



Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor

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ABSTRACT

Copper was continuously and selectively precipitated with Na₂S to concentrations below 0.3 ppb from water containing around 600 ppm of both Cu and Zn in a Continuously Stirred Tank Reactor. The pH was controlled at 3 and the pS at 25 ($pS = -\log(S^{2-})$) by means of an Ag₂S sulfide selective electrode. Copper's recovery and purity were about 100%, whereas the total soluble sulfide concentration was below 0.02 ppm. X-ray diffraction (XRD) analysis showed that copper precipitated as hexagonal CuS (covellite). The mode of the particle size distribution (PSD) of the CuS precipitates was around 36 μm. The PSD increased by high pS values and by the presence of Zn. Depending on the turbulence, the CuS precipitates can grow up to 200 μm or fragment in particles smaller than 3 μm in a few seconds. Zn precipitation with Na₂S at pH 3 and 4, in batch, always lead to Zn concentrations above 1 ppm. Zn precipitated as cubic ZnS (sphaerelite).

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1. Introduction

The sources of metal wastes are diverse in nature and in geographical distribution. The metal-related industry, like metal finishing and electroplating, generate large quantities of metal polluted wastewaters [1,2], while acid mine drainage (AMD) is one of the most widespread forms of pollution in the world [3,4]. Depending on the process, such wastestreams vary greatly in composition and volume. Discharges of these heavy metal contaminated wastewaters into the environment can lead to devastating effects on aquatic and terrestrial ecosystems. These may differ from acute toxic to chronic effects, depending on how the contaminants affect organisms and the concentrations involved [5]. Metals like Hg and Cd exhibit toxicity at extremely low concentrations, while others like Cu or Zn are micronutrients as well, becoming thus toxic at higher orders of magnitude [6–8].

Due to its relative simplicity and low costs, heavy metal precipitation with hydroxide has been widely used in industry [9]. However, it presents some serious limitations since it results in the production of a voluminous mixture of unstable metal hydroxides

leading to a greater disposal expense [10] and high investments necessary for dewatering the produced sludge [11]. A more sustainable option should be based on the recovery and reuse of heavy metals. The use of sulfide not only allows producing effluents with metal concentrations in the order of magnitude of ppm and ppb, but also gives the possibility of precipitation at low pH and selective precipitation for metal reuse [12]. However, if the amount of sulfide is not added stoichiometrically to the amount of metal(s), either excess of metals or excess sulfide will remain in solution [13]. Sulfidic metal precipitation became an applied technology often connected to biological sulfate reduction, since many wastewaters contain both metals and sulfate. Applications include full scale bioreactors where sulfate reduction is coupled to metal precipitation [9,14] and *in situ* treatment of contaminated soil [15].

Sulfide gives the possibility of selective precipitation due to the different solubility products of the different metal sulfides (Table 1). Having the solubility product defined as $K_{SP} = (Me^{2+})(S^{2-})$, it means that different sulfide concentrations (S^{2-} potentials) are required to precipitate different metals. Therefore, the addition of sulfide to selectively precipitate heavy metals can be controlled using an ion selective electrode for sulfide (S^{2-}), a so called pS electrode ($pS = -\log(S^{2-})$). Veeken and Rulkens [18] showed that at pH 6 different metals (Cd, Cu, Ni, Pb and Zn) had different pS curves when titrated and precipitated with sulfide. This paper presents a study on selective precipitation between copper and zinc controlled by a pS electrode in combination with a pH electrode in a completely

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Table 1

Solubility products from metal sulfides and hydroxides^a. The metal sulfide reactions are defined as $\text{MeS}(s) \leftrightarrow \text{Me}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$ or as $\text{Me}_2\text{S}(s) \leftrightarrow 2\text{Me}^+(\text{aq}) + \text{S}^{2-}(\text{aq})$.

Metal ion	Log K_{SP} (metal sulfide)	Log K_{SP} (metal hydroxide)
Hg(II)	–52.4	–25.5 ^b
Ag(I)	–49.7	–7.71
Cu(I)	–48.0, –48.5 ^c	–
Cu(II)	–35.1	–20.4, –19.7 ^b
Cd(II)	–27.7, –25.8 ^c	–14.4
Pb(II)	–27.0, –27.5 ^c	–15.3
Zn(II)	–23.8	–16.7, –16.9 ^b
Ni(II)	–20.7	–17.2, –13.8 ^b
Fe(II)	–17.3	–15.2

^a Data from Peters et al. [11], except.

^b Brown et al. [16] and.

^c Smith and Martell [17].

stirred tank reactor (CSTR) at 20 °C. The effect of pS and pH on the selective precipitation was investigated. The solid phase was characterized by particle size distribution (PSD) and X-ray diffraction (XRD).

2. Material and methods

2.1. Experimental set-up

Experiments were performed in a 1.5 L glass vessel (CSTR) with four baffles. The CSTR was mixed at 500 rpm using a magnetic stirrer and the temperature controlled at 20 °C by means of a water bath (Haake F3, Thermo Fisher Scientific, Karlsruhe, Germany). A pH controller (Lyquisys M, Endress + Hauser Holding AG, Switzerland) using a proportional control strategy, dosing 1 M HNO_3/NaOH (Merck, Darmstadt, Germany), in combination with a sulfide resistant pH electrode (Prosense, Oosterhout, The Netherlands), was used for pH control/reading. The pS was measured by a solid state Ag_2S ion selective electrode (Prosense, Oosterhout, The Netherlands). Two autosamplers (Metrohm 665 Dosimat, Herisau, Switzerland) were used, one for pS electrode calibration (containing 1 M HNO_3) and another for metal titration (containing 10 mM of Na_2S).

In the continuous experiments, the metal solution was pumped to the CSTR by a Watson Marlow 101U/R pump (Falmouth, UK), while a Masterflex Console Drive (Cole Palmer, IL, USA) was used to pump sulfide. Copper and zinc were always supplied as metal nitrates and the sulfide as sodium sulfide. All chemicals were of analytical grade (Merck, Darmstadt, Germany).

In all cases, the devices were connected to a DOS-based computer unit, equipped with the Control EG software, for data logging. Data were logged every 5 s. The same workstation was used for pS control proposes (see Section 2.4).

2.2. pS electrode calibration (ion selective electrode for S^{2-})

The calibration of the pS electrode followed a similar procedure as described by Veecken and Rulkens [18]. Approximately 10 mM (320 ppm) of Na_2S were titrated with 1 M of HNO_3 . The dissociation constants of sulfide ($\text{H}_2\text{S} \xrightleftharpoons{K_{a1}} \text{HS}^- + \text{H}^+$ and $\text{HS}^- \xrightleftharpoons{K_{a2}} \text{S}^{2-} + \text{H}^+$) are defined as

$$K_{a1} = \frac{(\text{H}^+)(\text{HS}^-)}{(\text{H}_2\text{S})} \quad (1)$$

$$K_{a2} = \frac{(\text{H}^+)(\text{S}^{2-})}{(\text{HS}^-)} \quad (2)$$

And the total sulfide concentration defined as:

$$\text{Sulfide}_{\text{TOTAL}} = [\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}] \quad (3)$$

As the ionic strength during a calibration is around 0.025 M, the activity factor for S^{2-} is around 0.6 as given by the Davies equation [7], which at pS 15 leads to an error on the pS of 1.4%. Considering that the ionic strength does not significantly change during the calibration, the following relationship can be deduced from Eqs. (1), (2) and (3):

$$(\text{S}^{2-}) = \frac{\text{Sulfide}_{\text{TOTAL}}}{1 + \frac{(\text{H}^+)}{K_{a2}} + \frac{(\text{H}^+)^2}{K_{a2}K_{a1}}} \quad (4)$$

where K_{a1} and K_{a2} are $10^{-7.0}$ and $10^{-13.9}$, respectively [7,17], $\text{Sulfide}_{\text{TOTAL}}$ is measured and (H^+) is given by the pH electrode. It is then possible to correlate the potential given by the pS electrode, E (mV), with the sulfide activity (S^{2-}) by the Nernst equation:

$$E = E^0 - \frac{RT}{ZF} \ln(10) \log(\text{S}^{2-}) = E^0 + \frac{RT}{ZF} \ln(10) \text{pS} \quad (5)$$

2.3. Experimental design

Two types of experiments were performed: titrations and continuous reactor experiments. Experiments were carried out either with only one metal (Cu or Zn), or with a mixture of both metals. Metals were supplied as metal nitrate. pH was controlled in all cases.

2.3.1. Titrations

Approximately 2 mM (around 130 ppm) of each metal were titrated with 0.1 M (3.2 g/L) of Na_2S [18]. All the solutions were prepared under anaerobic conditions and the reactor liquid (1.5 L) flushed for 1 h with N_2 at 25 mL/s, thus giving a dissolved oxygen concentration of 0.038 (± 0.006) ppm measured by a CellOx 325 sensor (WTW, Weilheim, Germany). The sulfide solution was dosed through an auto-doser and the pressure in the gas phase was controlled by a high precision Pressure Regulator 86606 (Brooks Instruments B.V., Veenendaal, The Netherlands) connected to a N_2 line and to a pressure transmitter PTX 1400 (Drucks, Leicester, UK) to compensate the pressure drop due to sampling.

2.3.2. Continuous reactor experiments

The used reactor volume during the continuous experiments was 1 L. The influent flow (Q_{in}) containing Cu or Cu and Zn was pumped from a 25 L container at a constant flow. Sulfide (Q_{sulf}) was pumped from a 25 L vessel by a Masterflex Console Drive connected to the control device. Influent concentrations (metal and sulfide) were around 600 ppm and the metal flow was set at 2 L/h. In order to minimize the loss of sulfide by oxidation, the water used for the preparation of the influent solutions was flushed with N_2 and a small overpressure of 20 mbar was applied in the headspace of the reactor.

2.4. Control strategy

Three variables were controlled during the continuous precipitation experiments: temperature, pH and pS. For the first two, commercially available devices were used, while for pS a proportional integral (PI) feedback control strategy was developed. In this feedback controller, the process variable pS is measured in the reactor and the manipulated variable Q_{sulf} (sulfide flow) is adjusted using the deviation ($\varepsilon(t)$) between the measured pS and a predefined pS set-point [19]. In general, the feedback controller parameters should be related to the process parameters. Analysing

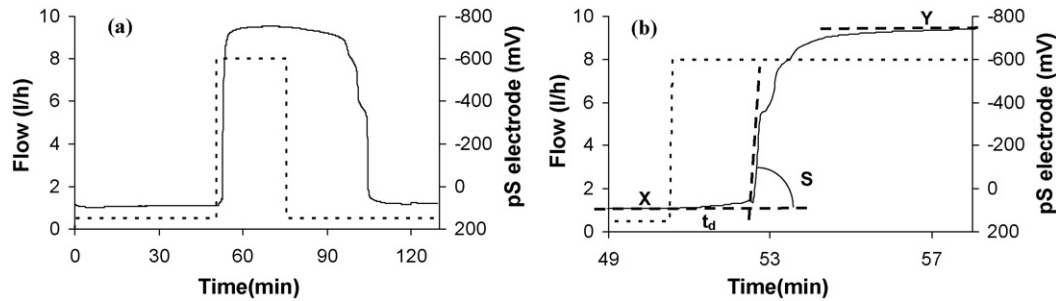


Fig. 1. (a) Step response curve, regarding the pS electrode response (—), for the determination of the PI control parameters. Sulfide flow (---) was increased from 0.5 L/h to 8 L/h. Both copper and sulfide influent solutions were 600 ppm. (b) X represents the mV given by the electrode before the increase, Y the mV at the top of the plateau, t_d the time delay between the flow increase and the electrode response and S the tangent to the step increase in mV/min.

the step response curve in Fig. 1(b), the following process parameters are determined:

$$\text{The process gain, } K = \frac{Y - X}{\Delta Q_{\text{Sulf}}}, \quad \text{with } Q_{\text{Sulf}} = \text{sulfide flow} \quad (6)$$

$$\text{The time constant, } \tau = \frac{Y - X}{S} \quad (7)$$

$$\text{The process delay, } t_d \quad (8)$$

The experiment consists on running the reactor at constant metal and sulfide flows and, at a sudden point, to increase the sulfide flow to another constant value. This flow step creates a response in the signal of the pS electrode. In the present case, the copper flow was 2 L/h and the sulfide flow step from 0.5 L/h to 8 L/h. Both (copper and sulfide) influent concentrations were 600 ppm. The controller gain (K_c) and the integral time constant (τ_i) from the PI controller were calculated using the Cohen-Coon tuning method [20]:

$$K_c = \frac{1}{K} \frac{\tau}{t_d} \left(0.9 + \frac{t_d}{12\tau} \right) \quad (9)$$

$$\tau_i = t_d \frac{30 + 3t_d/\tau}{9 + 20t_d/\tau} \quad (10)$$

The calculated parameters (K_c and τ_i) were inserted in the Control EG software to calculate $m(i)$:

$$m(i) = K_c \left(\varepsilon_i + \frac{T}{\tau_i} \sum \varepsilon_k \right) \quad (11)$$

where $m(i)$ is the change in sulfide flow and i the time instant.

2.5. Analytical methods and sampling

In the calibration, samples for total sulfide analysis were taken every half pH unit. For both titrations and continuous experiments, samples were taken and filtered with a 0.45 μm pore size filter (Schleicher & Schuell, Germany) for total soluble sulfide and soluble metal determination, as everything that goes through the filter is considered soluble. Also in both cases, samples for XRD analysis were collected, while for particle size distribution determination, samples were taken only in the continuous experiments. For the titrations only, samples were collected and filtered with a 0.45 μm pore size filter to quantify sulfide oxidation to sulfate and total sulfur determination.

Total sulfide was determined by the methylene blue method (Hach-Lange, Düsseldorf, Germany). Sulfate was determined by ion chromatography (IC) (Dionex Corporation, USA) as described by Lenz et al. [21]. After acidification with HNO_3 to 0.14 M, zinc, copper and total sulfur were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Varian Inc., USA) at the wave lengths of 213.857 nm, 324.754 nm and 181.972 nm, respectively.

A Coulter Laser LS 230 (Beckman Coulter, USA) was used for PSD measurements, applying the Fraunhofer refraction index in a range of 0.04–2000 μm . X-ray diffraction spectroscopy was conducted with a PANalytical Expert Pro System (Almelo, The Netherlands) by using nickel-filtered $\text{CuK}\alpha$ radiation (tube operating at 40 kV and 40 mA). The data were collected using an automated divergence slit (5 mm irradiated length) and a 0.2 mm receiving slit.

3. Results

3.1. Titrations

3.1.1. Single-metal titrations

Single-metal titrations were performed in order to evaluate the precipitation of each metal at different pH and to evaluate the course of the pS during the precipitation process. Copper was titrated with sulfide at pH 2 and 3, while zinc was titrated at pH 3 and 4 (Fig. 2). Such low pH values were chosen for optimization purposes: rather than steering the selective precipitation only based on pS, it was sought to steer it based on pH as well.

Precipitation of copper was not influenced by the pH values investigated, while zinc precipitation was worse at pH 3 than at pH 4. Moreover, in the case of copper, sulfide was only detected in solution for very low free metal concentrations, whereas it was detected almost from the beginning of the zinc titrations. Also, the minimum metal concentrations achieved with copper were in the order of ppb, while for zinc they were in the order of ppm (Table 2). Fig. 2(d) also shows that after the stoichiometric addition of sulfide, the soluble zinc concentration starts increasing. The titration of Zn at pH 3 was stopped due to the high amount of soluble sulfide (>5 ppm) detected in solution.

At the initial phase of a single-metal titration (Fig. 2), i.e. before the equivalent point (EP), the pS is characteristic of each metal, which means that it is driven by the solubility product of each metal. After the EP, the pS is more related to the dissolved sulfide and moreover, kinetic factors inherent to the solid phase start to play a role. One can therefore, from the initial plateau of the pS curve of a single-metal titration, calculate the solubility product of the respective metal by:

$$K_{\text{SP}} = (\text{Me}^{2+})(\text{S}^{2-}) \quad (12)$$

where (Me^{2+}) and (S^{2-}) are the metal and sulfide activities in equilibrium, respectively. While (S^{2-}) is obtained directly from the pS electrode (Me^{2+}) is obtained from the product of the concentration measured by the ICP-OES and the activity coefficient calculated by the Davies approximation [7]. The calculated solubility products (Table 3) show a good accordance with the values reported in the literature (Table 1). The observed ratios between metal and sulfide were all close to 1:1.

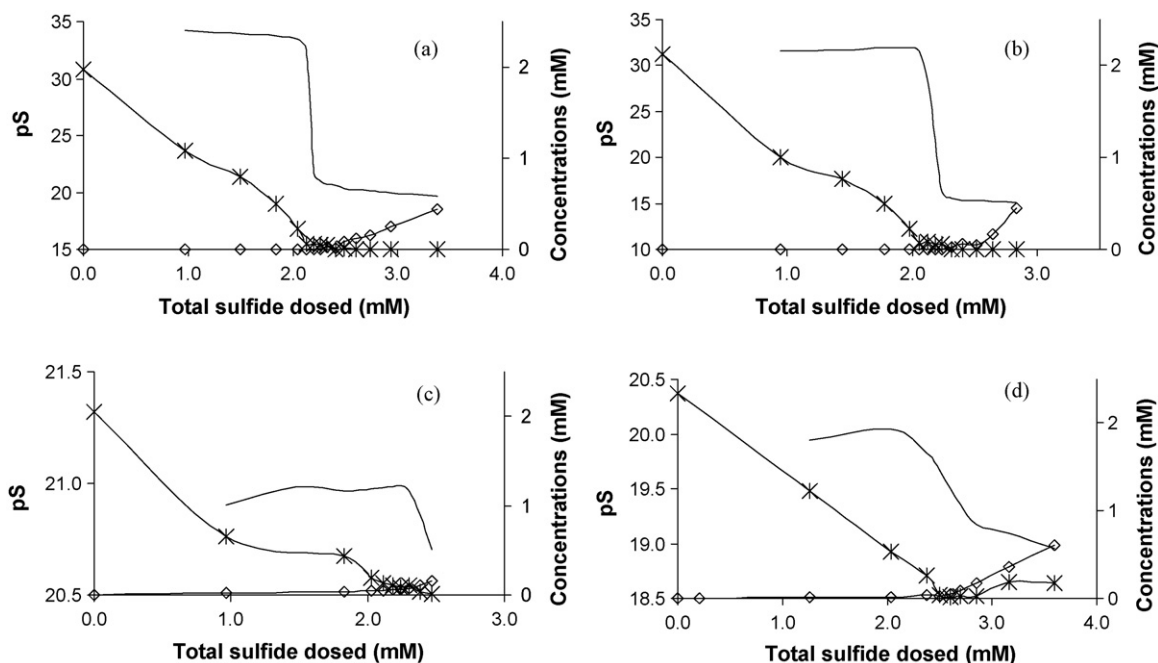


Fig. 2. Titrations of copper at (a) pH 2 and (b) pH 3; and Zinc at (c) pH 3 and (d) pH 4 with Na_2S . Evolution of pS (–), soluble metal (X) and total soluble sulfide (\diamond) within total sulfide dosage.

Table 2

Minimum metal concentration and correspondent sulfide concentration during the titrations.

Titrations	Minimum metal concentration (MMC) (ppm)			Soluble Sulfide _{TOTAL} at MMC (ppm)		
	Cu	Zn	Cu + Zn ^a	Cu	Zn	Cu + Zn ^a
pH 2	BDL ^b	–	–	3.86 ± 1.20	–	–
pH 3	BDL ^b	1.13 ± 0.03	0.002 ± 0.001	1.84 ± 0.37	5.08 ± 0.32	BDL ^c
pH 4	–	1.07 ± 0.05	–	–	1.37 ± 0.06	–

(–) Not analysed.

^a The minimum refers to Cu when all Zn is still in solution.

^b BDL, below ICP detection limit (0.3 ppb).

^c BDL, below spectrophotometer detection limit (0.1 ppm).

3.1.2. Bi-metal titrations

Bi-metal titrations were performed with the aim of studying the potential for selective precipitation. When both metals were mixed at pH 3, sequential precipitation was observed (Fig. 3). Copper was the first metal to precipitate, while zinc only started to precipitate when the copper concentration was already very low (2 ppb) (Table 2). Like in the single-metal titrations (Fig. 2), copper precipitates at higher pS (low S^{2-} potential) values than zinc (Fig. 3). Also, the observed reaction ratios between metal and sulfide were close to 1:1 for both metals (Table 3).

3.1.3. Precipitates characterization (XRD)

XRD analysis of the precipitates from the titrations of Cu at pH 3 and Zn at pH 4 identified crystalline structures in both cases (Fig. 4).

Table 3

Solubility product calculated from titrations and ratios observed between reacted metal and reacted sulfide.

	Solubility products (Log K_{SP}) ^a		Ratio (Me:S) observed	
	Cu	Zn	Cu	Zn
pH 2	–37.05 ± 0.20	–	1:1.1	–
pH 3	–35.20 ± 0.39	–24.16 ± 0.98	1:1.1	1:1.1
pH 4	–	–22.96 ± 0.53	–	1:1.1

(–) Not analysed.

^a Activity coefficients calculated by the Davies approximation [7].

Well defined spectra were obtained from a little amount of precipitate (less than 0.5 ml of sample) indicating highly crystalline structures: copper precipitated as CuS (covellite) and zinc as ZnS (sphaerelite). The same was obtained for Cu at pH 2 and Zn at pH 3 (data not shown).

3.2. Continuous experiments

3.2.1. Control strategy

The step response (Fig. 1(b)) shows a dynamic behaviour with an initial steep increase between 62 mV and –337 mV. This shape

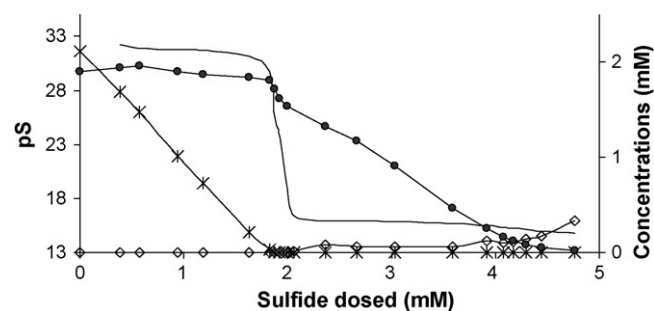


Fig. 3. Titration of a solution containing copper and zinc at pH 3 with Na_2S . Evolution of pS (–), soluble copper (X), soluble zinc (●) and total soluble sulfide (\diamond) within total sulfide dosage.

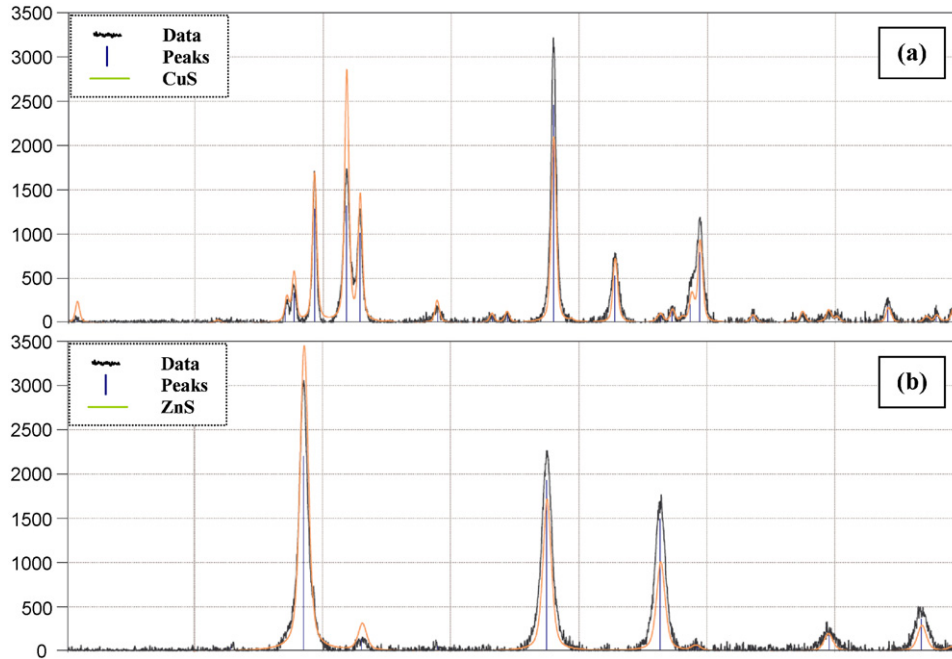


Fig. 4. Diffraction pattern and respective standard of the target compound identifying: (a) hexagonal CuS as covellite from the copper titration at pH 3 with standard in the background and (b) cubic ZnS as sphalerite from zinc titration at pH 4 with standard in the background.

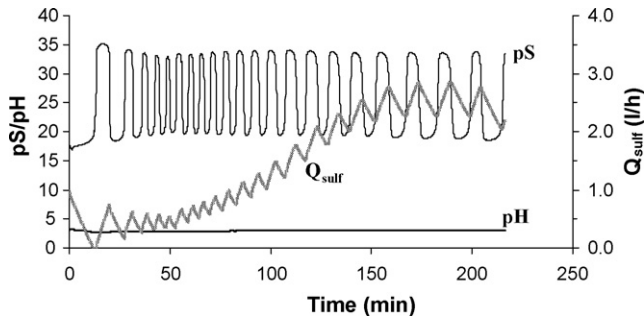


Fig. 5. Continuous precipitation of Cu controlled at pS 25 and pH 3. Q_{sulf} states for sulfide flow.

differs from the expected exponential curve with time delay of linear systems. In the initial and final phases of the step response (Fig. 1(a)), the electrode gave a positive reading when mostly copper was present in solution, whereas sulfide should always give a negative potential. Because the potential before and after the step dosing coincide, no decalibration of the electrode was observed

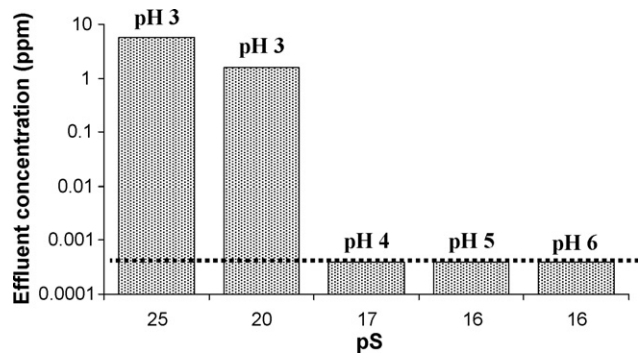


Fig. 6. Copper effluent concentration of several continuous experiments; variation with pH and pS. The dashed line represents the ICP detection limit (0.3 ppb).

during the experiment. From the step response curve (Fig. 1(b)), the PI control parameters were determined: $K_c = 0.07742 \text{ L}/(\text{min V})$ and $\tau_1 = 1.41 \text{ min}$.

3.2.2. Precipitation of Cu

Using the PI control parameters determined above, continuous experiments to precipitate copper were performed. The influent Cu concentration was around 600 ppm. Fig. 5 shows an experiment with large pS oscillations, which was typical for experiments at high pS values ($pS > 19$), thus at low sulfide concentrations. Nevertheless, the precipitation occurred with an average effluent concentration of 6 ppm at pS 25. By lowering the pS and/or increasing the pH, it was possible to further decrease the effluent Cu concentration to the ppb level (Fig. 6). An increase of the sulfide flow was observed during the experiments at low pH, but no build up was detected in the reactor. Sulfide was lost by volatilization due to the low pH, the overpressure applied and the fact that it was dosed close to the water surface. This can thus be avoided if the sulfide dosage is done at a bigger depth in the CSTR liquid.

3.2.3. Selective precipitation of Cu

Using the same PI control settings, experiments were performed with an influent containing both copper and zinc at concentrations around 600 ppm each. Fig. 7(a) and (b) shows the pS oscillating in the same way as in the case of copper alone. The recovery of copper was always over 99%, but only at pS 25 it was possible to recover it with a purity of nearly 100% (>99.9999%). At pS 20 there was already a considerable degree of co-precipitation, decreasing the purity to 61%. At pS 16 and pH 4 and 5, the zinc effluent was never higher than 22 ppm (Table 4).

At pS 22, the oscillations were smaller than at pS 25, disappearing completely at lower pS levels (Fig. 7).

For the same reason as explained for the precipitation of Cu, the flow of sulfide was found to increase with the time in the experiments at lower pH (Figs. 5 and 7), but no clear interference on the efficiency of the selective precipitation was noticed (Table 4).

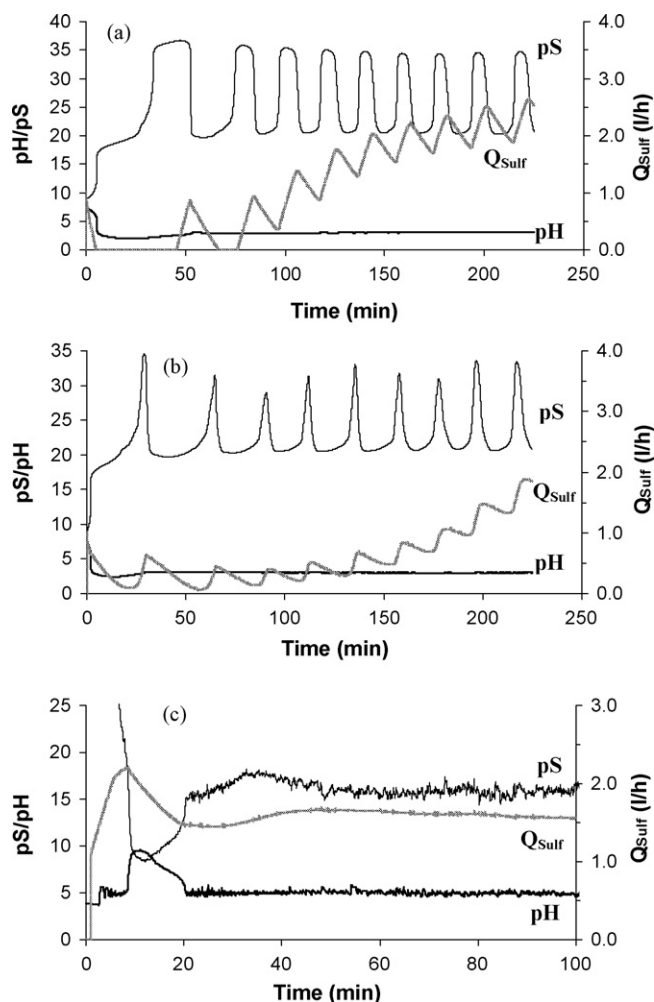


Fig. 7. Continuous selective precipitation of Cu from Zn controlled at (a) pS 25 and pH 3, (b) pS 22 and pH 3 and S 16 and pH 5. Q_{Sulf} states for sulfide flow.

3.2.4. Solid phase characterization

Fig. 8 shows that bigger particles were produced in experiments performed at higher pS values. Moreover, the presence of zinc enhanced the size of the particles compared to the case of copper alone (e.g. from around 22 μm to 36 μm at pS 25 and pH 3). The particles were found to be unstable: a sample from a pS 20 experiment with copper (Fig. 8(a)) was first allowed to settle prior to the PSD measurement and particles with PSD around 180 μm were formed (Fig. 9(a)). Then, the same sample was vigorously stirred for 5–10 s

Table 4

Results from the continuous selective precipitation between Cu and Zn, with final effluent concentrations, recovery and purity of the recovered copper.

	Effluent concentrations (ppm)		Copper in the effluent (%)	
	Cu	Zn	Recovery	Purity
pH 3				
pS 25	BDL	304 ± 18	>99.9999	101.6 ± 8.6
pS 22	BDL	388 ± 84	>99.9999	97.5 ± 9.8
pS 20 ^a	BDL	74.5	>99.9999	60.9
pH 4				
pH 16	BDL	16.9 ± 6.2	>99.9999	52.9 ± 0.5
pH 5				
pS 16 ^a	BDL	14.4	>99.9999	52.6

^a Only one sample analysed.

before measurement, which led to a decrease of the particle size below 3 μm (Fig. 9(b)).

The precipitates obtained in all the experiments at pH 3 were analysed by XRD. Like in the case of the titrations (Fig. 4(a)), also from the continuous experiments at pH 3 and pS 25, there was a clear identification of hexagonal CuS (data not shown). The same structure was identified in the case of Cu precipitation at pS 22 and when copper and zinc were mixed at pS 25 and 20 (data not shown).

4. Discussion

4.1. Titrations

Titrations indicate the possibility of selective precipitation of copper from zinc in waters containing both metals. Firstly, the low pH allows to precipitate copper at much lower concentrations than zinc (Table 2). Secondly, the pS required to precipitate copper (around 25) is higher than that to precipitate zinc (around 19). This lower sulfide potential (higher pS) has a direct relation with the lower solubility product of CuS compared to ZnS (Table 1) and shows the need of high pS values to remove only copper. This was also observed when both metals were mixed and selective precipitation occurred (Fig. 3).

König et al. [19] obtained concentrations below 0.1 ppm when titrating zinc with Na_2S at pH 6. Therefore, zinc titrations indicate that zinc is not efficiently removed at low pH (3 and 4) (Table 2). Moreover, sulfide is expected to be found in the effluent, which is a waste of resources as well as another source of pollution. At pH 4, the observed increase of soluble zinc at the end of the titration correlates well with the observations of Veeken et al. [13]. It shows that for ZnS precipitation the stoichiometric amount of sulfide should be added, since the excess dosage results in the solubilisation of zinc, possibly due to the formation of soluble zinc complexes [13,22].

4.2. Continuous experiments

4.2.1. Control strategy and pS electrode

The applied controller design methodology is for linear first-order systems with time delay. However, the system exhibits an unusual dynamic behaviour. The initial steep increase, between 62 mV and -337 mV (Fig. 1(b)), could be due to the interference of Cu with the electrode. An Ag_2S electrode is known to be selective not only to S^{2-} but to Ag^+ as well. As the response is a function of the cation and anion activities and the solubility product of the insoluble salt, the potential given by Ag^+ is positive and by S^{2-} negative [23]. Cu and Ag are both from the 11th group of the periodic table, with the *d* orbitals complete and one electron in the last *s* orbital, and both form highly insoluble salts with sulfide (Table 1). It is thus likely that Cu is responsible for the observed anomalous behaviour of the pS electrode. The presence of Cu(I) has been discussed in fresh waters [24] as well as in sulfidic solutions [25,26]. However, it is not known whether the interference is due to Cu^{2+} or Cu^+ ions. It should be noted that such interference was only observed for very low sulfide concentrations (pS > 19). On the other hand, it could be that the response of the electrode at such high pS does not follow the calibration line given by the Nernst equation, as it was only possible to calibrate the electrode until pS 20. Nevertheless, because the results of the solubility products (Table 3) are in accordance with the theory (Table 1), the deviations from the real pS should not be very considerable.

Selective precipitation of Cu from Zn was still achieved despite the steep variations in the high pS range very noticeable in some continuous experiments (Figs. 7 and 8). To change the electrode

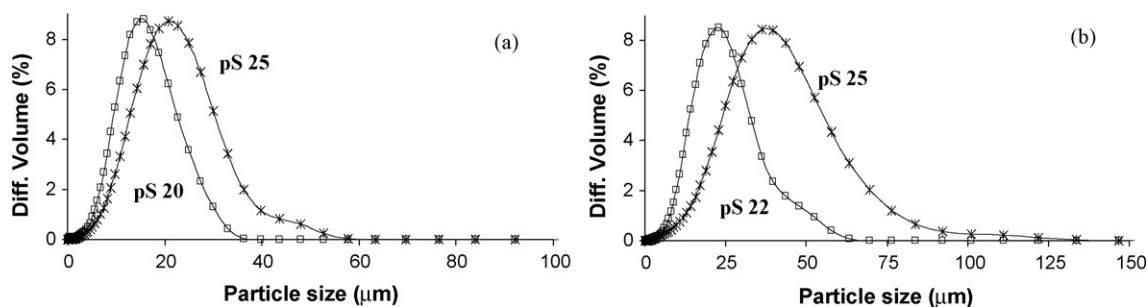


Fig. 8. Particle size distribution of copper sulfides produced at pH 3 in continuous experiment. (a) Single-metal experiments and (b) bimetal experiments (Cu and Zn) with Cu selective precipitation.

composition could be a way to solve the interference. The use of another more insoluble salt than Ag_2S could reduce the interference from the most common metals. Hg(II) , Sb(III) or Bi(III) could be candidates [27,28], but the sensitivity towards S^{2-} has to be investigated. Several electrodes based on the use of chalcogenides glasses have been used for metal determination in solution [27]. Chalcogenides glasses are amorphous vitreous solids obtained from the combination of certain chalcogenides (S, Se and Te) with some elements from the groups 13th, 14th and 15th of the periodic table (e.g. Al, Ge and As). Such solids are generally more stable than the corresponding crystalline materials and promising materials for ion selective electrodes [29]. As a S^{2-} selective electrode is based on the same principle, its sensitivity towards several metals would have to be tested to account for interferences. Miloshova et al. [30] illustrated the use of a chalcogenide sensor for S^{2-} , but did not describe it due to future patent applications.

Another more immediate solution could consist on performing a step response only in the mV range of the observed oscillations. However, due to the unusual dynamic behaviour observed, it might be difficult to select appropriate first-order or second-order models. The use of a sequence of linear systems described by a convolution model could be necessary [31]. In such case, the coefficients can be obtained directly from the factorization of the step response curve.

4.2.2. Precipitation of Cu

Copper was precipitated continuously in the CSTR at high pS (25), and concentrations below 1 ppb were reached at pS 17 and 16 (>99.999% recovery). Such a high efficiency corresponds to values below the groundwater clean-up standard (75 ppb) for residential landuse in The Netherlands [32]. Table 5 compares different processes for the removal of copper from waste and process water and clearly shows that sulfide precipitation is among the techniques with the highest efficiencies. It should be mentioned that for an accurate comparison between different techniques,

the same analytical methods and sampling procedures should be used. Nevertheless, sulfide precipitation can comply with very high Cu loading rates due to the fast kinetics (even at low pH), while others significantly loose efficiency at increasing influent concentration [34] or require high retention times to reach the ppb level [35]. Moreover, sulfide precipitation can be applied continuously without the need of stopping the process for regeneration [33] or harvesting [36] purposes.

In a two metal system, it was possible to selectively remove copper with virtually 100% purity (Table 4). This was only possible due to the very high pS (25) applied and because the solubility product of CuS is much lower than that of ZnS (Table 1). The presence of Zn allowed the precipitation of Cu at pS 25 to a lower level than in the case of copper alone. Moreover, not only the purity was nearly 100%, but the recovery as well, reaching the same level as the system with copper alone. This aspect might be due to the higher ionic strength that could play a role by decreasing the ion activities and thus the supersaturation (calculations not shown), which could decrease the formation of fines. It should however be mentioned that the increase of the ionic strength is due to the increase of ions that are not participating in the reaction (Zn^{2+} and NO_3^-), and that the effect of increasing the ionic strength by increasing Cu^{2+} and/or S^{2-} would result in the formation of more fines, as observed by van Hille et al. [41]. Good selectivity can also be reached with some ion exchangers [42], however, this type of processes require further steps to remove the metals from the concentrated waters eluted and their application to high loads is still questionable. Another interesting approach is the use of a redox electrode to selectively precipitate different metal sulfides at different redox potentials [43]. However, this presents a significant drawback when used with real wastewaters, as the fluctuations in concentrations and composition can change the required redox potential for an optimal selectivity.

In a system based on sulfidic precipitation with biogenic sulfide, Tabak et al. [10] were able to remove Cu from Zn with a purity of 82% at pH 2 by decreasing the temperature to 10°C . The effect of bio-

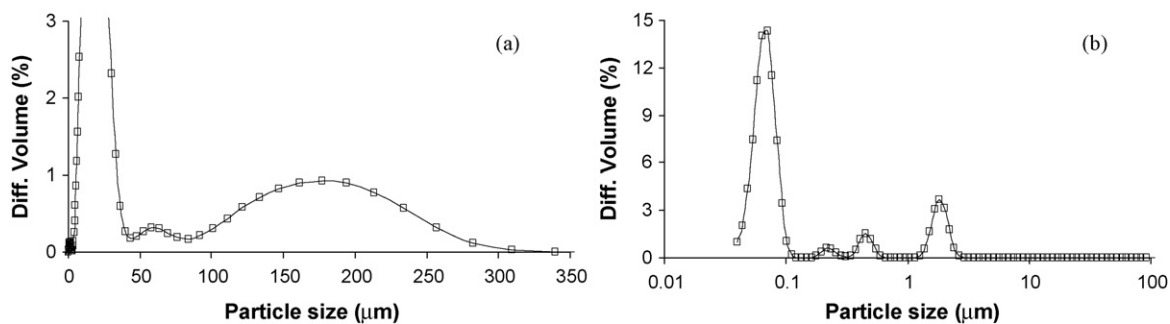


Fig. 9. Particle size distribution of copper sulfides produced at pH 3 and pS 20. (a) Formation of big size particles after allowing the sample to settle for a few minutes; (b) decomposition of the big particles into particles smaller than $3\ \mu\text{m}$ after 5–10 s of vigorous stirring. Note that the x-axis of (b) is in log scale.

Table 5
Comparison of several technologies to remove copper from wastewater at room temperature.

Method	Cu (ppm)		Removal (%)	pH	Cu load ^a (mg/Lh)	Author
	Initial ^b	Final				
Batch						
Ion exchange resin	100	–	99	4.2 (initial) 2.6 (final)	100 (1 h)	[33]
Electroflotation	50 500	–	99 71	5	50 (1 h) 500 (1 h)	[34]
Precipitation						
Pyridine-thiol ligand ^c	50	0.92 <0.0093	98.16 >99.98	4.5	50 (1 h) 12.5 (4 h)	[35]
Na ₂ S	127	<0.0003	>99.9999	2 and 3	Titration—not applied	Present study
Continuous						
Adsorption in sand column	100	–	91 87	10 3	10 (10 h) ^d	[36]
Adsorption in Mn oxide-coated activated carbon	2	<0.004	–	6	30 (4 min) ^e	[37]
Ion exchange resin	55–60	<0.05	–	3.3–3.5	900 (4 min) ^c	[38]
Ion exchange resin + electroextraction	40	<1.5	–	–	80 (30 min) ^f (current 2 A/m ²)	[39]
Precipitation						
Ca(OH) ₂ ^g	1.80	1.77 0.0051	–	4.4 9.1	–	[40]
Na ₂ S	–	0.01	–	6	953 (30 min)	[18]
Na ₂ S	600	<0.0003	>99.9999	3–6	1220 (20 min)	Present study

(–) Not given.

^a It is defined according to the operation time in batch systems and HRT in continuous systems (given between brackets). In the case of methods based on resins/sand columns, the volume of the resin/sand column is used; for the rest, the liquid phase reactor/bottle volume is considered, unless indicated otherwise. Calculated from author's data.

^b All the studies we performed with synthetic wastewater except Dobrevsky et al. [38] and Feng et al. [40], who used wastewater from electroplating plants and acid mine water from a South African gold mine, respectively.

^c Load of 15 L/(Lh).

^d Sand bed with 80 mm diameter and 1 m height. Flow of 0.1 m³/(m² h).

^e Flow of 5 mL/min and bed volume of 20 mL.

^f Flow of 0.09 L/h and volume of the cation exchange resin compartment of 0.045 dm³.

^g Other metals in solution. Al, Ca, Fe, Mg, Mn above 100 ppm and Cr, Ni, Si, Sr, Ti, Zn and Co above 10 ppm.

genic sulfide on Cu/Zn selective precipitation is not known, but pS control will be evaluated to optimize sulfide selective precipitation from more complex media.

4.2.3. Solid phase characterization

The PSD analysis showed that bigger particles were formed at lower supersaturation levels (higher pS), which is in accordance with previous studies [44–46]. Moreover, such particles are very sensitive to the hydraulic conditions applied, indicating that rather than crystal growth, enlargement due to agglomeration should be the ruling process on the formation of the ~30 μm particles. In the literature, several examples reporting the importance of the agglomeration phenomena in the case of very fast precipitations and supersaturated solutions are given [44,47–49]. As metal sulfides have very low solubility products and fast reaction kinetics, high levels of supersaturation cannot be avoided [50]. This means that primary nucleation predominates and is of much higher order than crystal growth. Consequently, the particle growth is ruled by the agglomeration phenomena [49].

Since all the metal that goes through the 0.45 μm pore size filter is considered soluble, the particle size has also implication regarding the sampling procedure. Precipitates smaller than 0.45 μm contribute to the increase of the soluble metal fraction. Veeken and Rulkens [18] reported Cu effluent concentrations from precipitation with sulfide of 0.01 ppm at pH 6. The difference to the present study (effluent <0.3 ppb) could be related with the formation of smaller particles that end up in the soluble fraction, due to the lower pS applied (pS 15), i.e. higher supersaturation. Another explanation could be that the slightly different reactor/stirrer con-

figuration created a more turbulent system and thus enhanced particle disruption.

XRD analysis showed that zinc precipitated as sphaerelite in the titrations (Fig. 4(b)), but no ZnS was identified in the continuous experiments at pS 25 and 20. Copper was found to precipitate as covellite, both in the titrations and in the continuous experiments and no Cu₂S was found. Despite the good spectra obtained, due to the small elevation observed in the background (not shown in the treated diffractogram of Fig. 4(a)) and the slight scattering shown by the measurements (Fig. 4), some of the precipitates might be amorphous. To identify and confirm this, more advanced X-ray techniques like XANES (X-ray absorption near-edge spectroscopy) should be used [51]. The XRD from the titrations matches well with the predicted ratios of 1:1 (Table 3), indicating that CuS and ZnS should be the only compounds resulting from the precipitation. The same type of crystal structures were identified by other authors in different systems. Labrenz et al. [52] observed sphaerelite in natural biofilms of sulfate reducing bacteria, and Jandová et al. [53] obtained covellite from the precipitation of copper from manganese deep ocean nodules with (NH₄)₂S. However, different results can be obtained as a function of the system applied and/or temperature. Rybicka et al. [54] obtained crystalline CuS and ZnS from the precipitation in clay columns at 80 °C, whereas the precipitates were amorphous at room temperature.

4.3. Applications

When real wastewater is used, conditions might change and a new pH/pS combination might be required. Moreover, real wastew-

aters contain several substances that might compete with sulfide or metals and affect the precipitation process in terms of kinetics, extension of precipitation or particle growth [7,45,55]. When biogenic sulfide is used, i.e. when biological sulfate reduction is combined with metal sulfide precipitation, organic compounds, micronutrients and washed sludge are present in the medium. Esposito et al. [46] showed that the precipitation efficiency of ZnS slightly decreased when biogenic sulfide was used, and that compounds like EDTA, acetate, phosphate and micronutrients had a negative influence on the precipitation.

When several metals are present in the wastewater, the importance of pS and pH control to avoid simultaneous precipitation increases. However, for metals with very similar values of solubility product and reaction kinetics like Ni and Co, the implemented pS and pH control strategy might not be sufficient if micromixing and supersaturated areas cannot be avoided [56]. If appropriate conditions cannot be achieved in a CSTR, other configurations should be investigated, e.g. membrane reactors [57]. In such type of reactor, the sulfide dosing is spread over a much larger surface area, which under the same loading conditions, reduces the local supersaturation compared to the single dosing point in the CSTR used in the present study.

5. Conclusions

- Copper can be continuously removed from solution in a CSTR at 20 °C by means of sulfide precipitation with pS control, from pH 3 to 6, below the groundwater clean-up standard (75 ppb) for residential landuse in The Netherlands.
- Selective precipitation of copper from zinc is possible in a CSTR at pS 25 and pH 3.
- Titration is a valuable tool to evaluate copper sulfide precipitation and selective precipitation between copper and zinc.
- Copper precipitates as CuS (covellite) at pH 2 and 3 and zinc and ZnS (sphalerite) at pH 3 and 4.

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