On-line estimation of the dissolved zinc concentration during ZnS precipitation in a CSTR

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Abstract In this paper a method is presented to estimate the reaction term of zinc sulphide precipitation and the zinc concentration in a CSTR, using the read-out signal of a sulphide selective electrode. The reaction between zinc and sulphide is described by a non-linear model and therefore classical observer theory cannot be applied directly, as this theory was initially developed for linear systems. However, by linear reparametrization of this non-linear system, the linear observer theory can be applied in an effective way. This is illustrated by a zinc sulphide example using real data.

Keywords Metal removal; Observers; State estimation; Sulphide precipitation; Zinc

INTRODUCTION

Numerous treatment technologies are available for the removal of heavy metals from natural waters and wastewaters, but most of them produce concentrated sludges that cannot be used in agriculture and need to be stored in controlled hazardous waste disposal sites. There is a need for new technologies that allow the recovery and reuse of the metals (Tabak *et al*., 2003). Consequently, treatment processes should also focus on metal recovery as the metal resources are depleting. The new technologies should be able to remove and recover heavy metals at acceptable costs and at a much higher efficiency than conventional technologies like hydroxide precipitation.

Recently a new promising technique has been developed in which heavy metals are separated by sulphide precipitation (Veeken *et al*., 2003a; Al-Tarazi *et al*., 2004; Al-Tarazi *et al*., 2005). The new sulphide process realizes an almost zero-emission at low costs. Furthermore the precipitation process can be controlled by pH and pS (Veeken *et al*., 2003b; König *et al*., 2006) to realize selective precipitation of individual heavy metals. This results in pure precipitates of metal sulphides that can be reused as a raw starting material in the metal industry.

For metal sulphide precipitation processes only limited amounts of process variables can be measured on-line. In fact, only the pH and the pS are measured online during the process (Veeken *et al*, 2003a). The metal concentration is measured by taking samples from the reactor at different time instants. This measurement procedure takes a lot of effort and time to observe the dissolved metal concentration. By creating an online estimator, it is possible to estimate the metal concentration during the process at any given time instant.

The process of the zinc sulphide reaction in a CSTR was modelled by König *et al*. (2006). Since the model is a non-linear model and current estimation theory for non-linear system has still some limitations, the *objective* of this research was to investigate a new method to estimate the zinc concentration in a CSTR online during the ZnS precipitation process.

METHODS

Observer theory

In this subsection some more theoretical information is given about the online estimation algorithm, in what follows indicated as the *observer* or *state estimator*. The first important aspect is that an observer needs an appropriate process model in order to obtain acceptable estimates. In this paper a so-called Luenberger observer (Luenberger, 1971) is developed to estimate the metal concentrations in the reactor. One of his theorems was: "An identity observer having *arbitrary* dynamics can be designed for a linear time-invariant system if and only if the system is completely observable." In other words, to apply such an observer, the system model has to be linear, time invariant and fully observable. In order to evaluate these properties, the process model is written in a so-called state space form, consisting of a state equation and an output equation:

$$\frac{dx}{dt} = Ax + Bu$$
$$y = Cx + Du$$

(1)

where x is the n-dimensional state vector of the system and u represents the input vector of the system. System matrices A, B, C and D are not allowed to contain any states, in order to maintain linearity. To determine whether the system model is observable, the so-called observability matrix W has to be constructed. This matrix depends on the system matrices A and C, *i.e.*

$$W = \begin{bmatrix} C & CA & CA^2 \end{bmatrix}^T$$

(2)

For the single output case, as in our application, the following holds: the model is observable if the determinant of the observability matrix W is not equal to zero. If the system is observable, the required estimates of the states can be obtained at every time instant and the estimation error tends to zero for time t tends to infinity. In practice, an observer can never determine the exact value of a state; it can only provide an estimate.
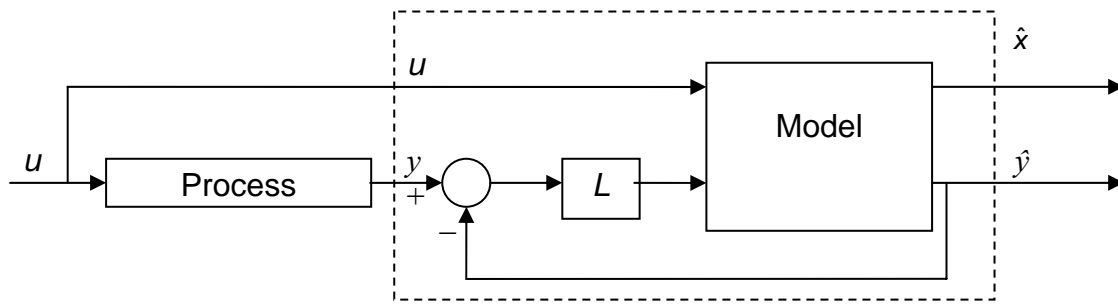
Figure 1 Observer system overview (part within dashed area is called the observer).

Figure 1 shows that the observer uses both the inputs and the outputs of the process. For a linear, time invariant (LTI) system, the estimates of states and outputs are given by the following equations:

$$\frac{d\hat{x}}{dt} = (A - LC)\hat{x} + Bu + Ly$$
$$\hat{y} = C\hat{x}$$

(3)

In order to let the estimates converge, the real parts of the eigenvalues of the $n \times n$ matrix $A-LC$, or of the poles of the observer system, have to be negative. Since A and C are given by the physical system, the observer gain (L) must be chosen such that the real parts of the eigenvalues of $A-LC$ are negative. Instead of the Luenberger observer, for example the Kalman filter that minimizes the estimation error within a least-squares context, could have been chosen for the on-line estimation of the zinc concentration in the reactor. The main advantage of our choice for the Luenberger observer is that in our case a symbolic expression for the observer gain will be found as a function of the system parameters.

Modelling

From figure 1 it is clear that for the observer design a reliable process model must be available. For the zinc sulphide reaction in a CSTR, König *et al.* (2006) developed a mathematical model. In this paper, a simplification of that model is used: the electron balance is denied and pH is considered as given from experimental data. Consequently, the following model results:

$$\frac{dTS}{dt} = \frac{Q_{buf}}{V_r} TS_{buf} - \frac{(Q_i + Q_{buf})}{V_r} TS - k[Zn^{2+}][S^{2-}] , \quad TS > 0$$

$$\frac{d[Zn^{2+}]}{dt} = \frac{Q_i}{V_r}[Zn^{2+}]_i - \frac{(Q_i + Q_{buf})}{V_r}[Zn^{2+}] - k[Zn^{2+}][S^{2-}] , \quad [Zn^{2+}] > 0 \qquad (4)$$

$$[S^{2-}] = \frac{TS}{\dfrac{[H^+]^2}{k_{a1}k_{a2}} + \dfrac{[H^+]}{k_{a2}} + 1}$$

where k_{a1} and k_{a2} are the reaction constants of the dissociation steps of H_2S. For ease of notation we introduce the state variables x_1, x_2 etc. (see Table 1).

Table 1. Symbols in state-space representation, their physical meaning and their steady state value

Symbol	Physical notation	Description	Steady state value, (pS = 15, pH = 5.5)[a]
x_1	TS	total sulphide conc. in reactor	$8.194*10^{-6}$ [mole/l]
x_2	$[Zn^{2+}]$	zinc concentration in reactor	$8.194*10^{-6}$ [mole/l]
y	$[S^{2-}]$	sulphide concentration	10^{-15} [mole/l]
u_1	Q_{buf}	flow from buffer tank	5.0 [l/h]
u_2	Q_i	influent flow, containing zinc	2.0 [l/h]
d_1	TS_{buf}	TS concentration in buffer tank	$30.0*10^{-3}$ [mole/l]
d_2	$[Zn]_i$	zinc concentration in influent	$75.0*10^{-3}$ [mole/l]
d_3	$[H^+]^2/(k_{a1}*k_{a2}) + [H^+]/k_{a2} + 1$	pH dependent factor	$8.194*10^{9}$ [-]
p_1	V_r	reactor volume	0.6 [l]
p_2	k	kinetic parameter for ZnS reaction	$3.050*10^{19}$ [l/(mole*h)]
	k_{a1}	equilibrium constant $H_2S \leftrightarrow HS^-$	10^{-7} [b]
	k_{a2}	equilibrium constant $HS^- \leftrightarrow S^{2-}$	$10^{-13.9}$ [b]

a König *et al* (2006) showed that at a pS of 15 ($[S^{2-}] = 10^{-15}$ mole/l) the lowest zinc concentration in a batch reactor is obtained.
b Data taken from Smith and Martell (1976)

Notice from (4) that constraints on the *TS* concentration and the zinc concentration have been added to avoid negative concentrations, which cannot occur in reality. The pH is an important

parameter: it determines the *TS* concentration in the reactor and the flow from the buffer tank, because $[S^{2-}]$ is controlled. Note that the model contains a non-linear reaction term. The amount of *TS* and zinc leaving the reactors define bilinear terms. Dynamics analysis of the linearized system show a two time-scale behaviour in this reactor: one driven by the reaction kinetics and one driven by the dilution (see Keesman (2002) for further details on time scales in (bio)reactors).

Observer design

Linearization methods. In order to apply observer theory, as presented before, the model has to be linear. In our application, two different approaches were applied: linearization around the steady state and linear reparametrization. Linearizing the non-linear system around a steady state leads to the so-called Extended Luenberger observer. Alternatively, in case of reparametrization the total reaction term ($k \, [Zn^{2+}] \, [S^{2-}]$) is replaced by a single term denoted by P. In both approaches, the new system becomes a linear system. Consequently, the linear observer theory, as presented in the first subsection, can be applied. Because of space limitations, in what follows, we will only consider the observer design based on the linearly reparameterized system.

System reparametrization. Basically the Extended Luenberger observer estimates the zinc concentration and the precipitation term around the steady state values without knowing the limitations of the linearization. Therefore in this subsection a method based on reparametrization is further worked out. This reparametrization results in the following system, with $x_3 = P$ (reaction term):

$$
\begin{aligned}
\frac{dx_1}{dt} &= \frac{u_1}{p_1} d_1 \;-\; \frac{(u_1 + u_2)}{p_1} x_1 \;-\; x_3, \quad x_1 > 0 \\[2mm]
\frac{dx_2}{dt} &= \frac{u_2}{p_1} d_2 \;-\; \frac{(u_1 + u_2)}{p_1} x_2 \;-\; x_3, \quad x_2 > 0 \\[2mm]
\frac{dx_3}{dt} &= 0 \\[2mm]
y &= \frac{x_1}{d_3}
\end{aligned}
\tag{5}
$$

The observability matrix of this *linear* system is given by:

$$
W = \begin{bmatrix}
\dfrac{1}{d_3} & 0 & 0 \\[4mm]
\dfrac{-u_1 - u_2}{d_3 * p_1} & 0 & -\dfrac{1}{d_3} \\[4mm]
\dfrac{(-u_1 - u_2)^2}{d_3 * p_1^{\,2}} & 0 & -\dfrac{(-u_1 - u_2)}{d_3 * p_1}
\end{bmatrix}
\tag{6}
$$

In this case, the determinant of the observability matrix is zero, so that this single-output system is not fully observable. Consequently, the eigenvalues of the observer, determining the rate of convergence, cannot be chosen arbitrarily. If we analyse the system equations, we directly see that x_2 is not affected by the measurements. Hence, it can be concluded that the initial dissolved zinc concentration (x_2) cannot be estimated uniquely from the data. In other

words, the second element of observer gain (l_2) is chosen to be equal to zero. This does, however, not imply that the dissolved zinc concentration cannot be estimated at all. Due to the stability of the process, the estimation error of the dissolved zinc concentration with $l_2=0$ tends to zero, anyway. Recall that in order to guarantee convergence of the estimates, all the eigenvalues of *A-LC* have to be negative. In this research, a second condition on the eigenvalues of *A-LC* is added. We require that in addition to the first condition that all the real parts of the eigenvalues have to be negative, all eigenvalues have to be real as well. Complex eigenvalues will cause oscillations in the estimates, which we would like to avoid.

Reparametrized observer system. Since the observer is used in a process, which is controlled by a PI-controller for the sulphide concentration and by a pH controller for the pH, the buffer flow Q_b and the pH vary in time. Therefore the observer system becomes *time-varying*. For this reparametrized system, the observer equations, with $l_2 = 0$, are given by:

$$\frac{d\hat{x}_1}{dt} = \frac{u_1}{p_1}d_1 - \frac{(u_1+u_2)}{p_1}\hat{x}_1 - \hat{x}_3 - \frac{l_1}{d_3}\hat{x}_1 + l_1 y$$

$$\frac{d\hat{x}_2}{dt} = \frac{u_2}{p_1}d_2 - \frac{(u_1+u_2)}{p_1}\hat{x}_2 - \hat{x}_3 \tag{7}$$

$$\frac{d\hat{x}_3}{dt} = -\frac{l_3}{d_3}\hat{x}_1 + l_3 y$$

The symbolic expressions of the eigenvalues belonging to this system are:

$$\lambda_1 = -\frac{(u_1+u_2)}{p_1}$$

$$\lambda_{2,3} = -\frac{(u_1+u_2)}{2p_1} - \frac{l_1}{2d_3} \pm \sqrt{\left(\frac{u_1+u_2}{2p_1} + \frac{l_1}{2d_3}\right)^2 + \frac{l_3}{d_3}} \tag{8}$$

The first eigenvalue, which is always negative, is the dilution rate. To meet our demands which respect to convergence and non-oscillating behaviour of the estimates, we require that:

$$-\frac{(u_1+u_2)}{2p_1} - \frac{l_1}{2d_3} \pm \sqrt{\left(\frac{u_1+u_2}{2p_1} + \frac{l_1}{2d_3}\right)^2 + \frac{l_3}{d_3}} \leq 0 \tag{9}$$

and

$$\left(\frac{u_1+u_2}{2p_1} + \frac{l_1}{2d_3}\right)^2 + \frac{l_3}{d_3} \geq 0 \tag{10}$$

After some manipulations we obtain the following inequality conditions, which should hold at any time instant:

$$-\left(\frac{u_1+u_2}{2p_1} + \frac{l_1}{2d_3}\right)^2 \leq \frac{l_3}{d_3} \leq 0 \tag{11}$$

Choosing $l_3 < 0$ and using the equality condition for l_1, the following results

$$l_1 = -d_3 \frac{u_1 + u_2}{p_1} + 2d_3{}^2 \sqrt{-\frac{l_3}{d_3{}^3}}$$ (12)

An initial value for l_3 can be derived from the zinc balance and the fact that the dissolved zinc concentration is in the order of 10^{-6} mole/l. To achieve such a concentration, the total reaction term has to be close to the total amount of zinc in the influent divided by the volume. Since the observation of the zinc concentration is the objective of this research, the change of the total reaction term should be in the order of the zinc concentration (10^{-6} mole/l). Due to the fact that the output (sulphide) in the experiments is controlled at 10^{-15} mole/l, l_3 should be in the order of magnitude of -10^9. Given this first guess, l_3 has to be fine tuned to obtain the desired results. This fine-tuning has been done for a specific data set minimizing the Mean Square Error (MSE) of the difference between the estimated and the observed output.


RESULTS AND DISCUSSION

In this section an application is presented based on experimental data of previous research (König, 2002). In Table 2, the process conditions for this experiment are presented.

Table 2. Process conditions during the simulation

Symbol in state space representation	Physical symbol	value
y	$[S^{2-}]$	$\pm\ 10^{-15}$ [mole/l] (experimental data)
x_1	TS	10^{-5} [mole/l] (initial value)
x_2	$[Zn^{2+}]$	10^{-5} [mole/l] (initial value)
x_3	$k[Zn^{2+}][S^{2-}]$	0.3580 [mole/(l*h)] (initial value)
u_1	Q_b	$\pm\ 7.09$ [l/h] (experimental data)
u_2	Q_{in}	2.58 [l/h] (fixed data)
d_1	TS_b	$29.365*10^{-3}$ [mole/l] (fixed data)
d_2	$[Zn^{2+}]_i$	$83.346*10^{-3}$ [mole/l] (fixed data)
d_3	$[H^+]^2/(k_{a1}*k_{a2}) + [H^+]/k_{a2} + 1$	$\pm\ 3.18*10^9$ [-] (experimental data, pH $\pm\ 5.71$)
p_1	V	0.6 [l] (fixed data)
l_1	-	time varying values
l_2	-	0
l_3	-	$-3.168*10^{11}$

Figure 2 shows the results of this application. In the first graph the measured output of the system ($[S^{2-}]$) is presented, where the objective of the control was to maintain a concentration of 10^{-15} mole/l. The second graph shows the estimates of the zinc concentrations (solid dark line) and the estimates of the TS concentrations (dashed light line). Notice the minor change in behaviour of the process after 1.2 hours. Especially, some unsteady behaviour can be seen which affects all the estimates. To further investigate these effects a correlation analysis has been performed. The cross-correlation function between $[S^{2-}]$ and the estimates of TS shows a clear peak of 0.62 for a lag of 0. The other estimates show much smaller correlations. In other words, the measured sulphide concentration does mainly affect the estimates of TS and has a limited effect on the other estimates. The third graph shows the estimate of the total reaction term.
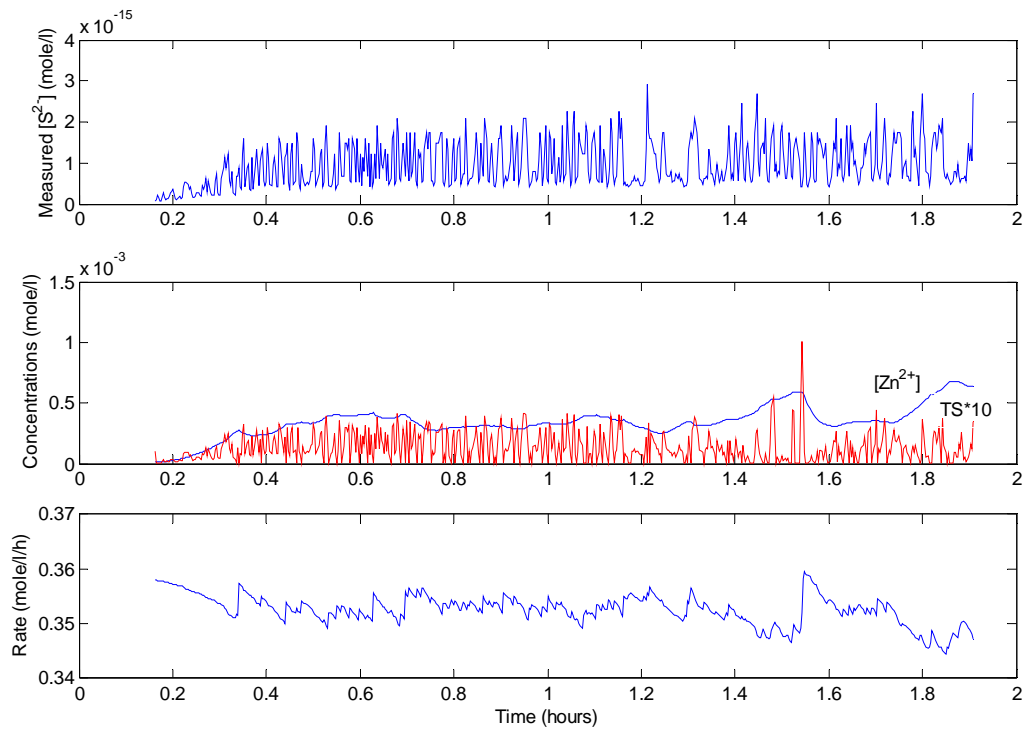
Figure 2 *Observer performance using experimental data from König (2002).*

During this experiment some samples were taken to measure the zinc concentration in the reactor. Figure 3 shows the effect of measured zinc concentrations, after 1, 1.25, 1.5 and 1.75 hours, on the estimates. Clearly after each measurement the estimated zinc concentration is directly affected.
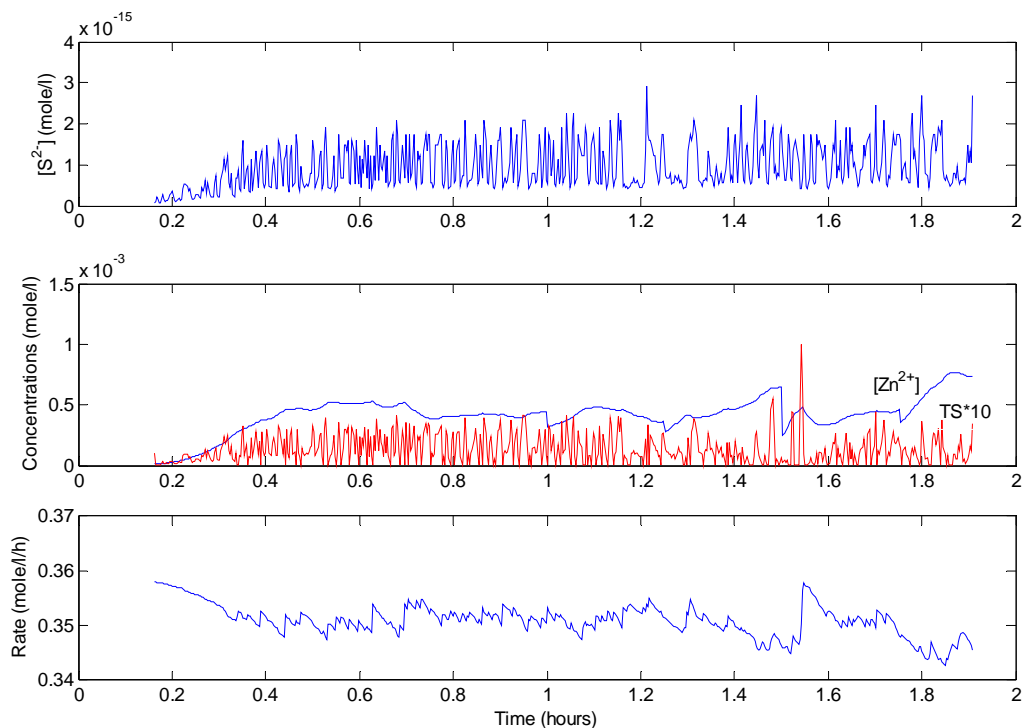
Figure 3 *Observer performance using experimental data of* $[S^{2-}]$ *and* $[Zn^{2+}]$.

The values of these zinc measurements were compared to the estimated zinc concentration from the observer, which are shown in Table 3.

Table 3. Comparison between the measured and estimated zinc concentration

time instant [h]	measured $[Zn^{2+}]$ [g/l]	estimated $[Zn^{2+}]$ [mole/l]	estimated $[Zn^{2+}]$ [g/l]	estimated $[Zn^{2+}]$ – measured$[Zn^{2+}]$ [g/l]
1.00	0.021	$4.490*10^{-4}$	0.029	0.008
1.25	0.018	$3.639*10^{-4}$	0.024	0.006
1.50	0.016	$6.518*10^{-4}$	0.043	0.027
1.75	0.023	$4.646*10^{-4}$	0.030	0.007

The last column of Table 3 shows that in general the estimated value is close to the measured value. Only at one and half hour, there is a large difference between the measured and observed value. This larger difference is caused by a low estimate of the total reaction term at that time instant.

Given the noise in the $[S^{2-}]$ measurements and its effect on the estimates, as an alternative to the observer of (7), an Extended Luenberger observer with or without repetitive linearization did not directly give appropriate results: a very careful tuning is needed and the calculations became slow. Thus our choice for an observer based on linear reparametrization.

CONCLUSIONS

After reparametrization of the non-linear system (4) and using the stability properties of this system, we were capable to properly estimate the reaction term of zinc sulphide and the zinc concentration in a CSTR based on pH and pS measurements only. Further research will focus on different process conditions with even lower concentrations and other divalent metal species.

REFERENCES

Al-Tarazi M., Heesink A.B.M., Azzam M.O.J., Yahya S.A. and Versteeg G.F. (2004). Crystallization kinetics of ZnS precipitation; an experimental study using the mixed-suspension-mixed-product-removal (MSMPR) method. Crystal Research and Technology. **39** (8), 675 – 685

Al-Tarazi M., Heesink A.B.M. and Versteeg G.F. (2005). Effects of reactor type and mass transfer on the morphology of CuS and ZnS crystals. Crystal Research Technology. **40** (8), 735 – 740

Keesman K.J. (2002). State and parameter estimation in biotechnical batch reactors. Control Engineering Practice **10** (2), 219 – 225

König J. (2002). Zinc precipitation with biogenic sulphide in a two-stage process. MSc thesis, Wageningen University: The Netherlands.

König J., Keesman K.J., Veeken A. and Lens P.N.L. (2006). Dynamic modelling and process control of ZnS precipitation. Separation Science Technology **41**(6), 1025-1042

Luenberger D.G. (1971). An introduction to observers. IEEE Transactions on Automatic Control **16** (6), 596-602

Smith R.M., Martell A.M.(1976) In: Critical stability constants, inorganic ligands, vol 4, New Year: Plenum Press

Tabak H.H., Scharp R., Burckle J., Kawahara F.K. and Govind R. (2003). Advances in biotreatment of acid mine drainage and biorecovery of metals: 1. Metal precipitation for recovery and recycle. Biodegradation, **14** (6): 423-436.

Veeken, A.H.M., Akoto, L., Hulshof Pol, L.W. and Weijma, J. (2003a). Control of the sulfide (S^{2-}) concentration for optimal zinc removal by sulfide precipitation in a continuously stirred tank reactor. Water Research. **37** (14): 3709-3717

Veeken, A.H.M., Vries, S. de; Mark, A van der; Rulkens, W.H. (2003b). Selective precipitation of heavy metals as controlled by a sulfide-selective electrode. Separation Science and Technology. **38** (1): 1-19