

Effect of microwave pretreatment on grinding and flotation kinetics of copper complex ore

Hamed Gholami¹⁾, Bahram Rezaei¹⁾, Ahmad Hassanzadeh²⁾, Akbar Mehdilo³⁾,
and Mohammadreza Yarahmadi⁴⁾

1) Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, Tehran 158754413, Iran

2) Department of Geoscience and Petroleum, Faculty of Engineering Science, Norwegian University of Science and Technology, NO-7491, Trondheim, Norway

3) Faculty of Engineering, University of Mohaghegh Ardabili, Ardabil 1136756199, Iran

4) Research and Development Division, Sarcheshmeh Copper Mine, National Iranian Copper Industries Company, Rafsanjan, Iran

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Abstract: The present study initially investigates the kinetics of microwave-assisted grinding and flotation in a porphyry copper deposit. Kinetic tests were conducted on untreated and microwave-irradiated samples by varying the exposure time from 15 to 150 s. Optical microscopy, energy-dispersive X-ray spectroscopy, and scanning electron microscopy were conducted to determine the mineral liberation and particle surface properties, and to perform mineralogical analyses. Results showed that the ore breakage rate constant monotonically increased by increasing the exposure time, particularly for the coarsest fraction size (400 μm) due to the creation of thermal stress fractures alongside grain boundaries. Excessive irradiation time (>60 s) led to the creation of oxidized and porous surfaces along with a dramatic change in particle morphologies that result in a substantial reduction of chalcopyrite and pyrite flotation rate constants and ultimate recoveries. We concluded that MW-pretreated copper ore was ground faster than the untreated variety, but the two types have slightly similar floatabilities.

Keywords: flotation kinetics; grinding kinetics; microwave technology; copper sulfide ore; recovery

1. Introduction

Application of microwave technology in mining and mineral processing industries has been extensively studied over the last four decades [1–5]. The microwave has been proven to considerably improve the overall grindability of materials by over 30% [6–9] while slightly influencing their floatabilities [10–12]. The microwave technology provides the best efficiency when it operates in an intensive power density instantly, whereas a notable difference exists among dielectric constants of the target and associated gangue minerals [13–14]. Most of the studies were conducted in batch conditions as a pretreatment process using a kitchen-type microwave except the recently fabricated and commercially utilized first industrial microwave operating at a throughput of 150 t/h [15]. Other industrial examples for different purposes were presented by Ju *et al.* [16].

Every mineral has a specific heat capacity, and its heating rate is different from that of other associated ones during exposure to microwave radiation. Some minerals absorb heat

more quickly, and others react less to heat or not at all [17]. By absorbing heat, phase transformation occurs at the boundary grains, which can be effective in froth flotation [18]. Kingman *et al.* [13] showed that the magnetic capabilities of a number of minerals, such as chalcopyrite (Cp), hematite, and wolframite, improved after microwave radiation. This enhancement has also been observed in pyrite (Py) and tetrahedrite [19–20]. Cp and Py have different thermal absorption rates due to differences in their dielectric constant. The heat absorption rate of Cp and Py is high, but Py is more resistant than Cp against microwave radiation. Thus, during a constant exposure period, its temperature is lower than that of Cp [21].

In general, microwave-assisted processes function physically or chemically by creating thermal stresses within (intra-granular) and alongside (intergranular or transgranular) grain boundaries. Meanwhile, surface modification of minerals induces an enhancement in mineral liberation degrees [22]. Alteration of particle surface properties is dependent, on the one hand, on the irradiation power and time and, on the other

Corresponding author: Bahram Rezaei Email: rezaei@aut.ac.ir

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hand, is affected by the particle surface characteristics such as oxidation affinity, roughness, and texture. Aside from the physical aspect, its chemical impact is highly dependent on the mineral type. For instance, in case of treating pure [23–24] and bulk [25–26] Cp samples, the grade and recovery were reduced in the flotation processes by increasing the irradiation time, but some researchers had reported the opposite [22,27]. Most recently, we found that the microwave location in a mineral processing circuit played a critical role in the floatabilities of Cp and Py [28], where their highest values were obtained when the domestic microwave was located before the crushing stage. Unlike identifying the main effect of dominant parameters, the synergetic and interlinked effects of a microwave system (power, exposure time, and location) on material grindability and floatability have not been reported in the literature. Another principal difficulty involved in microwave-related studies in froth flotation is that the floatability behavior of a pure mineral cannot be directly extended to its manner in a bulk matter. Thus, further comprehensive studies are needed to clarify the impact of microwave on froth flotation from fundamental to batch scales considering physical, chemical, and physicochemical properties of pure and bulk materials.

Kinetic rate of grinding and flotation determines how fast the material can be ground and floated in a mill and flotation cell, respectively [29]. The influential factors in the kinetic rate are classified into three categories: material properties, design factors, and operating parameters [30–31]. Many studies have focused on the acceleration of the kinetic rate by varying any of these parameters. Several studies have pointed out the positive impact of microwave on the kinetics of grinding [9,32–33] and flotation [12,22]. However, a comprehensive study on the grinding kinetics followed by the flotation kinetics has not been addressed in the literature yet. Table 1 presents a brief review of the previous works focused on the kinetics of only one of these processes. A crucial limitation of the microwaved-assisted kinetics of flotation studies is related to disregarding the selective separation of Cp from the main problematic gangue mineral (Py) in copper ores. We address this knowledge gap in the flotation kinetics section of this paper.

Although many studies have investigated the effect of microwave pretreatment on the grindability and floatability of materials, limited attention has been given to the grinding and particularly flotation kinetics. The motivation of this study is to address this deficiency for the first time by investigating the grinding kinetics of a porphyry copper ore followed by the flotation kinetic studies in a batch condition. Furthermore, the present study investigates the kinetic behavior of Cp and Py, as well as their selective separation through irradiation with a domestic microwave in comminution and froth flotation stages.

2. Experimental

2.1. Materials

The initial bulk sample (approximately 500 kg) was obtained from the input feed of Sarcheshmeh copper concentration plant ($d_{80} = 15$ mm) in Rafsanjan, Kerman province, Iran. This plant is one of the largest copper concentrators in the world, producing 50000 t copper concentrates with an average grade of 28%–32% Cu in the final re-cleaner flotation banks [36]. Hassanzadeh [37–38] described the operating units, grinding and flotation circuit schemes in detail, which is not discussed in this paper. The sampling process was conducted in 1 d after ensuring that the circuit operated under steady-state condition. The samples were taken from the conveyor belt after the primary ball mill was shut down. The given samples were treated, as shown in Fig. 1. First, they were carefully homogenized and split into two identical parts using splitting methods (cones and riffles). The first part was crushed by a jaw crusher (Retsch, BB100, Germany) and then milled by a stainless steel laboratory ball mill to reach $d_{80} = 74$ μm as a well-defined particle size suitable for the flotation experiments [39]. Similar to the previous part, samples for the second part were crushed, and 1 kg representative specimens were prepared for use in a domestic microwave (BER634GS1I, 2.45 GHz, Bosch, Germany) operating at 0.9 kW. Subsequently, similar to the first part and in an identical manner, the crushed samples were ground to reach 80% passing 74 μm . The role of microwave power level has been discussed in a previous study [40], where 0.9 kW was selected as the optimized magnitude. Eventually, all the untreated and MW-treated samples in a variety of exposure times were sieved, chemically characterized, and mineralogically analyzed.

Particle size distribution (PSD) is a crucial factor in relation to the microwave treatments. It was studied by varying the microwave location in three states, that is, before the jaw crusher ($d_{80} = 15$ mm), after the jaw crusher ($d_{80} = 1.5$ mm), and before the flotation (after the ball mill, $d_{80} = 0.074$ mm). A thorough description of the process was presented in a previous paper on froth flotation [28]. The PSD of an untreated representative sample after crushing and milling are exhibited in Fig. 2. In addition, we presented the roles of the PSD and microwave location on the grindability of a porphyry copper ore, which are both considered as constant in this study [41].

2.2. Material characterization

Semi-quantitative X-ray diffraction technique (Philips, PW17C, the Netherlands) and energy-dispersive X-ray spectroscopy (EDX) were performed to estimate the proportion of each mineral in the ore and elemental distributions. Particle surface properties before and after microwave irradiations were characterized through scanning electron microscopy

Table 1. Summary of reported studies in conjunction with kinetics of microwave-assisted grinding and flotation

Author(s)	Material	Microwave power/time	Notes
Kinetics of grinding			
Kingman <i>et al.</i> [17]	Lead–zinc ore (Sweden)	5, 10, and 15 kW 1, 5, and 10 s	Sample size range varied at –63+53 mm, –45+37.5 mm, –31.5+26.5 mm, –22.4+19 mm, and –16+13.2 mm. Preliminary tests were performed in a single-mode microwave cavity. Results showed strength reductions of 50% at 10 kW of microwave power with residence time of only 0.1 s. Ore softness was significantly increased compared with that of the untreated material.
Kumar <i>et al.</i> [34]	Iron ore (Orissa, India)	0.9 kW 30, 60, 90, and 120 s	The grindability test showed that the MW-treated iron ore ground much more rapidly than the unmicrowaved ore. Breakage function of microwaved and untreated iron ores was dependent on the particle size. The specific rate of breakage in MW-treated samples increased by an average of 50%.
Sahoo <i>et al.</i> [35]	High-ash Indian coal	0.9 kW 30, 60, 90, and 120 s	The –19.05+12.7 mm coal fraction size was microwaved. Bond work index (BWi) decreased by 15.4% after the sample was irradiated for 120 s. MW-treated samples were ground more rapidly than untreated ones while S_i increased 15% on average.
Koleini <i>et al.</i> [32]	Iron ore (Choghart iron mine, Iran)	1.1 kW 120 s	Effect of a microwave was examined on specific breakage rates of –2.36+2.00 mm, –1.40+1.18 mm, –1.00+0.85 mm, and –0.35+0.300 mm fraction sizes. MW-treated materials were broken faster than unmicrowaved ones.
Mendoza and Gómez [9]	Hematite (Fe ₂ O ₃)-rich ore (Guerrero, Mexico)	0.1–1.8 kW 60–240 s	Microwave indicated a significant effect on the production of fine particles. For each grinding time tested, the distribution of passing cumulative size was higher with respect to the untreated sample, particularly for short times.
Heshami <i>et al.</i> [33]	Venarj manganese ore mine (Iran)	1.1 kW 1–6 min	The particle size of samples was approximately –3.35 mm. The specific rate of breakage value increased to 8.42% as the particles became coarser after microwave treatment.
Kinetics of flotation			
Kingman <i>et al.</i> [25]	Palabora copper ore (South Africa)	1.3, 1.5, and 2.6 kW 10–300 s	A 1% initial increase in the recovery of copper was reported after microwave treatment. With prolonged exposure time, recovery decreased from 86.94% for untreated material to 77.7% under 4 min ore treatment at 2.6 kW.
Vorster <i>et al.</i> [26]	Neves Corvo copper ore (southern Portugal)	2.6 kW Different exposure intervals	The 80% passing size of all the samples was approximately 6500 μm. Flotation trials on a microwaved sample and untreated one showed insignificant improvement in copper grade and recovery.
Sahyoun <i>et al.</i> [27]	South African copper carbonatite ore	5–12 kW 0.1–0.5 s	Nine representative 1 kg samples of plant rod mill feed were used for all tests (100% passing 22 mm). Comparative batch flotation tests on MW-treated and untreated samples revealed improvements in copper recovery of between 6%–15%. Both recovery and cumulative grade increased with increasing treatment time and power.
Batchelor <i>et al.</i> [22]	Porphyry copper ore (Chile)	3–15 kW 0.1 s	Equivalent liberation could be obtained at a grind size of approximately 50–60 μm coarser than the nominal plant grind due to the effect of MW. An increase in copper recovery of approximately 1% could be achieved. The kinetics of the microwave-treated material was similar to that of the untreated material.
Azghadi and Barani [23]	Pure Cp (Qaleh-Zari vein copper mine, Iran)	0.9 kW 10, 30, 50, 70, 90, and 120 s	Particle size fraction of samples was approximately 100% passing 106 μm. The surface roughness of chalcopyrite decreased after microwave radiation. Particles with excessive surface roughness had higher flotation rates and kinetic constants. The surface wettability of Cp mineral increased with increasing microwave irradiation time.
da Silva and Waters [24]	Pure Cp, pentlandite, and pyrrhotite samples	3 kW 5, 10, and 20 s	Different particle size ranges were examined at –425+212 μm, –12+75 μm, –75+38 μm, and –150+38 μm. Formation of non-uniform oxidation or patched layers after MW treatment was proposed as the main reason for reducing Cp and pyrrhotite recoveries.

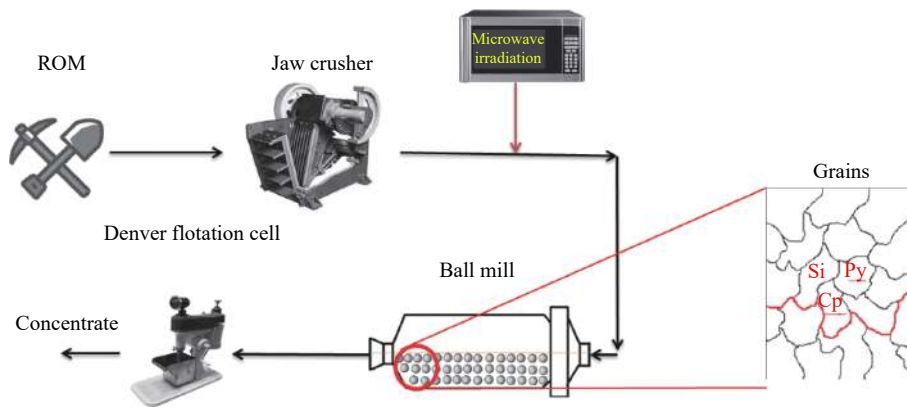


Fig. 1. Schematic view of material treatment.

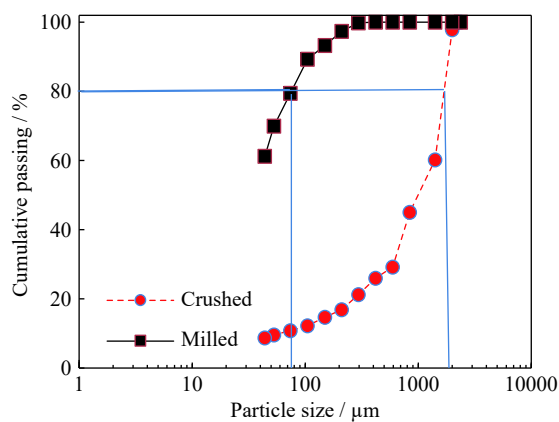


Fig. 2. PSD of untreated crushed and milled samples.

(SEM, Philips XL30, the Netherlands) and EDX analyzer. The mineralogical analyses, including the mineral liberation degrees, were determined through optical microscopy tech-

nique (Leica, DM-LP, Germany). Detailed information on the procedure can be found in another study [42]. Table 2 presents the chemical composition of the studied sample.

Commonly used Gaudin liberation model [43] (Eq. (1)) was applied to calculate the liberation degree (LD) [44].

$$LD = \frac{\text{Mass of free valuable mineral particles}}{\text{Total mass of variable minerals}} \quad (1)$$

The particles of Cp, as the most crucial copper-bearing mineral, were classified into three groups: liberated ($LD > 90\%$), middling ($30\% < LD < 90\%$), and locked ($LD < 30\%$). This methodology of estimating the LD suffers from a stereological bias along with a statistical dispersion in the light of a number of analyzed particles, which possibly results in an overestimation of mineral liberation degrees. Moreover, natural uncertainties are inherently linked to representativity and sample preparation limitations, which is discussed in detail by several researchers [45–47].

Table 2. Chemical analysis of crucial oxides of studied sample in

												wt%
CuO	Fe ₂ O ₃	MoO	SiO ₂	Al ₂ O ₃	SO ₃	CaO	MgO	K ₂ O	TiO ₂	P ₂ O ₅	LOI	
0.74	5.50	0.02	52.61	15.40	7.31	1.35	4.09	5.97	1.05	0.29	5.67	

Note: LOI—Loss on ignition.

2.3. Microwave pretreatment

Representative specimens (1 kg) were used in the microwave pre-treatment, which was performed using a domestic microwave oven (BER634GS11, 2.45 GHz, Bosch, Germany) with cavity dimensions of 382 mm × 594 mm × 318 mm. The treatment was conducted at a constant 0.9 kW power level for irradiation times of 0, 15, 30, 60, 90, 120, and 150 s. The samples were placed in a transparent Pyrex glass container inside the oven and then centered in the cavity for all experiments.

2.4. Experiments on grinding kinetics

Both the unmicrowaved and MW-pretreated samples were used for measuring the breakage distribution function and

specific rate of breakage by a direct experimental determination method. This approach is a standard top-size-fraction method that has been applied and detailed in several works [33,48–49].

First, the sample PSDs were measured and later prepared to achieve four single-sized fractions consisting of 420, 149, 74, and 53 μm. Then, 400 g of each fraction size was milled individually in a dry environment for a short time (10 s) through a standard batch Bond ball mill, and the mill discharge was sieved. Subsequently, the sample and charge media were re-loaded to the mill while it was operated until 45%–50% of the initial material passed through the top screen. After each grinding period (i.e., 10, 20, 40, and 80 s), the entire charge was discharged, and a representative sample

was taken for sieve analyses. The screening process was performed by using nine pans (400, 250, 177, 149, 105, 88, 74, and 53 μm) for 20 min. An in-house programmed breakage function distribution software [50] was utilized by taking advantage of the Berube model [51] in the breakage rate determination function. In this regard, detailed information concerning the modeling and estimation of breakage function (BF) and selection function (SF) can be found in other works [30,32].

The Berube model was applied to estimate the breakage function and its rate for both the fractionalized untreated and MW-pretreated samples based on the assumption that it follows the first-order disappearance kinetics (Eq. (2)) in a fully mixed batch mill.

$$w_1(t) = w_1(0) \exp(-S_1 t) \quad (2)$$

where $w_1(0)$ and $w_1(t)$ are the mass fractions of the top size fraction at time 0 and t (s), respectively. S_1 (min^{-1}) is a proportionality constant called the specific rate of breakage, which can be predicted from the slope of the following equation [52]:

$$\lg(w_1(t)) - \lg(w_1(0)) = -\frac{S_1 t}{2.303} \quad (3)$$

where the value of S_1 (min^{-1}) for various size fractions can be estimated by performing the same experiment with a uniform-sized material.

The primary cumulative breakage distribution (B_{ij}) is also defined in an empirical form by Austin and Luckie [53]:

$$B_{ij} = \varnothing_j \left(\frac{X_{i-1}}{X_j} \right)^\gamma + (1 - \varnothing_j) \times \left(\frac{X_{i-1}}{X_j} \right)^\beta, i > j \quad (4)$$

where B_{ij} is the mass fraction of primary breakage products; X_i is the coarsest size; and \varnothing_j , β , and γ are the model parameters that define the size distribution of the material [54]. γ is the slope of fine size end of the distribution, \varnothing_j is the extrapolated interception of this end, and β is the slope of the upper part of the curve as depicted somewhere else [55]. These parameters can be experimentally determined by plotting B_{ij} values versus relative size (x_i/x_j) on \lg - \lg scales. In general, the range of these parameters are $0 < \varnothing_j < 1.0$, $0.5 < \gamma < 1.5$, and $2.5 < \beta < 5.0$. Detailed information is provided in another study [49].

2.5. Experiments on flotation kinetics

Rougher flotation kinetic tests were performed on the untreated and MW-pretreated samples ($d_{80} = 74 \mu\text{m}$) using a 4.2 L mechanically agitated Denver flotation machine with 28% solid concentration and an impeller speed of 1400 r/min. To adjust the slurry pH at 11.8, we added 2 g lime (CaO) to the ball mill, and a sufficient amount of it was used during the flotation tests. The collectors and frothers were added with corresponding conditioning times of 1 and 2 min. These reagent types and dosages were selected according to the standard conditions of Sarcheshmeh copper processing plant

[29,56]. The mixture of sodium isopropyl xanthate ($\text{C}_4\text{H}_7\text{NaOS}_2$, Z11, 15 g/t) and butyl sodium dithiophosphate (Flomin 7240, 25 g/t) was used as the collector, while the mixture of methyl isobutyl carbinol ($(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OH})\text{CH}_3$, MIBC, 15 g/t) and polypropylene glycol ($\text{H}[\text{OCH}(\text{CH}_3)\text{CH}_2]_n\text{OH}$, F742, 15 g/t) was used as the frother. Detailed information regarding the functionality of these chemical agents [31], as well as the tap water properties and optimized dosages [57], is reported in other studies. The concentrate froth samples were collected at intervals of 1, 2, 3, 5, 8, and 12 min while the froth was manually scrapped every 10 s. These six concentrates and tailings were filtered, dried overnight in an oven at 60°C , weighed, and assayed. All the flotation tests were repeated twice for reproducibility.

The MW preconditioning naturally enhanced the grindability of the mineral, leading to variant product PSDs at the milling stage, prior to the flotation tests. Thus, to maintain the effectiveness of the PSD on the flotation experiments, we set the grinding time to reach $d_{80} = 74 \mu\text{m}$ for all the tests.

To estimate flotation rate constant, we used the following first-order flotation kinetic model [58–60]:

$$R(t) = R_{\text{max.}} \times (1 - \exp(-kt)) \quad (5)$$

where $R(t)$ (%) represents the recovery at the flotation time t (min), $R_{\text{max.}}$ (%) denotes the ultimate (infinite) recovery, and k (min^{-1}) is the flotation rate constant.

The recovery of Cp and Py was calculated using the following equation:

$$R = \frac{cC}{fF} \times 100\% \quad (6)$$

where R is the recovery; C (g) is the dry weight of the concentrate; c (%) denotes the grade of concentrate; F (g) and f (%) represent the dry weight of feed and its grade, respectively.

In addition to grade and recovery, selectivity index (SI) was a critical indicator to assess the metallurgical efficiency of the separation processes [60]:

$$\text{SI}_{\left(\frac{\text{M}_1}{\text{M}_2}\right)} = \frac{k_{\text{M}_1}}{k_{\text{M}_2}} \quad (7)$$

where k_{M_1} and k_{M_2} (min^{-1}) are modified kinetic rates of minerals 1 and 2.

The k_{M} is the modified rate constant defined as the product of infinite (ultimate) recovery and flotation rate constant (k):

$$k_{\text{M}} = k \times R_{\text{max.}} = \frac{\partial R}{\partial t} \Big|_{t=0} \quad (8)$$

3. Results and discussion

3.1. Kinetics of grinding

Fig. 3 displays the specific rate constants given for the selected mono-sized fractions as a function of microwave irra-

diation time. As shown, either coarser the size or longer the exposure time, more significant is the breakage rate. According to the results for the coarsest fraction, the breakage rate constant for the untreated and microwaved-pretreated (150 s) samples are 0.02219 min^{-1} and 0.030 min^{-1} , respectively. This condition implies that the microwaved sample is ground relatively faster than the untreated one. This result is in good agreement with the research findings of Rizmanoski [7], who applied a manufactured microwave to a porphyry copper ore. The results of drop weight tests (DWT) between the microwaved and unmicrowaved samples showed that material treatment for 5 s at 5 kW reduced the ore strength. Following this result, Heshami *et al.* [33] used a domestic microwave with 1.1 kW power and 2.45 GHz frequency to treat a manganese ore. They estimated the selection function for particles $<3350 \mu\text{m}$. An increase in S_i value was reported as the particles became coarser, in which the corresponding value obtained for the size fraction of $-3350+2360 \mu\text{m}$ increased to 8.42% after microwave treatment. Mendoza and Gómez [9] along with Javad Koleini *et al.* [32] investigated the impact of microwave on the grinding kinetics of Mexican and Iranian iron ores, respectively. Mendoza and Gómez [9] pointed out that the grinding kinetics led to a significant effect on producing fine particles for the treated sample (3, 5, 10, and 15 min), and consequently higher distribution of passing cumulative size compared with the untreated one. Kumar *et al.* [34] indicated an average improvement of 50% on the specific rate of breakage of MW-treated (0.9 kW, 30, 60, 90, and 120 s) iron ore (Orissa, India).

Fig. 3 shows that the effect of microwave pretreatment is only significant for the top size, that is, 400 μm . As the particle size becomes finer, the thermally stressed microfractures seemingly vanish, leading to the negligible role of

MW for sizes finer than 400 μm . Shahcheraghi *et al.* [61] recently evaluated the accuracy of the top-size-fraction method to estimate the selection function. This approach showed a relative error of 21%–34% with 95% confidence level. Therefore, the reproducibility of the results for this case study needs further investigation.

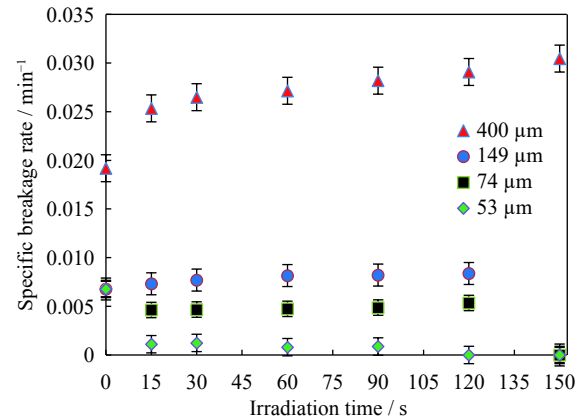


Fig. 3. Specific breakage rate compared with irradiation time in four mono-size fractions.

Fig. 4 shows the B_{ij} curves in connection with the untreated and MW-treated samples at irradiation times of 30, 60, and 150 s. The material becomes softer and easy to grind when subjected to longer irradiation. The discrepancy among the B_{ij} values shows that when the irradiation time is increased from 30 to 150 s, the deviation is explicitly noticeable in 150 s. The magnitude of related parameters, namely, β , γ , and ϕ_j , were obtained from the breakage curve by fitting Eq. (4) to the experimental data given in Fig. 4. As the irradiation time increases, the treated materials produce finer products compared with that for the untreated materials.

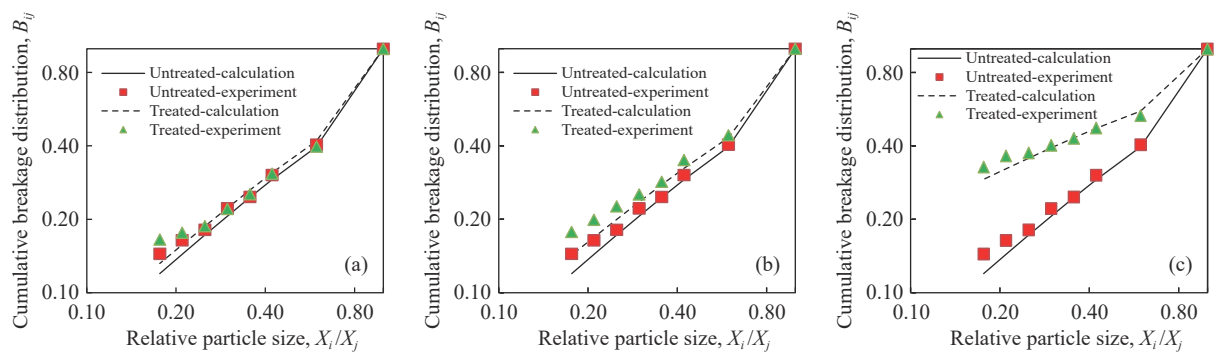


Fig. 4. Cumulative breakage distributions at (a) 30 s, (b) 60 s, and (c) 150 s microwave treatment.

Table 3 represents the predicted values for the breakage function parameters, which are calculated by a non-linear regression technique using the Solver function of Microsoft Excel, thereby minimizing the sum squared errors between the experimental and model values.

Data presented in Table 3 indicate a noticeable decrease in

γ and β values for the microwave-treated materials. In other words, the slope of the fine and coarse particles in Fig. 4 drops down in the presence of irradiation and extension of its duration. The microwave treatment substantially affects the value of γ at 150 s. A lower amount of γ indeed implies more effective breakage action with a maximum production of fine

particles. This condition may refer to the attrition or abrasion breakage mechanism, which is a surface phenomenon where shear stress causes the material to abrade. In general, softer materials display lower values of γ than harder materials [32]. Considering the results reported in Fig. 4 and the data presented in Table 3, we can conclude that the microwave irradiation affects all the relevant model parameters showing generation of finest product at 150 s treatment. Additionally, to support this outcome, we proved that overall Bond work index (BWi) of untreated and MW-treated samples at 30, 60, and 150 s were 13.7, 11.4, 11.2, and 10.8 kW·h/t [41].

Table 3. Descriptive constant characteristics of breakage function for untreated and MW-pretreated samples (0.9 kW, 30, 60, and 150 s)

Treatment state	γ	φ_j	β
Untreated	1.0653	0.7678	3.1481
MW-treated, 30 s	1.0239	0.7856	3.1167
MW-treated, 60 s	0.9807	0.7895	3.0967
MW-treated, 150 s	0.5894	0.8169	2.6437

We selected intermediate particle size ($-150+74 \mu\text{m}$) to demonstrate the role of studied irradiation times on Cp LD. This fraction size is known as the most favorably floatable particle spectrum in copper ores [62]. Fig. 5 exhibits the LD of Cp as the mineral of interest with respect to the unmicrowaved and microwaved samples at 30, 60, and 150 s. As shown in the figure, microwave pre-treatment for 60 s increases the LD from approximately 20% to 55%, which can potentially have a positive influence on its flotation in downstream processes. Enhancement of LD as a consequence of exposure time is extensively reported [22,63] and is in agreement with the results presented in Fig. 5.

3.2. Kinetics of flotation

The effect of microwave excitement on copper ores was typically shown by changing the copper recovery while the role of Py is often overlooked. Fig. 6 exhibits the impact of microwave preconditioning on Cp and Py flotation rate constants and their ultimate recoveries in response to the irradiation time.

The Py flotation rate constant does not show a notable response to the pretreatment in various irradiation times (Fig. 6(a)). However, the Cp flotation rate constant slightly improves by being exposed to the short irradiation time (30 s) possibly due to the creation of polysulphide functions [64], an increase in mineral LD (Fig. 5), and particle surface roughness [23]. However, for longer exposure times (>60 s), a reduction occurs seemingly due to the oxidation of particle surfaces [65], where the oxygen content of the microwaved sample is tremendously higher (30%) than that of the untreated one (6%). A microwave reduces the activation energy and enhances the mass transfer rate of chemical reactions involved in the metallurgical process, which is believed to be induced by microwave electric/magnetic field gradients [66]. In this regard, Batchelor et al. [22] subjected a porphyry copper ore to high-power density microwave treatments in a single-mode cavity at 15 kW and approximately 2 kWh/t. The kinetic tests showed that the estimated flotation rate constants by Klimpel model for the microwave-treated material were similar to the untreated ones. However, possible reasons concerning this phenomenon were not discussed further. Furthermore, the microwaved sample provided an approximate of 0.8% increased recovery, from

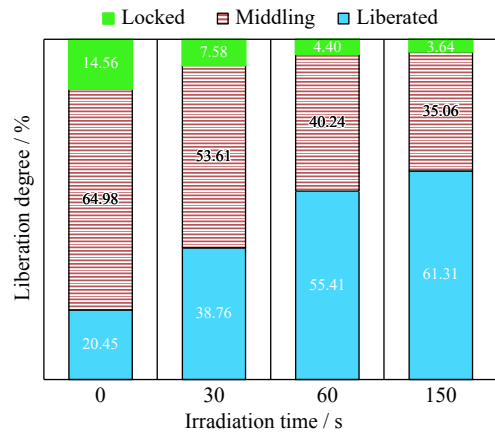


Fig. 5. Chalcopyrite LD vs. irradiation time.

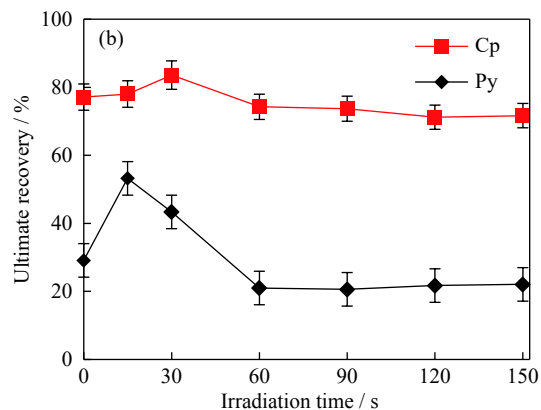
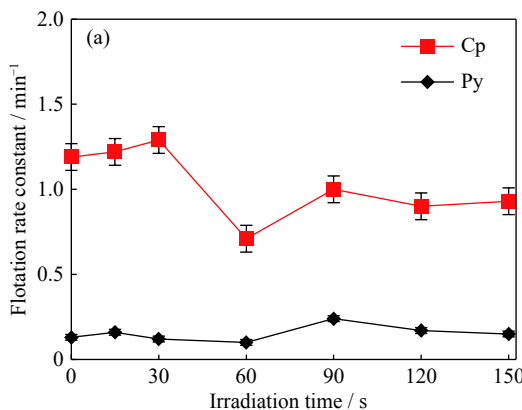


Fig. 6. Estimated (a) flotation rate constant and (b) ultimate recovery of Cp and Py as a function of irradiation time.

85.4% to 86.2%.

In addition to the flotation rate constants, ultimate recovery is also affected by the presence of microwave (Fig. 6(b)). The predictive Cp ultimate recovery increases from 77% (unmicrowaved) to 83% (30 s) and later reduces to 74% (60 s). Py shows almost the same behavior by rising from 29% (untreated) to 53% (15 s) and dropping to 21% (60 s), which remains relatively constant. In this regard, Marion *et al.* [12] investigated the effects of microwave radiation on the Voisey's Bay nickel and copper ore. It was found that copper recovery remained constant while nickel recovery increased by 33.6% after 120 s of microwave exposure at 0.8 kW, and by 34.4%

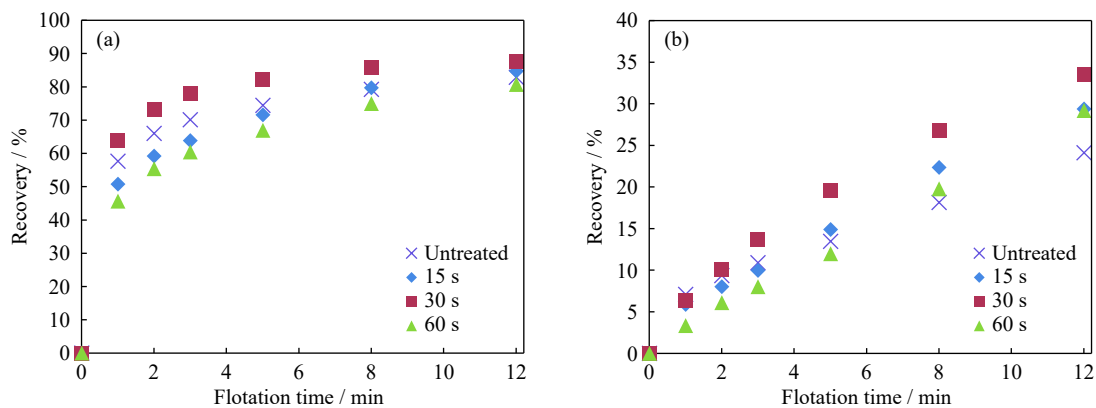


Fig. 7. Flotation kinetics of (a) Cp and (b) Py after MW pre-treatments for 15, 30, and 60 s at 0.9 kW.

Fig. 8 exhibits the elemental contents given by the EDX analyses for the untreated and MW-pretreated (60 and 150 s) samples. As shown in Fig. 8, irradiation of 60 and 150 s leads to the formation of moderate and intense oxide species on particle surfaces. As the figure shows, the oxygen content of the Cp surface increases to 30.42% and 42.1%, and that on the Py surface to 21.58% and 43.44% at 60 and 150 s irradiations, respectively (Figs. 8(a) and 8(b)). Despite the improvement in LD (Fig. 5), these species reduce the flotation kinetics rates in irradiation time of 60 and 150 s (Fig. 6). However, in case of 150 s, a significant increase in the amount of oxygen and iron indicates the presence of oxidat-

ive species and magnetic phases such as goethite (FeOOH) and hematite (Fe_2O_3) on the Cp and Py surfaces. Indeed, these species are oxides, hydroxides, and oxyhydroxides [65,67]. Studies show that the magnetic capabilities of some minerals have improved with increasing microwave irradiation time [13,19–20].

The given SEM images from the chalcopyrite (left) and pyrite (right) surfaces in Fig. 9 demonstrate the particle surface properties for the untreated (Figs. 9(a1) and 9(a2)) and MW-pretreated at 60 s (Figs. 9(b1) and 9(b2)) and 150 s (Figs. 9(c1) and 9(c2)). By pretreating the sample for 60 s, both mineral surfaces become oxidized. This result indicates

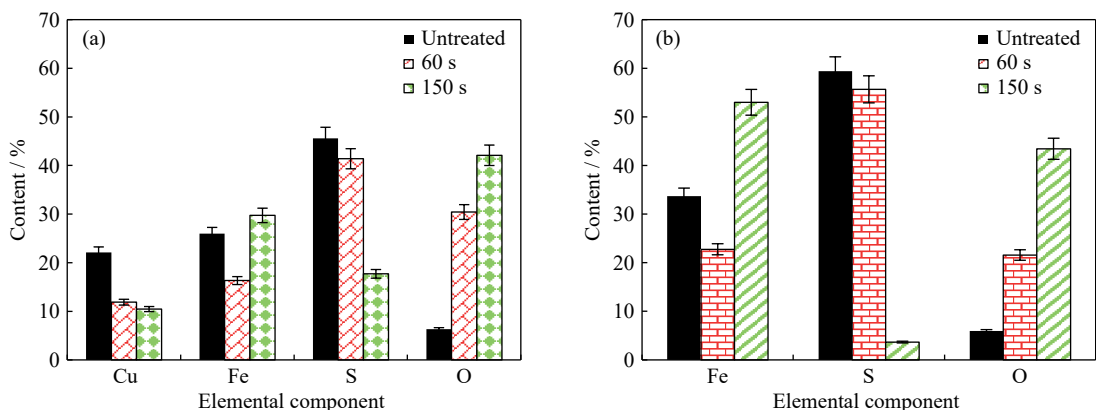


Fig. 8. Elemental components of (a) Cp and (b) Py surfaces for the unmicrowaved and microwaved samples (0.9 kW, 60 and 150 s).

that an exceeding irradiation time to 150 s creates a porous structure on the mineral surfaces, which can likely result in massive consumption of collectors. This may be another possible reason for reducing the recovery of Cp for the MW-treated samples in case of pretreating longer than 60 s, as shown in Fig. 6. If the irradiation time increases dramatically (to 150 s), the superficial layers in the lattice of Cp and Py are destroyed, as shown in Figs. 9(c1) and 9(c2).

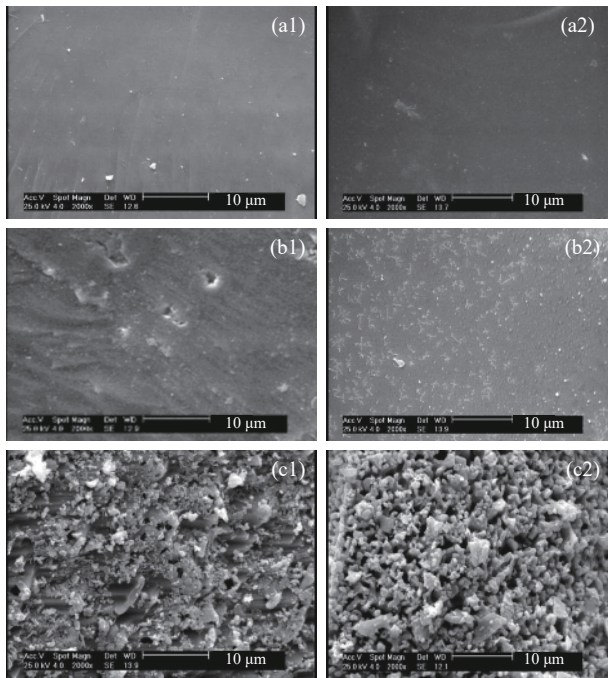


Fig. 9. SEM images from the chalcopyrite (left) and pyrite (right) surfaces of (a1, a2) un-microwaved and microwaved pretreated samples for (b1, b2) 60 s and (c1, c2) 150 s.

As the interpretation of experimental results based on k -values is somehow misleading [68], the selectivity index (SI) was utilized as an alternative and reliable criterion. As shown in Fig. 10, the microwave does not help in selective separation of Cp from Py. This condition may be attributed to the similar responses of both minerals (absorbers) to the mi-

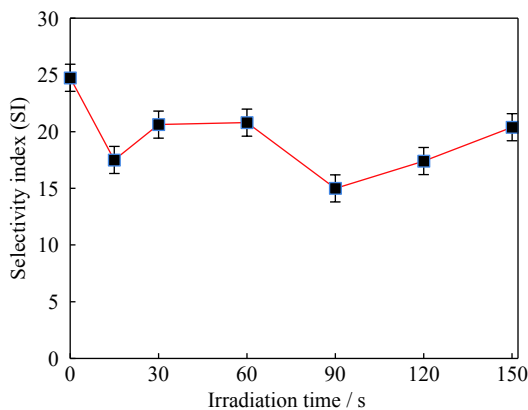


Fig. 10. Selectivity index of separation process vs. irradiation time.

crowave irradiation. Further studies should focus on an in-depth understanding of these phenomena.

4. Conclusions

The present study examined the kinetic behavior of microwave-assisted grinding, followed by flotation in a porphyry copper deposit. The grinding and flotation kinetics of the untreated and MW-pretreated samples were evaluated by varying the exposure time at 15–150 s. Optical microscopy, EDX, and SEM were used for characterizing mineralogical and particle surface properties. The results lead to the following conclusions.

(1) The results of the grindability tests confirmed that coarser-sized samples broke down faster during exposure to the microwave irradiation in the light of thermally created micro-fractures within and alongside the mineral boundaries.

(2) The flotation behavior of Cp and Py reacted the most to the shorter exposure times (<60 s), which led to an increase in Cp rate constant and Py maximum recovery. Longer irradiation time (≥ 60 s) not only caused surface oxidation (60 s) but also created a porous structure on mineral surfaces (150 s), inducing higher reagent consumption and destroying the superficial layers of particles, thereby leading to a reduction of k or R_{max} .

(3) The results from SI measurements showed that although the microwave pretreatment might selectively affect the improvement of mineral LDs in the grinding stage, selective separation of Cp from Py is not a promising technique because of their similar behavior during exposure to the microwave irradiation.

Thus, we conclude that further research is needed to clarify and comprehend the impact of microwave on the grindability and wettability of materials. In addition, the microwave location impact on grinding and flotation kinetics can be considered in future studies. Selection of microwave power, location, and time to simultaneously diminish the overall grinding energy consumption and increase the mineral grade, recovery, and selectivity in the flotation stage remains a challenging task.

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