



Zn–Ni sulfide selective precipitation: The role of supersaturation

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ABSTRACT

The selective removal of Zn with Na₂S from a mixture of Zn and Ni was studied in a continuously stirred tank reactor. At pH 5 and pS 18 the selectivity was improved from 61% to 99% by reducing the supersaturation at the dosing points by means of the reduction of the influent concentrations. The particle size distribution (PSD) of the precipitates increased as the supersaturation decreased up to a mode of about 22 μm at pH 5. PSD values on the 100–200 μm range were obtained when the sulfide was dosed through a polytetrafluoroethylene (Teflon) membrane at low supersaturation. Zn precipitated as sphalerite, whereas Ni mainly formed amorphous particles with a pH dependent stoichiometry.

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1. Introduction

Many industrial activities generate heavy metal contaminated wastewaters with very diverse compositions that pose serious environmental risks if not treated. There are numerous examples, from the mining activity [1,2] generating e.g. acid mine drainage (AMD) [3,4], to the metal finishing industry [5] like e.g. electroplating [6,7]. Zinc and nickel are among the several metals likely to be present in many of these wastewaters and though these metals are micronutrients for several organisms, they become toxic above certain concentrations depending on their speciation [8–11].

Sulfide can be a mean for the precipitation of a wide variety of metals [12,13] due to the low solubility of metal sulfides (Table 1). Full scale (reactor and *in situ*) applications for the removal and recovery of metals – including Zn – as metal sulfides already exist [14,15]. As a matter of fact, the precipitation of Zn with sulfide is a relatively well known process. Zinc and sulfide precipitate as ZnS, which has two polymorphs: the low temperature and most stable one, sphalerite, and the high temperature wurtzite [16]. Nevertheless, Zn and sulfide can also form soluble complexes [17–19] that decrease the precipitation efficiency. This can occur not only at high

pH (depending on ionic strength and salinity), but also when sulfide is dosed above the stoichiometric amount [20,21].

The chemistry of nickel sulfide, on the other hand, is rather more complex. Many forms of nickel sulfide have been reported in the literature, each one having its own solubility product (Table 1) [22–26]. However, correct and consistent solubility data is very difficult to assess and compare due to discussions regarding the conditions of formation and the existence of some polymorphs [27–30], to the variation in the available thermodynamic data [22,24–26,31,32] and to the definition of solubility product [8,22,31]. Despite the many discussions on this topic concerning phase transition behaviour and some of the high temperature phases, most of the low temperature forms of nickel sulfide, namely millerite (β-NiS), vaesite (NiS₂), polydymite (Ni₃S₄) and heazlewoodite (Ni₃S₂), are better characterized [27,33–37].

One of the greatest potentialities of sulfide precipitation is the selective precipitation, which can be achieved due to the difference in solubility product between the different metal sulfides [13]. Taking into account that in the simplest form $K_{sp} = (Me^{2+})(S^{2-})$, it has been shown that the steering of (S^{2-}) by means of a pS electrode ($pS = -\log(S^{2-})$) is an important factor to achieve selective precipitation [38]. Nevertheless, it cannot be neglected that due to the high rate of these reactions, and depending on the differences between solubility products, the occurrence of supersaturated areas can compromise the selectivity [39].

The aim of the present work is to study the selective precipitation between Zn and Ni with sulfide in a continuously stirred tank

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Table 1

Solubility products ($-\log K_{sp}$) for several zinc and nickel sulfide polymorphs at 298.15 K. The reaction is considered to occur in aqueous media with the metals and the sulfide in the form of Zn^{2+} (aq), Ni^{2+} (aq) and S^{2-} (aq).

Chemical formula	Mineral form	References			
		[22] ^a	[23]	[8] ^b	[24,25] ^c
Ni ₃ S ₂	Heazlewoodite	43.9	–	–	40.6
Ni ₆ S ₅	–	–	–	–	–
Ni ₇ S ₆	–	–	–	–	–
Ni ₉ S ₈	Godlevskite	–	–	–	–
NiS ^d	(α)	19.9	19.4	19.5	–
	(β) Millerite	25.1	24.9	25.0	21.0
	(γ)	26.9	26.6	26.7	–
Ni ₃ S ₄	Polydymite	58.1	–	–	–
NiS ₂	Vaesite	29.0	–	–	–
ZnS	(α) Sphalerite	24.5	24.7	24.8	24.6
	(β) Wurtzite	21.7	22.5	22.9	–

^a Recalculated with the $\Delta G^{\circ}_f(S^{2-})$ from Ref. [31].

^b Recalculated from original data given for $MeS(s) + H^+(aq) \leftrightarrow Me^{2+}(aq) + HS^-(aq)$ with the given $pK_{a2} = 13.9$.

^c K_{sp} was calculated as proposed by Licht [22]. References provided the ΔG°_f of the metal sulfide, whereas the ΔG°_f of S^{2-} (aq) and Me^{2+} (aq) are from elsewhere [31].

^d According to Thoenen [27] and Carlsson and Vuorinen [32] the α , β , γ denomination might be circumstantial and an artefact, since it originates from a work prior to the implementation of X-ray techniques and were therefore never confirmed. These seem to have spread through out many text books and databases, which is the case of references [22,23] and possibly [8]. More recently, the β -NiS and the α -NiS have been used to refer to millerite and to the high temperature NiAs-type, respectively [36,37]. However, no analogy should be made between the two denominations.

reactor (CSTR) at 20 °C controlled by a pS electrode in combination with a pH electrode. The effect of pS, pH and supersaturation on the selective precipitation was evaluated. In addition, the solid phase was characterized by particle size distribution (PSD), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Experimental set-up

Experiments were performed with the temperature controlled at 20 °C in a 1.5 l glass vessel (CSTR) stirred at 500 rpm as described by Sampaio et al. [38].

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

The pS electrode was calibrated by titrating approximately 10 mM (320 ppm) of Na_2S with 1 M HNO_3 . The methodology and its principles are described in Sampaio et al. [38]. The Nernst equation correlating the potential given by the pS electrode (mV) with (S^{2-}) is given by:

$$E = E^0 - \frac{RT}{ZF} \ln(10) \log(S^{2-}) = E^0 + \frac{RT}{ZF} \ln(10)pS \quad (1)$$

2.3. Experimental design

Two types of experiments were performed: titrations and continuous reactor experiments. Experiments were carried out either with only one metal (Zn or Ni), or with a mixture of both metals. Metals were supplied as metal nitrates and sulfide as Na_2S (Merck, Darmstadt, Germany). Temperature and pH were controlled in all cases.

Unless specified otherwise, hereforth “reaction ratio”, “dosing ratio” and “selectivity” will always be based on molar concentrations. Selectivity will be used to evaluate the separation between Zn and Ni and is defined as the amount of precipitated Zn regarding the total metal precipitated (Zn + Ni). Soluble metal concentration will be referred to as the concentration after filtration through a 0.45 μ m pore size filter.

2.3.1. Titrations

Approximately 2 mM (around 130 mg/L) of each metal (Zn and Ni) were titrated, either alone or mixed together, with 0.1 M of Na_2S

(3.2 g/L). The procedure and the material used has been described elsewhere [38].

2.3.2. Continuous reactor experiments

The used reactor volume during the continuous experiments was 1 L. The influent flow containing Zn, Ni or Zn and Ni was pumped from a 25 L container at a constant flow of 2 L/h. Sulfide (Q_{sulf}) was pumped from a 25 L vessel by a Masterflex Console Drive (Cole Palmer, IL, USA) connected to the control device. 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 .

Experiments with different combinations of metals and sulfide influent concentrations, as shown in Table 2, were performed at pH 4 and 5. This resulted in HRTs between 4 and 20 min. Additionally, there were also experiments where the sulfide was dosed via a polytetrafluoroethylene (Teflon) membrane (porosity 35%; pore size 4.5 μ m; surface area 36 cm²), but solely at pH 5 (Table 2).

2.4. Control strategy

During the titrations the temperature and the pH were both controlled at predefined set-points, while in the continuous experiments (besides pH and temperature) the pS was also controlled. Commercially available devices were used to control temperature and pH, whereas a proportional integral (PI) feedback control strategy was developed to control the pS [40].

For the development of the pS control strategy for the continuous precipitation of Zn, step responses were performed with a Zn influent concentration of 600 ppm at 2 L/h. The sulfide influent concentrations used were 600, 150 and 50 ppm, with steps in

Table 2

Layout of continuous experiments performed at different influent concentrations.

Metal influent (ppm)		Zn	Ni	Zn + Ni ^a	150	50
		600	600	600 ^b		
Sulfide influent (ppm)	600	✓	✓	✓ ^c		
	150			✓	✓	
	50			✓		✓ ^c

^a Values correspond to the concentration of each metal. All combinations were performed at pH 5.

^b Only the combinations with this metal concentration were performed both at pH 4 and 5 (except c).

^c Additional experiments with the sulfide dosed via a Teflon membrane (only at pH 5).

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