

Article

Effect of Mechanical Activation on the Kinetics of Copper Leaching from Copper Sulfide (CuS)

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Received: 17 December 2017; Accepted: 22 February 2018; Published: 26 February 2018

Abstract: The effect of mechanical activation on the copper leaching of copper sulfide, CuS, in 1 M HNO₃ (slurry density: 10 g/L) was investigated by analysis of the leachability and the apparent activation energy. Mechanical activation produced an increase in the leachability and a decrease of the activation energy in this leaching reaction. The leachability increased proportionally to the degree of mechanical activation, reaching 96.6% leaching within 60 min at 80 °C from CuS ground at 700 rpm for 15 min. This leaching process was controlled by surface chemical reaction following the shrinking-core model. The apparent activation energy of leaching for CuS (71.5 kJ/mol) in the range of 50 to 80 °C decreased with an increase of the degree of mechanical activation, reaching 44.3 kJ/mol for Cu leaching from CuS ground at 700 rpm for 15 min.

Keywords: mechanical activation (MA); leaching; copper sulfide; shrinking-core model; apparent activation energy

1. Introduction

Copper has been one of the most commonly used metals for thousands of years. Traditional industrial use of copper has continued to survive and flourish due to its excellent properties of corrosion resistance, machinability, conductivity, and malleability [1–3]. At present, copper and its alloys are used in various fields such as building construction, electrical and electronic equipment, industrial machinery equipment, transportation equipment, etc. Additionally, the promotion and security of copper as a non-conventional energy source and its application in solar heating is expected to prompt the further use of the metal in large quantities in the near future [4]. For these reasons, the demand and global market consumption of copper has been increasing steadily in recent decades, and this trend will be continued for decades to come [5,6].

As a traditional type of extractive metallurgy process for copper production, pyrometallurgical processes have been used to process sulfide minerals with a high grade of copper. However, falling grades of mined copper ore and stricter environmental protection legislations necessitate development of more selective and efficient hydrometallurgical processes to extract copper from minerals. This has led to increased interest in the extraction of copper from low-grade sulfides in aqueous solutions. Moreover, there has been a growing interest in secondary copper sulfides as the dominant mineral source of copper [7–9].

Among secondary sulfides, covellite (CuS) is a representative mineral containing 66% copper and is now considered to occur as a dimer (two molecules of CuS forming Cu₂S₂) with the copper existing as Cu(I). This occurs very often in nature, associated with such minerals as chalcopyrite and chalcocite, among others. In addition, covellite is also formed as an intermediate product during the leaching of

chalcocite, copper matte and other complex copper sulfide materials because covellite is more stable against oxidation in the presence of sulfur than other copper sulfides. In addition, during reactions to extract copper from covellite in strongly acidic conditions, elemental sulfur may be formed on the particle surface. This layer is called 'passivation layer', and it acts as a blocking layer for copper leaching in solution [10–16].

To overcome the passivation layer and improve leaching efficiencies (leachability, leaching rate, etc.), several alternative processes using mechanochemical, electrochemical and sonochemical treatments have been tested and reported, but they were focused mainly on primary sulfide minerals such as chalcopyrite and chalcocite. In particular, the mechanochemical process has advantages over the others, including no need for additional equipment and procedural simplicity, despite this method had some drawbacks such as agglomeration of fine particles and the relatively lower energy efficiency in the prolonged grinding [17–20].

For example, ultrafine grinding of chalcopyrite increases its activity so that less severe leaching conditions are required to recover the copper. Thus, the term of mechanical activation (MA) refers to mechanically induced enhancement of the chemical reactivity of a system produced through the action of mechanical energy without altering the chemical composition. In conventional ball milling, the particle size is reduced by fracturing, but the composition and microstructure of the particles do not change. During mechanochemical milling, however, the microstructure and chemistry of the powders change due to the occurrence of solid-state reactions between the particles. MA provides a number of favorable conditions to allow these solid-state reactions to occur [21–25].

For these reasons, our research group studied the applicability of MA treatment for copper extraction by comparing leachability in several kinds of covellite treated mechanically under different conditions. This research may provide information to facilitate the use of covellite as a main source of copper production.

2. Experimental Procedure

2.1. Materials

Copper sulfide with a purity of over 99.0% (CuS, –100 mesh, Aldrich, St. Louis, MO, USA) was used as an initial material in this research. MA treatment was conducted as follows: 4 g of the original sample (CuS) was added to a stainless pot (pot diameter: 3.8 cm, depth: 4.0 cm, inner volume: 45 cm³) with seven stainless-steel balls that were 15 mm in diameter. The ball filling ratio was 52 vol. % and the mass ratio of ball-to-sample was kept constant at 25:1. A planetary mill (model Pulverisette 7, Fritsch GmbH, Idar-Oberstein, Germany) was used for MA of the sample, and the activation was carried out for 15 min with two rotation speeds, 300 and 700 rpm. Three kinds of CuS (as received, two CuS ground at 300 and 700 rpm for 15 min) were prepared as the starting materials for the leaching procedure.

These samples were characterized by high-resolution X-ray diffraction (HRXRD) analysis (X'pert-pro MPD, PANalytical, Almelo, the Netherlands) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) to identify the phase changes during mechanical activation. In addition, the particle size and distribution were measured with a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., Malvern, Worcestershire, UK).

2.2. Leaching

Leaching experiments were carried out in a 500 mL three-necked reactor into which 400 mL of leaching solution and 4 g of the starting sample were added. One neck held a thermometer, another a Teflon stirrer, and the third was used for sampling. This setup provided stable conditions and allowed heating at constant temperature (50, 60, 70 and 80 °C). A 1 mol/L nitric acid (HNO₃) solution was prepared and used as a leaching reagent. 400 mL of HNO₃ at the adjusted concentration was added to the reactor and heated to the selected temperature. When the temperature was reached,

4 g of the starting sample was added, and the leaching commenced. The stirring speed was set to 400 rpm in all experiments. After selected time intervals between 5 min and 1 h, 1 mL of the sample solutions was taken for chemical analysis of Cu, which was carried out with an inductively coupled plasma spectrometer (ICP, OPTIMA 7300DV, Perkin Elmer, Waltham, MA, USA). To acquire more accurate data, each experiment was repeated at least three times and the results were averaged. The content of Cu in both the leached solution and leached residue was analyzed. To dissolve the residue completely, a wet chemical digestion method was adopted, using aqua regia at the boiling temperature of this solution. The leachability was determined via the following equation:

$$\text{Leachability of Cu (\%)} = \frac{\text{Cu content (A)}}{\text{Cu content (A)} + \text{Cu content (B)}} \times 100 \quad (1)$$

where Cu content (A) is the Cu mass calculated from the Cu concentration in the leached solution, and Cu content (B) represents the Cu mass in the leached residue after complete dissolution.

3. Results and Discussion

3.1. Mechanical Activation (MA) Treatment of CuS

Figure 1 shows the XRD patterns of as-received CuS and the two CuS samples ground for 15 min at 300 and 700 rpm, which were used as the starting materials in this study. As shown in Figure 1, all detected peaks corresponded to those of CuS (Hexagonal, JCPDS No. 65-3588), despite the decrease in their intensities and the broadening of peak width progressing gradually with an increase of rotation speed. These changes can be observed in the product of MA treatment as reduced particle size and crystalline defects in the CuS powder. Figure 2 shows the size distribution of the three kinds of CuS mentioned in Figure 1. In the case of the CuS ground at 300 rpm, the major particle size decreased slightly, despite that the portion of particles over 100 μm in size increased dramatically. In the CuS ground at 700 rpm for 15 min, changes in major particle size and the size distribution were also observed. In particular, the CuS ground at 700 rpm exhibited a bimodal particle size distribution wherein the distribution was focused approximately 10 and 420 μm . The particles with sizes approximately 420 μm might be strong agglomerates of fine particles, and these strong agglomerates have been reported previously in many cases of prolonged and intensive grinding under dry conditions [26–30]. Although the major particle size and the size distribution changed according to the grinding conditions, the average particle sizes calculated in the cumulative distribution curves were similar, approximately 23 μm , as shown in Table 1.

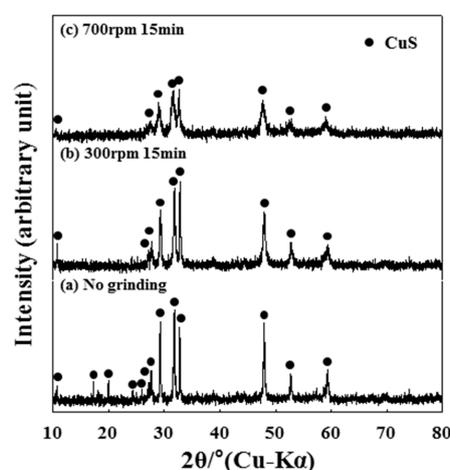


Figure 1. XRD patterns of CuS with various grinding conditions: (a) No grinding; (b) Ground for 15 min at 300 rpm; and (c) Ground for 15 min at 700 rpm.

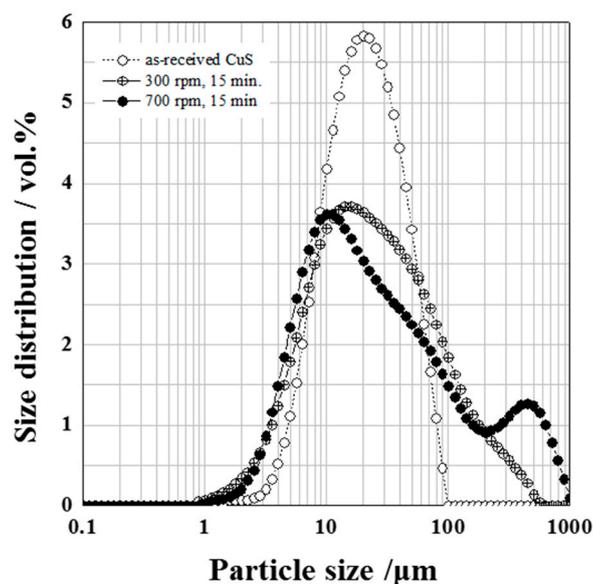


Figure 2. Particle size analysis profiles of CuS samples used as starting materials in this study.

Table 1. Representative particle sizes and specific surface area (SSA) of three types of CuS used as the starting materials in this study.

Starting Materials	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	SSA (m^2/g)
CuS as received	9.10	23.80	59.66	1.11
CuS ground at 300 rpm for 15 min	5.87	23.80	124.68	2.82
CuS ground at 700 rpm for 15 min	5.73	23.36	316.43	2.08

3.2. Copper Leaching of the Mechanically Activated CuS

Because the purpose of this study was to analyze the MA effect on leaching of Cu from CuS, leaching experiments were carried out for three kinds of CuS one as-received CuS and two mechanically activated CuS samples under varied leaching times and temperatures. The other conditions were fixed as follows: leaching reagent 1 M HNO_3 , slurry density 10 g/L and stirring speed 400 rpm. These results were organized in two graphs, Figures 3 and 4. In Figure 3, the leachabilities were presented in each leaching temperature in order that the effect of MA treatment on Cu leaching would be explained. In addition, the same leachabilities were arranged for each type of CuS to observe the temperature effect on Cu leaching from three kinds of CuS.

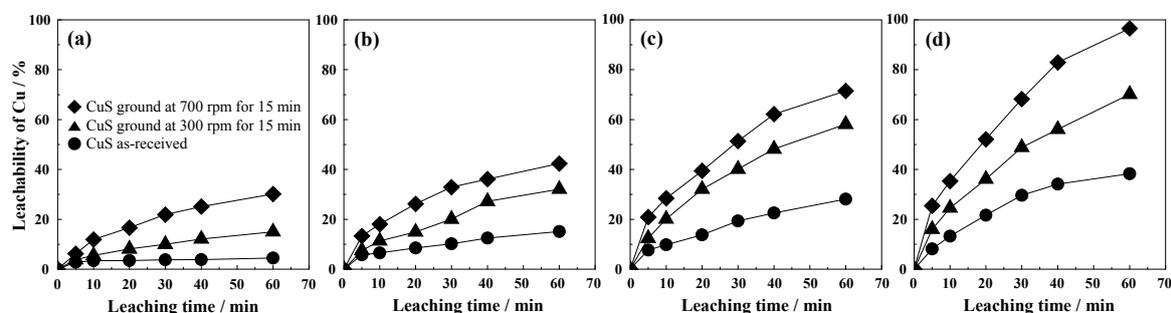


Figure 3. Effect of mechanical activation and leaching temperature on the dissolution of Cu from CuS: (a) 50 °C; (b) 60 °C; (c) 70 °C; and (d) 80 °C (1 M HNO_3 , slurry density 10 g/L, stirring speed 300 rpm).

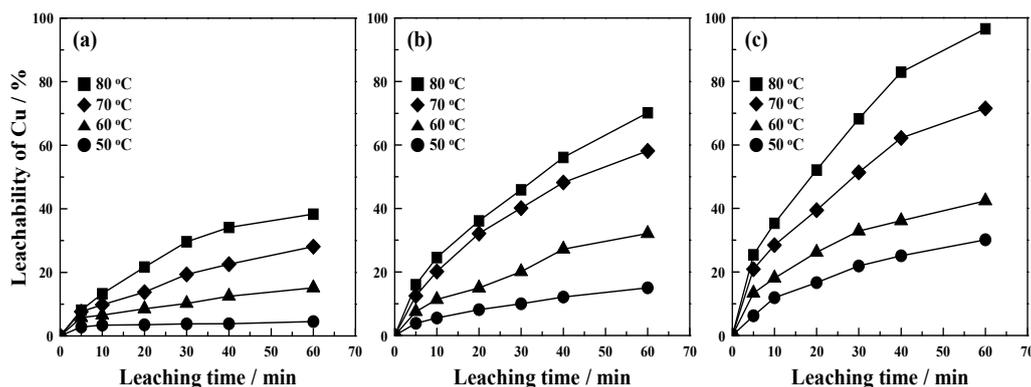


Figure 4. Leachability of Cu with the change of temperature from 50 to 80 °C (1 M HNO₃, slurry density 10 g/L, stirring speed 300 rpm): (a) CuS as-received; (b) CuS ground at 300 rpm for 15 min; and (c) CuS ground at 700 rpm for 15 min.

As shown in Figure 3, the leachability increased as an increase of grinding speed at all leaching temperature conditions, from 50 to 80 °C, even though the specific surface area (SSA) of CuS ground at 700 rpm for 15 min was lower than that of CuS ground at 300 rpm for 15 min (Table 1). These results imply that the Cu leachability of CuS can be improved by intensive grinding and it increases in sequence of grinding intensity.

In the case of the as-received CuS (Figure 4a), the extraction of Cu at 50 °C barely increased during 60 min of leaching, and it never reached 5%. This leachability increased proportionally to the leaching temperature as well as leaching time. The Cu extraction for 60 min at each temperature was 15.1% (60 °C), 28.1% (70 °C), and 38.3% (80 °C). However, though the extraction percentage increased considerably with rising leaching temperature, the maximum leachability for as-received CuS was only less than 40%. Especially at 50 °C, this low leachability and the extraction rate might be a result of the formation of elemental sulfur as well as the insufficient activation energy for the extraction reaction of Cu from CuS. This sulfur would build up as a protective layer, or “passivation layer”, on the surface of the CuS particles, and it might play a role in blocking acidic leaching for various sulfides including CuS [31–33].

Meanwhile, the leachability improved dramatically for the activated CuS. For the CuS ground at 300 rpm for 15 min, leachability increased with an increase in temperature and time. Within 60 min, it reached 15.0% (50 °C), 32.1% (60 °C), 58.1% (70 °C), and 70.1% (80 °C). This improvement was further enhanced by extending the degree of activation. Higher leachability was accomplished with the CuS ground at 700 rpm for 15 min, yielding 30.2% (50 °C), 42.4% (60 °C), 71.5% (70 °C), and 96.6% (80 °C). These results indicate that mechanical activation provides a way of overcoming leaching interruptions such as the development of an elemental sulfur layer. As seen from the results, the extraction of Cu from CuS could be improved considerably, attaining an excellent leachability of 96.6% within 60 min through the use of mechanical treatment.

3.3. Kinetics of Copper Leaching for the Mechanically Activated CuS

To evaluate the effect of MA on the leaching process, a study of the leaching kinetics was conducted using the obtained leachability data, with results presented in Figure 4. All of the linear fitting in least square method were carried out by using the data analysis and graphing software (OriginPro 8, OriginLab Co., Northampton, MA, USA).

Acidic leaching of sulfide minerals can be represented by many reaction models. Of these models, the previously established shrinking-core model plays an important role in the fluid-solid system and has been applied in the study of leaching for various sulfides [34–41]. Therefore, the shrinking-core

model was applied to describe the leaching kinetics for this experiment. The simplified equations of the shrinking-core model can be expressed as follows [41,42]:

$$\left[1 - (1 - \alpha)^{\frac{1}{3}}\right] = kt \quad (2)$$

$$\left[1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}}\right] = kt \quad (3)$$

where, α is the fraction of extracted Cu at time t and k is the apparent reaction rate constant. Equation (2) assumes that the controlling step is the chemical surface reaction, and Equation (3) assumes that the controlling step is the product layer diffusion.

In the literature, it is stated that the diffusion-controlled heterogeneous reactions (Equation (3)) are slightly dependent on temperature, while the chemically controlled processes (Equation (2)) are strongly dependent on temperature. In addition, the activation energy of a diffusion-controlled process is usually below 40 kJ/mol, while for a chemically controlled reaction, this value is usually greater than 40 kJ/mol [43–48]. To apply the reaction-controlling equation adequately for this study, the authors considered these two statements. As shown in Figure 4, the leachability increased significantly with an increase of leaching temperature for all samples. In addition, the apparent activation energies were substantially greater than 40 kJ/mol when they were calculated from Equation (3) on the basis of the leaching data. Therefore, the analysis of the leaching kinetics in this study was conducted using Equation (2).

Using the leaching results, plots of Equation (2) versus time are presented in Figure 5. For leaching of the as-received CuS at 50 °C, as presented in Figure 5a, the correlation coefficient, R^2 , calculated from the leaching data was below 0.9. An R^2 value lower than 0.9 implies that the application of the surface-reaction controlled Equation (2) may be inadequate for analyzing the kinetics of leaching for the as-received CuS at 50 °C. The unsound coefficient may be caused by the extremely low leachabilities, which is an effect that has been reported in previous research [10,49]. Except for this condition, the leaching data were fitted well by Equation (2), with a coefficient between 0.9208 and 0.9627 for the as-received CuS, 0.9538 and 0.9858 for the CuS ground at 300 rpm and 0.9556 and 0.9968 for the CuS ground at 700 rpm. Therefore, these results suggested that the leaching of the CuS used in this research was controlled by the surface chemical reaction. The apparent rate constant, k , was calculated from the slopes of the straight lines in Figure 5 and was used for the Arrhenius plot shown in Figure 6. The activation energy was determined by the Arrhenius equation, Equation (4):

$$k = A \times e^{\frac{-E_a}{RT}} \quad (4)$$

where k is the rate constant (min^{-1}), A is the frequency factor (min^{-1}), E_a is the apparent activation energy (kJ/mol), R is the gas constant (8.314 J/K·mol) and T is the leaching temperature (K).

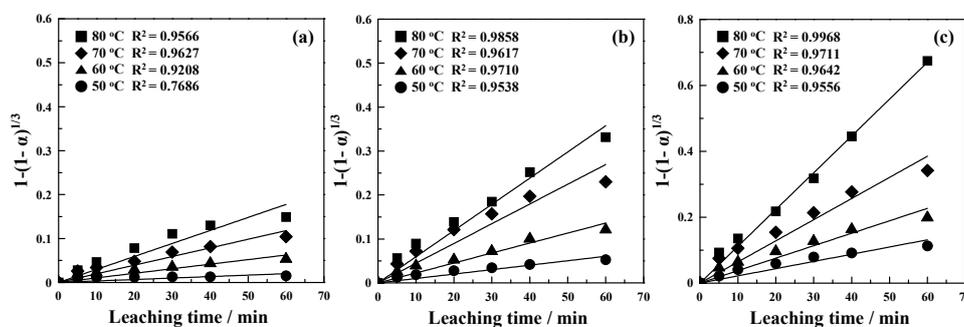


Figure 5. Plots of $[1 - (1 - \alpha)^{\frac{1}{3}}]$ versus time at various leaching temperature for (a) the as-received CuS; (b) the CuS ground at 300 rpm for 15 min; and (c) the CuS ground at 700 rpm for 15 min.

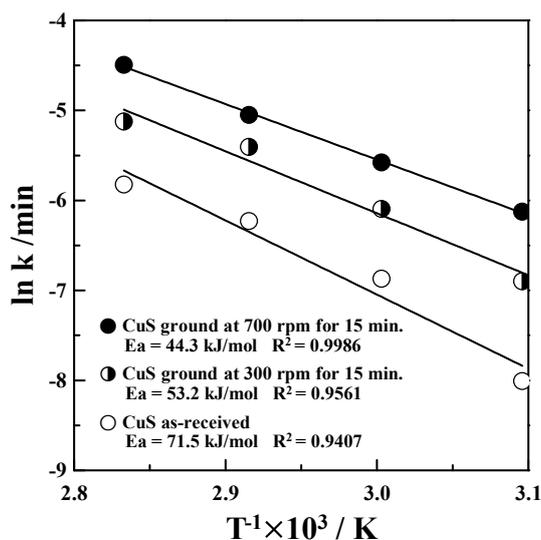


Figure 6. Arrhenius plots for the leaching of Cu from three different types of CuS.

Plots of $\ln k$ versus $1/T$ were straight lines with correlation coefficients of 0.9407 and 0.9986 (Figure 6). The apparent activation energy (E_a) for the as-received CuS was evaluated at 71.5 kJ/mol. This value is similar to that obtained by Cheng (1991) [34], and by Dutrizac (1974) [50], and the activation energy decreases with MA treatment. The activation energy of copper leaching in the temperature range of 50 to 80 °C was calculated at 53.2 kJ/mol for the CuS ground at 300 rpm for 15 min and at 44.3 kJ/mol for the CuS ground at 700 rpm for 15 min. These results imply that the activation energy decreases in reverse proportion to the grinding speeds, which can be interpreted as the degree of mechanical activation. This decrease resulted in the improvement of leachability, and 96.6% of Cu could be extracted from CuS at 80 °C in only 60 min.

4. Conclusions

The mechanical activation effect on the leaching kinetics of copper sulfide (CuS) was studied and discussed by means of the copper leachability and the apparent activation energy. Mechanical activation increases Cu leachability and decreases the activation energy of the leaching reaction. The rate of leaching was enhanced significantly by mechanical activation treatment, and it enabled us to achieve 96.6% Cu leachability at 80 °C in only 60 min from the CuS ground for 15 min at 700 rpm. The kinetics data showed a good fit to the shrinking-core model, and the rate-controlling step was also identified as a surface reaction. The apparent activation energy (71.5 kJ/mol) of leaching from CuS in the range of 50 to 80 °C, decreased with an increase of the degree of mechanical activation, and it descended to 44.3 kJ/mol for Cu leaching from the CuS ground at 700 rpm for 15 min.

Acknowledgments: This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry and Energy (MOTIE) of the Republic of Korea (No. 20165010100810). This work was also supported by Korea Energy and Mineral Resources Engineering Program funded by the Ministry of Trade, Industry and Energy.

Author Contributions: Jaeryeong Lee and Suyun Kim conceived and designed the experiments; Suyun Kim and Byoungjin Kim performed the leaching experiments and analyzed the ICP, particle size, and XRD data; Jae-chun Lee analyzed data and evaluated research results; Jaeryeong Lee wrote the paper and modified the paper; all authors contributed equally to the discussion.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Biswas, A.K.; Davenport, W.G.; Hopkins, D.W. *Extractive Metallurgy of Copper*, 2nd ed.; Pergamon Press: New York, NY, USA, 1974; pp. 64–69.

2. Burkin, A.R. *Topics in Non-Ferrous Extractive Metallurgy*; Blackwell Scientific Publications: Oxford, MS, USA, 1980; pp. 1–41.
3. Li, M. *Non-Ferrous Metals Metallurgy Process*; Chemical Industry Press: Beijing, China, 2010.
4. The World Copper Factbook. Available online: <http://www.icsg.org/> (accessed on 1 November 2017).
5. Mudd, G.M. The Environmental sustainability of mining in Australia: Key mega-trends and looming constraints. *Resour. Policy* **2010**, *35*, 98–115. [[CrossRef](#)]
6. Wang, M.; Chen, W.; Li, X. Substance flow analysis of copper in production stage in the U.S. from 1974 to 2012. *Resour. Conserv. Recycl.* **2015**, *105*, 36–48. [[CrossRef](#)]
7. Yin, Q.; Vaughan, D.J.; England, K.E.R.; Kelsall, G.H. Electrochemical Oxidation of Covellite (CuS) in Alkaline Solution. *J. Colloid Interface Sci.* **1994**, *166*, 133–142. [[CrossRef](#)]
8. Salmani Nuri, O.; Allahkarami, E.; Irannajad, M.; Abdollahzadeh, A. Estimation of selectivity index and separation efficiency of copper flotation process using ANN model. *Geosyst. Eng.* **2017**, *20*, 41–50. [[CrossRef](#)]
9. Xing, W.D.; Lee, M.S. Leaching of gold and silver from anode slime with a mixture of hydrochloric acid and oxidizing agents. *Geosyst. Eng.* **2017**, *20*, 216–223. [[CrossRef](#)]
10. Hirato, T.; Awakura, Y.; Majima, H. The leaching of sintered CuS disks with ferric chlorides. *Metall. Trans. B* **1989**, *20*, 485–491. [[CrossRef](#)]
11. Palache, C.; Berman, H.; Frondel, C. *Dana's System of Mineralogy*, 7th ed.; Wiley: New York, NY, USA, 1944; Volume 1, p. 248.
12. Ammou-Chokroum, M.; Sen, P.K.; Fouques, F. Electrooxidation of chalcopyrite in acid chloride medium: Kinetics, stoichiometry and reaction mechanism. In Proceedings of the 13th International Mineral Processing Congress, Warsaw, Poland, 4–9 June 1979; p. 527.
13. Parker, A.J.; Paul, R.L.; Power, G.P. Electrochemical aspects of leaching copper from chalcopyrite in ferric and cupric salt solutions. *Aust. J. Chem.* **1981**, *34*, 13–34. [[CrossRef](#)]
14. Downes, K.W.; Bruce, R.W. The recovery of elemental sulfur from pyrite and pyrrhotite. *Trans. Can. Inst. Min. Met.* **1955**, *58*, 77–82.
15. Sherman, M.I.; Strickland, J.D.H. Dissolution of Lead Sulfide Ores in Acid Chlorine Solutions. *J. Met.* **1957**, *9*, 795–800. [[CrossRef](#)]
16. Forward, F.A.; Veltman, H. Direct leaching zinc-sulfide concentrates by Sherritt Gordon. *J. Met.* **1959**, *11*, 836–840. [[CrossRef](#)]
17. Peters, E.; Loewen, F. Pressure leaching of copper minerals in perchloric acid solutions. *Metall. Trans. B* **1979**, *4*, 5–14. [[CrossRef](#)]
18. Ghali, E.; Dandapani, B.; Lewenstam, A. Electrodisolution of synthetic covellite in hydrochloric acid. *J. Appl. Electrochem.* **1982**, *12*, 369–376. [[CrossRef](#)]
19. Vereš, J.; Lovás, M.; Jakabský, Š.; Šepelák, V.; Hrdzák, S. Characterization of blast furnace sludge and removal of zinc by microwave. *Hydrometallurgy* **2012**, *129*, 67–73. [[CrossRef](#)]
20. Al-Harashsheh, M.; Kingman, S.; Bradshaw, S. The reality of non-thermal effects in microwave assisted leaching systems. *Hydrometallurgy* **2006**, *84*, 1–13. [[CrossRef](#)]
21. Palaniandy, S. Impact of mechanochemical effect on chalcopyrite leaching. *Int. J. Miner. Process* **2015**, *136*, 56–65. [[CrossRef](#)]
22. Baláž, P.; Achimovičová, M. Mechano-chemical leaching in hydrometallurgy of complex sulphides. *Hydrometallurgy* **2006**, *84*, 60–68. [[CrossRef](#)]
23. Hu, H.P.; Chen, Q.Y.; Yin, Z.L.; He, Y.H.; Huang, B.Y. Mechanism of mechanical activation for sulfide ores. *Trans. Nonferr. Met. Soc. China* **2007**, *17*, 205–213. [[CrossRef](#)]
24. Abdel Gawwad, H.A.; Abd El-Aleem, S.; Faried, A.S. Effect of internal sulfate attack on the properties of sulfate-resisting cement and alkali-activated slag. *Geosyst. Eng.* **2017**, *20*, 195–206. [[CrossRef](#)]
25. Minjigmaa, A.; Oyun-Erdene, G.; Zolzaya, T.; Davaabal, B.; Amgalan, J.; Temuujin, J. Phosphorus fertilizer prepared from natural Burenkhaan phosphorite (Mongolia) by a mechanical activation. *Geosyst. Eng.* **2016**, *19*, 119–124. [[CrossRef](#)]
26. Warris, C.J.; McCormick, P.G. Mechanochemical processing of refractory pyrite. *Miner. Eng.* **1997**, *10*, 1119–1125. [[CrossRef](#)]
27. Kim, J.K.; Han, S.H.; Lee, K.M. Estimation of compressive strength by a new apparent activation energy function. *Cem. Concr. Res.* **2001**, *31*, 217–225. [[CrossRef](#)]

28. Banza, A.N.; Gock, E. Mechanochemical processing of chrysocolla with sodium sulphide. *Miner. Eng.* **2003**, *16*, 1349–1354. [[CrossRef](#)]
29. Guo, X.; Xiang, D.; Duan, G.; Mou, P. A review of mechanochemistry applications in waste management. *Waste Manag.* **2010**, *30*, 4–10. [[CrossRef](#)] [[PubMed](#)]
30. Bujňáková, Z.; Baláž, P.; Zorkovská, A. Enargite concentrate processing by the combination of mechanochemical, hydrometallurgical and precipitation methods. *Int. J. Miner. Process.* **2014**, *127*, 28–36. [[CrossRef](#)]
31. Bredenhann, R.; Van Vuuren, C.P.J. Technical note the leaching behavior of a nickel concentrate in an oxidative sulphuric acid solution. *Miner. Eng.* **1999**, *12*, 687–692. [[CrossRef](#)]
32. Vračar, R.; Vučković, N.; Kamberović, Ž. Leaching of copper(I) sulphide by sulphuric acid solution with addition of sodium nitrate. *Hydrometallurgy* **2003**, *70*, 143–151. [[CrossRef](#)]
33. Sokić, M.; Vračar, R.; Ilić, I.; Marković, B. Leaching of polymetallic sulphide Cu-Zn-Pb concentrate with sulphuric acid in sodium nitrate presence. *CIM Mag.* **2008**, *101*, 1–9.
34. Cheng, C.Y.; Lawson, F. The kinetics of leaching covellite in acidic oxygenated sulphate-chloride solutions. *Hydrometallurgy* **1991**, *27*, 269–284. [[CrossRef](#)]
35. Thomas, G.; Ingraham, T.R.; MacDonald, R.J.C. Kinetics of dissolution of synthetic digenite and chalcocite in aqueous acidic ferric sulphate solutions. *Can. Metall. Q.* **1967**, *6*, 281–292. [[CrossRef](#)]
36. Mulak, W.; Niemiec, J. Kinetics of Cu₂S dissolution in acidic solutions of ferric sulphate. *ROCZNIKI CHEMII* **1969**, *43*, 1387.
37. King, J.A.; Burkin, A.R.; Ferreira, R.C.H. Leaching of chalcocite by acidic ferric chloride solutions. In *Leaching and Reduction in Hydrometallurgy*; Burkin, A.R., Ed.; Camelot Press: London, UK, 1975; pp. 36–45.
38. Warren, I.H. A study of the acid pressure leaching of chalcopyrite, chalcocite and covellite. *Aust. J. Appl. Sci.* **1958**, *9*, 36–51.
39. Gharabaghi, M.; Noaparast, M.; Irannajad, M. Selective leaching kinetics of low-grade calcareous phosphate ore in acetic acid. *Hydrometallurgy* **2009**, *95*, 341–345. [[CrossRef](#)]
40. Sokić, M.D.; Marković, B.; Živković, D. Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid. *Hydrometallurgy* **2009**, *95*, 273–279. [[CrossRef](#)]
41. Souza, A.D.; Pina, P.S.; Lima, E.V.O.; Da Silva, C.A.; Leão, V.A. Kinetics of sulphuric acid leaching of a zinc silicate calcine. *Hydrometallurgy* **2007**, *87*, 337–345. [[CrossRef](#)]
42. Sancho, J.P.; Ayala, J.; García, M.P.; Fernández, B. Leaching behaviour of a Bayer electrofilter fines in sulphuric acid. *Hydrometallurgy* **2009**, *96*, 35–41. [[CrossRef](#)]
43. Lee, I.H.; Wang, Y.J.; Chern, J.M. Extraction kinetics of heavy metal-containing sludge. *J. Hazard. Mater.* **2005**, *123*, 112–119. [[CrossRef](#)] [[PubMed](#)]
44. Uçar, G. Kinetics of sphalerite dissolution by sodium chlorate in hydrochloric acid. *Hydrometallurgy* **2009**, *95*, 39–43. [[CrossRef](#)]
45. Abdel-Aal, E.A.; Rashad, M.M. Kinetic study on the leaching of spent nickel oxide catalyst with sulfuric acid. *Hydrometallurgy* **2004**, *74*, 189–194. [[CrossRef](#)]
46. Safarzadeh, M.S.; Moradkhani, D.; Ojaghi-Ilkhchi, M. Kinetics of sulfuric acid leaching of cadmium from Cd–Ni zinc plant residues. *J. Hazard. Mater.* **2009**, *163*, 880–890. [[CrossRef](#)] [[PubMed](#)]
47. Baba, A.A.; Ayinla, K.I.; Adekola, F.A.; Bale, R.B.; Ghosh, M.K.; Alabi, A.F.; Sheik, A.; Folorunso, I.O. Hydrometallurgical application for treating a Nigerian chalcopyrite ore in chloride medium: Part I. Dissolution kinetics assessment. *Int. J. Miner. Metall. Mater.* **2013**, *20*, 1021–1028. [[CrossRef](#)]
48. Bell, S.L.; Welch, G.D.; Bennett, P.G. Development of ammoniacal lixiviants for the in-situ leaching of chalcopyrite. *Hydrometallurgy* **1995**, *39*, 11–23. [[CrossRef](#)]
49. Baba, A.A.; Balogun, A.F.; Olaoluwa, D.T.; Bale, R.B.; Adekola, F.A.; Alabi, A.G.F. Leaching kinetics of a Nigerian complex covellite ore by the ammonia-ammonium sulfate solution. *Korean J. Chem. Eng.* **2017**, *34*, 1133–1140. [[CrossRef](#)]
50. Dutrizac, J.E.; MacDonald, R.J.C. Kinetics of dissolution of covellite in acidified ferric sulphate solutions. *Can. Metall. Q.* **1974**, *13*, 423–433. [[CrossRef](#)]

