Membrane selective recovery of HCl, zinc and iron from simulated mining effluents

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ABSTRACT

This work proposes a flowsheet based on the combination of membrane processes for the effective recovery of value-added components contained in mining effluents with high concentration of hydrochloric acid and metal anionic and cationic chloro-complexes. A representative case of study has been selected consisting of a solution of zinc and iron that under the studied conditions were solubilized forming anionic and cationic chloro-complexes. The high complexity of the system requires of a selective membrane-based solvent extraction step to successfully achieve the separation of cationic iron from a solution containing the acid together with anionic species of zinc followed by a diffusion process through ion conductive membranes for acid recovery; in this step electrodialysis was selected searching for the optimum trade-off between process kinetics and separation selectivity. Although the quantitative results are case-dependent, the methodology can be well extended to any mining leaching effluent coming from the use of HCl as leaching agent and containing metal chloro-complexes.

1. Introduction

Hydrometallurgical beneficiation of mining ores involves different operations such as leaching, solvent extraction, ion exchange and precipitation, whose selection depends on the metal to be recovered [1]. Regarding the leaching step, processed materials from mining and extraction industry are commonly treated using strong acidic or basic solutions to selectively dissolve the metals of interest. Among the acids, sulfuric acid and hydrochloric acid are most frequently used. This results in moderate (0.35–$0.55\,g\,L^{-1}$) to high (1.5–$7.2\,g\,L^{-1}$) sulphate/chloride concentrated effluents also containing the metals of interest such as copper, zinc, cadmium, arsenic, manganese, aluminum, lead, nickel, silver, mercury, chromium, iron, rare earths (REs) as well as the platinum-group metals (PGMs) in a concentration that can range from 10^{-6} to $10^2\,g\,L^{-1}$ [1–3].

During the past decades the use of chloride hydrometallurgy has increased due to several reasons such as, i) the feasibility and success of the already existing operations, ii) new and more resistant construction materials and improved engineering know-how, iii) the extraordinary solution power of HCl for many minerals including oxides, hydroxides and carbonates, and iv) ease of separation of many chlorides through processes such as ion exchange, solvent extraction, valence changes, precipitation and crystallization. Thus, the potential of the chloride

systems to operate over a wide range of oxidizing conditions and acidity has triggered its use in hydrometallurgical operations [4]. Cheng et al. reported the benefits of acidic leaching using HCl to recover zinc from hemimorphite ores [5].

In chloride solution, metal ions react with Cl^- and different species are formed. For the systems $HCl + NiCl_2$ [6,7], $HCl + FeCl_2$ [6,8] $HCl + CuCl_2$ or $HCl + CrCl_3$ [6] cationic chlorocomplex species exist in the solution. For the system $HCl + ZnCl_2$ [6,7,9–11] the presence of anionic and cationic complexes with Cl^- has been reported, i.e. $ZnCl^+$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ depending on the relative concentration of HCl and Zn in the medium. The simultaneous presence of chlorides and anionic zinc chlorocomplex species makes their separation highly difficult thus being an interesting scientific challenge.

Application of membrane technology to the separation of metal ions in solution requires the use of selective and ion conductive membranes. Here, two groups of selective membranes that have reported excellent results so far, i) membrane-based solvent extraction, that combines the advantages of selective solvents to solubilize the target solute together with the use of membrane contactors to provide efficient equipment and process operation, and ii) electrodialysis (ED) with ion conductive membranes, that enhances the transport kinetics of the target species through charged membranes by means of electric current.

Among the membrane-based solvent extraction configurations,

Symbol used

A	membrane area, $[m^2]$
C	solute concentration, $[kmol\,m^{-3}]$
D	solute diffusion coefficient, $[m^2\,h^{-1}]$
D_0	diffusivity constant, $[m^2\,h^{-1}]$
F	Faraday constant, $[C\,mol^{-1}]$
I	electrical current, $[A]$
J	molar flux, $[kmol\,m^{-2}\,h^{-1}]$
$J_{Losses,i}$	lost ions molar flux, $[kmol\,m^{-2}\,h^{-1}]$
k	constant, $[m^3\,h^{-1}]$
L	thickness, $[m]$
n	number of moles, $[mol]$
N	number of cell pairs, $[—]$
R	universal gas constant, $[J\,mol^{-1}\,K^{-1}]$
Re	resistance, $[\Omega]$
$S_{HCl/Zn}$	selectivity of HCl towards Zn, $[—]$
t	time, $[h]$
T	temperature, $[K]$
V	volume, $[m^3]$
y	coordinate, $[m]$
z_i	charge number of the ion i, $[—]$

Greek letters

α_ι	constant, $[m^3\,mol^{-1}]$

β_ι	resistance parameter, $[—]$
η_ι	electric current efficiency, $[—]$
υ	species velocity, $[m\,h^{-1}]$
φ	electrical potential, $[V]$

Superscripts

global	total amount
m	membrane
tk	tank

Subscripts

C	concentrated solution
D	diluted solution
i	specie "i", (HCl, Zn)
in	inlet
initial	initial amount
final	final amount

Initial

out	oulet

non-dispersive solvent extraction (NDSX) using microporous hollow-fiber (HF) contactors has received considerable attention and has been proved to be very effective in the removal of solutes from aqueous solutions. Membrane-based non-dispersive extraction is characterized by the stabilization of the organic–aqueous interface at a porous material, avoiding the dispersion of the organic phase into the aqueous phase or vice versa and, thus, eliminating emulsion formation and phase entrainment. Additional advantages of non-dispersive solvent extraction have been widely mentioned in the literature. A number of successful applications has been reported so far with NDSX technology: (i) removal of Cr(VI) from groundwaters [12,13], (ii) removal of Cd from phosphoric acid [14], (iii) separation of Ni/Cd mixtures [15], (iv) removal of Cu(II) [16,17] and (v) selective separation of Zn(II) from spent pickling effluents [18–20].

ED is a technology in which, ion-exchange membranes in combination with an electrical potential difference are used to remove ionic species from aqueous solution [21,22]. ED was firstly developed for desalting brackish waters, brine production from seawater and demineralization of whey [23,24]. Recently, ED has been used for the treatment of various types of effluents from the food industry; biotechnology and chemical applications, which are steadily increasing [25–27]. Thus, ED is being widely applied for the production of organic acids, amino acids from fermentation processes, sugar demineralization, blood treatment, wine stabilization, fertilizers, etc. However, only few applications have been commercialized so far [21,28].

The development of new ion-exchange membranes improves the performance of electrodialysis technology (ED) and offers an attractive alternative to the treatment of industrial effluents such as waste acids and salts solutions [29,30]. In this field interesting works have been published i) on the purification and concentration of acids from metallurgical processes and surface treatment operations or spent industrial solutions [31,32], ii) the treatment of industrial copper and zinc electrolytes contaminated with multiple compounds [33], iii) the separation of aqueous $CuSO_4$ + H_2SO_4 solutions with a wide range of impurities and additives [34] or, iv) the separation of NaOH and NaAl (OH)$_4$ in alumina alkaline solution from alumina industries [30].

The main novelty of this work is the recovery of three valuable compounds namely Zn, Fe and HCl from acidic effluents using a combination of best available technologies (BAT) such as solvent extraction and electrodialysis [11,13,18,19]. In particular, this work aims to contribute to the definition of membrane processes based on their combination for the integral recovery of metal ions and mineral acids; as a case study, the methodology reported is focused on the separation of complex mixtures containing high concentration of iron (Fe^{+2}), zinc and hydrochloric acid; the difficulty of this separation lies first in finding a suitable technology for the separation of zinc and iron chloro-complexes from the acidic medium and second in the recovery of HCl from the mixture with high concentration of zinc chloro-complexes.

2. Experimental section

The separation of the multicomponent mixture containing iron, hydrochloric acid and zinc is carried out in two steps. The first step, based on the application of NDSX technology, provides two streams: an iron enriched raffinate for further reuse and a stripping phase containing HCl and $ZnCl_2$. The second step aims to separate both components, HCl from zinc species, employing electrodialysis in order to recover the acid and Zn that could be benefited by eletrowining (Fig. 1).

Fig. 2 shows the NDSX experimental set up. For the simultaneous extraction (EX) and back-extraction (BEX) steps, two HF modules are used, flowing the organic phase (extraction agent) from the EX module to the BEX one. Pure tributyl phosphate (TBP) and service water were selected as selective extractant and stripping agent, respectively. In the first module, the anionic and neutral species (zinc chloro-complexes and hydrochloric acid) are transfered from the aqueous feed to the organic phase, and, in the second module, the solutes are transported to the stripping phase. HF modules have an effective mass-transfer area of $1.4\,m^2$ (liquid cell-membrane).

In the experiments carried out for the technical assessment, the aqueous phases were pumped at $30.0 \times 10^{-3}\,m^3\,h^{-1}$ through the inner side of the microporous HF membranes whose pores were filled with the organic extractant. The organic extractant was pumped at $35.0 \times 10^{-3}\,m^3\,h^{-1}$ co-currently in the shell side of both HF modules. Three flow meters were used to monitor the flow rates of the feed,