Effect of pH, Concentration and Temperature on Copper and Zinc Hydroxide Formation/Precipitation in Solution

Trent William Jay Albrecht*, Jonas Addai-Mensah and Daniel Fornasiero
Ian Wark Research Institute, University of South Australia
Mawson Lakes Campus, Adelaide, South Australia 5095, AUSTRALIA
*Email: Albty001@mymail.unisa.edu.au

Abstract
Understanding the effect of temperature on the speciation of multivalent metals in solution is essential for many applications in industry. The results of the present Cu(II) and Zn(II) solutions speciation studies in tandem with thermodynamic calculations have shown that Cu\(^{2+}\) or Zn\(^{2+}\) ions proliferate in acidic solutions whilst in alkaline medium, solid Cu(OH)\(_2\) or Zn(OH)\(_2\) colloidal particles form. The extent of metal hydroxide precipitation accentuates with increasing Cu(II) and Zn(II) concentrations or temperature in the manner predicted by thermodynamic modelling. More solid Cu(OH)\(_2\) and Zn(OH)\(_2\) is formed and precipitates with increased temperature. The influence of temperature and concentration on the hydrolysis of Cu(II) and Zn(II) species, specific adsorption of the hydrolysis products and surface nucleation onto silica particles are shown to have a striking impact on the zeta potential at high pH.

Introduction
There is currently very limited information available in the literature on the effect of temperature on aqueous multivalent metal ion speciation in a broad pH range, despite many industrial processes being conducted under variable conditions. This study focuses on copper and zinc compounds that are employed in the ceramic industry for dye and pigment preparation, the mining industry as flotation reagents as well as fungicides in the agricultural industry (Durand-Keklikian and Matijević, 1990; Hidmi and Edwards, 1999). The speciation of the multivalent metals can have a detrimental effect on the environment as well as in the process industry with water recirculation and water reuse. The precipitation of metal hydroxides above a critical pH has long been used in the treatment of metal-ion-containing waste water (Baltpurvins et al, 1997; Hidmi and Edwards, 1999). This present study focuses on the changes in the hydrolysis and precipitation behaviour of Cu(II) and Zn(II) species as hydroxides and their adsorption onto a mineral surface (silica) as a function of pH, concentration and temperature. It is also our objective to establish how these processes can have important ramifications on temperature-mediated process water speciation changes during aqueous processing operations in the minerals industry.

Methods
The distribution of copper and zinc species in a 2×10\(^{-3}\) M potassium nitrate solution was investigated as a function of pH, temperature and copper or zinc concentration using UV-visible spectroscopy (CARY 1, Varian) at a fixed wavelength of 600 nm. For most metal ions dissolved in solution light absorption is negligible, however when they form colloidal species in solution, light is scattered and was measured as absorbance by the spectrometer. The metal ion solutions were conditioned at pH 3 for 3 minutes in a water jacketed vessel at the required temperature and pH was adjusted by small additions of
concentrated solutions of potassium hydroxide or nitric acid. A Malvern Zetasizer Nano was used to measure the zeta potential of silica particles with and without copper/zinc nitrate. A silica sample of 0.5 µm spherical particles was obtained from The Fibre Optic Centre Inc. The dilute (<0.01 wt%) solid mineral dispersion was conditioned for 30 minutes initially at pH 10.0 and then for 5 minutes at approximately 0.5 pH unit intervals in a water jacketed vessel at the required temperature. The zeta potential was measured from pH 10.0 to pH 3.0 with small additions of concentrated solutions of nitric acid, with a constant run time for each sample.

**Results and Discussion**

**Thermodynamic speciation study of copper and zinc**

A speciation study was conducted to investigate the effect of pH and temperature on the concentration of copper species. The thermodynamic speciation of copper shown as a function of pH in Fig. 1 at a temperature of 25°C was calculated based on Equations 1 to 4 and values of equilibrium constants obtained from free energy of formation, enthalpy and entropy values for each species involved (Garrels, 1960).

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2\text{O} &\rightleftharpoons \text{Cu(OH)}^+ + \text{H}^+ \quad (1) \\
\text{Cu}^{2+} + 2\text{H}_2\text{O} &\rightleftharpoons \text{Cu(OH)}_2 + 2\text{H}^+ \quad (2) \\
\text{Cu}^{2+} + 3\text{H}_2\text{O} &\rightleftharpoons \text{Cu(OH)}_3^+ + 3\text{H}^+ \quad (3) \\
\text{Cu(OH)}_{2(s)} &\rightleftharpoons \text{Cu(OH)}_{2(aq)} \quad (4)
\end{align*}
\]

![Diagram](image)

Fig. 1: Thermodynamic speciation of copper calculated using Equations 1 to 4 as a function of pH (top) at a fixed copper concentration of 1×10^{-3} M and (bottom) as a function of copper concentration at 25°C (only the dominant copper species are shown) (Eh=0.25 V SHE).
Fig. 1 (bottom) shows that at low copper concentrations, the copper ion, Cu\(^{2+}\), is the dominant species at low pH values up to pH 7.5. At higher pH values, copper hydroxide, Cu(OH)\(_2\), is the dominant species up to pH 12.3 where the copper ion Cu(OH)\(_3^-\) forms according to Equation 3. At higher copper concentrations, solid Cu(OH)\(_2\) is formed and precipitates out of solution at copper concentrations above the solubility product of copper hydroxide at 1×10\(^{-8}\) M. It is important to note that the domain of stability of solid Cu(OH)\(_2\) is expanding to lower and higher pH values with increasing copper concentration. A small but significant amount of an important Cu(II) complex Cu(OH)\(_+\) is formed at low pH (3-7), (Fig. 1, top). The thermodynamic speciation diagram for copper at temperatures of 5, 25 and 35\(^{\circ}\)C is shown in Fig. 2. It is observed that with increasing temperature, the domain of stability of the copper species shifts to lower pH values and therefore copper hydroxide forms and precipitates at lower pH values as temperature increases. The change in solubility product of copper hydroxide with temperature was small.

Fig. 2: Thermodynamic speciation diagram of dominant copper species calculated using Equations 1 to 4 as a function of pH, copper concentration and temperature (Eh=0.25 V SHE). The arrows show the change in the domain of stability of copper species with increasing temperature from 5 to 25 and 35\(^{\circ}\)C.

Similarly for zinc, the thermodynamic speciation was calculated as a function of pH, based on Equations 5 to 9. The thermodynamic speciation diagram is shown in Fig. 3. The changes in zinc species stability with pH and total zinc concentration are similar to those observed for copper in Fig. 1. At low zinc concentrations, the zinc ion, Zn\(^{2+}\), is the dominant species up to pH 8.7 while zinc hydroxide, Zn(OH)\(_2\), is the dominant species from pH 8.7 to pH 11.4. Above pH 11.4, Zn(OH)\(_3^-\) forms according to Equation 7. At higher zinc concentrations, solid Zn(OH)\(_2\) forms and precipitates out of solution at zinc concentrations above the solubility product of zinc hydroxide of 1×10\(^{-5}\) M. The domain of stability of the solid Zn(OH)\(_2\) is expanding to lower and higher pH values as zinc concentration increases, as was the case for copper. Notably, key, electropositive Zn(II) complex Zn(OH)\(_+\) is formed at the expense of Zn\(^{2+}\) ions at low pH values (Fig. 3, top). The thermodynamic speciation diagram for zinc at temperatures of 5, 25 and 35\(^{\circ}\)C is shown in Fig. 4. Similar to the effect of temperature on the thermodynamic speciation of copper (Fig. 2), the domain of stability of zinc species shifts to lower pH with increasing temperature, as observed in Fig. 4 and therefore Zn(OH)\(_2\) precipitates at elevated temperatures and lower pH values.
\[ \text{Zn}^{2+} + H_2O \rightleftharpoons \text{Zn(OH)}^+ + H^+ \quad (5) \]
\[ \text{Zn}^{2+} + 2H_2O \rightleftharpoons \text{Zn(OH)}_2 + 2H^+ \quad (6) \]
\[ \text{Zn}^{2+} + 3H_2O \rightleftharpoons \text{Zn(OH)}_3^+ + 3H^+ \quad (7) \]
\[ \text{Zn}^{2+} + 4H_2O \rightleftharpoons \text{Zn(OH)}_4^{2-} + 4H^+ \quad (8) \]
\[ \text{Zn(OH)}_{2(s)} \rightleftharpoons \text{Zn(OH)}_{2(aq)} \quad (9) \]

Fig. 3: Thermodynamic speciation of zinc calculated using Equations 5 to 9 as a function of pH (top) at a fixed zinc concentration of $1 \times 10^{-3}$ M and (bottom) as a function of zinc concentration at 25°C (only the dominant zinc species are shown) (Eh=0.25 V SHE).

Fig. 4: Thermodynamic speciation diagram of dominant zinc species calculated using Equations 5 to 9 as a function of pH, zinc concentration and temperature (Eh=0.25 V SHE). The arrows show the change in the domain of stability of zinc species with increasing temperature from 5 to 25 and 35°C (only the dominant zinc species are shown).
Study of copper species in solution

Fig. 5 shows the change in light scattered by a copper nitrate solution as a function of pH and copper concentration. The amount of light scattered at low pH values is negligible but it increases sharply at around pH 6 before reaching a plateau as the pH is further increased. Also, more light is scattered with increasing copper concentration above pH 6. The pH where the sharp change in light scattered occurs decreases with increasing copper concentration, pH of 6.7, 6.5 and 6.3 for copper concentrations of $2.5 \times 10^{-3}$, $4.5 \times 10^{-3}$ and $6.5 \times 10^{-3}$ M, respectively. The light scattered by the copper solution indicates that colloidal Cu(OH)$_2$ precipitate is formed (turbid solution), consistent with the speciation data in Fig. 1. Both the results of thermodynamic calculations and light scattering experiments show that the domain of stability of the solid Cu(OH)$_2$ extends to lower pH values as the copper concentration increases. Some hysteresis is observed between the acid and base titration curves and could be caused by the slow kinetics of dissolution (acid titration curve) and formation/precipitation (base titration curve) of copper hydroxide relative to the rate of pH change in the experiment. The change in light scattered at high pH (6.5<pH<10.5) may be due to the hydrolysis of solid Cu(OH)$_2$ to Cu(OH)$_3^-$ aqueous (Equation 9) resulting in a decrease in the intensity of light scattered.

![Fig. 5: Change in light scattered by a copper nitrate solution at 20°C measured at a fixed wavelength of 600 nm as a function of pH and copper nitrate concentration for base titration (filled symbols) and acid titration (empty symbols) ([KNO$_3$]= 2×10$^{-3}$ M).](image)

The effect of temperature (5, 15, 20 and 35°C) on the precipitation of copper hydroxide was also investigated at a fixed copper concentration of $4.5 \times 10^{-3}$ M. The results are shown in Fig. 6. The trends in the change in scattered light with increasing pH values at different temperatures are the same as those observed in Fig. 5 for different copper concentrations. Therefore it can be concluded that the number and/or size of precipitated Cu(OH)$_2$ colloidal particles increases when the temperature is increased. Also, as it was the case with increasing copper concentration, the critical pH for Cu(OH)$_2$ precipitation is shifted to lower pH values with increasing temperature, in
agreement with the results of thermodynamic calculations in Fig. 2. The change in light scattered with increasing and decreasing pH values at different temperatures are the same as those observed in Fig. 5 at different copper concentrations.

Fig. 6: Change in light scattered by a $4.5 \times 10^{-3}$ M copper nitrate solution measured at a fixed wavelength of 600 nm as a function of pH and temperature for base titration (filled symbols) and acid titration (empty symbols) ([KNO$_3$]$=2 \times 10^{-3}$ M).

Similar pH titration experiments were conducted for zinc as a function of zinc concentration (Fig. 7) and temperature (Fig. 8). The results reveal trends that are similar to those observed for copper in Figs. 5 and 6, respectively. The hysteresis in the base and acid titration curves increases with increasing zinc concentration. This is particularly noticeable at the highest zinc concentration where the amount of light scattered increases as the solution is acidified to pH~8 and the scattering sharply decreases. Again, this hysteresis in the acid and base titration curves is attributed to the slow dissolution/precipitation of zinc hydroxide relative to the rate of pH change in the titration experiments. Using the information provided by the thermodynamic calculations for zinc in Fig. 3, it can be therefore concluded that with increasing zinc concentration, more zinc hydroxide forms/precipitates. However, unlike copper, the pH where zinc hydroxide starts to form/precipitate, ~pH 7.5, appears to be independent of (or less affected by) zinc concentration.

More Cu(OH)$_2$ precipitates with increased temperature and the point of precipitation shifts to lower pH with increased temperature. In the case of zinc, increased formation and precipitation of Zn(OH)$_2$ occurs at higher temperatures and the pH of precipitation doesn’t appear to be affected by temperature. This could result in changes in industry performance or quality of recycled waste water as a result of changes in the environmental temperature. At the same time this could prove useful in improving waste water reuse via improved water quality by increasing solution temperature and reducing the amount of soluble metal ion species in solution.
Fig. 7: Change in light scattered by a zinc nitrate solution at 20°C measured at a fixed wavelength of 600 nm as a function of zinc nitrate concentration for base titration (filled symbols) and acid titration (empty symbols) ([KNO₃]=2×10⁻³ M).

Fig. 8: Change in light scattered (ABS(600 nm)) by a 4.5×10⁻³ M zinc nitrate solution measured at a fixed wavelength of 600 nm at temperatures of 5, 20 and 35°C for base titration (filled symbols) and acid titration (empty symbols) ([KNO₃]=2×10⁻³ M).

Zeta Potential Study

The zeta potential of silica was measured in order to investigate the effects of copper and zinc concentrations and solution temperature on the adsorption of copper and zinc species onto silica. The results in Fig. 9 show that the zeta potential of silica is negative in the pH range investigated and increases in magnitude with increasing pH. No or
A small hysteresis was observed during the acid-base titrations (results not shown), indicating that no marked dissolution and re-precipitation occurred at the silica-solution interface. The iso-electric point (IEP) of the silica was found to be at ~pH 3, which is in good agreement with that reported by Hunter (1981). The results in Fig 9 (right) show that the zeta potential of silica becomes more negative with decreasing temperature at pH values above 6, at pH values below 6 the zeta potential of silica becomes more positive, which results in a shift of the IEP to higher pH values from pH 3 or lower at 35°C to pH ~5 at 5°C. A similar observation was made by Fokkink et al. (1989) for the point of zero charge (PZC) of rutile and hematite with the change in temperature. The authors attributed the PZC shift with temperature change to specific interactions of the surface with protons in solution which are governed by the concomitant enthalpic changes (Fokkink et al., 1989). The temperature-mediated changes in rutile and hematite surface charge may also be explained by enhanced mineral dissolution and specific adsorption of dissolved Fe(III) and Ti(IV) hydrolyzed species upon pH change. With increasing copper concentration, the negative zeta potential of SiO$_2$ particles decreases in magnitude at alkaline pH values and even becomes positive (Fig. 9 left). The change in zeta potential of silica at pH > 6 with increasing copper nitrate concentration is due to Cu(II) hydrolysis, specific adsorption and surface nucleation of Cu(OH)$_2$ onto the SiO$_2$ mineral surface (Strumm and Morgan, 1995).

![Fig. 9: Zeta potential of silica as a function of pH at different copper nitrate concentrations, pH 10 and 20°C (left), and as a function of pH and temperature in the absence of copper nitrate (Si 0 M) and with the addition of 5x10^-5 M copper nitrate (right). The zeta potential of freshly prepared copper hydroxide is shown for comparison (acid titration; [KNO$_3$]= 2x10^-3 M; [Silica]=0.625 g dm$^{-3}$).](image)

Indeed, the zeta potential and IEP at the highest copper concentration are comparable to those of freshly prepared copper hydroxide. Furthermore in Fig. 9 (left), it can also be noted that the abrupt change in zeta potential occurs at pH values that coincide with the pH for the formation/precipitation or dissolution of solid Cu(OH)$_2$ in Fig. 1 and 5. The critical pH shifts to lower pH values as Cu(II) species concentration increases as was the case in the thermodynamic speciation calculations and light scattering experiments. No noticeable change in zeta potential is observed at pH < 5.5, which indicates that the extent of adsorption of the electropositive Cu(II) ions (Cu$^{2+}$ and Cu(OH)$^{+}$) onto the
negatively charged silica surface had no decisive impact on the interfacial chemistry. Similar observations were made by James and Healy (1972a, 1972b, 1972c) for the adsorption of cobalt onto silica or titania surfaces and was explained by the higher solvation energy associated with hydrated multivalent metal ions carrying higher charge (e.g. Cu$^{2+}$). Fig. 9 (right) shows that the changes in the zeta potential of silica in the presence of Cu(II) species with increasing temperature are quite similar to those observed in Fig. 9 (left) with increasing copper concentration. This implies that with increasing temperature, there is an increase in the Cu(II) dissolution, hydrolysis and surface adsorption of Cu(OH)$_2$ precipitation onto the silica surface at high pH (> 6). Similarly, Fig. 10 (left) shows that the zeta potential of silica becomes less negative with zinc nitrate addition at neutral and alkaline pH values. The maximum change in zeta potential occurs at around pH 9 where solid Zn(OH)$_2$ is the most dominant species (Fig. 3). Likewise, the results indicate the dissolution of Zn(II) species, followed by their hydrolysis and specific adsorption and Zn(OH)$_2$ precipitation onto silica surface. It is also observed in Fig. 10 (left) that the critical pH for Zn(OH)$_2$ dissolution/precipitation is around pH 7.5-8, which is in good agreement with the results in Fig. 3. As was the case for copper ions (Fig.9), Zn$^{2+}$ and Zn(OH)$^+$ ions are not specifically adsorbing onto the negatively charged silica surface at pH < 7. The changes in the zeta potential of silica in the presence of zinc nitrate with increasing temperature in Fig. 10 (right) are the same as those observed in Fig. 10 (left) with increasing zinc nitrate concentration. This confirms the previous observations that Zn(II) hydrolysis, specific adsorption and surface precipitation product formation are markedly reduced at low temperatures.

Fig. 10: Zeta potential of silica as a function of pH and zinc nitrate concentration at pH 10 and 20$^\circ$C (left), and as a function of pH and temperature in the absence of zinc nitrate (Si 0 M) and with the addition of 1.25×10$^{-4}$ M zinc nitrate (right). The zeta potential of freshly prepared zinc hydroxide is shown for comparison (acid titration; [KNO$_3$]= 2×10$^{-3}$ M; [Silica]=0.625 g dm$^{-3}$).

**Conclusions**

This study shows that Cu$^{2+}$ or Zn$^{2+}$ ions proliferate in aqueous acidic solutions, while their hydrolysis products, including colloidal Cu(OH)$_2$ or Zn(OH)$_2$ particles, proliferate in alkaline solutions. The concentrations of the Cu(OH)$_2$ or Zn(OH)$_2$ particles increase...
with increasing Cu(II) or Zn(II) concentrations and temperature, consistent with thermodynamic model predictions. More Cu(OH)_2 and precipitates Zn(OH)_2 with increased temperature. The zeta potential results show that specific adsorption of hydrolysed Cu(II) and Zn(II) complexes onto silica particles had a striking impact on particle zeta potential, the extent of which increased with increasing solution Cu(II) or Zn(II) concentration and temperature at alkaline pH. Under acidic conditions however, the temperature and/or Cu^{2+} or Zn^{2+} ion concentrations had no marked effect on the negatively charged silica particles. Solution temperature-mediated water quality/speciation may become an important, controlling factor when dealing with process water recirculation or aqueous processing improvement through process water treatment.

References
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Brief Biography of Presenter
Trent Albrecht has a background in general science and is currently completing the 3\textsuperscript{rd} year of his PhD at the Ian Wark Research Institute of the University of South Australia.