. Another way to interpret the Pourbaix diagram is illustrated in Figure A-2. Where aluminum metal is the stable species it has "immunity" from corrosion. It is thermodynamically impossible for it to react under those conditions of potential and pH. Where the soluble species Al^{3+} or AlO_2^- are present corrosion will occur. These species are soluble in water and will not provide any protection to the underlying metal. Where Al_2O_3 is the dominant species the aluminum will "passivate." The passivation is due to the presence of a solid species that forms on top of the metal. Two general cases exist for these solid species [30]. They may form as a non-porous film that essentially prevents further contact of the metal surface with the solution and are considered as providing "perfect" protection. The solid species may also form as a porous film that only reduces the contact between the metal surface and the solution. Porous films provide imperfect protection. The term passivation does not necessarily imply that no corrosion will occur. That will depend upon the solid species that forms. For the case of aluminum, Al_2O_3 is non-porous and provides perfect protection in most atmospheres. As with many metals the presence of chlorides is a notable exception.

To generate Figures A-1 and A-2 the activities (concentration) of the soluble aluminum species were set to 10^{-6} (1 ppm) which is typically used in corrosion to represent fresh waters. As the concentration of ions increase in solution, the stability of the Al_2O_3 will increase with respect to pH. Figure A-3 shows the stability regions when the ion activity is 1. The Al_2O_3 stability is extended to the approximate pH range of 2 to 14.5. This effect can help to reduce corrosion. As corrosion proceeds it will add aluminum ions to the local solution thus expanding the stability range for the Al_2O_3.

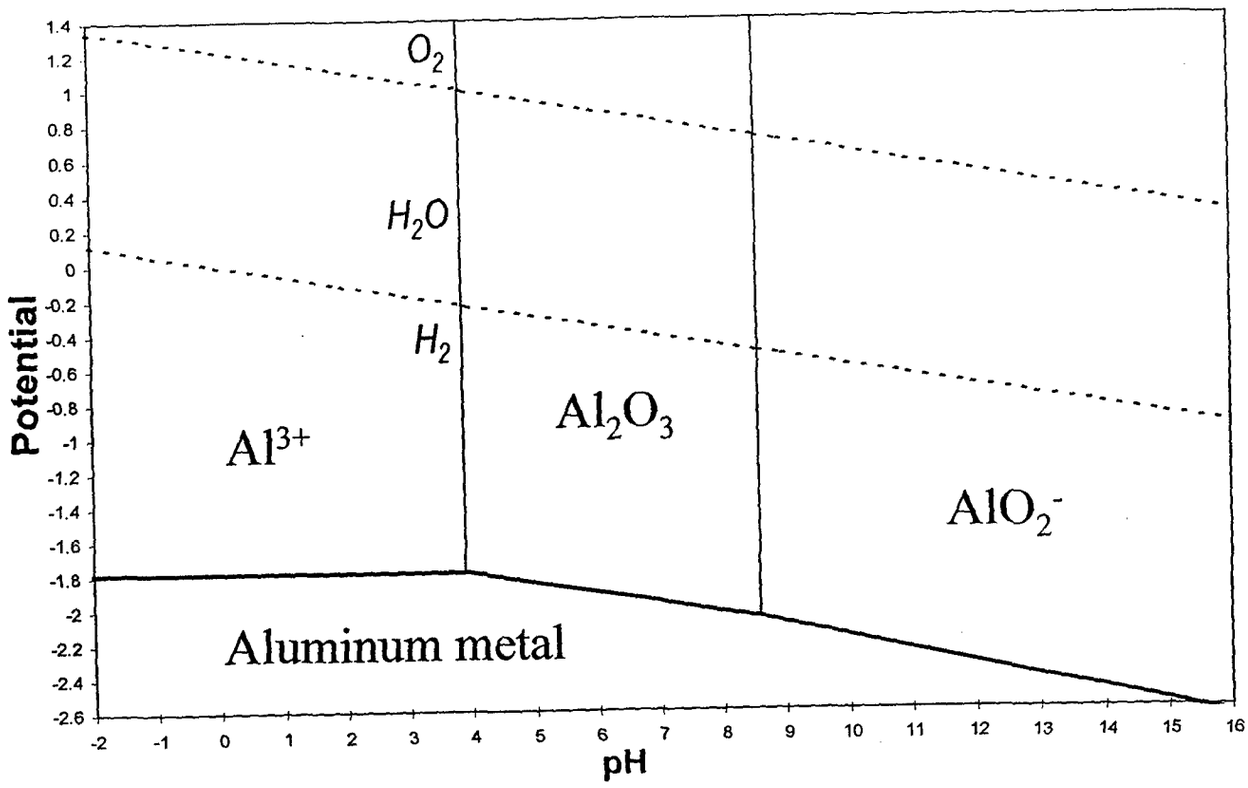

Fig. A-1 – Pourbaix diagram for the system aluminum-water, at 25 °C and activities for soluble species at 10^{-6} [30]

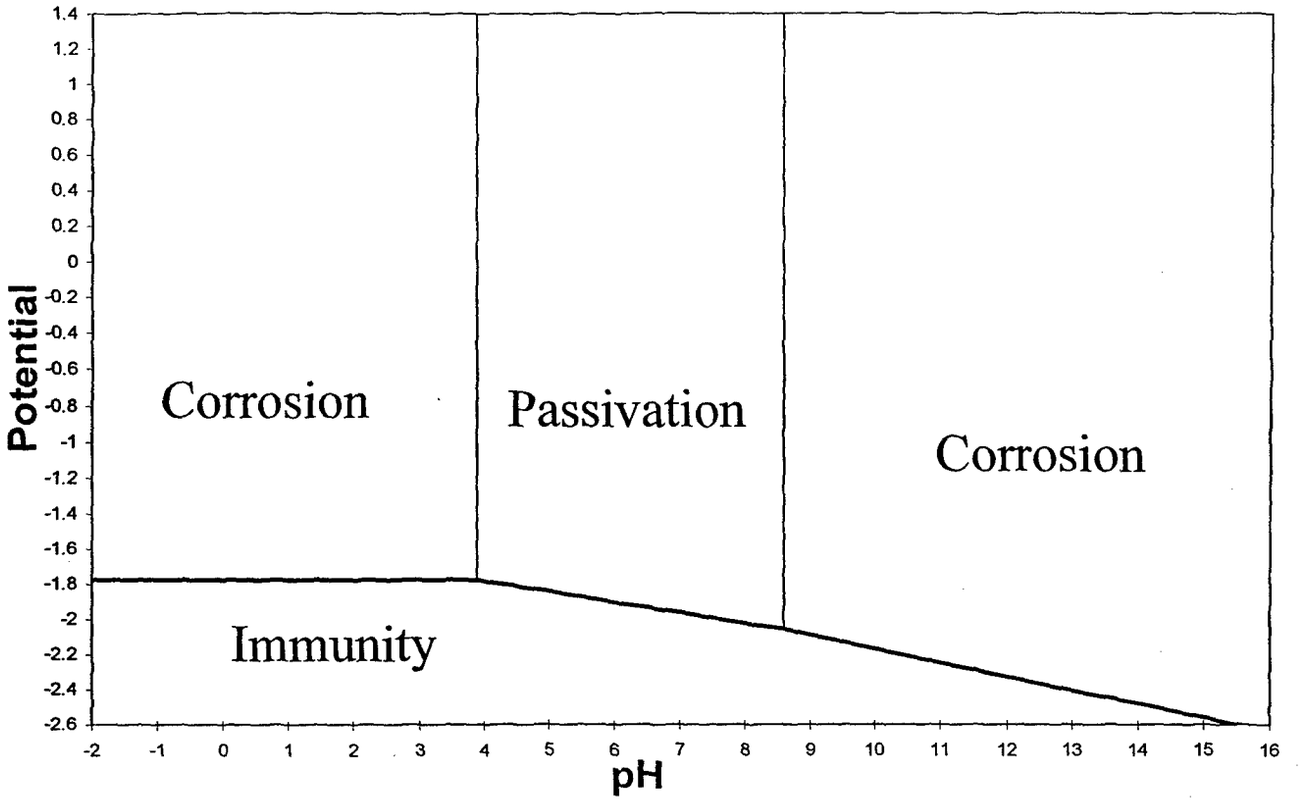

Fig. A-2 – Pourbaix diagram for the system aluminum-water at 25 °C and activities for soluble species at 10^{-6} showing regions of corrosion, passivity and immunity [30]

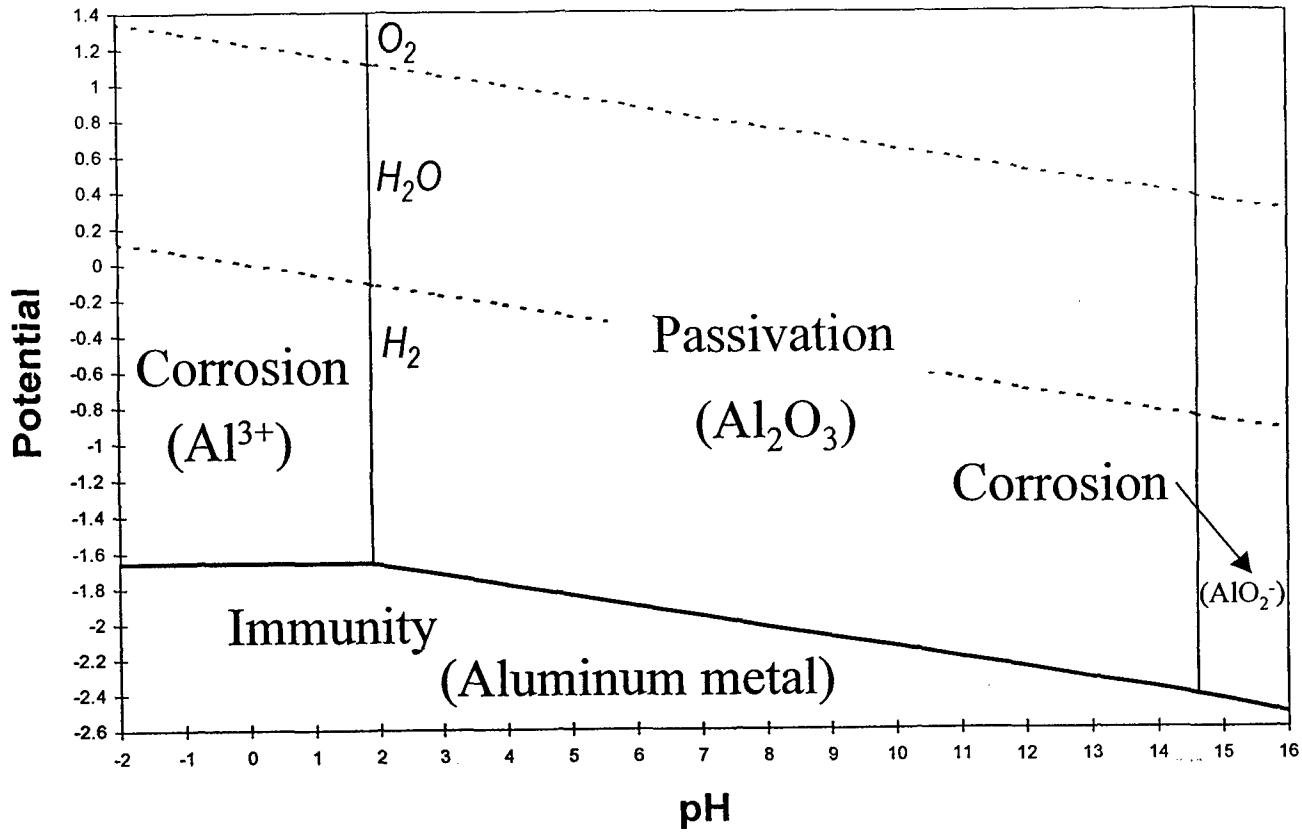

Fig. A- 3 – Pourbaix diagram for the system aluminum-water at 25°C and activities for soluble species at 1 [30]

The interpretation of the Pourbaix diagrams for aluminum - water is relatively straight forward because the stability of the corrosion products depend solely on pH. For example, in Figure A-1, the vertical line between Al^{3+} and Al_2O_3 indicates that potential plays no part in the equilibrium of these two species. Their relative stability is solely dependent upon pH. On the other hand, for some metal species such as iron, changes in potential due to the presence of oxidizers will effect the pH range over which the passive layer will be stable. This is shown in the iron - water Pourbaix diagram provided in Figure A-4 [30]. In this case, the interpretation of the Pourbaix diagram is less straight forward than for aluminum because the potential of the metal must also be known. For atmospheric exposures, the most common oxidizer is the O_2 in air. To interpret the Pourbaix diagram for atmospheric exposures, it is necessary to know the potential of the metal in the presence of O_2.

For example, it has been demonstrated experimentally that without the presence of O_2, the potential of iron is always below the H_2O - H_2 line, indicating the possibility of H_2 evolution (corrosion) [30]. At pHs between approximately pH 9.5 and 12.5, the potential is within the stability region of Fe_3O_4 and is very nearly identical to the Fe - Fe_3O_4 equilibrium line shown in Figure A-4. For all intents and purposes, the pH range over which passivation will occur without O_2 is defined by the equilibrium line between Fe (metal) and Fe_3O_4, i.e., pH 9.5 to 12.5.

In the presence of O_2, experimental data indicate that the potential of the metal is raised above the H_2O - H_2 line at pH 5 and above [30]. Below pH 5, the potential of iron is below the H_2O - H_2 line, indicating H_2 evolution and the formation of the non-protective species Fe^{2+}. Although the potential at pH 5 is above the H_2O - H_2 line, it does not automatically mean that iron will be passivated. At pH 5 and potentials above the H_2O - H_2 line, two species are potentially stable: Fe^{2+} and Fe_2O_3. Which species will form is dependant upon the actual potential. Experimental data indicate that the potential is not high enough for Fe_2O_3 to be the stable species until pH 8. Therefore, over the pH range 5 to 8, the potential is such that the non-protective Fe^{2+} is still the stable species. Corrosion will also occur over this pH range. It is not until pH 8 that the protective Fe_2O_3 becomes the stable species and iron will passivate.

It is not possible to use a Pourbaix diagram to predict the results described above. Data must be provided in order to use the Pourbaix diagram to predict the species that will form. The type of data needed will depend upon the particular metal and other species in the environment. In some cases, such as for the aluminum - water system, the exact potential is not needed. This is because firstly, the Pourbaix diagram indicates that when water is present, the aluminum metal stability region is always well below the H_2O - H_2 line. In other words, the potential is always above the aluminum metal stability. Secondly, for all potentials above the aluminum metal stability, only one species exists at a given pH. In order to determine which species will form in the presence of water, Al^{3+}, Al_2O_3, or AlO_2^-, only the pH is needed. On the other hand, for cases such as the iron - water system, several species may be stable at a given pH. It is necessary to know both the pH and the potential in order to use the Pourbaix diagram to predict corrosion.

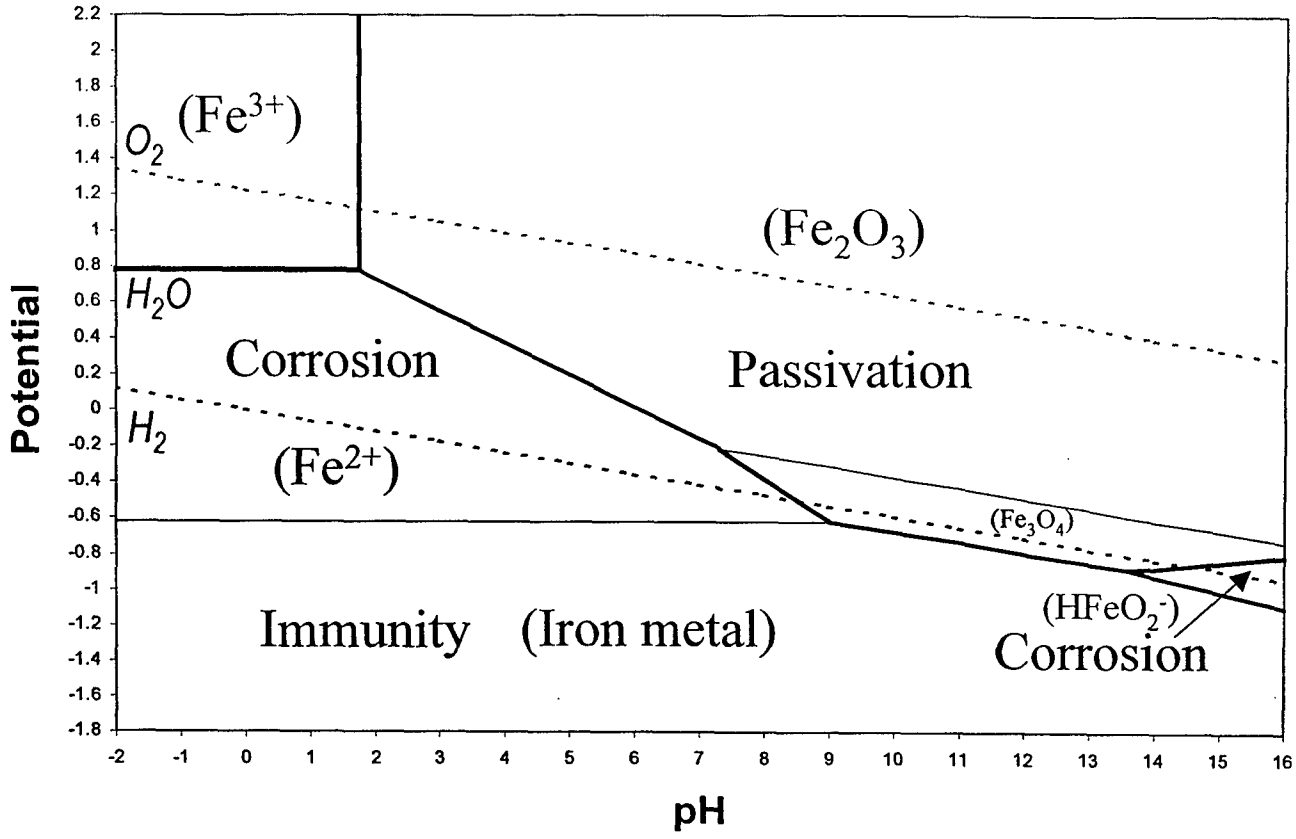

Fig. A-4 – Pourbaix diagram for the system iron-water at 25 °C and activities for soluble species at 10^{-6} [30]

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1. On the Cover Page, the author code is wrong. It should be NRL/MR/6180--99-8417, not NRL/MR/6170--99-8417.

2. On the Cover Page, F.W. Williams name is spelled wrong. It should be F.W. Williams not F.W. Willimas.

3. We regret any inconvenience.

Kathleen Parrish
Publications Branch