

Correlation between the hydrogen peroxide formed during grinding and the oxidized species present on the surface of sphalerite



Liuyin Xia^{a,b,*}, Brian R. Hart^a

^a Surface Science Western, University of Western Ontario, 999 Collip Circle, London, ON N6G 0J3, Canada

^b Mining and Minerals Division, Saskatchewan Research Council, 125-15 Innovation BLVD, Saskatoon, SK S7N 2X8, Canada

ARTICLE INFO

Keywords:

Complex sulphide ore
Sphalerite
Hydrogen peroxide
Surface chemistry

ABSTRACT

Flotation separation of sphalerite from chalcopyrite is significantly affected by the oxidation of metal species on the surface of sphalerite, partially contributed by production of the reactive oxygen species hydrogen peroxide (H_2O_2) and hydroxyl radicals (OH^\cdot) if any during wet grinding of a complex sulphide ore. This research experimentally measures the production of H_2O_2 during grinding of a Cu/Zn ore from Mine Matagami (Canada) with different grinding time and in different grinding environments. Results reveal that H_2O_2 was formed spontaneously when the ore was ground in the ball mill. The amount of H_2O_2 generated increases with an increased pyrite load to the ball mill. Grinding with mild steel shows a lower measurable concentration of H_2O_2 in slurry relative to grinding with stainless steel balls. This appears to be in conflict with other researchers. It is found that Fe ions released from mild steel balls benefits the conversion from H_2O_2 to (OH^\cdot), but in the current H_2O_2 detection program hydroxyl radicals (OH^\cdot) could not be measured. Surface analysis of mineral grains from the mill discharge samples has identified an obvious correlation between H_2O_2 detected in the pulp and sphalerite surface oxidation. Lower pulp H_2O_2 concentrations possibly correspond to the conversion of H_2O_2 to OH^\cdot which may be linked to a more pronounced sphalerite surface oxidation.

1. Introduction

This is part of a collaborative research project involving 6 industrial and 3 university partners, aiming at identifying opportunities for process optimization in flotation and extractive metallurgical processes through application of advanced surface characterization technologies. Results from previous work reported by Xia et al. (2016a, 2016b, 2017) on the depression of sphalerite in a Cu/Zn separation process identified that flotation selectivity is partially dependent upon pulp potential and dissolved oxygen content. Lab testing comparing mild steel versus stainless steel grinding medium identified that poor flotation of sphalerite is linked to both a lower pulp potential and dissolved oxygen content when using the mild steel in comparison to tests with stainless steel. It was speculated that the galvanic interaction between grinding medium and minerals as well as the mineral-mineral interaction during grinding and conditioning influences the iron hydroxyl species on the surface of sphalerite thus affects its flotation behavior. This electrochemical mechanism well explained the observed sphalerite flotation disparity from tests carried out in the plant and in the metallurgical laboratory (Xia et al., 2016b).

Pulp oxygenation and the galvanic interaction between minerals

and grinding medium can considerably alter the sulphide mineral flotation selectivity (Moslemi and Gharabaghi, 2017). The correlation between the flotation performance and the surface oxidation of sulphide minerals has been identified in numerous studies (for example: Martin, 1991; Senior and Trahar, 1991; Smart, 1991; Boulton et al., 2001; Ikumapayi et al., 2012; Owusu et al., 2013, 2015; Peng et al., 2003). Optimum levels of oxygenation improve chalcopyrite recovery because the presence of oxygen facilitates the interaction between collector and chalcopyrite surface (Boulton et al., 2001; Owusu et al., 2015). In contrast, oxygenation reduces some minerals floatability by forming hydrophilic stable metallic oxide/hydroxide coatings (Owusu et al., 2013; Peng et al., 2003). Hydrogen peroxide (H_2O_2) a much stronger oxidizing agent than oxygen, has been identified in flotation pulps during wet grinding in the presence of dissolved oxygen and when the solids were placed in water immediately after dry grinding (Nooshabadi and Rao, 2013a,b,c, 2014a,b, 2016). H_2O_2 is derived from water molecules. The relative proportion of H_2O_2 generated within a pulp can be linked to the presence of various sulphide minerals in the following order pyrite > chalcopyrite > sphalerite > galena (Nooshabadi and Rao, 2014b). Therefore, the authors concluded that the higher rest potential of a sulphide mineral the greater proportion of

* Corresponding author at: Surface Science Western, University of Western Ontario, 999 Collip Circle, London, ON N6G 0J3, Canada.

E-mail address: lxia22@uwo.ca (L. Xia).

<https://doi.org/10.1016/j.mineng.2018.09.023>

Received 4 May 2018; Received in revised form 26 September 2018; Accepted 27 September 2018

Available online 02 November 2018

0892-6875/ © 2018 Published by Elsevier Ltd.

H_2O_2 was generated. Pyrite generates more H_2O_2 than other examined sulphide minerals and when two sulphide minerals were mixed, increasing the pyrite fraction promoted H_2O_2 formation (Nooshabadi and Rao, 2014b). Moreover, formation of hydroxyl radicals (OH^\cdot) in pyrite/aqueous suspensions was demonstrated by Borda et al. (2003) and Cohn et al. (2004) using scavenging reactions because hydroxyl radicals (OH^\cdot) react nearly instantaneously with most organic molecules.

The reactive oxygen species H_2O_2 or hydroxyl radical (OH^\cdot) generated during the wet grinding of complex sulphide ore are strong oxidizing agents, can easily oxidize sulphide minerals and play a significant role in mineral surface modification. Castro and Baltierra (2003) reported that the floatability of pyrite was decreased after pre-treatment with hydrogen peroxide in alkaline conditions. Jones and Woodcock (1978) showed that hydrogen peroxide reacts with xanthates to form perxanthates which do not have collector properties. Observations by Shi and Fornasiero (2010) confirmed that conditioning of chalcopyrite in the presence of hydrogen peroxide induced oxidation of its surface and the formation of iron oxide/hydroxide and iron sulphate hydrophilic species, causing flotation depression.

Given the above-mentioned review, this paper reports on research which evaluates mineral surface chemistry linked to H_2O_2 generation in terms of sphalerite depression in Cu/Zn flotation separation process. The research measured the production of H_2O_2 during wet grinding of a complex sulphide ore using different grinding medium, reaction time, addition of reagents and different grinding environments. Surface chemistry of sphalerite grains from each test was analyzed by Time of Flight secondary ion mass spectroscopy (ToF-SIMS). The correlation of the production of H_2O_2 to sphalerite surface chemistry was extensively studied.

2. Methodology

2.1. Ball mill

Grinding was performed in a horizontal, cylindrical, rubber-lined laboratory ball mill, which had probes mounted in the grinding chamber to monitor pulp chemistry changes (pH, Eh, DO, and conductivity) during grinding. The grinding pulp density was 25%.

2.2. Ore

Sample ore was obtained from the Matagami mines (UNE Compagnie Glencore). The ore was crushed to 1.7 mm, homogenized, split, sealed and frozen prior to use. 200 g of homogenized sample was ground to 80% passing 75 μm with either mild steel or stainless steel balls. For each grind test, pulp density, mass and size of grinding medium were kept consistent. After grinding, the sample of pulp was immediately purged of oxygen using argon and frozen by liquid nitrogen for future analysis.

2.3. Measurement of H_2O_2

Spectrophotometric determination of H_2O_2 by using copper (II) ions and DMP (2,9-dimethyl-1,10-phenanthroline) were performed according to the method outlined by Baga et al. (1998) and Kosaka 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 with de-ionized water to a certain volume. After mixing, the absorbance of the sample at 454 nm was measured with Shimadzu (UV-1201) UV/Vis spectrophotometer. A blank solution was prepared in the same manner but no addition of H_2O_2 . Instrument calibration was performed for each test, multiple H_2O_2 concentration measurements were performed for each test; the variation among measured values was very little, so the selected data from the multiple tests is reported in this paper.

2.4. Surface chemistry analysis

Surface chemistry analysis by ToF-SIMS was performed on sphalerite from the mill discharge. To analyze the outer-most layer of samples, an ION-TOF, TOF SIMS IV™ secondary ion mass spectrometer was used. This technique allows for the analysis of the outermost 1–3 atomic layers of a surface by mass spectrometry. Each sample was mounted on indium foil, introduced into the instrument, pumped down in the vacuum and analyzed. From six regions on each sample, a minimum of six grains of each mineralogical type were examined, therefore for each sample more than 36 grains were identified and analyzed. This analysis provides a comprehensive survey of the surface species on the mineral grains in the various samples. The intensity of selected species detected on the sphalerite surfaces as positive or negative ions are plotted in vertical box plots and illustrate relative changes in surface species abundance for the mineral grain examined in the sample. In the vertical box plots, the medium is plotted as the solid line across the box, whereas the mean is plotted as the dashed line. All TOF-SIMS data presented (counts) are normalized by the total ion intensity (counts of the recorded total mass spectrum) for the region of interest (Hart, 2006).

3. Results and discussion

3.1. Influence of pyrite content

Initially the ore obtained from mine Matagami was being wet ground in a laboratory ball mill by using stainless steel grinding medium at natural pH. Slurry samples collected at pre-determined times were immediately filtered and the filtrate was analyzed for H_2O_2 concentration. As pyrite is more cathodic than other sulphide minerals, the reactive oxygen species generated during wet grinding are primarily produced by the redox reactions operating on the pyrite. Authors firstly tested the influence of pyrite load to the ball mill on the H_2O_2 production. In order to evaluate the influence of an increasing proportion of pyrite in the feed, a model ore comprising of 10% (20 g) of pure pyrite and 90% (180 g) of the complex sulphide base ore from mine Matagami were used for comparison. Measuring the H_2O_2 generation from the model ore during wet grinding was performed in the same manner as milling base mine Matagami ore. The measured H_2O_2 concentration from the two tests were recorded and presented in Fig. 1.

The data reveals that H_2O_2 is indeed generated during the wet grinding of the complex sulphide ore. The concentration of H_2O_2 increases as the ore gets finer likely in response to an increase in particle

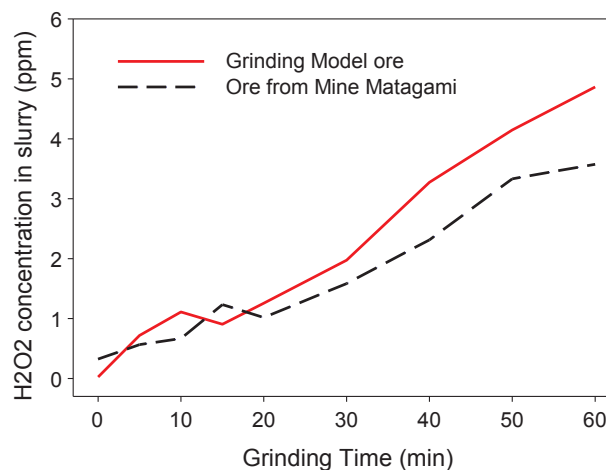


Fig. 1. Concentration of H_2O_2 formed during grinding with two ores, complex sulphide base ore from Mine Matagami and the model ore with higher content of pyrite.

surface area. In a previous study, Xia et al. (2016) reported pulp chemistry changes in pH, oxidation reduction potential and dissolved oxygen with increasing grinding time. When the ore was ground finer, the oxygen level in the slurry decreased, but the H₂O₂ content measured herein increased. This indicates the generation of H₂O₂ is dissolved oxygen independent, and it is well in agreement with other studies where it was observed that H₂O₂ is derived from water molecules (Borda et al., 2001, 2003). Nooshabadi and Rao (2013c) reported in extreme dissolved oxygen free conditions, where N₂ gas has been used to purge the mill during grinding, a greater proportion H₂O₂ was detected when compared to grinding in ambient conditions. The linked increase in the relative proportion of pyrite in the model ore and a significant increase in the proportion of H₂O₂ generated shows that pyrite plays a key role in the production of H₂O₂ from water. This finding may help explain operational experiences that, when the feed ore has a higher portion of pyrite, sulphides in the ore typically show a decrease in flotation response due to oxidation by H₂O₂ and/or the increased production of hydroxyl radicals (OH[·]) which are non selective and can result in partial depression (Owusu et al., 2014; Qin, 2015).

ToF-SIMS analysis of sphalerite grains from the mill discharge is shown in Fig. 2. Comparing the normalized intensity of FeO and FeOH on the sphalerite surface reveals that a much greater proportion of iron oxyhydroxyl species were detected in the ore with the increased pyrite content relative to the base ore. Previously results reported by Xia et al. (2017) linked the high content of pyrite in the model ore during grinding to an increase in oxygen consumption. Factors leading to the observed increase in the measured oxidative species on sphalerite were interpreted to reflect: an increase in the cathode to anode surface area ratio, a greater possibility for galvanic interaction between the mineral phases along with an increased rate of grinding medium corrosion. In light of the results presented here, the iron oxyhydroxyl species on sphalerite may also be attributed to the production of H₂O₂.

3.2. Two types of grinding medium

In a previous study Xia et al. (2016a) reported higher intensities of iron oxyhydroxyl species on sphalerite grain surfaces subsequent to grinding with mild steel balls. Given this, and data of the current test results, we believe the type of grinding medium could also affect the H₂O₂ production. Grinding tests were carried out with the complex sulphide ore from mine Matagami with mild steel or stainless steel balls at natural pH. The monitored H₂O₂ concentration with increasing grinding time in the two grinding tests is given in Fig. 3. The data reveals that there is less measurable H₂O₂ generated when grinding with mild steel balls relative to stainless steel balls. This appears to be in conflict with Nooshabadi and Rao (2013c), who reported that mild steel grinding balls produced a higher concentration of H₂O₂ relative to

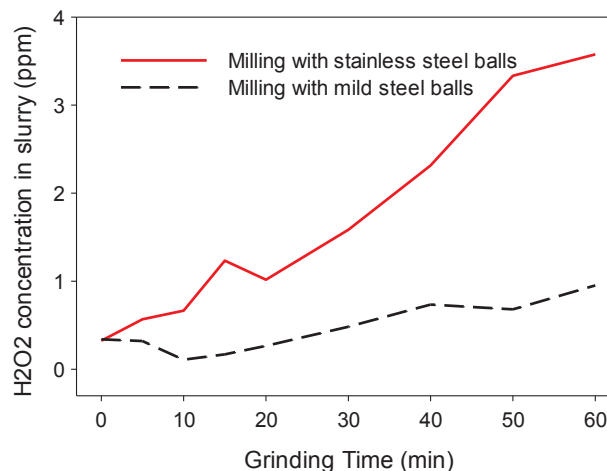


Fig. 3. Monitored H₂O₂ concentrations during wet grinding of a complex sulphide ore with two types of grinding medium.

stainless steel balls when grinding 100 g of pure pyrite in a lab size stainless steel mill. The presence of other sulphides in the tests performed with the complex sulphide ore in this work in comparison to the tests performed with pure pyrite by Nooshabadi and Rao (2013c) could potentially explain the disparity in results. Nooshabadi and Rao (2013c) pointed out that pulp potential (Eh) when using mild steel relative to stainless steel shows a greater and more rapid decrease likely due to the formation of oxidation species on mineral surfaces. In the current tests performed using a complex sulphide ore the greater proportion of other sulphides (sphalerite and chalcopyrite) likely consume majority of the generated H₂O₂ resulting in a lower overall measured H₂O₂ concentration. Implication here is that the pyrite should have generated more H₂O₂ in mild steel grinding test, in the meanwhile the consumption of H₂O₂ was super high by the rest of sulphide minerals, resulting in the detected H₂O₂ in mild steel much lower than in stainless steel.

The H₂O₂ generation and consumption plays a significant role for sulphide minerals surface oxidation. ToF-SIMS analysis of sphalerite surfaces from mill discharge samples are shown in Fig. 4. Tests with mild steel balls show a higher degree of FeO and FeOH on the sphalerite surfaces relative to tests with stainless steel balls. Most likely the reactive oxygen species hydrogen peroxide (H₂O₂) and hydroxyl radicals (OH[·]) generated (if any, not measured) during wet grinding is responsible for the oxidation of sulphide minerals.

3.3. Addition of reagents

There is a hypothesis that pyrite-generated H₂O₂ can react with

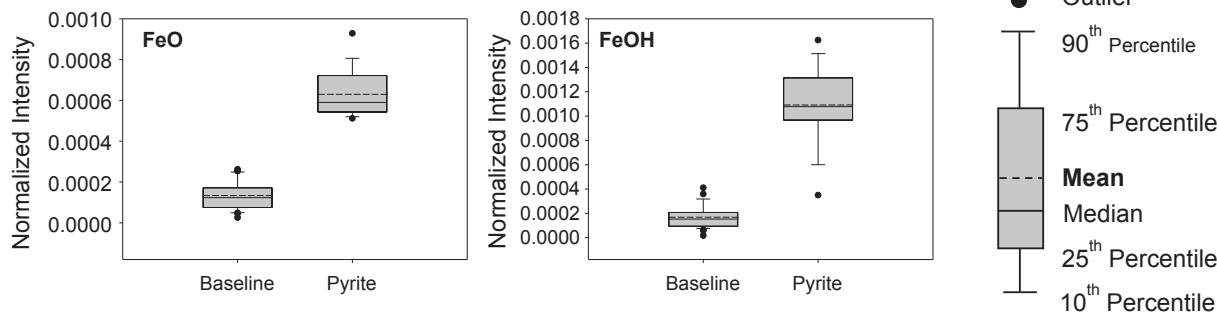


Fig. 2. Measured ToF-SIMS data for sphalerite surface chemistry analyze. Test parameters: milling with stainless steel only (baseline-no other added reagents) and with extra load of 10% pyrite (Pyrite).

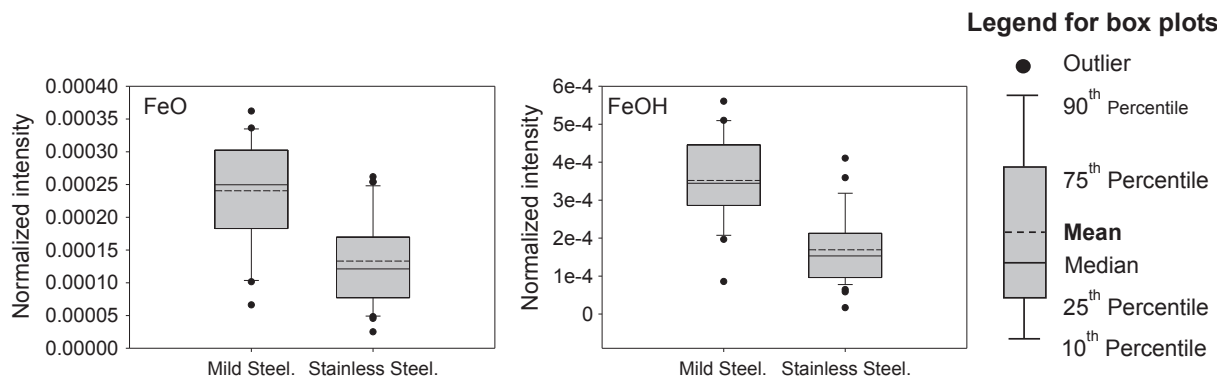
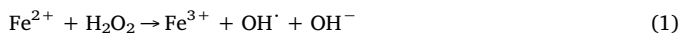


Fig. 4. Normalized intensity of iron oxide and oxyhydroxide species on the surface of sphalerite after grinding with two kinds of balls measured by TOF-SIMS.

Fe^{2+} at the pyrite surface or dissolved from pyrite to form (OH^\cdot) via the Fenton reaction as shown in Eq. (1)



This hypothesis has been confirmed with a simple test that addition of ethylenediaminetetraacetic acid (EDTA) to pyrite slurries significantly inhibited the formation of (OH^\cdot) , but not the formation of H_2O_2 (Cohn et al., 2006). Given the stability of EDTA chelating with both ferrous and ferric irons, the test suggests that EDTA prevents the hydrogen peroxide-to-hydroxyl radical conversion by chelation of dissolved iron species. Within this context, the authors believe that H_2O_2 to (OH^\cdot) conversion during ore grinding has a very high correlation to the Fe ions in the slurry. In order to evaluate the role of Fe ions in H_2O_2 formation and the hydroxyl radical conversion, a test was performed by adding 600 g/t of FeSO_4 to the ball mill prior to grinding. The monitored H_2O_2 level in the testing in the presence and absence of added Fe ions is shown in Fig. 5. The data from tests using the complex sulphide ore, ground with two types of grinding medium show that with addition of Fe ions, the detected H_2O_2 concentration in the slurry decreases.

This could be attributed to the limit of H_2O_2 detection method used by this paper, which is based on the color difference of $\text{Cu}(\text{DMP})_2$ and the final product of $\text{Cu}(\text{DMP})_2^+$ as shown in Eq. (2). With maximal absorbance at 454 nm, the differences of the absorbance between the sample and blank solutions are approximately proportional to H_2O_2 concentration. The hydroxyl radicals (OH^\cdot) may be undetectable by this method, thus we can see the decrease of measurable H_2O_2 concentration with addition of Fe ions. Interestingly, when stainless steel grinding balls were used, the decrease of H_2O_2 in response to Fe ions addition is more pronounced. The data may further indicate the link between

FeSO_4 addition and the conversion of hydrogen peroxide-to-hydroxyl radicals, because when compared to using mild steel medium, the iron content in the slurry is significantly lower when the ore is ground by stainless steel balls. In this grinding environment (nearly Fe ions free), any addition of Fe ions may have to dramatically affect the H_2O_2 to (OH^\cdot) conversion thus decreases the detectable H_2O_2 concentration. Considering that H_2O_2 may convert to (OH^\cdot) and not detected, the formation and consumption of H_2O_2 during grinding discussed above are complemented by another scenario: when the ore is ground with mild steel balls relative to stainless steel, the lower overall H_2O_2 concentration may be attributed to the conversion of H_2O_2 to (OH^\cdot) . However, concentration of hydroxyl radicals (OH^\cdot) is not measured.



ToF-SIMS analysis of sphalerite grains from grinding tests without the addition of FeSO_4 (labeled as baseline) and with the addition of FeSO_4 (labeled as FeSO_4) are shown in Fig. 6. Normalized intensity of FeO and FeOH on the sphalerite surface indicates that although the addition of FeSO_4 results in a lowering of the H_2O_2 level in the slurry, the surface of sphalerite still shows species indicative of surface oxidation. The supplying of Fe ions to the pulp prior to grinding offers a great opportunity of H_2O_2 -to- (OH^\cdot) conversion. Since hydroxyl radical (OH^\cdot) is stronger oxidizing agent than H_2O_2 , a slightly higher proportion of iron oxide and hydroxyl species were shown in ToF-SIMS data.

3.4. Aeration

Aeration of pulp in complex sulphide ores processing affects the flotation behavior of sulphide minerals as well as their selectivity (Kyhnowsky and Salman, 1970; Königsmann, 1973; Asian et al., 2003). In a previous study Xia et al. (2016a; 2017) have identified that the grade and recovery of sphalerite is dissolved oxygen consumption dependent; a greater surface oxidation of sphalerite when grinding with mild steel balls has been seen along with more rapid dissolve oxygen consumption. This appears to approve that adjusting oxygenation of the pulp can potentially affect the surface oxidation of sphalerite. In the following tests, the effects of aeration during grinding on production of H_2O_2 and the sphalerite surface chemistry were studied. The complex sulphide ore was wet ground with stainless steel balls in a closed ball mill and in an aeration tank where pressure air has been used to blow into the mill during grinding. The monitored H_2O_2 concentration with increasing grinding time in the two grinding tests is given in Fig. 7. The data reveals that there is a decrease of H_2O_2 concentration when the ore was ground in the aeration tank relative to in the closed system. This is in agreement with Nooshabadi and Rao (2013c) who reported that when the ball mill was operated in ambient conditions a decrease proportion H_2O_2 was detected in comparison to grinding in oxygen free conditions, where N_2 was adopted to purge the mill during grinding. ToF-SIMS surface chemistry analysis of sphalerite surfaces are shown in

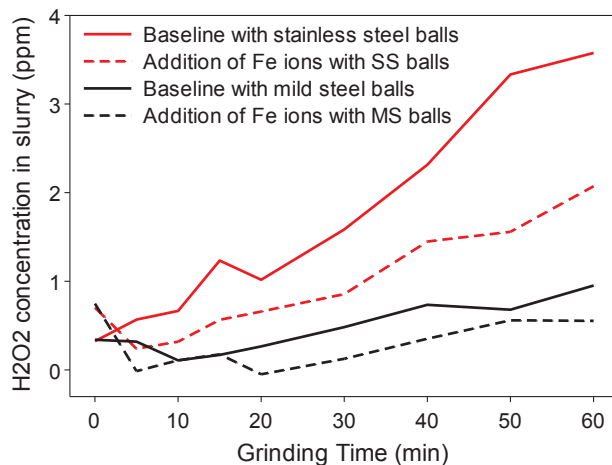


Fig. 5. Effect of Fe ions on the production of H_2O_2 during wet grinding with two types of grinding medium.

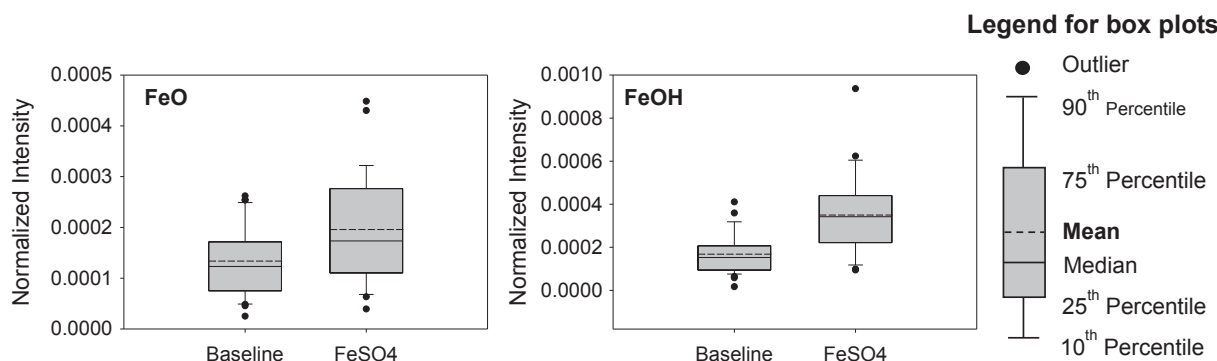


Fig. 6. Iron oxide and hydroxyl species on the surface of sphalerite after grinding with and without FeSO₄ measured by TOF-SIMS. Test parameters: milling with stainless steel only (baseline-no other added reagents), milling with addition of 600 g/t FeSO₄ (FeSO₄).

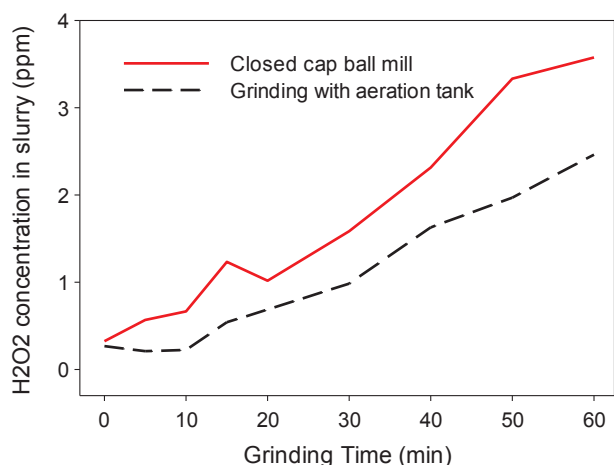


Fig. 7. Formation of H₂O₂ by grinding a complex sulphide ore in the closed ball mill and an aeration tank.

Fig. 8. Grinding with aeration shows sphalerite grains attach more iron oxide/hydroxyl/oxyhydroxyl species relative to tests with closed system. This could be explained by the undetectable hydroxyl radical (OH[·]) generation from H₂O₂ which leads to a much stronger surface oxidation or by the continuous air supply to the tank which offers more oxidizing environment during grinding. The exact electrochemical mechanism of grinding with an aeration tank need more search to be resolved. On the basis of the experiments reported in this study, the formation of H₂O₂ and its conversion to hydroxyl radical (OH[·]) (if any, but not measured) could be considered as part of the reason to surface oxidation of sphalerite.

4. Conclusions

Formation of H₂O₂ during wet grinding of a complex sulphide ore with different grinding time and in different grinding environments is measured. Surface chemistry of sphalerite grains from each test was analyzed by time of flight secondary ion mass spectroscopy (ToF-SIMS). The following conclusions can be derived based on the results presented in this paper:

- The reactive oxygen species H₂O₂ and OH[·] (if any, not measured) are formed spontaneously when the complex sulphide ore was wet ground in the ball mill. The measurable H₂O₂ concentration increases with increase in pyrite content of feed such as the model ore, indicating among all sulphide minerals pyrite dominantly generate the reactive oxygen species.
- Mild steel grinding medium produces lower overall concentration of H₂O₂ than stainless steel balls. We found that there are two scenarios related to such data. First, H₂O₂ likely oxidize other sulphide minerals such as sphalerite and chalcopyrite and thus are rapidly consumed when grinding with mild steel balls. Secondly the disparity of using two grinding medium potentially is related to the emergence of Fe ions in slurry when grinding with mild steel balls, because the speculative conversion of H₂O₂ to (OH[·]) is Fe ions dependent. The employed H₂O₂ detection method has its limit for hydroxyl radicals (OH[·]) thus the conversion is undetectable.
- Other grinding environments like addition of FeSO₄ and grinding in aeration tank are tested. Both show a lower level of H₂O₂ in the slurry and a greater oxidation on sphalerite surfaces relative to the baseline test. The exact electrochemical mechanism of grinding with FeSO₄ and with aeration need more search to be resolved. On the basis of the experiments reported here, the data potentially indicate a link between the lower measurable H₂O₂ concentrations in slurry and a more pronounced sphalerite surface oxidation.

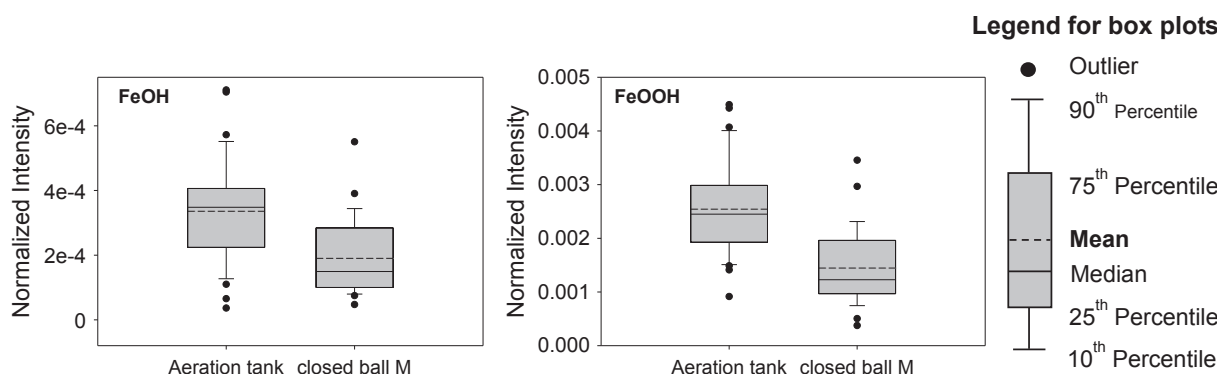


Fig. 8. Oxidation species on surface of sphalerite after grinding proceeded in the closed ball mill and an aeration tank.

Acknowledgement

Financial support from Natural Sciences and Engineering Research Council of Canada (NSERC CRD CRDPJ 439916-12) and UNE Compagnie Glencore Mine Matagami is gratefully acknowledged.

References

- Asian, A., Ekmekci, Z., Bayraktar, I., Aksani, B., 2003. The effect of reagent addition points and aeration on the flotation performance of sulphide minerals. In: 18th International Mining Congress and Exhibition of Turkey, conference proceeding.
- Baga, A.N., Johnson, G., Nazhat, N., Saadalla-Nazhat, R., 1988. A simple spectrophotometric determination of hydrogen peroxide at low concentrations in aqueous solution. *Anal. Chim. Acta* 204, 349–353.
- Borda, M.J., Elsetinow, A.R., Strongin, D.R., Schoonen, M.A., 2003. A mechanism for the production of hydroxyl radical at surface defect sites on pyrite. *Geochim. Cosmochim. Acta* 67 (5), 935–9939.
- Borda, M., Elsetinow, A., Schoonen, M., Strongin, D., 2001. Pyrite induced hydrogen peroxide formation as a driving force in the evolution of photosynthetic organisms on an early Earth. *Astrobiology* 1 (3), 283–288.
- Boulton, A., Fornasiero, D., Ralston, J., 2001. A comparison of methods to selectively depress iron sulphide flotation. In: Proceedings of the 4th UBC McGill International Symposium of Fundamentals of Mineral Processing -Interactions in Minerals Processing. Canadian Institute of Mining, Metallurgy and Petroleum Montreal, pp. 141–152.
- Castro, S.H., Baltierra, L., 2003. Redox condition in the selective flotation of enargite. In: Proceedings of Electrochemistry in Mineral and Metal Processing VI, pp. 27–36.
- Cohn, C.A., Borda, M.J., Schoonen, M.A., 2004. RNA decomposition by pyrite-induced radicals and possible role of lipids during the emergence of life. *Earth Planet. Sci. Lett.* 225 (3–4), 271–278.
- Cohn, C.A., Mueller, S., Wimmer, E., Leifer, N., Greenbaum, S., Strongin, D.R., Schoonen, M.A.A., 2006. Pyrite-induced hydroxyl radical formation and its effect on nucleic acids. *Geochem. Trans.* 7 (3), 1–11.
- Hart, B., Biesinger, M., Smart, R., 2006. Improved statistical methods applied to surface chemistry in minerals flotation. *Miner. Eng.* 19 (6–8), 780–798.
- Ikumapayi, F., Sis, H., Johansson, B., Hanumantha, R.K., 2012. Recycling process water in sulphide flotation, part B: effect of H₂O₂ and process water components on sphalerite flotation from complex sulphide. *J. Miner. Metall. Process.* 29 (4), 192–198.
- Jones, M.H., Woodcock, J.T., 1978. Perxanthates – A new factor in the theory and practice of flotation. *Int. J. Miner. Process* 5, 285–296.
- Konigsmann, K.V., 1973. Aeration in plant practice. In: 5th Annual Meeting of CMP, pp. 300–315.
- Kosaka, K., Yamada, H., Matsui, S., Echigo, S., Shishida, K., 1998. A Comparison among the methods for hydrogen peroxide measurements to evaluate advanced oxidation processes: application of a spectrophotometric method using copper(II) ion and 2,9-dimethyl-1,10-phenanthroline. *Environ. Sci. Technol.* 32, 3821–3824.
- Kyhnowsky, I.B., Salman, T., 1970. The role of oxygen in xanthate flotation of galena, pyrite and chalcopyrite. *J. CIM (Can. Mining Met.) Bull* 63 (698), 683–688.
- Martin, C.J., 1991. Review of the effect of grinding medium on flotation of sulphide minerals. *Miner. Eng.* 4 (2), 121–132.
- Moslemi, H., Gharabaghi, M., 2017. A review on electrochemical behavior of pyrite in the froth flotation process. *J. Ind. Eng. Chem.* 47, 1–18.
- Nooshabadi, A.J., Rao, K.H., 2013a. Formation of hydrogen peroxide by chalcopyrite and its influence on flotation. *Miner. Metall. Process.* 30 (4), 212–219.
- Nooshabadi, A.J., Rao, K.H., 2013b. Formation of hydrogen peroxide by sphalerite. *Int. J. Miner. Process.* 125, 78–85.
- Nooshabadi, A.J., Rao, K.H., 2013c. Formation of hydrogen peroxide by pyrite and its influence on flotation. *J. Miner. Eng.* 49, 128–134.
- Nooshabadi, A.J., Rao, K.H., 2014a. Formation of hydrogen peroxide by galena and its influence on flotation. *Adv. Powder Technol.* 25 (3), 832–839.
- Nooshabadi, A.J., Rao, K.H., 2014b. Formation of hydrogen peroxide by sulphide minerals. *Hydrometallurgy* 141, 82–88.
- Nooshabadi, A.J., Rao, K.H., 2016. Complex sulphide ore flotation: effect of depressants addition during grinding on H₂O₂ formation and its influence on flotation. *Int. J. Miner. Process.* 157, 89–97.
- Owusu, C., Aberu, S.B., Skinner, W., Addai-Mensah, J., Zanin, M., 2014. The influence of pyrite content on the flotation of chalcopyrite/pyrite mixtures. *Miner. Eng.* 55, 87–95.
- Owusu, C., Addai-Mensah, J., Fornasiero, D., Zanin, M., 2013. Estimating the electrochemical reactivity of pyrite ores-their impact on pulp chemistry and chalcopyrite flotation behaviour. *Adv. Powder Technol.* 24 (4), 801–809.
- Owusu, C., Fornasiero, D., Addai-Mensah, J., Zanin, M., 2015. Influence of pulp aeration on the flotation of chalcopyrite with xanthate in chalcopyrite/pyrite mixtures. *Int. J. Miner. Process.* 134, 50–57.
- Peng, Y., Grano, S., Fornasiero, D., Ralston, J., 2003. Control of grinding conditions in the flotation of galena and its separation from pyrite. *Int. J. Miner. Process.* 70 (1–4), 67–82.
- Qin, W., Wang, X., Ma, L., Jiao, F., Liu, R., Yang, C., Gao, K., 2015. Electrochemical characteristics and collectorless flotation behavior of galena: With and without the presence of pyrite. *Miner. Eng.* 74, 99–104.
- Senior, G.D., Trahar, W.J., 1991. The influence of metal hydroxides and collector on the flotation of chalcopyrite. *Int. J. Miner. Process.* 33 (1–4), 321–341.
- Shi, Y., Fornasiero, D., 2010. Flotation of oxidised chalcopyrite. In: Chemeca 2010: engineering at the edge, Hilton Adelaide, South Australia, pp. 541–550.
- Smart, R.S.C., 1991. Surface layers in base metal sulphide flotation. *Miner. Eng.* 4 (7–11), 891–909.
- Xia, L., Chen, Z., Hart, B., Nigim, J., 2016a. Effect of variability in grinding medium and its ball size on pulp chemistry. In: 28th International Mineral Processing Congress proceeding, Quebec Canada.
- Xia, L., Hart, B., Chen, Z., Furlotte, M., Gingras, G., Laflamme, P., 2017. A ToF-SIMS investigation on correlation between grinding environments and sphalerite surface chemistry: implications for mineral selectivity in flotation. *Surf. Interf. Anal.* 49 (13), 1397–1403.
- Xia, L., Hart, B., Furlotte, M., Gingras, G., Olsen, C., 2016b. Mechanism of sphalerite depression in an open Cu/Zn flotation separation circuit. In: 28th International Mineral Processing Congress proceeding, Quebec Canada.