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Editorial

Advances in Understanding of Unit Operations in Non-Ferrous Extractive Metallurgy 2021

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The high demand for critical materials, such as rare earth elements, indium, gallium, and scandium, raises the need for an advance in understanding the unit operations in non-ferrous extractive metallurgy. Unit metallurgical operation processes are usually separated into three categories: (1) hydrometallurgy (leaching, mixing, neutralization, precipitation, cementation, crystallization), (2) pyrometallurgy (roasting, smelting), and (3) electrometallurgy (aqueous electrolysis and molten salt electrolysis). In hydrometallurgy, the aimed metal is first transferred from ores and concentrates to a solution using a selective dissolution (leaching; dry digestion) under an atmospheric pressure below 100 °C and under a high pressure (40–50 bar) and high temperature (below 270 °C) in an autoclave and tube reactor. The purification of the obtained solution was performed using neutralization agents such as sodium hydroxide and calcium carbonate or more selective precipitation agents such as sodium carbonate and oxalic acid. The separation of metals is possible using a liquid/liquid process (solvent extraction in mixer-settler) and solid–liquid (filtration in filter-press under high pressure). Crystallization is the process by which a metallic compound is converted from a liquid into a solid crystalline state via a supersaturated solution. The final step is metal production using electrochemical methods (aqueous electrolysis for basic metals such as copper, zinc, silver and molten salt electrolysis for rare earth elements and aluminum). Advanced processes, such as ultrasonic spray pyrolysis and microwave-assisted leaching, can be combined with reduction processes in order to produce metallic powders. Some preparation for the leaching process is performed via a roasting process in a rotary furnace, where the sulphidic ore was first oxidized in an oxidic form, which is suitable for the metal transfer to water solution. During the smelting process, the target metal is further refined at high temperatures and reduced to its pure form. The pyrometallurgical treatment of the ore was performed in an electric furnace and combined with a refining during distillation. Unit Operations in Non-ferrous Extractive metallurgy can be successfully used for the recovery of non-ferrous metals from secondary materials.

The first Special Issue "Advances in Understanding of Unit Operations in Non-ferrous Extractive Metallurgy 2021" contains 17 papers divided in six groups:

1. Pyrometallurgical treatment (Thermal Decomposition and Kinetics of Pentlandite-Bearing Ore Oxidation in the Air Atmosphere [1])

The roasting of sulfide ores and concentrates is one of the most important steps in pyrometallurgical metal production from primary raw materials, due to the necessity of excess sulfur removal, present in the virgin material. Pentlandite is one of the main sources for nickel pyrometallurgical production. Raw pentlandite-bearing ore from the Levack mine (Ontario, Canada) was subjected to oxidative roasting in the air atmosphere. Thermochemical calculations, a phase analysis and construction of Kellogg diagrams for Ni-S-O and Fe-S-O systems at 298 K, 773 K, 923 K and 1073 K were used for proposing the theoretical reaction mechanism. A thermal analysis (TG/DTA—Thermogravimetric

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and Differential Thermal Analyses) was conducted in temperature range 298–1273 K, under a heating rate of 15 °C min^{-1}. A kinetic analysis was conducted according to the non-isothermal method of Daniels and Borchardt. Calculated activation energies of 113 kJ mol^{-1}, 146 kJ mol^{-1} and 356 kJ mol^{-1} for three oxidation stages imply that in every examined stage of the oxidation process, temperature is a dominant factor determining the reaction rate.

2 Dissolution of primary and secondary materials (1) Leaching, Processing Tests, Adjusted Cost Models and the Economies of Reprocessing Copper Mine Tailings in Chile; (2) NdFeB Magnets Recycling Process: An Alternative Method to Produce Mixed Rare Earth Oxide from Scrap NdFeB Magnets; and (3) Electrochemical Investigation of Lateritic Ore Leaching Solutions for Ni and Co Ions Extraction

To increase resource efficiency, mining residues—especially tailings—have come into the focus of research, companies, and politics. Tailings still contain varying amounts of unextracted elements of value and minerals that were not of economic interest during production. As for primary mineral deposits, only a small share of tailings offers the possibility for an economic reprocessing. To minimize exploration expenditure, a stepwise process is followed during exploration, to estimate the likelihood of a project to become a mine or in this case a reprocessing facility. During this process, costs are continuously estimated at least in an order of magnitude. Reprocessing flowsheets for copper mine tailings in Chile were developed, and costs and revenues of possible products from reprocessing were examined for a rough economic assessment. Standard cost models with capex and opex for flotation, leaching, and magnetic separation were adopted to the needs of tailings reprocessing. A copper tailing (around 2 Mt) that also contains magnetite was chosen as a case study [2]. A combination of magnetic separation and leaching gave the best economic results for copper and magnetite. The adopted cost models showed positive results at this early stage of investigation (semi-technical scale processing tests)

Spent NdFeB-magnets [3] and nickel lateritic ore [4] were chosen for the leaching process. The recovery of rare earth elements has become essential to satisfy this demand in recent years. In the present study, rare earth elements recovery from NdFeB magnets as new promising process flowsheet is proposed as follows; firstly acid baking process is performed to decompose the NdFeB magnet to increase in the extraction efficiency for Nd, Pr, and Dy. Than iron was removed from the leach liquor during hydrolysis. Finally, a production of REE-oxide from leach liquor was performed using ultrasonic spray pyrolysis method.

To examine the possible pathways of intrinsic electrochemical extraction of the crucial elements Ni and Co, it was necessary to make model solutions of these elements and to subject them to electrochemical examination techniques in order to obtain a benchmark. Beside Ni and Co, the model system for Fe had to be evaluated. The leachate examination results were compared to separate model solutions, as well as to their combinations in concentrations and to pH values comparable to those of the leachate [4].

3 Purification of solution during adsorption, precipitation and neutralization (1). Selenate Adsorption from Water Using the Hydrous Iron Oxide-Impregnated Hybrid Polymer; (2) Synergism Red Mud-Acid Mine Drainage as a Sustainable Solution for Neutralizing and Immobilizing Hazardous Elements; and (3) Basic Sulfate Precipitation of Zirconium from Sulfuric Acid Leach Solution

Hybrid adsorbent, based on the cross-linked copolymer impregnated with hydrous iron oxide, was applied for the first time for Se(VI) adsorption from water [5]. The influence of the initial solution pH, selenate concentration and contact time to adsorption capacity was investigated in detail. Adsorbent regeneration was explored using a full factorial experimental design in order to optimize the volume, initial pH value and concentration of the applied NaCl solution as a reagent. In addition to the experiments with synthetic solutions, the adsorbent performances in drinking water samples were explored, showing the purification efficiency up to 25%, depending on the initial Se(VI) concentration and water pH. Determined sorption capacity of the cross-linked copolymer impregnated with hydrous iron oxide and its ability for regeneration, candidate this material for further research, as a promising anionic species sorbent.

Acid mine drainage (AMD) and red mud (RM) are frequently available in the metallurgical and mining industry. Treating AMD solutions require the generation of enough alkalinity to neutralize the acidity excess. RM, recognized as a waste generating high alkalinity solution when it is in contact with water, was chosen to treat AMD from South Africa at room temperature. A German and a Greek RM have been evaluated as a potential low-cost material to neutralize and immobilize harmful chemical ions from AMD. Results showed that heavy metals and other hazardous elements such as As, Se, Cd, and Zn had been immobilized in the mineral phase [6]. According to European environmental standards, S and Cr, mainly present in RM, were the only two elements not immobilized below the concentration established for inert waste.

H_2SO_4 was ensured to be the best candidate for Zr leaching from the eudialyte. The resulting sulfuric leach solution consisted of Zr(IV), Nb(V), Hf(IV), Al(III), and Fe(III). It was found that ordinary metal hydroxide precipitation was not feasible for obtaining a relatively pure product due to the co-precipitation of Al(III) and Fe(III). A basic zirconium sulfate precipitation method was investigated to recover Zr from a sulfuric acid leach solution of a eudialyte residue after rare earth elements extraction. Nb precipitated preferentially by adjusting the pH of the solution to around 1.0. The precipitate contained 33.77% Zr and 0.59% Hf with low concentrations of Fe and Al. It was found that a high-quality product of ZrO_2 could be obtained from the basic sulfate precipitate [7]

4 Electrochemical methods for metal refining and winning (1) Electrorefining Process of the Non-Commercial Copper Anodes and (2) Aluminum Recycling in Single- and Multiple-Capillary Laboratory Electrolysis Cells

The electrorefining process of the non-commercial Cu anodes was tested on the enlarged laboratory equipment over 72 h [8]. Cu anodes with Ni content of 5 or 10 wt.% and total content of Pb, Sn, and Sb of about 1.5 wt.% were used for the tests. The real waste solution of sulfuric acid character was a working electrolyte of different temperatures (T1 = 63 ± 2 °C and T2 = 73 ± 2 °C). The current density of 250 A/m^2 was the same as in the commercial process. Tests were confirmed that those anodes can be used in the commercial copper electrorefining process based on the fact that the elements from anodes were dissolved, the total anode passivation did not occur, and copper is deposited onto cathodes.

The single- and multiple-capillary cells were designed and used to study the kinetics of aluminum reduction in LiF–AlF_3 and equimolar NaCl–KCl with 10 wt.% AlF_3 addition at 720–850 °C [9]. The cathodic process on the vertical liquid aluminum electrode in NaCl–KCl (+10 wt.% AlF_3) in the 2.5 mm length capillary had mixed kinetics with signs of both diffusion and chemical reaction control. The apparent mass transport coefficient changed from 5.6×10^{-3} cm s^{-1} to 13.1×10^{-3} cm s^{-1} in the mentioned temperature range. The dependence between the mass transport coefficient and temperature follows an Arrhenius-type behavior with an activation energy equal to 60.5 kJ mol^{-1}.

5 Synthesis of metallic, oxidic and composite powders using different methods (1) One Step Production of Silver-Copper (AgCu) Nanoparticles; (2) Synthesis and Characterization of a Metal Catalyst prepared by Ultrasonic Spray Pyrolysis as Pre-Definition Step for Titanium oxide-supported Platinum (3) Synthesis of Silica Particles Using Ultrasonic Spray Pyrolysis Method; (4) Atomic Layer Deposition of a TiO_2 Layer on Nitinol and Its Corrosion Resistance in a Simulated Body Fluid; (5) Spray-Pyrolytic Tunable Structures of Mn Oxides-Based Composites for Electrocatalytic Activity Improvement in Oxygen Reduction, and (6) Mixed Oxides $NiO/ZnO/Al_2O_3$ Synthesized in a Single Step via Ultrasonic Spray Pyrolysis (USP) Method

Synthesis of metallic, oxidic and composite methods using different methods was performed by ultrasonic spray pyrolysis method and atomic layer deposition. AgCu nanoparticles were prepared through hydrogen-reduction-assisted Ultrasonic Spray Pyrolysis (USP) and the Hydrogen Reduction (HR) method [10]. The changes in the morphology and crystal structure of nanoparticles were studied using different concentrated precursors. The average particle size decreased from 364 nm to 224 nm by reducing the initial solution concentration from 0.05 M to 0.4 M. These results indicate that the increase in concentration also increases the grain size. Antibacterial properties of nanoparticles against Escherichia coli were investigated. The obtained results indicate that the produced particles show antibacterial activity (100%).

Polygonal Pt nanoparticles were synthesized using ultrasonic spray pyrolysis (USP) at different precursor concentrations [11]. Physicochemical analysis of the synthesized Pt particles involved thermogravimetric, microscopic, electron diffractive, and light absorptive/refractive characteristics. Electrochemical properties and activity in the oxygen reduction reaction (ORR) of the prepared material were compared to commercial Pt black. Registered electrochemical behavior is correlated to the structural properties of synthesized powders by impedance characteristics in ORR. The reported results confirmed that Pt nanoparticles of a characteristic and uniform size and shape, suitable for incorporation on the surfaces of interactive hosts as catalyst supports, were synthesized. It is found that USP-synthesized Pt involves larger particles than Pt black, with the size being slightly dependent on precursor concentration. Among ORR-active planes, the least active (111) structurally defined the synthesized particles. These two morphological and structural characteristics caused the USP-Pt to be made of lower Pt-intrinsic capacitive and redox currents, as well as of lower ORR activity. Although being of lower activity, USP-Pt is less sensitive to the rate of ORR current perturbations at higher overpotentials. This issue is assigned to less-compact catalyst layers and uniform particle size distribution, and consequently, of activity throughout the catalyst layer with respect to Pt black.

Silica has sparked strong interest in hydrometallurgy, catalysis, the cement industry, and paper coating. The synthesis of silica particles was performed at 900 °C using the ultrasonic spray pyrolysis (USP) method [12]. Ideally, spherical particles are obtained in one horizontal reactor from an aerosol. The controlled synthesis of submicron particles of silica was reached by changing the concentration of precursor solution. The experimentally obtained particles were compared with theoretically calculated values of silica particles. The obtained silica by ultrasonic spray pyrolysis had an amorphous structure. In comparison to other methods such as sol–gel, acidic treatment, thermal decomposition, stirred bead milling, and high-pressure carbonation, the advantage of the ultrasonic spray method for preparation of nanosized silica controlled morphology is the simplicity of setting up individual process segments and changing their configuration, one-step continuous synthesis, and the possibility of synthesizing nanoparticles from various precursors.

Nitinol is a group of nearly equiatomic alloys composed of nickel and titanium, which was developed in the 1970s. Its properties, such as superelasticity and shape memory effect, have enabled its use, especially for biomedical purposes. Due to the fact that Nitinol exhibits good corrosion resistance in a chloride environment, an unusual combination of strength and ductility, a high tendency for self-passivation, high fatigue strength, low Young's modulus and excellent biocompatibility, its use is still increasing [13]. In this research, Atomic Layer Deposition (ALD) experiments were performed on a continuous vertical cast (CVC) NiTi rod (made in-house) and on commercial Nitinol as the control material, which was already in the rolled state. The ALD deposition of the TiO_2 layer was accomplished in a Beneq TFS 200 system at 250 °C. The pulsing times for $TiCl_4$ and H_2O were 250 ms and 180 ms, followed by appropriate purge cycles with nitrogen (3 s after the $TiCl_4$ and 2 s after the H_2O pulses).

Hybrid nanomaterials based on manganese, cobalt, and lanthanum oxides of different morphology and phase compositions were prepared using a facile single-step ultrasonic spray pyrolysis (USP) process and tested as electrocatalysts for oxygen reduction reaction (ORR). Electrochemical performance was characterized by cyclic voltammetry and linear sweep voltammetry in a rotating disk electrode assembly [14]. All synthesized materials were found electrocatalytically active for ORR in alkaline media. Two different manganese oxide states were incorporated into a Co_3O_4 matrix, δ-MnO_2 at 500 and 600 °C and manganese (II,III) oxide-Mn_3O_4 at 800 °C. The difference in crystalline structure revealed flower-like nanosheets for birnessite-MnO_2 and well-defined spherical nanoparticles for material based on Mn_3O_4. Electrochemical responses indicate that the ORR mechanism follows a preceding step of MnO_2 reduction to MnOOH. The calculated number of electrons exchanged for the hybrid materials demonstrate a four-electron oxygen reduction pathway and high electrocatalytic activity towards ORR.

Mixed oxides have received remarkable attention due to the many opportunities to adjust their interesting structural, electrical, catalytic properties, leading to a better, more useful performance compared to the basic metal oxides. Mixed oxides NiO/ZnO/Al_2O_3 were synthesized in a single step via USP method using nitrate salts, and the temperature effects of the process were investigated (400, 600, 800 °C) [15]. The synthesized samples were characterized by means of scanning electron microscopy, energy-dispersive spectroscopy, X-ray diffraction and Raman spectroscopy analyses. The results showed Al_2O_3, NiO–Al_2O_3 and ZnO–Al_2O_3 systems with spinel phases. Furthermore, the Raman peaks supported the coexistence of oxide phases, which strongly impact the overall properties of nanocomposite.

6 Characterization and behavior of the produced materials (Microstructural and Cavitation Erosion Behavior of the CuAlNi Shape Memory Alloy)

Microstructural and cavitation erosion testing was carried out on Cu-12.8Al-4.1Ni (wt.%) shape memory alloy (SMA) samples produced by continuous casting followed by heat treatment consisting of solution annealing at 885 °C for 60 min and, later, water quenching [16]. Cavitation resistance testing was applied using a standard ultrasonic vibratory cavitation set up with stationary specimen. Surface changes during the cavitation were monitored by metallographic analysis using an optical microscope (OM), atomic force microscope (AFM), and scanning electron microscope (SEM) as well as by weight measurements. The results revealed a martensite microstructure after both casting and quenching. Microhardness value was higher after water quenching than in the as-cast state. After 420 min of cavitation exposure, a negligible mass loss was noticed for both samples showing excellent cavitation resistance.

Finally, the combined process for the winning of rare earth elements and their oxides from primary and secondary materials was presented in the review paper: Advances in Understanding of the Application of Unit Operations in Metallurgy of Rare Earth Elements, prepared by B. Friedrich and S. Stopic [17].

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