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ISS Internal Active Thermal Control System (IATCS) Coolant Remediation Project

Russell H. Morrison
The Boeing Company

Mike Holt
NASA Marshall Space Flight Center

ABSTRACT

The IATCS coolant has experienced a number of anomalies in the time since the US Lab was first activated on Flight 5A in February 2001. These have included: 1) a decrease in coolant pH, 2) increases in inorganic carbon, 3) a reduction in phosphate buffer concentration, 4) an increase in dissolved nickel and precipitation of nickel salts, and 5) increases in microbial concentration. These anomalies represent some risk to the system, have been implicated in some hardware failures and are suspect in others. The ISS program has conducted extensive investigations of the causes and effects of these anomalies and has developed a comprehensive program to remediate the coolant chemistry of the on-orbit system as well as provide a robust and compatible coolant solution for the hardware yet to be delivered. The remediation steps include changes in the coolant chemistry specification, development of a suite of new antimicrobial additives, and development of devices for the removal of nickel and phosphate ions from the coolant. This paper presents an overview of the anomalies, their known and suspected system effects, their causes, and the actions being taken to remediate the coolant.

INTRODUCTION

The International Space Station (ISS) is under construction in low earth orbit by an international consortium led by the National Aeronautics and Space Administration (NASA) of the United States. On-orbit assembly began in 1998 with the launch of the Russian Zarya Module (aka Functional Cargo Block (FGB)). Active cooling of the internal elements of the United States On-Orbit Segment (USOS) of ISS began in February 2001 when the U. S. Laboratory (US Lab) Module was launched on STS-98 and docked to the Unity Module (aka Node 1). Even before February 2001, the cooling system in the US Lab had already undergone uncontrolled changes in oxygen content resulting in the need to change the specification of the coolant. After on-orbit activation in 2001, other changes in the coolant

chemistry have been observed which have led to additional remediation efforts, which are continuing to this day. This paper presents a history of anomalies observed in the coolant chemistry, the challenges that exist today, and an overview of the direction being taken in response to these challenges.

COOLANT SPECIFICATION HISTORY

Active cooling of power components, avionics, experiments and the environmental control elements in the US Lab and other pressurized elements of the USOS is provided by a pumped water system that rejects heat by way of an interface heat exchanger to an ammonia system and radiators mounted on the external truss elements of the ISS. There are two cooling loops currently on orbit. One controls temperature to about 40°F and is called the low temperature loop (LTL). The second controls temperature to about 60°F and is called the moderate temperature loop (MTL) [1].

The ISS Internal Active Thermal Control System (IATCS) coolant is an aqueous solution controlled by SSP 30573, Space Station Program Fluid Procurement and Use Control Specification, Table 4.1-2.8 Heat Transport Fluid (IATCS). The baseline and revision A versions of this specification did three things to limit corrosion in the IATCS primary materials of construction (CRES 347, Ni 201, BNi-2 braze, BNi-3 braze).

1. Chlorides were limited to less than 1.0 ppm max in response to testing which has shown clear evidence of pitting corrosion to the primary materials of construction in the IATCS.
2. Sodium borate (800-1200 ppm as B_4O_7) was added to provide a buffer for pH control.
3. Dissolved oxygen was held to less than 0.1 ppm using sodium sulfite as an oxygen scavenger

The coolant specification provided for control of microbial growth by maintaining total organic carbon (TOC) to less than 0.1 ppm and adjusting pH to 9.5 +/- 0.1 with sodium hydroxide (NaOH).

Coolant samples taken during US Lab Integration testing at the Boeing facility in Huntsville in 1997 revealed that the oxygen content of the coolant was increasing. Tests conducted on the Teflon lined flexhoses used throughout the IATCS revealed them to be permeable to air. As the air penetrated the flexhoses, it immediately consumed the sulfite scavenger, converting it to sulfate. The initial air concentration observed in the coolant was on the order of 1 to 2 ppm. This was considered too high to preclude microbial growth or provide an anaerobic environment against corrosion, and too low to ensure oxide passivation of active metal surfaces. Several options were considered for addressing this problem including exchanging the Teflon lined flexhoses for metal bellows flexhoses or covering the Teflon flexhoses with a gas impermeable overwrap material. There was some risk that these options would not be successful because they did not address another potential source for oxygen in the coolant, namely the gas trap. The gas trap is part of the pump package assembly (PPA) and is installed up-stream of the pump itself. It consists of hydrophobic membranes, through which air but not water can pass, surrounded by hydrophilic membrane tubes, through which water but not air can pass [2]. The hydrophobic tubes allow contact between the coolant and the cabin air and are a potential source for oxygen in the coolant. Given these potential limitations in effectiveness, these options were considered too expensive and too much of a schedule impact for further consideration.

It was finally decided that the coolant formulation needed to change to accept the elevated oxygen levels. First, higher oxygen content in the coolant (> 6 ppm) was specified to insure that active metallic sites would be passivated by oxidation. Di- or tri-sodium phosphate (200-250 ppm as phosphate ions) was added to boost corrosion resistance. This environment was anticipated to enhance the growth of microbes, so silver ions were added in the form of silver sulfate (0.1 to 3 ppm). It was expected that the silver would plate out on metallic surfaces in the IATCS, but it was not expected that it would lose all antimicrobial effectiveness once it was plated out. Microbial populations were limited and considered acceptable throughout the remainder of ground testing.

ON-ORBIT COOLANT CHEMISTRY CHANGES

The IATCS team did not fully appreciate the full impact of the gas permeability of the Teflon flexhoses until the US Lab module arrived on-orbit. The quality of the air in the pressurized elements of the ISS is controlled by a number of Russian and American devices, which generate oxygen, remove carbon dioxide (CO_2), remove trace contaminants, and control the temperature and humidity of the air. It was not anticipated that the CO_2 concentration in the US Lab on-orbit would deviate significantly from that experienced in ground testing. Typical ground CO_2 partial pressure levels are on the order of 0.2 millimeters of mercury (mm Hg). On-orbit, Flight Rules limit allowable CO_2 concentration to 5.3 mm

Hg averaged over 5 days or 6.0 mm Hg over 1 day. For crew comfort, ISS attempts to limit levels to below 4.5 mm Hg. Typically, CO_2 levels range from 2.6 to 5 mm.

The Teflon flexhoses are not only permeable to oxygen, but they are also permeable to CO_2 and this resulted in increases in total inorganic carbon (TIC) to levels on the order of 200 ppm and a reduction in coolant pH, Figure 1, as the borate/phosphate buffer was affected by the increasing concentration of carbon dioxide in the coolant.
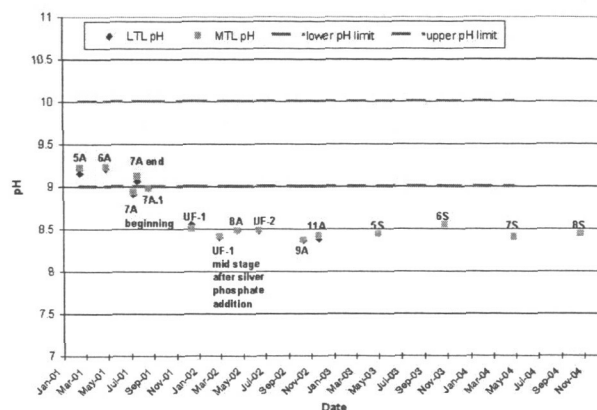

Figure 1. Coolant pH as measured in coolant samples returned from ISS for ground analysis.

The decrease in pH was accompanied by an increase in dissolved nickel ions within the coolant as illustrated in Figure 2. As the pH decreased and the nickel ion concentration increased, the point was finally reached when the phosphate in the coolant began to combine with the nickel to precipitate as nickel phosphate. The falling phosphate concentration is illustrated in Figure 3.
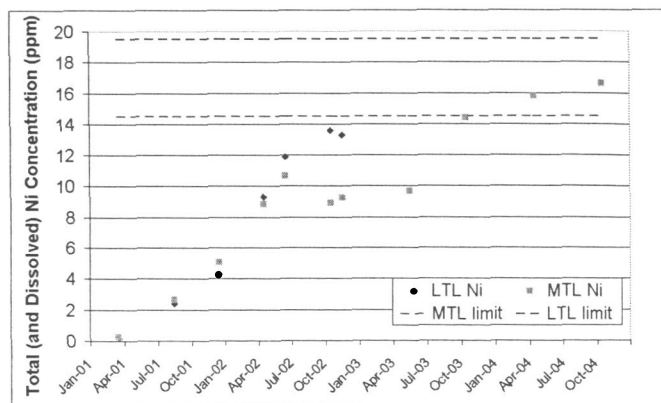

Figure 2. Total (approximately equal to dissolved) nickel concentration as measured in ISS coolant samples returned to ground for analysis
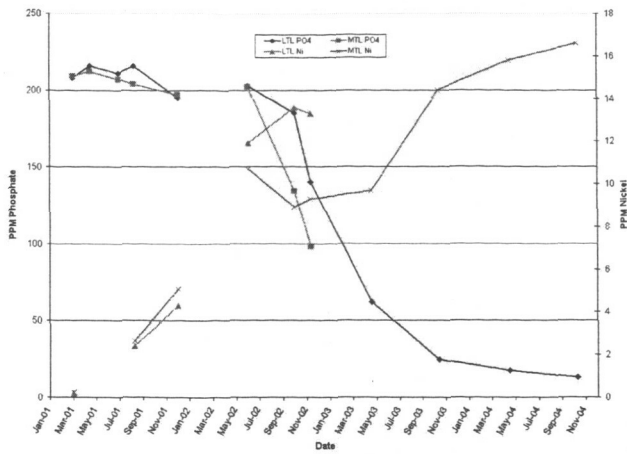
Figure 3. Phosphate and dissolved nickel trends showing nickel concentration leveling off as phosphate concentration drops (forming nickel phosphate)

CONSEQUENCES OF COOLANT CHEMISTRY CHANGES

CORROSION - The IATCS materials of construction, beyond the Teflon flexhoses, are largely CRES 347 and Titanium. The absence of other metal ions, however, pointed to the nickel brazed components as being most affected by the falling pH. The coldplates and heat exchanger cores in the system are primarily made of

Nickel 201 fins and CRES 347 parting sheets held together with BNi2 or BNi3 nickel braze as shown in Figure 4. Figure 5 [3] shows a highly magnified cross-section of a typical BNi3 brazed parting sheet. There is a layer of nickel braze that is approximately 0.001 inch thick which is in contact with the coolant. The bulk of this layer is "matrix" phase nickel, which is relatively pure nickel and very corrosion resistant. It is not significantly affected by the lower pH. Within this nickel layer are pockets of non-diffused "intermetallic" nickel. Intermetallic nickel within the braze layer is a blend of primarily nickel and silicon, from the braze itself. Both nickel and silicon concentrations were determined in the flight 7S coolant sample from April 2004 and were found to be 15.7 and 7.5 ppm, respectively, providing further evidence for this non-diffused intermetallic nickel as the source of the increasing nickel concentration. It is found in the fillet regions of all the nickel brazed components and in the flat surfaces of most of the BNi3 brazed components, which include the coldplates and some critical heat exchangers. This material becomes more and more susceptible to corrosion or dissolution in the IATCS coolant as the pH falls below 9.5 and leaves behind voids as shown in Figure 6. A survey of over 100 BNi3 samples has shown that the deepest void can extend down to within 0.0002 inch of the bottom of the braze layer. Life predictions for these components begin with the assumption that there is only 0.0002 inch of corrosion resistant matrix phase material before the

braze layer is penetrated. BNi2 components and BNi3 components that have been through an extended or second braze cycle do not have non-diffused intermetallic nickel in the flat sheets of nickel and always have at least 0.001 inch of matrix phase nickel above the parting sheet.
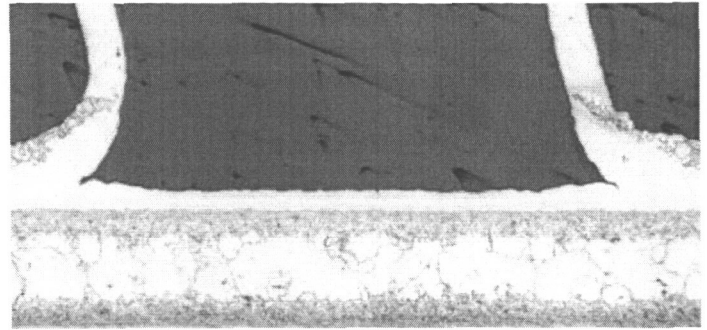

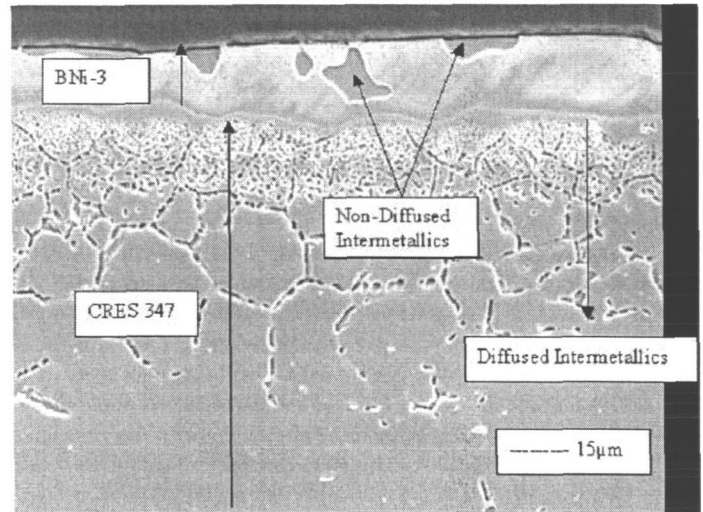
Figure 4 Typical HX cross-section

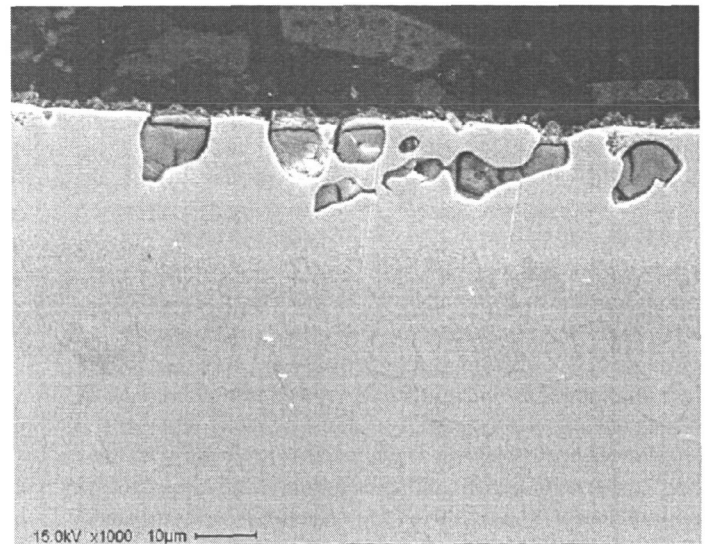Figure 5. Typical BNi3 Cross-section before exposure to IATCS Coolant

Figure 6. Typical BNi3 after non-diffused intermetallic are corroded away

Beneath the braze layer of nickel is another layer with a thickness, typically 0.001 to 0.002 inch of diffused intermetallic nickel into the CRES 347 parent material. Within this layer, the chromium at the grain boundaries within the CRES 347 alloy is bound up with boron introduced by the braze process. This layer is also highly susceptible to corrosive attack as can be seen in Figure 7 where the nickel braze was penetrated by coolant in this case, during Cyclic Potentiodynamic Polarization testing. In heat exchangers, the CRES 347 parting sheet is 0.006 inch thick and has a braze layer on both sides, so there may be only about 1/3 of the parting sheet with any real corrosion resistance. This corrosion rate is so high that when predicting component life for certain critical components, the coolant chemistry team typically considered penetration of the braze layer as being the life limiting event and would assign no additional life to the hardware for the parting sheet thickness. Once penetrated, iron oxide is produced from the 347 parent material and typically adheres close to point of penetration providing a clear marker for the penetration, as in Figure 8.
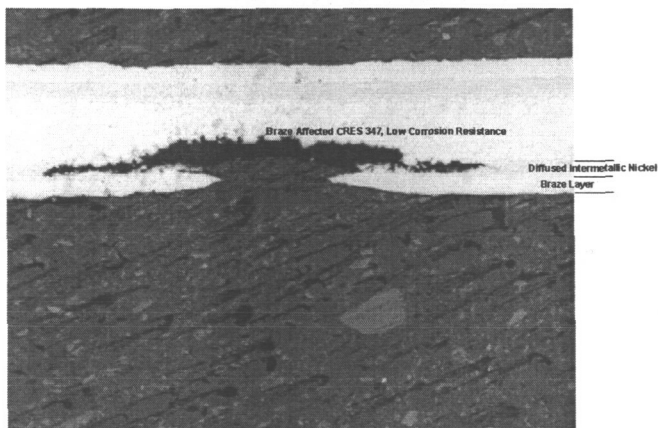

Figure 7. Effects of corrosive attack on diffused intermetallic in BNi3 braze coupon

Figure 8. Iron oxide in vicinity of braze layer penetration on SPCU qualification unit

A large team of NASA and contractor engineers performed a corrosion study over the course of about 2 years with multiple material coupons in various coolant formulations to understand these corrosion effects and make reliable, conservative life predictions for the hardware in the IATCS [4]. Another team evaluated the potential for microbiologically influenced corrosion in the IATCS materials of construction [5].

There are many components in the IATCS that contain nickel braze, but only a few represent potential catastrophic hazards. One is the Servicing and Performance Checkout Unit (SPCU) heat exchanger that is installed in the USOS Airlock. This provides cooling for the Extravehicular Maneuvering Unit (EMU) when the crew is in the airlock. On the IATCS side of that HX the pressure is normally 40 to 60 psia but can be as high as 115 psia. The maximum allowable pressure on the EMU side is about 30 psia. The EMU side is not protected by a relief function at this time and, should it over-pressurize, the likely failure point is in the liquid cooled undergarment worn by the crewmember underneath the Extravehicular Activity (EVA) suit. There are times in the normal procedures when the crewmember is attached to the EMU side of the SPCU HX while suited up and at vacuum. A rupture of the undergarment at that time could result in up to one gallon of IATCS coolant spilling into the suit. The risk then is that the crewmember will inhale the coolant and drown. The corrosion study team predicts that the nickel braze layer in a normal SPCU HX can be penetrated in about 4 years at pH 8.3. For that reason, the Airlock SPCU HX was replaced on March 15, 2005 with a spare unit that has undergone a second braze cycle and is expected to have a life in excess of 50 years.

A second potential catastrophic hazard exists with the Interface Heat Exchangers (IFHX). These are where the IATCS transfers its heat to the anhydrous liquid ammonia of the External Active Thermal Control System (EATCS) for rejection to space. The ammonia system operates at up to 500 psia. A breach of an IFHX would result in ammonia flooding and over-pressurizing the IATCS, followed by an IATCS component rupture and contamination of the atmosphere in the ISS pressurized elements with toxic levels of ammonia. The parting sheets in the IFHX are covered by BNi2 braze with a minimum matrix phase thickness of 0.001 inch. These devices are predicted to have a life in excess of 100 years in IATCS coolant at pH 8.3 and are of no additional corrosion concern at this time.

The coldplates and most other BNi3 components have sufficiently thick CRES 347 parent materials or are in applications such that leaks or breaches due to corrosion are not a concern and do not pose a catastrophic hazard. A pre-cooler heat exchanger in the US carbon dioxide removal system, however, was recently scheduled for replacement due to concerns about its BNi3 braze layer.

There was concern that the plating of antimicrobial silver onto the nickel-brazed materials would result in galvanic pitting. Corrosion testing [4] has shown the pitting concern to be unfounded although there does appear to be an increase in the general corrosion rate with multiple additions of silver. Also, an ionic exchange does occur at the surface when silver is added to the coolant, which results in a temporary increase in the release rate of nickel. Component life predictions have accounted for the increase in the general corrosion rate.

BIOFILM - Silver that has plated out of solution retains no anti-microbial effectiveness. As CO_2 permeated the flexhoses and entered the coolant, it provided a carbon source to some species of microbes. Residual isopropyl alcohol from hardware cleaning activities provided a nutrient source to some bacteria. As a consequence, by flight 7A the planktonic bacterial population had exponentially increased to 1.00E+06 to 1.00E+07 colony forming units (CFU) per 100 ml, Figure 9. For reference, the Environment Protection Agency (EPA) recognizes that the potable water upper limit for planktonic populations by similar analysis should be less than 5.0E+04 CFU/100 ml. There has always been some suspicion of the validity of these ground analyses of the on-orbit samples. These are populations in coolant samples that have been extracted from the loops and returned to the ground for analysis. Time periods ranging from 4 to 25 days typically pass between the time a sample is collected and it is analyzed, whereas standard methods would require analysis within 24 hours of sample collection. Kits for on-orbit analysis can only measure up 3.00E+02 CFU/100 ml. There is little that can be done about this at this time. Refrigeration of samples will likely be an option in the future. There has also been some evaluation of other analysis techniques and equipment that might be procured for future on-orbit microbiological characterization of fluids.
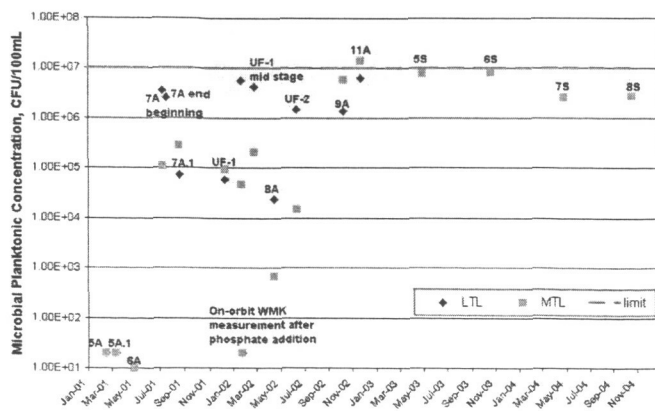

Figure 9. Planktonic microbial heterotrophic plate counts on R2A Agar as measured in ISS coolant samples returned to ground for analysis

The planktonic bacterial populations measured to date do not directly affect the functionality of the IATCS equipment. Bacterial affects on the crew in the event of exposure to the coolant by accidental ingestion or inhalation become more of a concern. These levels of planktonic microorganisms in the coolant are also capable of supporting biofilm formation on the wetted surfaces of the IATCS. These biofilms may actually represent a majority of the microbial biomass in a recirculated low nutrient system [5]. This could interfere with heat transfer or coolant flow. It could serve as nucleation sites for nickel precipitate formation. It could harbor microenvironments conducive to the growth of anaerobic bacteria or acid-producing bacteria capable of accelerating corrosion or pitting. The pits formed in the nickel braze by chemical corrosion of the non-diffused intermetallic nickel are suspected of being conducive to the formation of such microenvironments. A six-month ground experiment to study microbiologically influenced corrosion in the ISS coolant [6] showed microcolonization with surface populations reaching densities as high as 1.0E+06 CFU/cm2 after 180 days, but revealed no solid evidence of accelerated corrosion due to microbes. It is difficult to claim with conviction that the ground study captured all the microbiological species and environments existent on-orbit at that time or in the future. Nonetheless, this study did demonstrate that with the IATCS materials of construction and coolant chemistry, and no effective antimicrobial treatment, the program should expect a biofilm to grow. At the time of this publication, no IATCS hardware has been returned from the active on-orbit loops from which a complete assessment of the extent of biofilm in the loops can be provided. This will change with the first return to flight (RTF) space shuttle flight to ISS presently scheduled for May 2005, flight LF-1. That flight is expected to return with an SPCU HX and a short length of flexhose with quick disconnects on each end recently removed from the coolant loops. This hardware will be subjected to destructive examination and extensive biofilm evaluation.

PRECIPITATE FORMATION - The corrosion and biofilm effects on the IATCS are only based on literature reviews and ground testing. Nickel precipitation, on the other hand, has been a confirmed nuisance on orbit. Nickel phosphate becomes the most stable form for the dissolved nickel from the braze intermetallic layer as the pH of the coolant solution drops to 8.3. This is illustrated in a stability diagram, Figure 10, from an equilibrium model of the coolant chemistry [7]. As chance would have it, the CO_2 concentration on orbit is at exactly the right level to naturally drive the IATCS coolant, with its buffers, to a pH of about 8.4. It is expected that small changes in pH, either up or down, could result in the conversion of nickel precipitate from the phosphate form to the hydroxide form and vice versa. This is a potentially very unstable situation. Figure 3 clearly illustrates how the increasing nickel concentration flattened out at around 10 – 12 ppm beginning around March 2002, just as the coolant pH was dipping below 8.5, Figure 1, and the phosphate concentration plunged from over 200 ppm to about 50 ppm after which the nickel concentration began to rise again. Nickel phosphate is a hard, green, crystalline precipitate. At higher pH, nickel hydroxide is the stable form for the nickel to take and it is a gelatinous precipitate.
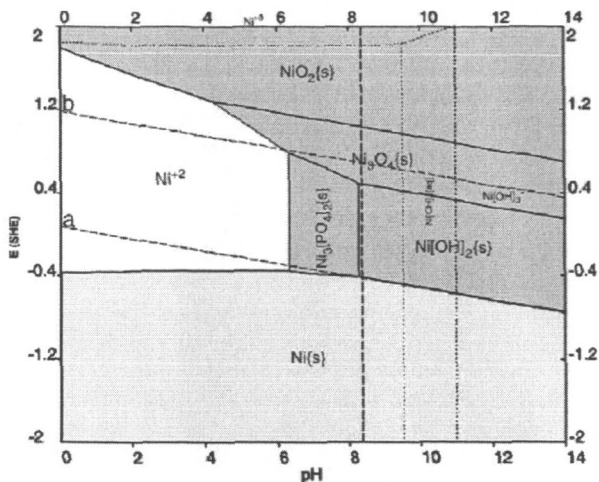
Figure 10. Stability diagram for Nickel in IATCS coolant showing that on-orbit equilibrium pH lies at boundary between nickel hydroxide and nickel phosphate formation.

Green Gas Trap, July 2001 - The effects of nickel precipitation were believed to be first observed in the IATCS in July 2001 when the pressure drop across a gas trap installed in the MTL had risen to 6 psid from a nominal 4.4 psid last observed in November 1999 [8]. The pressure drop across this gas trap had been rising even during ground testing of the US Lab. The last pressure drop observed on the ground before launch was 5.3 psid in September 2000. The US Lab was activated on-orbit in February 2001 and by May 2001, the gas trap pressure drop had risen to 5.7 psid. It was returned to the ground in August 2001. The hydrophilic membranes had a green appearance as illustrated in Figure 11, rather than the normal white. Tests revealed no significant microbiological contamination. Flushing with de-ionized water, isopropyl alcohol, and dilute hydrochloric acid cleaned the membrane module. At the time of its removal, the pH of the IATCS coolant was still around 9 and had never been below 9. Phosphate concentration was still in the normal range. Nickel concentration in the coolant was still below 2 ppm and was never high when the first increases in pressure drop were observed on the ground. Analysis of contamination from the membrane did reveal some nickel, phosphorus, silicon, aluminum and oxygen. It is not clear that these compounds were in large enough quantities to be responsible for the pressure drop observed. It is interesting that even in the surge of nickel phosphate precipitation that occurred over an 18 month period beginning in March 2002, it was not until one year into the process that the MTL gas trap pressure drop again reached 6 psid. It is not clear what role nickel precipitation played in the gas trap failure of July 2001, but it did alert the program to potential issues with nickel precipitates in the months to come.
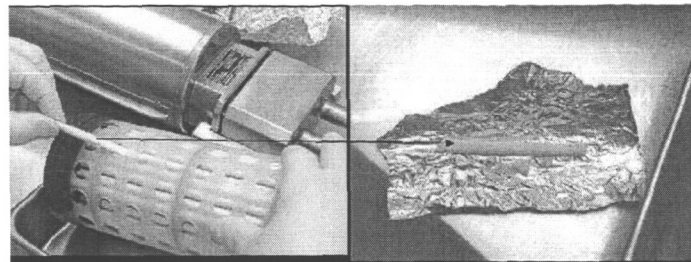

Figure 11. "Green gas trap" – contaminated with nickel precipitates, suspect primarily phosphate

Green Filter, October 2002 – This filter was installed on the MTL in January 2002 after having been seeded with silver phosphate in an attempt to achieve some measure of microbiological control. After dissolution of the silver phosphate, pressure drop fell to the normal 1.9 psid. By October 2002, well into the main nickel phosphate precipitation event, the pressure drop in this filter had risen to 4 psid. It was replaced and returned on flight 9A. Green precipitate was quite obvious on this filter as seen in Figure 12. Scanning Electron Microscope/Energy Dispersive X-Ray Fluorescence (SEM/EDXRF) analysis clearly showed strong nickel and phosphate peaks. Fourier Transform Infrared (FTIR) spectrum analysis also closely matched that for nickel phosphate. This filter was clearly consumed due to nickel phosphate precipitation.
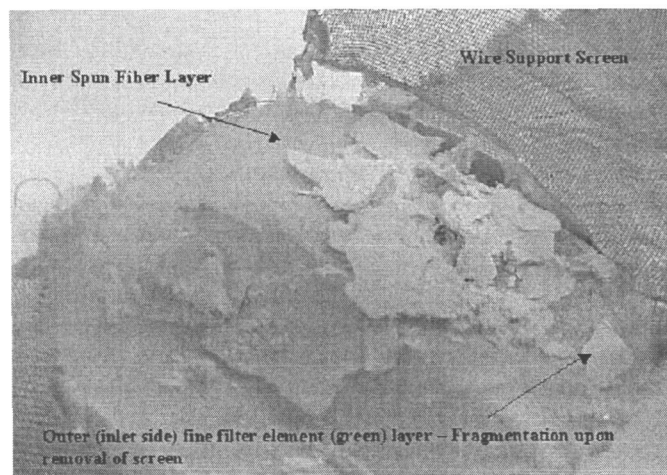

Figure 12. Green filter – contaminated with nickel precipitates, primarily phosphate

Pump Package Assembly, March 2003 – On March 16, 2003, after having experienced eight over current spikes in an 8 hour period, MTL pump package assembly (PPA) seized up and failed. From August 2002 until this time, the gas trap pressure drop on this PPA had risen from 4 to 6.6 psid. The filter pressure drop had not changed since its replacement in October 2002. This PPA with its gas trap installed is still on orbit at the time of this publication and planned to be returned with flight LF-1. It is premature to conclude that nickel phosphate played a role in this PPA failure, but it is high on the list of potential contributing factors. It is likely that nickel phosphate will be implicated in the gas trap pressure drop increase as well.

Quick Disconnect (QD), February 2004 – A temporary reconfiguration of the coolant loops to support a Soyuz vehicle relocation on ISS left four normally mated male and female QDs in a demated state for a period of approximately 56 hours. Two of the QD halves, one male, one female, had water blobs on their open faces totaling approximately 100 ml just before they were re-mated. The male QD water blob is visible in Figure 13. These parts remain in service. It is premature to conclude that nickel phosphate played a role in these leaks, but again, it is highly suspect. Procedural changes requiring the installation of caps or plugs on de-mated QD halves have been instituted. When this is not possible, the QD is cycled once before de-mating in the hopes of dislodging precipitate. One of the leaking QDs will be returned for failure analysis with a flexhose on flight LF-1.
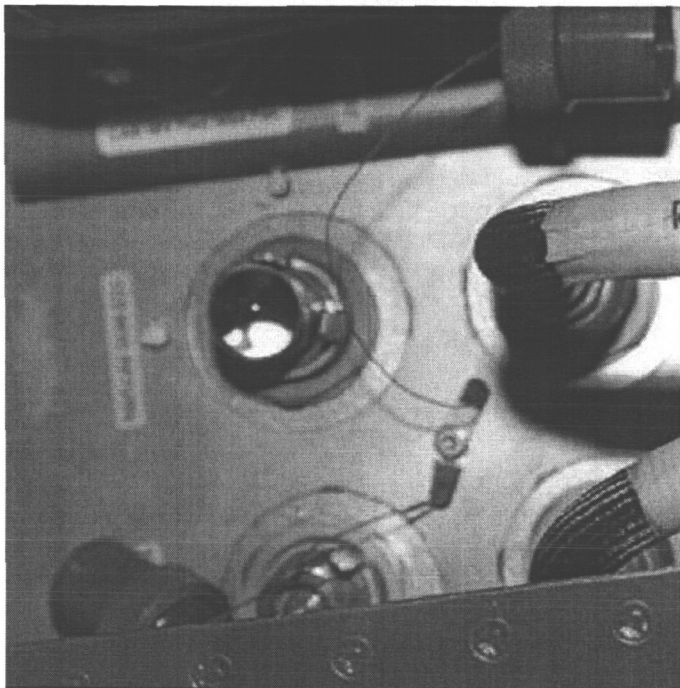

Figure 13. On-orbit quick disconnect leak

Gas Trap, In Service – The gas trap currently in service with the LTL PPA has had an increasing pressure drop since July of 2003 [9]. It would normally be replaced before the pressure drop exceeded 6 psid, but since there have been no operations introducing gas to the IATCS loops and since there is a shortage of gas traps, this unit remains in service. This gas trap exceeded 6 psid in March 2004 and currently has a pressure drop on the order of 6.6 psid. This gas trap will be replaced before flight LF-1 and returned on flight ULF1.1 in July 2005.

COOLANT REMEDIATION

PAST ATTEMPTS – Actions performed to remediate the coolant chemistry over the past four years have included modifications to the coolant specification and several actions aimed at correcting the observed symptoms. These have generally met with partial success, though one remediation attempt was aborted at the last minute due to late breaking ground test data as described below.

Revision B of Coolant Specification – The program decided not to change the permeability of the flexhoses. In order to insure that the oxygen concentration remains high enough to protect passivated surfaces, revision B of SSP 30573 was released in 2001 to raise dissolved oxygen from less than 0.1 ppm to greater than 6 ppm.

Di- or tri-sodium phosphate (200-250 ppm as $PO4$) was added to boost corrosion resistance as compensation for moving away from a deoxygenated coolant. In retrospect, this was an unnecessary move with negative solubility impacts.

Control of TOC to less than 0.1 ppm proved to be a practical impossibility due, among other things, to the use of solvents like isopropyl alcohol for cleaning during the assembly of many of the components in the IATCS. In revision B, the TOC limit was raised to 5 ppm. In an effort to provide for microbial control, silver sulfate between 0.1 and 3 ppm was specified.

Silver Addition – There has been considerable debate in the program about the use of silver for microbial control. It has demonstrated effective control of microbial populations when maintained at use concentrations and poses essentially no toxic hazard to the crew. These advantages have been offset by its tendency to plate out on the materials of construction in the IATCS, concerns about its effect on the general corrosion rate of matrix phase nickel in the presence of prolonged exposure, and its ineffectiveness against established biofilms. Considerable effort was invested in development of a silver ion generator for potential use on orbit in the 2000 timeframe [10], but production of flight hardware was never authorized.

Microbial concentrations were first observed to have undergone exponential increases in the flight 7A coolant samples collected before and after the airlock was installed in July 2001. Although the MTL gas trap pressure drop had been increasing to the point that it required replacement by this time and there was a rising nickel concentration, it would be several months before testing would bring nickel precipitation forward as the most likely root cause. Microbiological contamination of the gas trap was still considered a strong contender as the root cause for its performance degradation.

The program was also anxious to preserve what was believed to be a relatively biofilm-free cooling system up until that time. By October of 2001, a ground test of a technique to introduce silver ions to the loops by seeding PPA filters with silver phosphate had been satisfactorily performed on the US Lab module simulator at Marshall Space Flight Center, Figure 14. Over the course of the 92-hour test, silver concentration was raised from 0 to 0.7 mg/l and the bacterial population was reduced by a factor of 1000. In December 2001, on flight UF-1, the

program manifested PPA filters that were seeded with silver phosphate. These were installed in January 2002. A test was performed on-orbit with a water microbiology kit (WMK), normally used for monitoring ISS drinking water, shortly after the filters were installed. The results from this test showed that the planktonic microbial population had been reduced to 20 CFU/100 ml by the silver addition. Water samples taken at the same time and returned to the ground were not analyzed until 87 days later. These samples had microbial populations of up to 6.0E+06 CFU/100 ml. While the discrepancy between on-orbit and ground measurements is not surprising given the hold time on the ground analyzed sample, it remains unclear to what extent sample methods or contamination of either sample might have played a role in this discrepancy. Until November 2004, all coolant sample bags were made of Teflon and were gas permeable. This may contribute to discrepancies.
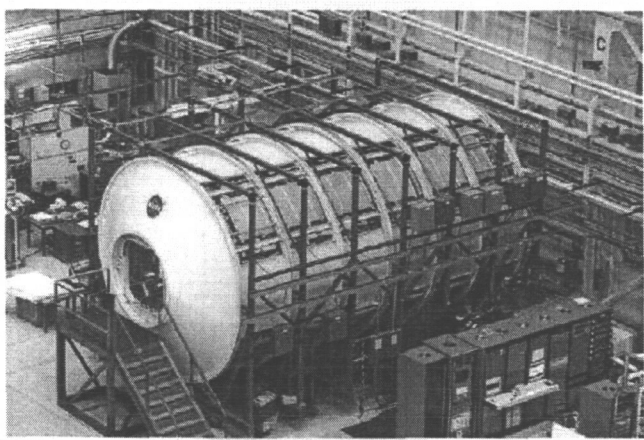

Figure 14. US Lab module simulator at Marshall Space Flight Center

Hold times for samples through mid-2004 are illustrated in Figure 15. In this figure it appears that longer hold times tend to be associated with higher microbial population measurements, although there are some inconsistencies. While this casts doubt on the accuracy of the microbial measurements, it suggests that they are at least conservative, and it is the general policy of the ISS program to use worst-case scenarios to drive decisions.
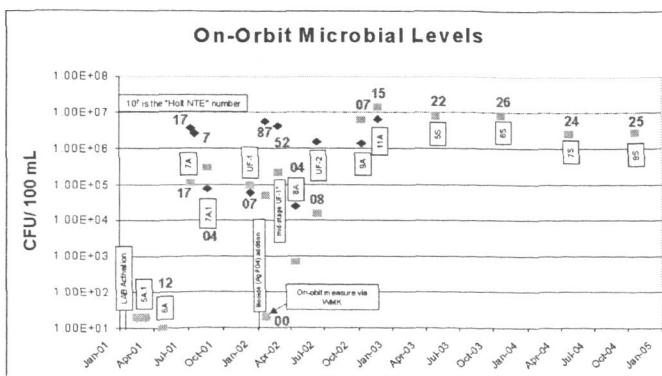
Subsequent ground test data suggests that the silver addition was effective for as much as several weeks, after which the planktonic population likely recovered. As the biofilm becomes more pervasive, the recovery time can be expected to become shorter because silver has been shown to be fairly ineffective against biofilms and these will provide the reservoir for planktonic population recovery.

Critical hardware life predictions are made assuming several cycles of silver exposure. Nevertheless, the risk of increased general corrosion rates in the matrix phase of the nickel braze due to repeated or continuous silver deposition have left the ISS program reluctant to pursue silver for microbiological control in the future.

Sodium Hydroxide Addition – The pH in the cooling loops was clearly falling by the fall of 2001. The IATCS coolant team considered raising the pH with an anion exchange resin bed and by directly injecting 0.08 Normal sodium hydroxide (NaOH) solution into the loops. The ISS NaOH Injection Kit (INIK) was developed on a very fast track and two kits were flown on flight 8A in April 2002. In parallel with this activity, a ground test on the US Lab module simulator at Marshall Space Flight Center was conducted, also in April. That test clearly showed that the injection of sodium hydroxide into the loops would cause a dramatic increase in filter pressure drop, enough to result in filter bypass and require filter removal and replacement. The speculation was that the nickel concentration in the coolant was high enough to form significant quantities of nickel hydroxide that would exist as a colloidal or gelatinous precipitate. The effect was dramatic enough that the program decided, only days to weeks before the INIK implementation was planned, to halt that remediation action. No attempt would be made to raise pH until the nickel concentration could be reduced.

CURRENT ACTIVITIES - The coolant chemistry effects to date have resulted in relatively minor system anomalies. One pump may have failed prematurely due to chemistry, but aside from that, it has resulted only in a fairly manageable but higher rate of coolant filter and gas trap consumption. Nonetheless, it is the nature of the ISS program to be proactive in preventing problems and there are serious risks in allowing the coolant to continue its deviation from specified conditions.

Our efforts to manage the chemistry, on the other hand, have come close to exacerbating our problems rather than solving them. As a result, the program has adopted a posture of requiring high fidelity tests of proposed solutions and withholding implementation until certain use criteria are met.

Some combination of the following conditions will need to be met before the program will authorize implementation of a chemical solution to the presence of nickel and nickel precipitates:

1. Failure investigation of the following items shows that any nickel precipitates were a contributing cause to the failure
    a. MTL PPA that failed in March 2003
    b. The quick disconnect that leaked in February 2004
    c. The Environmental Control and Life Support System (ECLSS) cabin air heat exchanger being returned on flight ULF1.1
2. Failure investigation of any failed gas traps or filters shows that nickel hydroxide or nickel carbonate were contributing causes to the failure (due to the potential ample supplies of these precipitates).
3. On-orbit data analysis indicates deleterious system symptoms such as reduced heat transfer rates or system flow and delta pressure degradation can be traced to scale formation as evidenced in analysis of returned orbital hardware.
4. A hardware failure after September 2003 (when phosphate levels were low) is traced to nickel phosphate formation

On-orbit antimicrobial solutions will be authorized for implementation after they have been through a rigorous development program including: screens for effectiveness in the on-orbit coolant chemistry, material compatibility and interference with ammonia detection in the coolant; toxicology assessment; ECLSS compatibility assessment; and hazard control plan development. An early implementation of a biocide that has not completed this program could be triggered by one of the following events or findings:

1. Planktonic microbial concentration as measured by heterotrophic plate count on R2A Agar is greater than 9.0E+06 CFU/100 ml.
2. Microbial planktonic concentration increases by greater than 2 logs or surface samples by more than 1 log in successive samples.
3. Confirmation of the presence of the sulfate reducing, iron or manganese oxidizing or anaerobic acid producing bacteria in coolant or surface samples.
4. Confirmation of the presence of pathogenic *Legionella* species.
5. ISS Common Environments team identifies unacceptable levels of opportunistic human pathogens in the coolant or surface samples.
6. Fluid chemistry changes, such as sulfate reduction, provide evidence of microbiologically influenced material degradation.
7. Increased rates of pitting corrosion or corrosion products are found beneath or adjacent to bacterial surface microcolonies or biofilms.

Meanwhile, the ISS program is actively preparing solutions to the observed coolant anomalies. A strategy is currently in place to control the level of nickel present in the coolant and to remove phosphate. Buffer solutions are under investigation that may provide for stable pH control in the 9 – 9.5 range even with the CO_2 concentration and permeable flexhoses in the flight coolant systems. Several antimicrobials are in test with the future coolant chemistry to define one or more best

solutions for stable reduction and control of microbes in the coolant and in biofilms. The key elements of the coolant remediation plan are summarized below.

Modeling – The IATCS coolant working group has enlisted the aid of specialists in the modeling of corrosion and water chemistry effects. Products of that effort, like the stability diagram in Figure 10, have proven invaluable in understanding observations from orbital coolant samples as well as those from tests performed on the ground at beaker, bench and full system levels. The models are refined with data and then used to predict the outcome of future tests and remediation efforts.

Nickel Removal Assembly (NiRA) – The IATCS coolant working group has performed extensive experimentation and perfected the application of a chelating resin produced by DOW Chemical for the removal of nickel ions from the IATCS coolant. A recirculating bench test of the NiRA performed in 2004 demonstrated its effectiveness at reducing nickel concentration, Figure 16. As the nickel concentration drops, nickel phosphate crystals distributed throughout the test bed were observed to re-dissolve and phosphate concentrations returned to their pre-precipitated levels. Subsequent bench testing proved the effectiveness of additional resin treatments for maintaining a constant pH during NiRA implementation. Ground NiRA units have been produced for experimentation and to support nickel ion removal from the Node 2 cooling systems while it is processed at the NASA Kennedy Space Center. Flight units are being manufactured and will be delivered to NASA by April 2005.
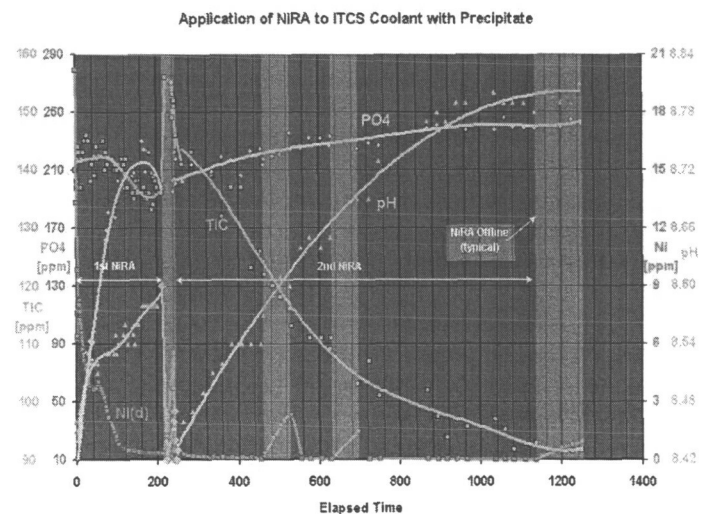

Figure 16. Recirculating bench test results of NiRA showing nickel removal (green) and phosphate redissolution (orange)

Phosphate Removal Assembly (PhosRA) – Phosphate was added to the coolant primarily as a corrosion inhibitor for the stainless steels in the system. Corrosion testing has shown that this is unnecessary at the pH levels the coolant is experiencing. Its propensity for forming nickel phosphate at the equilibrium pH of the on-orbit coolant has provided motivation to eliminate it. Future elements of the IATCS will be launched with

coolant that has no phosphate. In order that payload racks may be freely moved between the US Lab and other on-orbit elements, and to preclude future nickel phosphate formation, it will be necessary to remove the phosphate from the lab coolant. To that end, the program has completed an extensive development program to adapt a DOWEX ion exchange resin to this application. Figure 17 illustrates its effectiveness at the beaker level for phosphate removal without perturbing pH. Funding has been authorized for production of flight units of the PhosRA, based on the NiRA design, and delivery is expected by February 2006.

PhosRA Effect on ITCS Constituents
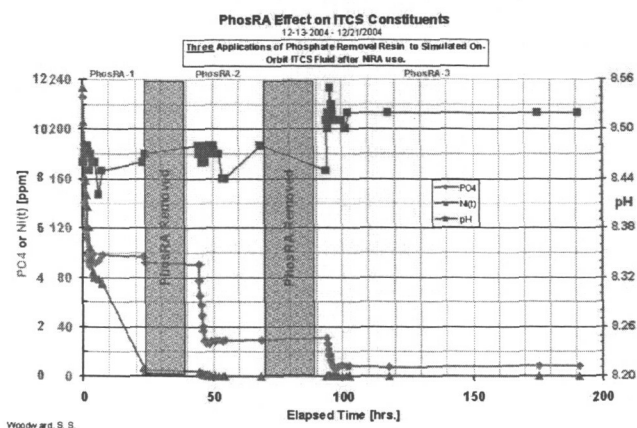12-13-2004 - 12/21/2004

Figure 17. Beaker scale testing of PhosRA resin showing phosphate removal effectiveness and ability to maintain a relatively constant pH

Buffer System – Chemical modeling of the coolant system in the fall of 2004 showed that it may be possible to control pH to near 9.5 by making adjustments in the buffer formula. Increasing the borate concentration from 1000 to 5000 ppm or higher has been shown by analysis and beaker level testing to hold pH to no lower than 8.8 with no phosphate in solution. Borate at concentrations of 5000 ppm and above has also been shown to be inhibitory to the predominant microbial species in the orbital coolant and may be synergistic with some antimicrobials. Carbonate/Bicarbonate systems in combination with borate or alone are thought to be capable of holding coolant pH above 9.2 in the presence of the on-orbit CO_2 levels. This has not yet been shown by test. Precipitate formation at these higher buffer concentrations is a key concern.

Holding the pH at a higher level holds the promise of not needing to use NiRAs for routine orbital nickel removal. When ISS assembly is complete, there will be a total of 9 cooling loops in the Lab, Node 2, Node 3, Japanese Experiment Module and Columbus Module. Without a higher pH, 9 to 18 NiRAs total will likely be needed to keep up with nickel concentrations on all 9 coolant loops. Eliminating the prospect of continued nickel corrosion and preserving margins in critical IATCS components would be a significant benefit of achieving a higher pH.

It will be necessary to have a final decision on the buffer formulation before continuing anti-microbial development. Re-evaluation of NiRA performance at other buffer formulations will also be required if the pH is

not maintained high enough for intermetallic nickel dissolution rates to go to zero.

Antimicrobials – The program has been looking into antimicrobials for several years. The first comprehensive program to competitively evaluate as many options as possible has been well documented and published [11], [12]. This effort led to the selection of glutaraldehyde at a use concentration of 250 ppm.

Several issues with glutaraldehyde have been identified and solutions are in work for each. For example, glutaraldehyde at a concentration of less than 10 ppm has been shown to be assimilated by some river water sediment microorganisms with aerobic metabolism to carbon dioxide [13]. As a consequence, maintenance of glutaraldehyde above minimum inhibitory concentrations in the IATCS is recommended. A resin is in development to lower its concentration to below 5 ppm should the need arise to remove it.

Another issue with glutaraldehyde is that it binds with ammonia and can mask an ammonia leak into the IATCS from current monitoring methods. It is essential to be able to monitor ammonia concentrations in the coolant to provide protection against leaks across the IFHX of ammonia from the external loops. A new ammonia monitoring kit is in development that raises the pH of the coolant sample before testing and, in so doing, produces a compound that reacts with the ammonia monitoring strips currently used on orbit just as the original concentration of ammonia would have.

Late in the development process, December 2003, an ECLSS analysis using conservative assumptions of glutaraldehyde evaporation rates and specification levels of coolant leakage into the cabin showed that on-orbit contamination control systems would not be capable of maintaining the atmospheric concentration of glutaraldehyde below the 180 day Spacecraft Maximum Allowable Concentration (SMAC) at use concentrations in the coolant above 25 ppm. At this level, glutaraldehyde is barely inhibitory. This has added to the burden already carried by glutaraldehyde when considering it for on-orbit use. To address this concern, tests are in work to obtain data to allow more realistic modeling of the rates that glutaraldehyde will enter the atmosphere. Evaporation experiments have already shown that glutaraldehyde concentrates as coolant evaporates. Its tendency to polymerize under these conditions will be quantified. Its vapor pressure at use temperatures will be quantified, and its degradation rate in light and the cabin atmosphere will be quantified. It is expected that as these data are incorporated into the ECLSS models, a workable range of use concentrations will be identified and incorporated into hazard controls associated with glutaraldehyde.

The issues with Glutaraldehyde remain significant. The program enlisted the help of two teams of outside consultants to perform new surveys of likely antimicrobial candidates in July 2004. After considerable review and

downselect, the program has decided to further evaluate and develop up to five candidates: glutaraldehyde, methyl isothiazolone, ortho-phthaldehyde (OPA), tetrakishydroxymethyl phosphonium sulfate (THPS) with the sulfate ion exchanged for carbonate, and hydrogen peroxide / silver (0.5 ppm / 10-20 ppb). Development of these candidates is continuing, but constrained by decisions pending on the buffer chemistry.

Implementation Schedule – An overview of the coolant remediation plan and implementation schedule is shown in Figure 18. This shows that flight LF-1 will yield key data that may initiate a rapid antimicrobial development effort. This would entail a re-prioritization of full-scale system test objectives and change the approach to the full-scale system test. The intent would be to deliver an early antimicrobial by flight 12A in December 2005. Absent a rush on the antimicrobial development, then the coolant remediation plan calls for a full scale system test in the MSFC US Lab Module Simulator beginning with NiRA testing in October 2005. This test is intended to mimic the on-orbit implementation with accelerations where stable equilibrium conditions allow.

The planned implementation scheme on orbit would be to deliver two NiRA units on or before flight 13A in April 2006. One unit would be installed with the US Lab configured to a single combined coolant loop before or at the beginning of docked operations. This unit will likely be spent within a few days. The second unit would be installed just before undocking and the spent unit returned with the 13A mission. The spent NiRA would then be quickly refurbished into a PhosRA and launched with the other two PhosRAs and a buffer implementation device on flight 13A.1 in July 2006. It is expected that simulation of the delays between 13A, 13A.1, and 15A can be shortened in the ground system test of this implementation scheme. During 13A.1 docked operations, the three PhosRAs would be installed serially two days apart followed by the buffer injection device. All four devices, along with the second NiRA will be returned with the 13A.1 mission. At the completion of flight 13A.1 the US Lab should be cleansed completely of ionic nickel, phosphate should be below 10 ppm, and the buffer system should be holding pH at least above 8.8 and possibly as high as 9.5. The rate of nickel dissolution should be significantly reduced, after this. The antimicrobial will be implemented on 15A. This schedule is aggressive and depends on funding to begin the work by May 2005.
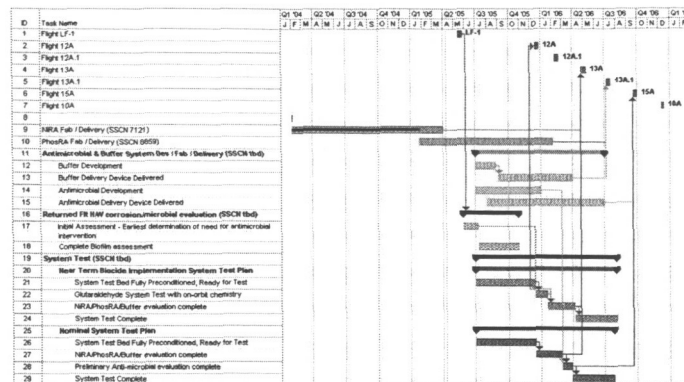

Figure 18. Coolant Remediation Plan

It was decided to fill Node 2 with SSP 30573 Rev. B fluid modified to delete the silver and phosphate and lower pH to 8.4 by sparging with CO_2 in April 2005. Glutaraldehyde at 200 ppm was added for microbial control. This coolant is circulated through the Node 2 loops 5 days per week, 8 hours per day using ground support equipment pumps as ground operations allow. Ground NiRA units are installed to remove nickel. The intent is to remove as much intermetallic nickel from Node 2 on the ground as possible, so as to minimize the necessity to use NiRAs in Node 2 on orbit. All hardware life predictions for Node 2 are based on this chemistry and are not an issue. Just before Node 2 is closed out for launch, this coolant will need to be replaced with coolant that has the planned on-orbit formula – hopefully buffered to a high pH.

Negotiations on coolant chemistry have not yet begun with the International Partners and Payload providers. Most continue to use de-ionized water as allowed by SSP 30573 for ground operations or are using the Rev. B formulation. Compatibility of the final coolant chemistry with all materials of construction in these other elements is a key concern of the coolant remediation team.

CONCLUSION

Early program decisions on the use of gas permeable Teflon flexhoses in the IATCS coolant system and the unexpected effects of higher on-orbit CO_2 levels have resulted in a lowered coolant pH. This has led to increased rates of corrosion in nickel brazed hardware throughout the system and precipitation events that have affected component performance. The lack of an effective antimicrobial in the IATCS coolant has created increased levels of planktonic and biofilm associated microorganisms. After some piecemeal remediation efforts reactive to the initial symptoms of coolant anomalies, the program is now well entrenched in a comprehensive program of test, analysis and development of the tools and devices required to drive the coolant chemistry to a stable and effective chemistry.

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CONTACT

Russell H. Morrison
Associate Technical Fellow
The Boeing Company
IATCS Subsystem Problem Resolution Team Co-Lead
Russell.h.morrison@boeing.com