Thermal Control System
Corrosion Study

Robert Yee, Rolfe A. Folsom, and Phillip E. Mucha

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Thermal Control System Corrosion Study

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EXECUTIVE SUMMARY

As a part of the Systems Autonomy Demonstration Project managed by Ames Research Center (ARC), the ARC Information Sciences Division is developing a thermal expert system which will automatically control the Space Station Thermal Control System (TCS) operation. This software will also provide fault diagnostics, recommend corrective actions to the Station crew, and perform some corrective actions in real time. Software development for this system was initiated using a “Brassboard” thermal bus made available to Ames by Johnson Space Center (JSC). This hardware was based on a Boeing Aerospace prototype, which was developed and manufactured by Sundstrand Aerospace Mechanical Systems of Rockford, Illinois. While at JSC, the equipment underwent modifications to interface with the the expert system.

PROBLEM

The modified brassboard was originally put into operation at ARC in May of 1988 and functioned without incident for about five months. At this time, reduced flow of the ammonia refrigerant to the bearings of the Rotary Fluid Management Device (RFMD) was noted. Examination showed that system filters were heavily clogged with a gray powdery residue. The filters were removed, cleaned in an ultrasonic Freon bath, and reinstalled. Subsequent operation revealed a gradual degradation in the flow rate, indicating the continuing accumulation of residue. At the same time, pitting of the aluminum filter connector seals was found, and a leaky condenser was removed which also showed surface corrosion. At this point, a formal investigation was initiated to determine the underlying cause of the corrosion and to develop corrective and preventive actions.

STUDY APPROACH

The corrosion study was planned to investigate two related areas thought to contribute to the contamination potential: the chemical reactions that cause the corrosion and their relation to specific design characteristics and materials composition of system elements; and the operating and maintenance procedures used at ARC. The latter issue is pertinent since at least two other similar systems are currently in operation, one at Boeing Aerospace and Electronics (BA&E) in Seattle, and one at JSC, neither having experienced the problems which occurred at ARC; the system design and the choice of materials used obviously play a role in creating the corrosive environment.

Chemical analysis was undertaken of both residue collected from system filters and of the anhydrous ammonia refrigerant. Since it had been postulated that the corrosion had been induced by residual traces of Freon constituents, with which the system had been cleaned, particular attention was directed toward detecting the presence of chlorides. Chlorides are known to contribute to corrosion mechanisms.
STUDY RESULTS

The residue was analyzed by four separate agencies, allowing a relatively accurate determination of the composition of this material. Constituents identified included aluminum, by far the largest metal contributor at about 30% by weight; ammonium, chlorides, and carbon at 3% to 5% each; and small amounts of organic compounds. Of great significance was the finding of a substantial amount of water trapped in the solid residue material, since water can facilitate a number of damaging effects. The water was introduced into the system via a leak in the condenser loop. The presence of fluorine was also detected, supporting the thesis that Freon residue remains in the system.

Samples of both the source ammonia and of ammonia used in the TCS were carefully analyzed with specific emphasis on the presence of water and chlorides. Results indicated the source sample to contain less than 200 ppm of water and less than 20 ppm of any other organic or metallic substance, including chlorides. The bus sample showed similar results, although the amount of chlorides detected, while still very small (<25 ppm), was at least 10 times greater than that in the source sample.

Considerable attention was given to the materials which comprise the ARC brassboard, particularly those coming in contact with ammonia. A comprehensive list of materials was generated by the Brassboard manufacturer, such that parts or components could be evaluated with respect to their compatibility with ammonia, Freon, or both. The metallic elements were also considered for potential galvanic corrosion when coupled with aluminum. Such potential was found to exist, most notably with respect to stainless steel. Furthermore, certain seal materials, principally ethylene propylene rubber (EPR), were used which are known to absorb Freon, thus providing a source of chlorine during subsequent operation in ammonia.

Operating, maintenance, and recharging procedures were sought and obtained from the three thermal bus systems now in operation: the ARC brassboard, the JSC Ground Test Article, and the Boeing Aerospace and Electronics (BA&E) Internal Research and Development (IRAD) unit. Significant differences were sought that could help to explain the ARC problems, which did not occur in the other systems. Differences were found, primarily involving the cleaning and handling processes used and in the purity of the ammonia with which the buses were charged. All users noted the difficulty of purging, evacuating, and adequately sealing the systems each time ammonia was purged and recharged.

SUMMARY CONCLUSIONS

Based on the chemical composition of the filter residue and the constituents of the ammonia, it was concluded that sufficient water was present to allow corrosion of the large aluminum parts merely by the reaction of the water with aluminum in a high pH (>9) solution. Although this reaction can proceed with no catalyst, the presence of chlorides will accelerate the process. Water is removed from the liquid phase by reaction with the aluminum surface. In addition, the chlorides may have formed an ammonia electrolyte which initiated galvanic corrosion when coupled with the more noble metals in the stainless steel,
and chloride salts alone will also corrode aluminum. Each of these corrosion reactions was facilitated by the lack of any protective coating on the aluminum components.

**SUMMARY RECOMMENDATIONS**

Recommendations to preclude recurrence of the corrosion experienced include design, materials, and procedural changes.

**Design Changes**—Recommendations include a revised specification for the condenser O-ring seal retention groove configuration and a change of material to neoprene for this seal. For the RFMD, it is recommended that the internal filter be eliminated to reduce pressure drops, since the bearing this filter protects has proven to be more robust than anticipated. Filter designs should allow servicing without requiring purging the system of ammonia. Of equal importance, a system design which minimizes the number of fittings will greatly improve the maintainability characteristics of the bus.

**Materials Changes**—It is recommended that components in contact with ammonia include the firm specification for neoprene for all seals, that all aluminum surfaces be protected by a chemical film process such as Alodine, and that as few different metals as possible be used. The ammonia used should be the purest available, at least 99.9995% pure.

**Operational and Procedural Changes**—It is recommended that the design include the capability to conduct leak checks at ambient and to establish optimum vacuum levels required during system charging. The cleaning process is equally important; it is recommended that components be cleaned in an ultrasonic bath of alcohol or hot distilled water rather than Freon of any kind. They must then be protected by proper packaging, handling, and storage procedures until installed. Strict conformance to procedural instructions must be observed, and rigorous quality control measures established and monitored during all phases of operation and maintenance.
<table>
<thead>
<tr>
<th>SYMBOL</th>
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<tbody>
<tr>
<td>ACBL</td>
<td>alpha chemical and biomedical laboratories</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>aluminum oxide</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>aluminum hydroxide</td>
</tr>
<tr>
<td>ARC</td>
<td>Ames Research Center</td>
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<tr>
<td>BA&amp;E</td>
<td>Boeing aerospace and electronics</td>
</tr>
<tr>
<td>BAO</td>
<td>Boeing aerospace operations</td>
</tr>
<tr>
<td>BPRV</td>
<td>back pressure regulator valve</td>
</tr>
<tr>
<td>CHN</td>
<td>carbon/hydrogen/nitrogen</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EPR</td>
<td>ethylene propylene rubber</td>
</tr>
<tr>
<td>H₂</td>
<td>hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>water</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>g</td>
<td>gas</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>IRAD</td>
<td>internal research and development</td>
</tr>
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<td>JSC</td>
<td>Johnson Space Center</td>
</tr>
<tr>
<td>LLNL</td>
<td>Lawrence Livermore National Laboratory</td>
</tr>
<tr>
<td>MDL</td>
<td>minimum detection level</td>
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<tr>
<td>MS</td>
<td>mass spectrometry</td>
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</tbody>
</table>
NCG  noncondensible gas
NH₃  ammonia
NH₄⁺ ammonium ion
OH⁻ hydroxide ion
pH  potential of hydrogen (hydrogen ion concentration)
ppm parts per million
RFMD rotary fluid management device
s  solid
SADP system autonomy demonstration project
TCS thermal control system
TEXSYS thermal expert system
WDX wavelength dispersive x-ray spectroscopy
THERMAL CONTROL SYSTEM CORROSION STUDY

INTRODUCTION

As part of the Systems Autonomy Demonstration Project (SADP), Ames Research Center (ARC) has undertaken the development of a thermal expert system (TEXSYS) to automatically monitor and control the TCS with minimal human involvement. TEXSYS will also identify, diagnose, report, and in some cases correct certain system malfunctions.

Problem Background

To implement the project, ARC acquired a version of the TCS fabricated by Sundstrand Corporation, which was subsequently modified at Johnson Space Center (JSC) for this autonomous operation. It was delivered to ARC in May 1988. The system was then put into service and operated intermittently in support of TEXSYS development until it was shut down in April of 1989, to investigate the corrosion problem. Table 1 describes the operational and abbreviated maintenance history of the system (ref. 1).

Table 1. ARC brassboard operation

<table>
<thead>
<tr>
<th>Date filled</th>
<th>Date emptied and notes</th>
<th>No. of runs</th>
<th>Total operation time, hr</th>
<th>Idle time, hr</th>
<th>Total time with NH₃, hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>05/14/88</td>
<td>05/16/88</td>
<td>4</td>
<td>9</td>
<td>58</td>
<td>67</td>
</tr>
<tr>
<td>05/25/88</td>
<td>06/01/88</td>
<td>3</td>
<td>6</td>
<td>160</td>
<td>166</td>
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<td>06/28/88</td>
<td>09/02/88</td>
<td>13</td>
<td>24</td>
<td>1561</td>
<td>1585</td>
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<tr>
<td>09/07/88</td>
<td>11/14/88</td>
<td>30</td>
<td>67</td>
<td>1563</td>
<td>1630</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/88 - noted reduced RFMD bearing flow</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/15/88</td>
<td>12/22/88</td>
<td>18</td>
<td>31</td>
<td>687</td>
<td>718</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12/28/88</td>
<td>03/06/88</td>
<td>5</td>
<td>5</td>
<td>1490</td>
<td>1495</td>
</tr>
</tbody>
</table>

During the first five months of operation, the system functioned normally. Following this, however, coolant flow rates gradually decreased, thus jeopardizing the ammonia pump bearings. Investigation revealed that a significant amount of metallic residue had accumulated in the system filters, apparently due to internal metallic corrosion. This residue was removed, the system was cleaned to the extent practical, and operation resumed. Although flow rates were initially improved, deterioration continued with each subsequent operating period, and the current study was initiated to determine the fundamental causes of the corrosion problem.
Study Participants

It became apparent early in the study that the roots of the problem were complex, probably involving the system design, operating and maintenance procedures, and cooling system chemistry. The study team was therefore organized to provide expertise in all these areas. Design support was provided by the original design team from Boeing Aerospace and Electronics (BA&E), Seattle, and from the system developer and manufacturer, Sundstrand Corp., Aerospace Mechanical Systems, Rockford, Illinois. Operating protocols and test, maintenance, and recharging procedures were provided by JSC (refs. 2 and 3) and BA&E, Seattle (refs. 4 and 5), for the respective similar systems being successfully utilized in their facilities, as well as by the Ames SADP Project staff (ref. 6). The important chemical analysis activities were shared by several groups:

1. Lawrence Livermore Laboratory produced an approximate analysis of filter residue.

2. The Advanced Technology Group of Sundstrand Aerospace Mechanical Systems performed a qualitative analysis of filter residue.

3. The Analytical Engineering Group of Boeing Aerospace and Electronics, performed a detailed qualitative analysis of filter residue and formulation of chemical reactions.

4. Alpha Chemical and Biomedical Laboratories performed a detailed quantitative analysis of filter residue and of source and bus ammonia samples.

In addition to the chemical analysis support, technical expertise was provided by the following groups:

1. The ARC Systems Autonomy Demonstration Project provided technical direction, design, and operational expertise.

2. Sundstrand Aerospace Mechanical Systems provided design and development expertise, thermal bus operational experience, RFMD inspection, and damage assessment.

3. Clay Engineering provided refrigeration systems consulting, hardware, and operational considerations.

4. Boeing Aerospace and Electronics, Seattle provided thermal bus operational and maintenance experience.

5. Boeing Aerospace Operations, ARC provided study coordination, comparative procedure evaluation, and quality assurance expertise.
SYSTEM DESCRIPTION

The Sundstrand Thermal Control System (TCS) is currently located at Ames Research Center, Moffett Field, California, with the System Autonomy Demonstration Project Office (SADP). The project utilizes the TCS as a testbed to develop and demonstrate a real-time thermal expert system (TEXSYS). TEXSYS controls setpoint temperatures, reconfigures the system, diagnoses problems, and performs certain corrective actions.

The TCS, also known as the Brassboard, is a prototype thermal system candidate for the Space Station Freedom. The Brassboard is a thermal bus which provides heat rejection for thermal-producing equipment (such as computers and manufacturing equipment) aboard the Station. The TCS employs a unique closed-loop, two-phase (liquid and vapor) ammonia system for waste heat acquisition, rejection, and transportation. Figure 1 is a simplified systems block diagram of the Sundstrand TCS; figure 2 is a detailed TCS schematic representation (ref. 7).

Evaporators

The Brassboard contains two evaporators for heat acquisition which serve as a heat sink for heat loads. Liquid ammonia is fed into an evaporator from a cavitating venturi; the circulating ammonia absorbs heat from the heat load by undergoing a phase change into vapor. The ammonia exits the evaporator as wet vapor, i.e., a liquid and vapor mixture.

Heat loads are simulated by electric strip heaters. The Sundstrand TCS is designed to handle 25 kW heat loads, but facility limitations restrict operations to a maximum of 6.6 kW.

Condensers

The Brassboard contains two condensers to provide TCS heat rejection by vapor condensation. Ammonia vapors generated by the heat loads on the evaporators are pumped into the condensers. The condensers are heat exchangers that chill the vapor below its saturation temperature, converting the ammonia back to a liquid state.

The condensers are kept below the ammonia saturation temperature by utilizing an external cooling cart to circulate a mixture of 50% methanol and 50% water coolant in the condensers. The cooling cart conditions the coolant to ensure proper condenser temperatures.

In actual practice aboard the Station, there would be no cooling cart. Instead, heat pipe radiators in contact with the condensers would radiate the excess heat out to space.

Back Pressure Regulating Valve

The Back Pressure Regulator Valve (BPRV) is a pressure activated servo, located upstream of the condensers. The BPRV provides discrete control of vapor flow into the condensers. When a predetermined vapor pressure threshold is exceeded, the BPRV opens up to relieve the upstream back pressure.
by allowing vapor to flow into the condenser. Once the back pressure is relieved and falls below the pressure threshold, the BPRV closes and vapor flow to the condensers ceases.

The BPRV maintains a constant vapor pressure by balancing the upstream back pressure with an internal servo pressure. The internal servo pressure is adjustable via a servo control spring force. By adjusting the BPRV control spring force, the vapor pressure and its corresponding saturation temperature of the liquid ammonia throughout the system—denoted as the setpoint temperature—can be raised or lowered. Setpoint temperatures are set from 35° to 70° Fahrenheit ±3° during normal operations.

Cavitating Venturi

Immediately upstream from each evaporator is a cavitating venturi. If the outlet/inlet pressure ratio is sustained below a critical level, the cavitating venturi maintains a constant liquid ammonia flow rate into the evaporator. This mass flow remains at a constant level, regardless of downstream pressure variations due to system fluctuations and various operating conditions such as heat load and setpoint changes.

Accumulator

The accumulator manages varying system liquid ammonia inventory due to heat load variations, sink temperature variations, and liquid thermal expansion. The accumulator maintains a constant ammonia liquid level throughout the system by automatically adding or removing liquid to accommodate changing inventory requirements of the system. The Brassboard is typically charged with 32 lb of anhydrous ammonia.

Rotary Fluid Management Device

The RFMD is a rotary pump that integrates the previously discussed components by performing the following functions: 1) pumps liquid ammonia through the evaporator loop, 2) separates liquid and vapor ammonia from the evaporator exit lines, 3) pumps ammonia vapor through the condenser loop, 4) restaturates subcooled liquid from the condensers, 5) controls liquid level with the accumulator, and 6) separates and collects noncondensible gases (NCG).

The RFMD pumps liquid ammonia into the evaporators through the cavitating venturis. The liquid and vapor mixture generated from the heat loads is returned to the RFMD where the liquid and vapor are separated.

A rotating drum in the RFMD separates liquid and vapor from the evaporator by centrifuge action. The centripetal acceleration produces a rotating liquid annulus and a vapor core within the RFMD main chamber.

A pitot probe is submerged in the liquid annulus to sense pump head pressure. The head pressure generated is proportional to the square of the annular radius and the square of the rotational speed of the liquid annulus.
The saturation conditions in the main chamber of the RFMD are regulated by the BPRV. The BPRV regulates the system vapor pressure (back pressure) from the RFMD and its corresponding fluid temperature within the RFMD.

Vapors released from the BPRV enter the condensers and are returned to the cold side of the RFMD as subcooled liquid. The subcooled liquid passes through peripheral holes in the RFMD thermal barrier and mixes in an intermediate chamber with liquid from the main chamber. The resulting subcooled mixture is pumped by a pitot through atomizers and mixed with the vapors in the main chamber. The atomized liquid is immediately saturated by condensing some of the vapor, which reenters the annular rotating liquid. This subcooled liquid resaturation process ensures that liquid pumped to the evaporators is at a temperature equal to the RFMD vapor saturation conditions set by the BPRV.

System liquid inventory changes in the condenser and evaporator loops are performed by a spring bellows accumulator. The accumulator's liquid side has a level probe within the rotating liquid annulus; the vapor side of the accumulator is vented to the RFMD vapor space. If more liquid is leaving the RFMD than is being returned, the liquid level in the RFMD will move radially outwards. The bellows spring force will exceed the liquid-vapor pressure difference, forcing liquid out of the accumulator and into the RFMD until bellows spring force equals the liquid-vapor pressure difference. If more liquid is entering the RFMD than leaves it, liquid will be forced into the accumulator from the RFMD.

Noncondensible gases such as hydrogen and helium do not condense at liquid ammonia pressures and temperatures. If present, these gases degrade system performance. They accumulate in the cold side of the RFMD and are periodically vented out of the TCS.

CORROSION STUDY

A partial disassembly of the Brassboard was conducted to resolve the source of contamination plugging the filters. Tight project schedules, limited facility resources, and manpower limitations prevented a complete disassembly for inspection.

Filter Inspection

All seven stainless steel filters were removed from the Brassboard and inspected. Each filter exhibited varying degrees of residue contamination. The residue was gray and powdery. The most severe clogging was found in the RFMD outlet filters. The filters that are in decreasing residue contamination order are the F3, the bearing flow filter; F2 and F7, BPRV filters; and F1, the accumulator and RFMD filter.

Moreover, the aluminum crush washers for the filter fittings were found to be pitted.

Condenser Leak

Prior to charging the Brassboard with anhydrous ammonia, a routine pressure rise test was attempted. For a pressure rise test, the TCS is purged of ammonia, evacuated to a 300-micron vacuum
level, and then valved off from the vacuum pump. A vacuum gauge measures the pressure rise during a 15-minute interval to determine the system leak integrity.

Unfortunately, the Brassboard could not be vacuum pumped below the 600-micron level, which indicated a severe leak problem. The problem was isolated to a particular condenser by chilling each one separately with the cooling cart, continuously pumping down the system, and monitoring the system vacuum level. Condenser 2 was the culprit, since chilling condenser 2 would not allow the system vacuum to drop below the 800-micron level during continuous vacuum pumping. Cutting off coolant flow to condenser 2 and allowing it to rise to ambient temperature dropped the system vacuum level back to 600 microns.

Condenser 2 was removed from the system and disassembled for O-ring replacements. Inspection of the ammonia side of the condenser revealed corrosive pitting of the aluminum surface (fig. 3). The corrosion is more pronounced around the ammonia entrance, diminishing towards the exit. Figure 4 shows deposits of residue and figure 5 shows pitting along the condenser grooves.

The O-rings were found to be permanently deformed into a rectangular cross section that matched the rectangular-shaped O-ring grooves. The O-rings were also found to have insufficient squash by approximately 0.004 in., resulting in leaky seals.

Coolant residue showed a possible leak path that enabled coolant to penetrate the metal plates that isolate the ammonia from the coolant (fig. 6). Failure of the coolant O-ring could have allowed the methanol-water mixture to bypass the metal barriers by seeping through bolt holes and into the ammonia if the O-ring on the ammonia side of the condenser also failed.

**Rotary Fluid Management Device Inspection**

The RFMD was sent to Sundstrand for teardown inspection, cleaning, repairs, and reassembly (refs. 8 and 9). The cutaway view of the RFMD in figure 7 illustrates the components mentioned in the inspection findings.

The RFMD disassembly and inspection revealed the RFMD interior was contaminated with a gray metallic powder similar to the residue found in the system filters. Corrosion was observed on all bare aluminum components. However, the anodized aluminum and stainless steel components exhibited no sign of corrosion.

The rotating drum (figs. 7 -70 and 8) and other bare aluminum parts showed considerable pitting on all surfaces. The interior of the rotating drum (figs. 9 through 11) was pitted and covered with the gray metallic residue similar to that found in the system filters.

The rotating housing end cap (figs. 7 -58 and 12) was anodized and showed corrosion only where the anodized coating was not present. Figure 12 also shows the centrifugal seal corrosion (fig. 7 -195) is similar to that on the rotating housing. The anodized aluminum parts, such as the vane disk (figs. 7 -181 and 13), exhibited no sign of corrosion.
The reverse thrust bearing (fig. 14) and mating surface (fig. 15; also fig. 7 [−146, −62]); showed signs of excessive wear. The electroless nickel/Teflon coating on the bearing was completely worn off and the bearing was scored.

The thrust bearing and mating surface (figs. 7 [−137, 138, 139] and 16) showed no sign of wear or corrosion.

The condenser end and evaporator end radial bearings (figs. 7 [−92] and 17) displayed no sign of wear or corrosion. Furthermore, the carbon-lined bearing bushing (figs. 7 [−61] and 18) showed almost no sign of wear. The evaporator end bearing and bearing bushing conditions were surprisingly good despite the residue clogging the filter screen, which severely restricted the lubrication supply (fig. 19).

The demisters (figs. 7 [−85, 93], 20, and 21) are fabricated from a stainless steel mesh which showed no sign of corrosion but were contaminated with a considerable amount of residue. The demister chem-filmed aluminum housings exhibited very little evidence of corrosion.

The thermal barrier (figs. 7 [−124] and 22), which is constructed from polyetheretherketone (PEEK), was contaminated but showed no sign of degradation. Other stainless steel components such as the pitots (figs. 7 [−99, −100, −155], 23 through 25) and the other housing (figs. 7 [−9], 26, and 27) were contaminated but showed no sign of corrosion.

The condenser pitot was damaged during disassembly; the excessive amount of contaminant present in the RFMD made disassembly very difficult.

Solid Residue Chemical Analysis

Residue collected from the TCS filters was analyzed by several organizations, each using somewhat different analytical techniques with varying accuracy levels. Table 2 is a summary of the results of these analyses; the following sections provide added details regarding each survey.

Lawrence Livermore National Laboratory-Lawrence Livermore National Laboratory performed a preliminary, semiquantitative analysis of the unknown solid residue from the system filter of the Thermal Control System (ref. 10). Carbon/hydrogen/nitrogen (CHN) analysis detected approximately 3.6%, 5.3% and 7.8% of carbon, hydrogen, and nitrogen, respectively; infrared (IR) analysis found trace organics; mass spectrometry (MS) revealed trace phthalates; and x-ray fluorescence detected approximately 36% aluminum, 17% chlorine, 13% nickel, 10% iron, 1% copper, and less than 1% each of chromium, manganese, zinc, and lead.

The Lawrence Livermore National Laboratory analysis showed that the solid residue compound is mostly inorganic (aluminum and stainless steel), and contains small amounts of carbon and ammonia. It was noted, however, that testing equipment was not fully calibrated, that the analyses were hastily accomplished, and that no testing techniques used were specific for fluorine.
Table 2. Analytical findings of thermal control system residue

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percent by weight</th>
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<tr>
<td></td>
<td>LLNL</td>
</tr>
<tr>
<td>Metals</td>
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</tr>
<tr>
<td>Aluminum</td>
<td>=36</td>
</tr>
<tr>
<td>Iron</td>
<td>=10</td>
</tr>
<tr>
<td>Nickel</td>
<td>=13</td>
</tr>
<tr>
<td>Magnesium</td>
<td>-</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Copper</td>
<td>=1</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Organics</td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td>=17</td>
</tr>
<tr>
<td>Carbon</td>
<td>=3.6</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>=5.3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>=7.8</td>
</tr>
<tr>
<td>Ammonium</td>
<td>-</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
</tr>
<tr>
<td>Not identified</td>
<td>=4.3</td>
</tr>
</tbody>
</table>

<sup>a</sup>In addition to the elements shown, Alpha Chemicals and Biomedical Laboratories found quantities of < .01% of Ag, As, Ba, Be, Cd, Co, Mo, Sb, Se, Sn, Ti, Tl, V, W, and Zr.

**Sundstrand Aerospace Mechanical Systems**—A solid residue contaminant sample from the RFMD bearing lubrication-line flow filter was analyzed by the Sundstrand Aviation Mechanical Systems Materials Laboratory (ref. 11). Results indicated that the contaminants consisted primarily of aluminum (and some aluminum oxide), and lesser amounts of chloride, iron, and nickel. A water soluble ammonium salt and 4% carbon were also present. A small percentage of minute metallic particles were visually observed in the gray, somewhat amorphous contaminants. Subsequently, the RFMD was shipped to Sundstrand Aviation Mechanical Systems for disassembly and inspection. During the inspection process, it was noted that the interior of the RFMD was very dirty and covered with a gray powder similar to that found in the system filter. Sundstrand reported that this residue is very similar to that which they have previously found when chlorides were inadvertently introduced into ammonia-based systems.

**Alpha Chemical and Biomedical Laboratories**—Alpha Chemical and Biomedical Laboratories (ACBL) provided testing support and chemical analysis for a sample of unknown solid residue from the RFMD outlet filter of the Thermal Control System (ref. 12). ACBL was required to determine percentages of all metals, chlorides and organochlorides, and other organic materials exceeding 1% by weight.
These analyses were accomplished using a series of techniques including gas chromatography and mass spectrometry (GC/MS).

The metal scan revealed a high concentration of aluminum (32.5%), relatively high traces of iron (0.57%) and nickel (0.22%), and trace amounts of numerous other metals. The extreme amount of aluminum, along with the trace amounts of iron and nickel, indicated that there is some significant decomposition of inner metal surfaces from corrosive substances. The chloride content was measured at 3.10%, and the carbon analysis revealed 2.64% organic carbon and 0.31% inorganic carbon for a total carbon content of 2.95%.

The GC/MS chromatogram of the solid residue indicated that there was a significant amount of organic material in the form of a branched aliphatic alcohol. The actual concentration of the alcohol contaminant was not determined, but a rough approximation of 0.1% to 0.5% was obtained by semi-quantitative analysis.

**Boeing Aerospace and Electronics**– Boeing Aerospace and Electronics (BA&E) performed chemical testing and analysis on a 0.6-gram solid contaminant sample from the in-line system filter of the Thermal Management System. The requirements were similar to those imposed on ACBL (ref. 13). Analysis techniques included Infrared Spectroscopy and Energy Dispersive X-ray Spectroscopy (EDX).

The EDX results confirmed that aluminum was the most abundant element in the sample (27.8%), followed by water (12.5%), chloride (5.5%), ammonium (3.3%), iron (0.9%), and nickel (0.7%), with trace amounts of magnesium, chromium, and copper. The infrared spectrum of the sample provided results characteristic of condensed, phase hydroxyl (water or water of hydration) and of oxides. Also, there were indications that ammonium salts, carbonates, and ammonium compounds were present. The water content of the sample was determined by heating it to 100°C, and carrying the vaporized water into the titration vessel with a stream of dry nitrogen gas.

In order to support the theory that the TCS had been contaminated with Freon, BA&E performed an additional analysis of the solid residue to determine the presence of fluorine, by using an electron microprobe with a wavelength-dispersive X-ray spectroscopy (WDX) attachment (ref. 14). The presence of fluorine in the solid residue was confirmed, therefore supporting the conclusion that Freon (a chlorofluorocarbon) had not been completely removed from the system prior to filling with ammonia.

**Chemical Analysis of the Anhydrous Ammonia**

Alpha Chemical and Biomedical Laboratories (ACBL) undertook a chemical analysis of samples of anhydrous ammonia from the ammonia source bottle and from the Thermal Control Bus (ref. 15). The controlled supply sample and the bus sample were each provided to ACBL in 2.25-liter pressurized stainless steel bottles. For each sample, ACBL, using a variety of techniques, determined the percentage of water, organic contaminants, indications of aluminum, and presence of chlorides.

The water detection tests originally conducted for the source and bus anhydrous ammonia could sense water in amounts exceeding 1% by weight. At this sensitivity, no water was detected in either sample. Chloride content was determined to be low in both samples: approximately 1.8 ppm in the source sample and 25 ppm in the bus sample. Aluminum traces of 0.6 ppm were detected in the source
sample and 1.0 ppm in the bus sample. Organic contaminants consisting of 20 ppm were also detected in both samples. The CG/MS chromatograms of the source ammonia and the bus ammonia did not indicate the presence of any substantial organic contaminants or organic reaction products. Therefore, it was concluded that the source anhydrous ammonia and the bus anhydrous ammonia were relatively free of any organic or inorganic contaminants.

Additional testing for water content within both ammonia samples was pursued. ACBL conducted another analysis on the same source and on bus samples in which the determination of water percentage was accomplished to a minimum detection level (MDL) of 0.02%. In this case, the MDL was established by using a very large gas sample (10 ml) that was introduced into the gas chromatograph via a gas syringe. This analysis detected no water at the 0.02% sensitivity level in either the source or bus anhydrous ammonia samples.

CONCLUSIONS

The corrosion study participants formulated a number of conclusions from the results of the chemical analyses, the evaluation of materials, and the operating and maintenance procedures. While they are not proven conclusively, they represent the consensus of the investigators for the most probable fundamental causes. The conclusions center around two basic types of aluminum corrosion: induced by water in a high pH environment and by the presence of chlorides.

Water-Induced Chemical Reactions

The presence of even very small amounts of water in the Brassboard thermal bus was found to be potentially damaging. The analysis confirmed that water did play a role in the corrosion process, since a substantial percentage of water was found in the solid residue from the system filters. Furthermore, the finding of alcohols in the ammonia indicates that a condenser leak allowed water and methanol to enter the ammonia loop.

Contamination by water alone could account for the corrosion. Untreated aluminum is resistant to corrosion within the pH range of 4 to 9 because of the protective oxide layer which immediately forms on all aluminum surfaces when exposed to oxygen in air. However, at pH values outside the 4 to 9 range, the ordinary oxide layer of unprotected aluminum is susceptible to attack by water. When any water is introduced into the Thermal Control System while using ammonia as a refrigerant, the effective pH will be greater than 10, and the protective aluminum oxide layer will be compromised.

Many reactions could be written to represent the action of water at the extreme pH values; however, since the products can exist in a variety of states of hydration, the process can most simply be expressed as

\[
\text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3
\]

The actual reactions will depend on the concentrations of both water and, in this case, hydrated ammonia. As a result of the high pH and resulting compromise of the aluminum oxide layer, additional
water will then directly attack and oxidize the underlying aluminum layer to the hydrated oxide or hydroxide in accordance with the above reactions. This reaction may be written

$$2\text{Al}(s) + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(	ext{OH})_3 + 3\text{H}_2(g)$$

Chloride or other ionic species are not essential to this process, but are corrosive to aluminum and probably contributed to the corrosion process.

**The Role of Chloride**

The presence of a significant proportion of chloride in the solid residue and the small but far higher amount in the bus ammonia than in the source supply, is compelling evidence that the use of Freon in some way introduced this contaminant; no element was found internal to the system from which chlorides could be released. Evidence of fluorine in the residue supports this view. However, BA&E concluded that the halides from the Freon were not the primary cause of the corrosion of the aluminum surfaces in the system. Chloride may, nevertheless, participate in the corrosion process by compromising the aluminum oxide layer, since chloride salts alone will corrode aluminum. The study team concluded that a possible source of the chloride and fluoride found in the system was residual Freon left in the system during the refrigerant change from Freon to ammonia. A more likely source was an improper cleaning procedure. During this process, internal EPR O-rings were inadvertently left in filters immersed in Freon while undergoing ultrasonic cleaning. The O-rings swelled and soaked up Freon during the cleaning process. When the filters were reassembled back into the system, they released chlorine into the ammonia. In addition, it is possible that chloride ions were freed from the solid residue. The chlorides, then, will enable galvanic corrosion by serving as charge carriers to form an ammonia electrolyte.

Aluminum and aluminum alloys are quite susceptible to galvanic action by virtue of their position on the electromotive force (emf) series. Table 3 is an abbreviated galvanic series showing the position of aluminum alloys and other more noble metals. Note that there is a significant difference in potential between aluminum and stainless steel. This couple is the most likely contributor to the corrosion process observed; all elements of the steel alloys used were detected in the residue analysis, and large quantities of both aluminum and stainless steel were used in the construction of the Brassboard system (ref. 16).

**Procedural Contributions**

The results of the study dramatically illustrate the importance of careful operating and maintenance procedures in addition to the design problems described above. The incompleteness of the cleaning due to limited time and manpower resources contributed to the problem, as did the lack of recognition of the potential degradation attributable to small amounts of water and residual chlorides. These findings demonstrate the need for carefully-prepared operating and maintenance procedures and the imposition of rigorous quality controls.
Table 3. Abbreviated galvanic series

<table>
<thead>
<tr>
<th>Element</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>+0.18 to -0.40</td>
</tr>
<tr>
<td>Nickel</td>
<td>-0.07</td>
</tr>
<tr>
<td>Silver</td>
<td>-0.08</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>-0.09</td>
</tr>
<tr>
<td>Copper</td>
<td>-0.20</td>
</tr>
<tr>
<td>Tin</td>
<td>-0.49</td>
</tr>
<tr>
<td>Lead</td>
<td>-0.55</td>
</tr>
<tr>
<td>Mild steel</td>
<td>-0.58</td>
</tr>
<tr>
<td>Cadmium</td>
<td>-0.82</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>-0.64 to -0.96</td>
</tr>
</tbody>
</table>

RECOMMENDATIONS

The following recommendations are based on the findings of chemical and physical analysis of the Brassboard. The recommendations are designed to alleviate corrosion and enhance system reliability. Most of the recommendations are sufficiently general to be valid for the Sundstrand TCS and other ammonia thermal systems. A few of the recommendations fall outside the scope of this corrosion report, but are reported anyway for future users contemplating ammonia-based thermal systems.

Condenser O-rings

Condenser 2 is a Boeing-designed heat exchanger utilizing EPR O-rings. The failure of these O-rings and a design that allowed coolant to seep through bolt holes resulted in water contaminating the ammonia. Future condenser designs should not allow coolant to flow so freely between the ammonia and coolant sides in the event of an O-ring failure.

Eliminating or minimizing the use of O-rings should be incorporated into future designs. O-rings, no matter how compatible with the coolant or ammonia, eventually break down and decompose.

During disassembly of condenser 2, the cross-sectional area of the O-rings appeared to be undersized. The O-ring grooves were measured and found to be ideal for a standard-size Parker O-ring which has a 0.210-in. actual diameter and a 0.1875 (3/16)-inch nominal size. The original O-rings appeared to have the smaller 0.1875 (3/16)-in. actual diameter. The drawing shows a 3/16 in. O-ring, but does not specify nominal or actual sizes.

The study team recommends that the standard-size Parker O-ring no. 2-388 with the larger 0.210-in. actual (3/16 nominal) diameter be used for condenser 2. This greater O-ring cross sectional area will permit a tighter fit for the O-ring grooves in condenser 2.
The permanent deformation of the EPR O-rings into a rectangular cross section matching the O-ring grooves is due to cold flow, an inherent property of EPR. Conversion to an ammonia-compatible neoprene would minimize this problem.

Ambient Leak Checks

Minor leaks in the Brassboard are detected with a helium mass spectrometer. The spectrometer pumps evacuate the TCS to a vacuum. Fittings and other suspected leak sources are then lightly sprayed with helium gas. If a leak is present, the helium gas is drawn into the vacuum and is eventually circulated into the mass spectrometer where a helium detector sounds an audible alarm in the presence of helium gas.

Leak checks of the Brassboard performed at ambient room temperatures were insufficient to detect condenser leaks under operating conditions. Thermal contraction of condenser 2 under coolant temperatures (20° to 30° F) was sufficient to produce leaks. Leak checks of the condensers were routinely performed with the coolant cart running.

If the O-rings leak, circulating coolant under pressure on the coolant side of the condenser would eventually work its way into the vacuum side. This leak path would introduce the methanol-water mixture into the ammonia side of the condenser, thus contaminating the ammonia when the system is charged.

It is recommended that if a condenser leak is detected while coolant is circulating, the condenser should be removed from the system for further examination. The TCS should be evacuated for a prolonged period (several days) to remove any moisture that might have crept into the system from the leaky condenser. During this period, a tight system should be required to prevent moisture from the ambient air from being continually drawn into the system.

Rotary Fluid Management Device Filters

Filtering of all inlet and outlet lines to and from the RFMD is recommended only if the filters are monitored (via flowmeters or delta-pressure transducers) and isolated with valves to permit on-line servicing with a charged system. Filters should be carefully selected and placed to minimize pressure losses. Instrumenting the filters permits measurement of filter clogging. Isolating filter inlet and outlet with valves in conjunction with a bleed valve permits evacuating the filter with a charged system. This method provides the convenience of servicing filters without purging and recharging ammonia for the entire system.

The degree of residue contamination found within the RFMD was high enough to show the robustness of the RFMD in maintaining proper thermal system operations. The evaporator bearing feed-flow filter screen internal to the RFMD showed significant clogging (fig. 19) and very restricted bearing flow. Contaminant residue had penetrated the filter screen and coated the bearing. The bearing and mating surface exhibited no signs of scoring.
The internal evaporator bearing feed flow-filter screen should be eliminated. If the contamination residue is present in the RFMD, there is a greater danger of bearing damage resulting from insufficient fluid flow than from residue abrasion on the bearing.

Rotary Fluid Management Device Reverse Thrust Bearing

The reverse-thrust bearing Teflon coating on the Brassboard was completely worn through. As a result, the bearing and mating surface showed excessive wear. Sundstrand recommends the Teflon reverse thrust bearing be replaced with a carbon reverse thrust bearing.

Untreated Aluminum

All bare aluminum surfaces and components exhibited signs of corrosion; stainless steel and anodized aluminum components did not exhibit this corrosion. The degree of corrosion on the bare aluminum RFMD rotating drum appears to be a major contributor to the residue contamination. Similar thermal systems at Johnson Space Center and Boeing have not exhibited this corrosion. Their rotating drums have been either anodized or chem-filmed.

From the Ames analysis and the analysis of other users, it is strongly recommended that all bare aluminum surfaces be coated with a material that provides a barrier to the corrosive ammonia. Alodining would be the preferred choice, followed by anodizing and (nickel and chrome plating) using Armoloy.

Dissimilar Metals

The major material components of the Brassboard are 6061 aluminum and types 304 and 316 stainless steel. In the presence of ions, the ammonia becomes a corrosive electrolyte with aluminum and stainless steel providing the potential difference.

To eliminate—or at least minimize—this galvanic corrosion, dissimilar metals in future ammonia thermal systems should be discouraged. A heterogeneous metal fabrication would be the ideal solution. Aluminum is a poor choice because it is readily attacked by halide ions, chlorine in particular. Type 304 stainless steel is satisfactory, but type 316 is more corrosion resistant due to the molybdenum alloying element.

Moreover, a heterogeneous metal construction would have the added advantage of permitting use of a uniform thermal expansion coefficient throughout the system, thereby minimizing temperature-induced leaks.

Minimizing Leaks

Leaks should be kept at an absolute minimum to maintain system efficiency and to prevent moisture from being drawn in when the system is pumped down to vacuum levels.

Each fitting is a possible leak source and therefore the number of fittings should be minimized. For example, whenever possible, surface thermocouples which does not require any fittings should be used in lieu of immersion thermocouples.
All fittings should be welded except in cases where removal of components for maintenance is required. This process would eliminate hundreds of potential leak sources. Tube cutters and automatic tube welders to make butt welds would facilitate this type of assembly. Of course, the tradeoff is a much more difficult disassembly and reassembly of welded components.

O-rings should be eliminated: they degrade and are a constant source of leaks. If O-rings must be used, neoprene should be used in preference to EPR. Neoprene offers greater resilience, lower thermal coefficient of expansion, and lower gas permeability.

Some vendors do not carefully distinguish neoprene (polychloroprene) from BUNA-N rubber (polyacrylonitrile). If neoprene is ordered from Parker Seals, parts with a “C” prefix (true neoprene) should be specified; O-rings with a “N” (BUNA-N) prefix part number are not acceptable.

Cleaning Processes

Cleaning components with a solution of HCl or Freon should be avoided. The potential chlorine residue will serve as a catalyst for galvanic corrosion.

Once a system has been contaminated with a gray powdery residue described in this paper, the system should be torn down for cleaning and inspection. The system should be thoroughly cleaned, piece by piece, to remove all residue. The ions locked in the residue can reintroduce chlorides back into the ammonia and start the galvanic corrosion process over again.

An alternative to the piece-by-piece approach would be flushing the whole system with water and alcohol to clean out the residue. Unfortunately, this approach would not work well for this system because the system contains a number of loops and cavities where liquid would stagnate and pool, making removal of the water difficult without disassembling large portions of the system.

To date, manpower and schedule limitations prevent the complete tear-down of the system at Ames. The authors hope in the near future for a complete tear-down and examination of the system to detect other major corrosion sites and alternative chlorine and/or water sources.

Ammonia Purity

The purity of the anhydrous ammonia used in the TCS is an important initial consideration and must be taken into account prior to operation of the system. The introduction of contaminants during the charging process, caused by anhydrous ammonia impurities, was a contributor to the corrosion problem.

An investigation into the purity levels of the ammonia used at ARC, JSC, and BA&E found that ARC purchased ammonia with a purity level of 99.98%, while BA&E and JSC (ref. 17) ammonia purities are currently 99.99% and 99.999%, respectively. Water is the major contaminant in anhydrous ammonia. The less-pure ammonia used at ARC possibly contributed to the TCS contamination problem, since it has been concluded that the presence of water was one of the primary causes of the TCS corrosion problem. In this application, the use of the purest available ammonia is warranted, and it was determined that 99.9995% purity is available and can easily be procured. Therefore, this purity level is recommended for use in all subsequent thermal bus operations. In addition, in order to ensure that
ammonia of superior purity and quality is procured for the TCS, periodic sample tests and analyses should be conducted.

Quality Assurance

Great care must be taken during all purging, cleaning, testing, and normal operation to assure the necessary levels of cleanliness and to avoid system contamination. It is strongly recommended that all procedures for test, operation, and maintenance of the TCS include the participation of Quality engineers in the preparation and implementation of the documents. All operations should require complete records of all activities during system development, test, and operation, formally monitored and signed off by Quality, as well as Project personnel.
REFERENCES


Thermal Bus System

ISSUE: ZERO-G TWO-PHASE FLOW
APPROACH: POSITIVE INTERFACE CONTROL

Figure 1.— TCS block diagram.
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Figure 4.— Condenser no. 2 residue.
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Figure 27.— Outer housing (~9).
Abstract

During the development at Ames Research Center of an expert system for autonomous control of the Space Station Thermal Control System (TCS), the thermal performance of the Brassboard TCS began to gradually degrade. This degradation was due to filter clogging by metallic residue. Ames Research Center initiated a study to determine the source of the residue and the basic cause of the corrosion. The investigation focused on the TCS design, materials compatibility, Ames operating and maintenance procedures, and chemical analysis of the residue and of the anhydrous ammonia used as the principal refrigerant.

It was concluded that the corrosion mechanisms involved two processes: the reaction of water alone with large, untreated aluminum parts in a high pH environment and the presence of chlorides and chloride salts. These salts will attack the aluminum oxide layer and may enable galvanic corrosion between the aluminum and the more noble stainless steel and other metallic elements present.

Recommendations are made for modifications to the system design, the materials used, and the operating and maintenance procedures, which should largely prevent the recurrence of these corrosion mechanisms.