STATISTICAL SIGNIFICANCE TESTING OF THE PARTICLE CIRCULARITY VALUES FROM VARIOUS PRODUCTS OF SPHALERITE COLUMN FLOTATION BENEFICIATION WITH ULTRASONIC PRE-TREATMENT

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Abstract: In this study, circularity of particles from various streams (such as feed and concentrates) of sphalerite beneficiation by column flotation with and without ultrasonic pre-treatment were measured by a recent technique; Dynamic image analysis (DIA) by counting more than 20 000 particles for each population. Then the statistical significance of mean circularity values was tested by using one way ANOVA (analysis of variance) and post hoc Tukey test. ANOVA results showed that circularity values of each particle from these product streams of column flotation with and without ultrasonic pre-treatment was statistically different from each other at the confidence level of 95%. DIA results showed that the highest circularity value was obtained in the concentrate of column flotation with ultrasonic pre-treatment which gives the highest zinc grade and recovery indicating that particle circularity has small but positive effect on the sphalerite column flotation beneficiation with ultrasonic pre-treatment.
Keywords: Zinc, circularity, column flotation, ultrasonic treatment, ANOVA

Introduction

Zinc is used by the industries such as rubber, chemical, paint, and agricultural. About three-fourths of zinc used is consumed as metal for coating, alloying metal, and zinc-based die casting applications and rolled zinc (http://www.niton.com/docs/literature/infographic_zinc3.pdf?sfvrsn=2). Zinc mine production in the world in 2014 was about 13 million tons (U.S. Geological Survey, 2015) indicating that it plays an important role in the global mineral economy.

Flotation is the most widely used separation process for the recovery of sphalerite from low grade complex Pb-Cu-Zn ores. Column flotation which is a patented process since 1962 have accomplished substantial industrial application over mechanical flotation since 1981 (Wheeler, 1988). Ameliorated concentrate grades and recoveries with decreased reagent consumption are the advantages ascribed to column cells which can operate with very deep froths and can be sprayed with wash water thus achieve high concentrate grades (Deglon, 1998).

Ultrasonic bath is a tool that uses high frequency sound waves (above the range of human hearing) to agitate an aqueous that in turn acts on contaminants adhering to substances like metals. By using ultrasonic effect with zinc column flotation our recent study has shown that ultrasound pre-treatment has improved column flotation performance with respect to zinc grade and recovery in multiple stages of column flotation (19.91 and 4.96 units, respectively) (Kursun and Ulusoy, 2015).

It is well known that flotation is a complex phenomenon in which particle shape is one of the affecting parameters of physical parameters of the particulates. Effect of particle shape on flotation has been investigated by various works regarding attachment-detachment process (Wotruba et al., 1991), the induction period for particle-bubble attachment in flotation (Verrelli et al., 2012), flotation kinetics constant of the particles (Dehghani et al., 2013; Rahimi et al., 2012), wettability (Ulusoy et al. 2004; Hiçyılmaz et al, 2004), flotation recovery (Forssberg and Zhai, 1985), and column flotation (Kursun and Ulusoy, 2006). Thus, the particle shape distribution of feed and concentrate streams of mineral flotation circuits needs to be characterized to understand how shape affects the recovery of minerals (Durney and Meloy, 1986). Dynamic Image Analysis (DIA) which is defined as image analysis methods while particles are in motion entails using techniques for dispersing particles in liquid, taking in focus, and analyzing the images using shape parameters (http://www.micromeritics.com/Repository/Files/The_Effects_of_Particle_Shape_on_Measured_Particle_Size_2011.pdf). DIA is a fast method that eradicates operator prejudice and fatigue. It brings reliability, accuracy and

reproducibility regardless who is performing the analysis. In addition, it allows statistically substantial sampling of 10 000 - 500 000 particles in one measurement.

One Way ANOVA (Analysis of variance) is an analysis of variance which is used to compare mean differences in two or more groups of measurements in image analysis. When the F-test is statistically significant, the null hypothesis is rejected. However, it is still necessary to determine which of the means were significantly different from each other. Post hoc tests are essential to determine which groups are actually different (Boslaugh and Watters, 2008; Ulusoy, 2008).

The aim of this work is to measure the particle circularity values of feed and column flotation concentrates with and without ultrasonic pre-treatment (Kursun and Ulusoy, 2015) and to corroborate the statistical significance of mean circularity values from these various column flotation streams tested by using one way ANOVA and post hoc Tukey test.

Materials and Methods

In this study, the same sphalerite ore which was taken from zinc feed of the selective zinc flotation circuit in a plant (GESOM A.Ş.) treating lead-zinc-copper complex ore (Kursun and Ulusoy, 2012; Kursun, 2014; Kursun and Ulusoy, 2015) in Turkey was used. The XRD of the ore which includes 3.23% Pb, 0.52% Cu and 2.71% Zn was already reported elsewhere (Kursun, 2014). The particle size of the sample was smaller than 74 μm (100 %) for the column flotation tests (Figure 1) which were performed by a 5 x 75 cm tubular flotation column cell (Ünal Mühendislik A.Ş., Turkey). The detailed information about the column flotation experiments by single and multistage was already described in the previous study (Kursun and Ulusoy, 2015). The pulp density was used as 30%. Flotation chemicals such as KAX (Dow Chemical), $CuSO_4$ (Merck), Aerofloat 211 (Cyanamid), 2-Ethyl hexanol (Merck) and Na_2SiO_3 (Merck) were used as collector, activator for sphalerite, collector for selective sphalerite flotation, frother and gangue depressant, respectively. Operational parameters of column flotation were optimized by single stage column flotation without ultrasonic pre-treatment. Optimized dosage values of these flotation conditions include 400 g/t of $CuSO_4$, 100 g/t of Aerofloat 211, 15 g/t of 2-ethyl hexanol, 50 g/t of Na_2SiO_3, 90 g/t of KAX, 160 rpm of stirring speed, 0.170 cm/sec of superficial wash water rate, 0.425 cm/sec of superficial feed rate, 1.5 cm/sec of superficial air rate, 4 min. of residence time, 0.437 cm/sec of tailing flow rate, 0.170 cm/sec of superficial wash water rate, 0.0123 cm/sec of bias flow rate, 0.425 cm/sec of superficial feed rate and 1.5 cm/sec of superficial air rate was. Tap water (pH: 8.2) was used for the experiments and pH was arranged as 11.5 by using lime (Merck). Collected concentrates were weighed and analyzed when the system was reached to steady state. Experiments were iterated until the consistent grade and recovery values were obtained as 3 repeats. Multiple stages (3 stages of cleaning and 3 stages of scavenging) of column flotation tests were carried out with and without ultrasonic pre-treatment after single stage column flotation experiments with and without ultrasonic pre-treatment. After column flotation tests, the feed and concentrates of multiple stages (3 stages of cleaning and 3 stages of scavenging) of column flotation tests were subjected to DIA analysis for the measurement of circularity values.

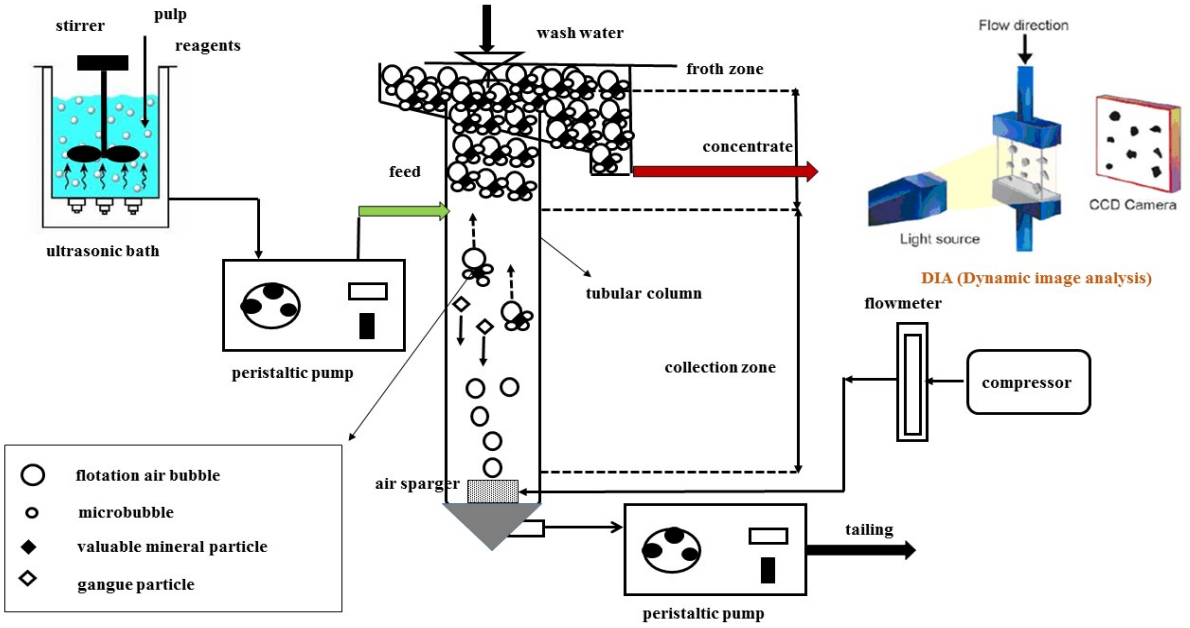


Figure 1. The experimental set-up used in this study (redrawn from Kursun and Ulusoy, 2015).

For the preparation of a few grams of representative sample to perform DIA, automatic rotary spinning riffler (Quantachrome® Instruments) was used. Then, prepared representative samples were placed in a 25 ml glass sample container added with water and hold in the ultrasonic bath for 5 min for good dispersion of the representative sample for DIA measurements.

Circularity (C) which is a fractional measure indicating shape of the particles and calculated from area (A) and bounding circle diameter (D_{BC}) as $4A/\pi D^2_{BC}$. For a spherical particle C is equal to 1 on the other hand C is lower than 1 for irregular particles such as elongated particles (Ulusoy and Yekeler, 2014).

Circularity values of sphalerite particles from three column flotation streams such as feed (C_F), concentrate with ultrasonic pre-treatment (C_{CFCUP}) and concentrate without ultrasonic pre-treatment (C_{CFC}) were determined as the average of three measurements by using a new 3D real-time dynamic image analyzer **(**Particle Insight Dynamic Image Analyzer, Micromeritics® Instrument Corp., Norcross, USA**).**

Results and Discussion

Shape results by DIA

Figure 2 illustrates the re-plotted grade and recovery results of sphalerite column flotation with and without ultrasonic pretreatment (Kursun and Ulusoy, 2015). As seen from Figure 2 ultrasonic pretreatment has increased the zinc grade and recovery obtained for both single stage and multi-stage column flotation.

Mean Circularity values of sphalerite particles from column flotation feed and concentrates with and without ultrasonic pre-treatment by DIA was shown by Figure 3 indicating that the highest circularity values obtained for concentrate with ultrasonic pre-treatment (C_{CFCUP}). Overall circularity trends were found as $C_F<C_{CFC}<C_{CFCUP}$.

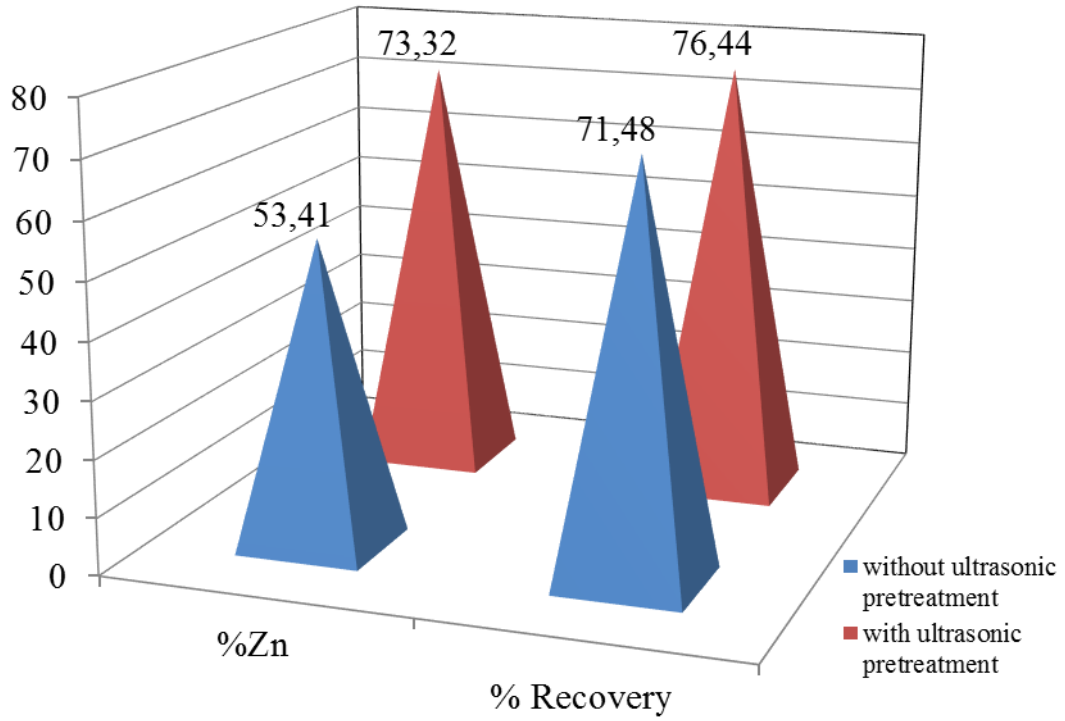


Figure 2. Zinc grade and recovery obtained for multi-stage zinc column flotation with and without ultrasonic pre-treatment (redrawn from: Kursun and Ulusoy, 2015)

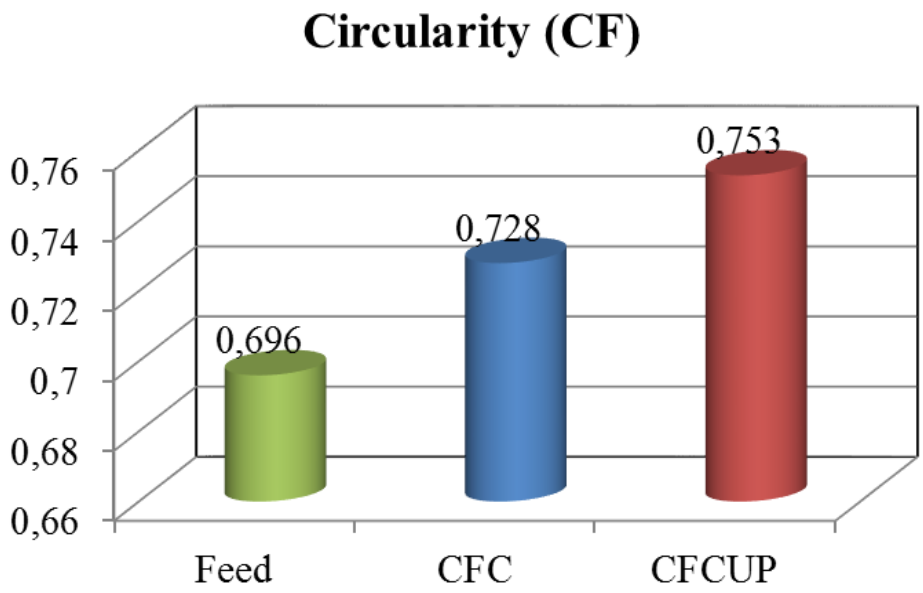


Figure 3. Circularity values measured by DIA from streams of zinc column flotation with and without ultrasonic pre-treatment (*where, F: Feed, CFC: Column flotation concentrate, CFCUP: Column flotation concentrate with ultrasonic pre-treatment)*

As seen from Figure 4 circularity values of sphalerite column flotation concentrates for multistage column flotation were increased with increased zinc grade of the concentrates. Fig. 5 illustrates the particle thumbnail images (C_F, C_{CFCUP} and C_{CFC}) from the circularity measurements by DIA. After analysis and a review of all particles in these thumbnail images which were only a small part of about 20 000 particles for each population, they consist of partly elongated particles and partly blocky (equi-dimensional) particles not represent one type of particle shape since there are small differences in circularity values of particles from each column flotation streams.

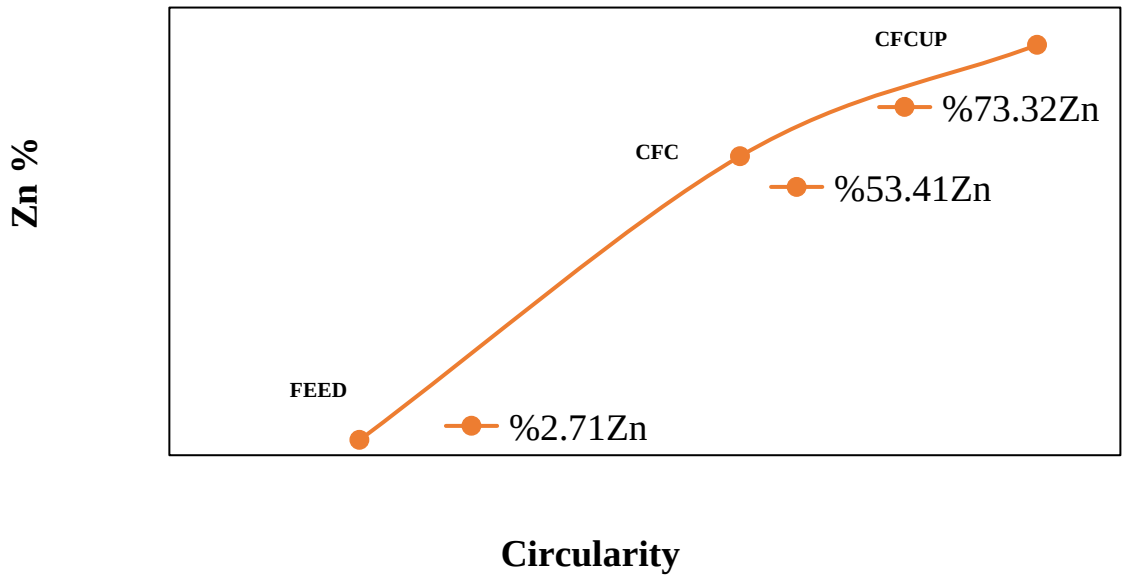


Figure 4. Changes of zinc grade with circularity values measured by DIA various streams of zinc column flotation with and without ultrasonic pre-treatment (Zn data from: Kursun and Ulusoy, 2015)

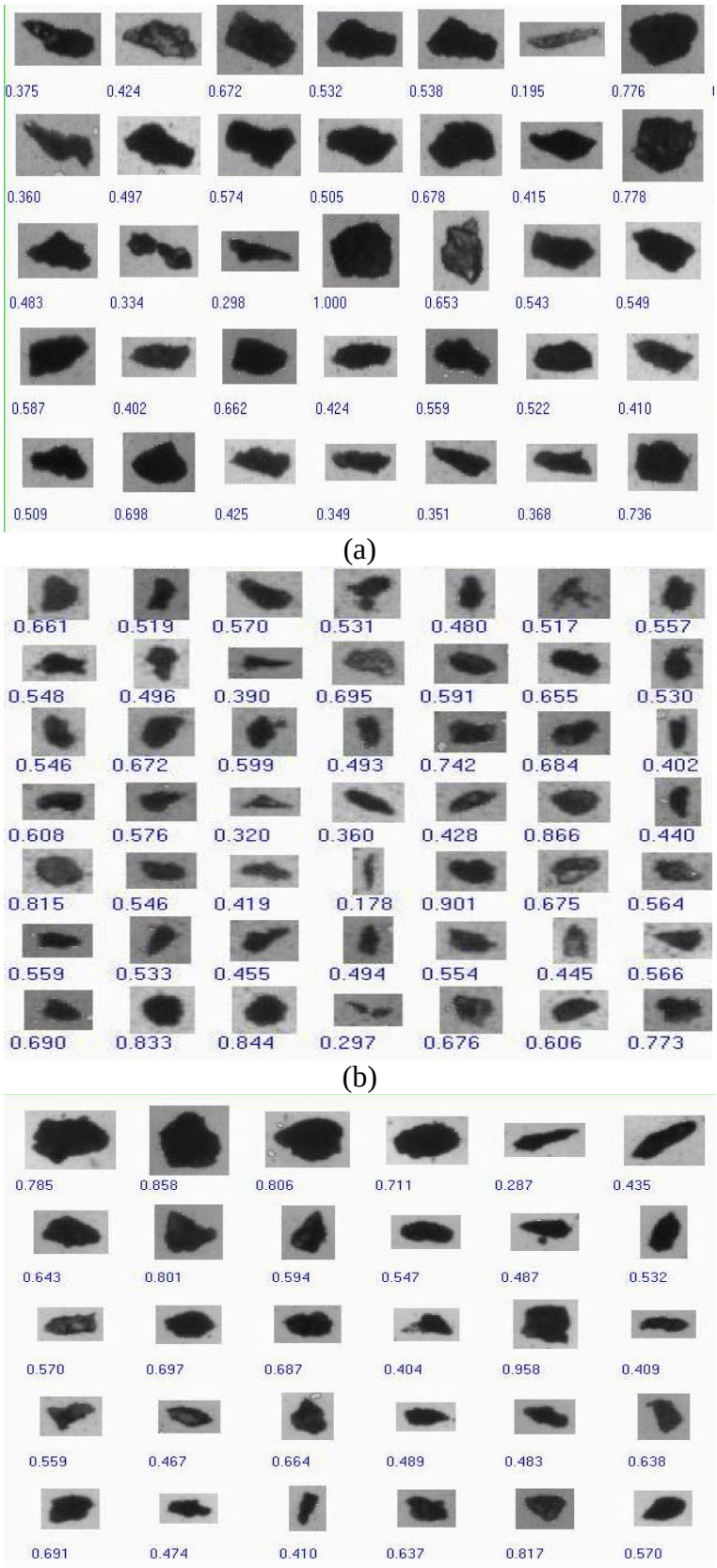


Figure 5. DIA thumbnail images of various streams of zinc column flotation with and without ultrasonic pre-teratment (a) Feed, (b) CFC, (d) CFCUP *(Where, F: Feed, CFC: Column flotation concentrate, CFCUP: Column flotation concentrate with ultrasonic pre-treatment)*

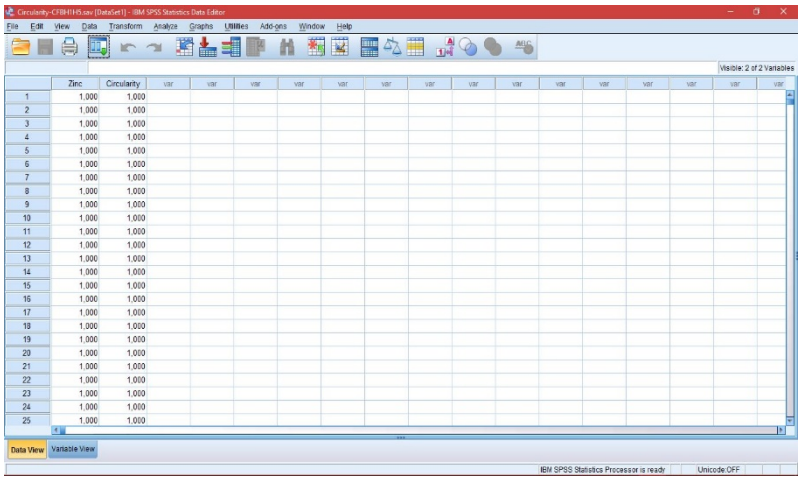
ANOVA Results

Since there is a small trend of increasing for circularity values considering the result of DIA, the significance of the circularity values of each sphalerite samples (feed, concentrate with ultrasonic pre-treatment and concentrate without ultrasonic pre-treatment) must be proved by the statistical test namely ANOVA.

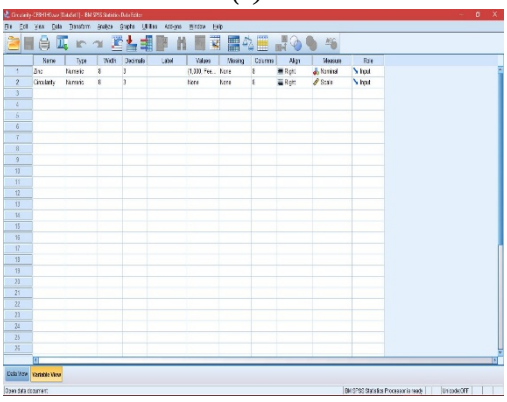
The purpose of ANOVA is to assess whether the observed differences among sample means are statistically significant. ANOVA tests the null hypothesis that the population means are all equal (H_0: $\mu_1 = \mu_2 = \mu_3$) while the alternative is that they are not all equal. This alternative could be true because all the means are different or simply because one of them differs from the rest. If H_0 is not rejected, we conclude that the population means are indistinguishable based on the data given. On the other hand, if H_0 is rejected, we would like to know which pairs of means differ. Multiple-comparisons methods address this issue. It is important to keep in mind that multiple comparisons methods are used only after rejecting the ANOVA H_0 (Moore et al., 2009).

Standard Excel™ spreadsheet data from the automated DIA analyzer were imported by a software called "Statistical Package for Social Science" 22.0 (SPSS Inc., Chicago, IL, USA) to determine whether the circularity parameter of three different sphalerite column flotation streams (feed, concentrate with ultrasonic pre-treatment, concentrate without ultrasonic pre-treatment) were statistically different from each other (Fig 6). Mean values of shape parameter for these products were compared by applying one way ANOVA (Ulusoy, 2008) and post hoc Tukey's multiple comparison tests at significance level of 0.05.

(a)



(b)



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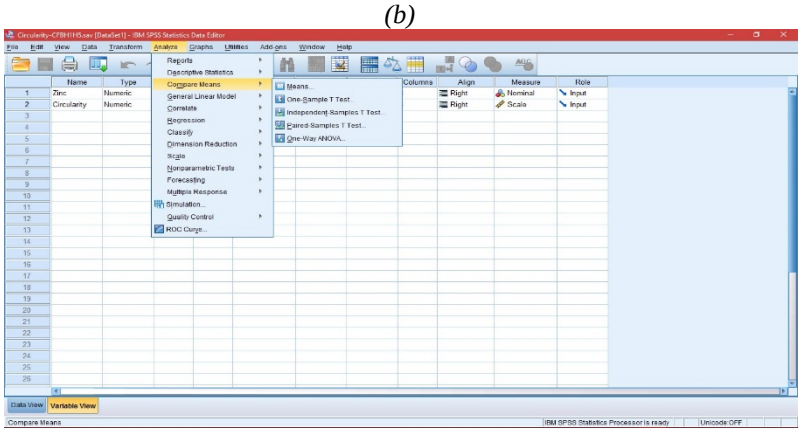

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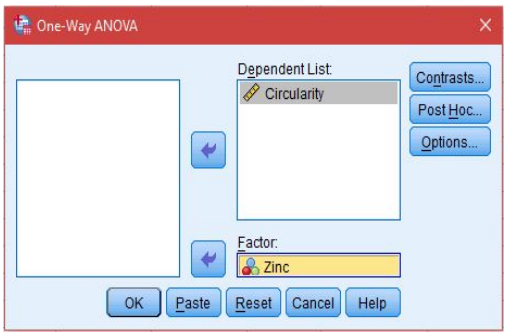

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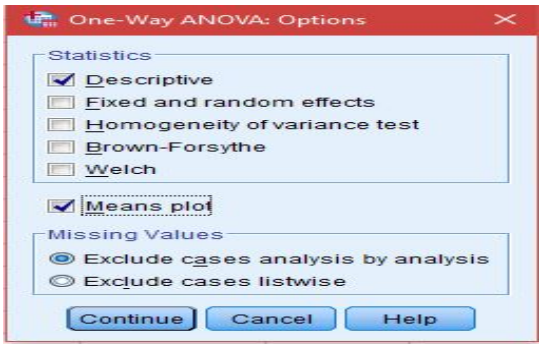
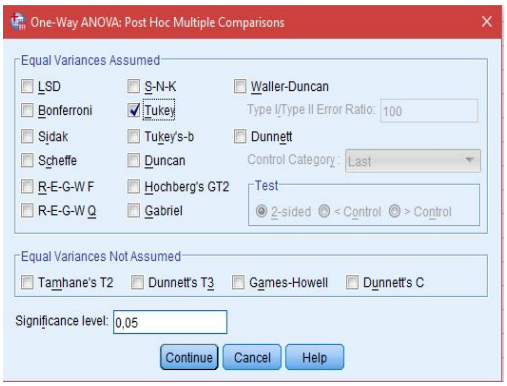


(f)



(g)

Figure 6. ANOVA study conditions by SPSS (a) version (b) data view (c) variable view (d) ANOVA menu (e) ANOVA variable (f) ANOVA options (g) Post hoc multiple comparisons.

In Table 1 there are group statistics, which provide the means and standard deviations of the groups. Table 2 shows the test of homogeneity of variances for circularity values of sphalerite column flotation streams. From Table 2, circularity results show that the test for homogeneity of variances is significant since p=.000 which is greater than 0.05. This means that (p-value is indicating not equal variances) in the homogeneity of variances assumption is not met. The One-Way ANOVA Output was given in Table 3.

Table 1. Descriptive ANOVA results of circularity values of streams of sphalerite column flotation with and without ultrasonic pre-treatment

					95% Confidence Interval for Mean			
Circularity	N	Mean	Std. Dev.	Std. Error	Lower Bound	Upper Bound	Min.	Max.
Feed	19764	.69610	.175971	.001252	.69365	.69856	.031	1.000
CFC	19514	.72368	.161446	.001156	.72141	.72594	.110	1.000
CFCUP	19452	.75422	.166987	.001197	.75187	.75656	.054	1.000
Total	58730	.72451	.169941	.000701	.72314	.72589	.031	1.000

Where, F: Feed, CFC: Column flotation concentrate, CFCUP: Column flotation concentrate with ultrasonic pre-treatment

Table 2. Test of homogeneity of variances for circularity values of streams of sphalerite column flotation with and without ultrasonic pre-treatment

Circularity			
Levene Statistic	df1	df2	Sig.
93.598	2	58727	.000

The results of the overall F test in the ANOVA summary table can be examined to determine whether group means are different. As shown in Table 3, the mean-square ratio experimentally derived (584.974) is higher than the sig. F ratio (0.00) for 95% confidence. So, it can be concluded with 95% confidence that there are significant

differences among circularity values obtained for three sphalerite column flotation streams (such as feed, concentrate without ultrasonic pre-treatment and concentrate with ultrasonic pretreatment).

If the significance value (which is usually labeled p in research reports) is less than alpha H_0 is rejected; if it is greater than alpha, H_0 is not rejected. As indicated, the overall F test is significant (i.e., p value < 0.05), indicating that means among circularity values of each groups are not equal. In other words, since the value of p value is 0.000 as shown in Table 3 there are significant difference among circularity values of each groups for at the 0.05 alpha levels. So, in this case, because the p value of .000 is less than 0.05 alpha level, the null hypothesis was rejected. The results of this ANOVA showed that there are significant differences among the groups.

Table 3. ANOVA results for circularity values of of streams of sphalerite column flotation with and without ultrasonic pre-treatment

ANOVA					
Circularity	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	33.129	2	16.565	584.974	.000
Within Groups	1662.963	58727	.028		
Total	1696.093	58729			

However, it is necessary to conduct post hoc comparison tests to determine which of the group means are different. Results of Tukey post hoc tests were presented in Table 4. From the Table 4 we can see that the circularity values of each sphalerite samples (feed, concentrate with ultrasonic pre-treatment and concentrate without ultrasonic pre-treatment) are significantly different from each other. Because the p value of 0.000 is less than alpha value of 0.05.

Table 4. Results of multiple comparisons by Tukey HSD post hoc tests

		Mean			95% Confidence Interval	
(I)	(J)	Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
Feed	CFC	-.027576*	.001698	.000	-.03156	-.02360
	CFCUP	-.058114*	.001700	.000	-.06210	-.05413
CFC	Feed	.027576*	.001698	.000	.02360	.03156
	CFCUP	-.030538*	.001705	.000	-.03453	-.02654
CFCUP	Feed	.058114*	.001700	.000	.05413	.06210
	CFC	.030538*	.001705	.000	.02654	.03453

*. The mean difference is significant at the 0.05 level.
Where, F: Feed, CFC: Column flotation concentrate, CFCUP: Column flotation concentrate with ultrasonic pre-treatment

The homogenous subsets table (Table 5) can help us to divide the three groups into homogenous subgroups. Within each sub-group the difference in means is statistically significant for circularity. The results also indicate that groups can be put into three subsets, based on mean differences. As the Table 5 indicates, circularity means of sphalerite particles from feed, concentrate without ultrasonic pre-treatment and concentrates with ultrasonic pre-treatment are not grouped together because their means are not similar.

Table 5. Homogeneous subsets of Tukey post hoc tests

		Subset for alpha = 0.05				
Tukey HSD[a,b]	N	1	2	3	4	5
Feed	19764	.69610				
CFC	19514			.72368		
CFCUP	19452					.75422
Sig.		1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 19575.741.
b. The group sizes are unequal. The harmonic mean of the group sizes is used.
Where, F: Feed, CFC: Column flotation concentrate, CFCUP: Column flotation concentrate with ultrasonic pre-treatment

The mean plots (graphically displays the circularity means for the three groups) that SPSS created are an effective way to illustrate the mean differences. The difference between groups was confirmed graphically by looking at the plot of means shown in Fig 7.

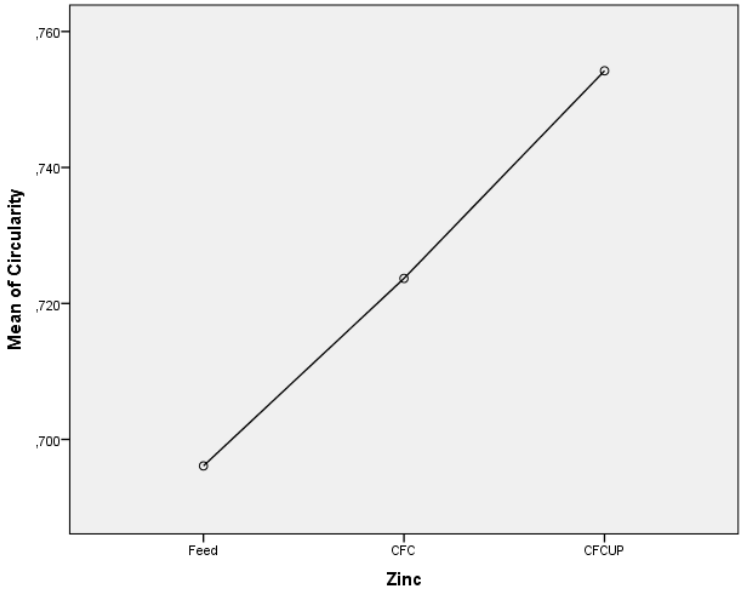


Figure 7. Mean plots for circularity of multiple comparisons for by SPSS

Conclusions

DIA results revealed that the highest mean circularity value was received in the concentrate of sphalerite column flotation with ultrasonic pre-treatment which gives the highest zinc grade and recovery pointed out that particle circularity has small but positive effect on the beneficiation by column flotation with and without ultrasonic pre-treatment.

The differences in circularity parameter of particles among the three populations from various column flotation streams were found statistically significant with a 95% confidence level. In other words, mean circularity values analyzed by counting more than 20 000 particles for each population using DIA were not identical.

Nomenclature

ANOVA	: Analysis of variance
C	: Circularity
CFC	: Column flotation concentrate
CFCUP	: Column flotation concentrate with ultrasonic pretreatment,
DIA	: Dynamic Image Analysis
F	: Feed
H_0	: Null hypothesis
p	: Significance value
μ_1	: Population mean
Alpha	: Confidence level

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