

# Advances in Selective Flotation and Leaching Process in Metallurgy

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## 1. Introduction and Scope

Metals are a finite resource that are necessary to maintain living standards in modern society, due to their countless applications, such as transportation vehicles, building and construction, household appliances, electronic devices, etc. In addition, the world is rapidly transitioning to “low-carbon technologies” using renewable energy sources (e.g., solar, wind, etc.) to combat climate change, and these technologies require vast amounts of metals per unit generation compared to that of conventional fossil generation; for example, 11–40 times more copper (Cu) for solar photovoltaic (PV) systems and 6–14 times more iron (Fe) for wind power stations [1].

Unfortunately, easily exploitable ore deposits are hard to find, which makes it unavoidable that mining industries must develop complicated ore deposits with low-grade and fine grain-size. The complexity of these ore bodies requires fine grinding to achieve the appropriate liberation of valuable minerals. Typically, there are two scenarios to extract metals from finely-ground ores; that is, (1) concentration of valuable minerals via “flotation” followed by smelting process and (2) direct extraction of metals from finely-ground ores by “leaching” followed by purification and recovery processes (e.g., solvent extraction and electrowinning (SX-EW)). Therefore, flotation and leaching, both of which are the first stage of each scenario, of finely-ground ores are of crucial importance to assure the continued supply of metals. Thus, this Special Issue introduces the latest scientific advances in selective flotation and leaching processes essential for the production of metals in a sustainable manner.

## 2. Contributions

Eleven articles have been published in the present Special Issue of *Metals*, encompassing the fields of flotation and hydrometallurgy. The papers are all of highly scientific value and will be of great interest to readers of *Metals*. The contents of the published papers will be briefly summarized as follows.

### 2.1. Flotation

Copper has been widely used in various applications, due to its excellent electrical/thermal conductivity, high corrosion resistance, etc. [2], approximately 60% of which is produced from porphyry copper deposits (PCDs) [3]. The beneficiation of porphyry copper ores is mostly achieved by a two-step flotation process; that is, (i) bulk flotation to recover Cu and molybdenum (Mo) minerals from gangue minerals and (ii) selective flotation of Mo minerals from Cu-Mo bulk concentrates using sodium hydrosulfide (NaHS) as a Cu depressant. Although this process is efficient and well established, the use of NaHS for Cu/Mo separation has several drawbacks. A review paper by Park et al. [3] introduced recent depression techniques, including alternative inorganic/organic depressants as well as oxidation treatments involving the use of ozone (O<sub>3</sub>), plasma, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and electrolysis. Moreover, Park et al. [4,5] developed a new depression technique (i.e.,



**Citation:** Park, I. Advances in Selective Flotation and Leaching Process in Metallurgy. *Metals* **2022**, *12*, 144. <https://doi.org/10.3390/met12010144>

Received: 11 January 2022

Accepted: 11 January 2022

Published: 12 January 2022

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microencapsulation using ferrous and phosphate ions), which preferentially coated chalcopyrite ( $\text{CuFeS}_2$ ) with ferric phosphate ( $\text{FePO}_4$ ) layers rather than molybdenite ( $\text{MoS}_2$ ). As a result, the floatability of chalcopyrite was selectively reduced, while molybdenite floated well by the addition of kerosene (Mo collector).

As high-grade and easily exploitable copper ores have been getting depleted, the development of flotation techniques for copper ores with low-grade and small grain size, as well as unconventional resources such as seafloor massive sulfide (SMS) ores, is becoming an important issue [6–8]. Hornn et al. [7] investigated the application of agglomeration using surfactant-stabilized oil emulsion to improve flotation recovery of finely-ground chalcopyrite. The recovery of fine particles ( $D_{50} < 5 \mu\text{m}$ ) by flotation is well known to be difficult due to the low collision probability between air bubbles and mineral particles [9–12]. A study by Hornn et al. [7] revealed that agglomeration using surfactant-stabilized oil emulsion was effective in increasing the apparent particle size of fine chalcopyrite particles from  $3.5 \mu\text{m}$  to  $\sim 10 \mu\text{m}$ , thereby improving Cu recovery from 68% to >97%. Meanwhile, Aikawa et al. [8] proposed a novel flotation procedure to recover chalcopyrite selectively from SMS ores. The major target minerals of SMS ores are chalcopyrite and sphalerite ( $\text{ZnS}$ ), so they should be recovered sequentially via a two-step flotation process whereby chalcopyrite is first recovered, followed by floating sphalerite. In the first stage of flotation, however, both chalcopyrite and sphalerite were recovered together even with zinc sulfate ( $\text{ZnSO}_4$ ; sphalerite depressant) because of the presence of anglesite ( $\text{PbSO}_4$ ) that releases  $\text{Pb}^{2+}$  and activates sphalerite. To address this problem, Aikawa et al. [8] employed EDTA washing before flotation, which was effective in removing anglesite, and thus chalcopyrite could be recovered selectively by flotation with  $\text{ZnSO}_4$ .

Apart from studies on the flotation of copper minerals, in this Special Issue, there are two papers on the recovery of fine bauxite [13] and elemental sulfur [14] by flotation. Zhang et al. [13] utilized a plate-packed flotation column (PFC) for fine bauxite, and the  $\text{Al}_2\text{O}_3$  recovery and grade increased by 2.11% and 1.85%, respectively, compared to the result obtained with unpacked flotation column (UFC). Additionally, they clarified the mechanism of how fine bauxite recovery was improved in a PFC by population balance model (PBM) incorporated with computational fluid dynamics (CFD) techniques; that is, installing the packing-plates significantly reduces the turbulent kinetic energy, which contributed to the formation of small-sized bubbles in the flotation column. A study by Liu et al. [14] demonstrated the recovery of elemental sulfur from the pressure acid leaching residue of  $\text{ZnS}$  concentrate. The recovery of elemental sulfur from high-sulfur residue can not only add economic value, as it is an important chemical material used for many applications, but also protect the environment. They compared three collectors (e.g., O-Isopropyl-N-Ethyl thionocarbamate (IPETC), ammonium dibutyl dithiophosphate (ADDTP), and sodium ethyl xanthate (SEX)), and among them, IPETC exhibited a superior collecting ability and selectivity to the elemental sulfur, which was further proved by density functional theory (DFT) calculation [14].

## 2.2. Hydrometallurgy

In this Special Issue, four articles deal with hydrometallurgical processing for Cu, gold (Au), and rare earth metals (REMs) [15–18]. Chae et al. [15] studied hydrochloric acid (HCl) leaching behaviors of Cu and antimony (Sb) in speiss obtained from top submerged lance (TSL) furnace. In general, the speiss containing Cu, Sb, and precious metals (e.g., Au, silver (Ag), etc.) is first processed by sulfuric acid ( $\text{H}_2\text{SO}_4$ ) leaching to extract Cu. However, it is reported that the leaching efficiency of Cu from the speiss in  $\text{H}_2\text{SO}_4$  media is decreased due to the increased amount of Sb in the speiss caused by the co-treatment of various secondary resources during the TSL process. The solubility of Sb in  $\text{H}_2\text{SO}_4$  is low, which hinders the leaching of Cu. In other words, Sb should be dissolved to improve the leaching efficiency of Cu, so HCl leaching experiments under various conditions were conducted by Chae et al. [15]. As a result, they found the optimum condition of HCl leaching where more than 99% of Cu could be dissolved.

As high-grade ores are depleted, the reprocessing of mine tailings to extract residual valuable metals/minerals is now getting increased attention. Godirilwe et al. [16] studied Cu recovery from mine tailings via flotation, high pressure oxidation leaching (HPOL), and SX-EW process. After flotation of mine tailings, the grade of Cu was upgraded from 0.24% to 0.65%, and the HPOL process of the concentrate yielded a high Cu leaching rate of 94.4%. Afterward, the pregnant leach solution (PLS) containing 2.9 g/L Cu and 102.9 g/L Fe was purified by solvent extraction using LIX-84I, which produced the stripped solution comprising of 44.8 g/L Cu and 1.4 g/L Fe where Cu could be electrowon with a current efficiency of about 95%.

The Cu-catalyzed ammonium thiosulfate leaching is one of the most promising alternatives to cyanidation for extracting gold from ores [17]. A major problem of thiosulfate leaching is its difficulty in recovering gold from the PLS; that is, the conventional Au recovery techniques (e.g., activated carbon (AC) adsorption and cementation using base metals) are inefficient. To address this problem, Jeon et al. [19,20] developed a novel recovery technique called enhanced cementation using AC and zero-valent aluminum (ZVAL), which yielded Au recovery of >99%. However, the previous studies on enhanced cementation using AC and ZVAL were conducted with relatively pure gold thiosulfate solutions [19,20], which significantly differs from the actual PLS where a variety of metal ions coexist. Thus, Jeon et al. [17] investigated the effects of coexisting metal ions (e.g., cobalt (Co), Cu, Fe, nickel (Ni), and zinc (Zn)) on Au recovery via enhanced cementation, and they found that the presence of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  showed the detrimental effects on Au recovery. However,  $\text{Cu}^{2+}$  acted as a catalyst that minimized the negative effects of these metal ions on Au cementation, yielding 85–90% of Au recovery.

Rare earth metals are essential to achieve a carbon-neutral society because significant quantities of REMs are utilized for manufacturing strong permanent magnets, a critical component used in generators for wind turbines and traction motors for electric vehicles (EVs) [21,22]. There are, however, only a few countries with exploitable rare earth deposits, so the production of REMs through the recycling of wastes is of topical importance. Choubey et al. [18] developed the hydrometallurgical process to extract REMs from Nd-FeB permanent magnets of waste hard disks. The demagnetized magnet was completely dissolved in 2 M  $\text{H}_2\text{SO}_4$  at 75 °C in 60 min, and then dissolved REMs and Fe were selectively precipitated from the leach liquor at pH 1.75 and 3.5–4.0, respectively. Finally, the precipitated REM hydroxides were converted to their oxides by heating at 120 °C for 2 h.

### 3. Conclusions and Outlook

A variety of topics have been covered in this Special Issue, presenting recent developments of flotation and leaching. Furthermore, the published articles effectively demonstrate the diversity of the recent research and development in the field. Nevertheless, there are still many challenges to overcome in this research field, so we hope that this Special Issue will serve as a springboard for future discussions and scientific debates on challenging topics related to flotation and leaching.

Having served as a Guest Editor, I am delighted by how well the contributions met the high standards of quality and originality that contributed to the success of this Special Issue. I would like to warmly thank all the authors for their contributions as well as the reviewers for their efforts to ensure a high-quality publication. In addition, I wish to extend my gratitude to the Editors of *Metals* for their continuous support and the *Metals* Editorial Assistants for their valuable and inexhaustible engagement and support during the preparation of this volume. My special thanks go to Mr. Toliver Guo for his support and assistance.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The author declares no conflict of interest.

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