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Monitoring ZnS Precipitation: Estimation, Error Analysis and Experiment Design

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Abstract: A mass balance model of total soluble sulfide and free zinc with a second-order reaction term is theoretically able to reconstruct the zinc effluent concentration and the kinetic parameter (k). However, under real conditions this model predicts the zinc effluent concentration four orders of magnitude higher than the measured ones. The applied error analysis, based on linearization of the model followed by first-order variance propagation, showed that the accuracy of several of the input variables (flows and influent concentrations) jeopardized the estimation of the Zn concentration in the effluent, which is a phenomenon expected for every fast reaction with low product concentration. In order to overcome the inaccuracy issue, an "apparent solubility product" as a function of pS (11–20) was calculated from the experimental data, allowing for the subsequent determination of an "apparent kinetic parameter" (k_A), that excluding parallel reactions was between $1.7 \times 10^{23} - 6.2 \times 10^{24}\ \mathrm{L/(mol \cdot h)}$. This allowed for further tuning of the model such that the estimates of the Zn effluent concentration became of the same order of magnitude as the measured ones (10^{-7} M Zn).

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INTRODUCTION

Several industrial activities, like mining and metallurgy, have lead to a great disposal of heavy metals in nature (Zn, Ni, Cu, Al, etc.) (1,2). If initially acute toxicity was of major concern, slow accumulation of these metals in living systems raised the awareness for their long term (chronic) effects (3). Therefore, legislation has become more stringent (4) and new technologies are being developed in order to reduce emissions.

With a very significant industrial production, Zn is one of the metals which emissions have to be controlled. According to the U.S. Geological Survey, around 10 thousand million tons of Zn were produced worldwide in 2005 (5). Such massive production generates wastewater or solid waste that needs to be treated. In the past years, more sustainable technologies focused on heavy metal recovery for later reuse started to be investigated and applied in industry. One of these technologies is based on metal sulfide precipitation and when optimized allows to reduce the effluent metal concentrations to the ppb level (6). In the case of zinc refineries, the use of sulfide to remove Zn from the wastewater is already successfully applied (7).

In view of the increasing emphasis on safety, efficiency, and high quality standards, process control has become very important and a prerequisite in many situations (8). In the case of ZnS precipitation, sulfide has to be stoichiometrically dozed in order to minimize both the Zn effluent concentration and the sulfide usage (9). As a consequence, a PI control protocol has already been applied, in combination with pS ($-\log(S^{2-})$) (10) and pH electrodes, for the optimization of ZnS precipitation in a laboratory scale Continuously Stirred Tank Reactor (CSTR) (11). This control strategy was based on the use of pS (see nomenclature) as the controlled variable and the sulfide flow as the manipulated variable.

In addition to control, it is also important to monitor reactants and products in a reliable and cost effective way (12). Because some variables cannot be measured online (due to the inexistence of reliable hardware sensors) or require offline analytical measurements, model-based sensors, usually indicated as soft sensors or estimators, represent an interesting alternative for their estimation (13,14). In order to evaluate the accuracy of the estimations, uncertainties have to be considered as well. These uncertainties in the estimates arise from modelling errors, including parameter uncertainties and errors in the input data, which consist of analytical and sampling errors (15).

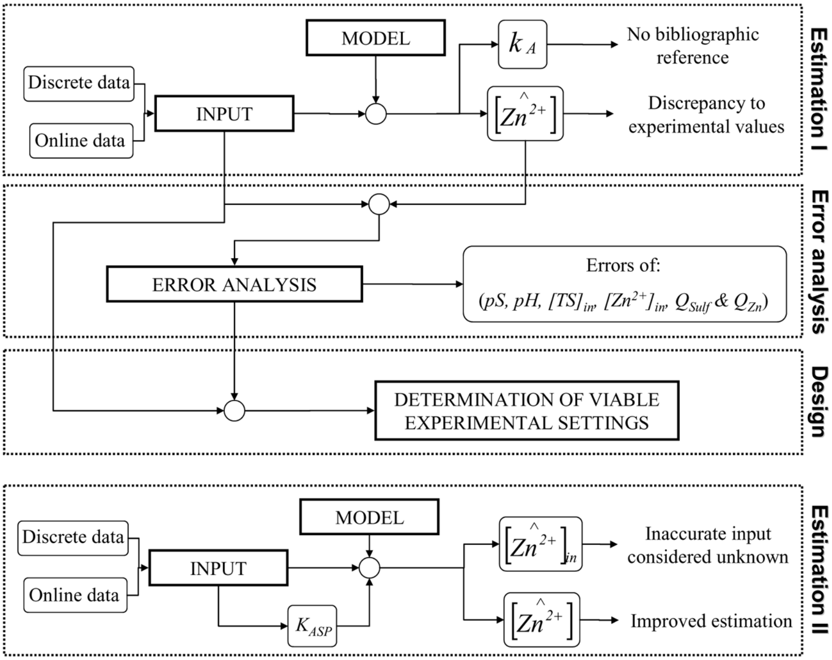


Figure 1. Schematic representation of the structure of the paper.

In this paper, a model previously proposed by König et al. (11) is used to estimate the zinc effluent concentration of a CSTR performing ZnS precipitation. The model is based on sulfide and zinc mass balances and a second-order reaction kinetic law, assuming a well-mixed reactor and the existence of only one (irreversible) reaction. It is a simplified approach to a system where indeed parallel reactions can occur and where micromixing phenomena associated to local supersaturation can affect the outcome of the process. Given this model, the goal of the paper is to derive an estimator for the ZnS precipitation process, to evaluate the inaccuracies, to suggest new experimental designs and approaches to finally obtain accurate estimations of the Zn effluent concentration and a second order "apparent kinetic parameter" k_A (Fig. 1).

MATERIAL AND METHODS

Experimental Set-up

A Continuously Stirred Tank Reactor (CSTR) of 600 ml equipped with a pS and a pH electrode was operated at 20°C (Fig. 2) (11) and used to

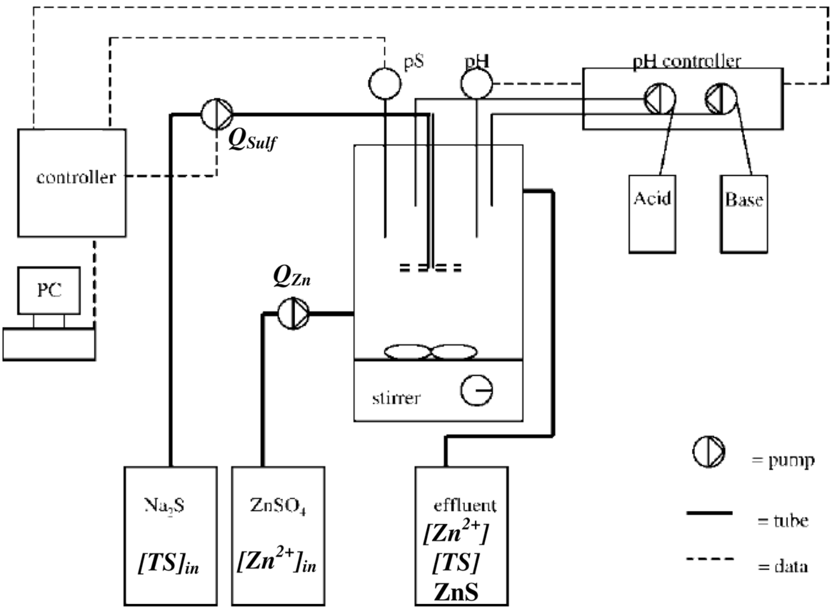


Figure 2. Experimental set-up used for ZnS precipitation (10).

generate the data processed in the present work. The pS electrode was used in a pS control strategy (11), with the aim of controlling the amount of sulfide pumped into the CSTR and therefore, the $[Zn^{2+}]$ concentration. Online data (pS, pH, Q_{Zn} and Q_{Sulf}) was recorded every 5 seconds. In addition to this, discrete data as $[Zn^{2+}]_{in}$ and $[Zn^{2+}]$ were analysed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Varian Inc., USA) and $[TS]_{in}$ by spectrophotometry (methylene blue method) (Hach-Lange, Düsseldorf, Germany). $[Zn^{2+}]_{in}$ and $[TS]_{in}$ were measured at the beginning of every experiment, while $[Zn^{2+}]$ was measured around five times per experiment, during the steady state period.

Mass Balance Model

In order to online estimate the effluent zinc concentration, the following model has been proposed (11):

$$\frac{d[Zn^{2+}]}{dt} = \frac{Q_{Zn}}{V_R}[Zn^{2+}]_{in} - \frac{Q_{Zn} + Q_{Sulf}}{V_R}[Zn^{2+}] - k[Zn^{2+}][S^{2-}] \qquad (1)$$

$$\frac{d[TS]}{dt} = \frac{Q_{Sulf}}{V_R}[TS]_{in} - \frac{Q_{Zn} + Q_{Sulf}}{V_R}[TS] - k\left[Zn^{2+}\right]\left[S^{2-}\right] \qquad (2)$$

This model (Eqs. 1–2) considers two influents flows, one of sulfide (Q_{sulf}) and another of zinc (Q_{Zn}), and a reaction between zinc and sulfide with the formation of ZnS. The mass balance is effectuated only to the free zinc and sulfide and no parallel reactions, like oxidation, volatilisation, or the formation of soluble species (e.g., $Zn(SH)_2$), are considered. Moreover, as in practice the model covers not only the reaction between S^{2-} and Zn^{2+}, but also possible parallel reactions and the whole precipitation process, including nucleation, agglomeration, aggregation and disruption, the reaction rate constant k is replaced by an "apparent kinetic parameter" k_A.

The relation between the total amount of sulfide ($[TS]$) and the sulfide concentration ($[S^{2-}]$) is given by (10):

$$[S^-] = \frac{[TS]}{\frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_{a2}} + 1} = \frac{[TS]}{c} \qquad (3)$$

where the variable c is introduced to facilitate formula manipulation.

Calculations and Considerations

Estimation of $[Zn^{2+}]$ and k_A (Estimation I)

The unknown total sulfide concentration in the effluent $[TS]$ can be directly estimated from Eq. 3, given measurements of pH and pS. In the following, it is shown how to estimate the two remaining unknowns, k_A and $[Zn^{2+}]$, from steady-state measurements of pH, pS, Q_{Zn} and Q_{Sulf} and from the predefined influent concentrations $[TS]_{in}$ and $[Zn^{2+}]_{in}$. Steady state was considered whenever the output variables pH and pS and the control input variable Q_{Sulf} were steadily around a constant value over a period of time, always longer than 30 min (Fig. 3).

By assuming steady state, the derivatives in Eqs. 1–2 are equal to zero and the system remains with only two unknowns, k_A and $[Zn^{2+}]$. Consequently, the following matrix equation is obtained:

$$\begin{pmatrix} \frac{Q_{Sulf}}{V_R}[TS]_{in} - \frac{Q_{Sulf}+Q_{Zn}}{V_R}10^{-pS}c \\ \frac{Q_{Zn}}{V_R}[Zn]_{in} \end{pmatrix} = \begin{pmatrix} 10^{-pS} & 0 \\ 10^{-pS} & \frac{Q_{Zn}+Q_{Sulf}}{V_R} \end{pmatrix} \begin{pmatrix} k_A\left[Zn^{2+}\right] \\ \left[Zn^{2+}\right] \end{pmatrix} \qquad (4)$$

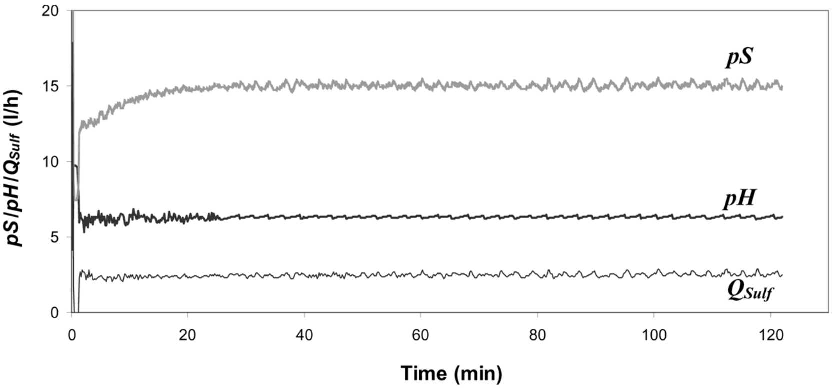


Figure 3. Example of a ZnS precipitation experiment controlled at pS 15 and pH 6.3 where steady state is reached after 30 minutes of operation and maintained over 90 minutes.

Solving this matrix equation and subsequently substituting the expression of $[Zn^{2+}]$ in $k_A[Zn^{2+}]$ gives the following relationships regarding the estimators of $[Zn^{2+}]$ and k_A:

$$[\widehat{Zn}^{2+}] = \frac{c10^{-pS}Q_{Sulf} + c10^{-pS}Q_{Zn} - Q_{sulf}[TS]_{in} + Q_{Zn}[Zn^{2+}]_{in}}{Q_{Sulf} + Q_{Zn}} \tag{5}$$

$$k_A = \frac{c10^{-pS}Q_{Sulf}^2 - 2c10^{-pS}Q_{Zn}Q_{Sulf} - c10^{-pS}Q_{Sulf}^2 + Q_{Sulf}^2[TS]_{in} + Q_{Sulf}Q_{Zn}[TS]_{in}}{10^{-pS}V_R(c10^{-pS}Q_{sulf} + c10^{-pS}Q_{Zn} - Q_{Sulf}[TS]_{in} + Q_{Zn}[Zn^{2+}]_{in})} \tag{6}$$

Recall that Eqs. 5–6 are valid on a steady-state interval. Therefore, it is in principle possible to reconstruct online estimates of $[Zn^{2+}]$ and k_A from given steady-state data. Consequently, Eqs. 5 and 6 can be used as an estimator. As will be shown later, the application of Eqs. 5–6 did not result in accurate estimates under noisy data conditions. Hence, there is a need to analyze the effect of errors on the uncertainty in the estimate of $[Zn^{2+}]$ and k_A. In what follows, the focus will be on the estimate of $[Zn^{2+}]$. In this analysis, it is assumed that the errors can be characterized in terms of simple stochastic properties, i.e., mean and variance. A similar procedure can be used for the determination of the uncertainty of the estimate of k_A.

Error Analysis of the $[Zn^{2+}]$ Estimate

In order to evaluate the variance of the estimated value of $[Zn^{2+}]$ and its dependence on the input variables, a Taylor series expansion aborted after the first-order term was applied to Eq. 5, followed by a first-order variance propagation. The Taylor series expansion is applied to provide a linearized form of Eq. 5 which facilitates the error analysis (see Annex A for details). Hence,

$$\begin{aligned} Var\left([\widehat{Zn}^{2+}]\right) = {} & F1\,Var(Q_{Sulf}) + F2\,Var(Q_{Zn}) + F3\,Var(V_R) + F4\,Var([TS]_{in}) \\ & + F5\,Var([S^{2-}]) + F6\,Var(c) + F7\,Var([Zn^{2+}]_{in}) \end{aligned} \tag{7}$$

with Fi, for $i = 1, \ldots 7$, *Factors* that depend on the steady state condition. Eq. 7 can also be represented as a sum of products:

$$Var\left([\widehat{Zn}^{2+}]\right) = P1 + P2 + P3 + P4 + P5 + P6 + P7 \tag{8}$$

Experimental Design

Equation 7 allows the evaluation of the uncertainty in the $[Zn^{2+}]$ estimate under different experimental settings (e.g., flows and/or concentrations) as well as under different variances of the measured variables. When Var($[Zn^{2+}]$) is predefined and set to a different value, and when the variances are fixed and one or more of the *Products* ($P1$ to $P7$) is larger than (or equal to) Var($[Zn^{2+}]$), the respective *Factors* ($F1$ to $F7$) of Equation 7 must be reduced.

$$\sum_{i=1}^{7} Pi \leq Var\left([\widehat{Zn}^{2+}]\right) \tag{9}$$

Taking into account that solutions exist for Equation 9, the *Factors* ($F1$ to $F7$) form a set of inequalities (see Annex B, Equation B1) allowing the determination of new flows and/or concentrations complying with the required Var($[Zn^{2+}]$). Such an approach can be used to design experiments, i.e., to determine the experimental conditions that would allow the use of certain online data as input, in the estimator (Eq. 5), for an accurate determination of the effluent Zn concentration ($[Zn^{2+}]$).

The following approach is suggested to solve the system of inequalities (Eqs. B1 – Annex B). First, given Var($[Zn^{2+}]$), upper limits on $F4$ and $F7$ (see Annex A, Eq. A6 for further specifications) are solved (since these two are closely related) as given by the following equation:

$$\frac{Q_{Sulf}}{Q_{Sulf} + Q_{Zn}} + \frac{Q_{Zn}}{Q_{Sulf} + Q_{Zn}} = 1 \tag{10}$$

Limit conditions for both flows (Q_{Sulf} and Q_{Zn}) can be established if the conditions given by the inequality $F4\ \mathrm{Var}([TS]_{in}) + F7\ \mathrm{Var}([Zn^{2+}]_{in}) < \mathrm{Var}([Zn^{2+}])$ and Equation 10 are fulfilled. In certain cases, where the variances of $[TS]_{in}$ and $[Zn]_{in}$ are too high, it can very well be that the upper limits for both flows do not fulfil Equation 10. This means that the measurements of $[TS]_{in}$ and $[Zn^{2+}]_{in}$ are not accurate enough and the system of inequalities does not have a solution.

If both the condition $F4\ \mathrm{Var}([TS]_{in}) + F7\ \mathrm{Var}([Zn^{2+}]_{in}) < \mathrm{Var}([Zn^{2+}])$ and Equation 10 are fulfilled, a solution set for Q_{Zn} and Q_{Sulf} can be found. Assuming that one of the *Factors* ($F4$ or $F7$) has a maximum, say x, then the other *Factor* is larger than $1 - x$, being both smaller than 1, as given by Eq. 10. Consequently, the following holds as the solution for $F4$ ($0 < (F4)^{1/2} < x$) and $F7$ ($1 - x < (F7)^{1/2} < 1$) and, therefore, for Q_{Zn} and Q_{Sulf} (see Annex B).

$$0 < Q_{Sulf} < \frac{xQ_{Zn}}{1-x}, \quad 0 < x < 1 \tag{11}$$

The next step is to solve $F1$ and $F2$. In this case, $\mathrm{Var}(Q_{Zn})$ and $\mathrm{Var}(Q_{Sulf})$ are considered equal, which means that the same type of pump with the same accuracy and precision would be used to pump both $[TS]_{in}$ and $[Zn^{2+}]_{in}$. Therefore, the square roots of both $F1$ and $F2$ have the same maximum, say y. After some algebraic manipulation, the following inequality appears as the solution for $F1$ and $F2$ and, consequently, for $[TS]_{in}$ and $[Zn^{2+}]_{in}$.

$$\frac{[TS]_{in} + [Zn^{2+}]_{in}}{z} < Q_{Sulf}, \ z = \frac{y}{x^2} \ and \ y > 0 \tag{12}$$

As a matter of fact, Eq. 12 allows a further specification of the solution set for $[TS]_{in}$, $[Zn^{2+}]_{in}$, Q_{Zn} and Q_{Sulf}. The remaining *Factors* do not enter in the specification of the final solution set, because *F5* and *F6* are only functions of *pH* and *pS*, respectively, and *F3* is equal to zero (see Eqs. A4 to A6 – Annex A). The final solution, for a given zinc concentration, is obtained after solving the system of inequalities defined by Eqs. 5, 9, 11, and 12.

Error Analysis of the Input Variables

Notice that in order to calculate $\mathrm{Var}([Zn^{2+}])$ (Eq. 7) or to design an experiment under a specified $\mathrm{Var}([Zn^{2+}])$, i.e., to determine $[TS]_{in}$, $[Zn^{2+}]_{in}$, Q_{Sulf} and Q_{Zn}, the variances of the several input variables have to be determined as well. That is, the variables *x, y* and *z* have to be specified (see Annex B). Subsequently, the following errors have to be taken into account: *controller errors* and *measuring errors*. The last one can be split in *analytical errors* and *sampling errors*. The first type of error relates to the oscillation generated by the controller and it is determined directly from the online data. The *analytical errors* are related to the calibration of the equipment (analytical apparatus, pumps and pH and pS electrodes) and require (like for $[Zn^{2+}]$) the application of a first-order variance propagation procedure to the calibration equations. The *sampling errors* are related to sample manipulation and are calculated from the multi-measurements of the discrete data, i.e., $[Zn^{2+}]_{in}$ and $[TS]_{in}$.

Regarding the *analytical errors*, the variables considered are pS, pH, $[Zn^{2+}]_{in}$, $exp[Zn^{2+}]$, $[TS]_{in}$, Q_{Sulf}, and Q_{Zn}. All of them have a calibration equation like:

$$Variable = Signal \times a + b \tag{13}$$

Where *Signal* corresponds to the electrode signal (mV) in the case of pS and pH, to the pump output signal (A) in the case of Q_{Sulf} and Q_{Zn} and to the intensity of the measurement in the case of $[Zn^{2+}]_{in}$, $exp[Zn^{2+}]$ and $[TS]$. Consequently, the variance of a measured variable becomes:

$$Var(Variable) = Var(Signal) \times a^2 \tag{14}$$

The variance of the *Signal* is the observed variance between all the effectuated calibrations. For $[TS]_{in}$, the variance cannot be determined, as one has no access to the calibration of the spectrophotometer. In this case, the standard deviation is considered as 1/10 of the limit of quantification of the device.

The variances of c and $[S^{2-}]$ appear as well in Eq. 7. Therefore, they have to be determined from their relationship with pH (see Eq. 3) and pS, respectively. For c, the same method as described before for $[Zn^{2+}]$, consisting of a linearization followed by first-order variance propagation, was applied. For $[S^{2-}]$, only the last step was used. After substituting $[H^+]$ by 10^{-pH}, this results in:

$$Var(c) = \left(\frac{-\ln(10)10^{-pH}}{K_{a2}} - \frac{-\ln(10)2^{1-2\,pH}5^{-2\,pH}}{K_{a1}K_{a2}} \right)^2 Var(pH), \text{ with } [H^+] = 10^{-pH} \tag{15}$$

$$Var([S^{2-}]) = (-\ln(10)10^{-pS})^2 \; Var(pS) \tag{16}$$

Estimation of $[Zn^{2+}]$ and k Using $exp[Zn^{2+}]$ (Estimation II)

Due to the outcome of the calculations described above (see Results section), an approach based on the adaptation of the model by experimental $[Zn^{2+}]$ data is also proposed. The model (Eqs. 1 and 2) can be slightly changed in order to incorporate the observed solubility product, or "apparent solubility product", of ZnS (K_{ASP}). This variable can be determined from pS and $exp[Zn^{2+}]$ considering that $K_{SP} = (S^{2-})(Zn^{2+})$ and that the ionic strength is low enough to assume $[Zn^{2+}] = (Zn^{2+})$ and $[S^{2-}] = (S^{2-})$. As a consequence, the solution for k_A becomes simpler and can be used instead of Eq. 6:

$$k_A = -\frac{c10^{-pS}Q_{Sulf} + c10^{-pS}Q_{Zn} - Q_{Sulf}[TS]_{in}}{K_{ASP}V_R}, \quad \text{with} \qquad (17)$$
$$K_{ASP} = \exp[Zn^{2+}] \cdot 10^{-pS}$$

By estimating k_A for every individual experiment with fixed pH, a function $k_A = \mathrm{f}(pS)$, that is a direct consequence of the $K_{ASP} = \mathrm{f}(pS)$, can be reconstructed and used for the estimation of $[Zn^{2+}]$. Consequently, $[Zn^{2+}]$ becomes the only unknown. Hence, $[Zn^{2+}]_{in}$ will be considered as the second unknown so that the system given by Eqs. 1 and 2 can be solved explicitly, under steady state conditions. The choice to consider $[Zn^{2+}]_{in}$ as unknown is based on the assumption that both $[TS]_{in}$ and $[TS]$ can be determined by means of the combination of a pS and pH electrode, and that both $[Zn^{2+}]_{in}$ and $[Zn^{2+}]$ cannot be frequently analyzed. In this way, both influent and effluent concentrations of zinc can be predicted by the following estimator:

$$[\widehat{Zn}^{2+}] = \frac{c10^{-pS}Q_{Sulf} + c10^{-pS}Q_{Zn} - Q_{sulf}[TS]_{in}}{k_A 10^{-pS}V_R} \qquad (18)$$

$$[\widehat{Zn}^{2+}]_{in} = \frac{(c10^{-pS}Q_{Sulf} + c10^{-pS}Q_{Zn} - Q_{sulf}[TS]_{in})(Q_{Sulf} + Q_{Zn} + k_A 10^{-pS}V_R)}{k_A 10^{-pS}Q_{Zn}V_R} \qquad (19)$$

Notice that the initial estimator (Eqs. 5 and 6) is based on all the measurements, while Eqs. 17–19 explore the uncertain $exp[Zn^{2+}]$ measurements, but skip the uncertainty of the $[Zn^{2+}]_{in}$ measurements that are in practice greatly affected by the dilution factor. In the Results section, it will be shown that this last approach has some significant advantages that compensate the costs related to the extra effort of measuring $[Zn^{2+}]$ offline. Furthermore, the same error analysis explained above can be performed in order to evaluate this approach (see Annex A).

RESULTS

Estimation of [Zn^{2+}] (Estimation I)

Applying Eqs. 5 and 6 to the average data of each experiment considered (see data in Annex C), led to estimates of *Zn* effluent concentrations ([Zn^{2+}]) that were in average three orders of magnitude higher than the measured values (Fig. 4a). Additionally, negative concentrations were obtained, but with the same order of magnitude as the positive ones.

Though more experiments were performed at *pS* around 15, giving it more statistical evidence compared to the results at the other two reported *pS* values, there is a clear trend regarding the number of positive average estimations of [Zn^{2+}] and the ratio between the zinc and the sulfide entering the reactor. The number of positive estimates (Fig. 4a) decreases from 80% at *pS* 20 (where zinc is in excess compared to sulfide), passing by 37% at *pS* 15 (where zinc and sulfide are approximately in equimolar concentrations), to 0% at *pS* 11 (where sulfide is in excess). For a better understanding of the reasons behind these observations, experiment 1 (see Annex C) will be elaborated as a case study.

Estimation of [Zn^{2+}] and k_A – Case Study (Estimation I)

By evaluating the estimator (Eqs. 5 and 6) at every data point of experiment 1, it results that not only most of the estimated [Zn^{2+}] values are several orders of magnitude higher than the measured ones (Fig. 5a), but some are also negative. When the "apparent reaction parameter" k_A is plotted (Fig. 5b), the same pattern is observed: positive and negative values with similar orders of magnitude and no intermediate values.

Therefore, to properly evaluate the reasons behind the observed pattern of having the results always within a certain order of magnitude (for both positive and negative estimates) higher than the measured values, all the input variables (flows and concentrations) were subjected to an error analysis.

Error Analysis of the [Zn^{2+}] Estimate – Case Study

Errors of Online and Discrete Data

In order to proceed with the error analysis, the variances of all the variables had to be determined. Table 1 shows how the magnitude of the variances relates with the different error sources. The variances resulting from the action of the controller were always higher for the same variable than the

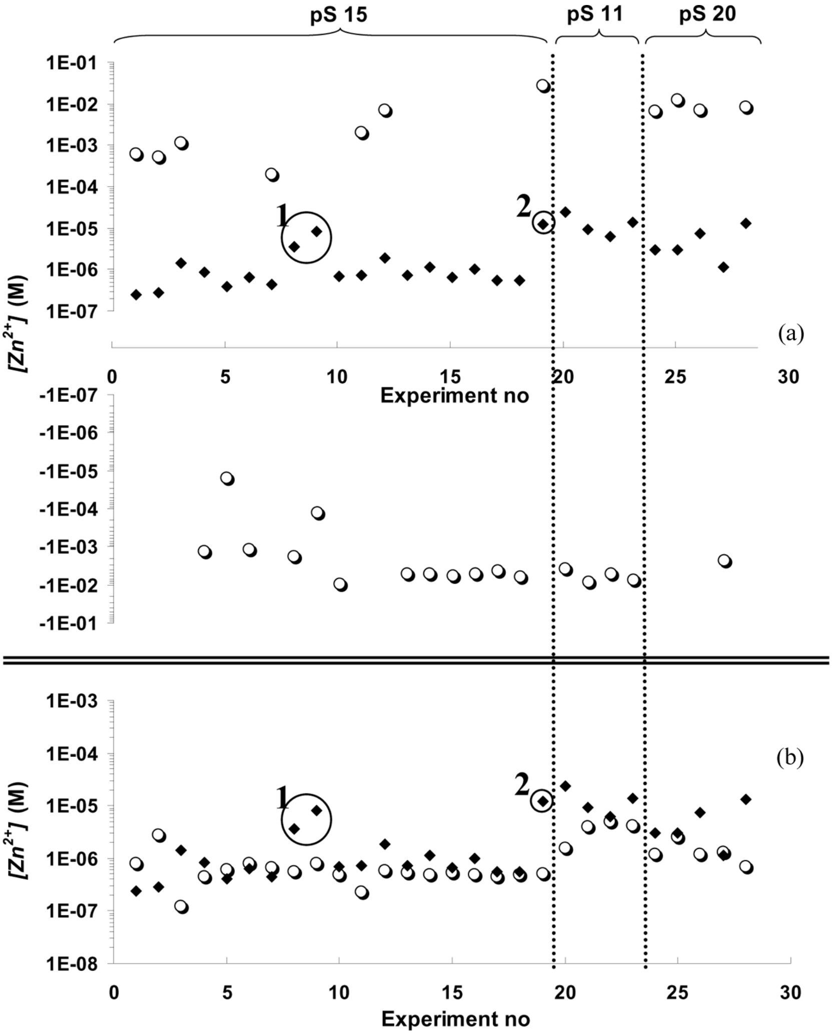
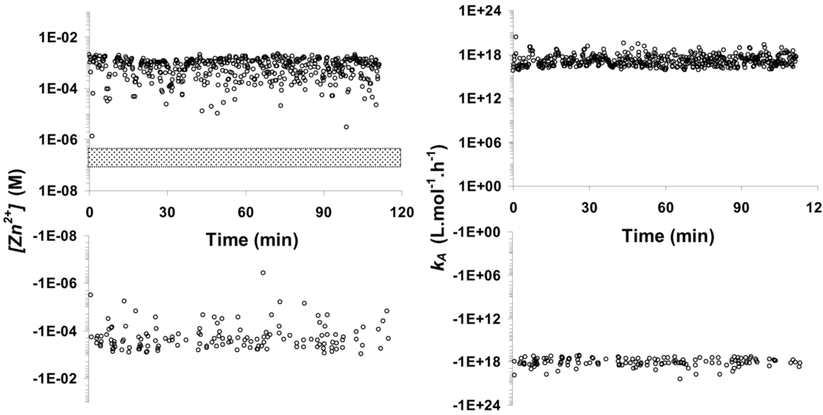


Figure 4. Average effluent zinc concentration calculated by the model (○), through Estimation I (a) and Estimation II (b) and measured by ICP-OES (◆) for every experiment shown in Annex C. Points 1 and 2 correspond to the usage of biogenic sulfide and *pH* 5, respectively, laying therefore above the expected average for the applied *pS*. The Y axis is given in log scale.

ones arising from the *measuring errors*. Moreover, the variances due to *sampling errors* always exceed the variances from the *analytical errors*.

As shown by Eq. 7, the product of the variance of each variable and the respective *Factor* (F_i) determines the final contribution to the variance of



(a) (b)

Figure 5. Estimate of Zn effluent concentration (a) and "apparent reaction parameter" (b) as function of time during experiment 1, as determined by the model (Eqs. 5 and 6) The bar (▨) represents the measured effluent concentration within the boundaries of its standard deviation. The Y axis is given in log scale.

$[Zn^{2+}]$. Table 2 shows that, for the controller error, the main contribution to the variance of the estimate of $[Zn^{2+}]$ is given by the *Product* containing the variance of the manipulated variable Q_{Sulf}. In contrast, when the *measuring errors* are taken into account, the *Products* containing the variances of $[TS]_{in}$ and $[Zn^{2+}]_{in}$ are the main contributors. Note that the order of magnitude of the variance of the estimate of $[Zn^{2+}]$ is almost the same in both cases.

Of relevance are also the variances of Q_{Sulf} and Q_{Zn}, which related *Products* (Table 2) are of lower order of magnitude than the variance of $[Zn^{2+}]$, but still higher than the variance of $exp[Zn^{2+}]$. Indeed, when only the *analytical errors* are considered, these are the *Products* (underlined in the last column of Table 2) with the highest values.

Experiment Design – Case Study

Prediction of $[Zn^{2+}]$ within the Current Laboratory Conditions and Experiments

It is relevant to know if under the laboratory conditions, in which the experiments were performed, it would be possible to achieve the variance of $exp[Zn^{2+}]$ by changing some of the experimental settings. By the same laboratory conditions, it is meant under the same procedures and with the same equipment (pumps, electrodes, reactor and analytical apparatus).

Table 1. Variances of the variables present in the model (Eqs. 1 and 2), Eqs. 7 and A9 (see Annex A)

	Controller error	*Measuring errors*		Variance required to achieve Var($exp[Zn^{2+}]$)[b] under current experimental settings	
Variable	Variance due to controller action[a]	Variance due to *sampling errors*	Variance due to *analytical errors*	Estimation I	Estimation II
$[Zn^{2+}]_{in}$	–	2.463×10^{-6}	6.093×10^{-28}[c]	$<1.154 \times 10^{-12}$	–
$[TS]_{in}$	–	7.408×10^{-8}	9.726×10^{-14}[d]	$<3.820 \times 10^{-14}$	$<7.151 \times 10^{-5}$
Q_{Sulf}	8.794×10^{-2}	–	2.675×10^{-4}	$<5.208 \times 10^{-9}$	$<1.084 \times 10^{1}$
Q_{Zn}	–	–	6.328×10^{-7}	$<1.735 \times 10^{-10}$	$<6.020 \times 10^{10}$
c	1.484×10^{16}	–	1.722×10^{-46}	$<1.104 \times 10^{16}$	$<1.240 \times 10^{26}$
$[S^{2-}]$	2.001×10^{-30}	–	2.556×10^{-39}	$<4.133 \times 10^{-31}$	$<1.093 \times 10^{-30}$
k_A	4.750×10^{41}	1.394×10^{41}	1.393×10^{41}	–	$<2.183 \times 10^{41}$

(–) Undetermined or not related to. [a]See Fig. 3 for visualising variances in pS (and thus in $[S^{2-}]$), pH (and thus in c) and Q_{sulf}. [b]See Table 2 for the values of Var($exp[Zn^{2+}]$). [c]6.093×10^{-25} if dilution of 1000 times from an influent concentration of 7.157×10^{-2} M (4.68 g/L). [d]9.726×10^{-11} if dilution of 1000 times from an influent concentration of 1.232×10^{-2} M (0.395 g/L).

Table 2. Values for all *Products* of Equation 8 compared to the variance of the estimate of $[Zn^{2+}]$ and $exp[Zn^{2+}]$. The variables associated to each *Factor* are also shown. The main contributors are underlined

		Product (P)		
		Controller error	*Measuring errors*	
Variable associated to the *Product*	*Product*		*Sampling errors*	*Analytical errors*
Q_{Sulf}	$P1$	$\underline{4.617 \times 10^{-7}}$	–	$\underline{1.405 \times 10^{-9}}$
Q_{Zn}	$P2$	0	–	$\underline{9.971 \times 10^{-11}}$
V_R	$P3$	0	–	–
$[TS]_{in}$	$P4$	0	$\underline{5.303 \times 10^{-8}}$	6.962×10^{-14}
$[S^{2-}]$	$P5$	1.324×10^{-13}	–	1.691×10^{-22}
c	$P6$	3.673×10^{-14}	–	4.264×10^{-76}
$[Zn^{2+}]_{in}$	$P7$	0	$\underline{5.838 \times 10^{-8}}$	1.444×10^{-29}
Variance of $[Zn^{2+}]$		4.617×10^{-7}	1.129×10^{-7}	1.504×10^{-9}
Variance of $exp[Zn^{2+}]^{a}$		2.734×10^{-14}	2.734×10^{-14}	6.093×10^{-28}

[a] As the variance observed on the measurements of the Zn effluent are a result of both the action of the controller and the *measuring errors* due to sampling, and they cannot be separated, it was decided to attribute the same value to both variances.

To know if such a scenario would be possible, the action of the controller is neglected, the variances due to all the *measuring errors* are used (Table 1) and the variance of the estimate of $[Zn^{2+}]$ (Eq. 7) is forced to be less or equal than the variance of $exp[Zn^{2+}]$. This implies that all the *Factors* ($F1$ to $F7$) have to be recalculated (Eqs. 7 and 9; see Annex B) in order to determine new flows and concentrations. Consequently, all *Factors* have now to comply with the new limits given by Table 3.

Table 3 shows that, under the current settings, only $F5$ and $F6$ are already beneath the upper limits considering all *measuring errors*. As a consequence, pS and pH (the variables associated to $F5$ and $F6$, respectively) are kept the same. However, because the other *Factors* are above their upper limits, new flows and concentrations have to be determined, following the steps previously explained in the Experimental design from the Material and Methods sections, i.e., using Eqs. 5, 9, 11, and 12.

When solving the inequalities for $F4$ and $F7$ independently, i.e., $F4$ $\mathrm{Var}([TS]_{in}) < \mathrm{Var}([Zn^{2+}])$ and $F7$ $\mathrm{Var}([Zn^{2+}]_{in}) < \mathrm{Var}([Zn^{2+}])$, it comes out that:

$$\frac{Q_{Sulf}}{Q_{Sulf} + Q_{Zn}} < 6.075 \times 10^{-4} \quad \text{and} \quad \frac{Q_{Zn}}{Q_{Sulf} + Q_{Zn}} < 1.054 \times 10^{-4}$$

Table 3. Maximum value for each *Factor* in Eq. 7 in order to achieve $exp[Zn^{2+}]$ variance under current lab conditions (all *measuring errors*) and without the *sampling errors* (minimum *analytical errors*), compared to the *Factors* under the current experimental settings

		Upper limits considering *measuring errors*	
Factor	Under current settings	All *measuring errors*	Minimum *analytical errors*
*F*1	5.251×10^{-6}	1.022×10^{-10}	4.321×10^{-8}
*F*2	1.576×10^{-4}	4.321×10^{-8}	4.321×10^{-8}
*F*3	0	–	–
*F*4	7.158×10^{-1}	3.691×10^{-7}	2.812×10^{-1}
*F*5	6.616×10^{16}	1.070×10^{25}	1.070×10^{25}
*F*6	2.476×10^{-30}	8.417×10^{32}	8.417×10^{32}
*F*7	2.370×10^{-2}	1.110×10^{-8}	4.487×10^{13}

As these solutions do not comply with the constraint given by Eq. 10, is not possible to solve Eq. 7. As a consequence, given the current experimental conditions, the system does not have a real solution.

Prediction of $[Zn^{2+}]$ Exclusively under Minimum *Analytical Errors*

As no solution was found when considering all the *measuring errors*, it would be important to know if in the absence of *sampling errors*, it would be possible to determine conditions and settings, i.e., to design new experiments, that allow the estimation of $[Zn^{2+}]$ with a variance in the order of magnitude of the variance of $exp[Zn^{2+}]$. For this case, all the considered errors result from the equipment. And except for Q_{Sulf}, the variances now considered are the variances resulting from *analytical errors* referred in Table 1. In order to minimize the errors, it was considered that the pump used for Q_{Sulf} has the same associated error as the pump used for Q_{Zn}.

Considering the upper limits defined by the minimum analytical errors, besides *F*5 and *F*6, only *F*7 is, under the current settings, already below those upper limits (Table 3). As the opposite occurs for *Factors* *F*1, *F*2, and *F*4 (Table 3), new values of concentrations and flows have to be calculated in order to achieve the variance of $exp[Zn^{2+}]$. Consequently, from the new upper limits, as defined in the last column of Table 3, it was found that $x < 5.302 \times 10^{-1}$ and $y < 2.079 \times 10^{-4}$. When applied to Eqs. 11–12, a universe of solutions for $[Zn^{2+}]_{in}$, $[TS]_{in}$, Q_{Sulf} and Q_{Zn} was found, as described by Fig. 6. It should be noticed that the order of magnitude of the flows is always higher than the one of the concentrations.

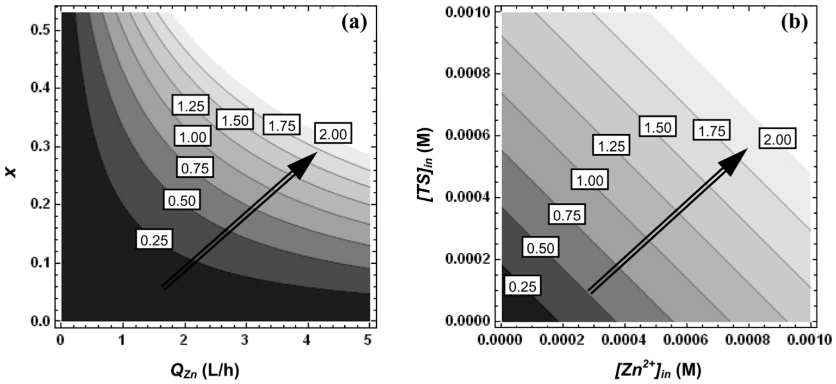


Figure 6. Graphical solution for Equations 11 (a) and 12 (b). The arrows indicate the increase of Q_{Sulf} from 01/h to 21/h, with increments of 0.25 as shown in the graphics. for b, both x and y were set at the maximum values, 5.302×10^{-1} and 2.079×10^{-4}, respectively.

Estimation of $[Zn^{2+}]$ and k_A using $exp[Zn^{2+}]$ (Estimation II)

The estimates of k_A obtained by Eq. 17 are strongly correlated with the supersaturation i.e., the pS (Fig. 7), varying from $1.9 \times 10^{14} - 9.2 \times 10^{15}$ L/(mol.h) at pS 11, $2.5 \times 10^{19} - 5.4 \times 10^{21}$ L/(mol.h) at pS 15, to $1.7 \times 10^{23} - 6.2 \times 10^{24}$ L/(mol.h) at pS 20. Replacing, in Eq. 18, k_A by the relationship given in Fig. 7 allows for estimating $[Zn^{2+}]$ at every data point and for every experiment. The result is that all the estimates become positive and of the same, or close to the same, order of magnitude as the $exp[Zn^{2+}]$ (Fig. 4b).

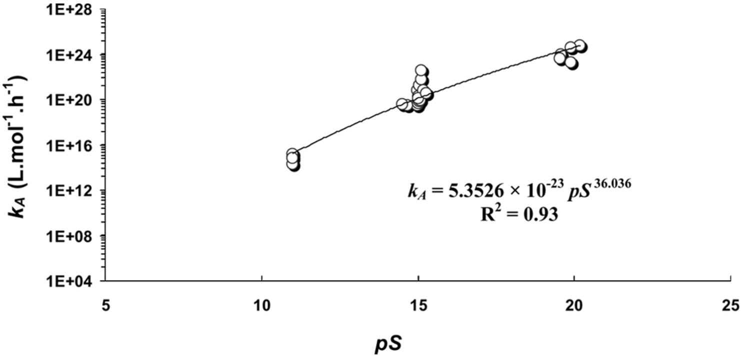


Figure 7. Correlation between the "apparent kinetic parameter" k_A and the pS. Experiments performed with biogenic sulfide and at pH 5 were excluded.

Considering the same case study as before (experiment 1), and applying the same error analysis as before (see Annex A – Eq. A9), it was noticed that this approach (Estimation II) does not bear the inaccuracy issues presented by the Estimation I. This is clearly shown in Table 1, where all the variances (of every input) are below the maximum variance allowed in order to achieve the variance of $exp[Zn^{2+}]$.

DISCUSSION

This study shows that the use of a mass balance model with a kinetic component to describe steady state periods of a CSTR used for ZnS precipitation is extremely susceptible to the quality of the input variables. Due to the low precision of some inputs and to the fact that the model incorporates variables with very high and very low order of magnitude (e.g., k and $[S^{2-}]$, respectively), very specific operational settings have to be applied in order to fit the experimental data (from ICP-OES) with the predicted ones (Eq. 5).

Estimation of $[Zn^{2+}]$ (Estimation I)

As the model (Eqs. 1 and 2) assumes an equimolar reaction between Zn and sulfide, it is normal to expect negative $[Zn^{2+}]$ estimates in the case of reactions that consume more sulfide than zinc. This corroborates with the fact that the percentage of negative estimates of $[Zn^{2+}]$ is correlated to the presence of sulfide in excess (more negative estimates at lower pS – see Figure 4a), since those reactions, like the formation of soluble $Zn(HS)_n$, occur mainly at a pS lower than 15 (9). However, when the pS is controlled at 15, the oscillation of Q_{Sulf} can generate lower pS values even during steady state. Within the range of the case study (experiment 1), values in the range of 1×10^{-3} to 5×10^{-3} ppm of Zn as $Zn(HS)_n$ can be expected (9). Assuming $n = 2$ (9) means that up to 1.5×10^{-7} M of sulfide can be "lost" and not quantified in the model. Other studies (17,18) have rather focused on other products like $Zn_2S_3^{2-}$, even reporting the absence of $Zn(HS)_2$ (18). However, of most importance is the fact that the stoichiometry of these reactions differs from that of ZnS formation, and can change the $[Zn^{2+}]$ estimate.

However, negative estimates were obtained even at pS 20, where sulfide is present under limiting amounts regarding Zn. This could indicate the existence of other phenomena related to the influents. The existence of negative $[Zn^{2+}]$ estimates can be caused by an underestimation of $[Zn^{2+}]_{in}$ and/or an overestimation of $[TS]_{in}$. Concerning the $[Zn^{2+}]_{in}$, it could only happen in the case where Zn would precipitate with hydroxide. Under the present experimental conditions this is very unlikely, as the $[Zn^{2+}]_{in}$ solutions were always acidified to pH 5. Regarding the $[TS]_{in}$, oxidation and volatilization of sulfide may play a very important role. However, this is very difficult to quantify as these phenomena depend upon specific area, exposure time, oxygen concentration, pH, etc (19). Nevertheless, the following two possibilities should be seriously considered regarding the loss of sulfide by oxidation/volatilization: in the influent vessel and/or when dosed to the reactor. As the influent vessel was flushed for several minutes and the pH was around 12, no volatilization and oxidation are expected to occur in large extend (19,20). On the other hand, as the sulfide was dosed above the reactor liquid surface, some oxidation could have occurred. For the current case study (experiment 1), assuming a common "metric" drop volume of 50 µL, that every drop takes about 0.5 seconds to reach the liquid surface and using 0.073 $\mu mol\, s^{-1}$ as the sulfide consumption rate due to oxidation (in artificial sea water) (21), the actual $[TS]_{in}$ becomes 1.159×10^{-2} M, lower than the measured one (see experiment 1 in Annex C). Of all these physical phenomena, the ones that create the greatest uncertainty regarding the estimation of $[Zn^{2+}]$ are the occurrence of parallel reactions consuming more sulfide than the one predicted by the model (Eqs. 1 and 2) and the oxidation of $[TS]_{in}$. Nevertheless, it was mainly the inaccuracy of some inputs that amplified the importance of these phenomena. Indeed, these should be considered mainly for fine tuning when input accuracy already fulfils the needs.

Error Analysis of the Determination of $[Zn^{2+}]$ – Case Study (Estimation I)

The error analysis of the case study (Annex C, experiment 1) shows that the variances of the estimates of $[Zn^{2+}]$ are several orders of magnitude larger than the variances of the experimental Zn effluent concentration (Table 2). This is a clear indication of an inaccuracy issue regarding the data used in the estimator (Eq. 5). The fact that the variances resulting from the action of the controller are the largest (Table 1) does not mean that the controller used in this study is inappropriate. The controller output directly depends on the *measuring errors*. In particular, the sample preparation method influences the final accuracy (22) (Table 2), as it can be seen from the discrepancy between the *sampling error* and the *analytical error* of $[Zn^{2+}]_{in}$ shown in Table 1. Indeed, the *sampling error* of $[Zn^{2+}]_{in}$ jeopardizes the accurate estimation of $[Zn^{2+}]$ (see Table 2), as it contributes to a very large value of $P7$. In the same way, the *sampling error* of $[TS]_{in}$ greatly contributes to the variance of the estimate of

$[Zn^{2+}]$ as shown by the large $P4$ in Table 2. This last error could be greatly reduced if pS and pH electrodes would be used to determine $[TS]_{in}$ in the same way as it was used for the effluent $[TS]$. Indeed, the development of an accurate online analytical apparatus is an elegant way of avoiding the usually large *sampling errors*.

Experimental Design – Case Study (Estimation I)

As within the current laboratory conditions it was not possible to solve Eq. 9, there is no set of flows and concentrations that would allow the use of the estimator presented in Eq. 5 for the estimation of $[Zn^{2+}]$. As discussed above, in particular the *sampling errors* of $[Zn^{2+}]_{in}$ and $[TS]_{in}$ are too high.

The impact of the *sampling errors* is even more emphasized by the fact that their exclusion from the error analysis allowed a feasible solution of Eqs. 5, 9, 11, and 12 (Fig. 6). However, as the concentrations must be of a smaller order of magnitude than the flows, the system could only be operated at a large difference of order of magnitude between flows and concentrations. This constraint implies that with the pumps used in the present study, only influent solutions of a few ppm of sulfide and zinc could be used. If the pumps would be more accurate (see *analytical errors* in Table 2), then lower flows could be applied for the used influent concentrations, or higher influent concentrations could be applied for the used flows. This would allow the treatment under more realistic conditions of flows and influent concentrations, as well as a more accurate prediction of $[Zn^{2+}]$ and k.

Estimation of $[Zn^{2+}]$ and k_A using $exp[Zn^{2+}]$ (Estimation II)

Based on the adaptation of the model by the sampled $[Zn^{2+}]$ data ($exp[Zn^{2+}]$), via determination of the kinetic parameter k_A (Eq. 17), the proposed approach successfully improved the estimation of $[Zn^{2+}]$ (Figure 4b), overcoming the existence of negative values of k_A that should only emerge in the case of dissolution (23).

The use of the experimentally calculated K_{ASP} is more correct than the direct use of the thermodynamically determined K_{SP}. First, the existence of other parallel reactions at low pS is not taken into account when only K_{SP} is used. Second, different pS values mean different levels of supersaturation, which have a different effect on the nucleation, crystal growth, and agglomeration and therefore on the extension of the precipitation (24,25) and on the overall kinetics (Fig. 7). However, as the formation of soluble zinc sulfide complexes starts at pS around 15 and proceeds to lower *pS* values (9), the function could consist of an inflection point at *pS* 15 rather than the function shown in Fig. 7.

Though the data range only permitted the build up of the function $k_A = \mathrm{f}(pS)$ (through K_{ASP}), also the influence of the *pH* should be considered, as it directly affects the precipitation of ZnS. Moreover, in order to fine tune the estimator of $[Zn^{2+}]$, the HRT should also be taken into consideration, provided that the model describes an inversely proportional relation between k_A and the HRT (Eqs. 6 and 17). However, the effect of the HRT should be mainly related to the growth and disruption of the precipitates, rather than exactly to the primary nucleation that occurs in time spans several orders of magnitude shorter than the HRTs.

The choice of taking $[Zn^{2+}]_{in}$ as an unknown together with $[Zn^{2+}]$ has a very practical reason. As the variance of $[Zn^{2+}]_{in}$ was the one with the highest *measuring error*, it makes sense to ignore its value and consider it as an unknown. On the other hand, if the goal was to estimate $[Zn^{2+}]$ in order to avoid its frequent measurements, it makes sense to avoid the frequent measurement of $[Zn^{2+}]_{in}$ as well. It was then shown that in the case of very fast reactions, the prior knowledge of the kinetic parameters is of crucial importance, as a mass balance model requires highly accurate inputs in order to determine such parameters, of very large order of magnitude, together with the effluent concentration of much lower order of magnitude. This is clearly shown in Table 1, as the variances required for a good estimation are much higher than with the Estimation I. Nevertheless, the complexity of the precipitation process (27) goes beyond a single rate constant. Hence, inclusion of $exp[Zn^{2+}]$ measurements allows the estimation of a global reaction parameter and thus from Eqs. 1 and 2, under steady state conditions, the online estimation of the unknown effluent (together with the influent) zinc concentration.

CONCLUSION

- Very fast reactions generating very low effluent concentrations, like ZnS precipitation, require an almost nonexistent accuracy of the input variables for a good estimation of the effluent concentration and the kinetic parameter from a mass balance model.
- The use of the first proposed estimator (Estimation I – Eqs. 5–6) for an accurate estimation of $[Zn^{2+}]$ requires the use of flows with a much larger order of magnitude than the influent concentration.
- The use of the accurate fraction of the data for the determination of the “apparent solubility product” (K_{ASP}) and considering the inaccurate influent data ($[Zn^{2+}]_{in}$) as unknown greatly improves the estimation and provides a reasonable soft sensor for steady state conditions.

- The value of the "apparent kinetic parameter" (k_A) for the studied reactor system, excluding parallel reaction but not micromixing effects and the HRT contribution, was determined between $1.7 \times 10^{23} - 6.2 \times 10^{24}$ L/(mol·h).

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The authors warrant that the article neither has been published before, nor it has been simultaneously submitted elsewhere.

NOMENCLATURE

k	Second order rate constant for the reaction of zinc and sulfide
k_A	Apparent kinetic parameter for the reaction of zinc and sulfide
Q_{Zn}	Influent flow of zinc
Q_{Sulf}	Influent flow of sulfide
V_R	Volume of the reactor
$[TS]$	Concentration of total soluble sulfide ($H_2S(aq) + HS^- + S^{2-}$)
$[Zn^{2+}]$	Concentration of free zinc
$exp[Zn^{2+}]$	Concentration of free zinc measured by ICP
$[S^{2-}]$	Concentration of S^{2-}
c	Function of pH ($[H^+]^2/(K_{a1}\, K_{a2}) + [H^+]/K_{a2} + 1$)
pS	$-\log(S^{2-}) \approx -\log[S^{2-}]$
$[H^+]$	Proton concentration (10^{-pH})
K_{a1}	Dissociation constant for H_2S (10^{-7})
K_{a2}	Dissociation constant for HS^- ($10^{-13.9}$)
K_{SP}	Solubility product of ZnS ($10^{-23.8}$)
K_{ASP}	Apparent solubility product of ZnS
in	Influent

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ANNEX A. ERROR ANALYSIS OF [Zn^{2+}]

Estimation I

Given Eq. 5:

$$\begin{aligned}
&[Z\hat{n}^{2+}]\left(Q_{Sulf}+\Delta Q_{Sulf}, Q_{Zn}+\Delta Q_{Zn},\ldots\right)= \\
&\frac{c10^{-pS}Q_{Sulf}+c10^{-pS}Q_{Zn}-Q_{sulf}[TS]_{in}+Q_{Zn}\left[Zn^{2+}\right]_{in}}{Q_{Sulf}+Q_{Zn}} \\
&\text{with } 10^{-pS}=\left[S^{2-}\right] \qquad \text{(A1)}
\end{aligned}$$

then the Taylor series expansion aborted after the first term becomes:

$$\begin{aligned}
&[Z\hat{n}^{2+}]\left(\tilde{Q}_{Sulf}+\Delta Q_{Sulf},\tilde{Q}_{Zn}+\Delta Q_{Zn},\ldots\right)\approx\left[Zn^{2+}\right]\left(\tilde{Q}_{Sulf},\tilde{Q}_{Zn},\ldots\right) \\
&+\left(\frac{\partial\left[Zn^{2+}\right]\left(\tilde{Q}_{Sulf},\tilde{Q}_{Zn},\ldots\right)}{\partial Q_{Sulf}}\Delta Q_{Sulf}+\frac{\partial\left[Zn^{2+}\right]\left(\tilde{Q}_{Sulf},\tilde{Q}_{Zn},\ldots\right)}{\partial Q_{Zn}}\Delta Q_{Zn}+\ldots\right) \qquad \text{(A2)}
\end{aligned}$$

Hence, without referring explicitly to the linearization point:

$$\begin{aligned}
\Delta[Z\hat{n}^{2+}]\approx{}&\frac{\partial[Z\hat{n}^{2+}]}{\partial Q_{Sulf}}\Delta Q_{Sulf}+\frac{\partial[Z\hat{n}^{2+}]}{\partial Q_{Zn}}\Delta Q_{Zn} \\
&+\frac{\partial[Z\hat{n}^{2+}]}{\partial V_R}\Delta V_R+\frac{\partial[Z\hat{n}^{2+}]}{\partial[TS]_{in}}\Delta[TS]_{in}+\frac{\partial[Z\hat{n}^{2+}]}{\partial[S^{2-}]}\Delta[S^{2-}] \\
&+\frac{\partial[Z\hat{n}^{2+}]}{\partial c}\Delta c+\frac{\partial[Z\hat{n}^{2+}]}{\partial[Zn^{2+}]_{in}}\Delta[Zn^{2+}]_{in} \qquad \text{(A3)}
\end{aligned}$$

Applying the first-order variation propagation rule gives:

$$\begin{aligned}
Var\left([Z\hat{n}^{2+}]\right)={}&\left(\frac{\partial[Z\hat{n}^{2+}]}{\partial Q_{Sulf}}\right)^2 Var(Q_{Sulf})+\left(\frac{\partial[Z\hat{n}^{2+}]}{\partial Q_{Zn}}\right)^2 Var(Q_{Zn}) \\
&+\left(\frac{\partial[Z\hat{n}^{2+}]}{\partial V_R}\right)^2 Var(V_R)+\left(\frac{\partial[Z\hat{n}^{2+}]}{\partial[TS]_{in}}\right)^2 Var\left([TS]_{in}\right) \\
&+\left(\frac{\partial[Z\hat{n}^{2+}]}{\partial[S^{2-}]}\right)^2 Var\left([S^{2-}]\right)+\left(\frac{\partial[Z\hat{n}^{2+}]}{\partial c}\right)^2 Var(c) \\
&+\left(\frac{\partial[Z\hat{n}^{2+}]}{\partial[Zn^{2+}]_{in}}\right)^2 Var\left([Zn^{2+}]_{in}\right) \qquad \text{(A4)}
\end{aligned}$$

This corresponds to Eq. 7:

$$Var\left([Z\hat{n}^{2+}]\right) = F1\ Var\left(Q_{Sulf}\right) + F2\ Var(Q_{Zn}) + F3\ Var(V_R) + F4\ Var\left([TS]_{in}\right) + F5\ Var\left([S^{2-}]\right) + F6\ Var(c) + F7\ Var\left([Zn^{2+}]_{in}\right) \tag{A5}$$

with:

$$F1 = \left(-\frac{Q_{Zn}\left([TS]_{in} + [Zn^{2+}]_{in}\right)}{\left(Q_{Sulf} + Q_{Zn}\right)^2}\right)^2,$$
$$F2 = \left(\frac{Q_{Sulf}\left([TS]_{in} + [Zn^{2+}]_{in}\right)}{\left(Q_{Sulf} + Q_{Zn}\right)^2}\right)^2,\ F3 = 0,$$
$$F4 = \left(-\frac{Q_{Sulf}}{Q_{Sulf} + Q_{Zn}}\right)^2,\ F5 = c^2, \quad F6 = [S^{2-}]^2,$$
$$F7 = \left(\frac{Q_{Zn}}{Q_{Sulf} + Q_{Zn}}\right)^2 \tag{A6}$$

In very compact notation, the variance of the estimate of $[Zn^{2+}]$ can be written as the sum of several *Products* (Eq. 8):

$$Var\left([Z\hat{n}^{2+}]\right) = P1 + P2 + P3 + P4 + P5 + P6 + P7 \tag{A7}$$

Estimation II

Given Eq. 18:

$$[Z\hat{n}^{2+}](Q_{Sulf} + \Delta Q_{Sulf}, Q_{Zn} + \Delta Q_{Zn}, \ldots) = \frac{c10^{-pS}Q_{Sulf} + c10^{-pS}Q_{Zn} - Q_{sulf}[TS]_{in}}{k10^{-pS}V_R} \quad \text{with} \quad 10^{-pS} = [S^{2-}] \tag{A8}$$

and applying the Taylor series expansion aborted after the first term, without referring explicitly to the linearization point, followed by the first-order variation propagation rule, gives:

$$Var([Z\hat{n}^{2+}]) = F1\ Var(Q_{Sulf}) + F2\ Var(Q_{Zn}) + F3\ Var(V_R) + F4\ Var([TS]_{in}) + F5\ Var([S^{2-}]) + F6\ Var(c) + F7\ Var(k) \tag{A9}$$

with

$$
\begin{aligned}
F1 &= \left(\frac{c[S^{2-}] - [TS]_{in}}{[S^{2-}]kV_R}\right)^2 \\
F2 &= \left(\frac{c}{kV_R}\right)^2 \\
F3 &= \left(-\frac{c[S^{2-}]Q_{Sulf} + c[S^{2-}]Q_{Zn} + Q_{Sulf}[TS]_{in}}{[S^{2-}]kV_R^2}\right)^2 \\
F4 &= \left(-\frac{Q_{Sulf}}{[S^{2-}]kV_R}\right)^2 \\
F5 &= \left(\frac{Q_{Sulf}[TS]_{\mathrm{ln}}}{[S^{2-}]^2 kV_R}\right)^2 \\
F6 &= \left(\frac{Q_{Sulf} + Q_{Zn}}{kV_R}\right)^2 \\
F7 &= \left(-\frac{c[S^{2-}]Q_{Sulf} + c[S^{2-}]Q_{Zn} + Q_{Sulf}[TS]_{in}}{[S^{2-}]k^2 V_R}\right)^2
\end{aligned}
\tag{A10}
$$

ANNEX B. EXPERIMENTAL DESIGN OF ESTIMATION I

In order to limit the value of $Var([Zn^{2+}])$, each one of the *Products* $P1 \ldots P7 < Var([Zn^{2+}])$. Therefore, according to Eq. 7, each of the *Factors* also has a maximum that is:

$$
\begin{aligned}
&F1 < \frac{Var([Z\hat{n}^{2+}])}{Var(Q_{Sulf})} \wedge F2 < \frac{Var([Z\hat{n}^{2+}])}{Var(Q_{Zn})} \wedge F3 < \frac{Var([Z\hat{n}^{2+}])}{Var(V_R)} \\
&\wedge F4 < \frac{Var([Z\hat{n}^{2+}])}{Var([TS]_{in})} \wedge F5 < \frac{Var([Z\hat{n}^{2+}])}{Var([S^{2-}])} \wedge F6 < \frac{Var([Z\hat{n}^{2+}])}{Var(c)} \\
&\wedge F7 < \frac{Var([Z\hat{n}^{2+}])}{Var([Z\hat{n}^{2+}]_{in})}
\end{aligned}
\tag{B1}
$$

These conditions are necessary but not sufficient. In fact, the following inequality (Eq. 9) must hold:

$$
\sum_{i=1}^{7} Pi \leq Var([Z\hat{n}^{2+}]) \tag{B2}
$$

Focusing on B1, as $F3$ is zero and $F5$ and $F6$ are functions of single variables ($[S^{2-}]$ and c, respectively, which are already accurate enough), only the others need to be evaluated. Let $(F4)^{1/2} < x$, then from $F4$ and $F7$ and Equation 10, the following inequality for the flows is found (Eq. 11):

$$\begin{aligned} &F4 = \left(-\frac{Q_{Sulf}}{Q_{Sulf} + Q_{Zn}}\right)^2 \wedge F7 = \left(\frac{Q_{Zn}}{Q_{Sulf} + Q_{Zn}}\right)^2 \\ &\Rightarrow \frac{Q_{Sulf}}{Q_{Sulf} + Q_{Zn}} < x \wedge \frac{Q_{Zn}}{Q_{Sulf} + Q_{Zn}} > 1 - x \Rightarrow 0 < Q_{Sulf} < \frac{x\ Q_{Zn}}{1 - x} \end{aligned} \tag{B3}$$

Subsequently, $F1$ and $F2$ are solved under the assumption that $Var(Q_{Sulf}) = Var(Q_{Zn})$ (see B1):

$$\begin{aligned} F1 &= \left(-\frac{Q_{Zn}\left([TS]_{in} + \left[Zn^{2+}\right]_{in}\right)}{\left(Q_{Sulf} + Q_{Zn}\right)^2}\right)^2 \wedge F2 \\ &= \left(\frac{Q_{Sulf}\left([TS]_{in} + \left[Zn^{2+}\right]_{in}\right)}{\left(Q_{Sulf} + Q_{Zn}\right)^2}\right)^2 \Rightarrow \frac{Q_{Zn}\left([TS]_{in} + \left[Zn^{2+}\right]_{in}\right)}{\left(Q_{Sulf} + Q_{Zn}\right)^2} \\ &< y \wedge \frac{Q_{Sulf}\left([TS]_{in} + \left[Zn^{2+}\right]_{in}\right)}{\left(Q_{Sulf} + Q_{Zn}\right)^2} < y \end{aligned} \tag{B4}$$

Given $(F4)^{1/2} < x$ and the expressions in B3:

$$\begin{aligned} &\frac{[TS]_{in} + \left[Zn^{2+}\right]_{in}}{Q_{Sulf} + Q_{Zn}} < \frac{y}{x} \wedge \frac{[TS]_{in} + \left[Zn^{2+}\right]_{in}}{Q_{Sulf} + Q_{Zn}} \leq \frac{y}{1 - x} \\ &\quad \Rightarrow [TS]_{in} + \left[Zn^{2+}\right]_{in} < \frac{y}{x^2} Q_{Sulf} \end{aligned} \tag{B5}$$

ANNEX C. Data compilation from all the experiments analysed in the present study. Part of the data provided by König et al., (8) and Esposito et al. (26)

Exp	Logged (online) data				Experimental data		
	Q_{Zn} (l/h)	Q_{sulf} (l/h)	pS	pH	$[TS]_{in}$ (M)	$[Zn^{2+}]_{in}$ (M)	$[Zn^{2+}]$ (M)
1	0.87	4.80	14.98	6.31	1.23×10^{-02}	7.16×10^{-02}	2.41×10^{-07}
2	2.58	6.95	15.05	5.77	3.03×10^{-02}	8.34×10^{-02}	2.80×10^{-07}
3	0.67	4.84	14.97	6.30	1.23×10^{-02}	1.37×10^{-02}	1.42×10^{-06}
4	0.67	2.70	15.01	6.33	1.23×10^{-02}	4.22×10^{-02}	8.41×10^{-07}
5	0.67	3.52	15.16	7.40	1.29×10^{-02}	6.70×10^{-02}	3.98×10^{-07}
6	0.67	7.84	15.11	6.26	7.08×10^{-03}	6.70×10^{-02}	6.42×10^{-07}
7	0.67	2.78	15.13	6.18	1.69×10^{-02}	6.70×10^{-02}	4.36×10^{-07}
8	0.67	3.24	14.89	6.32	1.20×10^{-02}	4.63×10^{-02}	3.56×10^{-06}
9	0.67	4.62	14.84	6.23	1.21×10^{-02}	8.14×10^{-02}	8.07×10^{-06}
10	0.60	2.84	15.03	6.31	8.89×10^{-03}	6.97×10^{-02}	6.99×10^{-07}
11	0.32	1.66	15.01	6.30	1.28×10^{-02}	5.43×10^{-03}	7.34×10^{-07}
12	0.89	4.48	15.03	6.36	1.01×10^{-02}	6.50×10^{-02}	1.86×10^{-06}
13	0.60	3.22	15.02	6.32	9.76×10^{-03}	9.10×10^{-02}	7.21×10^{-07}
14	0.60	3.17	15.07	6.29	1.22×10^{-02}	3.21×10^{-02}	1.14×10^{-06}
15	0.60	2.50	15.01	6.33	1.14×10^{-02}	2.68×10^{-02}	6.55×10^{-07}
16	0.60	2.47	14.66	6.31	1.56×10^{-02}	3.52×10^{-02}	1.00×10^{-06}
17	0.60	2.35	14.51	7.55	1.41×10^{-02}	3.14×10^{-02}	5.46×10^{-07}
18	0.60	2.27	15.26	8.95	1.33×10^{-02}	3.14×10^{-02}	5.46×10^{-07}
19	0.60	1.75	14.66	5.02	1.62×10^{-02}	3.06×10^{-02}	1.21×10^{-05}
20	0.32	1.22	11.00	6.30	1.35×10^{-02}	8.87×10^{-02}	2.37×10^{-05}
21	0.60	1.82	10.99	6.71	1.36×10^{-02}	8.87×10^{-02}	9.07×10^{-06}
22	0.89	2.63	11.01	6.51	1.40×10^{-02}	8.87×10^{-02}	6.12×10^{-06}
23	0.60	2.04	11.00	6.67	1.45×10^{-02}	9.10×10^{-02}	1.4×10^{-05}
24	0.60	2.49	19.57	6.32	1.27×10^{-02}	3.75×10^{-02}	2.99×10^{-06}
25	1.32	3.89	20.19	6.22	1.28×10^{-02}	3.44×10^{-02}	2.99×10^{-06}
26	0.60	2.39	19.53	6.36	1.63×10^{-02}	3.21×10^{-02}	7.38×10^{-06}
27	0.60	2.51	19.90	6.24	2.28×10^{-02}	3.36×10^{-02}	1.15×10^{-06}
28	0.32	0.994	19.90	6.33	2.13×10^{-02}	3.85×10^{-02}	1.29×10^{-05}