



## Formation of hydrogen peroxide by sulphide minerals



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### ABSTRACT

Formation of hydrogen peroxide ( $H_2O_2$ ), an oxidizing agent stronger than oxygen, by sulphide minerals during grinding was investigated. It was found that pyrite ( $FeS_2$ ), chalcopyrite ( $CuFeS_2$ ), sphalerite ( $(Zn,Fe)S$ ), and galena ( $PbS$ ), which are the most abundant sulphide minerals on Earth, generated  $H_2O_2$  in pulp liquid during wet grinding in the presence of dissolved oxygen in water and also when the solids are placed in water immediately after dry grinding. Pyrite generated more  $H_2O_2$  than other minerals and the order of  $H_2O_2$  production by the minerals found to be pyrite > chalcopyrite > sphalerite > galena. The pH of water influenced the extent of hydrogen peroxide formation where higher amounts of  $H_2O_2$  are produced at highly acidic pH. Furthermore, the effect of mixed sulphide minerals, i.e., pyrite–chalcopyrite, pyrite–galena, chalcopyrite–galena and sphalerite–pyrite, sphalerite–chalcopyrite and sphalerite–galena on the formation of  $H_2O_2$  showed increasing  $H_2O_2$  formation with increasing pyrite fraction in chalcopyrite–pyrite, galena–pyrite and sphalerite–pyrite compositions. The results also corroborate the amount of  $H_2O_2$  production with the rest potential of the sulphide minerals; higher rest potential of a sulphide mineral results in more formation of  $H_2O_2$ . Most likely  $H_2O_2$  is responsible for the oxidation of sulphide minerals and dissolution of non-ferrous metal sulphides in the presence of ferrous sulphide in addition to galvanic interactions. This study highlights the necessity of revisiting the electrochemical and/or galvanic interactions between pyrite and other sulphide minerals in terms of their flotation and leaching behavior in the context of inevitable  $H_2O_2$  existence in the pulp liquid.

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### 1. Introduction

Hydrogen peroxide, which is a strong oxidizing agent, stronger than molecular oxygen, causes non-selective oxidation of sulphide minerals. The oxidation of sulphide minerals takes place during the grinding process when the particle size is reduced for flotation. Recently it was shown that formation of  $H_2O_2$  takes place in the pulp liquid during wet grinding of complex sulphide ore (Ikumapayi et al., 2012). Previous work has highlighted the potential effect of reactive oxygen species (ROS),  $H_2O_2$  and hydroxyl radical ( $\cdot OH$ ), generated from milled sulphide concentrates on thermophilic Fe- and S-oxidizing bioleaching microorganisms through oxidative stress (Jones et al., 2011; 2013a; 2013b). To date, most studies dealing with sulphide mineral-induced ROS formation have made use of natural or synthetic mineral samples, of very high purity, suspended in solutions. Pyrite induced ROS formation has been studied most; however other sulphide minerals such as chalcopyrite ( $CuFeS_2$ ), sphalerite ( $ZnS$ ), pyrrhotite ( $Fe_{(1-x)}S$ ) and vaesite ( $NiS_2$ ) have also been studied with respect to ROS generation (Borda et al., 2001; Javadi Nooshabadi and Hanumantha Rao, 2013a; 2013b; Javadi Nooshabadi et al., 2013; Jones et al., 2011), and reactivities have been found to differ between sulphide minerals.

Buehler and Gottschalk (1910) noted that when pyrite was mixed with a second sulphide mineral, the second mineral oxidized more

rapidly. Harvey and Yen (1998) discovered that addition of galena to the sphalerite selective leaching system diminished the dissolution of sphalerite. Alternatively, a pyrite or chalcopyrite addition increased zinc extractions. Many authors have been reported that galvanic interactions are known to occur between conducting minerals and play a significant role in flotation (Ekmekçi and Demirel, 1997; Huang and Grano, 2005; Kelebek et al., 1996; Rao and Finch, 1988; Zhang et al., 1997), leaching (Abraitis et al., 2003; Akcil and Ciftci, 2003; Mehta and Murr, 1983), supergene enrichment of sulfide ore deposits (Sato, 1992; Thornber, 1975), environment governance (Alpers and Blowes, 1994), and geochemical processes (Banfield and Nealon, 1997; Sikka et al., 1991). In addition, other researchers (Dixon and Tshilombo, 2005; Holmes and Crundwell, 1995; Koleini et al., 2010, 2011; Mehta, and Murr, 1983) reported when the amount of pyrite in contact with chalcopyrite increases, the leaching rate of chalcopyrite increases.

However, participation of  $H_2O_2$  and  $\cdot OH$ , if any, in non-selective oxidation of the sulphide mineral pulp components and hence in deteriorating of the concentrate grade and recovery of metal-sulphides has not yet been explored. In an attempt to fill the gap, we have estimated the concentration of  $H_2O_2$  in pulp liquid during different grinding time intervals and in different grinding environments. The effect of pH, type of grinding (wet or dry grinding), and varying proportion of pyrite, chalcopyrite and galena mixed with sphalerite on the formation of hydrogen peroxide was investigated. The results are presented and discussed in the context of flotation and leaching phenomena of sulphide minerals.

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## 2. Experimental

### 2.1. Materials and reagents

Crystalline pure sphalerite (Sp), galena (Ga), pyrite (Py) and chalcocopyrite (Cp) minerals used in this study were procured from Gregory, Bottley & Lloyd Ltd., UK. Sphalerite contained 39.92% Zn, 20.7% S, 4.2% Fe, 1.32% Pb and 0.17% Cu, galena contained 73.69% Pb, 13.5% S, 1.38% Fe, 1.26% Zn, 0.2% Cu and some silica (quartz) impurity; pyrite contained 44.4% Fe, 50.9% S, and 0.2% Cu, and chalcocopyrite contained 29% Fe, 29.5% S, 25.8% Cu, 0.54% Zn, and 0.22% Pb. The XRD analyses of the samples showed that the main mineral phases were the pyrite (Fig. 1a), chalcocopyrite (Fig. 1b), sphalerite (Fig. 1c), and galena (Fig. 1d) in the respective mineral samples. All pyrite, chalcocopyrite, sphalerite and galena samples used in this study were separately crushed through a jaw crusher and then screened to collect the  $-3.35$  mm particle size fraction. The homogenized sample was then sealed in polyethylene bags. Potassium amyl xanthate (KAX) was used as collector and the frother was methyl isobutyl carbinol (MIBC) in flotation tests. Solutions of sodium hydroxide (1 M) and HCl (1 M) were added to maintain the pH at the targeted value during flotation. Deionized water was used in the processes of both grinding and flotation. Solutions of 2, 9-dimethyl-1, 10-phenanthroline (DMP), copper (II) (0.01 M), and phosphate buffer (pH 7.0) were used for estimating  $H_2O_2$  amount in pulp liquid by UV-Visible spectrophotometer. Zinc sulphate, copper sulphate, lead nitrate, ferrous sulphate and ferric sulphate chemicals were also used to investigate the effect of metal ions ( $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$ ) on the formation of  $H_2O_2$ .

### 2.2. Dry grinding

100 g of  $-3.35$  mm size fraction of sphalerite, pyrite, galena and chalcocopyrite minerals in each grinding test was separately ground in a laboratory stainless steel ball mill (Model 2VS, CAPCO Test Equipment, Suffolk, UK) with stainless steel medium for 60 min. 5 g of sphalerite, galena, pyrite or chalcocopyrite single mineral and 12.5 g in total of mineral mixture either sphalerite–pyrite or sphalerite–chalcocopyrite or sphalerite–galena or galena–pyrite or galena–chalcocopyrite or chalcocopyrite–pyrite that was  $< 106 \mu m$  was mixed with  $50 \text{ cm}^3$  water using magnetic stirrer. Then the slurry samples were collected at 0.5, 5 and 11 min, filtered and they were analyzed for hydrogen peroxide. The pH was regulated with HCl and NaOH solutions.

### 2.3. Analysis of hydrogen peroxide

The spectrophotometric method using copper (II) ions and DMP has found to be reasonably sensitive when applied to advanced oxidation processes (Kosaka et al., 1998). For DMP method (Baga et al., 1988) 1 mL each of 1% DMP in ethanol, 0.01 M copper (II), and phosphate buffer (pH 7.0) solutions were added to a 10 mL volumetric flask and mixed. A measured volume of liquid (filtrate) sample was added to the volumetric flask, and then the flask was filled up with ultrapure water. After mixing, the absorbance of the sample at 454 nm was measured with DU® Series 700 UV/Vis Scanning Spectrophotometer. The blank solution was prepared in the same manner but without  $H_2O_2$ .

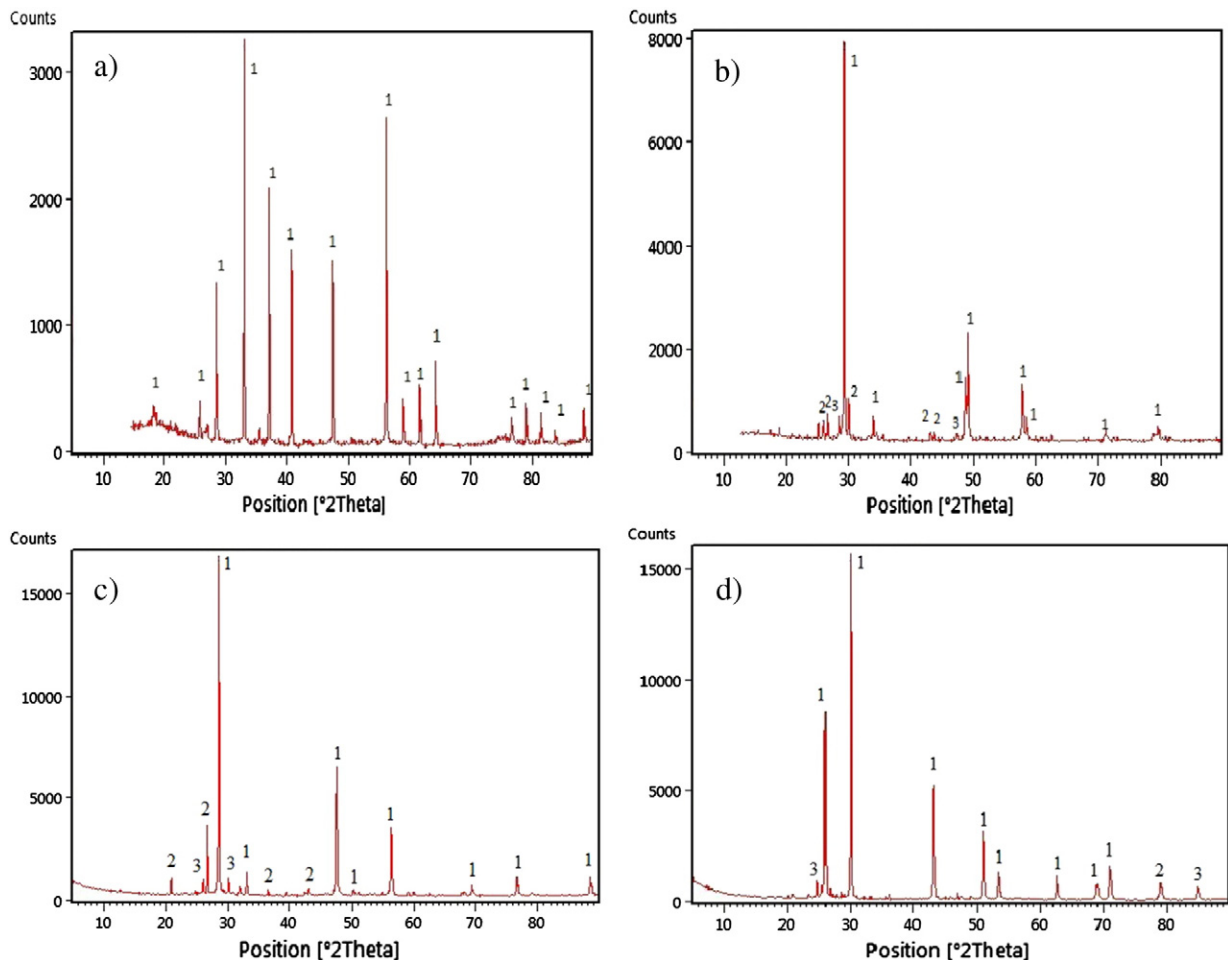


Fig. 1. XRD analysis of the mineral samples: (a) pyrite (1 – pyrite), (b) chalcocopyrite (1 – chalcocopyrite and 2 – pyrrhotite 3 – sphalerite), (c) sphalerite (1 – sphalerite 2 – galena 3 – quartz), and (d) galena (1 – galena 2 – sphalerite 3 – quartz).

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