

Electrochemical studies on interplay of mineralogical variation and particle size on bioleaching low grade complex sulphide ores

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Abstract: The interplay of mineralogical variation and mineral phase distribution within varying particle sizes on the dissolution behaviour of a low grade complex sulphide ore was investigated through bioleaching experiments and electrochemical technique. Investigations were carried out utilizing mineralogical data on the variations in mineral and phase distribution within particle sizes of <53 µm, 53–75 µm, 75–106 µm and 106–150 µm in mixed mesophilic cultures of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. Electrochemical behaviour was studied using particulate electrodes from the four varying particle sizes and from massive electrodes prepared from the two major sulphide mineral rich phases (sphalerite-rich and galena-rich) and a complex mineralogical phase of the bulk ore. Bioleaching studies reveal the highest recoveries at a particle size of 75 µm, while electrochemical investigations reveal the highest dissolution at particle size of 106 µm. Electrochemical results show that sphalerite rich phase has the highest dissolution rate while galena-rich complex phase has the least. SEM studies confirm the highest bacterial attack at the sphalerite-rich phase. The discrepancies between the dissolutions within particle sizes obtained from bioleaching experiments and electrochemical studies are consistent with and attributed both to the physical and mineralogical influences. Electrochemical behaviour is influenced and controlled by galvanic interaction resulting from mineralogical variation, while bioleaching behaviour is influenced by mineralogical variation as well as physical effect of particle size.

Key words: sulphide ore; ore mineralogy; particle size; bioleaching; electrochemical study

1 Introduction

The effectiveness of practically all mineral processing and hydrometallurgical operations is a function of the size of the particle treated. Due to the comparatively high cost associated with size reduction and the difficulties associated with separating minerals when over-or-under liberation occurs, it is important that the correct amount of size reduction is achieved. Particle size plays a very important role in mineral recovery, and according to MWALE et al [1], it is a key design variable in minerals beneficiation. Its analysis is commonly used to measure the extent of the liberation of the value from the gangue at various particle size fractions, to determine the optimum size of feed to the process for the maximum efficiency and to assess the size range at which losses occur in the plant, so that they may be reduced. Ore size

is specifically of great importance in the biohydrometallurgical processes, and a significant factor that determines bacteria-mineral attachment and detachment effectiveness. NEMATİ et al [2] observed that particle size distribution could influence both the activity and the bioleaching capacity of microbes, by affecting physical attrition, availability of mineral for leaching and mass transfer.

The relevance of ore size on microbial dissolution process has therefore drawn the attention of many researchers and several investigations have been reported [2–8]. Nevertheless, the interrelationship between particle size and bioleaching microbes is yet a matter of controversy as there is still no strong agreement on the effects of particle size on the overall bioleaching behaviour. SHRIHARI et al [3] reported that the highest metal recoveries were obtained at larger particle sizes during the dissolution of particles of pyrite and chalcopy-

rite minerals by *Acidithiobacillus ferrooxidans*. MAZUELOS et al[4] studied the effects of particle size amongst other parameters on ferrous iron biooxidation process in a packed bed bioreactor, and reported that ferric iron productivity increased with an increase in the particle size of the bed. The decrease in ferric iron production at smaller particle sizes was attributed to hindrance in biofilm development and consolidation, as biofilm is preferentially formed in the space between particles (NIKOLOV et al[5]). The dissolution of arsenic during the reduction of arsenic content in a complex galena concentrate by *Acidithiobacillus ferrooxidans* was reported by MAKITA et al[6] to be greater at larger particle size where the particle surface area was smaller. The work of DEVECI et al[7–8] on the effect of particle size and shape of solids on the viability of acidophilic bacteria during mixing in stirred tank reactors showed that the rate and extent of loss in the viability appeared to increase with decreasing particle size from 125–180 to 45–63 μm .

Contrary to the argument that higher particle sizes bring about higher metal recoveries, TORMA et al[10] reported the highest zinc recovery from the finest particles during the microbiological leaching of sphalerite concentrate. Similarly, PINCHES et al[11] reported increasing dissolution rates with a decrease in particle size during the bioleaching of chalcopyrite concentrates with *Thiobacillus ferrooxidans* in a batch culture. HOSSAIN et al[12] also reported that the bacterial leaching of zinc sulphide ore increases with decrease in size of particles, as the size of particles determines the surface area which also affects the bioleaching. GONZALEZ et al[13] observed that smaller particles bring about higher amounts of attached cells. This was attributed to the increased surface area of the finer particles that gave an increase in the number of active attachment sites. According to GONZALEZ et al[14], reduction of particle size causes an increase in the specific surface that results in an increase in the concentration of attached cells and its ratio with respect to suspended cells. Higher recoveries at smaller particle sizes compared with larger sizes can also be attributed to the negative effects of larger particles on bacterial cells. Large particle sizes especially at high stirring speed increase the frequency of particle–particle collisions that could cause bacteria shear and death resulting from friction and attrition.

In an attempt to therefore bring a correlation between the two arguments of higher recoveries at either larger or smaller particle sizes, NEMATİ et al[2] studied the effect of mineral particle size on the bioleaching of pyrite by acidophilic thermophiles in a batch bioreactor. It was observed that decreasing the particle size from a

mean diameter of 202 μm (size fraction: $(150\pm 180)\ \mu\text{m}$) to a mean diameter of 42.5 μm (size fraction: $(25\pm 45)\ \mu\text{m}$) enhanced the bioleaching rate from 0.050 to 0.098 $\text{kg}/(\text{m}^3\cdot\text{h})$. HANSFORD and CHAPMAN[15], worked on batch and continuous biooxidation kinetics of a refractory gold-bearing pyrite concentrate, and reported that there was a slight increase in the bioleaching rate when pyrite with a size distribution of $(53\pm 75)\ \mu\text{m}$ was used instead of a fraction containing particles smaller than 38 μm . This suggested that there is a threshold particle size value below and above which a further decrease or increase in the size will lead to a decrease in the dissolution rate. According to NEMATİ et al[2], decreasing the particle size of pyrite below this threshold value did not improve the rate of bioleaching due to the fact that fine particles adversely influenced the activity of the cells by apparently damaging the structure of the cells, resulting in their inability to oxidize pyrite.

Although the effect of particle size on microbial dissolution has been widely studied, it is observed that these studies were centered on the physico-chemical factors relating to particle size. The overall effect of these factors in obtaining optimum particle size and in understanding the interrelationship between microbial attack on minerals and oxidation behaviour is yet to be fully known and predicted. Since both larger and smaller particle size fractions have been reported to have inhibitory effects on both bacterial activity and ferrous oxidation, it is therefore believed that the dissolution process and trend will be best understood from a mineralogical perspective as dissolution of minerals depend mostly on their chemical and mineralogical compositions (OLUBAMBI et al[16]). Owing to the differences in the mineralogical compositions at different particle sizes, there exist some variations in microbial-mineral interaction that could lead to differences in dissolutions at varying particle sizes. This might result from the differences in the electrochemical galvanic interactions, as galvanic interactions depend on the mineralogical association between the phases present (CRUZ et al[17]).

An initial study on the effect of ore mineralogy on the microbial leaching of low grade complex sulphide ores have been initially investigated and reported in OLUBAMBI et al[16] with respect to zinc and copper recoveries. Mineralogical data on the variations in the mineral and phase distribution within varying particle sizes were used to provide an understanding of the influence of particle size and ore mineralogy on microbial dissolution behaviour of the ore. It was observed that mineralogical and elemental distribution within the various particle sizes both affect the mineral-microbe interaction, the galvanic interaction, as well as

precipitate formation on the surfaces. In the present work, a further understanding of the effects of particle size on bioleaching of the low-grade complex sulphide ore is provided by studying the interplay of ore mineralogy, particle size, and mineral phase distribution within varying particle sizes on the dissolution behaviour through bioleaching experiments with respect to zinc, lead copper, and iron recovery, electrochemical technique and scanning electron microscopy method.

2 Materials and methods

2.1 Ore

A complex sulphide ore obtained from Ishiagu, South Eastern part of Nigeria containing siderite, sphalerite, galena, quartz, chalcopyrite and pyrite was used for this study. The ore was stage crushed in the laboratory in a jaw crusher and a cone crusher. Size analysis of the ground product was carried out using the sieve analysis method in a laboratory test sieve. After sieving, 2 g each of homogenized particles of sizes of <53, 53, 75, and 106 μm were mixed together, further ground to powder and subjected to elemental analysis to give the composition of the bulk ore total. Identification of mineral distribution within the sizes and quantitative analysis of the mineralogical composition was carried out by X-ray diffractometer. Quantitative analysis of the elemental distribution within each particle size was determined by X-ray fluorescence with Magi "X Pro XRF spectrometer at 4 kV, using IQ⁺ "Standard less" analysis and optical emission spectrometer using the inductively coupled plasma-optical emission spectrometer(ICP-OES) model SPECTRO CIRO. The mineralogical and elemental composition of the ore as well as elemental composition within varying particle size fractions as previously reported in OLUBAMBI et al[18] is shown in Table 1.

2.2 Micro-organisms and sub-culturing

Mixed cultures of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* provided by MINTEK, South Africa, were used for the bioleaching studies. The cultures were routinely sub-cultured in an incubator shaker at 32–35 $^{\circ}\text{C}$ and pH 2.0 in 9 K medium consisting of 3.0 g

$(\text{NH}_4)_2\text{SO}_4$, 0.5 g K_2HPO_4 , 0.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g KCl, 0.01 $\text{Ca}(\text{NO}_3)_2$, and 44.2 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ used as energy source dissolved in 1 000 mL distilled water. After the cell has reached an exponential growth stage, the culture was filtered through a Whatman filter paper No.1 to remove the precipitate and centrifuged at 6 000 r/min for 30 min using a Sorval Centrifuge, Model RC 5C PLUS. The centrifuged cells were washed in sulphuric acid at pH 2.0. Washing and centrifugation were repeated until the cells were free from precipitates.

2.3 Bioleaching

Bioleaching experiments were carried out using mixed cultures of an initial population of 1.5×10^6 cell/mL in 1 000 mL glass reactor. The glass reactor had four holes for temperature measurement, pH measurement, aeration and sampling. The reactor was placed in a thermostatically controlled heated water-bath and agitated from above using mechanical stirrer. The mechanical stirrers had four twisted blades. In order to determine optimal particle size range where dissolution will be the highest, bioleaching tests were carried out at particles sizes of < 53, 53, 75 and 106 μm . The suspension was maintained at constant temperature of 32–35 $^{\circ}\text{C}$ and air sparged with simultaneously adjustment of desired solution pH with diluted sulphuric acid. Solution agitation was kept at a stirring speed of 150 r/min. The pulp density was kept at 10% (mass to volume), while the volume fraction of inoculum was 6%.

The amounts of zinc, lead, copper and total iron dissolved in the solution were analyzed periodically by atomic absorption spectrophotometry (AAS). All measurements were carried out in triplicate for each sample to ensure the reliability of the process. In all the experiments, very good reproducibility was achieved, as there were very little variations amongst the triplicates. The morphologies of the particles were observed by SEM analysis before and after bioleaching, while the mineral phases of the bioleached residues were identified by XRD.

2.4 Electrochemical study

2.4.1 Electrochemical cell

Electrochemical studies were conducted using a

Table 1 Composition and distribution of elements (mass fraction, %) (OLUBAMBI et al[17])

Sample	Zn	Fe	S	Pb	Si	Cu
Total bulk ore	25.53	12.59	13.82	9.78	4.79	0.45
Size 106 μm	26.63	11.98	13.55	9.02	3.02	0.52
Size 75 μm	25.81	12.23	13.67	9.45	3.10	0.47
Size 53 μm	25.05	12.96	13.91	10.15	4.23	0.42
Size –53 μm	24.51	13.11	14.03	10.41	5.51	0.39

conventional three-electrode system electrochemical cell. The cell was a 250 mL Pyrex glass electrochemical cell constructed for the electrochemical measurement. The cell consists of a silver/silver chloride, 3 mol/L KCl, reference electrode, graphite counter electrode, and the working electrode made from the ore sample.

2.4.2 Working electrode preparation

Two different kinds of working electrodes were used for this study. The first sets of working electrode were particulate electrodes made from the powdered samples of the four different particle size fractions used for the bioleaching experiments. These electrodes were prepared similar to the procedure described by MUNOZ et al[19] and LU et al[20]. 0.8 g of the base conductor material (powdered graphite) was mixed with 0.8 g of powdered sample and 0.4 mL of silicon oil from Sigma Aldrich as binder. They were compressed under pressure using a carbon paste electrode holder.

The second sets of working electrodes were massive electrodes prepared from the two major sulphide mineral rich phases (sphalerite-rich and galena-rich) and a complex mineralogical phase of the bulk ore (as shown in Fig.1). These working electrodes were prepared by cutting representative samples of the complex ore into 0.5 cm×0.5 cm×1.0 cm. The electrodes were mounted, with one surface exposed in a cold setting resin and the

other surface sealed with copper wire using aluminum (foil) conductive tape, which enabled electrical contact of the mineral with the copper wire. The exposed surface of the electrodes were polished with 220, 600, and 1 000 grit silicon carbide paper, rinsed in distilled water and washed in acetone to remove any species that might have remained on the electrode surfaces after polishing. The electrodes were further washed and polished with a 5 µm alumina polishing compound and finally with diamond paste.

2.4.3 Electrochemical measurements

Before electrochemical measurement, working electrodes were treated similar to the procedure described in MUNOZ et al[19] in an orbital shaker in a 9K nutrient medium containing the mixed culture bacterial cells of an initial population of 1.5×10^6 cell/mL. The electrodes were removed from the bioreactor at different treated intervals similar to the procedure described by MUNOZ et al[21] and tested in the corresponding electrochemical experiment. The electrolyte for the electrochemical measurement was the same 9 K nutrient medium used for the bioleaching. The leaching medium with the electrodes was placed on thermostatically controlled heated plate, and all measurements were conducted at 32–35 °C. Measurement was carried out without agitation, neither was oxygen eliminated from the medium.

Electrochemical tests were carried out using an Autolab potentiostat (PGSTAT20 computer controlled) using the general purpose, electrochemical software (GPES) version 4.9. Electrochemical measurements conducted on the powered electrodes included the open circuit potential(OCP) and potentiodynamic polarization techniques. Polarization curves were obtained at varying applied voltages and at constant scan rate of 1.6 mV/s from 100 to 1 200 mV. Before potentiodynamic polarization measurements, the cell was left for suitable time to stabilize the OCP after the immersion of the samples in the electrolytes. The OCPs of the electrodes were measured for 8 h. Potentiodynamic polarization test was only carried for the massive electrodes. On the 21st day of exposure to bacterial attack, the massive electrodes were however subjected to morphological and mineralogical analyses. The morphologies of the microbial attacked surfaces were examined using SEM, while the bioleached residues on mineral surface were identified with XRD.

3 Results and discussion

3.1 Bioleaching at varying particle sizes

The amounts of zinc, lead, copper and iron bioleached at varying size fractions are shown in Figs.2–5. The results reveal that dissolutions generally

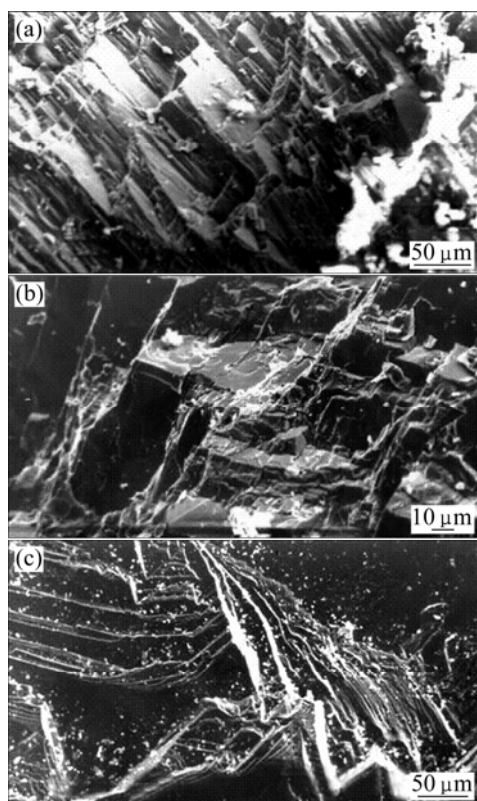


Fig.1 SEM micrographs of massive electrode showing morphologies of typical mineral rich phases: (a) Galena rich phase; (b) Siderite rich phase; (c) Sphalerite rich phase

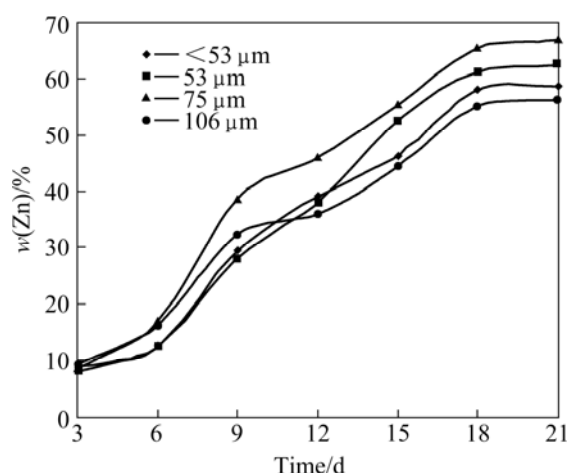


Fig.2 Effects of particle size on zinc dissolution (Stirring speed of 150 r/min, pH 2.0, 10% of pulp density and 6% of volume fraction of inoculum addition)

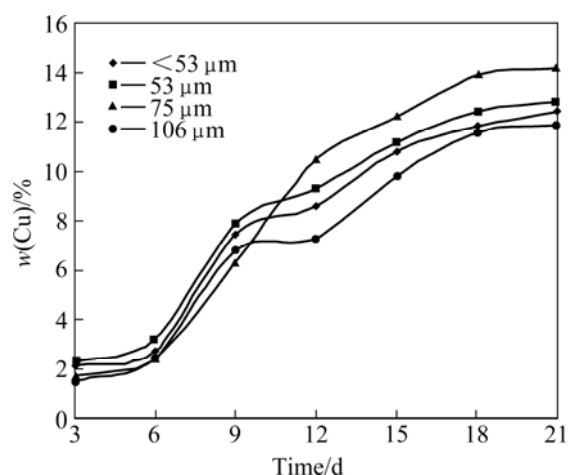


Fig.3 Effects of particle size on copper dissolution (Stirring speed of 150 r/min, pH 2.0, 10% of pulp density, and 6% of volume fraction of inoculum addition)

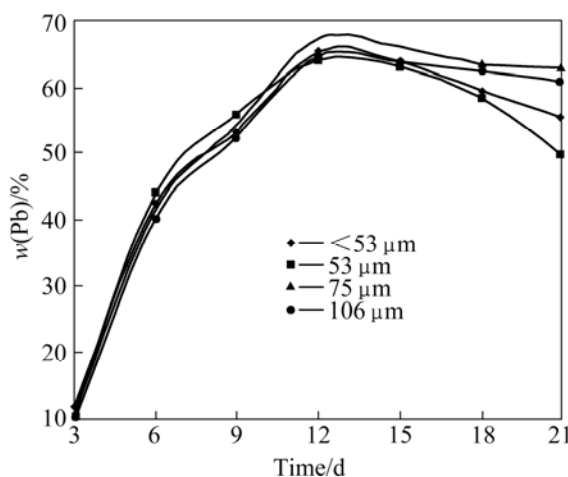


Fig.4 Effects of particle size on lead dissolution (Stirring speed of 150 r/min, pH 2.0, 10% of pulp density, and 6% of volume fraction of inoculum addition)

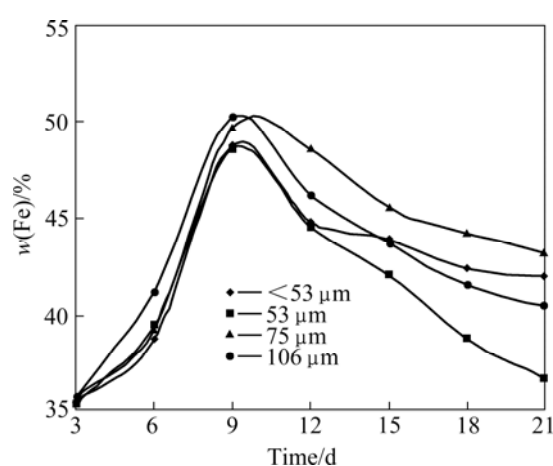


Fig.5 Effects of particle size on iron dissolution (Stirring speed of 150 r/min, pH 2.0, 10% of pulp density, and 6% of volume fraction of inoculum addition)

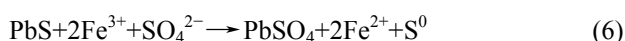
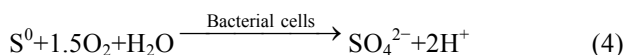
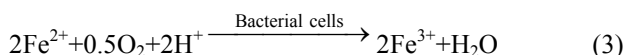
increased as particles decreased down to 75 μm , but later decreased as particle sizes reduced further to <53 μm . Lead and iron dissolutions exhibit an initial increase in dissolution up until the 12th day of bioleaching after which there was a general decrease. The dissolutions of zinc and copper followed a similar trend of increments with time with higher amounts of zinc dissolved than copper. Results show that zinc dissolution is the highest with the highest dissolution of 67% obtained on the 21st day of microbial attack.

The initial increase in iron and lead dissolution in the first 9 and 12 d of bioleaching respectively could be attributed to the high solubility of galena and siderite (Eqs.(1) and (2)). The hydrogen sulphide formed in Eq.(2) is immediately transformed by the oxidation of Fe(III), and the overall oxidation of galena can be represented by Eq.(3).

The initial increase in iron and lead dissolution in the first 9 and 12 d of bioleaching respectively could be attributed to the high solubility of galena and siderite (Eqs.(1) and (2)). The ferrous ion produced in Eq.(1) is immediately oxidized by the organisms to ferric ion (Eq.(3)), while the elemental sulphur formed in Eq.(2) is also oxidized by organisms to sulphate ions (Eq.(4)). The sulphate ion combined with ionic lead to form anglesite precipitate (Eq.(5)). The overall oxidation of galena can therefore be represented by Eq.(6).

The initial increase in iron and lead dissolution in the first 9th and 12th day of bioleaching respectively could be attributed to the high solubility of galena and siderite (Eqs.(1) and (2)). The ferrous ion produced in Eq.(1) is immediately oxidized by the organisms to ferric ion (Eq.(3)), while the elemental sulphur formed in Eq.(2) is also oxidized by organisms to sulphate ions (Eq.(4)). The sulphate ion combined with ionic lead to form

anglesite precipitate (Eq.(5)). The overall oxidation of galena can therefore be represented by Eq.(6).



Further decrease in dissolution at smaller particles sizes and after the 12th day could result from possible increase in the precipitation of lead as anglesite (Eqs.(5) and (6)) and soluble iron as secondary iron compounds. These precipitates could have increased the passivation of leaching surfaces, which might lead to limiting the transfer of both the reactants and the bioleaching products. This could thus result in a decrease in further oxidation and subsequently reducing the amounts of lead and other metals dissolved.

Lower amounts of zinc dissolution as compared with lead dissolution in the first 12 d of bioleaching could be attributed to the selective oxidation of galena to anglesite and a corresponding passivation of sphalerite surface. According to SILVA et al[22], the selective dissolution is due to galvanic interactions resulting from the differences in the rest potential values of both minerals in solution. Since galena is relatively more electronegative than sphalerite, a galvanic current would flow from galena to sphalerite in solution together, resulting in the selective oxidation of galena. Increase in zinc recovery after 12 d could be attributed to the preferential zinc dissolution resulting from a galvanic interaction effect occurring at the interface between the grain boundaries of sphalerite and anglesite precipitate. In the presence of more noble materials (the anglesite precipitate), the less noble (the sphalerite) will preferentially dissolve due to galvanic action. This observation was reported by SILVA et al[22], where once the majority of the galena had been oxidized, the rate of zinc extraction increased, indicating that sphalerite may leach in the presence of lead sulphate after all available galena has been oxidized.

Lower copper dissolution in comparison with zinc dissolution could be due to the low content of chalcopyrite in the ore and possible chalcopyrite passivation that could lead to its refractoriness. Apart from the fact that chalcopyrite is generally difficult to be bioleached at low temperatures using mesophilic bacteria, lower amounts of copper dissolved might also be attributed to the higher affinity of copper for

precipitates (HIROYOSHI et al[23], DEVECI et al[8]). Hence, instead of copper existing in ionic form in aqueous solution, it combines with the precipitated iron.

The bioleaching behaviour at varying particle size could be explained from the view point of the surface area of the mineral that is available for microbial attack. According to HOSSAIN et al[12]), the size of particles determines the surface area which also affects bioleaching. Smaller surface area of the larger particle size fraction of 106 μm could result in a decrease in the number of active microbial attachment sites that could promote dissolution. At larger particle sizes, less content of metals are exposed to the reacting solution, thereby reducing contact between the bacterial cells and metal content of the ore. Lower recovery at finer particle size fractions might be attributed to possible cell damage and deactivation (DEVECI[8]), which could be caused by finer particles arising from probable oxygen deficiency due to limiting air flow rate. According to NEMATİ et al [2], a reduction of particle size below a critical level could increase the extent of the particle—particle collision and impose severe attrition which might disrupt the structure of the cells. Possibility also exists that higher complexity of minerals may arise at smaller particle sizes that could have enhanced specific interactions. This is because, greater surface area could leave each particle exposed to a greater amount of different mineral species, which could increase the complexity of the medium thus affecting directly the dissolution (MAKITA et al[6]).

Optimal biodissolutions at a particle size of 75 μm could be attributed to the combined effects of surface area and its overall suitability for microbial viability and activities. Since larger particles and finer particles both have impeding effects on microbial-mineral activities, the dissolution results confirmed a particle size of 75 μm as the optimum size supporting, and accelerating biodissolution. It can therefore be concluded that particle size fraction of 75 μm satisfies both surface area effects and conduciveness for microbial growth, which leads to improved mass transfer and enhanced bioleaching rates.

3.2 Electrochemical behaviour at varying particle sizes

The polarization curves for the four varying particle sizes obtained from potentiodynamic studies on the 1st, 6th, 12th, 18th day of bioleaching are respectively shown in Fig.6. Polarization curves displayed a similar active dissolution trends for all the particles sizes in each day of measurement. The electrodes were however observed to display passivity as the day of exposure to microbial attack increased. Smaller particle size fractions of $\leq 53 \mu\text{m}$ displayed higher degree of passivity at lower

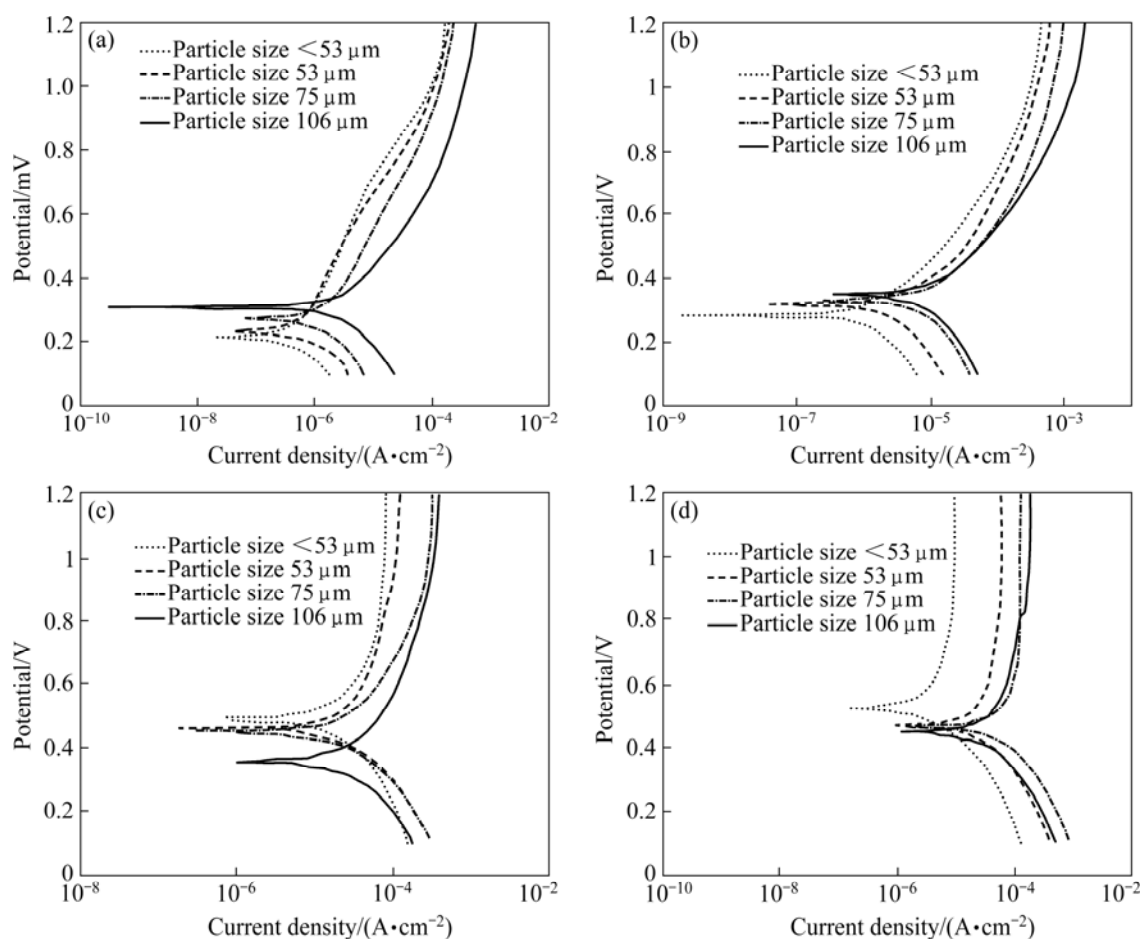


Fig.6 Polarization curves of four particle size fractions exposed to microbial attack on the 1st day (a), 6th day (b), 12th day (c) and 18th day (d)

potential values on the 12th and 18th day of microbial attack as compared with larger particle sizes. The passivity displayed by all the electrodes commencing from the 12th day of bioleaching confirmed that the decrease in lead and iron dissolution during the bioleaching experiments (Fig.4 and 5) were attributed to precipitation. The results for the dissolution current, dissolution current densities, and the dissolution rates that were derived from the electrochemical tests for the samples in the different solutions are summarized in Table 2. In all the bioleaching days, particle size fraction of 106 μm displayed the highest dissolution, while particle size fraction of $<53 \mu\text{m}$ displayed the least one.

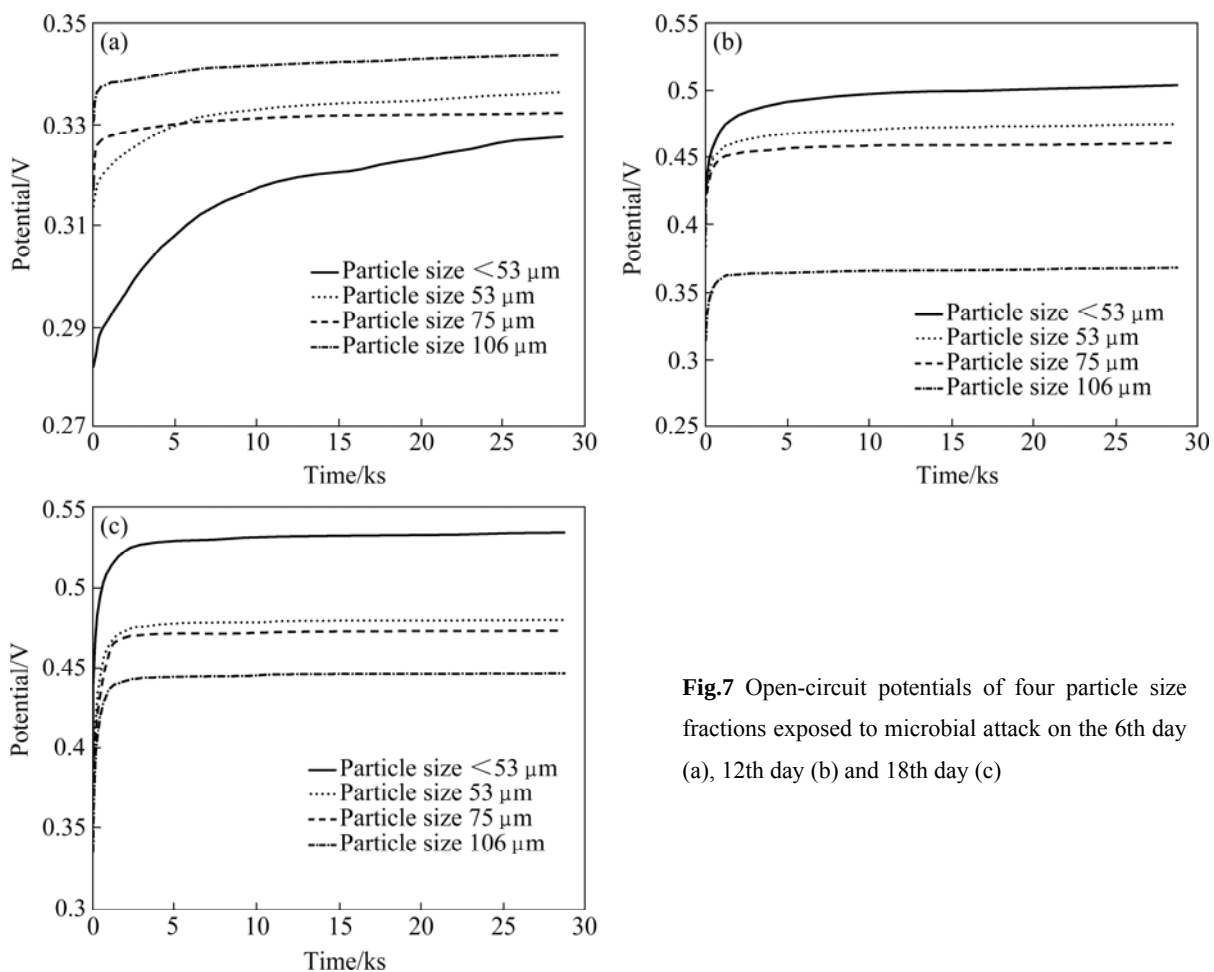
The electrochemical data in Table 2 show important differences between the OCP, dissolution current and corrosion rate values, indicating that galvanic interactions are prevalent as particle sizes increase. The values of the OCPs obtained from prior polarization measurement in the all the days of exposure to bacterial attack revealed variations in the OCPs of four varying particle size fractions as the duration of exposure to microbial attack increased. This variation could be an indication that their reactivity was influenced by the

mineralogical variations within these size fractions. In all the days of microbial attack, the OCP values of the varying particle sizes increased with duration of exposure. This indicates that the reactivity of the ore decreased with the duration of exposure to microbial attack. On the 6th day of microbial attack, the dissolution potentials of the electrodes were observed to increase with increasing particle sizes. However, on the 12th and 18th day, dissolution potential increased as particle sizes decreased. These observations indicate that smaller particles sizes were more susceptible to dissolution at the initial stage of microbial attack, while their amenability to dissolution decreased faster as the duration of microbial attack increased.

Typical variation of the OCPs of the electrodes from the four varying particle size fractions for the periods of exposure to microbial attack is shown in Fig.7. A small and progressive increase in potential from more negative values to positive values with time was observed as particle size fraction decreased. This was very significant for particle size fraction of $\leq 53 \mu\text{m}$ on the sixth day of microbial attack. The increased potential observed (Table 2) can be ascribed to the formation of passive films on

Table 2 Corrosion data obtained from electrochemical tests

Duration of exposure to microbial attack	Particle size fraction	$\varphi_{\text{corr}}/\text{V}$	$J_{\text{corr}}/(\text{A}\cdot\text{cm}^{-2})$	I_{corr}/A	Corrosion rate/ $(\text{mm}\cdot\text{a}^{-1})$
Day 1 (without bacteria)	$<53\ \mu\text{m}$	0.212	5.55×10^{-7}	1.08×10^{-7}	3.10×10^{-3}
	$53\ \mu\text{m}$	0.230	5.62×10^{-7}	1.10×10^{-7}	3.22×10^{-3}
	$75\ \mu\text{m}$	0.265	7.89×10^{-7}	1.55×10^{-7}	4.52×10^{-3}
	$106\ \mu\text{m}$	0.292	1.13×10^{-6}	2.20×10^{-7}	6.45×10^{-3}
Day 6	$<53\ \mu\text{m}$	0.282	6.81×10^{-7}	1.33×10^{-7}	7.91×10^{-3}
	$53\ \mu\text{m}$	0.317	3.42×10^{-6}	6.71×10^{-7}	3.97×10^{-2}
	$75\ \mu\text{m}$	0.330	8.11×10^{-6}	2.21×10^{-6}	9.54×10^{-2}
	$106\ \mu\text{m}$	0.335	1.17×10^{-5}	2.29×10^{-6}	1.36×10^{-1}
Day 12	$<53\ \mu\text{m}$	0.491	8.41×10^{-6}	1.65×10^{-6}	9.77×10^{-2}
	$53\ \mu\text{m}$	0.459	2.38×10^{-5}	4.68×10^{-6}	2.77×10^{-1}
	$75\ \mu\text{m}$	0.450	4.98×10^{-5}	9.77×10^{-6}	5.79×10^{-1}
	$106\ \mu\text{m}$	0.358	1.09×10^{-4}	2.13×10^{-5}	1.26×10^0
Day 18	$<53\ \mu\text{m}$	0.524	1.37×10^{-5}	2.69×10^{-6}	1.59×10^{-1}
	$53\ \mu\text{m}$	0.471	1.71×10^{-4}	3.36×10^{-5}	1.99×10^0
	$75\ \mu\text{m}$	0.467	2.01×10^{-4}	3.94×10^{-5}	2.33×10^0
	$106\ \mu\text{m}$	0.448	2.66×10^{-4}	5.22×10^{-5}	3.09×10^0

**Fig.7** Open-circuit potentials of four particle size fractions exposed to microbial attack on the 6th day (a), 12th day (b) and 18th day (c)

the surfaces of the minerals. According to SHI et al[24–25], the increase in potential signifies a growth of the passivating film on the surfaces of the electrode. This observation could therefore indicate that the growth of the passive film was more prevalent at lower particles

sizes. As the duration of microbial attack increased, the rate at which the OCP value increases with time was reduced. This was quite evident on the 18th day, where the OCP values initially increased within the first 600 s, before stabilization.

3.3 Bioleaching and electrochemical behaviour at varying particle sizes

The bioleaching and electrochemical behaviours respectively obtained from the bioleaching and electrochemical studies show a high degree of consistency with some discrepancies. The only exception is that, bioleaching revealed the highest recovery at particle size fraction of 75 μm , while electrochemical study revealed the highest dissolution at particle size fraction of 106 μm . The consistency and the slight difference (highest recovery from particle sizes fraction of 75 μm during bioleaching and highest dissolution particle size fraction of 106 μm during electrochemical study) in the results obtained from these studies are attributed to the mineralogical variations of the particles of the ore (Table 1). This is because mineralogical differences of particles could affect their responses and behaviour during bioleaching. Since there is variation in the amount of each element within the particles, percentage metal recovered during bioleaching will be a quotient of the percentage of the metal within a particular particle size. Mineralogical difference including higher amounts of acid consuming siderite, galena, and quartz at lower particle size fraction could negatively affect the major influencing factors for bioleaching; iron mobility and oxidation, and precipitate formation, which in turn could reduce metal dissolution at lower particle sizes (OLUBAMBI et al[16]).

The highest dissolutions at particle size fraction of 106 μm obtained through electrochemical studies can be attributed to the lower amounts of acid consuming siderite and galena, coupled with higher amount of Fe in the sphalerite matrix within the larger particles. The XRD analysis of the particle size fraction previously reported by OLUBAMBI et al[26] revealed that there were variations in the chemical composition of ferrous sphalerite for different particles as larger particle size fractions contained more solid solution iron. Higher amount of Fe within sphalerite of larger particle could decrease the activation energies for sphalerite leaching (WEISENER et al[27]) and also increase the availability of ferrous ions for ferric ion oxidation thereby accelerating metal dissolution through indirect mechanism.

The highest recovery would be expected at particle size fraction of 106 μm during bioleaching. Lower metal recovery at this particle size fraction in comparison with particle size fractions of 53 and 75 μm could be attributed to the negative effect of the physical influence of larger particle sizes on bacterial activity. It should be understood that during bioleaching, the reactor was continually agitated at 150 r/min, while electrochemical study was conducted without stirring. At higher stirring speed of 150 r/min during bioleaching, larger particle

size fraction of 106 μm could increase the frequency of particle–particle collisions. This might thus cause friction and attrition between bacterial cells and the ore that could result in cell damage, deactivation, disintegration, and inhibition of the attachment of bacteria to the minerals and the detachment of the cells from the mineral surface (d'HUGUES et al[28], ROSSI[29]; DEVECI[7]), consequently leading to lower dissolutions. Possibility also exists that there could be severe mass transfer limitations in the bioleaching reactor at this stirring speed. It can therefore be concluded that optimal recovery obtained at the particle size of 75 μm during bioleaching is due to the combined effects of mineralogical variation with those of the particle sizes which favour higher dissolution at larger particle sizes and that particle size of 75 μm was not too large to negatively affect microbial activity as does by larger particle size fraction of 106 μm .

3.4 Characterization of bioleached residues

The XRD and SEM analyses of the bioleached residues have been previously reported by OLUBAMBI et al[16]. SEM analyses revealed that the surfaces of the grains were covered and coated with precipitated products and that the morphologies of the ore were differently changed at the different particle sizes. The precipitates cover was reported to be an indication that dissolution might be hindered through the less-porous product layer over the mineral sulphides and the building up of the non-conducting product layers within the system. XRD analysis of the residues was reported to show the presence of jarosite, anglesite, elemental sulphur, hydroxides, and little secondary sulphides of pyrite and covellite in all the residues. Higher amounts of jarosite, anglesite and sulphur were obtained at smaller particle sizes of $\leq 53 \mu\text{m}$. Higher precipitates obtained at smaller particle size fractions of $\leq 53 \mu\text{m}$ were attributed to their higher amounts of siderite and galena contents. These insoluble products could thus built up a non-conducting product layer within the system, which reduced the dissolution rates of particle size fractions of $\leq 53 \mu\text{m}$ with time as compared with larger particle size fractions that had lower amounts of these precipitates. The higher amounts of these precipitates at smaller particle size fractions of $\leq 53 \mu\text{m}$ could have also accounted for the high degree of increase in the OCPs to more electropositive values as the duration of exposure to bacterial attack increased.

3.5 Electrochemical behaviour of constituent minerals phases

In order to confirm and provide a mineralogical understanding of dissolution behaviour at the varying particle sizes, massive electrode from three different

mineral rich phases of the ore (two major sulphide mineral rich phases consisting of sphalerite-rich and galena-rich, and a complex mineralogical phase) were subjected to electrochemical studies using potentiodynamic-potentiodynamic polarization method. The comparative electrochemical behaviours of the massive electrodes obtained from the potentiodynamic scans measured on the 6th, 12th, and 18th day of exposure to microbial leaching are shown in Fig.8. The polarization curves of the three phases were slightly similar, with basically no noticeable critical current density and active to passive transition. In all the measurements, current increased with applied potentials, indicating dissolution in all the potential ranges. Polarization curves also revealed that the three mineral phases displayed fairly high electropositive values with no spontaneous passivation. Galena displayed the fastest reactivity as revealed by its least dissolution potentials on the 6th day of exposure. As exposure time prolonged, reactivity at galena rich phase decreased, and became the least on the 12th and 18th day as indicated by its respective highest dissolution potential values of 371 and 426 mV. Reactivity was initially least at sphalerite-rich phase but became highest on the 18th day. In all the bioleaching days, dissolution was the highest at sphalerite-rich phase and the least at

galena-rich phase. The reactivity and dissolution results observed from this study can be attributed to the difference in the rest potentials and the type of precipitates that were formed on the surfaces of the various mineral-rich phases which might affect both the anodic and cathodic Tafel constants.

In all the days of exposure, it was noticed that the value of current density for sphalerite-rich phase starts to increase from a potential value of about 380 mV up till 850 mV. This could indicate that decomposition of the ore at sphalerite-rich phase occurs in the potential range of 380–850 mV. Beyond 850 mV, the rates of increase in current density with applied potential were very slow and could correspond to a decrease in dissolution. This decrease in dissolution can be attributed to the passivation of the mineral, which might result from the presence of elemental sulphur and insufficient ferric ions to oxidize sulphur chemically. The highest increase in the rate of current density with the corresponding applied potential observed between 380 mV and 850 mV shows that highest dissolution of the sphalerite rich phase could be attained within these potential ranges. Therefore, it can be concluded that the potential range for optimum dissolution is between 380 mV and 850 mV.

Careful observations revealed that the galena-rich

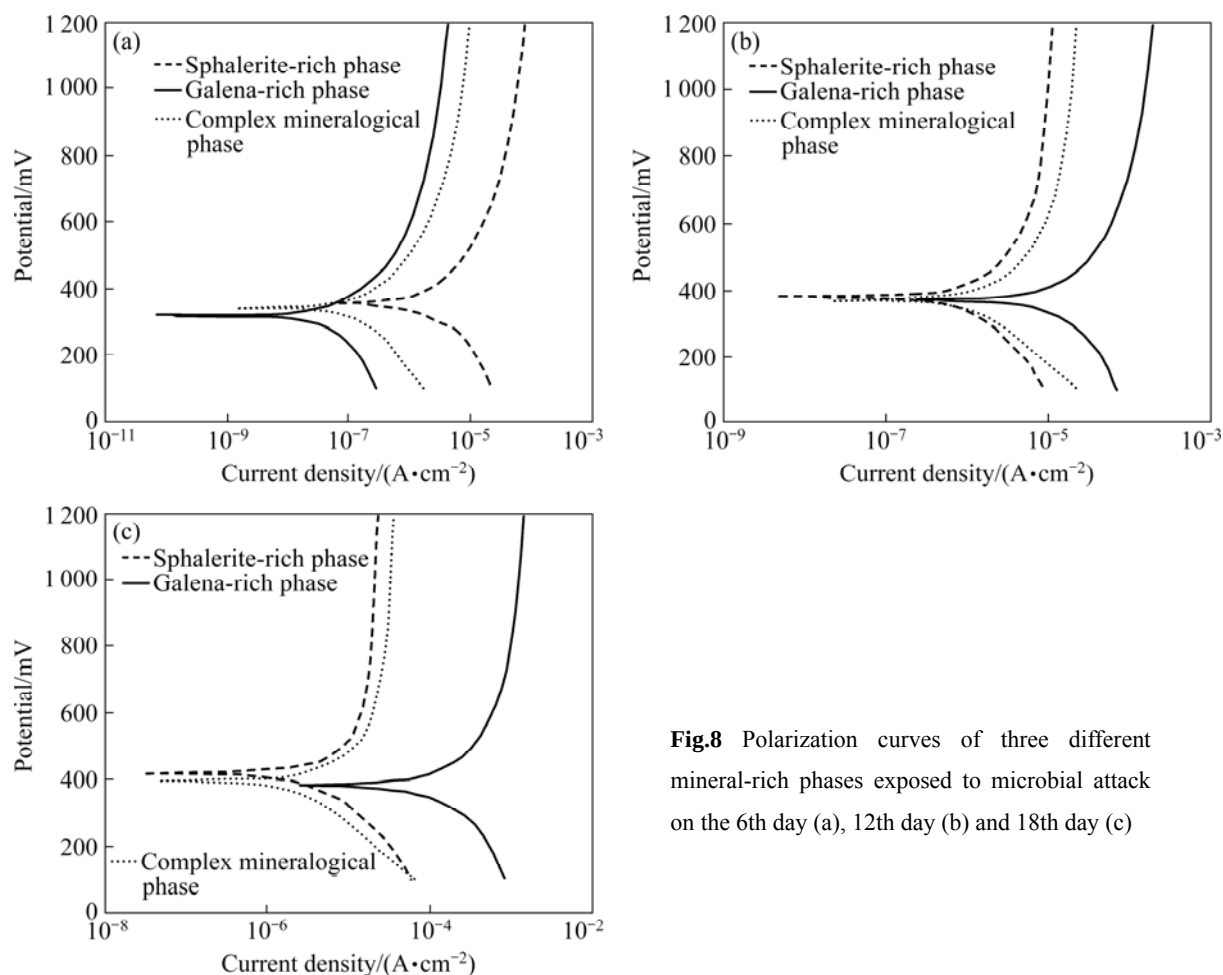


Fig.8 Polarization curves of three different mineral-rich phases exposed to microbial attack on the 6th day (a), 12th day (b) and 18th day (c)

phase exhibit higher passivity as compared with the sphalerite-rich phase. The potential ranges for increasing the applied potential corresponding to an increase in dissolution current was averagely between 400 mV and 650 mV. Beyond the potential range of 650 mV and 550 mV on the 12th and 18th day, this phase underwent passivity, as there was no significant increase in dissolution current as the applied potential increased. The general passivation observed for the galena-rich phase could be attributed to the formation of an insoluble precipitate layer on the mineral surface, which could be both non-conducting and non-permeable. According to SILVA et al[22], precipitates formed in the presence of galena pose diffusion limitations, which decreases dissolution. From the 12th day of bioleaching, reactivity began to decrease and passivity increased, which is presumed from the results that anglesite and sulphur precipitation increased.

For the complex mineralogical phase, polarization curves show that dissolutions were generally lower than that of sphalerite-rich phase but higher than that of galena-sphalerite-rich phase. Polarization curves show similarities between these two phases. With the exception of bioleaching on the 18th day, polarization curves show a consistent increase in the rate of current density with corresponding applied potential. The passivation observed on the 18th day, starting from a potential value of 600 mV, could be used to presuppose that the precipitate formed on this surface which inhibited dissolution became very significant on the 18th day.

3.6 XRD and SEM studies on dissolution at mineral phases

The various types of bioleached products were formed on the surfaces of the three different mineral-rich phases studied as revealed by XRD shown in Table 3. Sphalerite and pyrite with traces of covellite, sulphur and anglesite were the phases identified at sphalerite-rich phase, while anglesite and elemental sulphur were the major phases identified at galena-rich phase. Complex phases of jarosite, ferrous silicate and hydroxide, with traces of pyrite were observed on the surface of complex mineralogical phase.

The decreased dissolution on the galena-rich and complex mineralogical surface with increased potential could be attributed to the precipitate layers formed on

these surfaces. These precipitating films could have hindered bacterial access to the mineral surface and build up a non-conducting product layer within the system thereby lowering the galvanic interaction effect needed to promote further dissolution. In the case of sphalerite-rich phase, the none-limiting nature of the current could imply that the anodic process was not restricted by the diffusion of the minority transporters towards the surface (CABRAL and IGNATIADIS[30]). Since the presence of anglesite, sulphur and iron silica hydroxide precipitates were observed on the bioleached surfaces with variations at the three different phases, dissolutions would have been influenced by the types of precipitate formed on the three surfaces. On the sphalerite surface, it is believed that the zinc sulphate precipitate is formed during the bioleaching process, although this precipitate was not identified by XRD, probably because of its high solubility and transformation to ionic state in the leached solution. It is believed that this precipitate would have favoured microbial activity and permitted further dissolution through its high solubility. Formation of complex secondary iron products (e.g jarosite and iron silica hydroxide) for complex mineralogical phase might lead to the reduction in further dissolution.

Morphologies of the different mineral phases observed before and after the bioleaching experiments are presented in Fig.9–11. Surface observations of the bioleached samples showed different types of microbial attack. SEM micrographs of the surfaces revealed that the morphologies of different mineral phases were transformed by the microbial interaction. SEM micrographs revealed different types of pitting even at the same mineral phase.

Sphalerite rich phases were mostly attacked, confirming that dissolution was the highest at this phase. The galena-rich and the complex mineralogical phases did not show as much pitting as observed at the sphalerite rich phase. Fig.9 reveals higher deeper dissolution channels at sphalerite-rich phase. A similar situation was observed by SANTHIYA et al[31] where the sphalerite surfaces were eroded as a consequence of bacterial attack. Higher microbial attack observed on the sphalerite rich surfaces could be attributed to the type of soluble and conducting precipitate layer formed during biooxidation. The soluble and conducting zinc sulphate product formed favours microbial activity, permitting further bacterial access to mineral surface and aids

Table 3 Phases identified by XRD analysis of bioleached residues

Sample No.	Mineral phase	Major phases (order of abundance)
1	Sphalerite-rich	ZnS, FeS ₂ , with traces of CuS, S, and PbSO ₄
2	Galena-rich	PbSO ₄ , S, PbS, KFe ₃ (SO ₄) ₂ (OH) ₆ , FeS ₂
3	Complex mineralogy	KFe ₃ (SO ₄) ₂ (OH) ₆ , (K,H ₃ O)Fe ₃ (SO ₄) ₂ (OH) ₆ , KAl ₃ Si ₃ O ₁₀ (OH) ₂ , SiO ₂ , FeS ₂ , FeCO ₃

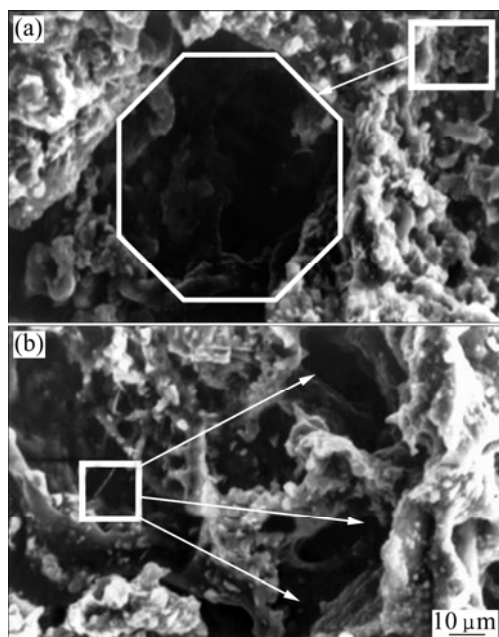


Fig.9 Typical SEM micrographs of sphalerite-rich phase morphologies after microbial attack: (a) Deep hollow dissolution pit; (b) Dissolution channels of elongated elliptical pits

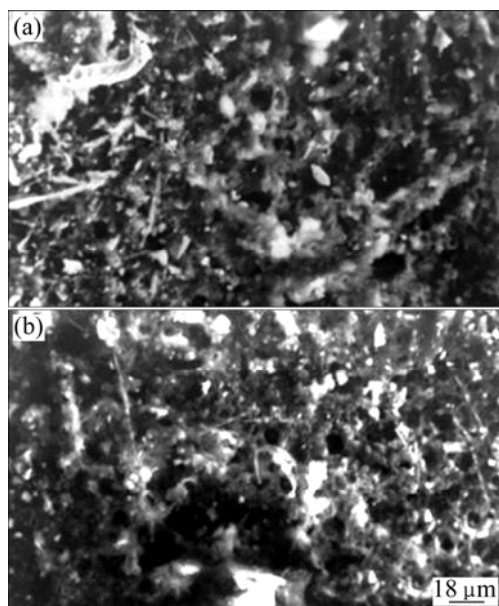


Fig.10 Typical SEM micrographs of galena-rich phase (a) and morphologies after microbial attack showing much precipitate cover with no distinct microbial induced pitting (b)

further dissolution. According to NDLOVU and MONHEMIUS[32], it is also possible that these pits are generated during initial stages of leaching, and with the subsequent generation of ferric iron, the pore sidewalls become susceptible to further enhance dissolution in the direction of high reactivity and enlarge the pores. The iron content within the sphalerite lattice would therefore

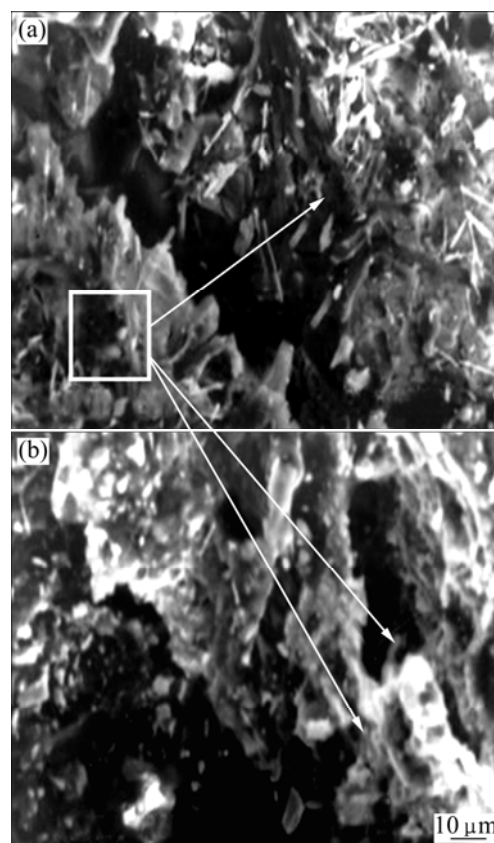


Fig.11 Typical SEM micrographs of complex mineralogical phase (a) and morphologies after microbial attack showing no regular microbial attack and dissolution pits (b)

enhance higher ferric generation, which is believed to have promoted higher dissolution pits observed through indirect mechanisms. From these observations, it can be concluded that indirect mechanism accelerated the oxidation rate of the sphalerite rich electrode, confirming the polarization curves shown in Fig.8.

At the galena rich phase, lower dissolution pits were observed. Lower dissolution could be attributed to the effects of the observed insoluble anglesite precipitate which limited the access of bacteria to mineral surface. According to SANTHIYA et al[33], lead sulphate formed on galena is insoluble and the cells are preferentially adsorbed onto anglesite surface. When this situation arises, cells will concentrate on anglesite instead of the mineral surface itself. According to PACHOLEWSKA [34], anglesite also covers the surface of the mineral, as well as reduce the penetration of solution components and oxygen inside the grain. Although there was pitting at the galena rich phase, higher bacterial attack was observed at the complex mineralogical phase than at the galena phase. Nevertheless, the formation of complex secondary iron products (e.g. jarosite and iron silica

hydroxide) at the complex mineralogical phase, might lead to the reduction in further microbial attack and dissolution, as some of the cells will adhere to the precipitate.

4 Conclusions

Bioleaching experiments, electrochemical technique and scanning electron microscopy method were used to study the interplay of mineralogical variation and mineral phase distribution within varying particle sizes on the dissolution behaviour of a low grade complex sulphide ore. Bioleaching studies revealed the highest recoveries at a particle size of 75 μm , while electrochemical investigations revealed the highest dissolution at particle size of 106 μm . The discrepancies between the dissolutions within particle sizes obtained from bioleaching experiments and electrochemical studies were attributed both to the physical and mineralogical influences. The combined effects of mineralogical variation, precipitation phenomenon as well as physico-chemical effect of particle size controlled bioleaching, while galvanic interaction resulting from variations in mineralogical distribution within particle size fractions controlled the electrochemical behaviour of the ore.

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