



Original Research Paper

Formation of hydrogen peroxide by galena and its influence on flotation



Alireza Javadi Nooshabadi, Kota Hanumantha Rao*

Mineral Processing Group, Division of Sustainable Process Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden

ARTICLE INFO

Article history:

Received 18 September 2013

Received in revised form 17 November 2013

Accepted 12 December 2013

Available online 27 December 2013

Keywords:

Hydrogen peroxide

Hydroxyl radical

Galena

Pyrite

Chalcopyrite

Flotation

ABSTRACT

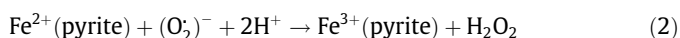
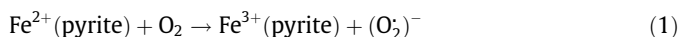
The formation of hydrogen peroxide (H_2O_2), an oxidising agent stronger than oxygen, during the grinding of galena (PbS) was examined. It was observed that galena generated H_2O_2 in the pulp liquid during wet grinding and also when the freshly ground solids were placed in water immediately after dry grinding. The generation of H_2O_2 during either wet or dry grinding was thought to be due to a reaction between galena and water, when the mineral surface is catalytically active, to produce OH^\cdot free radicals by breaking down the water molecule. It was also shown that galena could generate H_2O_2 in the presence or absence of dissolved oxygen in water.

The concentration of H_2O_2 formed increased with decreasing pH. The effects of using mixtures of pyrite or chalcopyrite with galena were also investigated. In pyrite–galena mixture, the formation of H_2O_2 increased with an increase in the proportion of pyrite. This was also the case with an increase in the fraction of chalcopyrite in chalcopyrite–galena mixtures. The oxidation or dissolution of one specific mineral rather than the other in a mixture can be explained better by considering the extent of H_2O_2 formation rather than galvanic interactions. It appears that H_2O_2 plays a greater role in the oxidation of sulphides or in aiding the extensively reported galvanic interactions. This study highlights the necessity of further study of electrochemical and/or galvanic interaction mechanisms between pyrite and galena or chalcopyrite and galena in terms of their flotation behaviour.

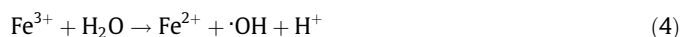
© 2013 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan. All rights reserved.

1. Introduction

Hydrogen peroxide 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 pulp liquid during wet grinding of complex sulphide ore [1]. Previous works showed that pyrite (FeS_2) [2–8], chalcopyrite (CuFeS_2) [7,9], sphalerite (ZnS) [10] and galena (PbS) [11–13] too generate hydrogen peroxide (H_2O_2) when placed in water. Cohn et al. showed that ferrous iron associated with pyrite in the presence of dissolved molecular oxygen, can form superoxide anion (O_2^\cdot)[−] (Eq. (1)), which further reacts with ferrous iron to form H_2O_2 (Eq. (2)) [4]. Thus hydrogen peroxide can then react with ferrous iron to form hydroxyl radicals through the Fenton reaction (Eq. (3)) [4].



Borda et al. showed that pyrite can also generate H_2O_2 in the absence of molecular oxygen [3]. They reported that an electron is extracted from water and a hydroxyl radical is formed (Eq. (4)). Combining two hydroxyl radicals leads to the formation of H_2O_2 :



Ahlberg et al. studied the oxygen reduction on pyrite and galena with a rotating ring disc electrode [11–13]. Their results suggest that the first electron transfer is the rate-determining step for the oxygen reduction at both galena and pyrite interfaces and hydrogen peroxide is found to be an intermediate. While galena is a poor catalyst for oxygen reduction, with minor formation of hydrogen peroxide, pyrite is a relatively better catalyst. This kind of difference may lead to different flotation behaviours. Numerous studies [14–19] on galena have shown that the floatability of galena can be affected by the grinding environment. The galena ground in an iron mill was much less floatable than galena ground in a ceramic mill [18]. Guy and Trahar demonstrated that the oxidation–reduction environment during grinding had a pronounced influence on the subsequent floatability of galena [14]. Peng et al. showed that galena had a lower floatability when ground with mild steel than with chromium grinding media [15]. According to

* Corresponding author. Tel.: +46 920 491705; fax: +46 920 491199.

E-mail address: hanumantha.rao@ltu.se (K. Hanumantha Rao).

the Nernst equation, the partial pressure of oxygen in the mill can also influence the grinding environment [16,19]. Oxygen purging causes the grinding environment to be more oxidising while nitrogen purging induces the opposite effect. Natarajan and Iwasaki studied the electrochemical aspects of grinding media and observed that galvanic coupling of mild steel medium with magnetite or pyrrhotite resulted in the formation of iron hydroxide species on the mineral surface [17]. Buehler and Gottschalk noted that when pyrite was mixed with a second sulphide mineral, the second mineral oxidised more rapidly [20]. The galena oxidation was accelerated electrochemically when in contact with pyrite [21,22]. However, Rao et al. demonstrated that in a 50:50 weight percent mixture of galena and pyrite the flotation response of galena was dramatically impaired compared with the same best performance with galena only [23]. They proposed that galvanic interactions may occur between conducting minerals and play a significant role in flotation.

However, participation of H_2O_2 and $\cdot OH$, if any, in the non-selective oxidation of the sulphide mineral pulp components and hence in the deterioration 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 times of grinding and in different grinding environments. The effects of pH, type of grinding (wet or dry grinding), grinding atmosphere (nitrogen/air) and the proportion of pyrite/chalcopyrite mixed with galena on the formation of hydrogen peroxide and on galena flotation were investigated.

2. Experimental

2.1. Materials and reagents

Crystalline pure galena, pyrite and chalcopyrite minerals used in this study were procured from Gregory, Bottley & Lloyd Ltd., United Kingdom. Table 1 shows the chemical composition of the minerals. The XRD analyses of the samples showed that the main mineral phase present was pyrite (Fig. 1a), chalcopyrite (Fig. 1b) and galena (Fig. 1c) respectively in these minerals. Pyrite, chalcopyrite 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 homogenised sample was then sealed in polyethylene bags. Potassium amyl xanthate (KAX) and methyl isobutyl carbinol (MIBC) used as collector and frother respectively were obtained from Boliden Mineral AB, and these samples are being used in the flotation plant concentrator. Dilute solutions of AR grade sodium hydroxide and HCl were added to maintain the pH at the targeted value during flotation. Deionised water was used in both grinding and flotation experiments. Solutions of 2,9-dimethyl-1,10-phenanthroline (DMP), copper (II) sulphate (0.01 M) and phosphate buffer (pH 7.0) used in the analytical method for determining H_2O_2 and lead nitrate, ferrous sulphate and ferric sulphate used for investigating the effect of these metal ions on the formation of H_2O_2 were purchased from VWR, Sweden.

2.2. Wet grinding and flotation test

Crushed galena sample (100 g) of -3.35 mm size in each grinding test was combined with 400 ml of water and ground in

Table 1
Chemical composition of the minerals used in the studies.

Minerals	% Pb	% S	% Fe	% Zn	% Cu
Galena	73.69	13.5	1.38	1.26	0.2
Pyrite	–	50.9	44.4	–	0.02
Chalcopyrite	0.22	29.5	29	0.54	25.8

a laboratory stainless steel ball mill (Model 2VS, CAPCO Test Equipment, Suffolk, UK) with stainless steel media. The amount of media, size of media ball, grinding time for the charge are 850 g, 1.87 cm and 60 min respectively. The slurry samples were collected at pre-determined time intervals and they were immediately filtered (Millipore 0.22 μm) and the liquid (filtrate) was analysed for hydrogen peroxide.

After grinding for 60 min, the mill was emptied and the pulp was screened and it was sampled to different portions. In each flotation test, 7.5 g of sample that was $<106 \mu m$ was transferred to a cell of 150 ml capacity (Clausthal flotation equipment), conditioned with pH modifier, collector and frother. The flotation concentrate was collected after 2.0 min at air flow rate of $0.5 \text{ dm}^3 \text{ min}^{-1}$. The flotation froth was scraped every 10 s. Dosages of collector for flotation was 10^{-4} M KAX. The conditioning times for adjusting pH and collector were 5 min and 2 min respectively. The frother dosage was one drop of MIBC in all cases. The flotation of galena was investigated at different pH. The Eh (pulp potential) was measured at room temperature and during the conditions of all our experiments using a platinum electrode and reference electrode and was expressed relative to the standard hydrogen electrode, SHE. The pH was measured using a glass electrode. The pH was regulated with NaOH and HCl solutions. Experiments were performed at room temperature of approximately 22.5 °C.

2.3. Dry grinding

100 g of galena, pyrite and chalcopyrite single minerals were separately ground in a laboratory stainless steel ball mill with stainless steel medium for 60 min. 5 g of either galena, pyrite or chalcopyrite mineral and 12.5 g in total of galena–pyrite blend or galena–chalcopyrite blend with particle size $<106 \mu m$ was mixed with 50 ml of water and conditioned with a magnetic stirrer. The slurry sample was collected after 0.5, 5 and 11 min conditioning time and was analysed for hydrogen peroxide. The pH was regulated with HCl and NaOH solutions. The Eh (pulp potential) of the suspension was measured at room temperature during mixing.

2.4. Gas purging

To study the effect of gaseous atmosphere, galena was wet-ground in a laboratory ball mill with stainless steel media in either air or N_2 atmosphere. For these tests, the jar of the laboratory ball mill was filled with 400 ml deionised water and purged with either air or N_2 gas for a minimum of 30 min. After 30 min, galena (100 g) was added to the jar and purged with either air or N_2 gas for a minimum of 30 min again and then galena was wet ground for 1 h. Though the dissolved O_2 concentration was not measured in these experiments, Butler et al. have reported that for 1 l solution of ultrapure water purged for 1 h with N_2 gas, O_2 concentrations do not exceed 0.19 ± 0.05 ppm [24]. The concentration of H_2O_2 in the pulp liquid was measured after 60 min of grinding.

2.5. Estimation of hydrogen peroxide

So far, various methods have been used for the measurement of H_2O_2 in oxidation processes. Such methods use metallic compounds such as titanium oxalate, titanium tetrachloride [25–28] and cobalt (II) ions [29] that form coloured complexes with H_2O_2 , which can then be measured spectrophotometrically. The spectrophotometric method using copper (II) ions and 2,9-dimethyl-1,10-phenanthroline (DMP) has been found to be reasonably sensitive when applied to advanced oxidation processes [30]. The principle of DMP method is reduction of copper(II) with H_2O_2 . The stoichiometry is as follows:

Download English Version:

<https://daneshyari.com/en/article/144833>

Download Persian Version:

<https://daneshyari.com/article/144833>

[Daneshyari.com](https://daneshyari.com)