Evaluation of the Relationship between the Milling Breakage Parameters and Mineralogical Data: A Case Study of Three Copper Ores from a Multi-Mineralised Deposit

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Abstract: The study evaluated the milling kinetics of three copper ores, from a multi-mineralised deposit, which were identified as sulphide 1 (with bornite as a dominant copper mineral), sulphide 2 (mainly composed of chalcopyrite) and oxide (with malachite as a dominant copper mineral) and related the breakage parameters to the mineral composition data. Five mono-size fractions between 1000 µm and 212 µm were dry milled for short grinding times in the laboratory ball mill in order to obtain data for predicting breakage rate parameters. The analytical and mineralogical characterisation of the ores were performed using X-ray fluorescence (XRF) analysis, scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) analysis, optical microscopy analysis and X-ray diffractometer (XRD). The mineralogy data showed that quartz was the abundant gangue mineral (average for each ore was above 60% (w/w)), followed by K-feldspar minerals (orthoclase and microcline) which constituted between 4% (w/w) and 6% (w/w) and the remainder are the minor calcite and dolomite minerals which are also in the host rock. The experimental milling kinetics parameters and mineralogical data were used to assess the robustness of the heterogeneous (two-component) and homogeneous (single-component) first-order rate breakage models. The mineral composition data were used for setting up the predictions of breakage parameters in the two-component and single-component first-order breakage models. The experimental data fitted better on the two-component breakage model than the single-component breakage model. These results highlighted the influence of two groups of minerals (generally classed as valuable and gangue minerals). The breakage data showed that the selection function for the hard component (the gangue minerals) has a dominant contribution to the overall selection function of the ores, with S_Sa correlating fairly well with experimental S. The parameter a in the Austin empirical breakage model was relatively similar (approximately 1) for all three ores, which confirms similar milling conditions to which the ores were subjected to. The data suggests that there is a relationship between breakage parameter α (material-specific parameter) in the Austin empirical breakage model and brittleness index βi (calculated from the mineralogical composition of the gangue phase). No clear trends could be deduced from the cumulative breakage distributions of the three ores. This highlights the complexity of developing relationships between the mineralogical composition data and breakage distributions of the ores which are extracted from the same deposit and with comparable gangue composition.

Keywords: mineralogy; copper ores; breakage distribution function; selection function; homogeneous first-order breakage model; heterogeneous first-order breakage model
1. Introduction

The current era of low-grade ores which are characterized by the intergrowth of very fine valuable minerals with the gangue has necessitated research in the mining industry in order to improve the understanding of the mineralogy of the available ores. In order to meet the market demands of metal and non-metal commodities in a world where industrialisation, coupled with population growth, continues to revolutionize, the mining industry has to process high tonnages. This comes at huge costs emanating from the capital investment in high-throughput technologies and high operating costs thereof. Another source of processing challenges in the mining industry is the complexity of ore mineralogy, e.g., within the same ore body there can be a variety of mineralisation zones (with distinct minerals), which may need different process flow sheets [1–3]. Process mineralogy, which is the practical application of mineralogy to help with the process plant design [4–7], has long been used in mineral processing to understand how the mineralogical data can be used to predict and understand the behaviour of the ores when subjected to comminution [8–15] and separation and recovery processes such as flotation [1,3,16,17], leaching [18–21] and gravity separation [22–24].

This paper was limited to the application of process mineralogy on the comminution of ores as it investigated the relationship between the mineralogical data and breakage parameters derived from the batch milling experiments which were conducted using three copper ores extracted from a multi-mineralized deposit. Several investigations attempted to study the relationship between mineralogical data and comminution parameters (e.g., Bond work index). The comprehensive work by Mwanga [13] used various ores including metal oxides (e.g., hematite and magnetite), metal sulphide (containing minerals such as chalcopyrite, sphalerite, pyrite and pentlandite) and non-metallic minerals (e.g., quartz and calcite) to develop a geometallurgical testing framework. The author attempted to develop the relationship amongst mineralogical data and comminution indices (e.g., Bond work index). Another geometallurgical modelling study by Mine [12] attempted to developed mathematical equations relating ore grindability (measured in terms of Bond work index) and mineralogical composition using the Aitik copper mine in Sweden as a case study. The present study build on the previous work to establish whether the variation in the mineralogical composition (in terms of valuable minerals (a minor constituent) and gangue minerals (a major constituent)) of the ores from the same deposit had an effect on their individual breakage characteristics (selection function and breakage distribution function) which can, in turn, have an implication on the milling circuit design.

It is well known that ores are characterised by varying mineral composition, grain size distributions and other structural discontinuities (e.g., cracks, voids, joints) which affect breakage patterns [25–27]. Mineralogically distinct ores of the same metal could thus fracture differently in a comminution device. The copper ores used in the study were sampled from the same pit with different mineralisation zones in the mine within the Pan African Damara Orogen, of the Northern Carbonate Platform section within the Mulden Group in the Otavi Mountain Land (OML) in Namibia [28–32]. The mineralisation is disseminated in the arkosic sandstone with minor calcite (CaCO₃) and dolomite (CaMg(CO₃)₂). The Tsumeb polymetallic (i.e., Cu, Pb, Zn along with As, Sb, Ag, Cd, Au etc.) deposit hosts several mineralisation facies, which are separated into three zones [28], namely the oxide, transition (with both oxide and sulphide copper minerals), and sulphide zones. The three copper ore samples (identified as namely sulphide 1, sulphide 2 and oxide) used in the study were obtained from the sulphide and transition zones and had different compositions of various copper minerals such as bornite (Cu₉FeS₈), chalcopyrite (CuFeS₂), malachite (Cu₂CO₃(OH)₂), and azurite (2CuCO₃·Cu(OH)₂), which are associated with minerals such as pyrite (FeS₂) and silicates such as quartz (SiO₂).
2. Theoretical Background

The fragmentation process in comminution devices such as crushers and mills is very complex, especially when there is interest in knowing the processes happening to the individual particles in the equipment. The numerical approaches such as the discrete element method provide useful insights into that aspect [33–37]. For mass balance purposes, which is relevant to this study, when only the initial and final masses of the material processed in the specific comminution equipment or circuit are considered, the population balance model, reviewed extensively by Solsvik & Jakobsen [38], is adequate to capture the changes in the mass fractions of various size classes. The operation parameters of the comminution machine (e.g., rotation speed, mill fill, and media size/fill in the case of tumbling mills) and material characteristics (e.g., brittleness and toughness) affect the product size distributions. It is acknowledged that the fragmentation process in comminution machines (e.g., in tumbling mill) is facilitated by a combination of two actions taking place simultaneously inside the mill: (1) a selection of the particle for breakage, and (2) breakage resulting in a particular distribution of fragment sizes after the particle is selected [39]. A population balance model, based on various size classes, accounting for both the selection and breakage of particles makes it possible to describe the grinding process mathematically. For a batch milling process treated as a first-order kinetic process, the breakage process is described mathematically using the following equation [40]:

\[
\frac{dw_i(t)}{dt} = -S_i w_i(t) + \sum b_j S_i w_j(t)
\]

where \( w_i \) is the mass fraction of material in size class \( i \), \( S_i \) is the selection function or rate of breakage of size class \( i \), \( b_j \) is the breakage function of fragments into size class \( i \) from size class \( j \), \( S_i \) is the selection function of size class \( j \), \( w_i \) is the mass fraction of material in size class \( j \), and \( t \) is the grinding time.

The selection and breakage functions are used to infer the breakage behaviour of ores in the comminution devices such as crushers and mills. The selection function \( S_i \) describes the rate of breakage (disappearance) of particles from a distinct size class \( i \) or \( j \), while the breakage function \( b_j \) describes the mass fraction breaking out of size class \( j \) that appears in size class \( i \) in the statistical limit \( t \to 0 \). The rate of breakage \( S_i \) is analogous to the first-order chemical reaction rate constant, and thus can be described mathematically as follows (Austin et al., 1984):

\[
\frac{dw_i}{dt} = -S_i w_i
\]

If \( S_i \) is a rate constant during the first-order milling process, then Equation (3) can be derived from Equation (2). The plot of \( \log \left( \frac{w_i(t)}{w_i(0)} \right) \) versus milling time is a straight line whose slope is \( S_i \). The selection function can thus be determined experimentally using mono-sized particles by milling for successive short-grinding times.

\[
\log \left( \frac{w_i(t)}{w_i(0)} \right) = -\frac{S_i t}{2.3}
\]

Gardner and Rogers [41] developed a heterogeneous (two-component) first-order breakage model shown in Equation (4) which is a modification of Equation (2). The equation is derived from the assumption that the total rate of breakage is the sum of breakage of hard component “\( A \)” and soft component “\( B \)”, with \( \varphi \) being the fraction of the hard component and \((1-\varphi)\) the fraction of the soft component of size class \( i \). The hard and soft components can be assumed to be the gangue and valuable minerals, respectively.

\[
\frac{d[w_i(t)]}{dt} = \varphi \frac{dw_{iA}(t)}{dt} + (1 - \varphi) \frac{dw_{iB}(t)}{dt}
\]

Modifying Equation (2), the rates of breakage of the two components in the ore, can be expressed by the following equations:
where $w_{iA}$ is the mass fraction of the hard component in size class $i$, $w_{iB}$ is the mass fraction of the soft component in size class $i$, $S_{iA}$ is the rate of breakage of hard component “A” in size class $i$, and $S_{iB}$ is the rate of breakage of soft component “B” in size class $i$.

For a feed size class $i$, integration by parts of Equation (4) yields Equation (7), the two-component first-order breakage model with two slopes presented as the selection function $S_{iA}$ and $S_{iB}$.

$$w_{i}(t) = \varphi e^{-S_{iA} t} + (1 - \varphi) e^{-S_{iB} t}$$

(7)

As with Equation (3), the breakage experimental data generated using the short-grinding times with mono-sized fractions (and mineral composition data from mineralogical characterisation) can be fitted to Equation (7) to determine the model parameters $S_{iA}$ and $S_{iB}$.

Austin et al. [39] related the rate of breakage to the milling conditions using Equation (8). The denominator in Equation (8) corrects for abnormal breakage which occurs when particle sizes fall outside the size range that the grinding media can nip. When only the normal breakage condition is considered Equation (8) simplifies to Equation (9).

$$S_{j} = \frac{a x_{j}^{q}}{1 + \left(\frac{x_{j}}{\mu}\right)^{\wedge}}$$

(8)

where $x_{j}$ is the upper limit screen in size interval $j$ in mm; $\wedge$ and $a$ are positive constants which are dependent on material properties; $a$ and $\mu$ are model parameters dependent on mill conditions.

$$S_{j} = a x_{j}^{q}$$

(9)

The breakage function in Equation (1) is usually represented as cumulative breakage function $(B_{ij})$, which can be estimated from the size distribution of the product obtained after grinding material in size class $j$ for a short period of time, as shown by Austin et al. [39]. This is summarized in what is known as the BII method represented by the following equation.

$$B_{ij} = \log\left[\frac{(1 - P_{i}(0))}{(1 - P_{j}(0))}\right]/\log\left[\frac{(1 - P_{i}(t))}{(1 - P_{j}(t))}\right], i > j$$

(10)

where $P_{i}(t)$ and $P_{j}(t)$ are the mass fractions of size classes $i$ and $j$ in the mill at the short grinding time $t$. The cumulative breakage function $B_{ij}$ can take the following general form [40]:

$$B_{ij} = \Phi(R_{ij})^{\beta} + (1 - \Phi)(R_{ij})^{\gamma}$$

(11)

where $R_{ij}$ is a relative size given by $\frac{x_{j+1}}{x_{j}}$, $\beta$ is a material-dependent parameter (values usually ranging between 2.5 and 5.0) which describes the slope at coarser sizes, $\gamma$ is also a material-dependent parameter (values ranging between 0.5 and 1.5) which describes the slope at fine sizes, and $\Phi$ is a fraction of fine particles resulting from a single breakage event (it is also dependent on the initial size of the parent material).

Fitting the ball milling data to the models described in this section does not always result in a high degree of fitness due to factors such as feed size distribution, minerals composition and milling conditions [39]. This study focused on how the mineral composition of three distinct copper ores affects the breakage parameters.
3. Methodology

This study used three copper ores, classified as sulphide 1, sulphide 2 and oxide. For each ore type, the homogenisation of about 300 kg sample (pre-crushed to −3.35 mm) was performed using the coning and quartering method to obtain a 75 kg sample for the test work. The 75 kg sample was rifle split into 18.75 kg sub-samples. One of the 18.75 kg samples was dry screened over the 300 µm and 75 µm sieves to obtain material in the −3350 + 300 µm and −75 µm size fractions. The masses were approximately 12 kg and 2 kg for the two size fractions, respectively. The −3350 + 300 µm material was rifle split into 3 kg sub-samples. One of the 3 kg samples was further rotary split to obtain 375 g samples which were used for chemical and mineralogical analyses.

For each ore, one of the 400 g samples of the −3350 + 300 µm was pulverized to −75 µm using the EQR-200 model vibratory disc mill (the rotation speed and time were set at 2000 rpm and 2 min, respectively). The pulverised samples were sub-sampled for chemical analysis which was performed using the benchtop X-ray fluorescence (XRF) spectrometer model NEX CG supplied by Applied Rigaku Technologies from Austin, Texas, United States of America (USA). This benchtop XRF machine uses an in-built calibration procedure referred to as the multi-channel analyser (MCA) calibration software. The remaining pulverised samples were used for the semi-quantitative determination of the bulk mineralogy for the gangue phases using the Bruker D8 Advance X-ray diffractometer (XRD) machine with a dynamic scintillation detector (sodium iodide thallium NaI(Tl) scintillator crystal) fixed divergence slit and an X-ray tube composed of copper, type: KFL Cu 2 K. The XRD machine and accompanying software were supplied by Bruker South Africa (Pty) Ltd, Johannesburg, South Africa. The machine was run from 5 to 55° at 2Θ and the samples were run with a step size of 0.02° at 2Θ with a counting time of 1 s per step. The XRD machine uses the Diffracplus package that has XRD wizard version 2.9.0.22 (Bruker South Africa (Pty) Ltd., Johannesburg, South Africa) for sample information entry, XRD commander version 2.6.1.0 to run the samples and EVA version 16.0.0.0 for data evaluation.

For each ore type, one of the 400 g samples (un-pulverised) of the −3350 + 300 µm was prepared for scanning electron microscope (SEM) analysis conducted using a JEOL JSM-IT300 (Joel, Baar, Switzerland) scanning electron microscope coupled with the Thermo Scientific N57 energy dispersive spectroscopy (EDS) software (Advancedlab, Baar, Switzerland). The samples were lightly carbon coated using the Quorum Q150T sputter coater (Advancedlab, Switzerland). SEM analysis was performed in a high vacuum in the backscattered mode (BSE) at an acceleration voltage of 15kV, a probe current of 50 nA, and a working distance of 15 mm.

For each ore type, the −75 µm sample was rotary split to obtain a 200 g sample which was observed in the reflection mode for phase identification using a model BX51 Olympus optical microscope. The samples for optical microscopy and SEM-EDS analyses were mounted in hot resin and then polished on Kemet waterproof silicon carbide grit papers using a 1 µm Kemet diamond slurry to obtain a reflecting surface.

The remaining 18.75 kg samples, after sub-sampling for chemical and mineralogical analyses, were combined and dry screened to obtain the following mono-sized samples:

- 1180 + 850 µm,
- 850 + 600 µm,
- 600 + 425 µm,
- 425 + 300 µm,
- 300 + 212 µm.

The mono-sized samples were rotary split to obtain 1 kg samples that were used to conduct short grinding times tests. The sub-samples of the mono-sized samples were also assayed using XRF to determine elemental deportment in various size fractions. The 305 × 305 mm mill, loaded with 19 mm steel balls, was used to perform the milling tests. Table 1 lists the milling conditions.
Table 1. Test conditions for dry milling experiments.

| Parameter                      | Description                  | Values |
|--------------------------------|------------------------------|--------|
| Internal diameter (mm)         |                              | 305    |
| Mill speed                     | Critical speed (rpm)         | 76.6   |
|                                | Fraction of critical speed (%)| 75     |
| Fill level factors             | \( f_c \) (%)                | 3.01   |
|                                | \( J \) (%)                  | 7.61   |
|                                | \( U \) (%)                  | 98.8   |
| Milling time (minutes)         | \( b_i \) experiments        | 0.5    |
|                                | \( S \) experiments          | 0.5, 1, 2, and 4 |

The powder filling \( (f_c) \), ball filling \( (J) \) and fraction of void space occupied by powder \( (U) \) were calculated, and kept constant in all experiments, and are shown in Table 1. The powder filling \( (f_c) \) is the volume of the powder material expressed as a fraction of the mill volume and is calculated using Equation (12). The porosity of the bed \( (\Phi) \) is theoretically 0.4 when the bulk density of steel balls is 4.65 g/cm\(^3\) [39]. The low-ball filling of 7.6\% \( (v/v) \) was selected to minimise the tendency of load slippage within the mill since the mill which was used had no lifter bars.

\[
f_c = \left( \frac{\text{Mass of powder}}{\text{Powder density}} \right) \times \frac{1}{(1 - \Phi)} \tag{12}
\]

The ball filling \( (J) \), which defines the volume of balls at rest expressed as a fraction of the mill volume, is calculated using Equation (13).

\[
J = \left( \frac{\text{Mass of balls}}{\text{Ball density}} \right) \times \frac{1}{(1 - \Phi)} \tag{13}
\]

The fraction of void space occupied by powder \( (U) \) is calculated using Equation (14), which expresses the relationship between \( f_c \) and \( J \). It is desirable that the value of \( U \) is kept close to or equal to 1 for efficient grinding [39,42,43].

\[
U = \frac{f_c}{0.4 J} \tag{14}
\]

To determine the mass disappearance, as a function of time, the 1 kg mono-sized samples were dry milled for 0.5, 1, 2, and 4 min successively. After each grinding time, dry sieving over the sieve of aperture size equal to the lower limit of the feed size interval was performed to determine the mass remaining in the feed size class.

4. Results and Discussion

4.1. Chemical and Mineralogical Characterisation of Copper Ores

The XRF results for the composite ore samples are shown in Table 2. The measurement errors are given after the ± sign. The major difference in the ore samples arises from the S and Ca contents, with the sulphide ores having a lower Ca content and a higher S content compared to the oxide ore. The scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) was also used to obtain the chemical composition of multiple particles, sampled from the bulk homogenised ore samples. It is observed that the XRF assays (in Table 2) were comparable to the assays estimated by SEM-EDS (see Table 3) for most elements.
Table 2. XRF analysis of −3350 + 300 µm composite samples.

| Element | XRF Assays (%) | Sulphide 1 | Sulphide 2 | Oxide |
|---------|----------------|------------|------------|-------|
| Ca      | 2.76 ± 0.0045  | 1.32 ± 0.0019 | 2.04 ± 0.0015 |
| Fe      | 1.18 ± 0.0039  | 1.34 ± 0.0024 | 2.75 ± 0.0002 |
| S       | 0.84 ± 0.0012  | 1.03 ± 0.0016 | 0.03 ± 0.0019 |
| Si      | 32.75 ± 0.068  | 30.27 ± 0.030 | 29.92 ± 0.038 |
| Ca      | 0.76 ± 0.0030  | 0.79 ± 0.0069 | 4.17 ± 0.0029 |
| Al      | 3.63 ± 0.041   | 6.87 ± 0.042  | 4.86 ± 0.0974 |
| K       | 3.35 ± 0.044   | 4.85 ± 0.012  | 3.49 ± 0.016  |
| Others  | 54.73 ± 0.024  | 53.53 ± 0.014 | 52.74 ± 0.023 |

Table 3. SEM-EDS analysis −3350 + 300 µm composite samples.

| Element | SEM EDS Assays (%) | Sulphide 1 | Sulphide 2 | Oxide |
|---------|-------------------|------------|------------|-------|
| Ca      | 2.55 ± 0.13       | 1.64 ± 0.10 | 1.63 ± 0.23 |
| Fe      | 0.33 ± 0.06       | 1.11 ± 0.10 | 0.51 ± 0.06 |
| S       | 0.79 ± 0.02       | 1.83 ± 0.02 | 0.13 ± 0.02 |
| Si      | 36.81 ± 0.14      | 34.97 ± 0.13 | 38.18 ± 0.14 |
| Ca      | 0.61 ± 0.05       | 0.52 ± 0.06 | 1.53 ± 0.05 |
| Al      | 2.79 ± 0.03       | 5.66 ± 0.03 | 3.34 ± 0.03 |
| K       | 1.04 ± 0.02       | 2.74 ± 0.04 | 1.16 ± 0.02 |
| Others  | 55.11 ± 0.064     | 51.53 ± 0.069 | 53.52 ± 0.079 |

The SEM-BSE micrographs for the plus 300 µm grains and optical micrographs of the −75 µm grains of the three copper ores are shown in Figure 1. Table 4 shows the elemental analysis performed in the scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) for the phases representing the grains of the valuable minerals (bright spots) in the three ores. The relative atom–gram proportions were also computed to enable mineral identification. The atom–gram proportions in Table 4 should be compared to the proportions of various copper minerals in Table 5. The atom–gram proportions identified in the oxide ore sample suggests the presence of malachite (Cu₂CO₃(OH)₂) and/or azurite (2CuCO₃·Cu(OH)₂). The optical microscopy results in Figure 1f also confirmed the presence of both malachite (Cu₂CO₃(OH)₂) and azurite (2CuCO₃·Cu(OH)₂) in the oxide ore. For sulphides 1 and 2, the atom–gram proportions of Fe and S in the ores (in Table 4) are equivalent to the theoretical ratio (in Table 5) for bornite (Cu₅FeS₄) and chalcopyrite (CuFeS₂), respectively. This can imply that the dominant copper minerals in the sulphides 1 and 2 are bornite and chalcopyrite, respectively. Similarly, from Figure 1, it was observed under the optical microscope that bornite is the dominant copper sulphide mineral in sulphide 1 ore (see Figure 1b) while chalcopyrite was a dominant copper sulphide mineral in sulphide 2 ore (see Figure 1d). However, it should be noted that Fe is not only existing in the copper-bearing minerals, it is also contained in Fe-S minerals such as pyrite (FeS₂) and pyrrhotite (Fe₁₋ₓS, where x = 0 to 0.2) as shown in Figure 1.
Figure 1. (On the left) SEM-BSE micrographs for +300 μm particles at the magnification of X50 (a,c,e), the numbers 1, 2, 3 and 4 in the SEM micrographs represent the selected grains for SEM EDS analysis, not relevant; (on the right) photomicrographs of reflected light microscopy for different copper ores (b,d,f). All optical photographs have a bottom length of 0.4 mm.
Table 4. Elemental analysis of the valuable mineral phases in the ore samples.

| Element | SEM-EDS Elemental Analysis (wt %) | Atom–Gram Ratio |
|---------|----------------------------------|-----------------|
|         | Sulphide 1 (Point 1 on Micrograph) | Sulphide 2 (Point 2 on Micrograph) | Oxide (Point 1 on Oxide Micrograph) | Sulphide 1 (Relative to Fe) | Sulphide 2 (Relative to Fe) | Oxide (Relative to O) |
| Cu      | 27.18 ± 0.80                     | 13.17 ± 0.49    | 59.44 ± 1.33                       | 2.5                        | 0.5                        | 1.6                      |
| Fe      | 11.03 ± 0.34                     | 24.08 ± 0.32    | 2.9                                | 1.0                        | 1.0                        | -                        |
| S       | 22.71 ± 0.17                     | 38.42 ± 0.17    | 2.0                                | 2.1                        | 1.2                        | -                        |
| O       | 25.99 ± 0.25                     | 15.38 ± 0.27    | 38.05 ± 0.34                       | -                          | -                          | 1.0                      |
| Si      | 12.82 ± 0.12                     | 4.78 ± 0.07     | 1.82 ± 0.11                        | -                          | -                          | -                        |
| Al      | 0.26 ± 0.05                      | 2.76 ± 0.04     | -                                  | -                          | -                          | -                        |
| Mg      | -                                | 0.24 ± 0.04     | -                                  | -                          | -                          | -                        |
| K       | -                                | 0.97 ± 0.07     | -                                  | -                          | -                          | -                        |
| Ca      | -                                | 0.19 ± 0.03     | 0.69 ± 0.12                        | -                          | -                          | -                        |
| Total   | 100.00                           | 100.00          | 100.00                             | -                          | -                          | -                        |

Table 5. Relative atom–gram proportions for common copper sulphide and oxide minerals.

| Element   | Relative Atom–Gram Proportions |
|-----------|--------------------------------|
|           | Bornite (CuFeS) Relative to Fe | Chalcopyrite (CuFeS) Relative to Fe | Malachite (CuCO3(OH)2) Relative to O | Cuprite (CuO) Relative to O | Azurite (2CuCO3.Cu(OH)2) Relative to O |
| Cu        | 5.6                            | 1.1                            | 1.6                               | 8.0                        | 1.6                          |
| Fe        | 1.0                            | 1.0                            | -                                 | -                          | -                            |
| S         | 2.3                            | 1.1                            | -                                 | -                          | -                            |
| O         | -                              | -                              | 1.0                               | 0.0                        | 1.0                          |

Table 6 shows the elemental analysis performed in the SEM-EDS for the gangue phases in the three ores (based on micrographs in Figure 1). The gangue phases comprise mainly of elements such as O, Si, K and Al. The XRD results in Table 7 show that the main gangue minerals are quartz (SiO2), and K-feldspar minerals such as microcline (KAlSi3O8) and orthoclase (KAlSi3O8). Although the chemical formulas for the K-feldspar minerals are the same, it is worth noting that there is a difference in their crystal structures as orthoclase is a high temperature monoclinic polymorph of K-feldspar with a partially ordered structure while microcline is a medium–low temperature triclinic polymorph of K-feldspar and is highly ordered. Analysis of gangue minerals is essential because, as we discuss later, the rate of breakage (S) is mainly dependent on the gangue mineral composition which is the main constituent of the ore.

Table 6. Elemental analysis of the gangue phases in the ore samples.

| Element | SEM-EDS Elemental Analysis (wt %) |
|---------|----------------------------------|
|         | Sulphide 1 (Point 3) | Sulphide 2 (Point 4) | Oxide (Point 4) |
| O       | 55.65 ± 0.36             | 47.94 ± 0.30         | 52.88 ± 0.34   |
| Al      | 0.92 ± 0.05              | 9.80 ± 0.08          | 0.17 ± 0.03    |
| Si      | 42.52 ± 0.19             | 30.50 ± 0.14         | 46.95 ± 0.19   |
| K       | 0.91 ± 0.06              | 11.42 ± 0.10         | -              |
| Na      | -                       | 0.34 ± 0.04          | -              |
| Total   | 100.00                   | 100.00               | 100.00         |
Table 7. XRD analyses of the gangue phases in the three copper ores (−3350 + 300 µm).

| Ore type  | Particle Size Range (µm) | Gangue Minerals Content (%) | Others in −3350 + 75 µm (%) |
|-----------|--------------------------|-----------------------------|-----------------------------|
|           |                          | Quartz | Microcline | Orthoclase | Total in −3350 + 75 µm | Others in −3350 + 75 µm |
| Sulphide 1| −3350 + 300              | 82.1   | -          | 5.1        | 89.1                  | 10.9                      |
|           | −300+75                  | 86.0   | -          | 6.0        |                       |                           |
| Sulphide 2| −3350 + 300              | 65.2   | 4.9        | -          | 75.0                  | 25.0                      |
|           | −300+75                  | 77.6   | 4.7        | -          |                       |                           |
| Oxide     | −3350 + 300              | 73.0   | 3.9        | -          | 67.9                  | 32.1                      |
|           | −300+75                  | 49.5   | 4.8        | -          |                       |                           |

4.2. Determination of Rate of Breakage (S_i) Parameters

For each ore type, the experimental mass fraction as a function of milling time \((w(t)/w(0))\) was fitted to both Equation (3) which assumes a homogeneous (single-component) feed, and Equation (7) which assumes a heterogeneous feed (two-component). The iterations had the objective of minimising the root mean square error (RMSE) between experimental and model values.

The chemical composition of the main gangue phases (quartz and feldspar minerals) in the −1180 + 300 µm size fraction was calculated based on the XRF assays of silicon listed in Table 8. The assays are for the pre-milling ore samples. The assays in all the size fractions (set of root two screens) between 1180 µm and 300 µm were similar, and are listed in Appendix A. The composition of quartz (SiO_2) was calculated from the Si content in Table 8. The chemical compositions of the total major gangue constituents (quartz and K-feldspar) were approximated using the ratio of quartz and K-feldspar minerals in the −3350 + 300 µm size class (see Table 7). The total mass fraction of the major gangue minerals (the hard component in the ore) was then fixed in Equation (7) to allow the determination of the rates of breakage of the hard and soft components. It is acknowledged that the minor gangue minerals such as calcite, dolomite and pyrite were not included in the calculations. The plotted results are shown in Figure 2 for size class −1180 + 850 µm (and the rest of the plots are in Appendix B). The model and experimental \(S_i\) values are listed in Tables 9 and 10. Figure 3 shows the experimental milling kinetics data versus the modelling data for both single-component and two-component models. The coefficients of correlation are listed in Table A2 in Appendix B.
Figure 2. Comparison of a single-component and a two-component model for feed size class −1180 + 850 μm; (a) sulphide 1, (b) sulphide 2, (c) oxide ore.
Figure 3. Comparing single-component and two-component models to the experimental milling kinetics data; (a) sulphide 1, (b) sulphide 2, (c) oxide ore.

Table 8. Composition of the hard (gangue) component in the three copper ores.

| Ore Type     | XRF Si Assays (ppm) | Calculated SiO$_2$ (%) | SiO$_2$ and K-Feldspar (%) |
|--------------|----------------------|-------------------------|----------------------------|
| Sulphide 1   | 327526               | 70.2                    | 74.5                       |
| Sulphide 2   | 302660               | 64.9                    | 69.7                       |
| Oxide        | 279608               | 59.9                    | 63.1                       |

Table 9. The model and experimental $S_i$ values.

| $x_i$ (µm) | Two-Component | Equation | Experimental | Two-Component | Equation | Experimental |
|------------|---------------|----------|--------------|---------------|----------|--------------|
|            | $q^p$ | $S_{IA}$ | $S_{IB}$ | ($3$) $S_i$ | $S_i$ | $q^p$ | $S_{IA}$ | $S_{IB}$ | ($3$) $S_i$ | $S_i$ |
| 850        | 0.75 | 1.47 | 35.71 | 1.96 | 0.83 | 0.70 | 1.99 | 36.21 | 2.64 | 0.88 |
| 600        | 0.75 | 0.33 | 31.11 | 0.53 | 0.44 | 0.70 | 0.58 | 3.37 | 0.90 | 0.57 |
| 425        | 0.75 | 0.56 | 37.98 | 0.89 | 0.43 | 0.70 | 0.53 | 4.63 | 0.87 | 0.51 |
The results in Figure 2 (and Appendix B) show that the disappearance of material in all feed size classes increases linearly with milling time. The slopes of the plots (see Figure 2, Tables 9 and 10) of various feed size classes show that the rate of disappearance increases with particle size. This is expected because it is well known in comminution, or fracture mechanics in general, that the resistance of particles to breakage decreases with particles size [44–48]. It is evident in Figure 2 (and Appendix B) that the two-component first-order model fits better on the experimental data than the single-component first-order model. Figure 3 and Table A2 in Appendix B, which present the experimental versus model data (both single-component and two-component models), show that both models have fair predicting power of the experimental data. The relative higher degree of fitness observed with the two-component model can possibly be attributed to the higher degree of freedom imposed by the separate specific rates of breakage of the hard and soft components in the ores. Nevertheless, that higher degree of fitness is also an indication of the effect of ore mineralogy (in terms of mineral composition, mainly classified as gangue and valuable phases) on the overall rate of breakage.

In order to assess if there is any relationship between the individual breakage rates of the two mineral groups (valuable and gangue minerals) and the overall rate of breakage, the specific rates of breakage for the hard and soft components ($S_iA$ and $S_iB$) in the heterogeneous model in Equation (7) were plotted against experimental $S_i$ values. The results are shown in Figures 4 and 5 for $S_i$ versus $S_iA$ and $S_i$ versus $S_iB$, respectively. It is evident in Figure 4 and Table 9 and 10 that, for the three copper ores, the experimental $S_i$ and the model $S_iA$ compare fairly well. If the two outliers are disregarded, the $R^2$ value will be above 0.9 as shown in Table 11. The data suggest that the gangue minerals have the dominant contribution to the breakage rates of the copper ores. The main gangue minerals are quartz ($\text{SiO}_2$), and K-feldspar minerals such as microcline ($\text{KAlSi}_3\text{O}_8$) and orthoclase ($\text{KAlSi}_3\text{O}_8$). The relative hardness for these gangue minerals on the Mohs scale is 7.0, 6.0–6.5, and 6.0, respectively. Since the relative compositions of quartz (abundant gangue minerals) and K-feldspar (second abundant gangue component) in the three ores are not significantly different, the $S_iA$ and experimental $S_i$ of the three ores compare fairly well (see Tables 9 and 10). This highlights the difficulty of deducing differences in the breakage characteristics of the ores which are extracted from the same deposit and with comparable gangue composition.

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### Table 10. The model and experimental $S_i$ values (continued).

| $x_i$ (µm) | Oxide | Two-Component | Equation (3) $S_i$ | Experimental $S_i$ |
|------------|-------|---------------|-------------------|------------------|
|            |       | $q_i$ | $S_{iA}$ | $S_{iB}$ |                      |                      |
| 850        |       | 0.63 | 1.08  | 2.27  | 1.40                | 0.88                |
| 600        |       | 0.63 | 0.70  | 4.85  | 1.20                | 0.73                |
| 425        |       | 0.63 | 0.43  | 4.91  | 0.87                | 0.37                |
| 300        |       | 0.63 | 0.22  | 39.87 | 0.54                | 0.25                |
| 212        |       | 0.63 | 0.16  | 2.81  | 0.41                | 0.19                |
Figure 4. Model $S_A$ versus experimental $S_i$.

Figure 5. Model $S_B$ versus experimental $S_i$.

Table 11. Statistical data on relationships between experimental $S_i$ and model $S_A$ and $S_B$.

| Statistical Measures | Model Parameter | Sulphide 1 | Sulphide 2 | Oxide |
|----------------------|----------------|-----------|-----------|-------|
| Correlation Coefficient | $S_A$ | 0.920 | 0.995 | 0.981 |
| | $S_B$ | 0.842 | 0.816 | $-0.443$ |
| p-value | $S_A$ | 0.037227 | 0.000752 | 0.001305 |
| | $S_B$ | 0.4793 | 0.4769 | 0.5125 |

Figure 5 and Table 11 show that there is no significant relationship ($p$-value greater than significance level of 5%) between experimental $S_i$ and $S_B$. A positive correlation exists...
between $S_i$ and $S_{ib}$ for the sulphides, but this was contrary for the oxide ore as shown in Table 11. A negative correlation coefficient of the oxide ore suggests that overall rate of breakage of the ore decreases with the specific rate of breakage of the oxide copper minerals, i.e., the increase in mineral composition of the oxide copper minerals does not necessarily contribute to the increase in the rate of breakage of the ore.

The experimental $S_i$ were also fitted to Austin model in Equation (9) using an iteration method to estimate the model parameters ($a$ and $\alpha$), with objective set to minimise the root mean square error (RMSE) between experimental and model $S_i$ values. It was assumed that the 19 mm balls were capable of nipping particles with top size of 3.3 mm, and therefore size reduction was through normal breakage. Figure 6 shows a plot experimental versus modelled (Equation (9)) $S_i$ values.

![Figure 6. Experimental versus modelling $S_i$ values.](image)

The data in Figure 6 shows that the experimental $S_i$ values and the modelled $S_i$ values compare fairly well, for all the copper ores. The predicted $S_i$ model parameters are listed in Table 12. The relative $a$ and $\alpha$, generated after normalisation to sulphide 1 values, are listed in Table 13 together with the relative brittleness index ($\beta_i$). The relative brittleness index was calculated using Equation (15), using the quartz content (in % $w/w$) from Table 7 (the composition of $\sim3350 + 300 \mu$m size fraction was used) which is reported to significantly influence to the brittleness of the ores [49-52].

Table 12. Selection function parameters.

| $S_i$ Parameters | Ore Type | $S_i$ Values | $S_i$ Values | $S_i$ Values |
|------------------|----------|--------------|--------------|--------------|
|                  |          | Sulphide 1   | Sulphide 2   | Oxide        |
| $a$              | 0.841    | 0.893        | 0.891        |
| $\alpha$         | 1.611    | 1.247        | 1.472        |

Table 13. Relative selection function parameters and relative brittleness index.

| Ore Type  | Relative $a$ | Relative $\alpha$ | Relative Brittleness Index ($\beta_i$) |
|-----------|--------------|--------------------|---------------------------------------|
| Sulphide 1| 1.0          | 1.0                | 1.0                                   |
| Sulphide 2| 1.1          | 0.8                | 0.8                                   |
| Oxide     | 1.1          | 0.9                | 0.9                                   |
It is evident in Table 13 that parameter $a$ is relatively similar for all three ores, which confirms similar milling conditions to the three ores were subjected to. The data suggests that there is a relationship between breakage parameter $\alpha$ and brittleness index $\beta_i$ (which is determined from the mineralogical composition of the gangue phase). However, it is acknowledged that an assessment of more data sets will be necessary to validate the relationship. Nonetheless, in Tables 9 and 10 it is observed that the rates of breakage ($S_i$) of the three ores are comparatively similar. This could be explained by the fact that the difference in the gangue composition (listed in Table 8) is not significant for the three copper ores. Since gangue composition affects the brittleness of the rocks [49,50,52], it can be assumed that for ores with distinctly different gangue compositions the relative $\alpha$ and relative brittleness index ($\beta_i$) will follow the same trend.

$$\text{Relative brittleness index (} \beta_i \text{)} = \frac{\% \text{SiO}_2 \text{ore type } i}{\% \text{SiO}_2 \text{ sulphide } 1}$$

(15)

4.3. Determination of Cumulative Breakage Distributions

The BII method in Equation (10) was used to calculate the cumulative breakage function ($B_{ij}$) from the size distributions of the fragments in size classes below the feed size class $j$ which were generated after milling the monosize samples for 30 s. $B_{ij}$ values obtained were fitted to the empirical model by Austin et al. [39] to estimate the best combinations of these parameters ($\beta$, $\gamma$ and $\Phi$) of the three ores which minimize the residual errors between the experimental $B_i$ and model $B_{e}$. The cumulative breakage distributions, both experimental and predicted, are listed in Appendix C for the three ores. A fair degree of fitness is observed for all feed size classes. To deduce the relationships among the three ores, the breakage distributions are plotted for each size fraction in Figures 7–11. It is observed in Figure 7 that, for the coarsest feed size class $\sim1180 + 850 \mu$m, the breakage distributions for sulphide 1 and oxide are similar. The sulphide 2 has a finer breakage distribution. The same trend is observed with the finest feed size class ($\sim300 + 212 \mu$m) in Figure 11.

Figure 7. Cumulative breakage functions for size class $\sim1180 + 850 \mu$m.
Figure 8. Cumulative breakage functions for size class −850 + 600 µm.

Figure 9. Cumulative breakage functions for size class −600 + 425 µm.
Figure 10. Cumulative breakage functions for size class −425 + 300 µm.

Figure 11. Cumulative breakage functions for size class −300 + 212 µm.

The trend in the breakage of the ores shown with the two feed size classes can be attributed to the trend in the work indices of the three ores which has already been discussed, i.e., similar work indices for sulphide 1 and oxide and a higher work index for the sulphide 2 (harder, but possibly more brittle than the other two ores). Contrary trends were obtained with the intermediate size classes as shown in Figures 8–10. In Figure 8, the breakage distributions for the sulphides are comparable (especially in the coarser size range, i.e., particle size above 150 µm) while a finer product was obtained with the oxide ore. For the −600 + 425 and −425 + 300 µm size classes in Figures 9 and 10, inconclusive results amongst the three ores were obtained, although the coarser product was generally produced with the oxide ore. This highlights the complexity of deducing relationships between the mineralogical composition data and breakage distributions for the ores which are from the same deposit and with comparable gangue composition. Since the gangue component of the ore determines its breakage behaviour, distinct relationships may only
be developed if the ores have distinct gangue minerals (or have significant differences in the compositions of similar gangue minerals of various ores).

The Bingham parameters ($\Phi$, $\gamma$, and $\beta$) are listed in Table A3 in Appendix C and plotted as functions of particle size in Figures 12–14, respectively. For $\Phi$ (which relates to the coarser end of the breakage distributions) and $\gamma$ (which relates to the finer end of the breakage distributions), we observe a comparable trend for the oxide ore in Figures 12 and 13. The parameters increase with feed particle size below 425 µm. For particles coarser than 425 µm, the two parameters remained relatively constant. It can be concluded that for the oxide ore, the two parameters vary with particle size, but for the particles coarser than 425 µm they are not independent of the feed particle size. The increase in the two parameters with the particle size (for the feed size less than 425 µm) can also be observed for sulphide 2. However, above 425 µm, both parameters decreased significantly. For sulphide 1, there is no relationship that could be deduced, and the authors do not have an explanation for such an anomaly. Further investigations will be undertaken in future to establish sustained trends.

![Figure 12. Parameter $\Phi$ as function of particle size.](image-url)

In Figure 14, it is observed that parameter $\beta$ remained relatively constant for the oxide ore while for the sulphides, there is no strong relationship that could be deduced. The absence of clear trends for the three breakage distribution parameters amongst the three ores proved the difficulty of developing relationships between the three parameters ($\Phi$, $\gamma$, and $\beta$) and mineralogical composition data.
Figure 13. Parameter $\gamma$ as function of particle size.

Figure 14. Parameter $\beta$ as function of particle size.

5. Conclusions

The main aim of the study was to establish whether the variation in the mineralogical composition of the ores from a multi-mineralised deposit had an effect on their individual breakage characteristics which can, in turn, have implications on the milling circuit design. The mineralogy data showed that quartz was the abundant gangue phase (average for each ore was above 60% (w/w)), followed by K-feldspar minerals (orthoclase and microcline) which constituted about between 4% and 6% (w/w) and the remainder are the minor calcite and dolomite minerals which are also in the host rock. The dominant copper minerals were identified using the optical microscope and it was confirmed that sulphide 1 had bornite as a dominant copper mineral, sulphide 2 had chalcopyrite and oxide was predominated by malachite. The experimental milling kinetics parameters and mineralogical data were used to assess the robustness of the heterogeneous (two-component) and
homogeneous (single-component) first-order rate breakage models. The mineral composition data were used in setting up the predictions of breakage parameters in the two-component and single-component first-order breakage models. A relative higher degree of fitness was observed with the two-component breakage model which was attributed to the high degree of freedom in the mathematical formulation, but also an indication of the effect of ore mineralogy (in terms of mineral composition, mainly classified as gangue and valuable phases) on the overall rate of breakage. The two-component model allowed investigation of the relationships between the specific rate of breakage of hard and soft components to the overall rate of breakage of the ores. The breakage data showed that the selection function for the hard component (the gangue minerals, abundant component) has a dominant contribution to the overall selection function of the ores. No clear trends could be established between the specific rate of breakage of the soft component (i.e., copper minerals) and the overall rate of breakage. The parameter $a$ in the Austin empirical breakage model was relatively similar (approximately 1) for all three ores, which confirms similar milling conditions to the ores were subjected to. The data suggests that there is a relationship between breakage parameter $a$ in Austin empirical breakage rate model and brittleness index $\beta_i$ (which is determined from the mineralogical composition of the gangue phase). However, it is acknowledged that an assessment of more data sets on ores from different deposits and possibly with distinguishable gangue composition, will be necessary to validate the relationship. Since the gangue minerals appear to have a dominant contribution to the overall breakage rate, and the composition is comparable in the three copper ores, it is difficult to conclude the effect of mineralogical composition on the breakage rate of the different ores. No clear trends could be deduced from the cumulative breakage distributions of the three ores. This highlights the complexity of developing relationships between the mineralogical composition data and breakage distributions of the ores which are extracted from the same deposit and with comparable gangue composition. Further work on the relationship between mineralogical data and breakage parameters should consider ores with distinct gangue minerals or having significant differences in the compositions of similar gangue minerals of various ores.

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Appendix A. Chemical Composition Results from XRF Machine

Table A1. XRF size-by-size metal assays in ppm.

| Size Range (µm) | Sulphide 1 | | | |
|-----------------|-----------|-----------|-----------|-----------|
|                 | Cu        | Fe        | Si        | Ca        |
| −1180 + 300     | 27,576    | 11,845    | 327,526   | 7550      |
| −300 + 212      | 31,471    | 18,987    | 340,865   | 6275      |
| −212 + 150      | 21,301    | 8299      | 345,942   | 5293      |
| −150 + 106      | 29,722    | 14,405    | 330,893   | 6899      |
| −106 + 75       | 27,498    | 13,939    | 337,652   | 6255      |
| −75             | 37,327    | 17,438    | 326,128   | 6142      |

| Size Range (µm) | Sulphide 2 | | | |
|-----------------|-----------|-----------|-----------|-----------|
|                 | Cu        | Fe        | Si        | Ca        |
| −1180 + 300     | 13,042    | 13,397    | 302,660   | 7941      |
| −300 + 212      | 9540      | 15,317    | 341,106   | 4766      |
| −212 + 150      | 10,312    | 10,640    | 308,237   | 6822      |
| −150 + 106      | 12,350    | 13,319    | 295,873   | 7961      |
| −106 + 75       | 13,199    | 15,549    | 291,599   | 9223      |
| −75             | 20,130    | 27,119    | 285,252   | 8092      |

| Size Range (µm) | Oxide     | | | |
|-----------------|-----------|-----------|-----------|-----------|
|                 | Cu        | Fe        | Si        | Ca        |
| −1180 + 300     | 27,758    | 32,941    | 279,608   | 42,936    |
| −300 + 212      | 13,760    | 33,219    | 328,267   | 19,119    |
| −212 + 150      | 9813      | 25,292    | 299,502   | 24,157    |
| −150 + 106      | 9470      | 26,720    | 297,838   | 25,040    |
| −106 + 75       | 20,612    | 50,958    | 270,221   | 38,314    |
| −75             | 19,360    | 58,322    | 260,513   | 37,432    |

Appendix B. Single and Two-Component Models Fitted to Experimental Data

(a) Sulphide 1
Figure A1. Comparison of a single-component and a two-component model for feed size class \(-850 + 600\) µm; (a) sulphide 1, (b) sulphide 2 and (c) oxide ore.
Figure A2. Comparison of a single-component and a two-component model for feed size class −600 + 425 µm; (a) sulphide 1, (b) sulphide 2 and (c) oxide ore.
Figure A3. Comparison of a single-component and a two-component model for feed size class $-4$ to $+300$ µm; (a) sulphide 1, (b) sulphide 2 and (c) oxide ore.
Figure A4. Comparison of a single-component and a two-component model for feed size class $-300 \div 212 \ \mu m$; (a) sulphide 1, (b) sulphide 2 and (c) oxide ore.

Table A2. Statistical data for model fitness.

| Model        | $-1180 + 850 \ \mu m$ | $-850 + 600 \ \mu m$ | $-600 + 425 \ \mu m$ | $-425 + 300 \ \mu m$ | $-300 + 212 \ \mu m$ |
|--------------|------------------------|-----------------------|-----------------------|-----------------------|------------------------|
|              | Sulphide 1   | Sulphide 2   | Oxide             | Sulphide 1   | Sulphide 2   | Oxide             | Sulphide 1   | Sulphide 2   | Oxide             | Sulphide 1   | Sulphide 2   | Oxide             |
| Homogeneous  | 99.92       | 99.80       | 99.94             | 98.92       | 99.52       | 99.33             | 97.74       | 99.15       | 99.15             | 95.53       | 96.93       | 95.04             |
| Heterogeneous| 99.97       | 99.94       | 99.94             | 99.05       | 99.91       | 99.85             | 99.62       | 99.99       | 99.28             | 99.37       | 100.00      | 99.28             |

Model
Appendix C. Cumulative Breakage Distribution Functions

|                | Sulphide 1 | Sulphide 2 | Oxide |
|----------------|-----------|-----------|-------|
| Homogeneous    | 85.34     | 97.41     | 94.50 |
| Heterogeneous  | 85.29     | 99.92     | 99.98 |

Figure A5. Appearance distributions for various size classes of sulphide 1.

Figure A6. Appearance distributions for various size classes of sulphide 2.
Table A3. Breakage function parameters.

| Size (μm) | Sulphide 1 (Bornite) | Sulphide 2 (Chalcopyrite) | Oxide |
|-----------|----------------------|--------------------------|-------|
|           | Φ   | γ    | β    | Φ   | γ    | β    | Φ   | γ    | β    |
| 850       | 0.15 | 0.00 | 1.54 | 0.01 | 0.01 | 1.31 | 0.48 | 1.17 | 3.00 |
| 600       | 0.51 | 1.48 | 7.28 | -   | -   | -   | 0.52 | 1.12 | 6.29 |
| 425       | 0.02 | 0.05 | 1.70 | 0.85 | 1.82 | 8.00 | 0.47 | 1.33 | 4.50 |
| 300       | 0.79 | 1.34 | 7.00 | 0.70 | 1.43 | 7.82 | 0.23 | 0.80 | 4.69 |
| 212       | 0.39 | 1.35 | 5.55 | 0.05 | 0.00 | 2.66 | 0.15 | 0.46 | 4.21 |
| Average   | 0.37 | 0.84 | 4.61 | 0.40 | 0.82 | 4.95 | 0.37 | 0.98 | 4.54 |
| Variance  | 0.093| 0.562| 7.916| 0.193| 0.903| 11.991| 0.029| 0.121| 1.391|

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