Advanced Chemical Stability Diagrams to Predict the Formation of Complex Zinc Compounds in Chloride Environment

M. E. McMahon *, R. J. Santucci Jr., and J. R. Scully

Supplementary Information

The derivation of ion predominance will be systematically illustrated. The stability of each ion was assessed using stability constants, with respect to Zn^{2+}. For example, for the $Zn(OH)^{+}$ ion:

$$Zn^{2+} + OH^{-} \rightarrow Zn(OH)^{+} \qquad \log \beta = 4.40 \qquad \text{Equation 16}$$

$$4.40 = log\frac{[Zn(OH^{+})]}{[Zn^{2+}][OH^{-}]} = \log [Zn(OH)^{+}] - \log [Zn^{2+}] - \log [OH^{-}] \qquad \text{Equation 17}$$

$$\boxed{[Zn^{2+}][OH^{-}] \cdot 10^{4.40} = [Zn(OH)^{+}]} \qquad \text{Equation 18}$$

These relations were derived for each ion and summated to quantify the total available Zn ion concentration with respect to Zn^{2+} (summation with other stability derivations based on additional predominant ions such as $Zn(OH)_4^{2-}$ yields the same overall results):

$$Zn_{total} = [Zn^{2+}] + [Zn(OH)^{+}] + [Zn(OH)_2^{0}] + [Zn(OH)_3^{-}] + [Zn(OH)_4^{2-}] + [ZnCl^{+}] + [ZnCl_2^{0}] + [ZnCl_3^{-}] + [ZnCl_4^{2-}] \qquad \text{Equation 19}$$

$$Zn_{total} = [Zn^{2+}] + [Zn^{2+}][OH^{-}]\cdot 10^{4.4} + [Zn^{2+}][OH^{-}]^{2}\cdot 10^{11.3} + [Zn^{2+}][OH^{-}]^{3}\cdot 10^{14.14} + [Zn^{2+}][OH^{-}]^{4}\cdot 10^{17.66} + [Zn^{2+}][Cl^{-}]\cdot 10^{0.43} + [Zn^{2+}][Cl^{-}]^{2}\cdot 10^{0.61} + [Zn^{2+}][Cl^{-}]^{3}\cdot 10^{0.53} + [Zn^{2+}][Cl^{-}]^{4}\cdot 10^{0.20} \qquad \text{Equation 20}$$

$$Zn_{total} = [Zn^{2+}]\,(1 + 10^{pH-14+4.4} + 10^{2pH-28+11.3} + 10^{3pH-42+14.14} + 10^{4pH-56+17.66} + [Cl^{-}]\cdot 10^{0.43} + [Cl^{-}]^{2}\cdot 10^{0.61} + [Cl^{-}]^{3}\cdot 10^{0.53} + [Cl^{-}]^{4}\cdot 10^{0.20}) \qquad \text{Equation 21}$$

$$\boxed{Zn_{total} = [Zn^{2+}]\,(1 + 10^{pH-9.6} + 10^{2pH-16.7} + 10^{3pH-27.86} + 10^{4pH-38.34} + [Cl^{-}]\cdot 10^{0.43} + [Cl^{-}]^{2}\cdot 10^{0.61} + [Cl^{-}]^{3}\cdot 10^{0.53} + [Cl^{-}]^{4}\cdot 10^{0.20})} \qquad \text{Equation 22}$$

Knowing the available total aqueous Zn ion content with respect to Zn^{2+}, the next step is to quantify the corrosion product equilibrium stability, derived here for $Zn(OH)_2$ (amorphous) as an example:

$Zn(OH)_2$ (Amorphous)

With Respect to Zn^{2+}

$$\log K = -15.42 = \log[Zn^{2+}] + 2\log[OH^{-}] \qquad \text{Equation 23}$$

$$[Zn^{2+}] = 10^{-15.42 + 28 - 2pH} = 10^{12.58 - 2pH} \qquad \text{Equation 24}$$

$10^{12.58 - 2pH} = [Zn^{2+}]$ Equation 25

With Respect to $Zn(OH)_3^-$

$Zn(OH)_2 = Zn^{2+} + 2OH^-$ $\log(K) = -15.42$ Equation 26
$Zn^{2+} + 3OH^- = Zn(OH)_3^-$ $\log(K) = 14.14$ Equation 27

$Zn(OH)_2 + OH^- = Zn(OH)_3^-$ $\log(K) = -1.28$ Equation 28

$$-1.28 = \log \frac{[Zn(OH)_3^-]}{[OH^-]} = \log[Zn(OH)_3^-] + pOH$$ Equation 29

$$\boxed{10^{-15.28+pH} = [Zn(OH)_3^-]}$$ Equation 30

With Respect to $Zn(OH)_4^{2-}$

$Zn(OH)_2 = Zn^{2+} + 2OH^-$ $\log(K) = -15.42$ Equation 31
$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-}$ $\log(K) = 17.66$ Equation 32

$Zn(OH)_2 + 2OH^- = Zn(OH)_3^-$ $\log(K) = -2.24$ Equation 33

$$-2.24 = \log \frac{[Zn(OH)^{2-}_4]}{[OH^-]^2} = \log[Zn(OH)_4^{2-}] + 2pOH$$ Equation 34

$$\boxed{10^{-30.24+2pH} = [Zn(OH)_3^-]}$$ Equation 35

Overall, derivation of the equilibrium solubility of the other corrosion products utilizing this method yielded the following equations, summarized in Table III:

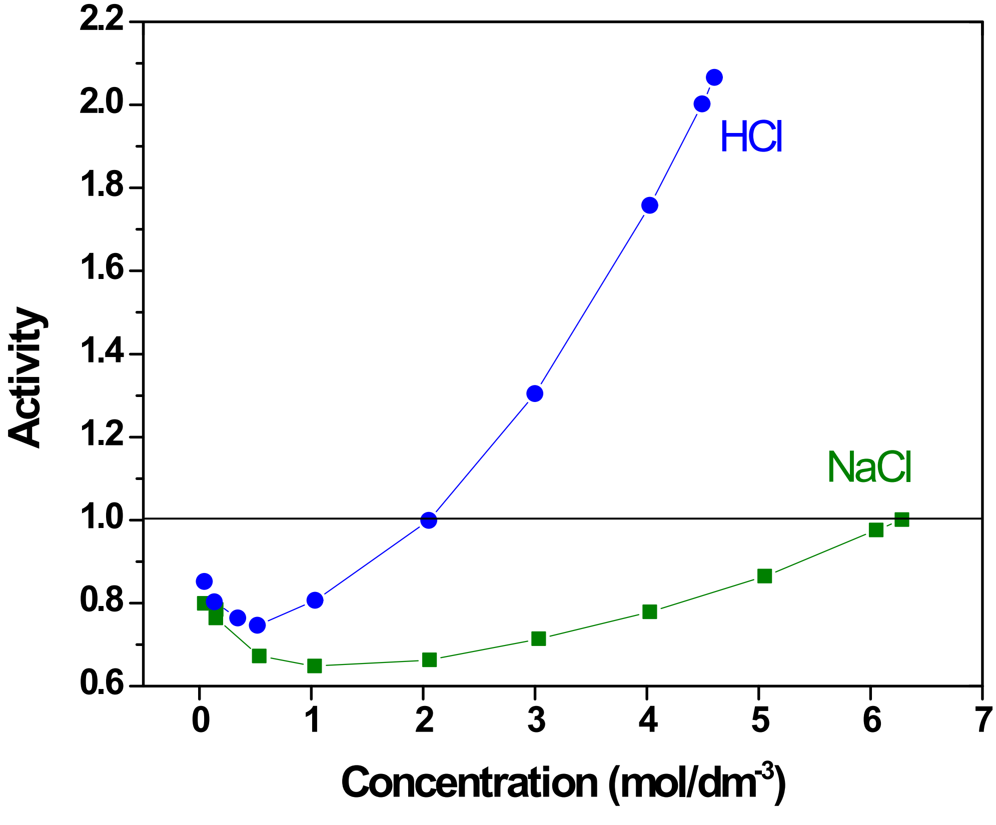
Table III: Equilibrium stability equations derived for each corrosion product

	Equilibrium Stability Equation		
Corrosion Product	**Zn^{2+}**	**$Zn(OH)_3^-$**	**$Zn(OH)_4^{2-}$**
Zinc Hydroxide (am)	$10^{12.58 - 2pH} = [Zn^{2+}]$	$10^{-15.28 + pH} = [Zn(OH)_3^-]$	$10^{-30.24 + 2pH} = [Zn(OH)_4^{2-}]$
Zinc Hydroxide (ε)	$10^{10.96 - 2pH} = [Zn^{2+}]$	$10^{-16.90 + pH} = [Zn(OH)_3^-]$	$10^{-29.62 + 2pH} = [Zn(OH)_4^{2-}]$
Zincite	$10^{11.35 - 2pH} = [Zn^{2+}]$	$10^{-16.51 + pH} = [Zn(OH)_3^-]$	$10^{-26.99 + pH} = [Zn(OH)_4^{2-}]$
Smithsonite	$10^{-10.92 - \log(CO_3 2-)} = [Zn^{2+}]$	$10^{-38.78 + 3pH - \log(CO_3 2-)} = [Zn(OH)_3^-]$	$10^{-49.26 + 4pH - \log(CO_3 2-)} = [Zn(OH)_4^{2-}]$
Hydroxycarbonate	$10^{1.28 - 1.2pH - 0.4\log(CO_3 2-)} = [Zn^{2+}]$	$10^{-26.58 + 1.8pH - 0.4 \log(CO_3 2-)} = [Zn(OH)_3^-]$	$10^{-37.06 + 2.8pH - 0.4 \log(CO_3 2-)} = [Zn(OH)_4^{2-}]$
Simonkolleite	$10^{7.64 - 1.6pH - 0.4\log(Cl-)} = [Zn^{2+}]$	$10^{-20.22 + 1.4pH - 0.4\log[Cl-]} = [Zn(OH)_3^-]$	$10^{-30.70 + 2.4pH - 0.4\log[Cl-]} = [Zn(OH)_4^{2-}]$

The summation of the three equations determined the equilibrium stability trend across the entirety of the pH range when no ion complexation effects due to Cl^- were considered. When complexation was considered, the available Zn^{2+} content was understood through use of Equation 24, which enabled the sole use of the Zn^{2+} relationship to calculate the chemical stability diagram.

Assumptions:

- Concentrations were expressed in molarity here. The importance of species activity is recognized, as activity more accurately describes the reactivity of a species and the thermodynamic stability of its reaction products. The framework used here necessitates the use of molarity, particularly for determining the dissolution trajectory expressions. Previous work[1] has demonstrated that the activity of NaCl has the following trend relative to concentration (Note: these data only apply to the pure environment case, with no foreign species such as pollutants):



  Therefore, the concentration assumption is considered to be less accurate in the case of low molarity of NaCl, but is increasingly accurate for the case of high concentration.

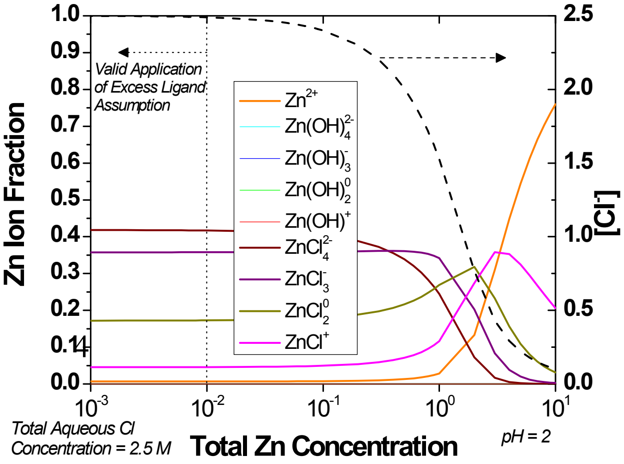
- The authors recognize that many different compounds and aqueous species exist. Some common examples of Zinc-based products were considered here, ranging from simple (ZnO) to complex ($Zn_5(OH)_8Cl_2 \cdot H_2O$) chemical formulae. Certainly other species could be considered and other systems modelled (SO_4-containing, for instance). This work establishes the framework which enables such analysis to be conducted by the reader.

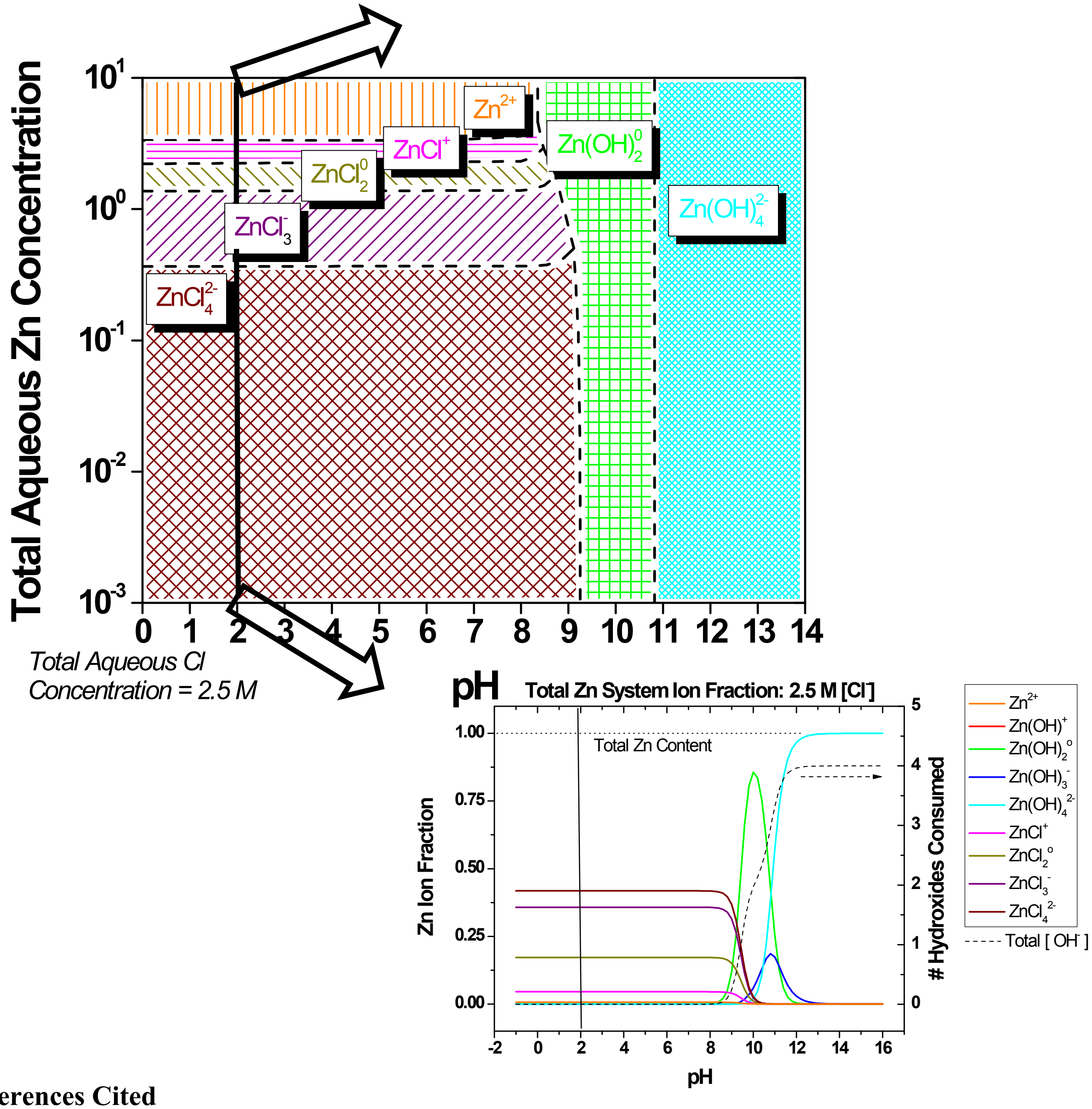
- Only thermodynamically stable phases were considered in the present work. The possibility of forming metastable (or kinetically stable) phases is recognized.
- Ligands were assumed to be in excess of the Zn ion. This allows [Cl^-], for example, to be approximated by the total Cl concentration. This approximation is insufficient when [Zn_{tot}] approaches [Cl_{tot}] (for example, this assumption is valid up to 10^{-2} M [Zn_{tot}] at 2.5 M [Cl^-], see the figure that follows). Generally, solid phases form before this condition is met. However, the graphical abstract was calculated exactly for the aqueous phases only (where solid phases were artificially suppressed/ignored) taking into account the consumption of Cl^- by Zn-Cl complexation. The procedure for this calculation is outlined below:

Equilibrium Calculations When the Ligand is Not in Excess

1. The equilibrium constants were calculated for successive, stepwise chlorination of Zn-Cl complexes, as for $Zn^{2+}/ZnCl^+$, $ZnCl^+/ZnCl_2^0$, $ZnCl_2^0/ZnCl_3^-$, $ZnCl_3^-/ZnCl_4^{2-}$. While these constants were not directly reported here, they are easily calculated by summing the appropriate reactions given in Table II. For each equilibrium, a condition is imposed where each Zn-based species is present in equal concentrations. This allows for the determination of [Cl^-] where this condition is valid.
2. A chloride mass balance is constructed where Cl_{tot} is solved for in terms of Cl^- and all of the Zn-Cl complexes. The concentration of the Zn-Cl complexes is dependent on [Cl^-] (which was just determined for each reaction) and [Zn^{2+}]. [Zn^{2+}] is solved for such that the Cl_{tot} expression is equal to the total chloride concentration in the system (2.5 M in the example of the graphical abstract).
3. A zinc mass balance is constructed for Zn_{tot} as shown in Equation 22 above. The Zn_{tot} is solved for such that [Zn^{2+}] is equal to the value determined by the chloride mass balance. Zn_{tot} will depend on [Cl^-] (which is fixed by the equilibrium calculation in step 1) and pH (which is incrementally varied from pH 0 to the pH at which $Zn(OH)_2^0$ dominance occurs).
4. The equilibrium constant for the reaction between $Zn(OH)_2^0$ and each of the Zn-Cl complexes is determined. When the Zn-Cl and $Zn(OH)_2^0$ are set equal then the equilibrium boundary can be calculated with respect to [Cl^-] and pH ([OH^-]). The [Cl^-] can be taken from the equilibrium condition between each successive Zn-Cl species, such that the pH can be calculated where $Zn(OH)_2^0$ become the most dominant species with respect to each Zn-Cl complex.
5. The equilibrium between the Zn-OH complexes can be determined directly from Table II.

<u>The excess ligand assumption</u>:





References Cited

1. Conway, B.E., *Electrochemical Data* (Houston: Elsevier, 1952).