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Zn and Pb marking of Ca binding to humic substances and PHREEQC speciation simulations

G. O. Bosire and J. C. Ngila

ABSTRACT

Power generating companies using and recycling cooling water usually experience deposition of insoluble salts on pipes carrying the water, leading to scaling problems. By controlling parameters that optimize competitive Ca complexation, the scaling potential could be reduced. This semi-empirical study determined the effect of ligands in binding, as well as the optimum parameters for Ca complexation experimentally using simulated water solutions before modelling. Experimental results showed that metal binding to ligands depended on the type of metal in competition, the pH and the humic substance used. Zn and Pb voltammetric peaks decreased with the addition of humic acid, tannic acid and catechol. Ca showed a synergistic phenomenon in the form of increased peak heights of the trace cations. Using PHREEQC model saturation index output results, the mineral phases likely to precipitate were successfully described. Furthermore, the effect of changing pH on scale formation was determined. For example, we successfully described the influence of pH on speciation and complexation through the formation of H-humate⁻ and humate²⁻. The models showed that pH may be manipulated to govern the incidence of scale. Predictive models were derived to determine what would be a useful tool in reducing the potential for scaling.

Key words | PHREEQC, saturation indices, scale

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INTRODUCTION

Scaling is a fundamental practical problem that Eskom (the Electricity Supply Commission, South Africa) is concerned with because of the expense of replacing their cooling water equipment. The dissolved constituents comprising scale increase with water recycling, and in some cases may increase scaling potential. Through chemical speciation and saturation index calculations, the PHREEQC code (Tipping 2002; Metreveli *et al.* 2010; Mostofa *et al.* 2013) has been shown to accurately describe the scaling potential of metal constituents in simulated water solutions. The resulting predictive models could indicate what physico-chemical parameters and which constituents could be manipulated to govern the incidence of scale; such models would act as useful scale management tools and thus avoid unnecessary costs.

Physico-chemical changes in cooling water can trigger scale formation (Gabielli *et al.* 1996). The predominant

scale deposits in cooling water have been found to be Ca or Mg-carbonates or Ca-sulphate (Parsons *et al.* 1997). Chelating organic compounds contained in natural organic matter (NOM) help to reduce these cations from deposit-forming salts by forming stable soluble complexes. Metal-NOM formation is of fundamental importance in metal ion chemistry, and can control the occurrence of free metals in water (Mostofa *et al.* 2013). Metal-NOM interactions have been studied as a function of various physico-chemical properties such as pH, temperature and ionic strength. Metreveli *et al.* (2010), for example, reported that the binding capacity of the NOM for metals increased as the pH value increased in the order: Zn > Pb > Cu > Pt. Fundamentally, the precipitating salts are inhibited by NOM in water by complexing the free ions in solution, thereby lowering the state of saturation (Hoch *et al.* 2000).

In this work, a semi-empirical approach is employed, complementing experimental results with modelling. To achieve these objectives, the authors of this article equilibrated trace metal ions (namely Pb^{2+} , Cu^{2+} and Zn^{2+}) separately with catechol, tannic acid and humic acid. Furthermore, the influence of Ca was investigated by measuring the peak height increases or decreases by adding it to the metal solutions before equilibration. By doing this, the influence of Ca/Mg ions in solution could be accurately accounted for. Finally, examples of scaling phases were studied by predictive simulations generated by the PHREEQC code. The simulative results show that, within a timeframe of the continuous recycling of real cooling water at Eskom, the saturation indices can be determined and manipulated, if the concentrations of the solutes dissolved in the cooling water are known, in order to manage scale formation.

MATERIALS AND METHODS

Humic acid, tannic acid and catechol (obtained from Sigma–Aldrich Company) and other reagents were of analytical grade unless otherwise stated. For solutions, Millipore water was used throughout the experiments. The concentrations of the free metal ion tracers (Zn and Pb) were determined by anodic stripping voltammetry. Voltammetric measurements were performed on an Autolab/PGSTAT128N workstation (Metrohm AG, Switzerland). The resulting peak heights were related to concentration using the Randles–Sevcik equation (at 25 °C) (Sato *et al.* 1996). The concentrations formed part of the input files in the PHREEQC code simulations.

Experimental

Preparation of humic acid, tannic acid and catechol solutions

The ligand solutions (1,000 mg/L) were prepared by dissolving 1 g of humic acid, tannic acid and catechol (1, 2-dihydroxybenzene) in Millipore water, obtained from a Milli-Q-Plus (0.22 μm pore membrane) purification system (Millipore Corporation). Fresh solutions were

prepared prior to each experiment and stored in the dark at 4 °C. Complete dissolution of humic acid was only possible in $\text{pH} > 7$. Solutions containing 20 mg/L of Pb, Cu and Zn were prepared by diluting appropriate amounts of 1,000 mg/L reference standard solutions (Sigma–Aldrich, AR grade) in 0.1 M KNO_3 . A stock solution of catechol was freshly prepared by dissolving solid catechol in ultra-pure water prior to each experiment to avoid degradation by air. At the beginning of all tests by electrochemical methods, the test solutions were purged with ultra-high purity argon gas for 10 min.

Determination of complexing capacities

Humic substances and metal solutions were mixed together, and the pH of the mixture was adjusted to 4 and 8 using 1.0 M NaOH. The Pb(II) and Zn(II) complexing capacities were determined by adding amounts of known concentration of tannic acid, humic acid and catechol to 6 mL of 20 mg/L of Pb and Zn ions at pH 4 and pH 8. Separately, these solutions were spiked with 50 μL of 1,000 mg/L Ca ions, and relative complexation measured. This method is based on the assumption that metal–ligand complexes are formed in different ratios, and that the temperatures at which the complexing capacities are established do not vary. The runs were conducted in triplicate and average peak heights were recorded.

Computation of free metal activities

The peak current I_p , measured by square wave anodic stripping voltammetry (SWASV), which is proportional to the labile fraction of metal in the voltammetric measurement, is a weighted average of the diffusion of all metal species (free + complexed). For a fully labile system (that is, a system in which all the relevant metal species (M (Cu, Fe, Pb, Zn) and ML in our system) are electroactive, the peak current I_p is expressed as (Cheng & Allen 2006):

$$I_p = -\pi^{-1/2} n F A D^{-1/2} C_{M,T}^* \tau^{-1/2} \quad (1)$$

where F is the Faraday constant, A is the electrode surface area, n is the number of moles of electrons transferred per

mole of metal oxidized or reduced, $C_{M,T}^*$ is the total soluble metal concentration in the bulk solution, τ is characteristics time, and \bar{D} is the weighted average of the diffusion coefficient of all metal species (free + complexed), which is expressed as:

$$\bar{D} = \frac{[M]^*}{C_{M,T}^*} D_M + \frac{[ML]^*}{C_{M,T}^*} D_{ML} \quad (2)$$

where $[M]^*$ is the free metal ion concentration in bulk solution, $[ML]^*$ is the complexed metal concentration in bulk solution, D_M and D_{ML} are the diffusion coefficients of the free and complexed metal ion. The mass balance of metal in bulk solution is:

$$[M]^* + [ML]^* = C_{M,T}^* \quad (3)$$

Defining normalized current Φ as the ratio of peak current in the presence of ligands to that of a ligand-free reference:

$$\Phi = \frac{I_P^L}{I_P} + \left(\frac{\bar{D}}{D_M} \right)^{1/2} \quad (4)$$

where Φ is the normalized current, I_P^L is the peak current in the presence of ligands and I_P is that of the ligand-free reference. Combining Equations (2)–(4), the free metal ion activity in bulk solution is expressed as:

$$[M]^* = \frac{\left(\left(\frac{I_P^L}{I_P} \right)^2 - D_{ML}/D_M \right)}{(1 - D_{ML}/D_M)} C_{M,T}^* \quad (5)$$

Equation (4) is used to compute free Zn, Pb and Cu ion concentrations for labile Cu/Pb/Zn–NOM systems in our experiments. Normalized current is obtained by comparing the peak current in the presence of ligands and that of the ligand-free reference. For a fully labile system, the value of D_{ML}/D_M can be estimated under conditions when the ligand concentration is in large excess of the total zinc concentration so that $[M]^* \ll [ML]^*$ and the weighted average tends to D_{ML} (Equation (2)).

RESULTS AND DISCUSSION

The results and discussion are divided into two parts: (1) complexation reactions and (2) model simulations. The first part shows complexing capacities of Pb and Zn ions to organic ligands, which were assessed by SWASV. The impact of Ca and Mg, at different pH, in competing for binding ligands was marked by the changes in the Zn and Pb peaks. The second part describes the scaling potential of the labile ions in solutions, using PHREEQC model simulations.

Metal–ligand interactions at basic and acidic pH

The Randles–Sevcik Equation (at 25 °C) (Sato *et al.* 1996) was used to calculate the concentrations of the labile Zn and Pb ions from the peak height currents. The diffusion coefficients of various labile ions used for the concentration computations are shown in Table 1. The differences in concentrations of the labile Zn and Pb ions in the presence of Ca and Mg (attributed to competitive binding to the organic ligands used) were also measured (Tables 2 and 3).

Pb-complexation to chelating agents

Voltammetric results showed a decrease in peak heights of labile Pb when humic acid, tannic acid and catechol were added into the reaction flasks, as expected. Figure 1 shows a synergistic phenomenon in the form of increased peak heights of Pb in the presence of Ca. This phenomenon was used to determine the influence of Ca on metal–ligand complexation. The synergistic response, however, showed

Table 1 | Diffusion coefficients (D) of selected hydrated cations in water, at T = 298.15 °K and infinite dilution (Buffle *et al.* 2007)

Hydrated metal ion	D (10 ⁻¹⁰ m ² s ⁻¹)	Hydrated metal ion	D (10 ⁻¹⁰ m ² s ⁻¹)
Fe ³⁺	6.04	Ca ²⁺	7.92
Mg ²⁺	7.06	Cd ²⁺	7.19
Mn ²⁺	7.12	Co ²⁺	7.32
Ni ²⁺	7.05	Cr ³⁺	5.95
Pb ²⁺	9.45	Cu ²⁺	7.14
Zn ²⁺	7.03	Fe ²⁺	7.19

Table 2 | Concentration of labile Pb after complexation equilibration using humic acid, tannic acid and catechol as chelating ligands (in the presence and absence of Ca)

Matrix	Peak concentration (ppm) at pH 4	Peak concentration (ppm) at pH 8	Significance at 0.1	Significance at 0.05
Pb + HA	1.134	3.19	Values significantly different ($P = 0.0944$, RMSE = 5.9)	Values not significantly different ($P = 0.0944$, RMSE = 5.9)
Pb + CAT	1.32	14		
Pb + TA	2.64	19.6	Values not significantly different ($P = 0.7118$, RMSE = 4.7)	Values not significantly different ($P = 0.7118$, RMSE = 4.7)
Pb + Ca + HA	2.9	1.26		
Pb + Ca + CAT	6.61	4.69		
Pb + Ca + TA	5.4438	13.5		

RMSE = root mean square error.

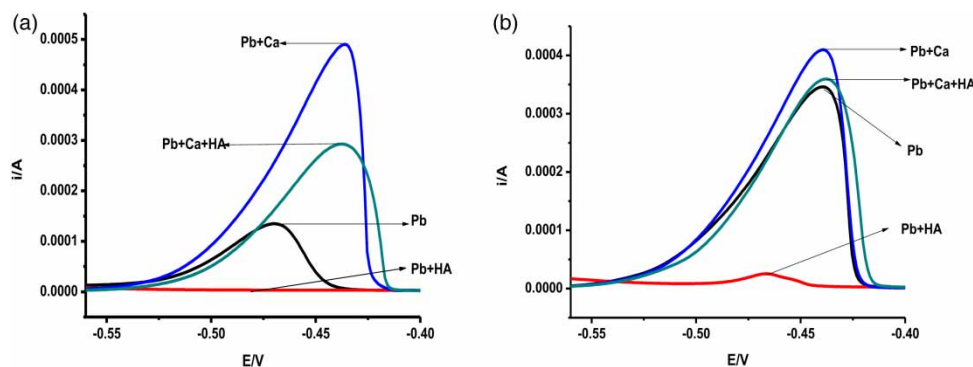
Table 3 | Differences in Pb and Zn complexing concentrations (in ppm) in humic acid (represented as HA), tannic acid (represented as TA) and catechol as a function of Ca influence

Solution	pH = 4		pH = 8	
	Pb	Zn	Pb	Zn
HA	1.77	2.68	1.94	3.74
TA	5.59	-2.49	6.15	1.50
Catechol	2.8	6.27	9.31	1.07

significant differences which were dependent on the type of chelating agent and pH. Statistical analysis, which revealed distinct significance differences at a confidence level of 0.05, was achieved using the originLab software version 8. Table 2 shows the differences in experimental concentrations in the absence and presence of Ca and corresponding analyses of variance. Pb-complexation showed no significant differences at pH 8, statistically (at 0.05 confidence levels), in all experiments. However at 0.1 confidence levels, values

of labile Pb at pH 4 and 8, in the absence of Ca, were significantly different (Table 2). Besides statistical differences, the greatest complexation of Ca in the equilibration mixtures was observed at pH 8. It is also expected that alkaline conditions enhance Pb binding to a range of chelating agents (Pinheiro *et al.* 1999). This was not the case in this study. Compared to Ca, Pb competed least for tannic acid at pH 8. The complexation of Pb to humic acid is shown in Figure 1.

A number of studies have shown that increasing complexing ligand concentration influences metal complexation (Hoop *et al.* 1995; Iglesias *et al.* 2003; Guthrie *et al.* 2005; Zhou *et al.* 2005; Mostofa *et al.* 2013). Figure 2 shows the effects of increasing HA acid concentration at a pH of 4. Clearly, increased HA increases the complexation of Pb, as shown by the peak currents, proportionately. As discussed earlier, the synergistic effect (competitive effect) of Ca enhanced Pb peaks. The humic acid complexation discussions are imperative since their Ca-metal stability constants

**Figure 1** | Linear scan ASV of Pb using a glassy carbon electrode: Ca/Pb competitive binding as a function of pH at pH 4 (a) and pH 8 (b); measured at constant ionic strength ($I = 0.1$ M KNO_3).

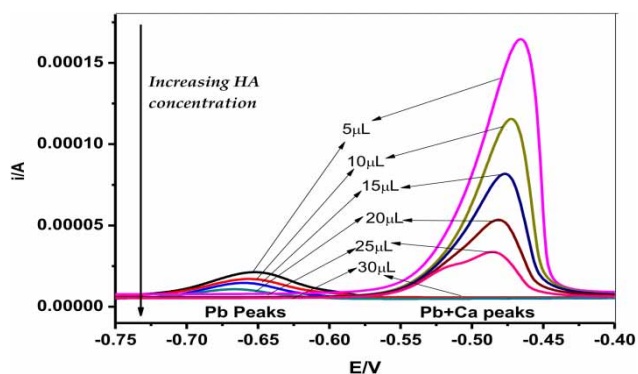


Figure 2 | ASV voltammograms of Pb and Pb + Ca binding to different concentrations of HA at pH = 4. The ionic strength is constant $I = 0.1 \text{ M KNO}_3$. The increasing amounts of 200 ppm HA were added to the reaction mixtures (at constant Pb and Ca concentrations, throughout).

guide in reducing scaling potential in water pipes carrying cooling water. This could be the basis of significant studies on scale formation in the future. The scaling simulations are discussed in the section ‘Geochemical simulations’.

Zn-complexation to chelating agents

Similar to Pb, the lability of Zn also depended on pH and the type of chelating agent used during equilibration. In the complexing mixture with Ca and humic acid, labile Zn concentrations were higher than labile Pb at both pH 4 and pH 8 (Figure 3 and Table 3). This implied that within the experimental conditions, Pb ions were more binding to HA than Zn ions. As a direct consequence, Ca competes better for HA binding in the presence of Zn than Pb. For these two trace metal ions, the binding scenario for humic acid applies when catechol is used at pH 4. However, the binding results obtained when using catechol at pH 4 and tannic acid at pH 4 and pH 8 showed that Ca competes for binding sites better in the presence of Pb than Zn (Table 3). This leads us to one argument: much as the trace metals are highly polarizing and therefore act as better coordinating centres to chelating agents, Ca will compete for ligands better in a solution mixture with one of the trace metals than the other. However, the capacity of Ca to bind will also depend on (1) the type of chelating ligand and (2) the physico-chemical conditions. At any point in time, therefore, one trace metal will be preferred to mark the capacity of Ca to bind, especially with

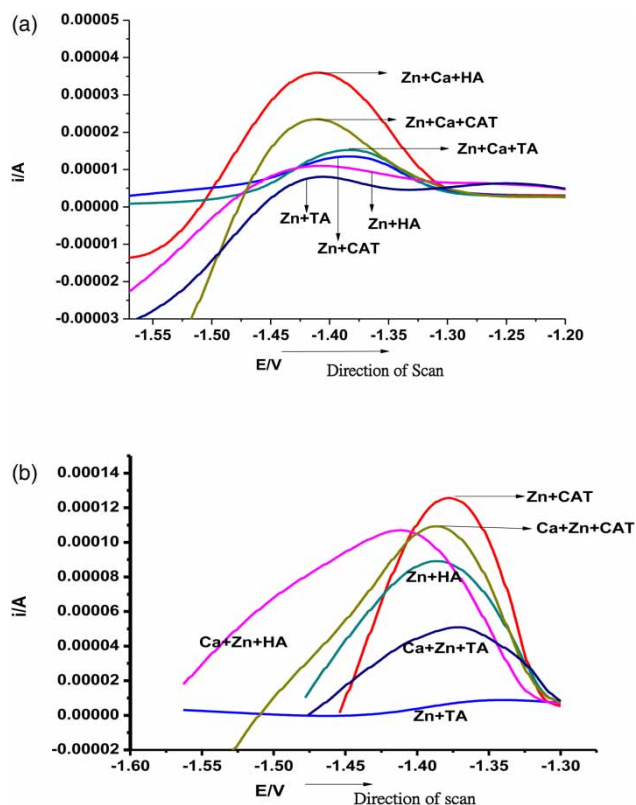


Figure 3 | Linear scan ASV of Zn using a glassy carbon electrode, Ca/Zn competitive binding as a function of pH at pH 4 (a) and pH 8 (b); measured at constant ionic strength ($I = 0.1 \text{ M KNO}_3$).

voltammetric procedures. Besides competition for humic ligands, it is worth bearing in mind that competitive interactions of H^+ , inorganic Pb and Zn species, and major cations with NOM will affect the pH, and at the same time affect Pb and Zn speciation (Pinheiro *et al.* 1999).

Table 3 shows the calculated concentration differences for Pb and Zn, respectively, using peak current plots (detailed calculations are shown in the Appendix, available with the online version of this paper). The concentrations were obtained via the difference between labile trace metals in the presence and absence of Ca. The labile concentrations of the trace metals form part of the PHREEQC model inputs. The negative value in concentration of Zn ions at a pH of 4 could be explained by the fact that tannic acid binds the least Ca, hence all the Zn is energized. This anomaly could further be explained by the fact that the labile Ca will energize the Zn ions, leading to increased deposition per unit of time and, as a result, the observed high voltammetric peak differences.

Geochemical simulations

Labile Pb and Zn scaling simulations

Positive saturation indices imply the potential to precipitate mineral phases. If the saturation index is negative, the mineral cannot precipitate. If the saturation index is positive, the mineral may precipitate. The precipitation is governed by a number of factors. The minerals likely to precipitate are presented in Tables 4 and 5. In all the three organic chelating substances used, the mineral assemblages were increasing saturation as the pH increased. The presence of Pb forms cerrusite, which further aggravates scaling (Table 4). The Zn saturation indices' simulations were all negative, indicating no precipitation of mineral phases. This agrees with experimental data that Ca is more coordinating to humic acid in the presence of Zn, hence the more precipitation experienced with Pb than Zn, relatively.

The minerals most likely to generate scale, being those containing calcium, are under-saturated in the model samples. In the actual cooling water at Eskom, the cooling water undergoes constant recycling, resulting in evaporation that leads to the increased concentration of the water constituents. The resulting saturation and speciation scenario

could be further simulated to show the effect of changing physico-chemical parameters.

Pb, Zn and Ca speciation

Speciation calculations show that there are significant differences in the distribution of scaling species. Scale formation could be reduced by a reduction in concentration of the free calcium ion, and other ions that combine with anions to form precipitates. If the Ca ion binds with organic compounds (such as catechol, tannic acid and humic acid), it will form discrete chemical complexes, a process that will reduce the concentration of the free calcium ion in solution, hence reducing the scaling potential.

The distribution of the species at pH are shown in Tables 6 and 7. According to the modelling calculations, the Ca ions going into solution remained constant at all pH values for the three chelating ligands, while the Pb and Zn species concentrations changed according to the pH (Table 6).

The pH influences complex formation as well as precipitation. A typical example of pH influence using PHREEQC runs shows the formation of H-humate⁻ and humate²⁻ in the concentrations of Pb²⁺ simulations,

Table 4 | PHREEQC model saturation indices of the main Pb/Ca mineral assemblages at basic pH values for humic acid, catechol and tannic acid

Mineral phases	Saturation indices					
	At pH = 4			At pH = 8		
	Humic acid	Catechol	Tannic acid	Humic acid	Catechol	Tannic acid
Aragonite (CaCO ₃)	-9.05	-9.06	-9.05	-2.75	-2.87	-2.95
Calcite (CaCO ₃)	-8.91	-8.91	-8.91	-2.60	-2.72	-2.80
Cerrusite (PbCO ₃)	-5.38	-4.81	-5.81	0.36	0.77	0.87

Table 5 | PHREEQC model saturation indices of the main Zn/Ca mineral assemblages at basic pH values for humic acid, catechol and tannic acid

Mineral phases	Saturation indices					
	At pH = 4			At pH = 8		
	Humic acid	Catechol	Tannic acid	Humic acid	Catechol	Tannic acid
Aragonite (CaCO ₃)	-8.89	-8.89	-8.89	-2.54	-2.54	-2.54
Calcite (CaCO ₃)	-8.74	-8.74	-8.74	-2.39	-2.39	-2.42
Smithsonite (PbCO ₃)	-3.3	-8.19	-8.34	-1.81	-1.71	-1.24

Table 6 | PHREEQC speciation outputs based on the total Ca and labile Pb. Alkalinity was expressed as hydrogen carbonate in the PHREEQC input files

Species	Humic acid		Catechol		Tannic acid	
	Log (Molality)					
	pH = 4	pH = 8	pH = 4	pH = 8	pH = 4	pH = 8
HCO ₃ ⁻	-7.08	-4.78	-7.08	-4.90	-7.08	-4.976
CO ₃ ²⁻	-13.429	-7.131	-13.429	-7.249	-13.429	-7.326
PbHCO ₃ ⁺	-9.286	-7.547	-9.286	-7.136	-9.286	-7.017
CaHCO ₃ ⁺	-9.907	-7.607	-9.907	-7.723	-9.907	-7.801
CaCO ₃	-14.174	-7.871	-14.174	-7.991	-14.174	-8.068
PbCO ₃	-11.331	-5.591	-11.331	-5.180	-11.331	-5.061
Ca ²⁺	-3.858	-3.858	-3.858	-3.858	-3.858	-3.858
Pb ²⁺	-5.068	-5.633	-5.068	-5.102	-5.068	-4.905
CaOH ⁺	-12.605	-8.663	-12.605	-8.664	-12.605	-8.664
PbOH ⁺	-8.806	-5.368	-8.806	-4.838	-8.806	-4.642
CO ₂	-4.78	-6.407	-4.78	-6.626	-4.78	-6.603

Table 7 | PHREEQC speciation outputs based on total Ca and labile Zn. Alkalinity was expressed as hydrogen carbonate in the PHREEQC input files

Species	Log (Molality)					
	Humic acid		Catechol		Tannic acid	
	pH 4	pH 8	pH 4	pH 8	pH 4	pH 8
CO ₂	-4.708	-6.358	-4.708	-6.36	-4.078	-6.384
CO ₃ ²⁻	-13.419	-7.703	-13.442	-7.075	-13.422	-7.093
HCO ₃ ⁻	-7.078	-4.729	-7.079	-4.731	-7.079	-4.754
ZnHCO ₃ ⁺	-9.256	-7.265	-9.651	-7.165	-9.796	-6.701
CaHCO ₃ ⁺	-9.742	-7.388	-9.74	-7.391	-9.738	-7.419
ZnCO ₃	-12.443	-6.451	-12.837	-6.352	-12.983	-5.889
CaCO ₃	-14.012	-7.658	-14.009	-7.661	-14.009	-7.69
Zn(CO ₃) ₂ ⁻²	-21.532	-9.193	-21.929	-9.096	-22.075	-8.652
Ca ²⁺	-3.86	-3.68	-3.686	-3.686	-3.686	-3.686
CaOH ⁺	-12.501	-8.508	-12.499	-8.498	-12.498	-8.502
Zn ²⁺	-4.231	-4.593	-4.628	-4.491	-4.774	-3.999
ZnOH ⁺	-9.394	-5.753	-9.788	-5.651	-9.934	-5.163
Zn(OH) ₂	-13.178	-5.536	-13.572	-5.434	-13.718	-4.947
Zn(OH) ₃ ⁻	-20.666	-9.025	-21.061	-8.934	-21.207	-8.435
Zn(OH) ₄ ⁻²	-29.431	-13.793	-29.828	-13.691	-29.974	-13.198

using humic acid (Figure 4). These are ions arising from humic acid, and they can combine with metals to form stable complexes.

Since this study was focussed on Ca, the formation of insoluble mineral phases such as calcium carbonate were imperative to describe scaling. However, the labile Zn and

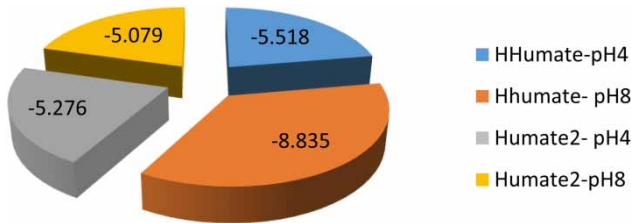


Figure 4 | Distribution of humate species as a function of changing Pb input on a modified PHREEQC with Windermere's Humic Acid Model (WHAM).

Pb ions could lead to insoluble phases such as lead carbonate and zinc carbonate, i.e., cerussite and smithsonite, respectively. Therefore, the availability of Zn ions and Pb ions could also aggravate scaling. This is because they combine with anions, and in some cases, precipitate out. Figure 5 shows the ratio of Zn and Pb ions to the Ca ion after equilibration with humic acid, tannic acid and catechol. The versatility of PHREEQC has been proved to be important in determining the scaling formation when metals and ligands are present in cooling water. Thus this study shows the ease with which these metals form scale, as well as the formation of their complexes with chelating substances.

CONCLUSIONS

Metal binding to ligands depends on the type of metal in competition, the pH and the humic substance used as the organic

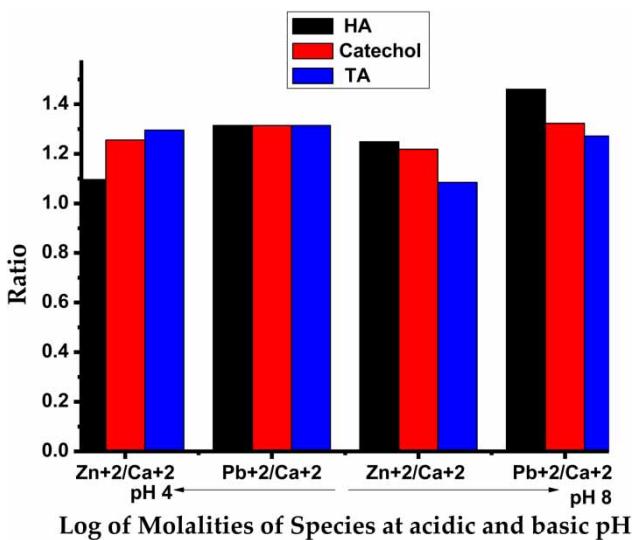


Figure 5 | Metal binding to HA, catechol and TA; ratio differences between Zn and Pb to Ca ions.

compound. Model water solutions containing known concentrations of trace metals and ligands were successfully used to trace the Ca influence on their complexation. Zn and Pb voltammetric peaks decreased with the addition of humic acid, tannic acid and catechol. Ca showed a synergistic phenomenon in the form of increased peak heights of the trace cations, which depended on the type of chelating agent and pH. Labile trace ions, total Ca, were modelled by PHREEQC and the minerals that were most likely to generate scale, and were identified. The PHREEQC modelling can accurately generate speciation and saturation indices of various phases, and henceforth can be translated to scaling. The resulting saturation and speciation scenario in the model solutions could be applied in the real cooling waters at Eskom, which undergo constant recycling, resulting in evaporation that leads to the increased concentration of the water constituents. In addition, we simulated speciation to show the effect of changing physico-chemical parameters. We successfully described the influence of pH on speciation and complexation through the formation of H-humate⁻ and humate²⁻. The competition between major cations such as Ca and the trace metals such as Pb and Zn, for complexation with ligands in water, was shown to play a role in the mineral phases that contribute to scaling. Thus by controlling parameters that optimize Ca complexation, the scaling potential could be reduced.

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