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INFLUENCES OF GRINDING CONDITIONS ON GALENITE-SPHALERITE FLOTATION KINETICS

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Keywords

Flotation,
Dry grinding
Wet grinding

Abstract

Grinding is more than just crushing, it is also a process that causes a chemical reaction on the surface of the mineral. Water used in the grinding process significantly affects the galvanic interaction.

Different grinding conditions result in different pulp chemistries. This becomes especially important in sulfide flotation in terms of recovery and selectivity. There are limited studies examining the effects of dry and wet grinding prior to the flotation of sulfide minerals. This study compared the effects of wet and dry grinding on the flotation kinetics of complex Pb-Zn sulfide ore at P_{80} of 20 and 50 µm grind sizes. Results showed that dry grinding positively affected the sphalerite ore flotation compared to wet grinding in terms of recovery and grade in both galenite and sphalerite rougher flotation stages. Considering that the effect of dry grinding was due to the difference in pulp chemistry, the reasons were explored based on particle morphology, and pulp potentials.

The results showed that grinding the same ore under dry and wet conditions significantly affected the flotation performance. In light of the pulp potential measurements, it was determined that the reducing environment obtained in the wet grinding negatively affected the flotation performance, while the oxidizing environment formed during the dry grinding affected the flotation performance positively. This was attributed to the fact that galvanic interactions that occurred during wet grinding were significantly reduced during dry grinding. Hence, better galenite and sphalerite flotation was obtained following dry grinding.

ÖĞÜTME KOŞULLARININ GALENİT-SFALERİT FLOTASYON KİNETİĞİ ÜZERİNDEKİ ETKİLERİ

Keywords

Flotasyon,
Kuru öğütme
Yaş öğütme

Öz

Öğütme, sadece kırmanın ötesinde, mineralin yüzeyinde kimyasal reaksiyona neden olan bir işlemdir. Öğütme işleminde kullanılan su, galvanik etkileşimi önemli ölçüde etkiler.

Farklı öğütme koşulları, farklı pülp kimyalarının oluşmasına neden olmaktadır. Bu durum özellikle sülfürlü mineral flotasyonunda verim ve seçimlilik açısından önem arz etmektedir. Flotasyon öncesi kuru ve yaş öğütmenin, sülfürlü mineral flotasyonu üzerindeki etkilerini inceleyen sınırlı sayıda çalışma bulunmaktadır. Bu çalışmada, yaş ve kuru öğütmenin P_{80} 20 ve 50 µm tane boyutundaki kompleks sülfürlü galenit-sfalerit flotasyon kinetiği üzerindeki etkileri karşılaştırılmıştır. Sonuçlar, kuru öğütmenin hem galenit hem de sfalerit flotasyon devrelerinde verim ve tenör açısından yaş öğütmeye kıyasla flotasyon performansını olumlu etkilediğini göstermiştir. Gözlemlenen olumlu etkinin pülp kimyasındaki farklılıktan kaynaklandığı düşünülerek sonuçlar tane

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morfolojisi ve pülp potansiyeli özelinde araştırılmıştır. Sonuçlar, önceki çalışmada kullanılan 50 µm boyutundaki numunelerin galenit flotasyon devresinden elde edilen sonuçları ile karşılaştırmalı olarak verilerek tartışılmıştır.

Elde edilen bulgular, aynı cevherin farklı koşullar altında öğütülmesinin flotasyon performansı üzerinde önemli etkileri olduğunu göstermektedir. Pülpün elektrokimyasal ölçümleri ışığında yaş öğütmede oluşan indirgeyici ortamın flotasyon performansını düşürdüğü belirlenmiştir. Kuru öğütme işlemi sırasında yeni açığa çıkan mineral yüzeyleri su, pH veya E_h gibi kimyasal reaksiyonlardan etkilenmez ve böylece flotasyon verimi olumlu yönde etkilenir. Öğütme sırasında oluşan oksitleyici ortam nedeniyle galenit-sfalerit minerallerinin yüzebilirliği artmaktadır.

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1. Introduction

In dry areas such as South Africa, Australia, Chile and China, water depletion has a significant negative impact on the environment, which is becoming more pronounced due to the high consumption level of water (Franks, Forbes, Oshitani, Batterham, 2015; Gunson, Klein, Veiga, Dunbar, 2012; Kökkiliç, Langlois, Waters, 2015; Nguyen, Ziemski, Vink, 2014; Rivas-Perez, Sotomayor-Moriano, Perez-Zuñiga, 2017). Besides these regions, countries such as Sweden have procedures to conserve and recycle water in mining operations to obtain better resource usage and environmental benefits (Ranängen and Lindman, 2017; SIP STRIM, 2019). In this context, the use of dry grinding systems gains importance. A limited number of studies comparing the effects of dry and wet grinding on flotation in complex sulfide ores are included in the literature (Feng and Aldrich, 2000; Seke, 2005; Başaran, 2006; Chapman, Shackleton, Malysiak and O'Connor, 2013).

In this study, the effects of dry and wet grinding on the flotation kinetics of complex Pb-Zn sulfide ore were examined comparatively in the case of two different grind sizes, emphasizing particle morphology and pulp potential change.

2. Literature Review

2.1. Dry and Wet Grinding

In mineral processing, wet grinding is preferred to dry grinding because of the ease of material handling and higher energy efficiency in wet grinding. It is known that wet grinding requires less energy consumption than dry grinding i.e., about 20-25 % lower compared to wet grinding. As a result of wet grinding, products with the desired surface formation and less deformation of the particle surface are obtained (Feng and Aldrich, 2000).

On the other hand, dry grinding has many advantages, including less wear of the grinding media than wet grinding, a smaller proportion of fine products, and the potential to improve downstream process efficiency (Bruckard, Sparrow and Woodcock, 2011; Kanda, Abe, Yamaguchi and Endo, 1988; Koleini, Abdollahy and Soltani, 2012; Ogonowski, S., Wołosiewicz-Głab, M., Ogonowski, Z., Foszcz, D., Pawełczyk, F., 2018; Routray and Swain, 2019)

In an experiment with sphalerite mineral that was crushed by a high-pressure roller mill (HPGR) or conventional methods and wet ground by rod mill, it was observed that the highest sphalerite recovery and grade values were obtained after dry grinding regardless of the crushing method (Figure 1)(Chapman et al., 2013). In parallel with these results, Seke (2005) showed that higher sphalerite recovery values and positive pulp potential were obtained as a result of dry grinding compared to wet grinding.

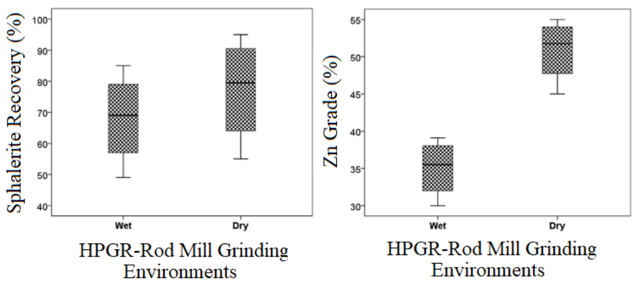

Figure 1. Flotation Performance of Sphalerite in Different Grinding Environments (Chapman et al., 2013)

Figure 2 shows the time-dependent changes in lead and zinc recovery of the ore from the Rosh Pinah mine under different grinding conditions (50 g/t sodium n-propyl xanthate (SNPX)). It is seen that zinc recoveries after dry grinding are higher and lead recoveries are lower compared to wet grinding. One of the reasons for the lower zinc recovery after wet grinding may be that the steel is more anodic than sphalerite, resulting in electron flow from steel to sphalerite (Seke and Pistorius, 2006). These electrons cause the formation of hydroxyl ions by reacting with water, and hydroxyl ions can react with metal ions in the environment to form stable metal hydroxides on the mineral surface, and as a result, they can make the mineral surface hydrophilic or reduce its suitability for collector absorption (Palm et al., 2010).

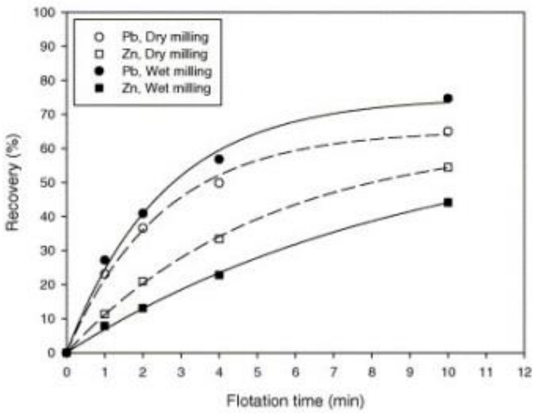

Figure 2. Flotation Recovery of Galenite and Sphalerite Under Various Grinding Conditions (Seke and Pistorius, 2006).

In another study conducted with complex sulfide ores, it was stated that particle surface deterioration occurred as a result of the exposure of particles with denser pulp (90% solids) in the dry grinding process to higher stress. In addition, as a result of new surface formation, it has been observed that dry milling consumes more energy compared to wet milling. This indicates that more energy is conserved in the surface deterioration resulting from dry grinding. Surface weathering plays an important role in the subsequent particle dissolution and reactive absorption (Feng and Aldrich, 2000). In this context, it was determined that the SIBX (Sodium Isobutyl Xanthate) absorption kinetics of dry ground activated mineral surfaces were faster.

Dry-ground samples have higher surface energy and faster flotation kinetics compared to wet grinding, while wet-ground samples provide higher grades and slightly higher recovery values. Dry grinding creates activated layers on the particle surface by causing high stress on the particles. On the other hand, grinding in an aqueous medium increases the sample's surface area. Feng and Aldrich (2000) pointed out the improvement in flotation kinetics and grade due to the combined use of wet and dry grinding.

2.2. Pulp Potential

Pulp potential is one of the important electrochemical parameters that can be associated with flotation efficiency and can be used in many situations, such as the oxidation/reduction control of minerals in the pulp. The pulp potential can be used to determine the surface conditions of sulfide minerals and to estimate the optimum flotation conditions.

The potential measured in the flotation system is the mixing potential and is somewhere between the mineral and solution potential values. The separation of the minerals in the flotation stage depends on the pulp potential (Trahar, 1984; Richardson and Walker, 1985).

Electrochemical studies using mineral electrodes with high purity sulfide mineral samples have shown that the interaction of a mineral with the collector can be controlled by the electrochemical potential measured at the mineral surface (Buckley and Woods, 1982; Allison, Goold, Nicol and Granville, 1972; Ruonal, Heimala & Jounela, 1997).

The potential value of the flotation pulp cannot be easily estimated due to galvanic interactions occurring in the system (Rao, Moon and Leja, 1976; Martin, McIvor, Finch and Rao, 1992). It has been observed that the pulp potential values vary between +50 and +200 mV in the applications made in the facilities where sulfide mineral flotation takes place (Grano, 2004).

Pulp potentials in aerated systems are too oxidizing to provide maximum mineral separation by flotation. For each mineral, there is a unique potential value at which flotation begins. The recovery values corresponding to the changing potential value of the galenite are shown in Figure 3. Galenite floats at values between 0 and 410 mV (SHE), the flotation efficiency is quite low below and above these values. By determining and controlling the pulp potential ranges in which the minerals float, these minerals can be selectively separated from each other. However, at very anodic potential values, specific ranges of values may overlap and cause simultaneous floating of some minerals, reducing selectivity (Ralston, 1991; Chander, 2003). By observing the potential changes in the flotation cell, the addition points of the reagents can be determined, and the grade and recovery values can be increased (Chander, 2003). In addition, the collection of E_h-pH data allows for obtaining additional information that can help reduce reagent quantities and solve problems in flotation plants (Johnson and Munro, 1988).

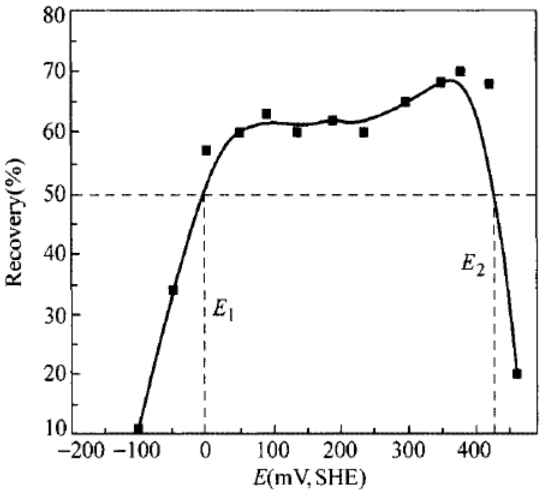

Figure 3. Galenite Recovery versus Pulp Potential (Hu et.al.,2010)

Due to the high electrical resistivity of sphalerite, very few studies have examined its electrochemical behavior. The relationship between sphalerite recovery and pulp potential is shown in Figure 4. Sphalerite flotation takes place between 0 and 310 mV (SHE) values.

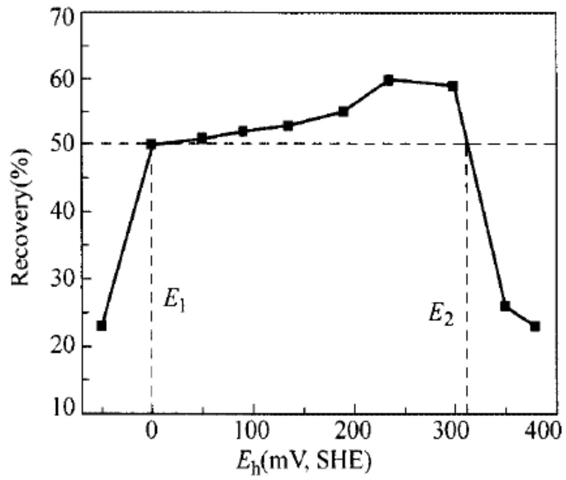

Figure 4. Sphalerite Recovery versus Pulp Potential (Hu et.al., 2010)

In many of the sulfide mineral systems, the pulp potential values reach more reducing (cathodic) values, that is, decrease as the dissolved oxygen moves away from the system. It has been observed that the pulp potentials are very low since sulfide minerals are mostly ground in steel mills (Woodcock and Jones, 1970 a, b; Graham and Heathcote, 1982; Grano et al., 1994). Since the absorption of thiol collectors depends on the E_h values, the floatability of the minerals can be greatly reduced if adequate aeration is not provided before flotation.

The oxidation of the medium, which reacts with oxygen, continues until the oxygen in the mill is depleted. Afterward, while a sudden decrease in pH values is observed, hydroxyl ions begin to form on the mineral surfaces. The reducing effect of the interaction between the grinding medium and sulfide minerals on the flotation pulp has been included in many studies (Forssberg and Subrahmanyam., 1993; Leppinen, Hintikka and Kalapudas., 1998; Martin et al., 1992; Yuan et al., 1996 a,b).

The pulp potential change of the lead-zinc sulfide ore belonging to the Rosh Pinah Mine, which is ground dry and wet in the steel mill, is shown in Figure 5. Dissolved oxygen and pulp potential were higher after the dry grinding of the composites. Similar results were observed in the study of Koleini et al. (2012). The increase in pulp potential with the onset of aeration is clearly due to the increase in the amount of oxygen in the pulp.

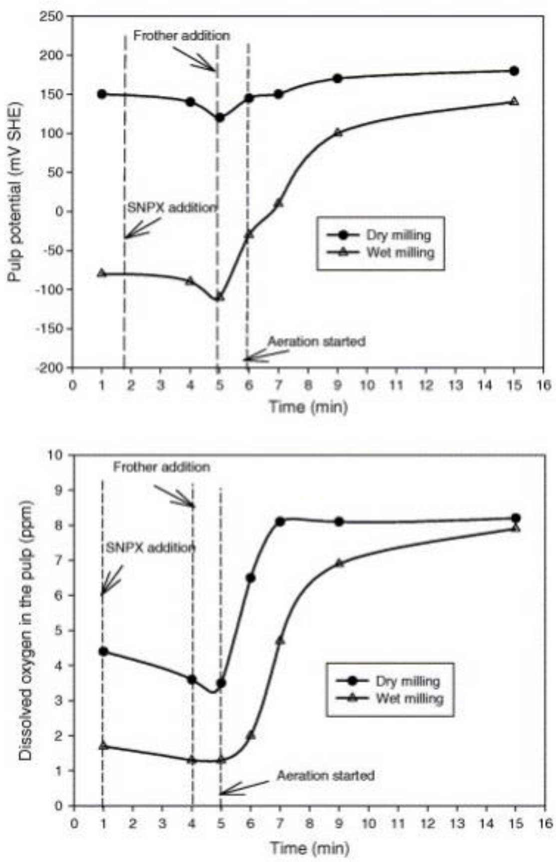

Figure 5. Effect of Dry and Wet Grinding on Pulp Potential and Dissolved Oxygen (Seke and Pistorius, 2006).

After dry grinding, further oxidation of minerals is inevitable due to aeration in the flotation cell. On the contrary, more negative pulp potential values and lower dissolved oxygen content are detected in wet grinding. Under these conditions, less oxidation of minerals occurs during conditioning. It is known that the flotation of sphalerite in complex lead-zinc ores increases under oxidized conditions. Therefore, it can be expected that the flotation efficiency of sphalerite will increase and the selectivity between lead-zinc will decrease after dry grinding. The presence of dissolved oxygen in the environment improves the flotation efficiency of sphalerite by depressing pyrite and preventing the formation of hydrophobicity on the mineral surface (Ek, 1985; Bulatovic and Wyslouzil, 1985; Dávila-Pulido, Uribe-Salas and Espinosa-Gómez, 2011).

3. Material and Method

3.1. Material

The sample studied was complex Pb-Zn sulfide ore originating from South America. Chemical analyses of the sample were performed using the multi-element inductively coupled plasma optical emission spectrometry (ICP-OES) method carried out by Bureau Veritas Commodities Canada Ltd. The chemical analysis is given in Table 1. The ore contains sulfur minerals, principally galenite (PbS), sphalerite (ZnS), pyrite (FeS_2), and minor amounts of chalcopyrite ($CuFeS_2$). The lead mineral in the ore consists of 99% galenite, while the zinc mineral consists of 98.78% sphalerite. The primary iron minerals are goethite (FeO(OH)), which accounts for 81.64% of the total, with hematite and pyrite accounting for the remainder.

Table 1. Chemical Analysis of the Flotation Feed (Tokcan, 2017)

Pb %	Zn %	Fe %	Cu %	S %	Ag g/t
1.07	2.74	23.22	0.08	2.65	24.00

3.2. Method

3.2.1. Grinding Tests

The crushed ore sample was utilized in wet grinding (WM) while part of it was dry ground (DM) by the pilot scale Loesche GMBH vertical roller mill system in Germany (P_{80}: 50 and 20 μm) and delivered to Eskişehir Osmangazi University, Mining Engineering Department Mineral Processing Laboratory. Samples to be ground by wet grinding for P_{80} 50 μm (DM-50) and P_{80} 20 μm (DM-20), and also dry ground samples were kept frozen to avoid surface oxidation after riffling.

A stainless steel rod mill (Ø200x 250 mm) with 12.9 kg of stainless-steel rods was used to grind bulk samples used in wet grinding at 60% solids. Wet ground samples were ground for 85 minutes to obtain a P_{80} of 20 μm (WM-20) and for 52 minutes to obtain a P_{80} of 50 μm (WM-50). In wet grinding experiments, depressants and lime were added to the mill with the sample to affect the newly formed mineral surfaces and maintain the pH.

3.2.2. Particle Size Analysis

A particle size measurement device Malvern Mastersizer Hydro 2000 MU-Malvern Co., Ltd., UK working with the laser diffraction method was used for the particle size analyses. At the end of each wet grinding test, samples were taken with the help of a syringe from the conditioned pulp in the flotation cell.

3.3.3. Scanning Electron Microscopy (SEM) Analysis

SEM analyzes of dry and wet ground samples were carried out at the Anadolu University Ceramic Research Center. The Zeiss Supra VP50 model SEM device was used in the measurements.

3.3.4. Image Analysis

The shape characterization was performed at Cumhuriyet University Mining Engineering Laboratory with a Particle Insight Dynamic Image Analyzer, One Micromeritics Drive, Norcross, GA30093-1877.

Many methods have been developed to characterize the shape of the particles. One of the scientific methods that analyze the shape parameters of the particles is the image analysis method which is frequently used. The Particle Insight Analyzer uses two important features: random routing and recirculation of samples. These features help obtain precise data about the sample and give its true description. Roundness is calculated using the area (A) and the radius of the bounding circle (DBC) (Equation 1). This measurement is fractional, with perfect roundness expressed as 1. The closer the value is to 1, the more rounded it is. The roundness value is not affected by the minor irregularities around the particle and the errors in the circumference measurement.

$$\text{Circularity} = 4A / \pi DBC^2 \qquad (1)$$

An Ellipse Length Ratio (EEAL) is calculated using equivalent ellipse area length and width values. Smoothness refers to the measurement of regional fluctuations around the particle cross-section. A value of 1 indicates that there is no roughness on the surface, while lower values indicate that the roughness on the surface is increasing.

3.3.5. Kinetic Flotation Tests

Batch flotation tests were conducted using the Denver D12 type with an impeller speed of 1,300 rpm at an air flow rate of 6 $dm^3\ min^{-1}$ and a 2,5 L flotation cell. All flotation tests were conducted at about 35% solids. In the galenite flotation stage, the slurry pH was set at 8, and lime was used in solid form to adjust the pH. Aerophine 3418A (3418-A) and Aerofroth 70 (AF-70) from Solvay Chemicals were utilized as collector and frother respectively. Sodium metabisulfite ($Na_2S_2O_5$) and sodium cyanide (NaCN) were used as sphalerite and pyrite depressants. The froth was scraped into separate pans at intervals of 1, 3, 5, 7, 10, and 12 minutes.

In the sphalerite flotation stage, the slurry pH was set at 11. Sodium isopropyl xanthate (SIPX) and copper sulfate ($CuSO_4$) were used as sphalerite collectors and activators, respectively. The froth was scraped at intervals of 1, 3, 5, 7, and 10 minutes. The effects of particle sizes P_{80} of 50 µm and P_{80} of 20 µm on galenite and sphalerite flotation kinetics were investigated in the cases of dry and wet grinding conditions.

In both flotation stages, the flotation rate constants (k) were also calculated to compare the effect of different grinding conditions based on a classical first-order flotation kinetics model (Equation 2).

$$R = R_{max}\,(1 - e^{-kt}) \qquad (2)$$

where, R is the calculated recovery, R_{max} is the theoretical maximum recovery, k is the flotation first-order rate constant, and t is time.

3.3.6. Pulp Potential Measurements

A Hach HQD Portable Meter with a pH and platinum ORP electrode was utilized to monitor the pH and pulp potential (E_h) values throughout the flotation tests. The measured potential values were converted from the Ag/AgCl scale to the SHE (Standard Hydrogen Electrode) scale using Equation 3.

$$E_{SHE} = E_{Ag/AgCl(volt)} + 0.207 \qquad (3)$$

The research has been prepared by analyzing in accordance with publication ethics.

4. Results

4.1. Particle Size Analysis

Particle size analysis data of dry and wet ground galenite-sphalerite ores measured by laser diffraction method are presented in Figure 6. 50 µm sized samples that were used in the previous study (Tokcan and Bozkurt, 2021) were shown in grey color in the graphics.

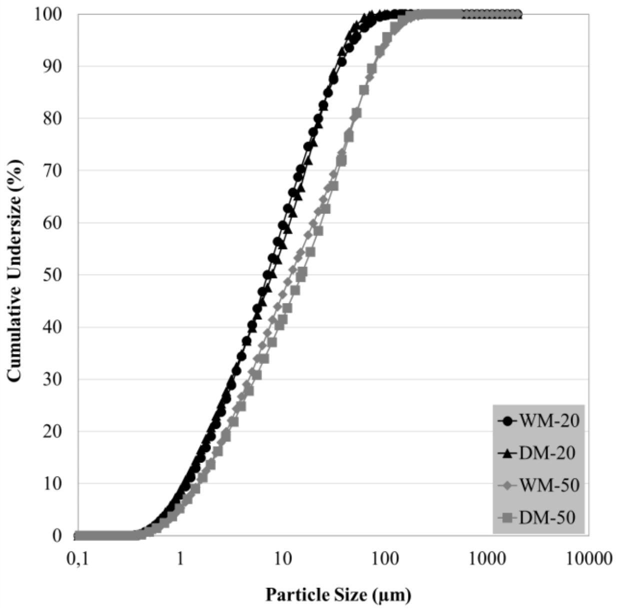

Figure 6. Particle Size Analysis of Samples (Tokcan, 2017)

The particle size distributions of the samples ground under different conditions are quite similar. Therefore, it is assumed that the flotation performance differences are related to the differences between dry and wet grinding.

4.2. Effect of Grinding Conditions on Particle Shape and Morphology

Unlike other separation processes, flotation is directly affected by the surface properties of minerals and thus by the grinding process. The deformation mechanism that takes place in grinding has a significant effect on the mineral surface properties. Ocepek, Strazisar and Kanduti-Sumej (1990) found that the way flotation reagents react with minerals depends on how different the surface shapes of the minerals are.

Different breaking mechanisms of traditional tumbling mills change the surface properties, such as physical, chemical, and roughness, differently. These changes can vary according to the material and mill characteristics, the grinding method, ambient temperature, and pressure (Orumwense and Forssberg, 1991). The surface roughness of the particles can affect flotation performance after grinding. The particle shape and morphology of the product obtained during the grinding process should be examined using image analysis systems to examine the effects of the enrichment process and to predict their behavior (Petruk, 1986, 1988, 1989; Jones, 1987).

The effects of different grinding schemes (VRM versus Rod Mill) on particle shape and morphology were investigated. The effect of different grinding mechanisms on the particle shape was examined with a Particle In-sight Analyzer to determine the roundness, smoothness, and EEALs. The data for the aforementioned shape parameters is shown in Table 2.

Table 2. Particle Shape Analysis Results (Tokcan, 2017)

Sample	C.P.	CIRC	S.D.	S.	S. D.	EEAL	S. D.
WM	6530	0.63	0.12	0.84	0.08	1.66	0.33
DM	6436	0.64	0.11	0.83	0.07	1.64	0.31

C.P.: Counted Particles S.D.: Standard Deviation
S.: Smoothness EEAL: Ellipse Length Ratio
CIRC:: Circularity

As a result of the examinations, it was observed that slightly more rounded and rougher particles were obtained after dry grinding, and relatively longer and smoother particles were obtained after wet grinding. The difference between the particle characteristics was quite negligible when comparing different grinding schemes, confirming that the main difference in flotation response would be due to the dry and wet grinding conditions. In the literature, it has been observed that the samples ground in the rod mill have a longer particle shape compared to the ball and autogenous mills (Yekeler, Ulusoy and Hiçyılmaz, 2004). It is also among the findings that the high liberation and round particle shape obtained in autogenous grinding provide a high concentrated grade and higher recovery values (Forssberg and Zhai, 1985). On the other hand, the low floatability of the mineral was attributed to the round shape of the particles (Hoberg and Scheneider, 1978). It has been shown that the separation of round particles from the air bubble is higher compared to particles with a high length ratio (Wotruba, Hoberg and Schneider, 1991). As it is understood, studies on the effects of particle shape on flotation performance are contradictory to each other. Particle morphologies vary depending on the ore type, grinding mechanisms, and grinding times.

It is stated in the literature that, as a result of dry grinding, the particle surfaces are rougher than those after wet grinding (Feng and Aldrich, 2000). Dry ground samples have faster flotation kinetics compared to wet ground samples. The performance of dry grinding is higher than wet grinding, both on a recovery and grade basis. It is thought that the defects occurring on the mineral surfaces after dry grinding make the surface more suitable for collector adsorption and thus increase the flotation efficiency. From this point of view, the wet grinding sample with a smoother surface has lower surface energy, so it is expected that the flotation kinetics will be slower (Feng and Aldrich, 2000).

As indicated before, there are slight differences in shape analysis. SEM images were examined in detail for each fraction to visually find any difference. However, when the SEM images of dry and wet samples were compared, no noticeable difference was found between them (Figure 7).

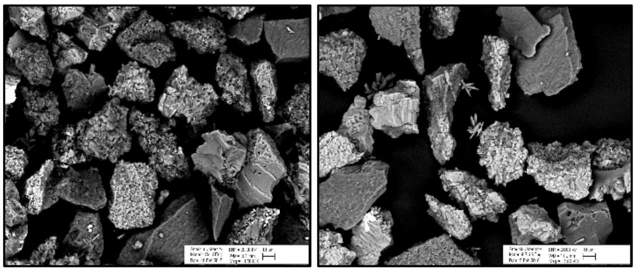

Figure 7. SEM Images of Wet (left) and Dry (right) Ground Samples from the -38+25 µm Fraction (Tokcan, 2017)

4.3. Effects of Grinding Conditions on Galenite Flotation Kinetics

The effect of different grinding conditions on the galenite flotation was determined by performing kinetic tests at the optimum conditions at which the highest recovery was obtained. Galenite rougher flotation concentrates were collected over time, and the data was analyzed based upon cumulative Pb recoveries and grades. Experimental conditions are presented in Table 3.

Table 3. Experimental Conditions for Galenite Flotation

	Reagents (g/t)	Dry Grinding	Wet Grinding
pH		8	8
Depressants	$Na_2S_2O_5$	1000	1500
	NaCN	200	250
Collector	3418-A	30	60
Frother	AF-70	40	40

Figure 8 shows the variation of the cumulative Pb recovery with flotation time. While the highest recovery value was obtained at 20 µm grind size following dry grinding (DM-20) during the flotation period, the lowest recovery was obtained at 20 µm grind size following wet grinding (WM-20). Similar results were previously acquired at 50 µm grind size following dry (DM-50) and wet grinding (WM-50) conditions (Tokcan and Bozkurt, 2021). Higher recoveries were obtained after dry grinding at both grinding sizes. Even though minerals were expected to be more liberated at a 20 µm grind size, in contrast to dry grinding, slightly lower recovery values were acquired at the 20 µm size compared to the 50 µm size for wet grinding. The decrease in recovery could be attributed to the prolonged grinding time at 20 µm size. Recovery values for both in the case of different grinding conditions and particle sizes were quite similar at the end of the flotation.

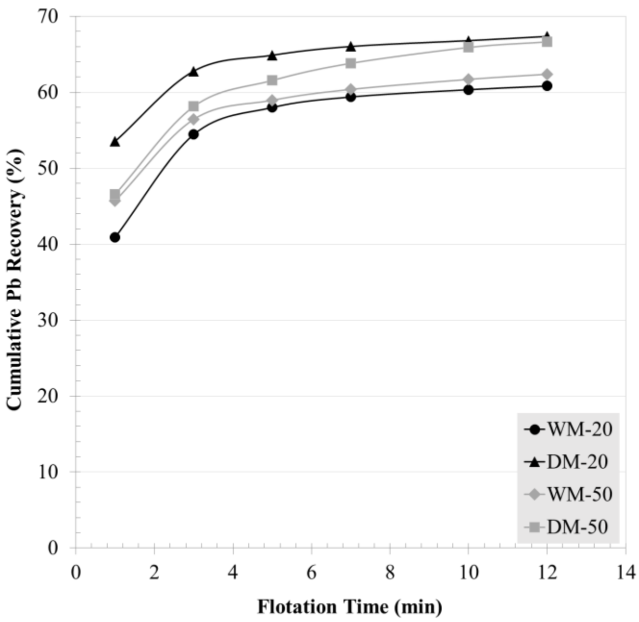

Figure 8. Cumulative Pb Recovery over Time

In studies with galenite mineral, it has been observed that the flotation kinetics are higher in autogenous and stainless-steel mills, that is, in more oxidizing environments, compared to reducing media such as steel mills (Learmont and Iwasaki, 1984, Rey and Formanek, 1960, Thornton, 1973, Cases, de Donato, Kongolo and Michot, 1989).

When the Pb grade over time is examined according to particle sizes, it is seen that in the case of dry grinding, lower grade values were acquired at 20 µm compared to wet grinding, while having higher grade values at 50 µm (Figure 9).

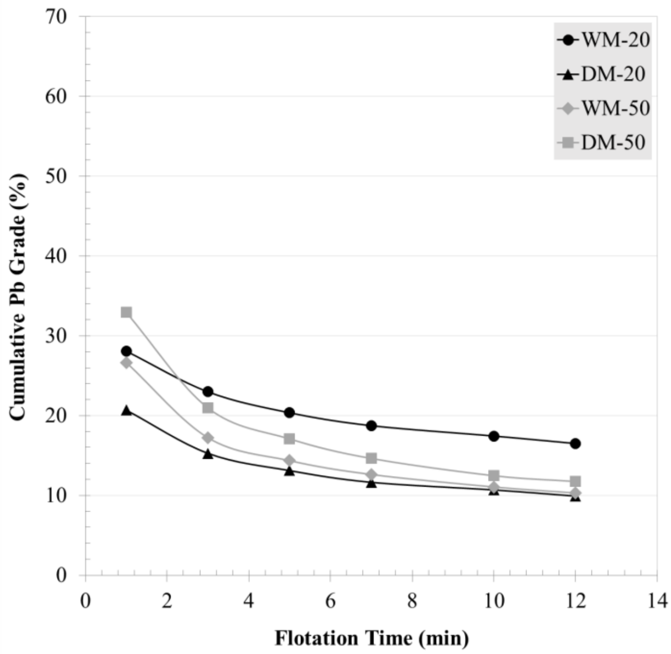

Figure 9. Cumulative Pb Grade over Time

The best results were obtained with the DM-50 sample in terms of both grade and recovery. Overall, it can be said that the dry grinding condition improved both Pb recovery and grade values at 50 µm compared to wet grinding, while having only higher Pb recoveries and lower Pb grades at 20 µm compared to wet grinding. This indicates that further grinding to 20 µm diminishes the flotation selectivity in dry grinding, perhaps due to the non-selective adsorption of fine particles on the mineral surfaces and causes a sudden decrease in the Pb grade values as the flotation time progresses, which is parallel with the highest Pb recoveries obtained at the same condition. Generally, it is also worth mentioning that better Pb grade values were obtained at 20 µm compared to 50 µm in wet grinding with similar Pb recoveries. This indicates that a 20 µm grind size has better flotation selectivity than a 50 µm grind size in wet grinding. Further grinding from 50 µm to 20 µm may be advantageous only in the case of wet grinding, possibly due to the improved dispersion conditions obtained in wet grinding, which protect the non-selective adsorption of fine particles onto mineral surfaces.

Figure 10 shows the flotation selectivity in the galenite flotation stage. In the case of dry grinding at both grind sizes, Zn recoveries in the Pb concentrate were quite high compared to wet grinding. This indicates that dry grinding resulted in the unintentional activation of sphalerite and hence selectivity loss in the galenite flotation. This could be attributed to the oxidizing environment provided during dry grinding (Seke and Pistorius, 2006; Chapman et al., 2013; Nooshabadi and Rao, 2014). It is also worth noting that selectivity loss, i.e., sphalerite reporting to the Pb concentrate, was higher at 50 μm compared to 20 μm in both grinding conditions, despite similar Pb recoveries, indicating that further grinding to 20 μm resulted in relatively better selectivity compared to 50 μm.

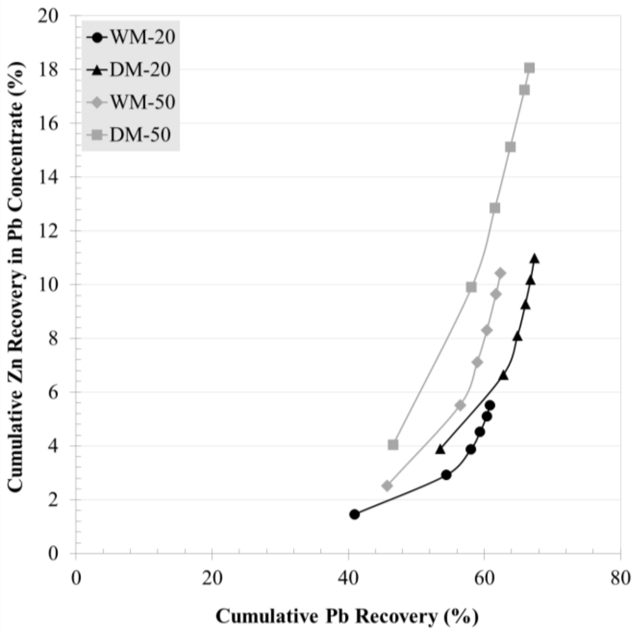

Figure 10. Cumulative Zn Recovery in Galenite Concentrate versus Cumulative Pb Recovery

In the galenite flotation stage, the flotation rate constants were also calculated to compare the effect of different grinding conditions based on a classical first-order flotation kinetics model (Equation 3).

$$R = R_{max}\,(1 - e^{-kt}) \quad (3)$$

where, R is the calculated recovery, R_{max} is the theoretical maximum recovery, k is the first-order flotation rate constant, and t is time. The results are presented in Table 4.

Table 4. First-Order Rate Constants of Galenite Flotation

		20 μm		50 μm	
		Pb	Zn in Pb	Pb	Zn in Pb
Rate constants, k	Dry grinding	1.66	0.38	1.31	0.27
	Wet grinding	1.13	0.26	1.25	0.22

The results indicate that the k values obtained at both grind sizes are higher for the dry grinding conditions compared to the wet grinding conditions, meaning faster flotation kinetics in the case of dry grinding. Furthermore, the higher rate constant values obtained at 20 μm compared to 50 μm grind size in the case of both grinding conditions imply faster flotation kinetics at 20 μm grind size. Furthermore, the kinetics of sphalerite reporting to Pb concentrate was also faster in the case of dry grinding and at 20 μm grind size.

4.4 Effects of Grinding Conditions on Sphalerite Flotation Kinetics

Experimental conditions for sphalerite rougher flotation kinetic tests are given in Table 5. The results of sphalerite flotation tests are shown in Figures 11 and 12.

Table 5. Experimental Conditions for Sphalerite Flotation

	Reagents	Dry & Wet Grinding Samples
pH		11
Activator	$CuSO_4$ (g/t)	1250
Collector	SIPX (g/t)	60
Frother	AF-70 (g/t)	40

Figure 11 shows the variation of the cumulative Zn recovery over flotation time. The Zn recoveries obtained in the first five minutes appear to be quite high, indicating that the majority of the sphalerite was recovered within the first five minutes, except for dry grinding at 50 μm. The highest Zn recoveries were obtained in the case of dry grinding at 20 μm grind size, while the lowest Zn recoveries were at 50 μm with dry grinding for all other conditions ultimate zinc recoveries are same. This is parallel with the results of the highest Zn recoveries reported to the Pb concentrate (Figure 10). In the case of wet grinding, Zn recoveries were low at shorter flotation times but increased at both grind sizes, particularly at longer flotation times. The Zn recovery differences in different grinding conditions got smaller and became quite similar at longer flotation times. As a result, in the case of sphalerite flotation, the enhanced flotation response of sphalerite observed after dry grinding may have been diminished due to the longer exposure time of sphalerite surfaces to water.

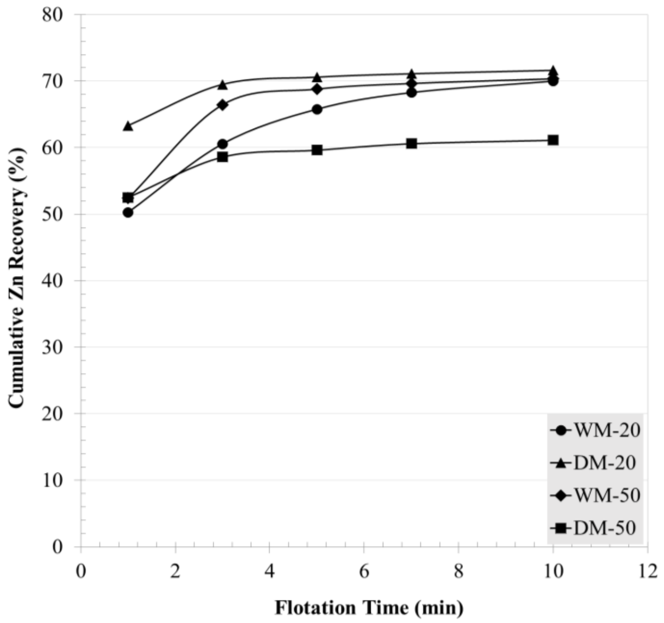

Figure 11. Cumulative Zn Recovery over Time

The variation of the cumulative Zn grade with flotation time is depicted in Figure 12. The lowest Zn grades were acquired at a 50 μm grind size in the case of dry grinding, in accordance with the obtained Zn recoveries under the same conditions. The highest grade values obtained at the grind size of 20 μm with similar Zn recoveries could be attributed to the better liberation of the sphalerite compared to 50 μm.

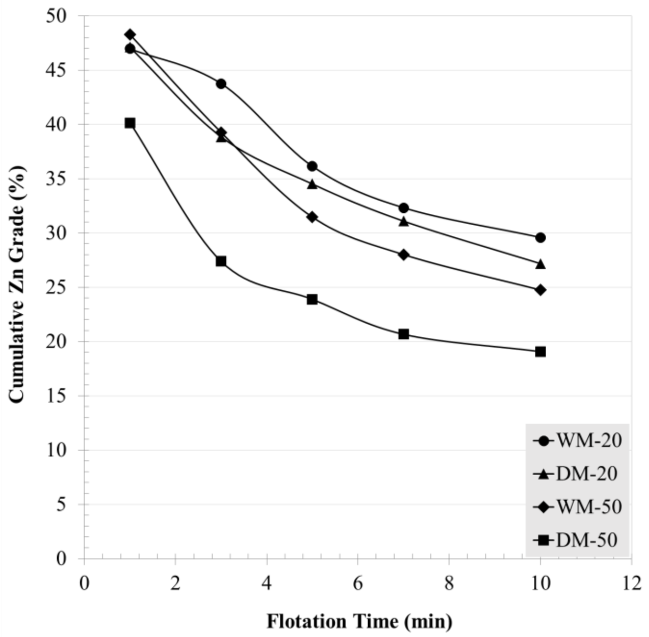

Figure 12. Cumulative Zn Grade over Time

Calculated first-order flotation rate constants are presented in Table 6. The k values obtained at both grind sizes are higher for the dry grinding conditions compared to the wet grinding conditions, meaning faster flotation kinetics in the case of dry grinding. Furthermore, the rate constant values obtained at both grind sizes are quite similar in the case of dry and wet grinding conditions.

Table 6. First-Order Rate Constants of Sphalerite Flotation Stage

		20 μm	50 μm
		Zn	Zn
Rate constants, k	Dry grinding	2.11	2.07
	Wet grinding	1.10	1.40

4.4. Effects of Grinding Conditions on the Pulp Chemistry

In flotation, pulp chemistry, especially in terms of -*interactions between minerals and minerals and the grinding medium, plays a vital role. Pulp potential (E_h), an indication of the pulp chemistry, is a critical monitoring tool and control parameter affecting the success of the flotation process. E_h is used as an indicator in oxidation-reduction environments and is affected by the pulp's pH and dissolved oxygen amounts. It is known that E_h values are directly dependent on grinding conditions. Thus, grinding conditions play an essential role in sulfide minerals' flotation recovery and selectivity.

The change in E_h values during flotation stages was monitored over time following dry and wet grinding. The monitored E_h values are shown in Figure 13. The E_h values of the dry grinding samples are very close to each other, while the pulp potentials are significantly reduced after wet grinding. There is a potential difference of around 350 mV between the dry-ground and wet-ground samples. Due to the longer grinding time, this difference becomes even more remarkable at a 20 μm grind size. High pulp potential values of dry ground samples show superior flotation performance compared to wet grinding at both particle sizes studied, especially in the galenite flotation stage, bearing in mind that sphalerite reporting to galenite concentrate was increased as well. In the literature, it has been shown that dry grinding prior to flotation may have advantages over wet grinding, particularly in sulfide ores. In a dry grinding environment, the newly liberated mineral surfaces are not affected by galvanic interactions during grinding and are affected much less during the following flotation process. Hence, better flotation responses were observed after dry grinding compared to wet grinding.

In the case of the following sphalerite stage, the enhanced flotation response of sphalerite observed after dry grinding was diminished since the E_h difference observed in the case of dry and wet grinding conditions was minimized along with the longer exposure time of sphalerite surfaces to water. Similar results were observed in the literature and attributed to the rapid oxygen consumption in the steel grinding medium, which is generally electrochemically active. The E_h and dissolved oxygen values decrease, and a reducing environment is formed. The problem with the reduction in pulp potential values is usually related to preventing thiol collectors' adsorption to the surface of the sulfide minerals and resulting in the inhibition of flotation (Forssberg et al., 1993; Leppinen et al., 1998; Martin et al., 1992; Yuan et al., 1996a, b). The low potential values observed after wet grinding also indicate the presence of oxygen consumers, such as metallic iron, in the pulp (Bruckard et al., 2011). The observed low potential and dissolved oxygen ratios cause a decrease in the oxidation of minerals during the conditioning phase (Koleini et al., 2012). Due to the lower pulp potential of the steel grinding medium, iron hydroxide products are formed in the pulp, and as discussed earlier, these formed species may have adversely affected the galenite-sphalerite flotation. This difference in pulp potentials after dry and wet grinding shows how the products form as a result of galvanic interaction during wet grinding and affect the pulp chemistry and floatability of the ore.

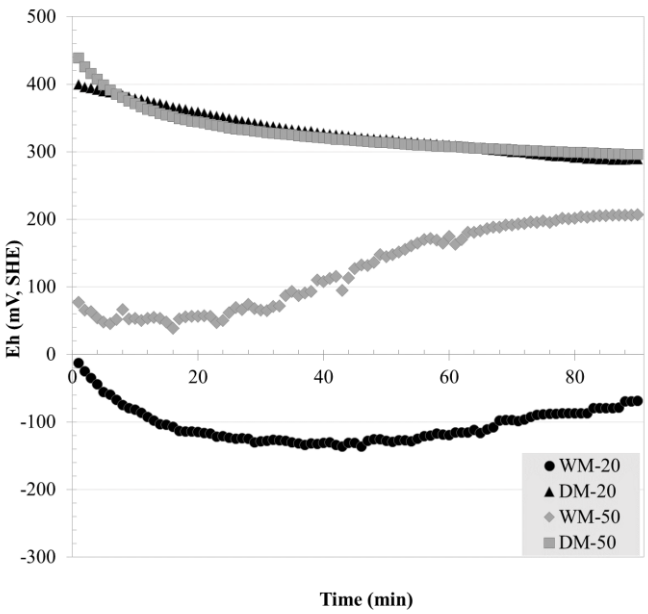

Figure 13. Pulp Potential and Time Relationship

5. Conclusions

Particle size analysis, together with the particle shape and morphology characterization tests performed on the Pb-Zn complex sulfide ore, revealed that the difference between the samples utilized in the kinetic flotation test was negligible; therefore, the difference in flotation response of the ore might be due only to pulp chemistry differences generated by the dry and wet grinding conditions. Overall, kinetic flotation tests showed a significant difference between the flotation performances of the ore following dry and wet grinding conditions.

In the galenite flotation stage, higher Pb-recoveries were obtained at 50 and 20 µm grind sizes following dry grinding compared to wet grinding, but with a significant loss in selectivity due to the unintentional activation of sphalerite. This was attributed to the significantly higher positive pulp potentials, i.e., the highly oxidizing environment provided during dry grinding. Calculated flotation rate constants at 50 and 20 µm in the case of dry and wet grinding conditions also further confirmed these results.

In the sphalerite flotation stage, the highest Zn recoveries were obtained in the case of dry grinding at 20 µm grind size, while the lowest Zn recoveries were at 50 µm due to the highest Zn recoveries reported to the Pb concentrate. The Zn recovery differences following dry and wet grinding conditions were quite similar, indicating that the enhanced flotation response of sphalerite observed after dry grinding may have been diminished due to the longer exposure time of sphalerite surfaces to water, as confirmed by the measured E_h values. The highest Zn grade values obtained at the grind size of 20 µm were attributed to the better liberation of the sphalerite. Calculated flotation rate constants at 50 and 20 µm in the case of dry and wet grinding conditions were also in accord with the results.

This study showed that differences in grinding schemes in terms of dry and wet grinding affect flotation performance significantly and necessitate an elaborate reagent regime with strict control of pulp Eh and pH.

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Author Contributions

Işıl Tokcan contributed to the implementation of the research, analysis of the results, and writing of the manuscript. Murat Mümtaz Volkan Bozkurt contributed to the design of the research, analysis, and discussion of the results and review of the manuscript.

Conflict of Interest

No conflict of interest was declared by the authors.

References

Allison, S.A., Goold, L.A., Nicol, M.J.& Granville, A. (1972). *A determination of the products of reaction between various sulphide minerals and aqueous xanthate solution, and a correlation of the products with electrode rest potential*. Metall. Trans. 3, 2613–2618.

Başaran, Ç. (2006). *Kuru öğütmenin sülfürlü cevherlerin flotasyon performansına etkisi*, Yüksek Lisans Tezi, Hacettepe Üniversitesi, Ankara, Türkiye.

Bruckard, W.J., Sparrow, G.J. & Woodcock, J.T. (2011). *A review of the effects of the grinding environment on the flotation of copper sulphides*, International Journal of Mineral Processing, 100,1-13. http://dx.doi.org/10.1016/j.minpro.2011.04.001

Bulatovic, S., & Wyslouzil, D.M. (1985). *Selection of reagent scheme to treat massive sulphide ores, Complex Sulphides, Processing of Ores, Concentrates and By-Products* (Ed. By A.D. Zunkel, R.S. Boorman, A.E. Morris and R.J. Wesely), Metallurgical Society, 101-141.

Cases, J.M., de Donato, P., Kongolo, M., & Michot, L. (1989). *The influence of grinding media on the adsorption and abstraction of potassium amyl xanthate on finely ground galena and pyrite*, SME Preprint, SME, Littleton Colorado, 89-62.

Chapman, N. A., Shackleton, N. J., Malysiak, V., & O'Connor, C. T., (2013). *Comparative study of the use of HPGR and conventional wet and dry grinding methods on the flotation of base metal sulphides and PGMs*, The Journal of the Southern African Institute of Mining and Metallurgy, 113, 407-413.

Dávila-Pulido, G.I., Uribe-Salas, A., & Espinosa-Gómez, R., (2011). *Comparison of the depressant action of sulfite and metabisulfite for Cu-activated sphalerite*, International Journal of Mineral Processing, 101(1-4), 71-74. https://doi.org/10.1016/j.minpro.2011.07.012

Ek, C. S., (1985). *Selective flotation of different complex pyritic ores*, In Complex Sulfides, Zunkel A.D. and others (Eds.), TMS-AIME, Warrendale, 83-101.

Fahlstrom, P.H. (1974). *Autogeneous grinding of base metal ores at Boliden Aktiebolag*. CIM Bulletin, 78, 127-141.

Feng, D., & Aldrich, C. (2000). *A comparison of the flotation of ore from the Merensky Reef after wet and dry grinding*, International Journal of Mineral Processing, 60 (2), 115-129. https://doi.org/10.1016/S0301-7516(00)00010-7

Franks, G. V., Forbes, E., Oshitani, J., & Batterham, R.J. (2015*). Economic, water and energy evaluation of early rejection of gangue from copper ores using a dry sand fluidised bed separator*, Int. J. Miner. Process., 137, 43–51. https://doi.org/10.1016/j.minpro.2015.03.001.

Forssberg, E., & Subrahmanyam, T.V., (1993). *Grinding, pulp chemistry and particle floatability*, Proceedings of the XVIII International Mineral Processing Congress, Sydney, Vol. 1. The Australasian Institute of Mining and Metallurgy, Melbourne, 1-6.

Grano, S.R., Wong, P., Skinner, W., Johnson, N.W. & Ralston, J., (1994). *The effect of autogenous and ball mill grinding on the chemical environment and flotation of the copper ore of Mount Isa Mines Limited*, In III Latin American Congress on Froth Flotation (University of Concepcion Publ.), Concepcion, Chile, 351-388,

Grano, S., (2004). Private Communication, Ian Wark Institute. Uni.S. Aus., Adelaide, Australia.

Gunson A.J., Klein, B., Veiga, M. & Dunbar, S., (2012). *Reducing mine water requirements,* Journal of Cleaner Production, 21 (1), 71-82. https://doi.org/10.1016/j.jclepro.2011.08.020

Houot, R., & Duhamet, D. (1990). *Importance of oxygenation of pulps in the flotation of sulphide ores*, International Journal of Mineral Processing, 29, 77-87. https://doi.org/10.1016/0301-7516(90)90006-K

Kanda,Y., Abe, Y., Yamaguchi, M. & Endo, C. (1988). *A Fundamental Study of Dry and Wet Grinding from The Viewpoint of Breaking Strength,* Powder Technol.,56, 57-62, 10.5188/ijsmer.7.195

Kökkiliç, O., Langlois, R., & Waters, K.E. (2015). *A design of experiments investigation into dry separation using a Knelson Concentrator*,. Miner. Eng. 72, 73–86. https://doi.org/10.1016/j.mineng.2014.09.025

Koleini, S.M.J., Abdollahy, & M., Soltani, F. (2012). *Wet and dry grinding methods effect on the flotation of Taknar Cu-Zn sulphide ore using a mixed collector*, XXVI International Mineral Processing Congress (IMPC) 2012 Proceedings, New Delhi, India, 5113-5119. 10.13140/2.1.3508.9606

Learmont, M.E., & Iwasaki, I. (1984). *Effect of grinding media on galena flotation*, Minerals and Metallurgical Processing, 136.

Leppinen, J.O., Hintikka, V.V. & Kalapudas, R.P. (1998). *Effect of electrochemical control on selective flotation of copper and zinc from complex ores*, Minerals

Engineering,11(1),39-51. https://doi.org/10.1016/S0892-6875(97)00137-4

Martin, C.J., McIvor, R.E., Finch, J.A., & Rao, S.R., (1992). *Review of the effect of grinding media on flotation of sulfide minerals*, Minerals Engineering 4(2), 121-132.

Nguyen, M.T., Ziemski, M. & Vink, S. (2014). *Application of an exergy approach to understand energy demand of mine water management options*, J. Clean. Prod. 84, 639–648. https://doi.org/10.1016/j.jclepro.2014.04.004

Nooshabadi, A.J. & Rao, K. H. (2014). *Formation of hydrogen peroxide by sulphide minerals*. Hydrometallurgy,141,82–8. https://doi.org/10.1016/j.hydromet.2013.10.011

Ocepek, D., Strazisar, J. & Kanduti-Sumej, B. (1990). *Comminution and surface properties of minerals. In: Schonert*, K. (Ed.), 7th European Symposium Comminution: Clausthal, Zellerfeld. BRD, 273–282.

Ogonowski, S., Wołosiewicz-Głab, M., Ogonowski, Z., Foszcz, D., & Pawełczyk, M. (2018). *Comparison of wet and dry grinding in electromagnetic mill*, Minerals,8(4). https://doi.org/10.3390/min8040138

Orumwense O. A., & Forssberg E. (1991). *Surface and structural changes in wet ground minerals*, Powder Technology,68,23-29. https://doi.org/10.1016/0032-5910(91)80060-V

Palm, N. A., Shackleton, N. J., Malysiak, V. & O'Connor, C.T. (2010). *The effect of using different comminution procedures on the flotation of sphalerite*, Minerals Engineering, 23, 1053-1057. https://doi.org/10.1016/j.mineng.2010.08.001

Petruk, W. (1986). *The MP-SEM-IPS image analysis system*, CANMET Report 87-IE (CANMET, Dept Energy, Mines and Resources, Canada), Ottawa.

Petruk, W. (1988). *Automatic image analysis for mineral beneficiation,* J. Metals, 40,29-31. https://doi.org/10.1007/BF03259018

Petruk, W. (1989). *Short course on image analysis applied to mineralogy and earth sciences*, Mineralogical Ass. Canada: Ottawa.

Ranängen, H., & Lindman, Å. (2017). *A path towards sustainability for the Nordic mining industry*, J. Clean. Prod.151,43–52. https://doi.org/10.1016/j.jclepro.2017.03.047

Rao, S.R., Moon, K.S., & Leja, J., (1976). *Effect of grinding media on the surface reactios and flotation of heavy metal sulphides in flotation*, M.C. Fuerstenau (Ed.), AIME Newyork, 509-527.

Routray, S & Swain R. (2019). *Effect of chemical additives on reduction in Mill power during continuous grinding of chromite overburden materials in a tumbling Mill: a case study*. J Inst Eng (India): 100:123–8. http://dx.doi.org/10.1007/s40033-018-0170-7.

Ruonal, M. Heimala, S. & Jounela, S. (1997). *Different aspects of using electrochemical potential measurements in mineral processing,* International Journal of Mineral Processing, 51, 1–4, 97-110. https://doi.org/10.1016/S0301-7516(97)00023-9

Rivas-Perez, R., Sotomayor-Moriano, J. & Perez-Zuñiga, C.G., (2017). *Adaptive Expert Generalized Predictive Multivariable Control of Seawater RO Desalination Plant for a Mineral Processing Facility*, IFAC-PapersOnLine50,10244–10249. https://doi.org/10.1016/j.ifacol.2017.08.1284

Seke, M. D. (2005). *The optimization of the selective flotation of galena and sphalerite at Rosh Pinah Mine*, Doctoral thesis, University of Pretoria, Pretoria, South Africa.

Seke, M. D., & Pistorius, P.C. (2006). *Effect of cuprous cyanide, dry and wet milling on the selective flotation of galena and sphalerite*, Minerals Engineering,19,1-11. https://doi.org/10.1016/j.mineng.2005.03.005

SIP STRIM, (2019). *Strategic Research and Innovation Roadmap for the Swedish Mining*. Mineral Metal Prod. Ind.

Tokcan, I. (2017). *Farklı öğütme koşullarının kurşun-çinko flotasyonu üzerindeki etkisi*, Doktora tezi, Eskişehir Osmangazi Üniversitesi, Türkiye. http://hdl.handle.net/11684/1625

Tokcan, I & Bozkurt, M.M.V. (2021). *Öğütme Şartlarının Galenit Flotasyonuna Etkisi*, ESOGÜ Müh. Mim. Fak. Derg.,29(2),224-234. https://doi.org/10.31796/ogummf.936105

Thornton, E. (1973). *The effect of grinding media on flotation selectivity,* Canadian Mineral Processors Annual General Meeting, 223.

Wotruba, H., Hoberg, H., & Schneider, F.U.,(1991). *Investigations on the separation of microlithe and zircon-the influence of particle shape on floatability*, XVII International Mineral Processing Congress, Federal Republic of Germany, Dresden, 83-95.

Yekeler, M., Ulusoy, U., & Hiçyılmaz, C., (2004). *Effect of particle shape and roughness of talc mineral ground by different mills on the wettability and floatability*, Powder Technology, 140 (1), 68-78. https://doi.org/10.1016/j.powtec.2003.12.012

Yuan, X.M., Pålsson, & B.I., Forssberg, K.S.E., (1996a). *Flotation of a complex sulfide ore, I. Cu/Zn selectivity control by adjusting pulp potential with different* gases, International Journal of Mineral Processing, 46, 155–179. https://doi.org/10.1016/0301-7516(95)00094-1

Yuan, X.M., Pålsson, B.I., Forssberg, K.S.E., (1996b). *Flotation of a complex sulfide ore, II. Influence of grinding environments on Cu/Zn sulfide selectivity and pulp chemistry*, International Journal of Mineral Processing,46,181–204. https://doi.org/10.1016/0301-7516(95)00095-X