

## Selectrodialysis and ion-exchange resins as integration processes for copper and zinc recovery from metallurgical streams containing arsenic

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**Highlights:** SED is an innovative technology for metallurgical effluents treatment; IEX resin is an efficient methodology for metal separation and concentration steps; Cu and Zn were recovered by means of integration processes (SED and IEX resins)

**Keywords:** selectrodialysis; ion-exchange process; metal recovery; free-arsenic stream; metallurgical industry; circular economy.

### 1. Introduction

Nowadays, the shortage of water and the need to reduce the associated environmental impacts make it necessary not only to treat it but also to reuse the wastewater. In addition, all industrial sectors generate waste effluents with great potential to be valorized. The metallurgical sector is an industry that produces acid currents that contain heavy metals (e.g. copper (Cu), zinc (Zn)) and impurities (e.g. arsenic (As)). Heavy metals have an added value, which could be obtained by the metallurgical waste-stream treatment.

In this study, a circular economy scheme is proposed in order to be able to take advantage of an acidic effluent produced in the copper and zinc metallurgical industries. From this point of view, two ion-exchange (IEX) technologies were used to separate and concentrate its main elements (Cu, Zn and As): (i) selectrodialysis (SED) following by (ii) IEX resins. Figure 1 shows the flowchart of integrated processes (SED and IEX resins) for copper and zinc recovery and arsenic removal from acidic metallurgical streams.

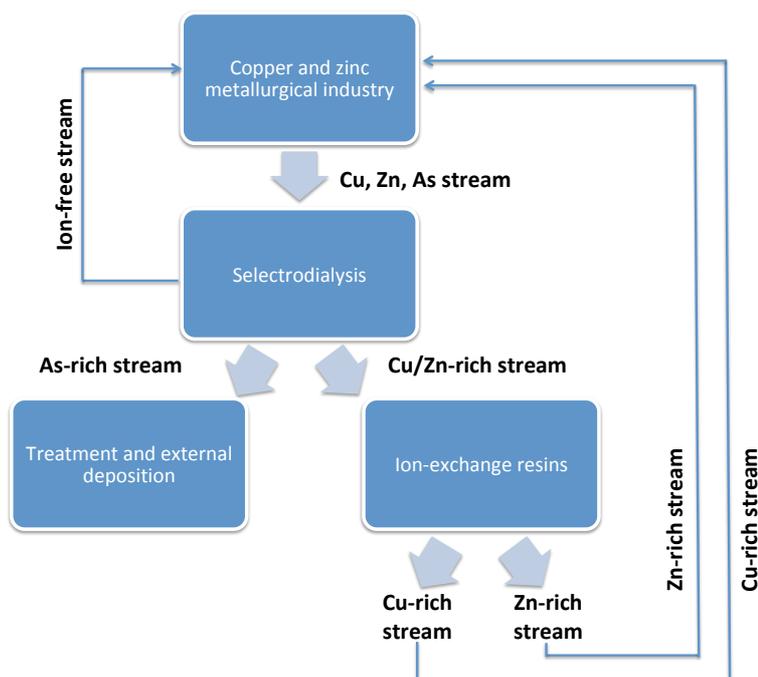


Figure 1. Circular economy scheme purposed for copper and zinc recovery and arsenic removal in the metallurgical industry.

By means of a novel electrodialysis-based technology, named SED, is possible to separate different charged ions when electrical current is applied, using standard and mono-selective membranes (Zhang et al. 2012; Reig et al. 2018). In this study, SED was used to separate As from Cu and Zn. Afterwards, the obtained As-rich stream could be treated properly for external disposal, taking into account the arsenic toxicity. Besides, after the SED process, a Cu/Zn-rich stream was also obtained. Subsequently, two ion-exchange resins were used to separate both ions (Cu and Zn) in order to reuse both streams in the copper and zinc metallurgical industries, respectively (Juang et al. 1992).

## 2. Material and Methods

An ED lab-scale set-up (ED 64-4) supplied by PCCell (Germany) was employed to conduct the SED experiments. Fujifilm Manufacturing Europe B.V (Netherlands) membranes (standard anionic, standard cationic and monovalent selective cation-exchange) were placed between two electrodes and constant voltage of 7 V was applied. An acidic metallurgical stream containing 170 mM Cu(II), 70 mM Zn(II) and 110 mM As(V) was treated in order to be able to separate the As from Cu and Zn. Initial solution in the Cu/Zn-rich compartment was 300 mM H<sub>2</sub>SO<sub>4</sub>; whereas initial solutions in the As-rich compartment and electrode rinse streams were 100 mM Na<sub>2</sub>SO<sub>4</sub>. Samples collected during the experiments were analysed by inductively coupled plasma (ICP) to determine Cu, Zn and As concentrations in each stream along the time.

Once an As-free stream was obtained, the Cu/Zn-rich stream was treated by IEX resins in a fixed-bed configuration (1.1 cm internal diameter and 7.5 cm height), using 2.75 g of resin at 1.95 mL/min of flow rate, in order to separate Cu from Zn. Two different IEX resins were used: Purolite S960 (chelating resin) and Lewatit OC VP 1026 (solvent-impregnated resin), for testing which resin has the highest separation factor of both cations (Cu and Zn).

## 3. Results and Discussion

SED experiments were stopped when the feed solution conductivity was reaching a value around zero. For this reason, conductivity was monitored in each stream during the trials. The electrode rinse stream has no interactions with the other operational streams, so its conductivity remains constant during the tests. As exhibited in Figure 2, As concentration increased in the As-rich stream, while Cu and Zn concentrations increased in the Cu/Zn-rich stream one. Overall, SED process allowed to recover 49.1 % of As (for its subsequent treatment and disposal) and 81.9 % of Cu/Zn. The energy consumption of the SED process was about 4.8 kWh/kg Cu+Zn produced.

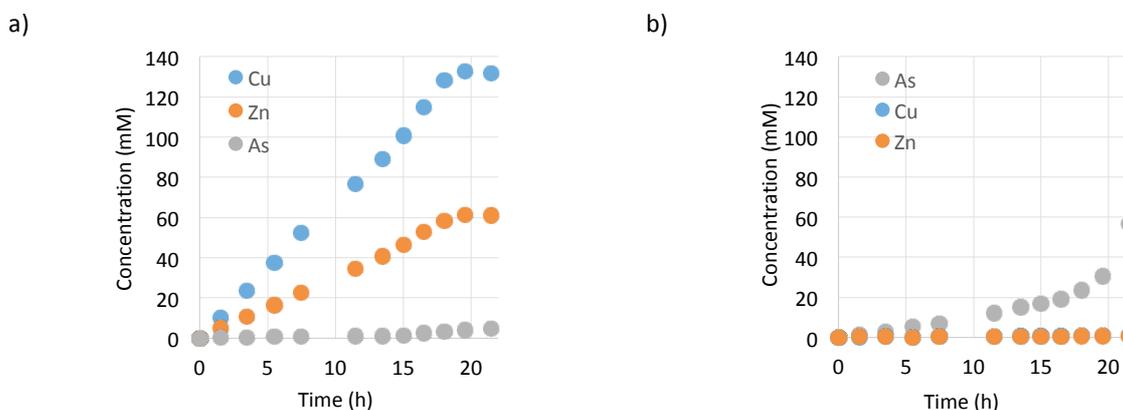


Figure 2. SED results a) in the Cu/Zn-rich stream and b) in the As-rich stream over time

Afterwards, IEX resins were used to treat the Cu/Zn-rich stream in a fixed-bed column set-up. Best Cu and Zn separation factors were obtained using the Lewatit 1026 resin. In this case, the acidic metallurgical stream (at pH 2.7) was treated by the IEX solvent-impregnated resin followed by an elution step using H<sub>2</sub>SO<sub>4</sub> 1 M, which allowed to recover 69 % of Zn (Figure 3a). Then, the pH was increased up to 4.7 to exchange Cu ions (elution step was also conducted using H<sub>2</sub>SO<sub>4</sub> 1 M) achieving 97 % of Cu recovery (Figure 3b).

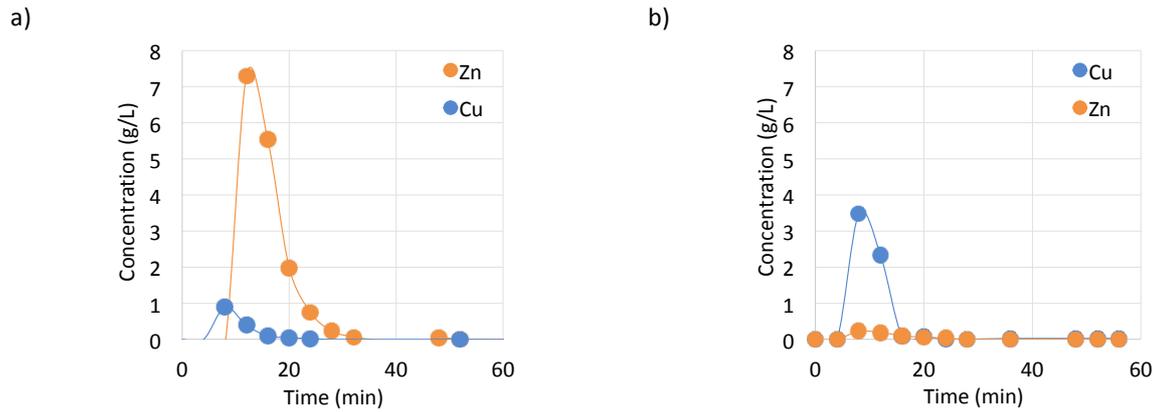


Figure 3. IEX elution curves by Lewatit 1026 resin for a) Zn and b) Cu recuperation, respectively.

#### 4. Conclusion

To summarize, it was possible to separate As from an acidic metallurgical stream containing mainly As, Cu and Zn by SED technology and also it was possible to separate and concentrate Cu and Zn streams by IEX resins. Furthermore, copper and zinc streams can be reused in the copper and zinc metallurgical industries, respectively; promoting in this way the circular economy in the metallurgical sector.

#### References

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