Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Veeken, A. H. M. , de Vries, S. , van der Mark, A. and Rulkens, W. H.(2003) 'Selective Precipitation of Heavy Metals as Controlled by a Sulfide-Selective Electrode', Separation Science and Technology, 38: 1, 1 — 19
To link to this Article: DOI: 10.1081/SS-120016695
URL: http://dx.doi.org/10.1081/SS-120016695

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 1, pp. 1–19, 2003

Selective Precipitation of Heavy Metals as Controlled by a Sulfide-Selective Electrode

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ABSTRACT

Sulfide precipitation is superior to hydroxide precipitation for removal of heavy metals from wastewaters as it results in lower effluent concentrations and less interference from chelating agents. However, sulfide precipitation is not widely applied in practice because the dosing of sulfide cannot adequately be controlled, and excess sulfide in the effluent is toxic and corrosive. A new process was developed where a sulfide-selective electrode (pS-electrode) controls the sulfide addition. Experiments were performed on lab-scale in batch and continuous systems for synthetic wastewater containing Cd, Cu, Ni, Pb, and Zn. The heavy metals were removed to ppb levels ($<0.05\,\mathrm{mg\,l^{-1}}$) at pH 6.0 by sulfide precipitation while maintaining the total sulfide concentration $<0.02\,\mathrm{mg\,l^{-1}}$. The response of the pS-electrode during precipitation was unique for each heavy metal and was directly related to the solubility

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DOI: 10.1081/SS-120016695
0149-6395 (Print); 1520-5754 (Online)
www.dekker.com

product of the corresponding metal sulfide. By control of the pS at different levels, the metals in mixtures of Cu—Zn and Pb—Zn were selectively precipitated from solution. This resulted in the production of pure metal sulfide sludges that possibly can be reused. Formation of colloidal sulfide precipitates was prevented by applying a membrane to keep the solids in the reactor to offer high surface area for growth and by controlling pS at optimal levels. The precipitate was separated from the water phase by a microfiltration membrane at a flux of $1000\,\mathrm{l\,m^{-2}\,h^{-1}\,bar^{-1}}$ at a total solids content of $30\,\mathrm{g\,l^{-1}}$. Control of sulfide precipitation by the pS-electrode results in very low metal effluent concentrations, and the selectivity of the precipitation results in pure metal sulfide sludges, which can be reused.

Key Words: Membrane; Wastewater; Selectivity; Sulfide precipitation; Removal; Heavy metals.

INTRODUCTION

Hydroxide precipitation is the most frequently applied treatment technology for removing heavy metals from industrial wastewaters and polluted groundwaters.[1,2] Disadvantages of hydroxide precipitation include the relatively high residual effluent metal concentrations ($0.5–2\,\mathrm{mg\,l^{-1}}$), the interference of chelating compounds, and unsuitability of metal sludge reuse in case more metals are present.[1] A well-known alternative is sulfide precipitation, which can achieve very low effluent concentrations ($<0.01\,\mathrm{mg\,l^{-1}}$) with less interference from chelating compounds.[1] Sulfide precipitation is not widely applied because the dosing of sulfide cannot adequately be controlled, and excess sulfide is toxic and corrosive. Moreover, precipitation by sulfide results in colloidal metal sulfide precipitates that are poorly separable from the water phase by sedimentation or filtration.[1,3,4]

Determination of the sulfide ion (S^{2-}) by sulfide-selective electrodes (pS-electrode) is widely used for analytical purposes[5,6] and could possibly be used for process automation for the control of sulfide addition. The production of colloidal precipitates could be prevented when a high specific surface area for crystal growth is offered and nucleation is minimized.[4] A possible reactor configuration is a membrane reactor in which the solids are retained in combination with control by a pS-electrode to keep the supersaturation level low. In theory, it should be possible to precipitate heavy metals selectively if the response of the pS-electrode is directly related to the solubility product of the metal sulfides.

This study explores the application of a solid state AgS electrode to monitor S^{2-} in heavy metal-containing wastewaters for control of sulfide addition in such a way that heavy metals are almost completely precipitated with negligible amounts of sulfide left in the effluent. Experiments with monometal solutions were performed in batch and continuous reactors for the divalent heavy metals Cd, Cu, Ni, Pb, and Zn. Selective precipitation of heavy metals was studied in a batch reactor for metal mixtures of Cu–Zn and Pb–Zn and in a continuous-flow, stirred tank reactor (CSTR) for Cu–Zn. The performance of a membrane reactor for sulfide precipitation was studied for Zn in a 40-L membrane reactor where the metal sulfide particles were separated by both ultra- and microfiltration units. The separation efficiency with respect to Zn and the fluxes of the two membranes were measured for increasing levels of ZnS precipitate in the membrane reactor.

EXPERIMENTAL SECTION

Sulfide Ion-Selective Electrode (pS-Electrode)

The tip of the solid-state pS-electrode is a layer of Ag_2S plated on silver (MicroScale Measurement, The Netherlands). The potential between the pS-electrode and the reference electrode is related to the activity of fully dissociated sulfide (S^{2-}). The double junction Ag/AgCl reference electrode (Schott Geräte, Germany) was applied with an inner solution of saturated 3 M KCl with AgCl and an outer solution of 3 M KCl, to prevent precipitation of AgS in the inner solution. The sulfide activity is related to the total sulfide concentration, S_{TOT} ($S_{TOT} = [H_2S] + [HS^-] + [S^{2-}]$) and pH according to:

$$(S^{2-}) = \frac{S_{TOT}}{1 + \frac{(H^+)}{K_{A2}} + \frac{(H^+)^2}{K_{A1} \cdot K_{A2}}} \quad (1)$$

where (S^{2-}) is the sulfide activity, (H^+) the proton activity as measured by a glass electrode, K_{A1} the first dissociation constant of hydrogen sulfide ($H_2S \leftrightarrow H^+ + HS^-$), and K_{A2} the second dissociation constant of hydrogen sulfide ($HS^- \leftrightarrow H^+ + S^{2-}$). The pS-electrode was calibrated with a solution of 10 mM Na_2S that was titrated with 0.1 M HNO_3 from high to low pH values. Solution pH was measured by a combined glass electrode (Schott Geräte, Germany) which was calibrated with pH buffers 4.0 and 7.0 (Merck, Germany). During calibration, the entrance of oxygen and stripping of undissociated sulfide (H_2S) were prevented to keep S_{TOT} constant. The electrode response (in mV) as a function of pH is shown in Fig. 1A. The electromotive force (E in mV) of the electrode is described by the Nernst

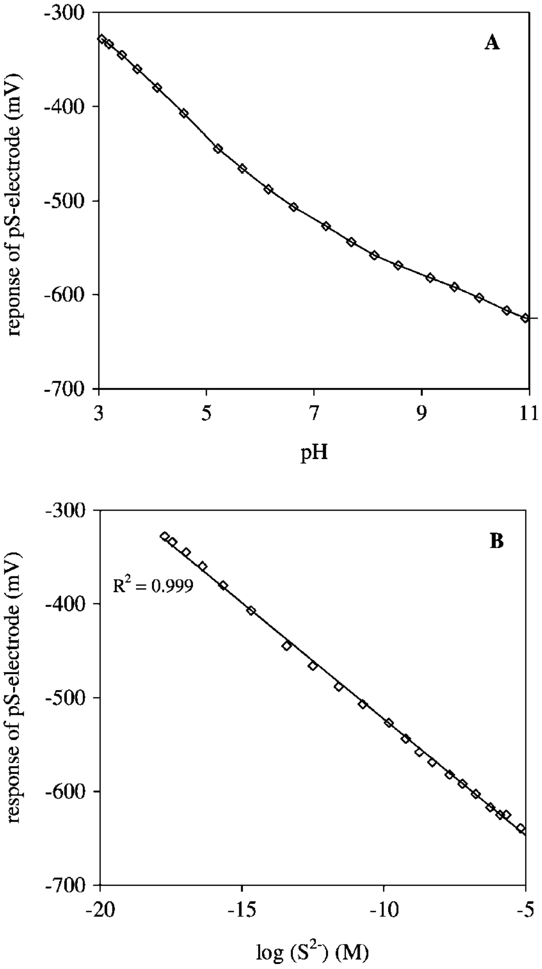

Figure 1. Response of pS electrode as function of pH (A) and as function of log(S^{2-}) (B).

equation[7] and should be a linear function of the logarithm of the activity of sulfide (S^{2-}):

$$E = a + b \cdot \log(S^{2-}) \qquad (2)$$

where a is the intercept and b the slope of the electrode response. Applying Eq. (1), the electrode response versus (S^{2-}) can be plotted for the data of Fig. 1A where values of $10^{-7.0}$ M for K_{A1} and $10^{-13.9}$ M for K_{A2} were used.[8] Figure 1B shows that the electrode behaves perfectly according to the Nernst equation ($R^2 = 0.999$) within the measured range. During a period of 1 year the slope and intercept of the electrode ranged from −24.3 ± 0.6 mV to −763 ± 16 mV, respectively. In analogy to pH measurements the term pS is introduced: $pS = -\log(S^{2-})$. The electrode response (mV) can be directly converted to pS units, applying Eq. (2).

Precipitation Experiments in Batch and Continuous (CSTR) Reactors

The CSTR experiments were performed in a 1000-mL glass vessel (120 mm in diameter) with four baffles, which was ideally mixed by a magnetic stirrer at 500 rpm (as confirmed by a retention time distribution test using LiCl as tracer) and operated at room temperature (Fig. 2). The pH- and pS-electrodes were connected to proportionally integrated controllers (Endress + Hauser, Germany) and equipped with stock solutions of HNO_3/NaOH and Na_2S, respectively, to control pH and pS levels in the reactor. The stock solutions of NaOH and Na_2S were mounted with

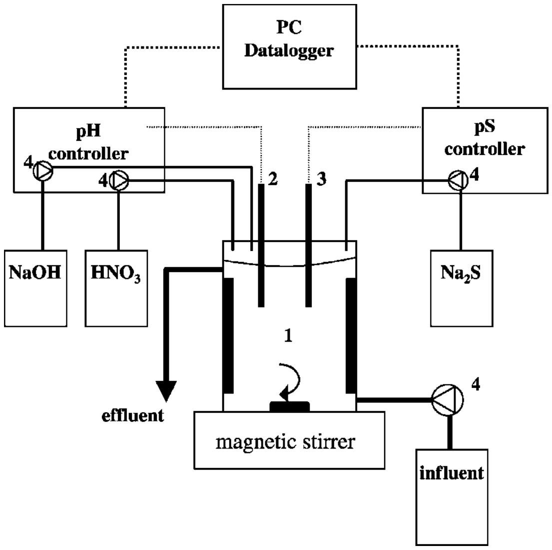

Figure 2. Schematic presentation of the experimental set-up for batch and CSTR experiments (1: reactor, 2: pH-electrode, 3: pS-electrode, 4: peristaltic pumps).

$Ca(OH)_2$ pellet columns to prevent absorption of CO_2 into solution. The pS- and pH-controllers were connected to an automatic data logging system (Data Electronics Ltd., Australia) to record pH and pS on-line. The batch experiments were performed with the same experimental set-up, except that the influent and effluent openings were closed and only pH was controlled.

For the batch experiments, monometal solutions of approx. 1 mM and 3 mM of $Me(NO_3)_2$ salts (Me = Cd, Cu, Ni, Pb, or Zn) were titrated by hand with 100 mM Na_2S. The pH was controlled at 6.0 by the pH-controller. After constant readings of pH and pS, the next aliquot of Na_2S was added. When reaching the equivalence point, EP (the point where metal is almost completely precipitated and pS starts to drop drastically), the titration was ended after a small overdose of Na_2S. The pS and pH were recorded online and periodically 5–10 mL samples were taken from the reactor for metal analysis. The samples were filtered through 0.45 μm membranes (Schleicher & Schuell, Germany), the filtrate acidified to 0.1 M HNO_3 and stored at 4°C until analysis by ICP-AES.

Two batch titration experiments were performed with mixtures of Cu and Zn (7 and 10 mM) and Pb and Zn (2 and 10 mM) at pH 6.0 to study the selective precipitation of the metals.

CSTR experiments were performed with monometal solutions of $Me(NO_3)_2$ salts (Me = Cd, Cu, Ni, Pb, or Zn) at pH 6.0 and pS 15.0. This condition corresponded to a total sulfide concentration S_{TOT} of 0.03 mg l^{-1} as calculated by Eq. (1). Experiments were performed at hydraulic retention times (HRT) of 1, 5, and 30 min for Cu, Pb, and Zn and at 30 min for Cd and Ni. The metal load rate was kept constant at 0.25 mM min^{-1}. The experiments were run for 10–15 HRTs. The effluent of the reactor was sampled 1–2 times per HRT, samples filtered through 0.45 μm, filtrate acidified to 0.1 M HNO_3 and stored at 4°C until analysis by ICP-AES.

The selective precipitation of heavy metals was studied for a mixture of Cu and Zn (3.8 mM each) at pH 6.0 at various pS levels at an HRT of 30 min. The pS was maintained at a constant level for 3–4 HRTs and Cu and Zn in the effluent were measured periodically.

Precipitation in a Membrane Reactor

Figure 3 shows the flow scheme of the membrane reactor system. The reactor system was constituted of a 40-L glass reactor, centrifugal pump (CDXM 70/07, Ebara, Italy), and two membrane modules in series. The circuit was equipped with three ball valves to control the pressure over the centrifugal pump and the membranes. The reactor was ideally mixed (as confirmed by

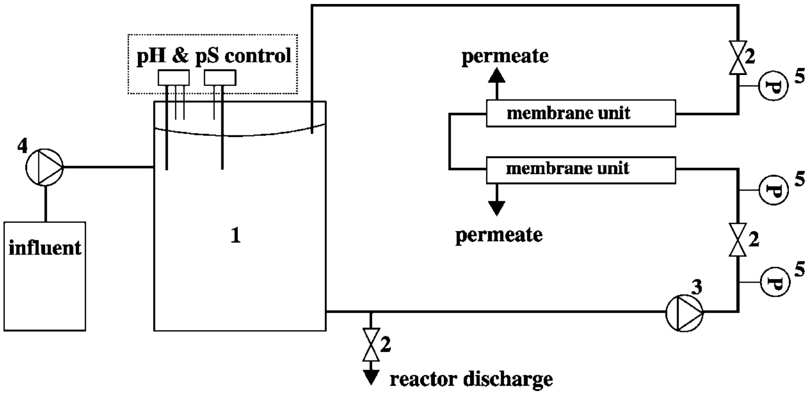

Figure 3. Schematic presentation of the membrane reactor (1: reactor, 2: ball valves, 3: centrifugal pump, 4: peristaltic pump, 5: pressure gauges).

a retention time distribution test using LiCl as tracer) by the high pumping rate of the centrifugal pump (about 200 L per min). The temperature in the reactor was controlled at 25°C by a heat exchanger (not shown in Fig. 3). The experiment was performed with two different membranes in series: an ultrafiltration (UF) membrane with mean pore size of 0.01 μm (WFS 0120, Stork, The Netherlands) and a microfiltration (MF) membrane with mean pore size of 0.1 μm (WFS 0171, Stork, The Netherlands). The pS and pH in the membrane reactor were controlled by the PI-controllers as shown in Fig. 2. An influent solution of 8 mM $Zn(NO_3)_2$ was precipitated at pH 6.0 and pS 15.0 at a HRT of 30 min. The ZnS content in the reactor was concentrated up to $60\,g\,l^{-1}$ for both the MF and UF membranes. The permeate flux was measured as a function of the ZnS content in the reactor. The ZnS content of the reactor was measured periodically by drying samples from the reactor at 40°C for 2 days. Samples of the permeate were taken periodically, acidified to 0.1 M HNO_3 and stored at 4°C until analysis by ICP-AES.

Analyses and Reagents

All reagents were of analytical grade (Merck, Germany) and demineralized water was used to prepare the solutions. Metals were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at Central Lab, Department of Soil Quality, Wageningen University, The Netherlands; both standards and samples were measured at a background of 0.1 M HNO_3. The detection limit of ICP-AES was $0.05\,mg\,l^{-1}$ for the metals which corresponded to the following molarities: Cd 0.47 μM, Cu 0.8 μM, Ni 0.9 μM, Pb 0.2 μM, and Zn 0.8 μM. Total sulfide (S_{TOT} defined as the sum of H_2S, HS^-, and S^{2-} species) was determined colorimetrically using the methylene blue method.[9]

RESULTS

Batch Experiments

The pS, metal concentration and Na concentration during the titration for an initial metal concentration of 1 and 3 mM are shown in Fig. 4. The batch titrations, except for Ni, showed a typical pS response which can be divided in 2 regions: before and after the equivalence point, EP (point where metal was almost completely removed and pS suddenly decreases). Before the EP, pS remained constant at a characteristic level for each heavy metal: Cd 27.5–28.5, Cu 39.5–40.5, Pb 28.5–29.5, and Zn 18.5–19.5. After the EP, when the metal is completely precipitated, the electrode response is dictated by the dissolved sulfide in solution. The heavy metals reached the detection limit for all metals except Cu. This is most probably due to the presence of CuS particles that were visually observed in the filtrate after 0.45 μm membrane filtration.

Figure 5 shows the metal concentrations and pS during the titration of mixtures of Pb–Zn and Cu–Zn. For both titrations, the metals are precipitated consecutively, the metal with the lower solubility (Cu and Pb) first and then Zn. The precipitation of both metals also corresponded with the two EPs in the pS curves. Both titrations showed two constant pS-levels during precipitation, again showing that the levels of pS during precipitation were unique for every heavy metal.

CSTR Experiments

The pH and pS level were controlled at 6.0 ± 0.2 and 15.0 ± 0.3, respectively throughout the runs (data not shown). Figure 6 shows the average effluent concentrations over the last period (6–10 HRT) of the runs. The effluent concentration was independent of the hydraulic retention time for both Pb and Zn but Cu showed a strong effect. The concentrations were in the

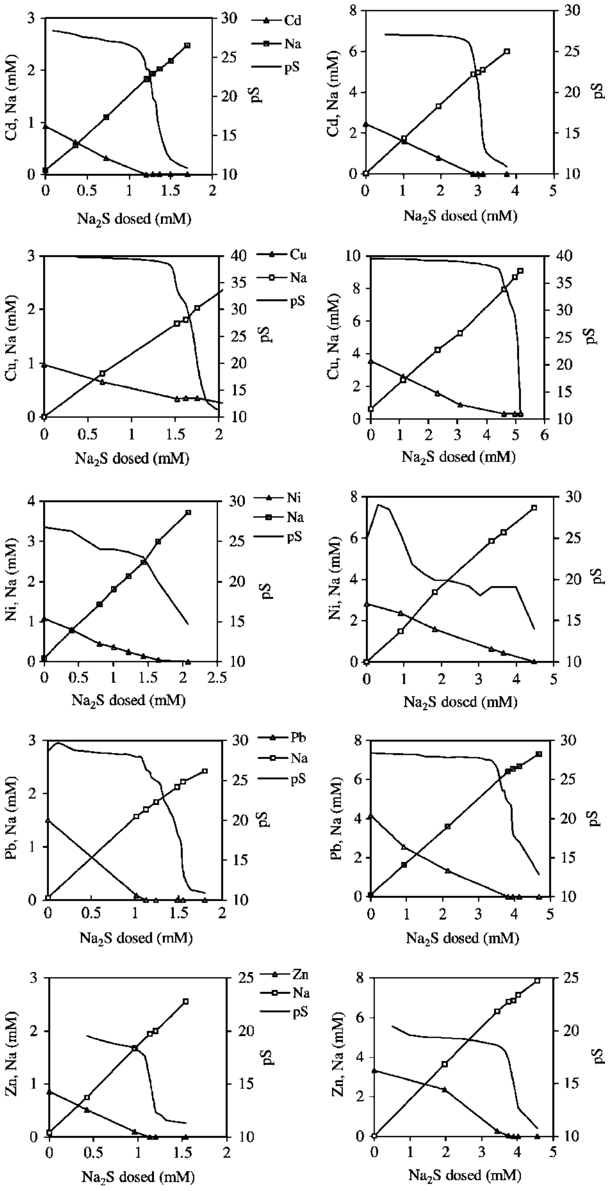

Figure 4. Batch titrations of 1 and 3 mM metal nitrate solutions (Cd, Cu, Ni, Pb, and Zn) with Na_2S at pH 6.0.

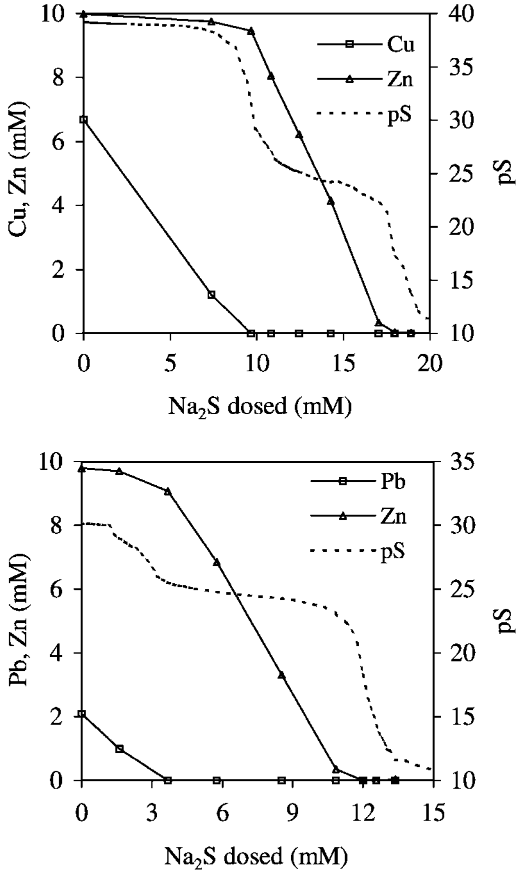

Figure 5. Selective precipitation in batch of Cu–Zn and Pb–Zn mixtures at pH 6.0.

range of the detection limit of ICP-AES for Cd, Pb, and Zn, i.e., the metals were precipitated to very low levels. However, Cu and Ni showed high levels even for an HRT of 30 min indicating that the precipitation reaction was slow or that metal sulfide particles smaller than 0.45 μm were produced. The presence of metal sulfide particles in the filtrates was visually observed for Cu but not for Ni.

For the selective precipitation experiment, the pH and pS level were controlled accurately within 0.2 units by the PI-controllers (data not shown). The average Cu and Zn concentrations in the effluent as a function of pS levels are shown in Fig. 7. As is expected from the solubility product, Cu is

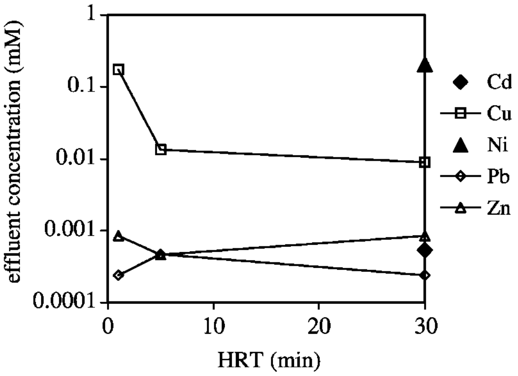

Figure 6. Effluent metal concentration (Cd, Cu, Ni, Pb, and Zn) as function of the hydraulic retention time in CSTR precipitation experiments at pH 6.0.

precipitated at higher pS levels than Zn. The experiment showed complete, selective precipitation in the pS range 30–37.

Membrane Reactor

The influent concentration of 8 mM $Zn(NO_3)_2$ was precipitated in the membrane reactor at pH 6.0 and pS 15.0. The measured Zn

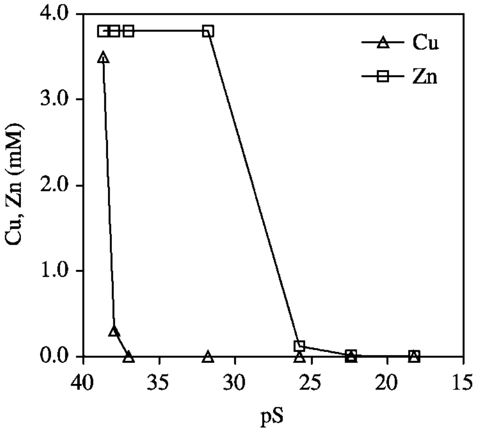

Figure 7. Selective precipitation of Cu–Zn mixture in CSTR at pH 6.0.

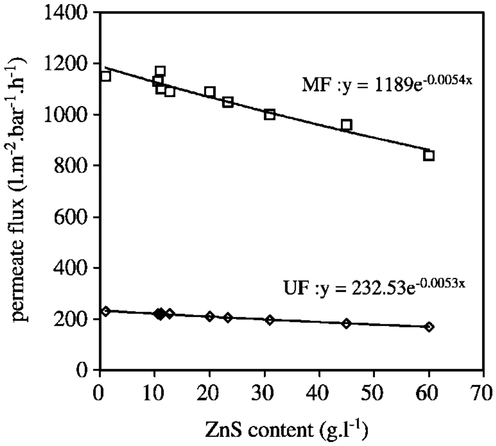

Figure 8. Permeate flux of MF and UF membranes as function of ZnS content in the reactor.

concentration in the permeate was below the detection limit ($<0.8\,\mu$M) during accumulation of ZnS to $60\,g\,l^{-1}$ for both the UF and MF membranes. This is in agreement with the batch and CSTR experiments. The permeate flux of both the MF and UF membrane during accumulation of ZnS is shown in Fig. 8. Both membranes showed a decrease in permeate flux at increasing ZnS levels.

DISCUSSION

Heavy Metal Sulfide Precipitation

The batch titrations for Cd, Cu, Pb, and Zn show a typical response of the pS-electrode. Before the equivalence point, sulfide is completely removed by metal precipitation. After complete precipitation of the metal, pS sharply drops and the response of the pS-electrode is determined by the dissolved sulfide concentration. The dissolved sulfide depends on the excess of total sulfide and pH of the solution according to Eq. (1). Ni does not show this typical response in pS, which can be explained by the slow precipitation reaction of Ni and sulfide as was also observed by Simons[10] and Brooks.[11] In the experiment of 1 mM Cu, the metal was not completely removed. This can be due to two reasons: 1) colloidal CuS particles which were not retained by the 0.45 μm filter, or 2) the precipitation reaction was too slow. Indeed, a black cloudiness was observed in the filtrate and indicated that CuS particles smaller than 0.45 μm had formed. These particles were also measured by ICP-AES and contribute to the total amount of soluble Cu. Moreover, a constant pS level during precipitation and a sharp drop at the EP, confirms that the precipitation reaction was fast.

The batch titrations indicate that, by controlling pS at approximately 15.0, the heavy metals will be removed to low levels accompanied by low sulfide concentrations ($< 0.02\,\mathrm{mg\,l^{-1}}$ as calculated by Eq. (2)). Experiments in CSTR were performed at pH 6.0 and pS 15.0 to confirm this idea. Cd, Cu, and Zn were in the range of the detection limit of ICP-AES for all HRTs and shows that the precipitation reaction is very fast for these metals. As CuS particles were not completely retained by the 0.45 μm membrane filter, also CuS was measured as soluble Cu and contributed to the high Cu concentration in the effluent. The formation of small particles is due to the extremely low solubility product of CuS (or Cu_2S) which results in high supersaturation and high nucleation rates (as discussed later). Ni however was completely retained by 0.45 μm membrane filters but still showed very high effluent concentrations. This is due to the slow reaction rate between Ni^{2+} and S^{2-} as reported by Simons.[10] The precipitation reaction of NiS was almost instantaneous when seeds were added to the system,[10] indicating that nucleation was the rate-limiting step.

Both batch and CSTR experiments show that the pS-electrode can be used to control sulfide precipitation of heavy metals where the heavy metals are removed to very low concentration (detection limit of ICP-AES) and no total sulfide is present in the effluent.

Solubility Products of Metal Sulfides

The batch experiments showed that each heavy metal has its characteristic pS level before the equivalence point. This pS level is determined by the solubility product of the metal sulfide when the solution is in thermodynamical equilibrium, i.e., kinetics effects are negligible. The solubility product (K_{SP}) of a metalsulfide (MeS) is given by:

$$K_{SP} = (Me^{2+})^{*}(S^{2-})^{*} \qquad (3)$$

where $(Me^{2+})^{*}$ is the equilibrium activity of metal ion Me^{2+} and $(S^{2-})^{*}$ the equilibrium activity of S^{2-}. The activity of S^{2-} is directly measured by the pS-electrode but the metal concentration $[Me^{2+}]$ as measured by

ICP-AES has to be converted to activity by[12]:

$$(\mathrm{Me}) = \gamma_{\mathrm{Me}}[\mathrm{Me}^{2+}] \tag{4}$$

where $[\mathrm{Me}^{2+}]$ is the concentration of the metal ion (M), (Me^{2+}) the activity of the metal ion (M), and γ_{Me} the activity coefficient of the metal ion. The activity coefficient can be calculated by the Davies equation up to an ionic strength of 0.3 M[12]) according to:

$$\log \gamma = -\mathrm{A}Z^2\left(\frac{\sqrt{\mathrm{I}}}{1+\sqrt{\mathrm{I}}} - 0.2\,\mathrm{I}\right) \tag{5}$$

where I is the ionic strength I which is defined as $\frac{1}{2}\sum C_i Z_i^2$, $\mathrm{A} = 1.82 \times 106(\varepsilon \mathrm{T}),^{-3/2} = 0.5$ for water at 25°C, Z is the charge of ion i, C the concentration of ion i, and ε is the zdielectric constant. The solubility products for Cd, Cu, Ni, Pb, and Zn only can be calculated accurately if the metal concentration is above the detection limit of ICP-AES. The average $\log(K_{SP})$ values for the experiments at 1 and 3 mM are given in Table 1 together with the literature values of stability constants for metal sulfide precipitates. The values from the experiments are in the same order of magnitude as the literature data but there is some discrepancy as is also the case for the literature data. This is mainly the result of differences in experimental conditions (e.g., mixing intensity, supersaturation, solids concentration, reaction time) which result in different types of precipitates with different solubility products.[4,13] The measured solubility products should therefore be regarded as conditional K_{SP}s and in dynamic situations, e.g., treatment of metal-containing wasterwaters, metastable precipitates may control solubility.[14]

Table 1. Comparison between MeS solubility products ($\log K_{SP}$) as obtained from the batch experiments and literature data.

Metal	1 mM	3 mM	Literature data[a]
Cd	− 28.8 ± 0.3	− 29.8 ± 0.6	− 25.8, − 28.2[b]
Cu	− 41.5 ± 0.5	− 41.0 ± 0.3	− 36.1 (CuS), − 48.5 (Cu_2S)
Ni	− 26.0 ± 0.9	− 25 ± 2	− 19.4 (α), − 24.9 (β), − 26.6 (γ)
Pb	− 30.6 ± 0.9	− 30.8 ± 0.4	− 27.5
Zn	− 20.9 ± 0.3	− 22.1 ± 0.3	− 22.5 (α), − 24.5(β), − 18.4[c]

[a] Ref. 8.
[b] Ref. 14.
[c] Ref. 13.

The solubility product for Cu is in between the values for Cu^{2+} and Cu^{+}. This is most probably due to a redox reaction where Cu^{2+} is reduced to Cu^{+} and sulfide is oxidized to sulfate. This redox reaction is thermodynamically favorable[12] and occurrence of the redox reaction was confirmed by the presence of sulfate at the end of the titration (results not shown).

In this study, a value of $10^{-13.9}$ M for the second dissociation constant (K_{a2}) of H_2S[8] was used for the calibration of the pS electrode. The corresponding solubility products of the metal sulfides are related to this value for K_{a2}. Myers[15] showed that K_{a2} of H_2S of $10^{-13.9}$ M is not correct due to the oxidation of sulfides yielding polysulfides S_xS^{2-}. The exact value of K_{a2} is highly uncertain but its approximate value is 10^{-19} M. Therefore, Myers[15] concluded that S^{2-} is never a principal species in normal aqueous solutions and proposed an alternative solubility product for metal sulfides based on the reaction $MeS(s) + 2H^+ \leftrightarrow Me^{2+} + H_2S$, which does not involve K_{a2} of H_2S. However, our study and the results of others[5,6] showed that the response of the pS-electrode vs. S^{2+} gives a linear relationship in pH range 3–11 (Fig. 1) where S^{2-} is calculated on basis of $10^{-13.9}$ for K_{a2} (see Eq. (1)). This would suggest that the species S^{2-} is relevant in normal and acidic aqueous solutions. We could have chosen a value of 10^{-19} M for K_{a2} but this only affects the intercept of the electrode response in Fig. 1. We believe that the true value of K_{a2} is of academic importance but not relevant for the engineering aspects with respect to the control of metal sulfide precipitation by the pS-electrode. In our opinion, both the definition of the solubility products according to Myers[15] and the definition $MeS \leftrightarrow Me^{2+} + S^{2-}$ can be applied as long as both definitions and corresponding equilibrium constants are not mixed up.

Selectivity of Sulfide Precipitation

As the response of the pS-electrode is directly coupled to the solubility product of the metal sulfide precipitate and pS and pH level can be controlled accurately, we have a control parameter to selectively precipitate heavy metals. The batch titration of Cu–Zn and Pb–Zn mixtures shows that Cu and Pb with lower solubility are precipitated first at their characteristic pS level of 39.0 and 30.0, respectively. Zn precipitates at pS 24, corresponding to a $\log(K_{SP})$ of -25 which is in better agreement with the solubility product of Smith and Martell.[8] This shows that the K_{SP} depends on the experimental conditions (e.g., HRT, mixing, reactor configuration, presence of seed crystals) and should be considered a conditional solubility product. The selectivity of precipitation is 100% for Cu–Zn and 95% for Pb–Zn.

The selectivity will become lower when the values of the solubility products are closer together.

The experiment was repeated for a mixture of Cu–Zn in a CSTR at pH 6.0 and control at various pS levels. Cu was completely removed at pS 37 at which pS level Zn was still completely soluble. At pS 22 both Cu and Zn are completely removed. Thus by a sequential precipitation in two steps where both reactors are controlled at different pS levels, both Cu and Zn can be precipitated in pure form which increases the possibilities of reuse of the produced metal sulfide sludges. The selectivity of the precipitation will depend upon the differences in solubility product. However, also differences in the rate of the precipitation reaction can possibly be applied for selective precipitation, e.g., Ni shows much slower kinetics than Cd, Pb, and Zn.

Membrane Precipitation Reactor

The Zn concentration in the permeate of both UF and MF membranes was below the detection limit of ICP-AES. This is in accordance with the batch and continuous experiments and showed that ZnS was completely retained by the membrane filter. This shows that the smallest ZnS particles were larger than $0.45\,\mu m$ and the results are in accordance with Peters and Ku.[16] The particle size distribution (PSD) of precipitates depends on the competition between nucleation and crystal growth. Nucleation results in very small particles ($< 0.05\,\mu m$) and crystal growth in larger particles. In general, high supersaturation levels favor nucleation and should therefore be minimized to produce large particles.[4,17] For precipitates with low solubility products, very small particle sizes ($< 1\,\mu m$) normally prevail in CSTRs as the supersaturation level cannot be controlled at low levels.[17] and because local supersaturation at the feed points due to micromixing limitation cannot be prevented.[18] However, by controlling pS at very low levels with the pS-electrode and by offering a high specific surface for crystal growth, local supersaturation can be minimized and therefore large particles can be produced in a membrane reactor. These large particles are easily separated from the liquid by using membranes with large pore sizes resulting in very high permeate fluxes and thus low costs. This concept was confirmed by the measured high permeate fluxes for ZnS even at very high total solids contents. The membrane reactor was run for 6 days up to a ZnS content of $60\,g\,l^{-1}$ without fouling of both UF and MF membranes. Both MF and UF membranes showed the same relative drop in permeate flux as function of the solids content in the reactor. This indicates that the permeate flux is controlled by the viscosity of the liquid.[19] The ZnS particles do not have a direct effect on the performance of the membranes due to the large size of the ZnS particles and the hydrophobic nature of the precipitate. The solids concentration can be kept constant by discharging of the reactor content continuously by control on basis of density measurement.

CONCLUSIONS

The pS-electrode measures the activity of S^{2-} ions in the liquid and can be used to monitor and control the pS level in the reactor. Simultaneous control of pS and pH provides an excellent method for precipitating heavy metals to very low concentrations and at the same time negligible amounts of sulfide are present in the effluent. The flexibility of the pS–pH control allows control in a continuous reactor system that can handle fluctuations in flow rate and heavy metal concentration.

Every precipitating metal has a unique pS level for sulfide precipitation which is directly related to its solubility product. The experimentally obtained solubility products and data from literature are in good agreement but span several orders of magnitude. This is due to the different experimental conditions which result in different precipitates with different solubility products. The uniqueness of the pS level for each metal was successfully applied as a control parameter to precipitate metals selectively and to obtain pure metal sulfide, which have better chances for reuse.

By adopting a membrane reactor in combination with the pS–pH control, a large specific surface area and low supersaturation levels are offered, which promote crystal growth and suppresses nucleation. In this way, even wastewaters with very low amounts of metals that are difficult to treat in conventional CSTRs can be removed.

ACKNOWLEDGMENTS

This research was financialy supported by NOVEM within the framework of the Environment and Technology Program 1999 (project 351340/5010). We thank Triqua bv for supplying the membrane reactor and Witteveen + Bos for information on the safety aspects and the economic evaluation of the sulfide precipitation process.

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Received April 2001
Revised April 2002