

Preliminary Study on the Total Dissolved Organics Measurement and Their Contribution to Conductivities at Elevated Temperature

Kwang-Rag Kim, Hee-Suk Kang, Seung-Woo Paek, Sung-Ho Lee, Do-Hee Ahn, Han-Soo Lee, Hongsuk Chung, and Ki-Woung Sung

Korea Atomic Energy Research Institute

Abstract

Total organic carbon (TOC) derived from organics is one of the possible contamination in the reactor water system and causes of *pH* change and high conductivity levels. Measurements of total dissolved oxidizable carbon were carried out and its contribution to conductivities at elevated temperature was studied by using the thermodynamic equilibrium analysis in carbonic acid system. The calculated conductivities were in good agreement with the levels observed for the formation of carbonic acid from salicylic acid solution.

1. Introduction

A wide variety of organic compounds can enter the secondary cycle of reactor water systems, e.g., resins, lubricating oils, cleaning solvents and organics in the makeup water source. Total organic carbon (TOC) has been recognized for many years as a contaminant in high-purity water systems used in power generation, and causes for concern. The nature of these materials or their decomposition products at high temperatures may impact on materials corrosion. Analysis for most organic species presents significant difficulty to plant staffs because of the limited capability of conventional plant equipment to identify and quantify such species.

Recent field experience has shown that organics can contribute a significant amount towards the cation conductivity of a solution in the secondary water systems. Of particular concern is coolant conductivity. Conductivity is a measure of ionic concentrations. Low conductivity is important because it indicates low concentrations of ions which promote stress corrosion cracking (SCC) and to increase crud transport[1].

Carbonic acid, H_2CO_3 , formed from the breakdown of an organic compound reduces pH by dissociation to H^+ and the bicarbonate ion, HCO_3^- . Carbon dioxide that dissolves according to



Equilibrium in this reaction favors concentration of the bicarbonate as pH increased, and also increase corrosion in steam-condensate systems by lowering the pH . Although carbonates have been identified as accelerating intergranular attack of alloy 600 tubing, there is currently no data available on which to base a value. Various amines of the form R-NH_2 are routinely added to steam and condensate waters to neutralize acidity caused by carbon dioxide. They currently hydrolyze to OH^- by



which neutralizes the acidity produced by this reaction.

This study is to describe the aspects of water chemistry pertaining to conductivity which could be directly in connection to the dissolved oxidizable carbon. The conductivities were calculated by using the thermodynamic equilibrium analysis in carbonic acid system based on the total organic carbon content. These values were compared with observed levels for the formation of carbonic acid from salicylic acid solution.

2. Thermodynamic equilibrium analysis in carbonic acid system

The carbonic acid ($\text{CO}_2(\text{aq})$) would be saturated at a certain equilibrium with dissolved organic contaminant for the existing environment condition such as temperature, presence of catalyst, and radiation, etc. Radiation from nuclear reactor would increase the oxidation rate of organic contaminants.



The usefulness of the TOC meter arises from ones ability to calculate how much of the conductivity is due to carbon species. One can see that carbon dioxide is formed from the breakdown of an organic compound and is directly proportional to the initial TOC concentrations. The inorganic carbon content, given as total dissolved carbon species ($\text{CO}_2(\text{aq})$, HCO_3^- , and CO_3^{2-}), can be derived using carbonic acid-water equilibrium from conductivity data, and visa-versa.

This value includes carbon in the form of carbonates or bicarbonates which may have been present. At various reactor operating condition, the equilibrium constant of Eq.(3) could be accomplished by subtracting inorganic carbon content from TOC values. The conductivity readings can be mainly given because of dissociation into H^+ and HCO_3^- .

The basic reactions of the dissolution and ionization of the carbon dioxide can be written as follows:



and



Here, K_0 , K_1 , K_2 and K_w are the equilibrium constants of the corresponding reactions. The molality of each species is assumed to be defined by the equilibrium of the relevant reactions. The ionization constant of water, K_w , can be found in several sources.

The total charge concentration of the positive ions should be equal to that of the negative ions in the solution for the charge neutrality of the system. Thus the final molality of H^+ is derived from the charge balance equation:

$$[\text{H}^+] - [\text{HCO}_3^-] - [\text{OH}^-] - 2[\text{CO}_3^{2-}] = 0 \quad (8)$$

The ionization constant of water ($K_w = [\text{H}^+][\text{OH}^-]$) was taken from the recommendation by Marshall and Frank[2].

Furthermore, the total dissolved carbon concentration is the sum of the following species concentrations:

$$\Sigma[\text{C}] = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (9)$$

The estimated molal ionic activity coefficients γ_z were calculated in accordance with the extended Debye-Hückel expression:

$$\log \gamma_z = (-z^2 A I^{0.5}) / (1 + 1.5 I^{0.5}) \quad (10)$$

where z = ionic charge

$$I = \text{ionic strength} \left(= \frac{1}{2} \left\{ [\text{H}^+] + [\text{HCO}_3^-] + [\text{OH}^-] + 4[\text{CO}_3^{2-}] \right\} \right)$$

$$A = \text{Debye-Hückel limiting slope, estimated in accordance to Mesmer, Baes, and Sweeton[3].}$$

The equilibrium constants K for the dissolved carbon species reactions were calculated from the free-energy change of the reaction by the following thermodynamic relation:

$$\Delta G^o(T) = -RT \ln K^o(T) \quad (11)$$

and $\Delta G^o(T)$ was estimated from the free energy of formation $[\Delta G_f^o(T)]$ values of the reactant and product species. Because of the lack of reliable experimental data on $\Delta G_f^o(T)$ for dissociation of carbon dioxide in aqueous solution at elevated temperatures, they were calculated by applying the

following expression:

$$\begin{aligned} \Delta G^{\circ}(T) = & \Delta G^{\circ}(298.15) - \Delta S^{\circ}(T - 298.15) \\ & + \overline{\Delta C_p^{\circ}}(T - 298.15) - \overline{\Delta C_p^{\circ}} T \ln(T/298.15) \end{aligned} \quad (12)$$

Where $\overline{\Delta C_p^{\circ}}$ represents the average standard heat capacity change at the temperatures involved, and $\Delta S^{\circ}(298)$ is the standard state entropy change at 25°C. Corresponding thermodynamic values are summarized in Table 1 [4].

Finally, the specific conductance of solute solutions of electrolytes can be obtained by summing the product of ionic conductances of species (Table 2 [4]). A table of the results for these calculations at 25 °C can be found in Table 3. Also a graph relating TOC to conductivity at 25 and 50°C can be found in Fig1. The conductivities were measured after the complete oxidation (water flow through the UV-illuminated thin film of TiO₂) of the organics present in the salicylic acid solution to CO₂. The calculated conductivities were shown to have a good agreement with the levels observed for the formation of carbonic acid from salicylic acid solution.

3. Conclusion

Results show that total organic carbon derived from organics is one of the possible contamination in the reactor water system and is the cause of *pH* change and high conductivity levels. To assist in evaluating the maximum tendency for acid formation in regions where local concentrations develop, resource can be made to cation conductivity levels to access the total anion concentration in a given reactor water system. Where the observed cation conductivity is greater than that predicted from the observed ions, another ionic species such as carbonic acid derived from organics would have to be present and considered.

For further work, the inclusion of TOC oxidation processes such as use of 185 nm UV lamps is on going in KAERI.

References

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3. R. Mesmer, C.Baes, and F. Sweeton, "Boric Acid Equilibria *pH* in PWR Coolants," *Proc. 32nd Int. Conf. Water*, Pittsburgh, Pennsylvania, p.55 (Nov. 1971)
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Table 1. Equilibrium properties for carbonic acid - water system

Reactions	Equilibrium properties
$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$	$\Delta G_{298}^{\circ} = 2003 \text{ cal mol}^{-1}$, $\Delta S_{298}^{\circ} = -23.0 \text{ cal mol}^{-1} \text{ deg.}^{-1}$ and $C_p = 36 \text{ cal mol}^{-1} \text{ deg.}^{-1}$
$\text{CO}_2(\text{aq}) + \text{OH}^- = \text{HCO}_3^-$	$\Delta G_{298}^{\circ} = 10,406 \text{ cal mol}^{-1}$, $\Delta S_{298}^{\circ} = -372 \text{ cal mol}^{-1} \text{ deg.}^{-1}$ and $C_p = 19.5 \text{ cal mol}^{-1} \text{ deg.}^{-1}$
$\text{HCO}_3^- + \text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O}$	$\Delta G_{298}^{\circ} = 5000 \text{ cal mol}^{-1}$, $\Delta S_{298}^{\circ} = -16.1_6 \text{ cal mol}^{-1} \text{ deg.}^{-1}$, and $\Delta C_p = -21.0 \text{ cal mol}^{-1} \text{ deg.}^{-1}$

Table 2. Limiting ionic conductances of the ions (Siemens $\text{cm}^2 \text{ eq}^{-1}$)

Ion	Temperature ($^{\circ}\text{C}$)					
	0	18	25	100	200	300
H^+	225	315	349.8	634	824	894
OH^-	105	171	198.3	447	701	821
HCO_3^-	24	43.9	51.5	156	306	460

Table 3. Equilibrium concentrations(molal) of dissolved carbon species as a function of CO_2 partial pressure at 25°C

P_{CO_2} (bar.)	CO_2 (aq.)	H^+	HCO_3^-	OH^-	CO_3^{2-}	Ionic strength	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Total carbon species (ppm)
1.10E-07	3.74E-09	1.06E-07	1.46E-08	9.16E-08	6.18E-12	1.06E-07	6.97	5.61E-02	1.05E-03
1.00E-06	3.40E-08	1.54E-07	9.12E-08	6.31E-08	2.66E-11	1.54E-07	6.81	7.12E-02	7.06E-03
2.00E-06	6.80E-08	1.95E-07	1.45E-07	5.00E-08	3.35E-11	1.95E-07	6.71	8.54E-02	1.18E-02
3.00E-06	1.02E-07	2.28E-07	1.85E-07	4.27E-08	3.66E-11	2.28E-07	6.64	9.77E-02	1.58E-02
4.00E-06	1.36E-07	2.57E-07	2.19E-07	3.79E-08	3.84E-11	2.57E-07	6.59	1.09E-01	1.93E-02
5.00E-06	1.70E-07	2.83E-07	2.49E-07	3.44E-08	3.96E-11	2.83E-07	6.55	1.19E-01	2.26E-02
6.00E-06	2.04E-07	3.07E-07	2.75E-07	3.17E-08	4.04E-11	3.07E-07	6.51	1.28E-01	2.58E-02
7.00E-06	2.38E-07	3.29E-07	2.99E-07	2.96E-08	4.10E-11	3.29E-07	6.48	1.36E-01	2.87E-02
8.00E-06	2.72E-07	3.50E-07	3.22E-07	2.78E-08	4.15E-11	3.50E-07	6.46	1.44E-01	3.16E-02
9.00E-06	3.06E-07	3.69E-07	3.43E-07	2.64E-08	4.19E-11	3.69E-07	6.43	1.52E-01	3.44E-02
1.00E-05	3.40E-07	3.88E-07	3.63E-07	2.51E-08	4.22E-11	3.88E-07	6.41	1.59E-01	3.71E-02
2.00E-05	6.80E-07	5.40E-07	5.22E-07	1.80E-08	4.36E-11	5.40E-07	6.27	2.19E-01	6.17E-02
3.00E-05	1.02E-06	6.57E-07	6.42E-07	1.48E-08	4.41E-11	6.57E-07	6.18	2.66E-01	8.41E-02
4.00E-05	1.36E-06	7.57E-07	7.44E-07	1.29E-08	4.44E-11	7.57E-07	6.12	3.06E-01	1.05E-01
5.00E-05	1.70E-06	8.45E-07	8.33E-07	1.15E-08	4.46E-11	8.45E-07	6.07	3.41E-01	1.26E-01
6.00E-05	2.04E-06	9.25E-07	9.14E-07	1.05E-08	4.47E-11	9.25E-07	6.03	3.73E-01	1.46E-01
7.00E-05	2.38E-06	9.98E-07	9.88E-07	9.76E-09	4.47E-11	9.98E-07	6	4.02E-01	1.65E-01
8.00E-05	2.72E-06	1.07E-06	1.06E-06	9.14E-09	4.48E-11	1.07E-06	5.97	4.29E-01	1.84E-01
9.00E-05	3.06E-06	1.13E-06	1.12E-06	8.62E-09	4.49E-11	1.13E-06	5.95	4.55E-01	2.03E-01
1.00E-04	3.40E-06	1.19E-06	1.18E-06	8.18E-09	4.49E-11	1.19E-06	5.92	4.79E-01	2.22E-01
2.00E-04	6.80E-06	1.68E-06	1.68E-06	5.80E-09	4.51E-11	1.68E-06	5.77	6.76E-01	4.02E-01
3.00E-04	1.02E-05	2.06E-06	2.05E-06	4.74E-09	4.52E-11	2.06E-06	5.69	8.27E-01	5.74E-01
4.00E-04	1.36E-05	2.38E-06	2.37E-06	4.10E-09	4.52E-11	2.38E-06	5.62	9.54E-01	7.43E-01
5.00E-04	1.70E-05	2.66E-06	2.65E-06	3.67E-09	4.53E-11	2.66E-06	5.58	1.07E+00	9.10E-01
6.00E-04	2.04E-05	2.91E-06	2.91E-06	3.35E-09	4.53E-11	2.91E-06	5.54	1.17E+00	1.08E+00

Table 3. Equilibrium concentrations(molal) of dissolved carbon species as a function of CO₂ partial pressure at 25°C (continued)

P _{CO2} (bar.)	CO ₂ (aq.)	H ⁺	HCO ₃ ⁻	OH ⁻	CO ₃ ²⁻	Ionic strength	pH	Conductivity (μS/cm)	Total carbon species (ppm)
7.00E-04	2.38E-05	3.14E-06	3.14E-06	3.10E-09	4.53E-11	3.14E-06	5.5	1.26E+00	1.24E+00
8.00E-04	2.72E-05	3.36E-06	3.36E-06	2.90E-09	4.53E-11	3.36E-06	5.47	1.35E+00	1.40E+00
9.00E-04	3.06E-05	3.57E-06	3.56E-06	2.74E-09	4.53E-11	3.57E-06	5.45	1.43E+00	1.56E+00
1.00E-03	3.40E-05	3.76E-06	3.76E-06	2.60E-09	4.54E-11	3.76E-06	5.43	1.51E+00	1.73E+00
2.00E-03	6.80E-05	5.32E-06	5.31E-06	1.84E-09	4.54E-11	5.32E-06	5.27	2.13E+00	3.32E+00
3.00E-03	1.02E-04	6.51E-06	6.51E-06	1.50E-09	4.55E-11	6.51E-06	5.19	2.61E+00	4.89E+00
4.00E-03	1.36E-04	7.52E-06	7.52E-06	1.30E-09	4.55E-11	7.52E-06	5.12	3.02E+00	6.44E+00
5.00E-03	1.70E-04	8.41E-06	8.41E-06	1.16E-09	4.56E-11	8.41E-06	5.08	3.38E+00	8.00E+00
6.00E-03	2.04E-04	9.21E-06	9.21E-06	1.06E-09	4.56E-11	9.21E-06	5.04	3.70E+00	9.54E+00
7.00E-03	2.38E-04	9.95E-06	9.95E-06	9.84E-10	4.56E-11	9.95E-06	5	3.99E+00	1.11E+01
8.00E-03	2.72E-04	1.06E-05	1.06E-05	9.20E-10	4.57E-11	1.06E-05	4.97	4.27E+00	1.26E+01
9.00E-03	3.06E-04	1.13E-05	1.13E-05	8.68E-10	4.57E-11	1.13E-05	4.95	4.53E+00	1.42E+01
1.00E-02	3.40E-04	1.19E-05	1.19E-05	8.23E-10	4.57E-11	1.19E-05	4.92	4.78E+00	1.57E+01
2.00E-02	6.80E-04	1.68E-05	1.68E-05	5.83E-10	4.58E-11	1.68E-05	4.77	6.76E+00	3.10E+01
2.10E-02	7.14E-04	1.73E-05	1.73E-05	5.69E-10	4.59E-11	1.73E-05	4.76	6.93E+00	3.25E+01
2.20E-02	7.48E-04	1.77E-05	1.77E-05	5.55E-10	4.59E-11	1.77E-05	4.75	7.09E+00	3.40E+01
2.50E-02	8.50E-04	1.88E-05	1.88E-05	5.21E-10	4.59E-11	1.88E-05	4.72	7.56E+00	3.86E+01
3.00E-02	1.02E-03	2.06E-05	2.06E-05	4.76E-10	4.59E-11	2.06E-05	4.69	8.28E+00	4.62E+01
4.00E-02	1.36E-03	2.38E-05	2.38E-05	4.12E-10	4.60E-11	2.38E-05	4.62	9.57E+00	6.13E+01
5.00E-02	1.70E-03	2.67E-05	2.67E-05	3.69E-10	4.61E-11	2.67E-05	4.57	1.07E+01	7.65E+01
6.00E-02	2.04E-03	2.92E-05	2.92E-05	3.37E-10	4.61E-11	2.92E-05	4.53	1.17E+01	9.16E+01
7.00E-02	2.38E-03	3.16E-05	3.16E-05	3.12E-10	4.62E-11	3.16E-05	4.5	1.27E+01	1.07E+02
8.00E-02	2.72E-03	3.38E-05	3.38E-05	2.92E-10	4.62E-11	3.38E-05	4.47	1.35E+01	1.22E+02
9.00E-02	3.06E-03	3.58E-05	3.58E-05	2.75E-10	4.62E-11	3.58E-05	4.45	1.44E+01	1.37E+02
1.00E-01	3.40E-03	3.78E-05	3.78E-05	2.61E-10	4.63E-11	3.78E-05	4.42	1.52E+01	1.52E+02
1.00E+0	3.40E-02	1.20E-04	1.20E-04	8.30E-11	4.73E-11	1.20E-04	3.92	4.82E+01	1.50E+03

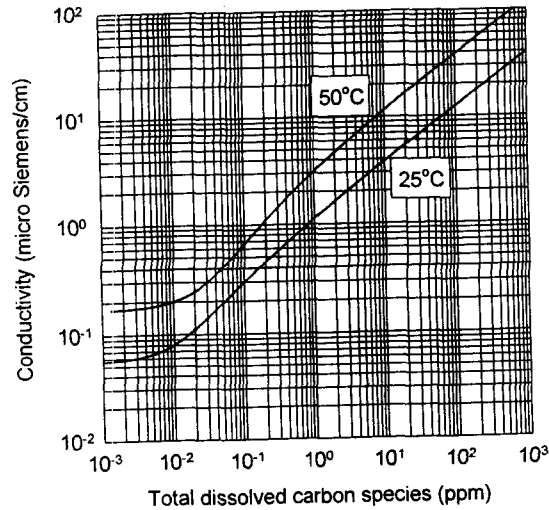


Fig. 1 Specific conductivity of aqueous CO₂ solutions at 25°C and 50°C.