

Internal Active Thermal Control System (IATCS) Sodium Bicarbonate/Carbonate Buffer in an Open Aqueous Carbon Dioxide System and Corollary Electrochemical/Chemical Reactions Relative to System pH Changes

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The International Space Station (ISS) Internal Active Thermal Control System (IATCS) experienced a number of chemical changes driven by system absorption of CO₂ which altered the coolant's pH. The natural effects of the decrease in pH from approximately 9.2 to less than 8.4 had immediate consequences on system corrosion rates and corrosion product interactions with specified coolant constituents. The alkalinity of the system was increased through the development and implementation of a carbonate/bicarbonate buffer that would increase coolant pH to 9.0 – 10.0 and maintain pH above 9.0 in the presence of ISS cabin concentrations of CO₂ up to twenty times higher than ground concentrations. This paper defines how a carbonate/bicarbonate buffer works in an open carbon dioxide system and summarizes the analyses performed on the buffer for safe and effective application in the on-orbit system. The importance of the relationship between the cabin environment and the IATCS is demonstrated as the dominant factor in understanding the system chemistry and pH trends before and after addition of the carbonate/bicarbonate buffer. The paper also documents the corollary electrochemical and chemical reactions the system has experienced and the rationale for remediation of these effects with the addition of the carbonate/bicarbonate buffer.

Nomenclature

IATCS = Internal Active Thermal Control System
ISS = International Space Station
EATCS = External Active Thermal Control System
[CO₂(aq)] = the concentration of aqueous carbon dioxide
PCO₂ = Partial Pressure of CO₂
Q = $K_p * A * (dP/L)$ = Rate of mass flow

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Kp	= Permeation Rate Constant
A	= Area normal to gas flow
dP	= Difference in partial pressures
L	= Length of flow path (wall thickness)
CO	= CO ₂ Concentration in Cabin Air
CI	= CO ₂ Concentration in Coolant
TIC	= Total Inorganic Carbon
LTL	= Low Temperature Loop
MTL	= Moderate Temperature Loop
ANC	= Acid Neutralization Capability
ORP	= Oxidation Reduction Potential

I. Introduction

The IATCS aboard the ISS is primarily responsible for the removal of heat loads from payload and system racks. The IATCS is a water based system which works in conjunction with the EATCS (External Active Thermal Control System), an ammonia based system, which interface through a heat exchanger to facilitate heat transfer. On-orbit issues associated with the aqueous coolant chemistry began in 2001 shortly after system activation and operations. These changes were primarily associated with unexpected increases in O₂ and CO₂ levels in the coolant aboard ISS. This caused an increase in total inorganic carbon (TIC), a reduction of system pH, increased corrosion, and precipitation of specified constituents (i.e. phosphate).

These anomalous conditions resulted in coolant chemistry parameters that were outside the specified range and undesirable for future on-orbit performance. The resulting increased corrosion rates that reduce hardware life and foul system filters and gas traps were deemed unacceptable. The programmatic desire was to establish a new coolant chemistry that could return the system to a more basic pH able to persist in the on-orbit CO₂ environment. The newly established chemistry must be implementable via the remediation of the U.S. Laboratory (USL).

The understanding of the chemistry of carbon dioxide in aqueous systems identified the relationship of carbon dioxide in the Space Station cabin environment and its resulting effects on the IATCS chemistry. This document details the chemical basis for coolant anomalies and provides the rationale and understanding that form the core for changes that have been implemented to remediate this system and provide new coolant chemistry to the ISS thermal loops.

II. Relationship of Carbon Dioxide in ISS Cabin to that in the IATCS Coolant

Water open to a gas will establish equilibrium between the gas and the gas molecule in aqueous form. In dry air on earth the carbon dioxide mole fraction percentage averages 0.035%. In the on-orbit cabin environment the CO₂ concentrations have nominal values greater than 0.035% and range from 0.20% to 0.75%. Initially the coolant has no inorganic carbon specified.

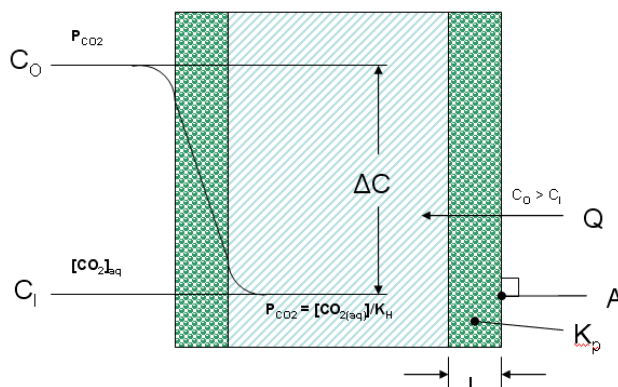


Figure 1. Flexhose Permeability

When exposed to the on-orbit conditions, this difference in cabin air concentrations (CO) and the internal concentration of aqueous CO₂ establishes a concentration gradient of the partial pressures of CO₂ across the Teflon® hose material used extensively in the IATCS coolant loops. This gradient allows permeation of CO₂ into the IATCS coolant (Figure 1).

The rate of mass flow is governed by the permeability of CO₂ through the Teflon® flexhoses. CI is determined by Henry's Law. Henry's Law states that the CO₂ concentration in the coolant is proportional to the CO₂ concentration in the cabin air by a constant known as Henry's Law Constant (KH) ~ (mole/Litre - atm).

Figure 2 shows the increase in inorganic carbon for the on-orbit IATCS over time. Because of the Henry's Law relationship for the concentration of aqueous CO_2 ($[\text{CO}_2]_{\text{aq}}$) relative to the Partial Pressure of CO_2 (PCO_2), any change in cabin CO_2 establishes a driving force for mass flow through the flexhose membrane. The rate of mass flow is determined by the permeability of the membrane separating the gas from liquid. Under initial rates of permeation of $0.72 \text{ mg C}^{12}/\text{L-days}$ the IATCS absorbed 151 mg of CO_2 per day. After the U.S. airlock, which is

parasitic to the USL, was attached, the macroscopic rate in the entire system was 0.45 mg of CO_2 per litre per day. In the 257 litre system the permeation rate equates to 115 mg of CO_2 per day.

The absorption rate of CO_2 into the ITCS occurred with an effective Permeation Rate Constant (K_p) value of $\sim 0.00124 \text{ g/day atm ft}$. Qualitative observations have been that CO_2 into the IATCS occurs at a faster rate of permeation than CO_2 out of the IATCS. This is probably due to the lower kinetics of gasses in liquids than with air. The consequence of this phenomenon is that as CO_2 cabin environment increases, the IATCS pH will drop faster than it will go up when the cabin has lower CO_2 concentrations.

This relationship between dissolved CO_2 ($\text{CO}_{2\text{aq}}$) and partial pressure of CO_2 (PCO_2)

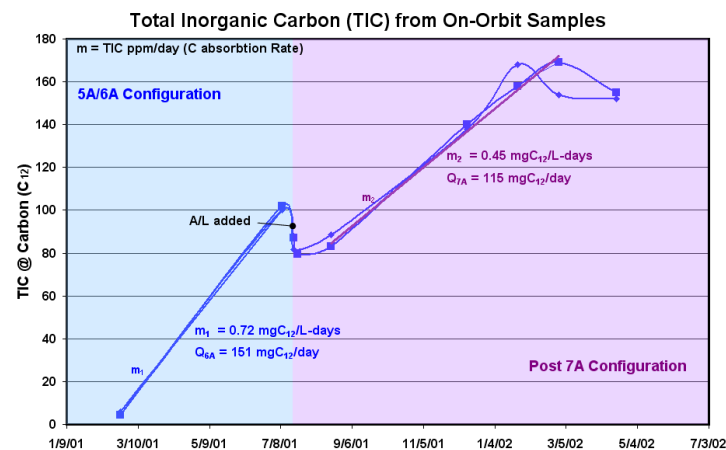


Figure 2. Initial On-orbit Increase in TIC

occurs in both directions. Once equilibrium is established, when the partial pressure of cabin CO_2 goes up the concentration of aqueous CO_2 goes up. When the partial pressure of cabin CO_2 goes down the concentration of aqueous CO_2 goes down.

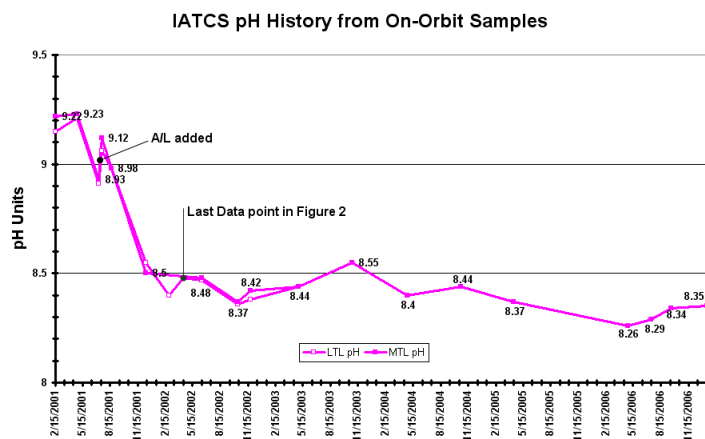


Figure 3. On-orbit pH History

The source of acidity in the on-orbit coolant that resulted in a decrease in system pH is directly due to dissolved carbon dioxide.

III. CO_2 Induced pH Changes On-orbit

As shown in Figure 3, on-orbit pH history indicates that the initial pH of the system on-orbit was 9.23. Shortly after the exposure to increased ISS cabin carbon dioxide levels the pH dropped to below 8.4 and appears to have stabilized between 8.25 and 8.5. This pH drop was accompanied by a sharp increase in Total Inorganic Carbon (TIC, C_T) in the system as shown in Figure 2.

Figure 4 shows a stability diagram for matrix phase nickel braze material utilized in the

coldplates of the ISS. This Pourbaix diagram is based on the on-orbit chemistry as defined and measured by samples returned from ISS flight 11A (11/24/02). The pH range of thermodynamic stability for nickel orthophosphate is approximately 6.4 where approximately half the nickel would be nickel orthophosphate vs. ionic nickel and 8.4 pH units where half would be nickel orthophosphate vs. nickel hydroxide. The increase in ORP nickel corrosion produced increased corrosion products by their interaction with specified hydroxides and phosphates in the system.

IV. Carbon Dioxide Equilibrium in an Open Aqueous System

Because the coolant on-orbit is freely exchanging CO_2 with the cabin environment, the system is defined as an "open" carbon dioxide system. In an open carbon dioxide system the total inorganic carbon (TIC) is not constant but will change in accordance with Henry's Law.

Once CO₂ enters water a series of equilibrium reactions take place.

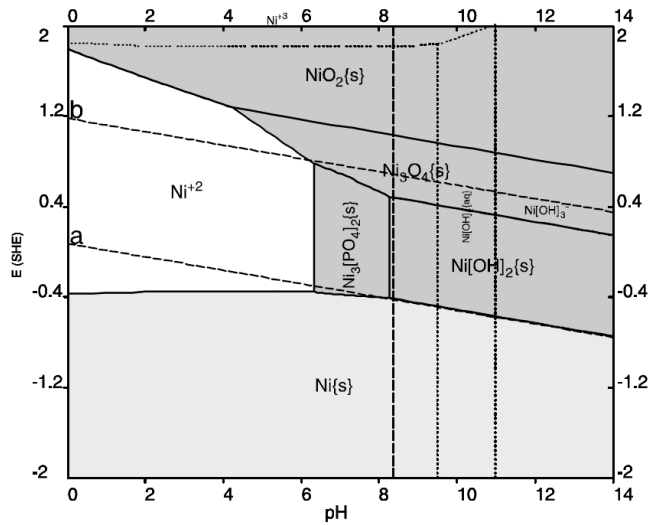
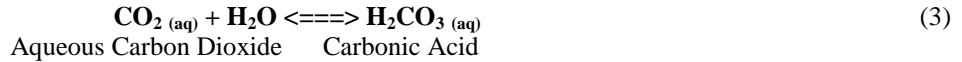


Figure 4. Pourbaix Diagram Nickel-Water system

Carbon dioxide is slightly soluble in water and that solubility decreases with increased temperature. A close look at Figure 3 On-orbit pH History shows that the Low Temperature Loop (LTL; Temperature ~ 10°C) consistently has a lower pH than that of the Moderate Temperature Loop (MTL; Temperature ~ 20°C). This is due to colder water absorbing more CO₂ than that of the warmer water. This is reflected in the temperature dependence of Henry's Law constants in the relationship $[\text{CO}_2]_{\text{aq}} = P_{\text{CO}_2} K_H$. As shown in Figure 5, as the temperature increases, Henry's Law constants decrease. Derivation of the basic equilibrium equations relative to terms of the partial pressure of CO₂ start as shown in equation 1.

$$[\text{CO}_2]_{\text{aq}} = P_{\text{CO}_2} K_H \quad (2)$$

Once the carbon dioxide dissolves a small fraction of this is converted to carbonic acid (H₂CO₃).



There is a standard practice that carbonic acid (H₂CO_{3(aq)}) concentration and hydrated carbon dioxide (CO_{2(aq)}) concentration are treated together. This is due to the following logic. "True" carbonic acid (H₂CO₃) is a strong acid (pK_a of 3.4 to 3.8) however it only exists in aqueous solutions in equilibrium with CO₂. The [H₂CO₃] is 650 times smaller than [CO₂]. $[\text{CO}_{2(\text{aq})}] = 650 [\text{H}_2\text{CO}_3]$ Therefore:

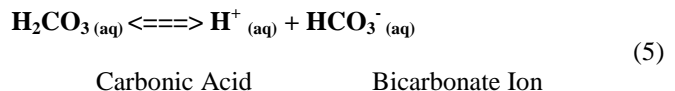
$$[\text{H}_2\text{CO}_3^*] = [\text{H}_2\text{CO}_3] + [\text{CO}_2]_{\text{aq}} \text{ or } \approx [\text{CO}_2]_{\text{aq}} \approx [\text{H}_2\text{CO}_3^*] \approx [\text{CO}_2]_{\text{aq}} \quad (4)$$

Thus what is referred to as "dissolved carbon dioxide" is mostly CO_{2(aq)} with a small amount of carbonic acid. This mixture or composite is referenced as [H₂CO₃*]. The dissociation constants in Table 1 were computed using this assumption. It should be noted that as equation 3 points out, the concentration of aqueous CO₂ is independent of the pH (-log([H⁺])) of the aqueous medium. It has no [H⁺] dependent term. It is purely a function of the partial pressure of CO₂ in the environment.

Temp (oC)	pK _H	K _H (mol/L/atm)
0	1.11	0.0769
5	1.19	0.064
10	1.27	0.0536
15	1.34	0.0455
20	1.41	0.0392
25	1.46	0.0345

Table 1. Henry's Law Constants

Carbonic acid (H₂CO₃) is diprotic; it has two hydrogen atoms which can dissociate and therefore two dissociation constants. Any loss of H₂CO_{3(aq)} from the system during dissociation is replaced by the environment. Carbonic acid may lose protons to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions. In this case the proton is liberated to the water, decreasing pH.



Therefore combining reactions (3) and (5),



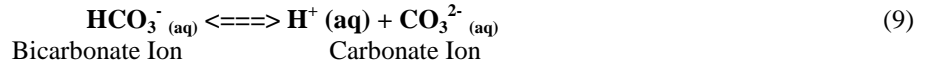
The dissociation constant (K_a) determines the relative concentrations of molecules on both sides of the equilibrium equation.

$$K_{a1} = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_{2(aq)}] \quad (7)$$

Relative to the reaction 6 and reworking the first dissociation constant, equation 7 via equation 2 redefines the bicarbonate concentration in terms of P_{CO_2} : Therefore:

$$K_{a1} = [\text{H}^+][\text{HCO}_3^-]/P_{\text{CO}_2} K_H \quad [\text{HCO}_3^-] = P_{\text{CO}_2} K_H K_{a1} / [\text{H}^+] \quad (8)$$

The bicarbonate ion can also lose the other proton to form a carbonate ion (CO_3^{2-}). The proton is again liberated to the water, increasing acidity and decreasing pH.



Similarly, relative to the reaction 9 and reworking the second dissociation constant, equation 10 via equation 8 redefines the carbonate concentration in terms of P_{CO_2} :

$$K_{a2} = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]; K_{a2} = [\text{H}^+][\text{CO}_3^{2-}]/(P_{\text{CO}_2} K_H K_{a1} / [\text{H}^+]); [\text{CO}_3^{2-}] = P_{\text{CO}_2} K_H K_{a1} K_{a2} / [\text{H}^+]^2 \quad (10)$$

The total carbon (C_T) in solution in pure water is defined as the sum of all of the inorganic carbonate species. Total Inorganic Carbonates (TIC) = Total Carbon (C_T):

$$C_T = [\text{CO}_{2(aq)}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (11)$$

These relationships of carbonate species are best viewed and understood graphically. The best graphical approach is a log-log diagram since pH is a logarithmic function of the $[\text{H}^+]$ and the concentrations of the bicarbonate and carbonate ions are also a function of $[\text{H}^+]$. Assuming the partial pressure of CO_2 in the environment is a constant:

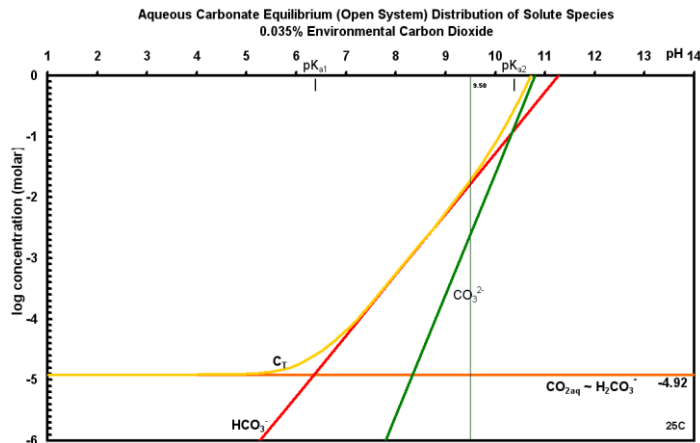


Figure 5. Open Carbon Dioxide System 0.035% CO_2

For Carbonic Acid:

$$\log[\text{H}_2\text{CO}_3^*] \sim \log[\text{CO}_{2(aq)}] = \log(P_{\text{CO}_2}) + \log(K_H)$$

For bicarbonate:

$$\log[\text{HCO}_3^-] = \log(P_{\text{CO}_2} K_H K_{a1}) + \text{pH}$$

For carbonate:

$$\log[\text{CO}_3^{2-}] = \log(P_{\text{CO}_2} K_H K_{a1} K_{a2}) + 2\text{pH}$$

Figure 5, Open Carbon Dioxide System, graphically depicts water in equilibrium with nominal ground concentrations of gaseous CO_2 and provides the following observations:

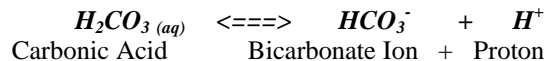
- Carbon dioxide concentration is independent of pH as evidence of having a slope of zero (orange line).
- The bicarbonate line always has a slope of 1 (red line)
- The carbonate line always has a slope of 2 (green line).
- The intersection of the CO_2 line and HCO_3^- lines is always at $\text{pH} = \text{p}K_{a1}$; $\text{p}K_{a1} = -\log(K_{a1})$
- The intersection of the HCO_3^- and the CO_3^{2-} lines is always at $\text{pH} = \text{p}K_{a2}$

Because of the constraints placed on the interrelationship of carbonate species in an open aqueous carbon dioxide system, the relationship between the total carbonates and the pH at a given level of environmental CO₂ is therefore constrained. Knowing any two parameters of CT, pH, or PCO₂ the third is defined.

V. Alkalinity

A basic understanding of the chemistry of alkalinity in open aqueous carbon dioxide systems is used to show the quantitative behavior of the system under the influence of the on-orbit carbon dioxide environment.

Alkalinity (Alk) is the ability of a fluid to neutralize strong acids to a given degree.



In this example carbonic acid has the capability to donate a proton so it is by definition an acid. In the reverse reaction the bicarbonate ion can accept a proton to form carbonic acid, so the bicarbonate ion in this reaction is by definition a base. The difference in the concentration of the base (C_B) to the concentration of the acid (C_A) will be the alkalinity of the solution. Any net excess base provides for the capability to neutralize acids (i.e. alkalinity).

$$[Alk]_M = C_B - C_A \quad (12)$$

[Alk]_M is the concentration of moles of protons per litre (M) required to reach the end point. A thousand times the [Alk]_M is the expression for milliequivalents (meq/L) of protons per litre. If the concentration of strong acid and strong base are equal, the alkalinity is zero (the end point condition). When a strong acid or strong base is added to a solution, the alkalinity will change in accordance to equation 12. In order for a solution to neutralize acid (H⁺) there must be an excess amount of anions (negatively charged ions) (e.g. OH⁻) that will react with that added hydrogen and form a neutral molecule (e.g. H⁺ + OH⁻ ==> H₂O).). It is the Acid Neutralization Capability (ANC) that determines how much acid (hydrogen protons) it takes to neutralize the solution to reach a certain end point. The end point in carbon dioxide systems (including the IATCS) will be where the bicarbonate concentration equals the hydrogen ion concentration ([HCO₃⁻] = [H⁺]) in a closed system. This point corresponds to a pH of approximately 4.2.

$$[Alk]_M = [ANC] = C_B - C_A \quad (13)$$

Alkalinity is the parameter that has determined the pH of the IATCS in the USL carbon dioxide (CO₂) cabin environment and will continue to determine the pH of the IATCS after the new buffer is present.

ISS USLab Initial Total Alkalinity

The total alkalinity in the ISS system is then given by the sum of the contributors to acid neutralization capability (ANC). The ISS system before the new buffer addition has an alkalinity of :

$$[Alk]_{T \text{ Initial}} = \Sigma(ANC)$$

$$[Alk]_{T \text{ Initial}} = C_B - C_A = [OH^-] - [H^+] + [B(OH)_4] + 2[PO_4^{3-}] + [HPO_4^{2-}] - [H_3PO_4] - [HSO_4^-]$$

$$[Alk]_{T \text{ Initial}} = \Sigma(ANC) = 15.4 \text{ to } 23.4 \text{ meq/L}$$

A. Rules for Open Carbon Dioxide System Alkalinity

The ISS chemical changes have occurred primarily because of the absorption of CO₂. The relationship between CO₂ absorption and alkalinity are defined by the following two rules.

1. *There is no alkalinity in a CO₂ water system, unless other sources of base are added*

Deionized (DI) water exposed to CO₂ gas will not have any alkalinity regardless of how much CO₂ is absorbed into the water.

2. The absorption of CO₂ into the ISS system does not change the IATCS alkalinity

This means that even though total carbonates have increased in the system, the alkalinity of the system does not change. Even though carbonic acid dissociation produces two species that support the acid neutralizing capability of the system, [HCO₃⁻] and [CO₃²⁻], the alkalinity of the system does not change with the absorption of CO₂. The best way to understand this is that CO₂ is a neutral molecule (has no charge) and water H₂O has no charge. So when they combine to form carbonic acid they have not increased the acid neutralization capability of the solution. They increase the acidity of the solution (which is why the pH drops) but do not change the alkalinity.

Because the alkalinity does not change with CO₂ absorption, the distribution of species that make up alkalinity must change.

3. A given value of alkalinity prescribes one and only one pH in an open system of fixed P_{CO2}

This simple rule states that in an open carbon dioxide system, the pH is prescribed by the alkalinity of the system. Each value of alkalinity prescribes one and only one pH. This rule defines the solution to the ISS pH problems in the CO₂ environment induced by the Cabin Air. Alkalinity in a pure carbon dioxide system would be the sum of all of the acid neutralization capable (ANC) parameters associated with CO₂ absorption in an open aqueous system.

$$[\text{Alk}]_T = C_B - C_A = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (14)$$

Note that the alkalinity term for carbonate ions is multiplied by a factor of two because it can take two protons. Substituting the relationships established derives an expression for the total alkalinity in a pure carbon dioxide system in terms of the partial pressure of P_{CO2} and the pH.

$$[\text{Alk}]_T = P_{\text{CO}_2} K_H K_{a1} / [\text{H}^+] + 2 P_{\text{CO}_2} K_H K_{a1} K_{a2} / [\text{H}^+]^2 + [\text{OH}^-] - [\text{H}^+] \quad (15)$$

This relationship is displayed as a [Alk]_T line in Figure 6 Carbonate Alkalinity. The pH would be changed by the addition of a strong acid or strong base. Figure 6 details the relationships between the concentration of individual carbon species and alkalinity in a 0.031% CO₂ environment (ground concentrations). Notice that at pH 8 – 9, the major contribution to the system alkalinity is due to the bicarbonate concentration ([HCO₃⁻]). At pH 9-10 the contribution of carbonate ions can be seen.

Chemical Change	Alkalinity Response Notes
Increase in CO ₂	None Increased Acidity C _T Increases
Increase in [H ₂ CO ₃] (Same as increased CO ₂)	None Increased Acidity C _T Increases
Add NaHCO ₃	Increases (x1) C _T Increases
Add Na ₂ CO ₃	Increases (x2) C _T Increases
Add Strong Acid C _A (e.g. H ⁺)	Decreases C _T Decreases C _T Unchanged (Closed System)
Add Strong Base C _B (e.g. OH ⁻)	Increases C _T Increases C _T Unchanged (Closed System)
Dilution	Decreases C _T Decreases
Temperature	None Proton balance maintained
Pressure	None Proton balance maintained

Table 2. Conservative Response in Carbon Dioxide Systems

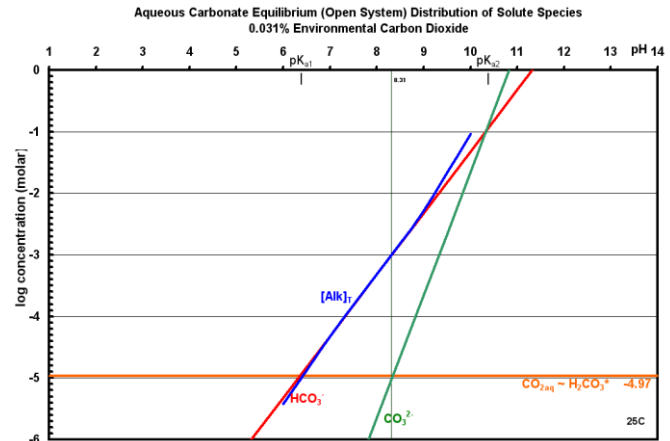


Figure 6. Carbonate Alkalinity

Table 2 shows the response of alkalinity to chemical changes in an open aqueous system (e.g. the IATCS).

B. Alkalinity of Mixtures (Pankow)

Because of the conservative nature of alkalinity, the alkalinity of a mixture of two fluids is merely the weighted mean of the mixing process. When solutions of

Type I and II are mixed in proportions of x parts of I and y parts of II the resulting alkalinity will be:

$$\text{Alk}_{\text{mix}} = (\text{xAlk}_I + \text{yAlk}_{II})/(\text{x+y}) \quad (16)$$

	Addition of Molar Increments of:				
Capacity	C _B	C _A	H ₂ CO ₃ [*] (CO ₂)	NaHCO ₃	Na ₂ CO ₃
C _T , M	0	0	+1	+1	+1
[Alk] (eq/L)	+1	-1	0	+1	+2

Table 3 Capacity Change Responses

the alkalinity is increased by 1 eq/l and for every mole of sodium carbonate 2 eq/l is added.

The significance of equation 16 is that the resulting mixed alkalinity for the ISS coolant loops can be determined for conditions of dilution or additions of make-up fluids.

Table 3 provides a quantified look at the changes occurring with the addition of sodium bicarbonates/carbonates. For the addition of each mole of sodium bicarbonate

C. New Coolant Specification Alkalinity

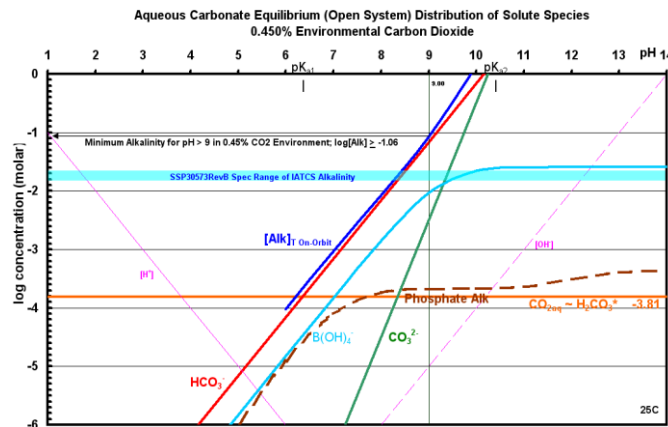


Figure 7. Minimum Alkalinity Requirement in a 0.45% CO₂ Environment

carbonate species in terms of the partial pressure of CO₂ and [H⁺].

Cabin CO ₂ mole%	Alkalinity meq/L	Temperature °C	pH
0.4%	140.9	20°C	9.23
0.7%	118.9	10°C	8.92

Table 4 Nominal Envelope Parameters

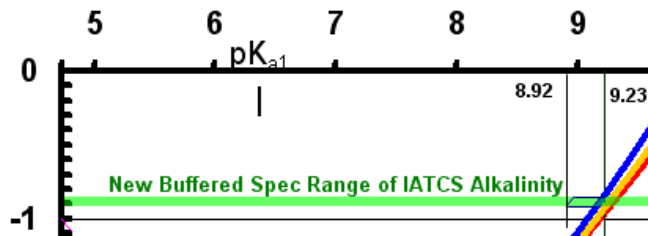


Figure 8. Performance Parallelogram for new Buffer

Figure 7, Minimum Alkalinity Requirement in a 0.45% CO₂ Environment, indicates that in order to maintain a pH ≥ 9 in a 0.45% CO₂ environment for the USL the log[alkalinity] ([Alk]_{T On-Orbit}) must be ≥ -1.06. At pH 9.0 that means that the [Alk] ≥ 0.085M or 85.0 meq/L. The pre-buffer alkalinity was 15.4 to 23.4 meq/L. Within specified tolerances the new alkalinity is 118.9 to 140.9. The new equation for coolant alkalinity will be:

$$[\text{Alk}]_{\text{New}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] \quad (17)$$

Because the IATCS system is an open carbon dioxide system, equation 17 will have to be rewritten to incorporate the relationship of the

In an open system, in order to increase the pH of the system, the alkalinity must be increased. The relationship defined by equation 18 is represented by the 'New Buffered Spec Range of IATCS Alkalinity' in Figure 8. Based on the conservative response to the addition of bases and the natural existence of bicarbonate in solution, an 0.4 equi-molar mixture of sodium bicarbonate and sodium carbonate was chosen. The ideal model results are shown in Table 4.

This theoretical chemical model (assumes ideal behavior) was used to assess the expected performance for the range of potential buffer concentrations, thermal effects and CO₂ environmental conditions.

$$[\text{Alk}]_{\text{New}} = P_{\text{CO}_2} K_H K_{a1} / [\text{H}^+] + 2 P_{\text{CO}_2} K_H K_{a1} K_{a2} / [\text{H}^+]^2 + B_T K_b / ([\text{H}^+] + K_b) + [\text{OH}^-] - [\text{H}^+] \quad (18)$$

Figure 8 is a close-up of the parallelogram that is produced under these conditions for the new buffer. The top

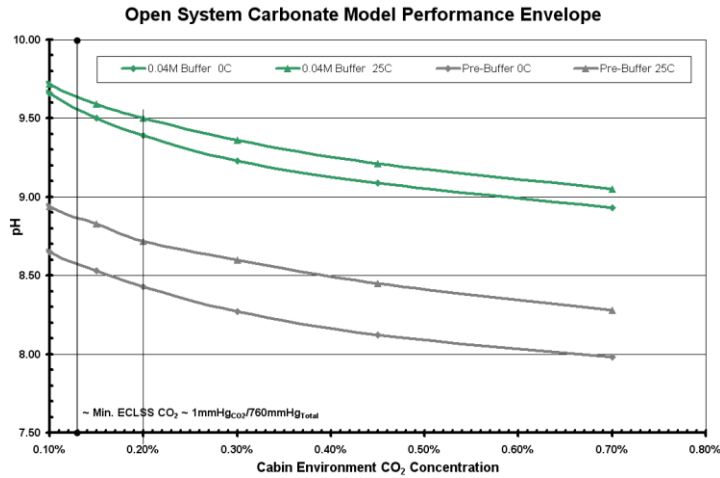


Figure 9. 0.4M Buffer vs. Pre-Buffer Performance

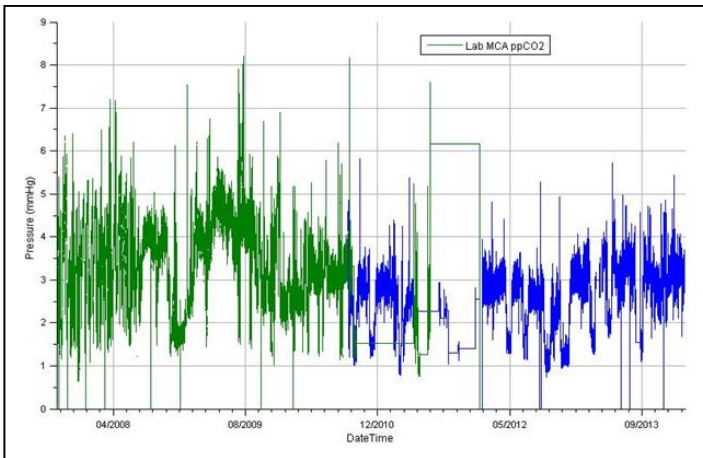


Figure 10. On-orbit US Lab CO₂ Environment

slightly higher pH than is observed. A 0.31% Cabin environment equates to a pH of 9.3 based on this ideal model. However, a 0.4 equal molar solution of sodium carbonate and sodium bicarbonate in conjunction with existing ions creates a solution with ion strength of approximately 0.16. This is high enough to have to consider ionic strength when calculating the resultant pH. This ionic strength shifts the pK_{a1} value from 6.42 to 6.27 and pK_{a2} from 10.43 to 10.05. The result of the pH calculation with these dissociation constants is a pH of 9.14.

Figure 11 provides the results of the calculated average alkalinity and resulting pH prior to buffer addition as well as the measured alkalinity and resulting pH when the 0.4 equi-molar bicarbonate/carbonate buffer is added.

This higher pH has decreased the oxidation and reduction potential (ORP) of the coolant that manifests itself in decreased corrosion rates of the systems nickel hardware. These interactions were governed by the thermodynamic state of the coolant and solubility laws relative to the precipitates.

and base of the parallelogram are defined by the alkalinity range as specified. The top is defined by the maximum alkalinity specification and the base being the minimum. The sides of the parallelogram are defined by the highest and lowest CO₂ partial pressures to which the coolant is exposed. The left side is defined by the alkalinity under high cabin CO₂ conditions. The right side is defined by the alkalinity of the low CO₂ condition. These are the extremes of equilibrium values and these extreme conditions would have to be maintained for some time for the system to fully equilibrate to these conditions.

The grey curves in Figure 9 represent the pre-buffer performance of the IATCS. The green curves are for the expected performance of the 0.04M bicarbonate/carbonate buffer. Both sets reflect temperature dependence from 0°C – 25°C and P_{CO2} from 0.10% to 0.70% CO₂ in the cabin environment. The lowest curve in each group represents the lowest performance conditions of low alkalinity and cold water (more CO₂ absorbed in cold water). The 0.04M bicarbonate/carbonate buffer assumes the range as specified for USL conditions via the Buffer Delivery Applicator (BDA) as well as the waiver chemistry composition in the other IATCS loops.

Figure 10 shows the historic CO₂ concentrations of the ISS Cabin.

The ideal curves shown will estimate a

VI. Conclusion

Early ISS Program decisions on the use of gas permeable Teflon flexhoses and the unanticipated effects of higher on-orbit CO₂ concentrations in the cabin environment created a lower pH in the IATCS. This lower pH has

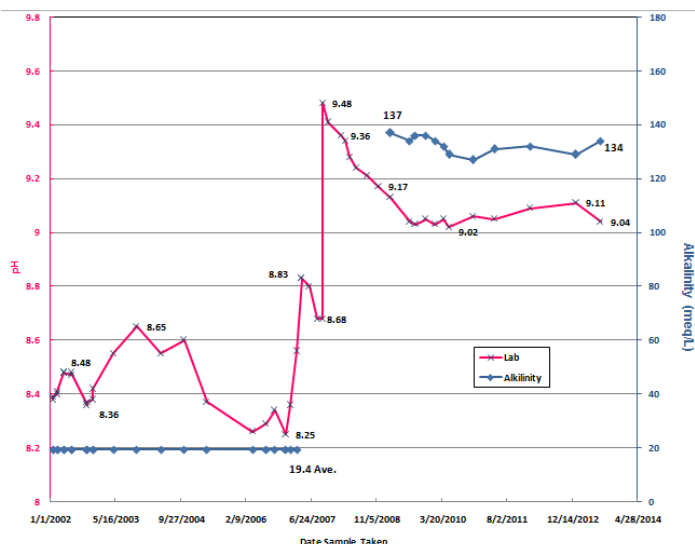


Figure 11. 0.4M Buffer On-Orbit Results

more stable passive layer. The reduced corrosion activity has resulted in the lower production of insoluble nickel precipitates in the system (namely nickel hydroxide). Phosphates no longer react with nickel to form nickel orthophosphate. Understanding the effects of the water coolant with its environment provided all the knowledge required to ensure a safe and effective implementation and maintenance.

increased the oxidation and reduction potential of the coolant that manifests itself in increased corrosion rates of the system's nickel hardware. The increase in nickel corrosion produced increased corrosion products by their interaction with specified hydroxides and phosphates in the system. These interactions were governed by the thermodynamic state of the coolant and solubility laws relative to the precipitates. The chemical principles governing the changes that occurred in the IATCS are still in existence even after the addition of a bicarbonate/carbonate buffer. However, the system behavior is now in a more acceptable condition.

The new system chemistry has maintained a higher pH, which has minimized the nickel corrosion activity by lowering the system ORP and provides a

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