Implementation of biological and chemical techniques to recover metals from copper-rich leach solutions

Hedrich, Sabrina; Kermer, René; Aubel, Tim; Martin, Mirko; Schippers, Axel; Johnson, D. Barrie; Janneck, Eberhard

Hydrometallurgy

DOI:
https://doi.org/10.1016/j.hydromet.2018.06.012

Published: 01/08/2018

Publisher's PDF, also known as Version of record

Hydrometallurgy 179 (2018) 274–281

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Implementation of biological and chemical techniques to recover metals from copper-rich leach solutions

Sabrina Hedrich[a,*], René Kermer[b,*], Tim Aubel[b], Mirko Martin[b], Axel Schippers[a], D. Barrie Johnson[c], Eberhard Janneck[b]

[a] Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany
[b] G.E.O.S. Ingenieurgesellschaft mbH, Schwarze Kiefern 2, 09633 Halsbrücke, Germany
[c] School of Biological Sciences, Bangor University, Deiniol Road, Bangor LL57 2UW, UK

ARTICLE INFO

Keywords:
Pregnant leach solution
Metal recovery
Solvent extraction
Biological sulfate reduction

ABSTRACT

Pregnant leach solutions (PLS) resulting from (bio)leaching of copper ores are characterized by low pH, high concentrations of Fe (III), Cu, Zn and often significant amounts of Ni and Co. In order to make the metals available for further processing they require selective recovery form the acidic, multi-metal solution. Commonly, copper and other base metals are recovered by solvent-extraction/electro-winning (SX/EW) technologies from acidic, metal-rich solutions. This study describes the application of chemical and microbiological process steps for the selective recovery of base metals from the PLS. A multi-stage metal recovery system, involving initial Cu-SX/EW to recover copper, followed by iron hydroxy sulfate precipitation to recover the high amounts of these two metals before introducing the more sensitive biological step, is proposed. The biological route is based on a sulfidogenic bioreactor housing acidophilic bacteria producing hydrogen sulfide directly from the acidic, sulfate-rich PLS. The bioreactor promotes and controls the selective precipitation of CuS and ZnS in two connected vessels and the recovery of Ni and Co as metal sulfides within the bioreactor. The sulfidogenic system has additionally the advantage of lowering the sulfate concentration of the PLS and contribution to an increase in pH. A parallel alternative chemical metal recovery pathway allows the selective recovery of remaining Cu and other metals (e.g. Zn, Co, Ni) via ion exchange (IX). Both the biological and chemical routes lead to a modified PLS which can be reintroduced into the bioleaching operation. Silver and lead are recovered from solid (bio) leach residues by hot brine leaching. The system has been designed to selectively recover all relevant metals from the PLS following a zero waste concept, and its modular arrangement allows an independent operation of the units and the integration of further modules, depending on the nature of the leach solutions.

1. Introduction

Bioleaching and chemical leaching of ores and residues for the recovery of valuable metals have become an increasingly attractive technology over recent years (Schippers et al., 2014). During the (bio) leaching process, most of the metals are brought into solution whereas some valuable trace metals remain in the solid (bio)leach residues, which can be recovered by secondary treatment steps. Bioleaching or chemical leaching of copper sulfide and copper oxide ores, respectively, is mainly applied in heaps or dumps; stirred tank bioreactor processes for copper concentrates has received increased attention in recent studies (Brierley, 2016). Pregnant leach solutions (PLS) resulting from these processes are characterized by low pH and high concentrations of various transition metals, metalloids and sulfate. Metal separation and recovery from these solutions are commonly achieved by technologies such as solvent extraction (SX), electrolysis/electro-winning (EW), ion exchange (IX) or selective precipitation reactions, well approved techniques commonly applied to most hydrometallurgical processes in which base metals are recovered (Dutrizac, 1987; Jergensen, 2009; Sole et al., 2016). For example, SX and EW are widely applied for the recovery of Cu from various leaching operations (Schlesinger, 2011). However, intermediate products like hydroxide, sulfide precipitates or cement-copper are also possible, but some of these techniques are not always efficient when metals are present in relatively low

Abbreviations: PLS, Pregnant leach solution; IX, Ion exchange; SX, Solvent extraction; EW, Electro-winning; SRB, Sulfate reducing bacteria; SE, Strip electrolyte; RE, Rich electrolyte; O/I, Organic/Inorganic ratio; T-RFLP, terminal restriction fragment length polymorphism

* Corresponding authors.
E-mail addresses: sabrina.hedrich@bgr.de (S. Hedrich), r.kermer@geosfreiberg.de (R. Kermer), t.aubel@geosfreiberg.de (T. Aubel), m.martin@geosfreiberg.de (M. Martin), axel.schippers@bgr.de (A. Schippers), d.b.johnson@bangor.ac.uk (D.B. Johnson), e.janneck@geosfreiberg.de (E. Janneck).

https://doi.org/10.1016/j.hydromet.2018.06.012
Received 9 March 2018; Received in revised form 6 June 2018; Accepted 23 June 2018
Available online 27 June 2018

concentrations as investment and operation costs are disproportionately high. Precious metals remaining in the leached solid residues can be recovered using cyanide or more aggressive reagents (Spolaore et al., 2009; Attia and El-Zeky, 1990). While the production of metallic copper as well as the recovery of zinc and nickel from acidic waters via these state-of the art techniques is commonplace, the application of less cost-intensive and aggressive methods for the selective metal recovery from more complex solutions has received little attention.

Alternatives to the conventional applied metal recovery technologies are biological methods, such as biosorption (Fomina and Gadd, 2014) or biomineralization (Janneck et al., 2010; Boonstra et al., 1999). One promising biological approach, which has been intensively studied for the treatment of acid mine drainage, harnesses the abilities of sulfate-reducing bacteria (SRB) which convert sulfate to H_2S and HS^- (e.g. Ñancucheo and Johnson, 2012). Chalcophilic metals (such as Cu, Zn, Ni and Co) can be selectively precipitated as metal sulfides under pH-controlled conditions, and metals recovered from the sulfidic precipitates formed. Biological sulfidogenesis has the secondary advantage of removing some of the sulfate present and increasing solution pH, as sulfate-reduction is a proton-consuming reaction in low pH liquors. A commercial process utilizing neutrophilic sulfate-reducing bacteria (e.g. Boonstra et al., 1999) is e.g. operated by the Dutch company Paques (ThioTeq). Most sulfate-reducing bacteria are, however, sensitive to low pH and high metal contents, therefore sulfate-reduction and metal sulfide precipitation must necessarily take place in separate vessels.

Recently, a novel laboratory-scale low pH sulfidogenic bioreactor that mediates the selective biomineralization of chalcophilic metals in acidic waters has also been described (e.g. Ñancucheo and Johnson, 2012; Santos and Johnson, 2017). The system uses acidophilic and acid-tolerant strains of sulfate-reducing bacteria indigenous to mine-impacted environments, which are tolerant to moderate acidity and elevated concentrations of some transition metals. This has previously been applied to selectively recover valuable metals and to remove sulfate from acidic liquors (Ñancucheo and Johnson, 2012; Ňancucheo and Johnson, 2014). The design and application of biosulfidogenic systems can vary with the nature of the solution being treated, and can also be used in tandem with other selective metal recovery methods (Hedrich and Johnson, 2012).

This study describes the development of a system for recovering metals from pregnant leach solutions (PLS) generated by bioleaching of a copper concentrate, using a combined chemical and biological approach. The proposed technique involves two chemical recovery steps (i) initial SX/EW stage for Cu recovery and (ii) subsequent selective precipitation of excess soluble ferric iron. In a next step, the process flow splits into (iii) a further chemical main path (precipitation and IX) and (iv) an alternative path of biological metal sulfide precipitation.

2. Materials and methods

2.1. Pregnant leach solution chemistry

Biological metal recovery experiments were carried out with synthetic PLS (PLS 1) to establish the process and due to the sensitivity of the biological system. Chemical recovery experiments also used synthetic PLS 1 in preliminary experiments and a PLS from tank reactor bioleaching (PLS 2) to test actual conditions and reproducibility. The synthetic PLS was based on the chemistry of that generated by the bioleaching of flotation copper concentrate (provided by the company KGHM, Poland) from *Kupferschiefer* (a black shale ore, found throughout central Europe) in stirred tank bioreactors using acidophilic, moderately-thermophilic bacteria (Spolaore et al., 2011; Hedrich et al., 2016, 2018). The PLS had an average pH of 1.6 and elemental composition as in Table 1. All elements were added as sulfate salts, except chloride as sodium salt (NaCl). PLS 2 had a pH of 1.3 and a higher copper content of ca. 47 g/L but otherwise showed an elemental composition similar to PLS 1 (Table 1).

Table 1
Composition of synthetic PLS (PLS 1) and actual PLS (PLS 2) from copper concentrate bioleaching (g/L).

	As	Cu	Fe	Zn	Ni	Co	SO_4^{2-}	Ca	Mg	Cl
PLS 1	0.45	31	7.4	2.3	0.07	0.35	86	0.56	4.0	0.39
PLS 2	0.26	47	7.9	4.6	0.12	0.56	115	0.68	5.9	0.95

2.2. Chemical metal recovery path

2.2.1. Copper recovery by SX/EW

2.2.1.1. Cu-SX. For Cu-SX experiments the extraction agent LIX984N (25% LIX984N in Exxsol D100) was applied. Initially, extraction and stripping isotherms were generated followed by deduction of suitable parameters using the McCabe-Thiele-method. The defined parameters were applied in experiments simulating a counter-current-flow extraction using PLS 1 and 2, and a typical strip electrolyte (SE) to generate a Cu-reduced raffinate and a rich electrolyte (RE). The experiments were conducted in glass beakers at room temperature under magnetic stirring (1000 rpm, 15 min). Phase separation was accomplished by separating funnels after 3–5 min of segregation. Aqueous and organic phases were analyzed for Cu and Fe. Feed PLS and produced raffinate were analyzed in more detail.

2.2.1.2. Cu-EW. Tests on Cu-EW were carried out in a glass tank (~1.5 L) filled with artificial RE ($CuSO_4/H_2SO_4$ solution, ~55 g/L Cu, ~180 g/L H_2SO_4) or with actual RE produced by SX of PLS 2. In case of actual RE an additional filtering step with active carbon had to be performed prior to the EW-step to remove residual traces of extraction agent. The actual RE from the SX step was applied to a 100 mL column filled with 35 g of washed and conditioned activated carbon under continuous flow (100 mL/h). The EW-test cell comprised up to three stainless steel sheets (cathodes, 60 × 115 × 1 mm) and up to four lead sheets (anodes, 65 × 120 × 1.5 mm) which were mounted in alternating order and connected in parallel. A current intensity of up to 5 A (voltage: 2–3 V) was applied. Electrolysis took place for ca. 5–7 h under continuous mixing of the electrolyte by magnetic stirring.

2.2.2. Precipitation of iron and remaining copper

In order to precipitate excess iron, the pH of the previously produced SX-raffinate was increased to 3.2 by adding 10% $CaCO_3$ suspension (chalk, permanently stirred during addition) under continuous mixing. The Fe/gypsum precipitate was separated by centrifugation followed by washing with distilled water. The clear solution including washing water was treated with 2 M NaOH to increase the pH to 5.5. The further procedure was analogous to the previous precipitation. Samples of the clear solution including washing water of both precipitation steps were analyzed by ICP-MS.

2.2.3. Separation of other metals

The metals still remaining in the PLS after the previous recovery steps (mainly divalent cations such as Zn, Co and Ni) were separated using ion exchange (IX) columns. The weakly acidic IX resin Lewatit TP 207 (Lanxess Germany) suitable for adsorption of divalent metal cations (Me^{2+}) was chosen for this purpose. The solution which was produced by passing PLS 2 through all previous recovery steps (SX, Fe and Cu precipitation steps) served as test solution. A total volume of 400 mL test solution was applied to a test column filled with 50 g of washed and conditioned IX resin under continuous flow (100 mL/h). The effluent liquors were sampled after each 100 mL and analyzed by ICP-MS for relevant Me^{2+}.

2.2.4. Bioleach residue treatment and lead/silver recovery

Metals still remaining in the bioleached residues, such as lead and silver, were recovered by secondary leaching tests using hot brine solutions. The tests included mixing of the residue material (5 or 10% (*w/v*)) with solutions that contained different NaCl concentrations (100 g/L, 175 g/L or 350 g/L) and were adjusted to different pH values (I: without pH adjustment, II: pH 2 by addition of 5% (w/v) HCl solution, III: pH 0 by addition of 35% (w/v) HCl solution, IV: pH 0 by direct application of 5% (w/v) HCl solution as reaction media) followed by stirring the mixture at 85 °C for 2 h. After cooling to room temperature, solid-liquid separation took place. A sample of each of the separated leaching solutions was analyzed by ICP-MS. The experiments comprised initial test series using 5 g dry mass each in 100 mL volumes to study different NaCl concentrations and pH adjustments. Several residues derived from bioleaching under different conditions were used for this and contained on average ca. 6% Pb, 3–4% Fe, 1.5–2% Cu, 0.5% Zn and ca. 850 mg/kg Ag. A final approach with 50 g dry mass in 1 L was conducted by using optimized conditions to produce a sufficient volume of leaching solution for subsequent silver and lead recovery tests. These tests involved a slow pH increase with Na_2S-solution and Na_2S-/NaOH-solution to pH 0, pH 2 or pH 4. After solid-liquid-separation samples of the clear solution were analyzed.

2.3. Biological metal recovery

The recovery of chalcophilic metals (Cu, Zn, Co and Ni) was achieved as metal sulfides via controlled biomineralization using a sulfidogenic bioreactor system. Biological metal sulfide recovery was tested for its potential as economic and environmental-benign alternative to chemical metal recovery.

2.3.1. Sulfidogenic system and set up

The system consisted of an acidic, sulfidogenic upflow biofilm reactor which contained a mixed microbial community of acidophilic, sulfate-reducing and other bacteria immobilized on porous glass beads (Poraver Dennert GmbH, Germany). The bioreactor used a low cost electron donor (glycerol) and had the additional advantage of lowering the sulfate content of the liquor as sulfate served as electron acceptor for the sulfidogens and was converted to hydrogen sulfide, which then reacted with the metals to form metal sulfides.

The design and operation of the system is similar to that described by Ñancucheo and Johnson (2012). The working volume of the system was 2.3 L, temperature was set at 30 °C and a continuous stream of nitrogen (200 mL/min) was used to maintain a slight positive pressure within the reactor vessel and to remove excess H_2S present. The bioreactor was operated in continuous mode and the pH varied between 2.0 and 6.0. The bioreactors were fed with (iron-free) PLS (pH ~2.0) additionally containing various amounts of glycerol as electron donor for the bacteria, yeast extract (at 0.01%, *w/v*) as a source of growth factors and basal salts (Ňancucheo et al., 2016). Metals were added to the synthetic liquor as sulfate salts, and NaCl was included to give the equivalent amount of chloride as in actual PLS 1. In order to determine at which stage in the metal recovery process the sulfidogenic system could be integrated, experiments were carried out using concentrated PLS 1 (Table 1) as well as pre-treated PLS (e.g. after chemical metal recovery).

2.3.2. Selective metal recovery

Selective metal precipitation with the sulfidogenic system was achieved by controlling the pH of the process, as the metal sulfides concerned have different solubility products and form at different pH values, since the relative concentration of the reacting sulfide species (S^{2-}) is pH-dependent (Table 2).

In order to selectively recover chalcophilic metals from PLS 1, several facts have to be considered when setting up the system. First of all the solubility products of the metal sulfides (Table 2), which determine the precipitation order of the metals in the following order Cu → Zn → Ni = Co. The solubility products of CoS and NiS are very similar, leading to a concurrent precipitation. Secondly, H_2S predominantly reacts with the high amounts of ferric iron in the PLS reducing it to ferrous iron and thereby consuming a lot of H_2S and producing elemental sulfur, which requires the ferric iron to be removed upfront. Thirdly, the high sulfate content (0.9 M) of the PLS could be toxic for the sulfate-reducers and slow down their activity.

Table 2
Solubility products of target metal sulphides (Monhemius, 1977).

metal ion	Cu^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	Fe^{2+}
log K_{sp}	−35.9	−24.5	−22.1	−21.0	−18.8

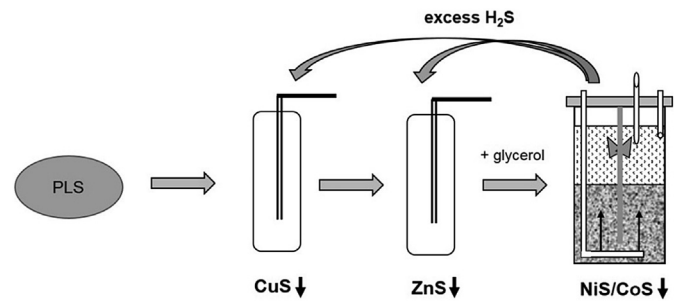

Fig. 1. Final treatment scheme for the recovery of chalcophilic metals via sulfidogenesis.

The optimum operational conditions for the selective recovery of target metals (Cu, Zn, Co and Ni) from the PLS using the sulfidogenic system were investigated. Therefore, the metal sulfides were precipitated in the order displayed in Fig. 1, with Cu and Zn recovered by sparging 150 mL PLS 1 in 250 mL bottles with biogenic H_2S. Ni and Co were recovered within the 2 L-bioreactor. The sulfidogenic bioreactor was fed with Cu-, Fe- and Zn-free PLS supplemented with glycerol (4–31 mM) and yeast extract (at 0.01%, *w/v*) and pH was adjusted to about 2.0. The optimum operational conditions (e.g. pH and glycerol concentration) for the selective recovery of target metals from the PLS using the sulfidogenic system were determined by replicating each experiment 3 to 5 times.

2.4. Analytical methods

2.4.1. Chemical analyses

pH measurements were carried out using a Blueline 18 pH electrode (Schott, Germany). Dissolved metals were determined in filtered, acidified samples using ICP-OES (Varian SpectrAA-300). Metal sulfide precipitates were washed, dried and analyzed by X-ray diffraction for purity. Glycerol and acetate concentrations were analyzed by HPLC with a diode array detector using an Applichrom ABOA SugarSep-H column or an Eclipse Plus C8 column, respectively. Sulfate was determined by ICP-OES (Spectro).

2.4.2. Bioreactor community analysis

To determine the microbial community composition during the course of the experiment about 5 mL of slurry sample was centrifuged for 10 min at 13,000 × *g*. The resulting pellet was subject to DNA extraction using the FastDNA Spin Kit for Soil (MP Biomedicals) following a modified extraction protocol (Webster et al., 2003). Polymerase chain reaction and terminal restriction fragment length analysis (T-RFLP) was carried out as described by Hedrich et al. (2016).

3. Results and discussion

3.1. Chemical metal recovery

3.1.1. Copper recovery by SX/EW

3.1.1.1. Solvent extraction. The generation of isotherms and application of McCabe-Thiele-method provided the following parameters: three extraction steps with organic/aqueous (O/A) ratio 3.7/1 for production of a raffinate with ~5 g/L Cu and two stripping steps with O/A ratio 3.1/1 for generation of RE with ~55 g/L Cu. The defined parameters were applied in a subsequent counter current flow extraction experiment to produce RE with the predicted copper content. The analyzed copper concentrations in the different fractions was in good accordance with the theoretical values of the isotherms. The raffinate contained ~5.2 g/L Cu corresponding to an extraction of ~85% (Fig. S1). No further metals of interest were co-extracted (with the exception of ca. 5 mg/L molybdenum). The raffinate produced was subject to further precipitation steps.

The SX-tests with PLS 2 yielded comparable results to those with PLS 1. As the SX process was established for a PLS with a much lower copper content the overall copper extraction was lower and reached ca. 73% (Fig. 2), though the raffinate still contained ca. 12.9 g/L Cu. The co-extraction of other metals likewise was very low (few mg/L of molybdenum, zinc, vanadium and lead, no iron co-extracted). A modified variant of the SX process was performed with PLS 2 by using an increased O/A ratio of 7.5/1, which led to an increase of the Cu-extraction by 10%. In total 82% of Cu were extracted and the raffinate resulting from this treatment contained ca. 8.5 g/L Cu (data not shown).

3.1.1.2. Electrowinning. The initial EW tests used artificial $CuSO_4$-solutions, one cathode-anode pair and concentrated on adjustment of the current intensity in relation to the selected active cathode surface (fixed by electrode number, size and immersion depth) to get an optimal current density and a good copper deposition at the cathode (assumed quality criteria for copper cathodes: light/metallic color, fine grained deposition). Finally, a setup with three cathodes and four anodes at a current density of 250 A/m^2 was tested simulating a larger scale application. The copper cathodes produced met the visual quality criteria. In addition, the available active cathode surface, separable copper mass and deposition speed were increased using this setup. The electrolysis efficiency reached ca. 99% which was not surprising as the used artificial solution did not contain iron which often impairs electrolysis of actual RE solutions. An energy consumption of ca. 2000 kWh per t of Cu was achieved which was comparable to values reached in other projects (Jergensen, 2009; Sole et al., 2016). Due to the usage of artificial $CuSO_4$-solutions a purity analysis of the copper cathodes produced was omitted. However, in a larger scaled process such analyses are obligatory for copper quality evaluation.

The EW tests with actual RE produced via SX of PLS 2 used the optimized electrode setup and current density. A prior filtering step with activated carbon was performed which allowed 92% of the residual traces of extraction agent to be removed. The copper cathodes produced again met the visual quality criteria (light metallic color, finely grained copper deposition). The achieved electrolysis efficiency (96.3%) and energy consumption (ca. 2100 kWh per t of Cu) were also very satisfactory and well comparable to previous tests.

3.1.2. Precipitation of iron and remaining copper

During further processing of the SX raffinate, Fe was precipitated within a mixture of iron hydroxy sulfate/schwertmannite/gypsum, and copper as hydroxide. Both precipitation steps led to only low losses of other metals (e.g. Zn, Co, Ni) (Fig. S1b, Fig. 2b). Iron precipitation resulted in a nearly complete removal of arsenic by co-precipitation. This effect is generally considered as a benefit, but also raises new questions concerning costs for the waste material generated. The copper precipitate produced was proposed to be re-introduced into the Cu-EW step by dissolution into the electrolyte, given that the precipitate's purity is sufficient, or may be directly utilized as a chemical compound. Further tests on sedimentation and solids separation of both precipitates were also carried out (data not shown). The results achieved with both solutions based on PLS 1 and 2 were in good accordance and showed a good reproducibility despite the higher copper content in the original solution of PLS 2 (Fig. 2).

3.1.3. Separation of other metals

The IX studies with the weakly acidic cation exchange resin Lewatit TP 207 showed that all relevant divalent metal cations could be completely removed from the solution. The highest residual metal concentration of the solution leaving the IX column was ca. 2 mg/L of both Zn and Mn; Table 3). Exceptions to this were Mg and Ca, which were

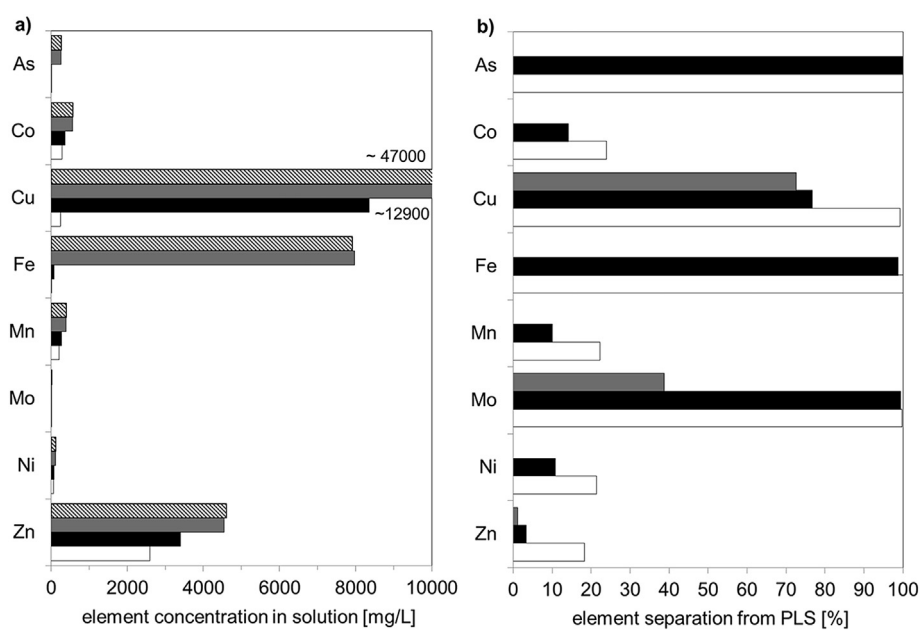

Fig. 2. Results of metal recovery studies with PLS 2 (hatched) after Cu-SX (grey), iron precipitation (black) and copper precipitation (white): (a) elemental concentration in solution; (b) the percentage of metal separation after each recovery step. Percentage values refer to analyzed element masses of the PLS.

Table 3
Results of ion exchange (IX) studies: metal concentrations after the respective volume that passed the IX column.

Volume [mL]	100	200	300	400
Element	Concentration [μg/L]			
Ca	240	< 20	1170	7970
Cd	2.8	2.9	1.4	13.5
Co	10.5	< 0.2	< 0.2	379
Cu	< 1.0	< 1.0	< 1.0	< 1.0
Mg	20	20	602,000	4,330,000
Mn	2.0	< 1.0	< 1.0	1880
Ni	< 1.0	< 1.0	< 1.0	< 1.0
Zn	698	1620	808	2060

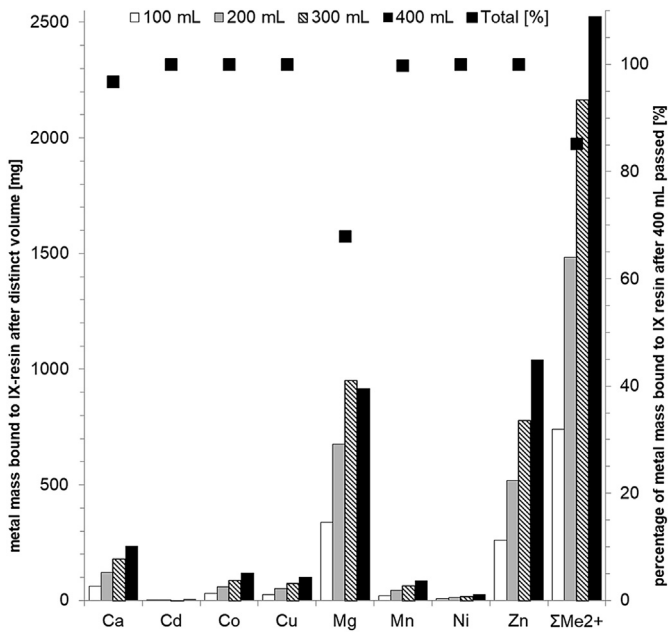

Fig. 3. Results of ion exchange (IX) studies with the solution produced by Cu-SX and Fe/Cu-precipitation of PLS 2 (Fig. 2). The figure shows the metal masses bound to IX resin (each calculated from the difference between the metal masses in the applied solution and the metal mass in the solution leaving the column after distinct volume of the solution passed shown) for single metal cations (bars) and for the total of divalent metal cations (ΣMe^{2+}).
Key: 100 mL - white, 200 mL - grey, 300 mL - hatched, 400 mL – black, total % - ■.

still present at higher concentrations but not in the immediate focus of the recovery test (low selectivity of the IX resin). The summarized metal masses of Cd, Co, Cu, Mn, Ni and Zn present in the applied solution were bound to the IX resin to 100% (total % in Fig. 3). Overall, 2.5 g of divalent transition metals was adsorbed to 50 g of IX resin, corresponding to a recovery rate of ca. 85% of the relevant Me^{2+} present in the applied solution.

The concentrate of separated Me^{2+} resulting from IX may be utilized by conventional processing routes depending on the metal content. The solution leaving the IX step will have to be subjected to further cleaning steps, e.g. for the removal of sulfate and Mg (see below, Fig. 7). Afterwards the clean solution may be directly reused, e.g. by re-introduction into the bioleaching step.

3.1.4. Bioleach residue treatment and lead/silver recovery

Bioleaching failed to mobilize elements like silver and lead from sulfidic matrices due to the fact that Ag is likely contained as recalcitrant sulfide or partially transformed to poorly soluble chloride and Pb is oxidized to lead sulfate which has very low solubility. For the recovery of metals remaining in the residues after bioleaching a series of tests were conducted using hot brine leaching, utilizing the fact that Pb and Ag are complexed by chloride in acidic solutions, e.g.:

$$PbSO_4 + 4NaCl \rightarrow Na_2[PbCl_4] + Na_2SO_4 \quad (1)$$

$$AgCl + NaCl \rightarrow Na[AgCl_2] \quad (2)$$

Initial tests were carried out with 5% (*w/v*) residual material in 100 mL final volume and by using different NaCl concentrations and solution pH (adjusted with HCl). The results showed that leaching performed remarkably better for the assays adjusted to pH 0 than for those adjusted to pH 2 or without pH adjustment. Changing NaCl concentrations had little impact on metal extraction. Assays containing 100 and 175 g/L NaCl provided only slightly better results. In addition, the achieved metal extraction was very similar for the different bioleaching residues processed. In conclusion the extraction tests reached a mobilization of 75–100% Pb, 60–90% Ag, up to 40% Cu, up to 30% Fe and Zn each (data not shown).

To produce sufficient leaching solution for a subsequent test on Pb and Ag separation, larger (1 L) extraction volumes and the same methodology (with optimized pH/NaCl; (Table 4) were used. For one approach (T1) an increased solid load of 10% (*w/v*) was applied to potentially yield a higher concentration of mobilized metals in the solution afterwards. As a result, the relevant metals were mobilized in similar range as in previous tests: ca. 80% Pb, 90% Ag, 40% Cu, 30% Fe, 20% Zn (Fig. 4). The metal concentrations in the leaching solution after hot brine treatment indeed were highest for test T1 and so this solution was used for further tests on Pb and Ag separation. The solution contained ca. 3 g/L Pb, 1.8 g/L Fe, 1 g/L Cu, 130 mg/L Zn and 25 mg/L Ag. The separation of Pb and Ag took place by step wise increasing the pH using Na_2S solution. The results showed that an increase to pH 0 lead to separation of ca. 40% Pb and 100% Ag and Cu each (data not shown). Increasing the pH to 2.0 was sufficient to precipitate 100% Pb. Zinc and iron were completely precipitated after pH increase to pH 4 and pH 7, respectively.

3.2. Biological metal recovery

Biological metal recovery was integrated in the treatment scheme to selectively recover the remaining Cu, Zn, Co and Ni. A single sulfidogenic bioreactor was used, which was responsible for both in-line precipitation of NiS and CoS and off-line precipitation of CuS and ZnS. In order to operate the biological metal recovery system effectively, the initial recovery of ferric iron via the chemical route was essential. The high ferric iron concentrations in the PLS interferes in the sulfidogenic system, as most of the hydrogen sulfide reacts with ferric iron, reducing it to ferrous iron and generating elemental sulfur. This means that the sulfidogenic system would need to produce much more H_2S (113 mM) than that required just to precipitate metal sulfides. Also an additional treatment step would have to be integrated in the process scheme to oxidize the ferrous iron again and precipitate it in order to recover iron from the PLS, which would increase costs of the process. Therefore, we suggest that in a first step soluble ferric iron is precipitated as described in Section 3.1.2.

The advantage of this system in the recovery flow, apart from the selective recovery of chalcophilic metals, is the low-cost operation of these sulfidogenic systems by directly feeding PLS into the bioreactors

Table 4
Conditions of hot brine leaching tests: solid content, NaCl content and final pH.

Test number	T1	T2	T3	T4
Bioleaching residue	1	1	1	2
Solid load [%(w/v)]	10	5	5	5
NaCl [g/L]	175	175	175	175
Final pH	1.96	1.70	−1.22	ca. -1.0

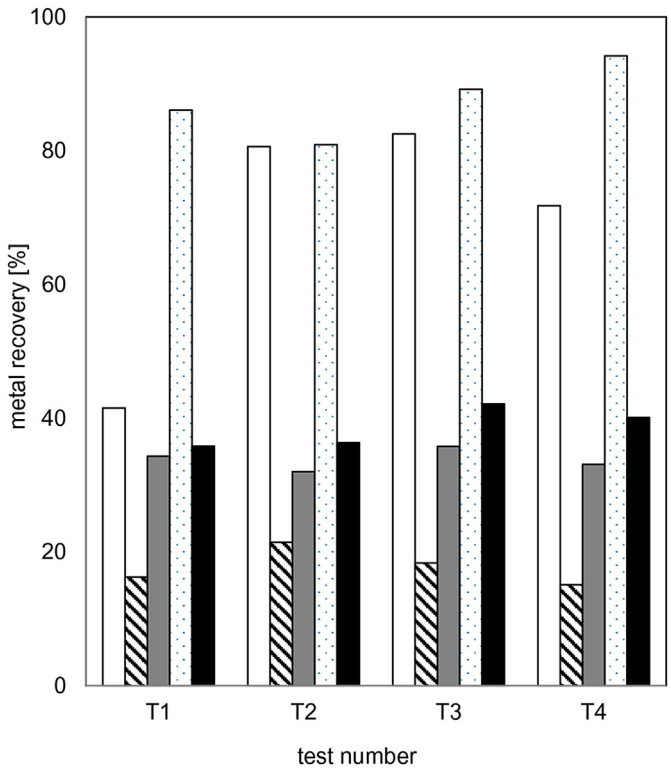

Fig. 4. Results of hot brine leaching tests, showing the percentage of metal recovery for different test conditions T1 – T4 (test conditions are given in Table 4). Pb-white, Zn-hatched, Fe-grey, Ag-dotted, Cu-black.

and removal of the sulfate at the same time.

3.2.1. Copper sulfide precipitation

Copper has the least soluble sulfide phase of the target metals, therefore it requires recovery upfront to avoid co-precipitation with other metals that have larger solubility products and which form at higher pH values. Most of the Cu was recovered via solvent extraction upfront (see Section 3.1.1). There was however still some copper (2.57 g/L) remaining after the first round of solvent extraction (Table 5), which at this concentration could be recovered via biogenic H_2S.

Copper was recovered by flushing the original pre-treated PLS (Table 5) containing 2.57 g/L Cu and a pH of 3.2 with the hydrogen sulfide produced in the SRB reactor when the reactor was operated with 162 mM sulfate and 23 mM glycerol.

Over 99.9% copper recovery from the pre-treated PLS (pH 3.2) as CuS without co-precipitation of other chalcophilic metals (as confirmed by ICP-OES analysis) was achieved at an HRT of 4.0H (Fig. 5). The pH of the PLS dropped from 3.2 to 1.5 (Fig. 5). Chemical and XRD analyses confirmed that no other chalcophilic metals co-precipitated with the CuS.

The chemistry of the pre-treated PLS as given in Table 4 served for all further metal sulfide precipitation experiments.

3.2.2. Zinc sulfide recovery

After successful recovery of copper, the PLS was transferred to a

Table 5
PLS composition (g/L) after Cu recovery via solvent extraction and iron recovery.

Cu	Zn	Ni	Co	SO_4^{2-}	Ca	Mg
2.57	1.16	0.04	0.18	15.56	0.52	2.07

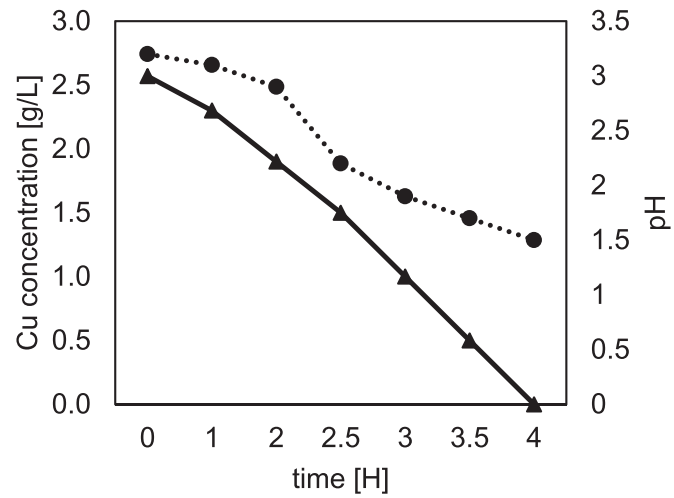

Fig. 5. Copper sulfide precipitation in off-line vessels filled with PLS after Cu recovery by SX/EW flushed with biogenic H_2S from the sulfidogenic bioreactor. The figure depicts changes in Cu concentrations (solid line) and pH (dotted line).

second vessel for zinc sulfide precipitation in the same way as described above for copper. As the sulfidogenic bioreactor was set up to produce enough excess H_2S to precipitate all four chalcophilic metals, a second N_2-gas stream carrying the H_2S was transferred into the zinc precipitation vessel. Since the pH of the PLS was now 1.5, the total acidity (proton plus bisulfate ions) in t, leading to a prolonged hydraulic retention time for full zinc recovery. The final HRT after complete zinc recovery was determined as 3.3 h and a pH of 1.2. Zinc sulfide precipitation could however be enhanced by increasing the pH of the PLS after copper recovery, e.g. by mixing with pre-treated Cu-free liquor from the chemical recovery route or the sulfidogenic bioreactor effluent (see Fig. 1). Nickel and cobalt both remained in solution while zinc was precipitated, leading to a pure ZnS product. The CuS and ZnS produced from the PLS in the separate vessels could therefore directly be used for recovery of pure Cu and Zn without any further metal separation steps.

3.2.3. Nickel and cobalt sulfide recovery

While Cu and Zn were selectively precipitated by sparging the PLS with H_2S in off-line vessels, NiS and CoS were directly precipitated within the bioreactor vessel. Treated PLS from the zinc recovery vessel served as feed medium for the bioreactor. The pH of this liquor was adjusted with NaOH to about 2.0 and glycerol was added up to 23 mM to produce excess H_2S for the recovery of all four target metals. When adding > 23 mM glycerol, its oxidation was incomplete most likely due to the dominance of *Desulfosporosinus* spp. which are incomplete oxidizers and form acetate (Fig. 6) and acetate formation was enhanced. Over 99.9% of the Ni and Co were co-precipitated as sulfide phases. Fine tuning of parameters, such as the bioreactor pH and the glycerol concentration, did not lead to a successful separation of CoS and NiS within the bioreactor (data not shown) as their solubility products are too close (Table 2). The final HRT of the sulfidogenic bioreactor at 162 mM sulfate and 23 mM glycerol was 19.6H. Also the sulfate concentration was no longer a problem for the sulfidogenic bioreactor as the sulfate content (162 mM) after the Cu and Fe recovery was below the inhibition limit (200 mM).

Under these conditions at pH 5.5 only the acid-tolerant *Ds. acididurans* and a bacterium distantly related to *Clostridium* were detected in the sulfidogenic community together with the acetate-consumer *Ac. aromatica* Jones et al., 2013. Other common acidophilic, sulfate-reducing bacteria were absent likely due to the relatively high pH.

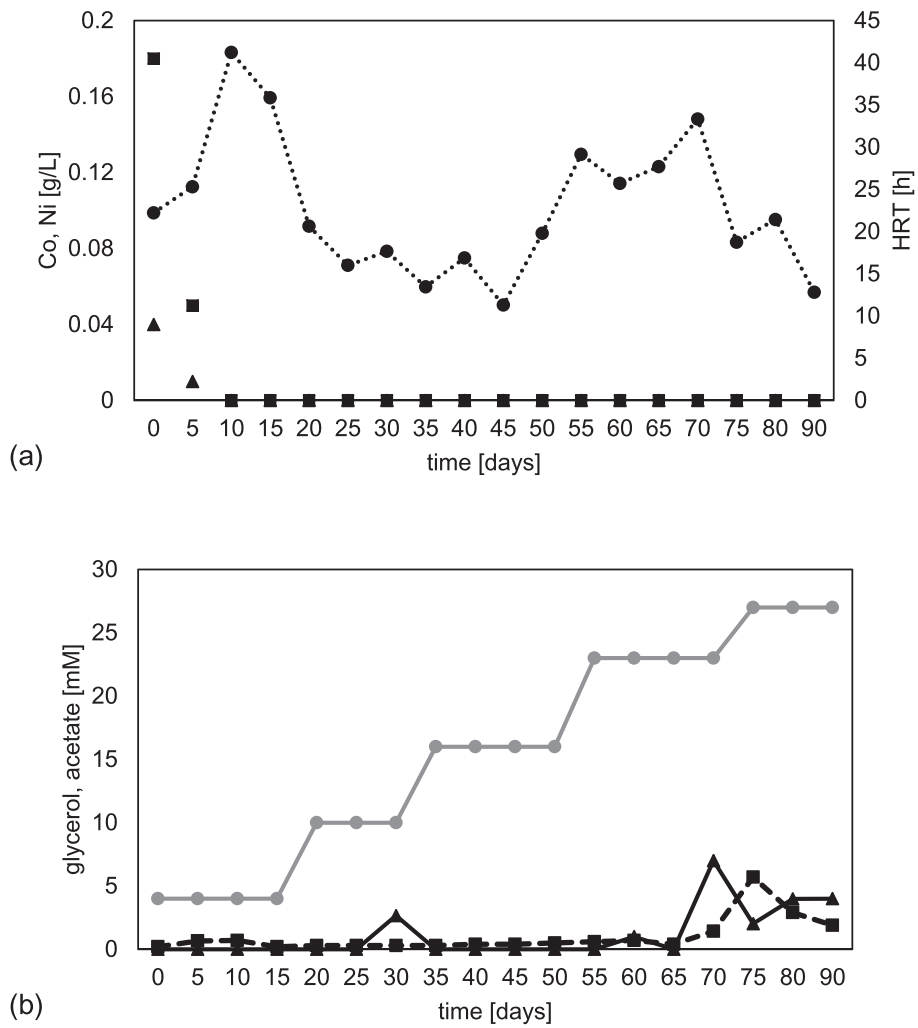

Fig. 6. Precipitation of CoS and NiS at pH 5.5 within the sulfidogenic bioreactor: changes in concentrations of (a) Co (■) and Ni (▲) (and corresponding HRT; dotted line), and (b) glycerol (solid black line) and acetate (dotted black line) (and corresponding glycerol concentration in the feed liquor; grey solid line).

3.3. Summary of the overall metal recovery process

After separately testing the various chemical and biological metal recovery process steps the following combined flow sheet is proposed (Fig. 7). The process starts with two chemical process steps comprising an initial SX/EW stage for soluble Cu recovery and subsequent selective precipitation of soluble ferric iron as iron hydroxy-sulfate. After this step, the process flow is split into a further chemical main path (Cu precipitation and IX) and an alternative one using biological metal sulfide precipitation. For the biological route a sulfidogenic bioreactor is applied to produce hydrogen sulfide from the PLS to precipitate under controlled conditions NiS and CoS within the bioreactor and CuS and ZnS in separate off-line vessels. The parallel chemical route involves precipitation of remaining Cu and IX for the recovery of the remaining mainly divalent metal cations. Both, the biological and chemical route lead to a “metal-free” PLS, which can be reintroduced into the bioleaching operation (after further cleaning steps, in particular for sulfate and Mg removal). As the chemistry of the PLS fed into the metal recovery plant can vary depending on the mineral and the bioleaching efficiency, the alternative routes are integrated to be able to counteract the varying PLS chemistries.

4. Conclusion

A multi-stage metal recovery system is proposed for selectively recovering metals from a low pH, mixed-metal (bio)leach solution, which combines chemical process steps and metal sulfide precipitation via biological sulfidogenesis. The system involves initial SX/EW to extract and recover copper, followed by excess iron precipitation to remove the high amounts of these metals before the final biological step, involving a sulfidogenic bioreactor and two connected vessels to selectively precipitate remaining CuS, ZnS and NiS/CoS. An alternative chemical pathway allows the selective recovery of remaining Cu and other metals (e.g. Zn, Co, Ni) using IX. Another important component of the system uses hot brine to extract Ag and Pb from the (bio)leach residues. The system has been designed to selectively recover all relevant metals from the PLS in line with a zero waste strategy, and its modular arrangement allows an independent operation of the units and the integration of further modules depending on the compositions of various leach solutions, either generated in bioleaching processes for sulfide ores or chemical acid leaching of oxide ores.

Acknowledgement

This study as part of the project Ecometals was funded by the German Federal Ministry for Education and Research (BMBF), funding number is 033RF001. We are grateful to the project partner BRGM (France) for supply of the data for the synthetic PLS, and KGHM (Poland) for providing a copper concentrate. We thank at G.E.O.S. Anke Patzig and Jacqueline Engel for support with experiments. We thank at

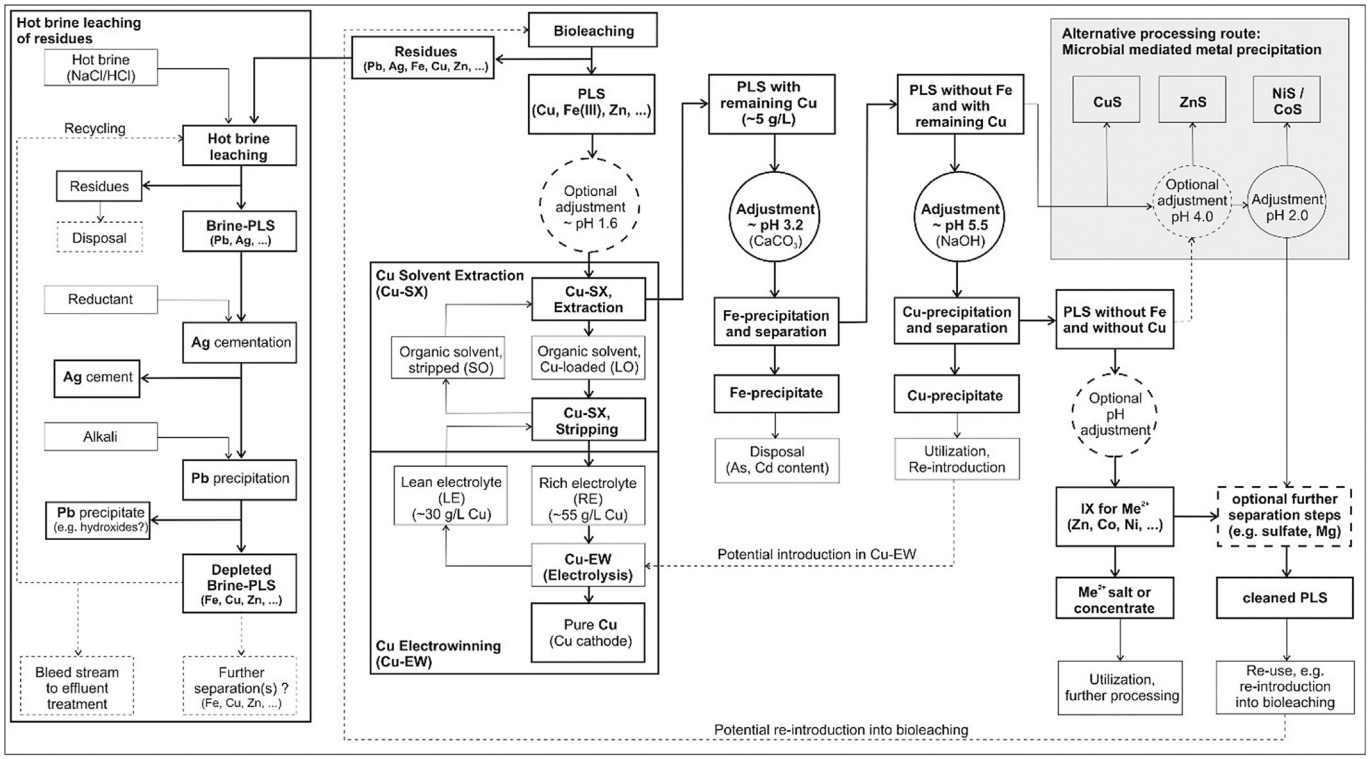

Fig. 7. Proposed treatment scheme for PLS resulting from copper concentrate bioleaching.

BGR Isabell Kruckemeyer for support with experiments, Detlef Spier for HPLC measurements and method development and Jens Stummeyer for ICP-OES analyses.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2018.06.012.

References

Attia, Y.A., El-Zeky, M., 1990. Effects of galvanic interactions on sulfides on extraction of precious metals from refractory complex sulfides by bioleaching. Int. J. Miner. Process. 30, 99–111.

Boonstra, J., van Lier, R., Janssen, G., Dijkman, H. Buisman, C.J.N., 1999. Biological treatment of acid mine drainage in: R. Amils, R.A. Ballester (Eds.) Biohydrometallurgy and the Environment toward the Mining of the 21st Century. Process Metallurgy vol. 9B, Elsevier, Amsterdam, pp 559–567.

Brierley, C.L., 2016. 2016. Biological processing of sulfidic ores and concentrates – integrating innovations. In: Lakshmanan, V.I., Roy, R., Ramachandran, V. (Eds.), Innovative Process Development in Metallurgical Industry. Springer International Publishing, Switzerland, pp. 109–135.

Dutrizac, J.E., 1987. An Overview of Iron Precipitation in Hydrometallurgy. In: Strathdee, G.L., Klein, M.O., Melis, L.A. (Eds.), Crystallization and Precipitation. Proceedings of the International Symposium, Saskatoon, Saskatchewan, Canada, 5–7 October. Burlington. Elsevier Science, pp. 259–283.

Fomina, M., Gadd, G., 2014. Biosorption: current perspectives on concept, definition and application. Bioresour. Technol. 160, 3–14.

Hedrich, S., Johnson, D.B., 2012. A modular continuous flow reactor system for the selective biooxidation of iron and precipitation of schwertmannite from mine-impacted waters. Bioresour. Technol. 106, 44–49.

Hedrich, S., Guézennec, A.-G., Charron, M., Schippers, A., Joulian, C., 2016. Quantitative monitoring of microbial species during bioleaching of a copper concentrate. Front. Microbiol. 7, 2044.

Hedrich, S., Joulian, C., Graupner, T., Schippers, A., Guézennec, A.-G., 2018. Enhanced chalcopyrite dissolution in stirred tank reactors by temperature increase during bioleaching. Hydrometallurgy 179, 125–131.

Janneck, E., Arnold, I., Koch, T., Meyer, J., Burghardt, D., Ehinger, S., 2010. Microbial synthesis of schwertmannite from lignite mine water and its utilization for removal of arsenic from mine waters and for production of iron pigment. In: Wolkersdorfer, C., Freund, A. (Eds.), Mine Water & Innovative Thinking: Proceedings of the International Mine Water Association Symposium 2010. Cape Breton University Press, Sydney, Canada.

Jergensen, G.V., 2009. Copper Leaching, Solvent Extraction, and Electrowinning Technology. Society for Mining, Metallurgy and Exploration (SME), Littleton, CO, USA.

Jones, R.M., Hedrich, S., Johnson, D.B., 2013. Acidocella aromatica sp. nov.: an acidophilic heterotrophic alphaproteobacterium with unusual phenotypic traits. Extremophiles 17, 841–850.

Monhemius, A.J., 1977. Precipitation diagrams for metal hydroxides, sulfides, arsenates and phosphates. Trans. Inst. Min. Metall. 86, C202–C206.

Ňancucheo, I., Johnson, D.B., 2012. Selective removal of transition metals from acidic mine waters by novel consortia of acidophilic sulfidogenic bacteria. Microb. Biotechnol. 5, 34–44.

Ňancucheo, I., Johnson, D.B., 2014. Removal of sulfate from extremely acidic mine waters using low pH sulfidogenic bioreactors. Hydrometallurgy 150, 222–226.

Ňancucheo, I., Rowe, O.F., Hedrich, S., Johnson, D.B., 2016. Solid and liquid media for isolating and cultivating acidophilic and acid-tolerant sulfate-reducing bacteria. FEMS Microbiol. Lett. 363 (10) (fnw083).

Santos, A.L., Johnson, D.B., 2017. The effects of temperature and pH on the kinetics of an acidophilic sulfidogenic bioreactor and indigenous microbial communities. Hydrometallurgy 168, 116–120.

Schippers, A., Hedrich, S., Vasters, J., Drobe, M., Sand, W., Willscher, S., 2014. Biomining: metal recovery from ores with microorganisms. In: Schippers, A., Glombitza, F., Sand, W. (Eds.), Geobiotechnology I – Metal-Related Issues, Advances in Biochemical Engineering & Biotechnology. vol. 141 Springer, Heidelberg.

Schlesinger, M.E., 2011. Extractive Metallurgy of Copper. Elsevier, Amsterdam, Boston.

Sole, K.C., Mooiman, M., Hardwick, E., 2016. Present and Future Applications of Ion Exchange in Hydrometallurgy: An Overview. In: International Ion Exchange Conference IEx. At Cambridge, UK, pp. 2016.

Spolaore, P., Joulian, C., Gouin, J., Ibanez, A., Auge, T., Morin, D., D'Hugues, P., 2009. Bioleaching of an organic-rich polymetallic concentrate using stirred-tank technology. Hydrometallurgy 99, 137–143.

Spolaore, P., Joulian, C., Gouin, J., Morin, D., d'Hugues, P., 2011. Relationship between bioleaching performance, bacterial community structure and mineralogy in the bioleaching of a copper concentrate in stirred-tank reactors. Appl. Microbiol. Biotechnol. 89, 441–448.

Webster, G., Newberry, C.J., Fry, J., Weightman, A.J., 2003. Assessment of bacterial community structure in the deep sub-seafloor biosphere by 16S rDNA-based techniques: a cautionary tale. J. Microbiol. Meth. 55, 155–164.