



Influence of High Chloride Concentration on pH Control in Hydroxide Precipitation of Heavy Metals

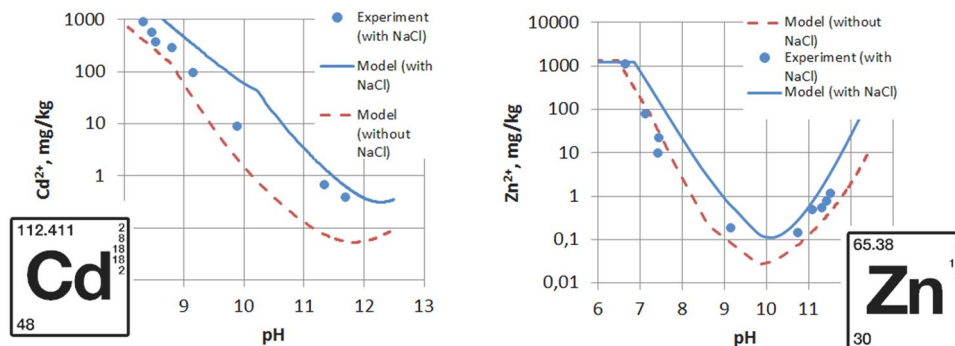
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Abstract

Removal of zinc and cadmium from highly saline solutions by hydroxide precipitation is discussed. Experimental solubilities of zinc and cadmium in highly saline solutions were compared to modeled results obtained using Pitzer's approach. An amphoteric character of zinc and cadmium and an influence of chloride ion on the concentration of dissolved metals were investigated. In order to avoid errors linked to pH measurements in concentrated aqueous solutions, the method of calibration of glass pH electrodes was developed and evaluated. The method uses easily prepared buffers whose pHs were determined with the Pitzer ion-interaction approach. The presented investigations address two issues of high significance in industrial wastewater treatment, namely: precise pH measurements and rigorous modeling of highly saline wastewaters. The results can be implemented in the treatment of hydrometallurgical wastewaters such as zinc refinery wastewater. Additionally, an implementation of the presented investigations is not limited to wastewater treatment but can easily be extended to other high-chloride metallurgical processes wherein the pH measurements in highly saline streams are required.

Graphical Abstract



Keywords pH measurements · High ionic strength · Wastewater treatment · Hydroxide precipitation · Heavy metals

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Introduction

The continuous progress of industrialization significantly affects the environment by contamination with heavy metals [1, 2]. Harmful effects of heavy metals contamination against living organisms are well known and well documented. To address this significant aspect, several methods of removal of heavy metals from wastewater have been developed but precipitation of metals remains the most popular technique on an industrial scale. The biggest advantages

of the precipitation of the heavy metals are low cost and relative simplicity [3, 4]. Lime or caustic precipitation is particularly suitable for wastewaters containing high heavy metals content, e.g., electroplating or metallurgical wastewaters. Despite tremendous work done to optimize precipitation processes, there are still several challenges present. One such challenge is that heavy metals precipitation forms highly saline wastewaters.

The mobility of heavy metals depends on their binding forms and the different chemical species and minerals in which the metals prevail. The high concentration of background salts in wastewaters affects the solubility of heavy metals. For example, in hydrometallurgical wastewater such as the zinc refinery wastewater, the chloride ion is frequently present in concentration over $10,000 \text{ mg dm}^{-3}$ [5]. Such a high concentration of chloride causes the formation of soluble complex chlorides of heavy metals. In fact, this phenomenon is so efficient that it is often used as a method to extract heavy metals from residues—brine leaching [6]. Unfortunately, the high solubility of heavy metals in highly saline solutions, being an advantage in the case of brine leaching, is a significant drawback in wastewater treatment [7, 8].

The quality of treatment by chemical precipitation depends strongly on the precision of the pH control, which in turn depends on the quality of pH measurements and dosing of chemicals. The pH measurements are the straightforward and frequent measurement performed in the wastewater industry. Typically, standard combined glass electrodes are utilized in both laboratory and industrial practice as pH measuring equipment. The combined glass electrode pH measurements are easy in use and precise equipment, however, several precautions have to be taken to guarantee the highest quality of measurements. The latest IUPAC Recommendations concerning pH measurements [9] describe the detailed procedure of pH measurements using glass electrodes and present limitations of their usage. The authors stress that pH measurements using pH meters calibrated on standard buffers are limited to solutions of low ionic strength ($I < 0.1 \text{ mol kg}^{-1}$). This aspect is not important when dealing with diluted wastewater streams, but its importance rises when, for example, the zinc refinery wastewater treatment is considered. The same drawbacks occur in other high-chloride processes wherein precipitation and pH measurements are required, e.g., HydroCopper™ technology, aimed to produce copper directly from concentrates. In the HydroCopper™ process, the copper concentrate is leached into a strong ($250\text{--}300 \text{ g dm}^{-3}$) sodium chloride solution and in the next phases, divalent copper is precipitated as hydroxychloride by increasing the pH of the solution to 4–5 with sodium hydroxide and Zn, Pb, Ni, etc., are removed as carbonates by increasing the pH to 6–7 using sodium carbonate [10]. Another process, wherein precipitation in highly loaded solutions has to be conducted, is Outotec Nickel Matte

Chloride Leaching Process. The process incorporates metals leaching into a calcium chloride solution and subsequent iron precipitation using slaked lime or limestone [11].

Currently, there is no common and standardized convention describing recommendations on how to measure pH values in electrolyte solutions of moderate and high ionic strength. The main inconsistencies in pH measurements of high ionic strength solutions rise from the convention of assigning pH values to buffers. The assigned pH values for buffers, in line with IUPAC recommendations, are obtained using the Bates–Guggenheim convention and are only valid for dilute ($I < 0.1 \text{ mol kg}^{-1}$) solutions [12]. The Pitzer's approach to ion interactions is widely appraised and offers an alternative to the Bates–Guggenheim suitable for use in solutions of higher ionic strengths [13].

The aim of this study is to introduce a possibility of using Pitzer's approach to estimate the composition of simple buffers of high ionic strength and to model the precipitation of heavy metals from high ionic strength solutions. Further, the theoretical calculations are compared with the zinc and cadmium precipitation experiments, conducted in concentrated NaCl solutions. During the experimental works, the pH meter was calibrated against high ionic strength buffers, established using the above approach.

Experimental

Chemicals

Zinc(II) chloride (ZnCl_2 , Chempur, Poland) and cadmium(II) chloride hemi(pentahydrate) ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, Chempur, Poland) were used to prepare heavy metal solutions. The salinity of the solutions was increased by adding sodium chloride (NaCl, Avantor, Poland). The solutions were prepared by dissolving the chemicals with distilled water. The standard pH buffers at pH 4.0 (citrate) and 9.0 (borate) for pH meter calibration were purchased from Chempur, Poland. 1 M NaOH, 1 M HCl (Chempur, Poland) standard solutions, and sodium bicarbonate (NaHCO_3 , Chempur, Poland) were used to prepare high ionic strength buffers. The ionic strength of the buffers was fixed using sodium chloride (NaCl, Avantor, Poland). All chemicals were of analytical grade.

pH Measurements

Solution pH was measured with a combined, refillable glass electrode (Elmetron ERH-11, filling solution of a reference electrode: 3 M KCl + sat. AgCl, reference half-cell: Ag/AgCl) and an Elmetron CPC-461 pH meter. Purchased, commercial secondary standard buffers [9] at pH 4.0 (citrate) and

9.0 (borate) were used to calibrate the meter for pH measurements in the ISO scale [14]. In the case of highly saline solution pH measurements, the meter was calibrated against high ionic strength buffers (molality ~ 1.0 m) prepared in the laboratory. The composition of the high ionic strength buffers was established using PHREEQC software as described in the subsequent chapter.

In order to distinguish whether the standard buffers or the high ionic strength buffers were used to calibrate the meter, the following notation is used within the article: pH_{ISO} —depicts measurements carried out using meter calibrated against secondary standard buffers and pH_{HSW} —using the high ionic strength buffers. The potential difference and temperature measured by the pH meter during calibrations were recorded and further used to convert to pH using a two-point calibration procedure, in line with IUPAC Recommendations [9].

The calibration of the pH meter was validated against two test solutions: acidic and alkaline. The solutions consisted of HCl, and NaOH + NaHCO_3 , respectively. The ionic strength of the solutions was changed by the cumulative addition of weighted portions of solid NaCl. The potential difference and temperature were recorded during NaCl addition.

Sample measurements and calibrations were carried out in jacketed glass beakers (100 ml and 250 ml). The temperature of water conveyed in the beakers' jacket was held constant using the Julabo F25-HE thermostat.

Software Calculations

High Ionic Strength Buffers Calculations

In order to evaluate the theoretical pH of the prepared high ionic strength buffers, PHREEQC modeling software was used. The PHREEQC software is a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations [15]. The software offers several approaches to address electrolyte solution thermodynamics, among others: Debye–Hückel, Davies, Truesdell–Jones, SIT—implements extension of the Debye–Hückel theory introduced by Brønsted [16], WATEQ4F—uses extended Debye–Hückel equation [17], and Pitzer. The latter is especially suitable in the case of modeling of high ionic strength solution speciation [18] and therefore this approach was chosen.

The Pitzer's model implementation in the PHREEQC is based on PHRQPITZ computer program [19] and excludes Pitzer interaction coefficients for several chemicals used in standard buffers (for example, phthalic acid, acetic acid, citric acid, or phosphoric acid). In order to avoid the necessity of manual addition of missing interaction coefficients, the prepared buffers were composed of constituents included in

Table 1 Values of the Pitzer's pure-electrolyte parameters

Electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference
NaCl	0.07722	0.25183	0.00106	[20]
CdCl ₂	0.01624	0.43945	0.00109	[20]
ZnCl ₂	0.22825	1.73138	−0.06553	[21]

Table 2 Values of the Pitzer mixing interaction parameters

System	Mixing interaction parameters	Reference
NaCl–CdCl ₂ –H ₂ O	$\theta_{\text{NaCd}} = -0.7940$ $\psi_{\text{NaCdCl}} = 0.3456$	[22]
NaCl–ZnCl ₂ –H ₂ O	$\theta_{\text{NaZn}} = -0.366$ $\psi_{\text{NaZnCl}} = -0.0082$	[23]

the default PHREEQC Pitzer's database, namely: sodium hydroxide, sodium bicarbonate, sodium chloride, and hydrochloric acid. Such an approach is beneficial due to the usage of only high quality and well-documented Pitzer interaction parameters of sodium, chloride, or carbonate ions. In fact, a lack of Pitzer's coefficients for relevant buffer media is claimed to be the main obstacle in the application of Pitzer's model in pH measurements [13].

Subsequent advantage of using simple inorganic substances as buffer components is extending the shelf life of the buffers. Such high ionic strength buffers have a shelf life of at least one year when stored properly.

Zinc and Cadmium Solubility Predictions

The solubility of zinc and cadmium was also calculated using package PHREEQC and Pitzer's approach [19]. In contrast to calculations of the high ionic strength buffers described above, zinc and cadmium solubility predictions required an extension of the default PHREEQC Pitzer's ion-interaction parameters database. Contrary to components of the standard buffers, such data for cadmium and zinc chlorides are available in the literature. Implementation of the new species involved adding their pure-electrolyte and mixture interaction parameters. Interaction Pitzer parameters for Cd²⁺ and Zn²⁺ systems, together with its literature sources, are reported in Tables 1 and 2.

Anstiss and Pitzer [23] have pointed that in the case of CdCl₂ there is some error in the value of ion-interaction parameters of Kim and Frederick [20]. Despite that, it was decided to include the parameters in the database because of their usage by Wang et al. [22] in establishing ternary mixing interaction parameters for NaCl–CdCl₂–H₂O system. Such an approach ensures that all interaction parameters are compatible [24].

PHREEQC Pitzer's database was also constrained to include only those solid phases that were found to govern

solubility. In the case of Cd^{2+} and Zn^{2+} dissolved in solutions containing high chlorides concentration, apart from hydroxides, zinc and cadmium hydroxy chlorides, can be formed during hydroxide precipitation [25, 26]. Therefore, in the case of $\text{NaCl-ZnCl}_2\text{-H}_2\text{O}$ system considering $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ precipitate [27, 28], and in the case of $\text{NaCl-CdCl}_2\text{-H}_2\text{O}$ system CdOHCl are valid [29]. Thermodynamic constants for both aqueous and solid phases were selected from the PHREEQC databases for their relevance to the systems under study.

Precipitation Experiments

In order to check the solubility of cadmium and zinc in highly saline solutions and to compare experimental results with the model, the following solutions were prepared: $\text{ZnCl}_2 + \text{NaCl}$ (20 mmol $\text{kg}^{-1}_{\text{water}} + 1300$ mmol $\text{kg}^{-1}_{\text{water}}$, respectively) and $\text{CdCl}_2 + \text{NaCl}$ (30 mmol $\text{kg}^{-1}_{\text{water}} + 1300$ mmol $\text{kg}^{-1}_{\text{water}}$, respectively).

For each metal solution, ten 50 mL polypropylene vials were filled with approx. 45 g of the solution. Further, the vials were made up with 1 M NaOH ensuring heavy metal (zinc or cadmium) to hydroxide mole ratio ranging from 0 to 2.5. The addition of 1 M NaOH caused the immediate occurrence of white flocs. The vials were vigorously shaken to mix the constituents and left for 30 min. Next, the solutions were filtered using cellulose paper filters. The filtrate was collected and its pH_{HSW} was measured. The concentrations of zinc and cadmium in the filtrate were determined on the iCAP 6500 Duo (Thermo Scientific, USA) inductively coupled plasma optical emission spectrometer (ICP-OES) according to EN ISO 11885:2009 “Water quality—determination of selected elements” by inductively coupled optical emission spectrometry (ICP-OES). To calibrate the spectrometer, calibration standard solutions were prepared from single standard element solutions from SCP Science Company with the addition of nitric acid.

The same procedure was used for both metals, namely zinc and cadmium, resulting in the obtention of 20 samples.

Results and Discussion

pH Meter Calibration

It was decided to calibrate the pH meter by a two-point calibration procedure using two buffer solutions. Such a procedure is recommended for the majority of glass electrode practical applications [9]. In such a case, the unknown $\text{pH}(X)$ is obtained from the equation:

$$\text{pH}(X) = \text{pH}(S_1) - [E_V(X) - E_V(S_1)]/k' \quad (1)$$

where the practical slope factor (k') is given by

$$k' = [E_V(S_1) - E_V(S_2)]/[\text{pH}(S_2) - \text{pH}(S_1)] \quad (2)$$

and $\text{pH}(S_1)$ and $\text{pH}(S_2)$ are pH values of standard buffers and $E_V(X)$, $E_V(S_1)$, $E_V(S_2)$ are respective potential differences measured. The IUPAC Recommendations claim that target uncertainty in $\text{pH}(X)$ calibrated by a two-point calibration procedure should not exceed 0.03 in the case of usage of standard buffer solutions with an uncertainty 0.01. The overall uncertainty becomes higher if buffers with lower uncertainties are used.

In the case of the pH_{ISO} calibration, the pH meter was calibrated by measuring potential differences of two secondary standard buffers at 20 °C in accordance with the manufacturer’s guidelines and IUPAC Recommendations [9]. Buffers data and measured potential differences are summarized in Table 3.

The procedure of calibration in high ionic strength buffers (pH_{HSW} calibration) was similar to above. The high ionic strength buffers were prepared individually. Bearing in mind the limitations of the Pitzer’s database in PHREEQC, the following buffer solutions were used: $\text{NaCl} + \text{HCl}$ (pH 2.0 at 20 °C) and $\text{NaHCO}_3 + \text{NaOH} + \text{NaCl}$ (pH 10.0 at 20 °C). The composition of the buffers is adapted from Robinson and Stokes [30], but with the difference that NaCl is added to increase the ionic strength to 1.0 m. The amounts

Table 3 The pH meter calibration data

Parameter	pH_{ISO}	pH_{HSW}
Acidic buffer (S_1)	Citrate, pH 4.0 at 20 °C	$\text{NaCl} + \text{HCl}$, pH 2.0 at 20 °C
Alkaline buffer (S_2)	Borate, pH 9.0 at 20 °C	$\text{NaHCO}_3 + \text{NaOH} + \text{NaCl}$, pH 10.0 at 20 °C
$\text{pH}(S_1)$	4.0	2.0
$\text{pH}(S_2)$	9.0	10.0
Potential difference $E_V(S_1)$, mV	160.6	283.8
Potential difference $E_V(S_2)$, mV	− 133.8	− 184.9
Temperature, °C	20.0 °C	20.0 °C
Practical slope factor (k'), mV	58.880	58.661

Table 4 Calculated compositions of the high ionic strength buffers determined by Pitzer's approach in PHREEQC

Acidic NaCl + HCl buffer pH 2.0 at 20 °C		Alkaline NaHCO ₃ + NaOH + NaCl buffer pH 10.0 at 20 °C	
NaCl	58.44 g	NaCl	58.44 g
1 M HCl	10.64 g	NaHCO ₃	1.68 g
Water	1000.0 g	1 M NaOH	15.54 g
		Water	1000.0 g

Table 5 Calculated pH values of the high ionic strength buffers used

t, °C	Theoretical pH values (Pitzer's approach)	
	Acidic NaCl + HCl buffer	Alkaline NaHCO ₃ + NaOH + NaCl buffer
10	1.993	10.111
15	1.996	10.053
20	2.000	10.000
25	2.004	9.952
30	2.008	9.909
35	2.012	9.869
40	2.017	9.833

of constituents in the buffer solutions were determined by PHREEQC simulations.

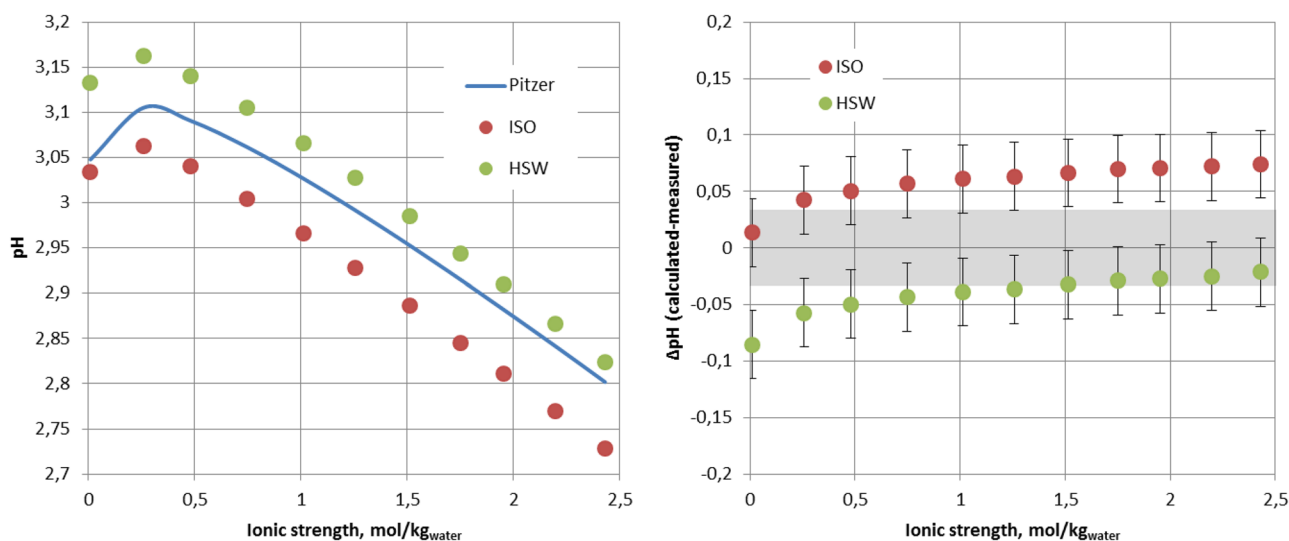
PHREEQC offers extreme flexibility in calculations and allows, among others, determination of the amount of reagent necessary to maintain selected pH. This procedure was used to calculate high ionic strength buffers composition. In the case of the acidic buffer, PHREEQC was programmed

to calculate the amount of the 1 M HCl necessary to fix the pH of the 1 m NaCl solution to 2.0. Similarly, in the case of the alkaline buffer, the amount of 1 M NaOH necessary to fix the pH of the 1 m NaCl + NaHCO₃ solution to 10.0 was established. Further, the pH of the buffers at temperatures from 10 to 40 °C was calculated. The simulation source files used to calculate both buffer compositions and properties are included in the electronic supplementary material that accompanies this article. The results of the simulations are shown in Tables 4 and 5.

Two buffer solutions were prepared, in accordance with Table 4 and the pH meter was calibrated against them using the manufacturer's guidelines. The calibration procedure was the same as in the case of calibration against the standard, diluted DIN buffers.

In order to validate the calibration of the meter, pH of two test solutions (acidic and alkaline) was recorded while changing the ionic strength, by addition of weighted portions of solid NaCl. A measured potential difference was converted to pH scale using two calibrations—using standard buffers (ISO scale) and high ionic strength buffers (HSW scale). Experimental data were compared with the theoretical pH of the solutions, calculated with PHREEQC software, using Pitzer's approach. Calculated and measured pH of acidic and alkaline samples are shown in Figs. 1 and 2, respectively.

The gray band, shown in Fig. 1 (right) and Fig. 2 (right), represents the uncertainty of the procedure. The uncertainty of the procedure, as well as the uncertainty of measurement (depicted as vertical error bars), was estimated to $\Delta\text{pH} \pm 0.03$, likewise in the IUPAC Recommendations for pH measurements [9]. As shown in the figures, the experimental measurements obtained by pH meter calibrated using

**Fig. 1** Calculated and measured pH for the acidic test sample (Color figure online)

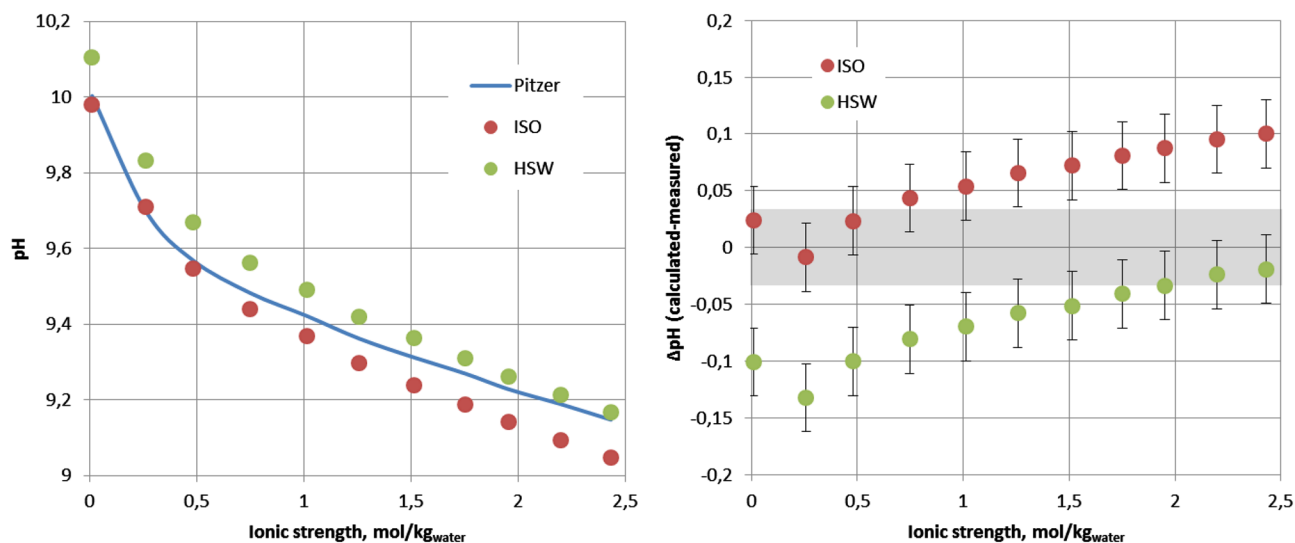


Fig. 2 Calculated and measured pH for the alkaline test sample (Color figure online)

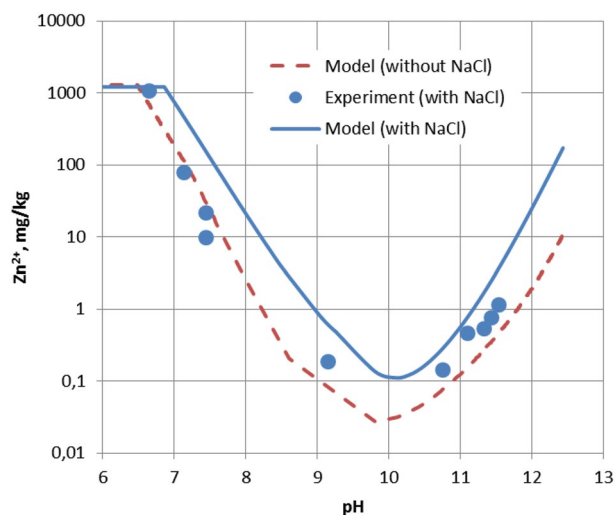


Fig. 3 Solubility for zinc system (Color figure online)

the ISO scale, fall into error limits for low ionic strength, which is consistent with the IUPAC Recommendations. The Bates–Guggenheim convention, used for the pH meter ISO calibration (as described in the recommendations), permits the applicability of the ISO procedure for ionic strength up to 0.1 mol kg^{-1} . It can be seen that ISO calibration correlates pH fairly well for higher ionic strength, up to 0.5 mol kg^{-1} .

However, further increase of the ionic strength makes the ISO-calibrated pH measurements unreliable. Unlike, the performance of HSW-calibrated pH is satisfactory for the higher ionic strength. The utility of high ionic strength buffer pH meter calibration is thus proved.

The result of the validation is a confirmation of purposefulness of using high ionic strength buffers for calibration

of the pH meter when the examined solution has high ionic strength. The devised pH measurement methodology was used in further research on the solubility of zinc and cadmium in highly saline solutions, outlined below.

Zinc System

A comparison of the generated solubility and the experimentally observed precipitation profile for the zinc system is given in Fig. 3. The plot contains modeled solubility of zinc in solutions containing only zinc chloride (dashed line) and having additionally the high amount of NaCl ($1300 \text{ mmol kg}^{-1} \text{ water}$, identical as in the experimental sample). It is clearly visible that a high concentration of Cl^- anion causes an increase in zinc solubility. The minimum solubility is observed at pH 10.0. The Cl^- concentration lowers pH of the minimal zinc solubility to some extent, reducing the optimal value. A typical amphoteric solubility relationship exists for zinc systems with and without the addition of the NaCl, with the onset of precipitation occurring at pH 7–9 and resolubilization occurring at pHs > 10.

A variation in the calculated and experimentally observed solubilities of zinc is visible, especially in lower pH region. This phenomenon may be explained by considering the kinetics of the precipitation. An analysis presented by Cousy et al. [26] shows that in the case of Zn solutions containing a high concentration of Cl^- anion, a zinc hydroxide salt $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ —simonkolleite—is dominating component of the precipitates in the lower pH regions, while $\text{ZnO}/\text{Zn}(\text{OH})_2$ is present in a higher extent at pHs > 10. Further, the relation in the amount of both precipitates changes with time. Takada et al. subjected to aging for up to 200-h suspensions of ZnCl_2 and NaOH and proved that the composition of

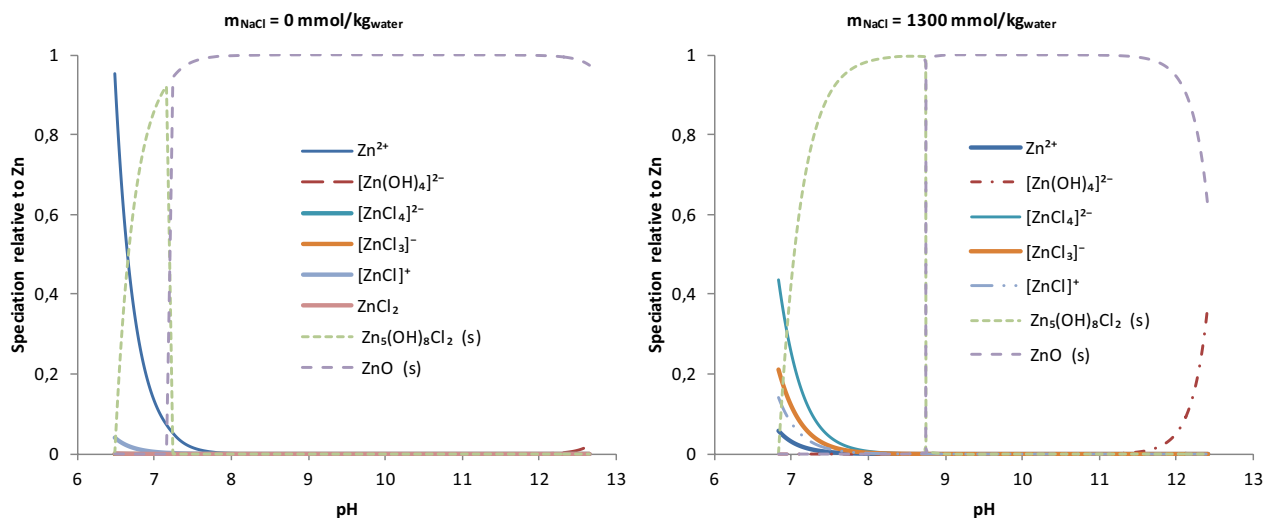


Fig. 4 Distribution of precipitates, molecular, and ionic species of Zn at different pH values (Color figure online)

precipitates changes over that time [27]. Taking into account that reaching equilibrium in such systems is prolonged, we can assume that the experimental samples shown in Fig. 3, subjected to aging for 30 min, have not reached final, equilibrium solubility. Despite the variation in the calculated and experimentally observed solubilities shown in Fig. 3, the increase in solubility of zinc caused by the high concentration of chloride ion is clearly visible.

PHREEQC simulations were used to quantify speciation of zinc systems containing no additional chlorides source and with a high concentration of NaCl. A comparison of speciations at different chlorides concentration as a function of pH is shown in Fig. 4. Figure 4 (left) shows that

ZnCl₂ solution without background NaCl contains mainly Zn²⁺ cation and [ZnCl]⁺ chloride complex in a minor extent. An increase of pH in the solution causes precipitation of Zn₅(OH)₈Cl₂ in a narrow pH range from 6.5 to 7.2. Further increase of pH favors precipitation of ZnO. Above pH 12.5, the ZnO precipitate is being dissolved as a hydroxide complex anion [Zn(OH)₄]²⁻. Speciation of ZnCl₂ with background NaCl at a concentration of 1300 mmol kg⁻¹ water, shown in Fig. 4 (right), is more complex. At lower pH, complexed forms of zinc are dominant of which [ZnCl₄]²⁻ anion is prevailing, while free Zn²⁺ cation is almost absent. The addition of NaOH (an increase of pH) causes precipitation Zn₅(OH)₈Cl₂ and its pH range is much wider than in the

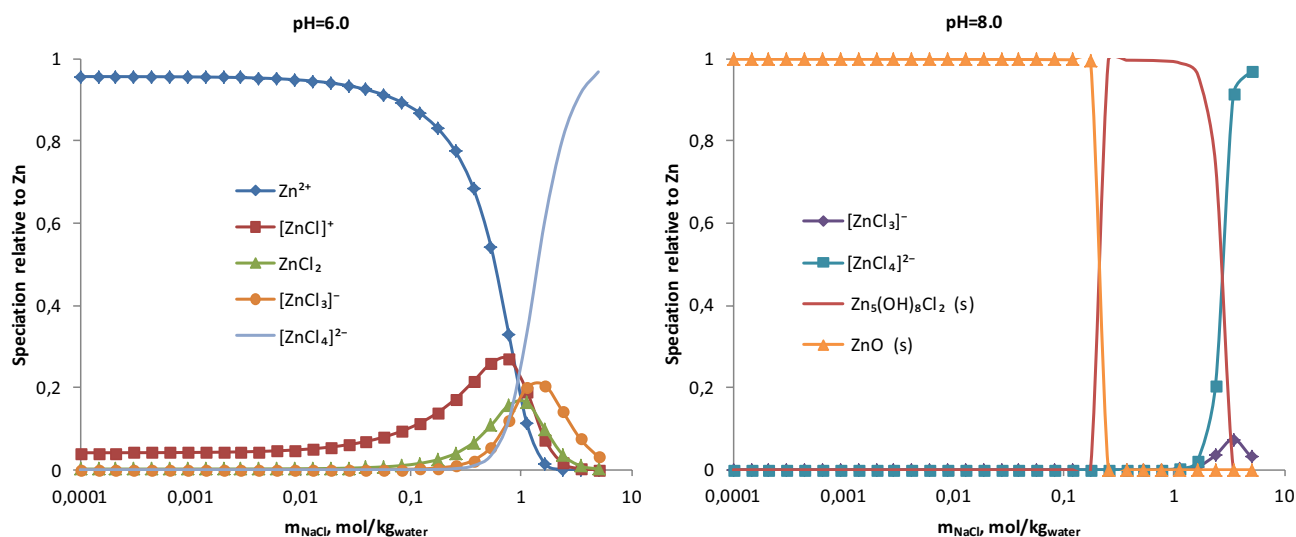


Fig. 5 Distribution of ionic, molecular species, and precipitates of Zn at different sodium chloride background salt concentrations at pH 6.0 (left) and pH 8.0 (right) (Color figure online)

case of the solution without background NaCl. In solution having background NaCl, precipitation occurs at higher pH comparing to pure ZnCl_2 solution. In the former solution, precipitation is observed at pH 6.8, while in the latter at pH 6.5. In the solution having a high concentration of background salt, a change in the precipitate composition from $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ to ZnO occurs at much higher pH 8.8 comparing to 7.2 in the pure ZnCl_2 solution. Further, the resolubilization of precipitate as a hydroxide complex occurs at lower pH 11.5 and is much prominent than in the case of pure ZnCl_2 solution. Presented speciation analysis proves that chlorides and hydroxides present in a high concentration in zinc solutions affect both either speciation of solution and composition of precipitates. The relevance of the various hydroxy and chloro species distributions becomes evident in predicting the degree of solubility of the zinc precipitates. The shown analysis is in line with the calculations of Hahne

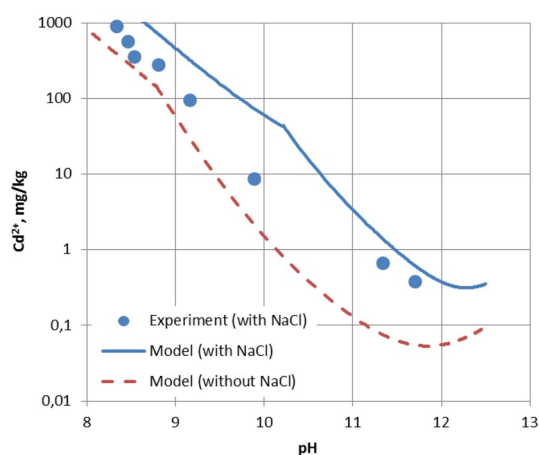


Fig. 6 Solubility for cadmium system (Color figure online)

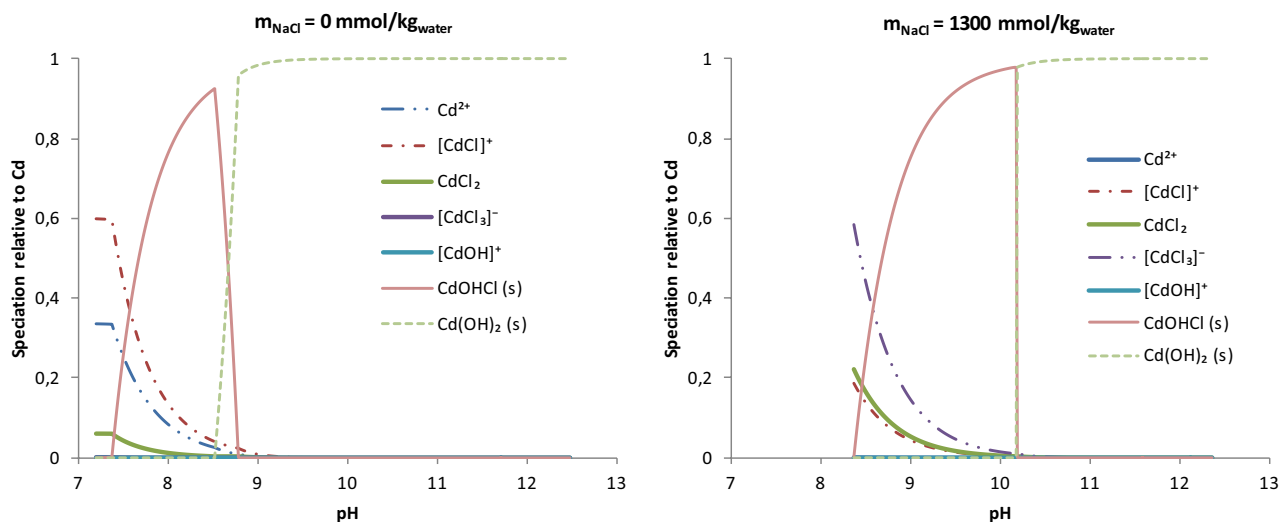


Fig. 7 Distribution of precipitates, molecular, and ionic species of Cd at different pH values (Color figure online)

and Kroontje [8] and extends mentioned work with precipitates composition.

A significant strength of chloride complexes of zinc is further demonstrated in Fig. 5, showing distribution of zinc species at different sodium chloride background salt concentrations in ZnCl_2 solution (concentration $m_{\text{ZnCl}_2} = 20.0 \text{ mmol kg}^{-1}_{\text{water}}$). The speciation plots were generated using PHREEQC, fixing pH at constant values and changing the concentration of background NaCl salt, and keeping ZnCl_2 amount constant. At pH 6.0, no precipitation occurred, irrespective of chlorides concentration. An amount of chloro complex ions of zinc increases at NaCl concentrations greater than $0.1 \text{ mol kg}^{-1}_{\text{water}}$. In solutions being nearly saturated with NaCl, free Zn^{2+} cation is absent while complexed $[\text{ZnCl}_4]^{2-}$ is a major form of zinc in the solution. In the case of the solution having pH 8.0, shown in Fig. 5 (right), zinc exists in precipitated form as ZnO or as $\text{Zn}_5(\text{OH})_8\text{Cl}_2$, depending on background NaCl concentration. The composition of precipitates changes from ZnO to $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ at NaCl concentration greater than $0.3 \text{ mol kg}^{-1}_{\text{water}}$. Further increase of chlorides concentration (above $1.0 \text{ mol kg}^{-1}_{\text{water}}$) causes a dissolution of the precipitate. The induction of a zinc precipitate dissolution is used in brine leaching, aimed to selectively dissolve zinc in the presence of iron [31, 32].

Cadmium System

Figure 6 shows the response of chloride complexed cadmium metal to hydroxide precipitation in comparison with uncomplexed metal where only NaOH is used for pH increase. PHREEQC-generated results show that the increase in chlorides concentration to $1300 \text{ mmol kg}^{-1}_{\text{water}}$ increases an equilibrium solubility of cadmium in the

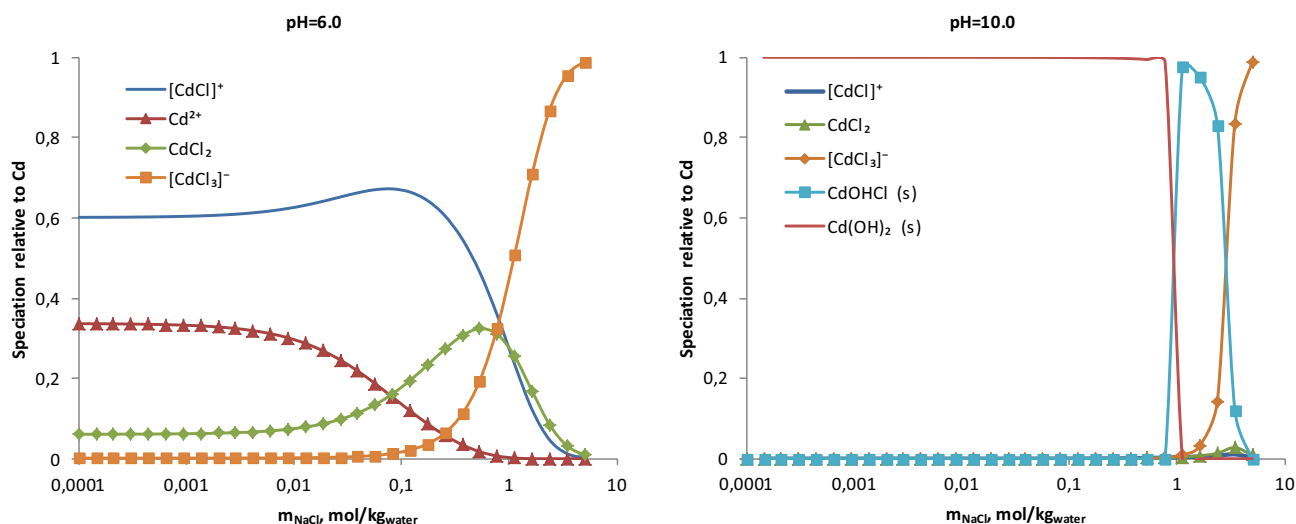


Fig. 8 Distribution of ionic, molecular species, and precipitates of cadmium at different sodium chloride background salt concentrations at pH 6.0 (left) and pH 10.0 (right) (Color figure online)

solution by an order of magnitude. Resolubilization of cadmium at higher pH confirms its amphoteric character [33], but the effect occurs at significantly higher pHs, comparing to zinc (Fig. 3). A shift of the pH of minimal Cd solubility is also affected by the chlorides concentration. The addition of $1300 \text{ mmol kg}^{-1}_{\text{water}}$ of background NaCl to CdCl_2 causes shift of the minimum solubility pH from pH 11.8 to 12.2. The shift is much more prominent, compared to zinc system (Fig. 3). In Fig. 6, experimentally observed solubilities of cadmium are included. Bearing in mind that the chemistry of cadmium is very much like that of zinc, except that it is less active and not as acidic in alkaline solution [34], the analogous rationale explaining the variation in the calculated and experimentally observed solubilities can be expressed as in the case of zinc (see the previous chapter).

In the case of cadmium–chloride system, two precipitates compete: Cd(OH)_2 and hydroxy salt CdOHCl . Composition of the precipitate is related to the pH and to the concentration of background chlorides. Similarly, as in the case of zinc, the range of pH where CdOHCl is dominant in the precipitate is wider for the solution having a high NaCl concentration (see Fig. 7).

The analysis of Fig. 7 (left) shows that chloride anion strongly complexes cadmium. Even in the absence of additional NaCl background salt, chlorides concentration (Cl^- anion in the solution is originated only from CdCl_2) is sufficient to complex over 60% of cadmium present. Further decrease in the concentration of free Cd^{2+} and the increase of concentration of complexes of cadmium are observed with increasing Cl^- concentration (Fig. 8).

As with zinc, chloride anion acts as a typical complexing agent inhibiting metal hydroxide precipitation [35] and if present in sufficiently high concentration can even dissolve

the precipitate. An example of such a phenomenon is shown in Fig. 8 (right)—cadmium bearing precipitate is being dissolved even at pH 10.0, if the concentration of Cl^- exceeds $2 \text{ mol kg}^{-1}_{\text{water}}$.

Chloride complexation affects the performance of hydroxide precipitation to a much lesser extent, compared to stronger complexing agents like EDTA, NTA [36], but still increases the solubility of zinc and cadmium, especially in chloride bearing streams like metallurgical wastewaters.

Conclusions

Hydroxide precipitation of zinc, cadmium, and other heavy metals is still the most common and effective method of treatment of heavy metal bearing wastewaters. Although widely used, hydroxide precipitation also has some limitations: the presence of complexing agents in the wastewater, being one of them. The aim of this study was to assess zinc and cadmium solubility in solutions containing a high amount of background chlorides, acting as a complexing agent, in a theoretical and experimental manner. An analysis of such solutions, having extreme ionic strengths exceeding $1.0 \text{ mol kg}^{-1}_{\text{water}}$, required the introduction of Pitzer's model to address electrolyte solution thermodynamics. To generate speciation of solutions and to model precipitation, PHREEQC modeling software was used. The high ionic strength of analyzed solutions affects also a methodology of pH measurements. To avoid errors, connected with using pH combined glass electrodes in highly saline solutions, the method of calibration of pH electrodes was developed and evaluated.

The present analysis showed that both heavy metals zinc and cadmium exhibit similar properties in highly saline solutions. The hydroxide precipitation in such solutions is possible, however, is started to be inhibited by chlorides in concentrations exceeding $\sim 0.1 \text{ mol kg}^{-1}_{\text{water}}$. Minimum solubility of zinc and cadmium in presence of a high concentration of background salts (i.e., sodium chloride in concentrations $> 1.0 \text{ mol kg}^{-1}_{\text{water}}$) is decreased by an order of magnitude, compared to solutions lacking background NaCl. The presence of chlorides affects also a composition of the precipitates. The high concentration of chlorides favors the formation of hydroxo salt precipitates $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ or CdOHCl instead of typical metal hydroxides.

The relative simplicity and flexibility of the PHREEQC application, created as a geochemical software, proved its value for utilization in wastewater treatment calculations.

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