

Effect of water quality on formation of hydrogen peroxide and its behavior on flotation

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Article History:

Received: 16 December 2020.

Revised: 17 August 2021.

Accepted: 24 September 2021.

ABSTRACT

Water is one of the important parameters in flotation and represents 80–85% of the volume of mineral pulp processed in flotation circuits. In our recent studies revealed was found that sulphide minerals generated H_2O_2 in pulp liquid during wet grinding and also the solids when placed in water immediately after dry grinding but the effect of type of water on the oxidation of pulp components and hence in deteriorating the concentrate grade and recovery in flotation has not been explored yet. In this study, the effect of two types of water on the formation of H_2O_2 as an oxidizing agent stronger than oxygen was investigated. process water is water that is used for a flotation process in Bama Company. It was shown that process water generated $482 \mu M H_2O_2$ but deionized water generated $16 \mu M$. The result shows the recovery of chalcopyrite in pH 6 is 60% and 40% in process water and deionized water respectively. Also, recovery of galena in pH 6 is 30% and 20% in process water and deionized water respectively.

Keywords: Hydrogen peroxide, Oxidizing agent, Pyrite, Process water

1. Introduction

The billions of gallons of water also a number of chemicals such as collectors, depressants, activators, regulators are used in the flotation process. It is however pertinent to recycle a greater percentage of the used process water within the flotation cycle due to different reasons which include scarcity of freshwater resources as well as to minimize the discharge of the contaminated water to the environment [1-3]. Identifying specific effects of recycled water on the quality of flotation has been a difficult task as there is no common agreement on its impact on flotation, it appears to be detrimental in some studies where the accumulation of species such as calcium, sulphate, carbonate, rest reagents and their oxidation products, thiosalts and other metal ions leads to reduced flotation grade and recoveries [4-6] while in other studies they appear to be beneficial to the flotation process [3-4,7-8]. However, the chemistry of the recycled water is different from that of freshwater because several chemicals and other components such as rest flotation reagents, suspended solid/colloid particles, cations of metals, and anions of organic and inorganic pollutants are now present in the process of water, which inhibit collector adsorption to some extent. It can also be observed that the mineral is generally depressed in process water; this could be due to the presence of a number of dissolved iron [9-11] in the process water which could form hydrophilic layers or iron oxidation species on the surface of chalcopyrite, in addition to the formation of copper hydroxide [12] and iron hydroxide; these hydrophilic species usually play a major role in the depression of chalcopyrite flotation [10]. Our recent studies have illustrated the formation of hydrogen peroxide (H_2O_2) by metal-sulfides during grinding in the presence and absence of oxygen [13-16]. In the absence of oxygen, it was found that the pyrite surface is catalytically active and able to break down water molecules to form OH^\cdot free radical and thereby deriving oxygen in the formation of H_2O_2 from water molecules [11]. The in-situ formation of H_2O_2 and its influence on sulphide

flotation have not been addressed yet.

In this study, the effect of water types on the formation of H_2O_2 , as an oxidizing agent stronger than oxygen was investigated. In mineral processing, this is the first time that the effect of water types during grinding on the formation of H_2O_2 was investigated.

2. Materials and methods

Pure chalcopyrite and galena minerals were procured from Gregory, Bottley & Lloyd Ltd., United Kingdom. The minerals were crushed, ground, and classified into different size fractions. $5 \mu m$ fractions were used in the FTIR study. The chemical composition of the minerals is shown in Table 1. The typical concentration range of various chemical species in Bama Co. process water is shown in Table 2.

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

Minerals	% Cu	% Fe	% Zn	% Pb	% S
Galena	0.2	1.38	1.26	73.69	13.5
Chalcopyrite	25.8	29	0.54	0.22	29.5

2.1. Diffuse reflectance FTIR spectroscopy measurements

The measurement was carried out with the aid of an FTIR spectrometer. The $5 \mu m$ fraction of the mineral pre-treated at different conditions based on the present study flotation requirements were subjected to FTIR measurements. In each measurement, about 10 mg of $5 \mu m$ fraction of the mineral is pre-treated at a solids concentration of about 10 mg/100 ml of solution. The pH was adjusted with solutions of HNO_3 and KOH accordingly. The required concentration of each solution and species was usually prepared followed by the addition of

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the mineral, conditioning for 10 minutes, and addition of other required reagents and species. The pulp was subsequently filtered and the solids left to dry on the filter paper at room temperature. The pH of the suspension after all conditioning prior to filtration is always regarded as the pH of the measurement. Diffuse reflectance infrared Fourier transform (DRIFT) method was used in the measurement with 2.8 wt% concentration in potassium bromide (KBr) matrix. Each spectrum was recorded after 256 scans.

Table 2. Chemical species and their concentration range in Bama Co. process water.

Species		Concentrations		
		From	To	Unit
Sulphate	SO ₄	200	1700	mg/l
Calcium	Ca	100	850	mg/l
Iron	Fe	0.1	1900	mg/l
COD	(Cr)	<30	130	mg/l
Nitrogen	N	0.1	10	mg/l
Phosphorus	P	<0.050	0.7	mg/l
Magnesium	Mg	4.3	400	mg/l
Manganese	Mn	4.4	3100	µg/l
Zinc	Zn	12	4100	µg/l
Aluminium	Al	55	51000	µg/l
Cadmium	Cd	0.10	5.8	µg/l
lead	Pb	2.7	3500	µg/l
copper	Cu	2.7	200	µg/l
Mercury	Hg	<0.1	<0.11	µg/l
Conductivity at 25°C		91	156	ms/m

2.2. Analysis of hydrogen peroxide

So far, various methods have been used for the measurement of H₂O₂ in oxidation processes. Such methods use metallic compounds such as titanium oxalate, titanium tetrachloride, and cobalt (II) ion that form colored complexes with H₂O₂, which can then be measured spectrophotometrically. The spectrophotometric method using copper (II) ions and DMP has been found to be reasonably sensitive when applied to advanced oxidation processes [17-20]. For the DMP method [21] one milliliter each of DMP, copper (II) sulphate, 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 H₂O₂.

3. Results and discussion

Table 3 shows H₂O₂ generation at two water types that processed water produced more H₂O₂ than deionized water. The effect of different ions on the formation of H₂O₂ was investigated as shown in Table 3. Table 3 shows that Fe²⁺ ions generate substantial H₂O₂ and Pb²⁺ and Zn²⁺ give higher concentrations than Fe³⁺, Cu²⁺, Ca²⁺ and Mg²⁺. In the presence of dissolved molecular oxygen, ferrous ion forms superoxide (O₂)⁻ (eq. 1) that reacts with ferrous ion to form H₂O₂ (eqs. 2-4), [22]. This is in agreement with other studies where it was observed that metals-induced formation of free radical generates the superoxide and hydroxyl radical [22-24].



The recovery of chalcopyrite and galena at different pH ranging from 3 to 11.5 in both deionized (DW) and process (PW) water is shown in Fig. 1. It can be seen that the recovery of chalcopyrite decreases generally from low to high pH until pH 10 when it begins to rise again. The recovery of galena decreases generally from pH 3 to pH 6 and rises at pH 7, stabilizes to pH 9 where it begins to rise again. The recovery of both minerals in process water is generally lower than in deionized water. In addition, the recovery of galena in process water is generally lower than in deionized water. In literature reported that reason of depressing of minerals in process water; this could be due to the presence of a number of species including SO₄²⁻, SO₃²⁻ [25] dissolved iron [9,11] in the process water which could form hydrophilic layers or iron oxidation species on the surface of chalcopyrite, in addition to the formation of copper hydroxide and iron hydroxide; these hydrophilic species usually play a major role in the depression of chalcopyrite flotation while the strong depressing action of H₂O₂ on galena may be attributed to its strong oxidizing action on lead xanthate in galena surface giving rise to the oxidation and decomposition of lead xanthate by the reaction of (5) [12, 26]:

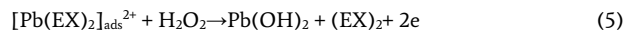


Table 3. H₂O₂ generation at two water types (natural pH, and 22 °C).

	H ₂ O ₂ (µM)
Process water	482
Deionized water	16

Table 4. Effect of metal ions on H₂O₂ generation at two initial concentrations (conditioning time 1 h, natural pH, and 22 °C).

Concentration of ions	H ₂ O ₂ (µM)	
	1 mM	10 mM
water	0	0
Fe ²⁺	551	465
Fe ³⁺	4.1	60
Cu ²⁺	0.6	15
Pb ²⁺	13	96
Ca ²⁺	0	6
Mg ²⁺	0	0
Zn ²⁺	0.6	88

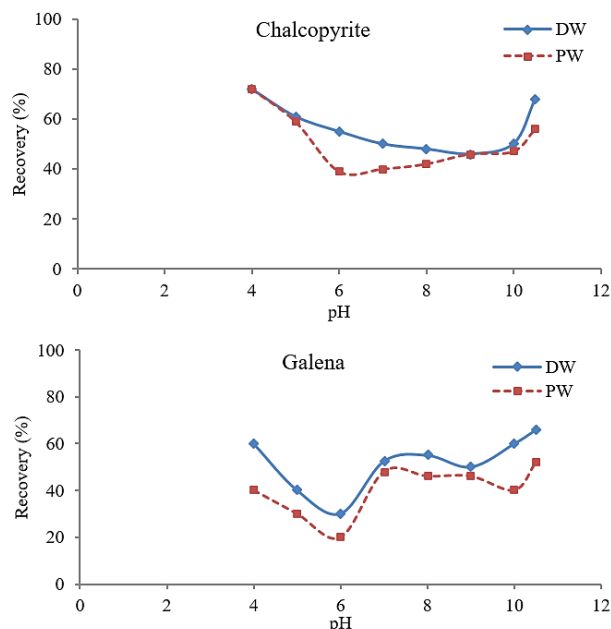


Fig. 1. Recovery of chalcopyrite and galena at different pHs in deionized and processed water.

Therefore, at certain pH and H_2O_2 concentrations, the complete decomposition of lead xanthate preadsorbed on galena renders galena surface hydrophilic and depression of galena, whereas the dioxanthogen prefixed on chalcopyrite remains stable, which confers chalcopyrite surface hydrophobic and floatable, which was proved by voltammogram method [27].

3.1. Diffuse reflectance FTIR studies

Since H_2O_2 can oxidize surfaces, the solid fraction was subjected to FTIR analysis to examine the surface species. The FTIR spectra of $-5 \mu m$ pure chalcopyrite and chalcopyrite treated with H_2O_2 at different times are shown in Fig. 2. Untreated chalcopyrite spectrum exhibits two broad bands centered around 1009 cm^{-1} and 467 cm^{-1} , and weak bands at 1189 , 796 , 684 , 631 , and 517 cm^{-1} frequency. In addition to these bands, the oxidized chalcopyrite sample display bands at 3622 , 3554 , 3390 , and 1090 cm^{-1} . The intensity of all bands in the H_2O_2 treated sample spectra increases with increasing time of treatment, implying that these bands relate to surface oxidized sulfoxyanion and hydroxide species. The bands at 1189 and 1009 cm^{-1} can be assigned to S–O stretch vibrations in sulphate and sulphite structures respectively, while the band at 631 cm^{-1} represents S–O bend vibrations. The superficial iron oxy-hydroxide species display bands in the $796\text{--}630 \text{ cm}^{-1}$ region and iron sulphate at 467 cm^{-1} ; however, the several bands around 470 and 780 cm^{-1} could also arise due to Si–O vibrations caused by silicate impurity in the sample. The bands in the region $3000\text{--}3700 \text{ cm}^{-1}$ of the H_2O_2 treated sample characterize O–H stretching vibrations of surface hydroxyl groups. The spectra with increasing time of H_2O_2 treatment and in process water, the intensity of O–H bands increased. While comparing the pure chalcopyrite spectrum to the spectra oxidized by H_2O_2 , it is clear that the pure chalcopyrite sample used in experiments is partially oxidized.

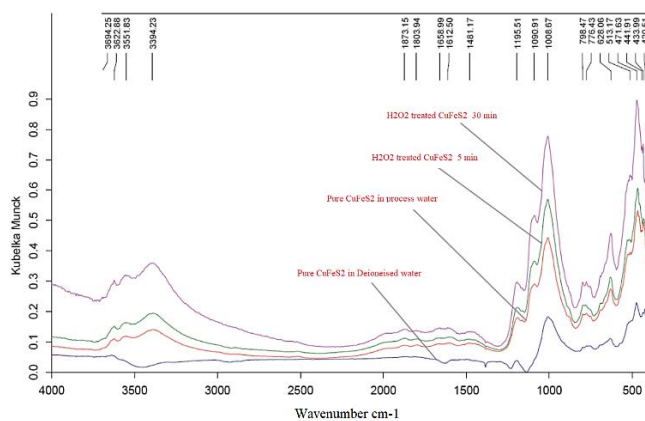


Fig. 2. Pure and H_2O_2 treated chalcopyrite DRIFT spectra.

The diffuse reflectance spectrum of the $-5 \mu m$ galena powder sample is shown in Fig. 3. The spectra of the same sample conditioned with H_2O_2 at different times are also presented in this figure. Since galena exhibits a fundamental vibration below 200 cm^{-1} , the several bands seen in the spectrum of the pure sample are due to oxidized species on the surface. An increase in the intensity of these bands when the sample is treated with an H_2O_2 oxidant substantiates that these bands are characteristic of oxidized species present on the sample. The oxidized surface state of galena mainly consists of lead sulphate and thiosulphate, and lead carbonate. The bands at 598 , 629 , 1051 , 1093 , and 1160 cm^{-1} can be assigned to S–O vibrations in lead sulphate. Lead thiosulphate bands that could appear at about 985 and 1120 cm^{-1} were not noticed in the spectra. Absorption bands characteristic of C–O vibrations in lead carbonate are seen at about 679 , 838 , 1051 , 1409 , and 1425 cm^{-1} . With increasing time of H_2O_2 treatment and in process water, the intensity of sulphate bands increased. While comparing the pure galena spectrum to the spectra oxidized by H_2O_2 , it is clear that the pure galena sample used in experiments is partially oxidized.

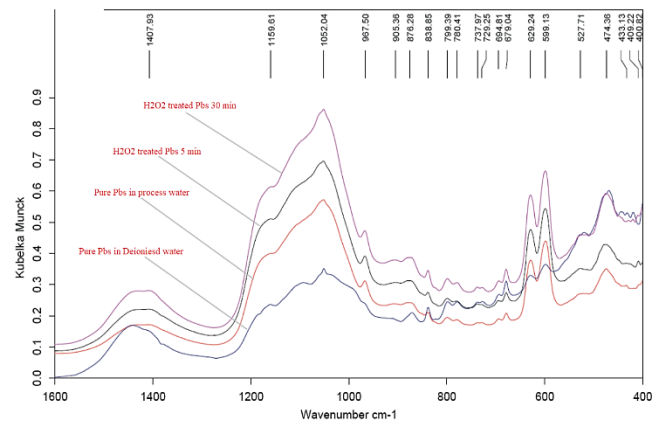


Fig. 3. DRIFT spectra of pure and H_2O_2 treated galena.

The spectra of chalcopyrite treated with xanthate in deionized and process waters after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 without xanthate are shown in Fig. 4. Within a maximum xanthate concentration of $5 \times 10^{-5} \text{ M}$ used, the difference spectra with increasing xanthate concentration in deionized water show three prominent bands at 1201 , 1157 , and 1098 cm^{-1} , and a band at 1011 cm^{-1} appears at a higher concentration. These bands are associated with adsorbed xanthate species where the higher intensity band 1098 cm^{-1} can be assigned to C–O–C vibrations and the bands at 1201 and 1011 cm^{-1} are due to S–C–S and C–O–C stretching vibrations [28–31]. The bands characteristic of copper xanthate (1157 cm^{-1}) and dioxanthogen (1201 cm^{-1}) are observed. In process water, the S–O stretching band (1008 cm^{-1}) dominates over xanthate species bands, weak and low-intensity bands (1181 , 1144 , 1084 cm^{-1}) inferring lower adsorption of xanthate.

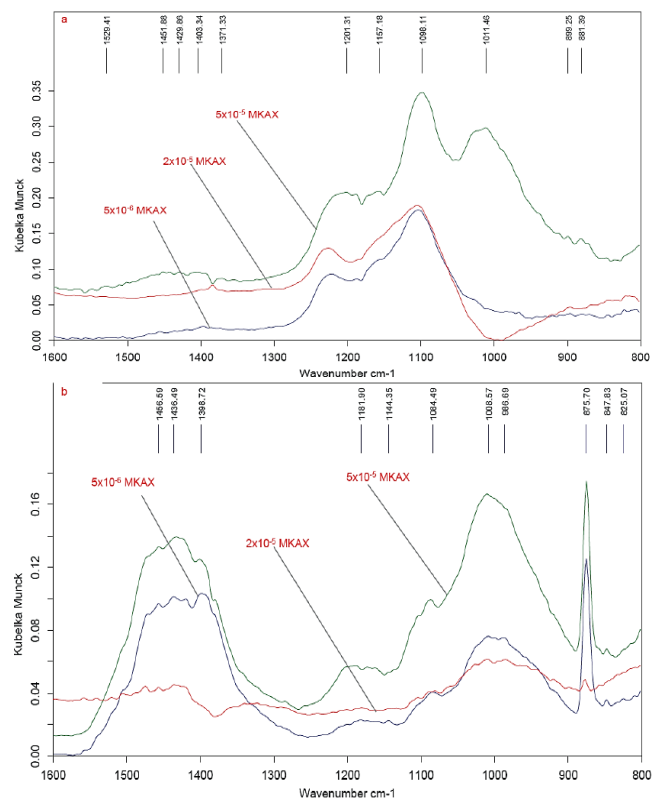


Fig. 4. Difference DRIFT spectra of chalcopyrite treated at different xanthate concentrations at pH 10.5 in deionized (a) and process (b) waters after subtracting the respective pure mineral reference spectrum.

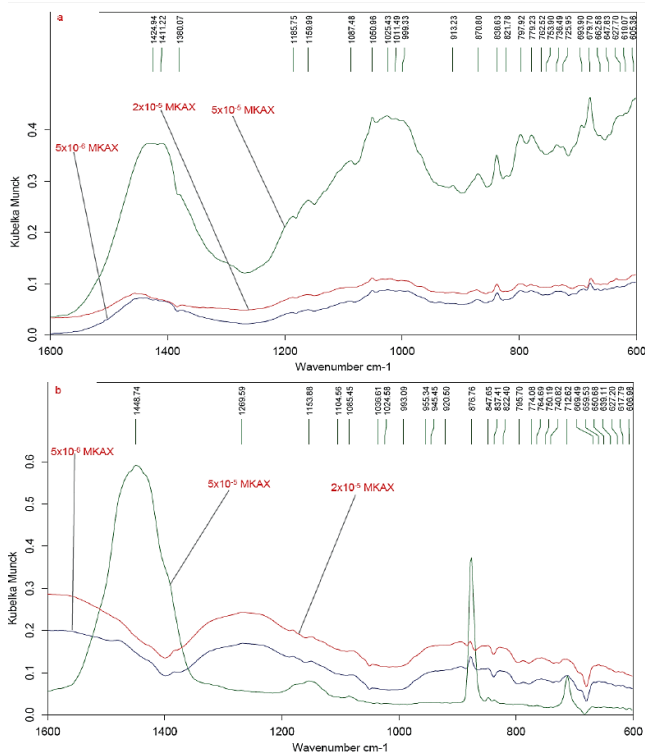


Fig. 5. Pure mineral subtracted from galena treated at different xanthate concentrations at pH 10.5 in deionized (a) and process (b) waters.

Spectra of galena after interaction with amyl xanthate at 5×10^{-6} , 2×10^{-5} , and 5×10^{-5} M concentrations in deionized (a) and process (b) waters are shown in Fig. 5. These were the difference spectra after subtracting the mineral spectrum from the xanthate treated spectra. In deionized water, the spectra exhibit the C-O-C and S-C-S symmetric stretching vibration band at 1187 cm^{-1} and the stretching vibration band of the S-C-S group at 1024 cm^{-1} [28-31]. Comparing the corresponding bands in the lead amyl xanthate (1:2) compound, these bands are shifted from 1220 cm^{-1} to a lower value of 1187 cm^{-1} and from 1022 to 1024 cm^{-1} . These bands can be assigned to a monocoordinated form of lead xanthate. Furthermore, increasing xanthate concentration to 5×10^{-5} M, the intensity of these bands is seen to increase illustrating increased amyl xanthate adsorption on galena surface. However, the lead sulphate (1160 , 1132 , 1025 cm^{-1}) and lead carbonate (1051 , 838 cm^{-1}) bands although diminished can be seen in these spectra. The surface oxidized products of galena are expected to be removed during the abstraction of xanthate. The presence of oxidation products indicates that the maximum initial xanthate concentration of 5×10^{-5} M used is not adequate to form monolayer coverage. In process water and at low xanthate concentrations of 5×10^{-6} and 2×10^{-5} M, the spectra show only the oxidized substrate bands and are devoid of xanthate bands. The absence of xanthate bands could be that xanthate is in complex formation with the metal ions in process water. However, at the 5×10^{-5} M xanthate concentration spectrum, xanthate bands can be seen. The presence of positive and negative lead sulphate and lead carbonate bands illustrates the different levels of surface oxidation compounds in the xanthate treated galena spectra compared to the mineral spectrum that was subtracted.

4. Conclusion

The recovery of both minerals in process water is generally lower than in deionized water. In addition, the recovery of galena in process water is generally lower than in deionized water. In literature reported that reason of depressing of minerals in process water; this could be due to the presence of a number of species including SO_4^{2-} , SO_3^{2-} dissolved iron

in the process water which could form hydrophilic layers or iron oxidation species on the surface of chalcopyrite, in addition to the formation of copper hydroxide and iron hydroxide; these hydrophilic species usually play a major role in the depression of chalcopyrite flotation while the strong depressing action of H_2O_2 on galena may be attributed to its strong oxidizing action on lead xanthate in galena surface giving rise to the oxidation and decomposition of lead xanthate. This study showed that Fe^{2+} ions in process water generate substantial. In the presence of dissolved molecular oxygen, ferrous ion forms superoxide (O_2^-) that reacts with ferrous ion to form H_2O_2 . The DRIFT spectra of chalcopyrite and galena pure samples showed that the surfaces are partially oxidized depicting surface sulfooxy, oxyhydroxide, and carbonate species absorbance bands. These oxidized species bands are evidenced by the bands that developed when the samples are oxidized with H_2O_2 oxidant.

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