

Effect of Microwave Radiation on the Floatation of Copper Sulfide Ores

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The objective of this study is to evaluate the floatation behaviour of microwave pre-treated 2 sulfide copper ores containing different mineralogy. Each ore was subjected to microwave radiation for varying time periods before grinding and subsequent floatation testing. The changes in floatation recoveries and grades with the microwave exposure time were quantified by batch type laboratory tests. The results of the floatation tests indicated essentially the same recoveries at low temperatures for both the microwave treated copper ores compared to untreated samples. On the other hand, the results showed that high microwave radiation temperatures were detrimental to floatation recovery for both the copper ores due possibly to microwave energy induced oxidation of minerals at relatively high temperatures. The existence of significant oxidized areas on high-grade chalcopyrite particles were shown when heated with microwaves. Differing ore mineralogy has been shown to affect the floatability of the ores treated with microwaves.

Key Words: Microwave irradiation, Floatation, Copper ore.

INTRODUCTION

The application of microwave radiation to minerals is relatively new and previously it was mainly limited with the measurements of heating characteristics of minerals¹⁻³. Over the past three decades, significant amounts of research work has been undertaken to investigate the applications of microwave radiation in mineral processing and extractive metallurgy and the results of many studies have been published immensely. Much of the work performed in the field of microwave assisted comminution has been carried out by the former U.S. Bureau of Mines⁴⁻⁶ and by the University of Utah's Comminution Center⁷⁻⁹. More recently, the Universities¹⁰⁻¹⁷ of Birmingham and Nottingham and other researchers^{18,19} have also published in this area. The findings have shown significant improvements in comminution for certain minerals after microwave pretreatment.

Encouraging results from a variety of pioneering applications of microwave radiation were also reported in the literature implying that microwave heating of many different minerals resulted in improved mineral liberation²⁰⁻²², partial desulfurization^{23,24}, enhanced magnetic susceptibility²⁵⁻²⁸, leaching²⁹⁻³² and beneficiation^{31,33-35}. For all the applications of microwave radiation, there are several

mechanisms identified from the literature^{4,13,20,30}. First, unequal thermal expansion of microwave energy absorbing minerals in a non-heating gangue matrix may cause micro-fractures at the mineral grain boundaries by overcoming the tensile strength of the ore. In general, most metal sulfides and oxides heat readily when subjected to a microwave field. On the other hand, common gangue minerals containing silicates and carbonates are nearly transparent to microwaves and heat slightly. Second, internal pressure created from super-heated water vapour and gases (for example, SO₂ forming from the reactions of metal sulfides converting to metal oxides) may also cause fissures in the host rock. A third mechanism may involve structural changes, chemical alterations or reactions of minerals contained in the ore with the intense heat generated by the absorption of microwave energy.

Most recently, microwave pretreatment to increase the floatability of sulfide and oxide minerals has received considerable attention from a number of researchers. The published reports on a variety of geological materials, indicated that although microwave radiation pretreatment was effective in modifying surface properties of minerals, successful application of microwave treatment is not always ensured. Floatation results in the literature from the application of microwave heating vary. Fan *et al.*³⁶ greatly improved the floatability of a massive ilmenite ore after microwave induced thermal pretreatment. Ozbayoglu *et al.*³⁷ reported that the floatation tests of microwave treated coal by using heptanol and octanol lead to a higher yield and ash removal than original coal. Sahyoun *et al.*³⁸ have showed significantly improved floatation recoveries with a copper carbonatite ore exposed to a short microwave durations of time, but, the authors reported that the recovery was sensitive to applied power level and duration of microwave exposure. Vorster *et al.*³⁹ investigated the effect of microwave radiation upon the processing of two Neves Corvo massive sulfide copper ores. The authors showed no change in the floatation performance of this copper ore after microwave pretreatment of 90 s, although up to 70 % reductions in work index were attained.

Kingman *et al.*⁴⁰ however, reported significant reductions in the floatation recovery of a Palabora copper ore exposed to a prolonged microwave exposure, even after 10 s. Similarly, Can and Bayraktar²⁸ showed that the floatability of pyrite, chalcopyrite and galena were decreased when microwave energy and the duration of treatment were increased, owing to oxidation of the mineral surfaces caused by relatively high temperature. The floatability of sphalerite was unchanged. Orumwense and Negeri⁴¹ investigated the impact of microwave irradiation on the processing of a complex sulfide ore containing pyrite, sphalerite, galena and chalcopyrite. They found that copper recovery decreased sharply at long irradiation times. Liberation values decreased in the following order: sphalerite, galena and chalcopyrite.

Although researchers have attained much knowledge and experience on the application of microwave radiation, current status of this research work is still

fundamental. In general, these studies have been exploratory in nature and have been mostly performed on a laboratory scale. Further research is needed to advance the application of the microwave energy in the mineral industry.

This research work is aimed to investigate the floatation behaviour of microwave pretreated two copper sulfide ores containing different mineralogy. Floatation results of microwave-treated samples were compared with untreated samples.

EXPERIMENTAL

Ore characterization: Two different complex copper sulfide ores with differing mineralogies were selected in present study. The ore samples, collected from two copper concentrator plant feeds, were crushed to below 25.4 mm (1 inch) in a jaw crusher and screened into size fractions. Minus 3.4 mm (6 U.S. mesh) material was discarded in this investigation. Plus 3.4 mm samples were divided into 1 kg samples and bagged. The characterization work, completed on plus 3.4 mm fractions only, included optical microscopy analysis of polished sections, quantitative X-ray diffraction analysis and chemical analysis.

The first copper ore is a medium hard monzonite porphyry copper ore. Its main gangue minerals are quartz (45.7 %), K-feldspar (18.9 %), plagioclase (1.4 %), muscovite (11.5 %), pyrite (2.9 %), kaolinite (4.4 %) and iron oxides (2.3 %). Copper bearing phases are predominantly mixed sulfide minerals. They are relatively coarse grained and associated with iron sulfides and copper-iron sulfides. Copper occurs as chalcopyrite, covellite, chalcocite and digenite. The ore contains 0.62 % total copper and 0.045 % copper oxide with 0.011 % of molybdenite and 0.04 g/t of gold. The ore's Bond work index is measured as 11.4 kWh/t.

The second copper ore is a medium hard andesite-hosted mineralization with veins, tabular or lens like breccia bodies. Its gangue mineralogy is dominated by magnetite (18 %), K-feldspar (33 %), quartz (11 %), biotite (8 %), plagioclase (5.1 %), kaolinite (1.6 %). Sulfide gangue consists of varying proportions of pyrite (7 %), pyrrhotite and trace sphalerite. Copper mineralogy is dominated by chalcopyrite with little secondary speciation. Chalcopyrite textures are present in fine and coarse disseminations mostly in veins. The ore contains 1.39 % total copper, 0.014 % copper oxide and 0.21 g/t gold. The ore's Bond work index is measured as 16.7 kWh/t.

Microwave treatment: A batch type microwave oven (Microdry, Inc., Crestwood, KY, USA) with a variable power output range of 1-6 kW, a volume of 1.3 m³ applicator and a frequency of 2.45 GHz was used. The 1 kg sample batches with plus 3.4 mm size were irradiated in the microwave oven at a power of 6 kW for varying durations of time. Samples were placed on a 0.09 m² ceramic surface and positioned in the centre of the oven.

Average bulk surface temperatures of the ore particles were measured using a Model Raytec Ranger 3I infrared thermometer after switching off the microwave

power. It is desirable to heat the sulfide minerals present in the ore quickly and to a high temperature. Since it is not feasible to measure the temperature of each sulfide mineral grain, a bulk surface temperature of the ore is recorded as an indication of the extent of sulfide mineral grain heating. Temperature readings within a given sample varied from particle to particle and decreased rapidly with time, therefore, the average surface bulk temperatures of each sample were recorded for the duration of *ca.* 2 s. It is assumed that the bulk surface temperature is a measure of the coupling between the microwave energy and the sulfide minerals. Therefore, this is an indication of the effect on milling properties. In simpler words, heating the samples to a higher temperature may increase the effect of microwave irradiation.

Floatation procedure: To investigate the advantages of microwave pretreatment on floatation, each ore with plus 3.4 mm size was subjected to microwave irradiation for varying time periods. All microwaved and untreated reference samples were crushed further and ground to minus 208 μm (65 mesh) in a rod mill for floatation testing. Floatation tests with microwaved and untreated copper samples were carried out in a 2 L Denver D-12 batch cell under the conditions listed in Table-1. The collector was AP 6594, a modified thiocarbamate collector, received from Cytec Industries, Inc. (CT, USA). Tap water was used with all the floatation tests. The tests were replicated and the results are presented as the mean of two readings. Concentrates and tails were analyzed for total and copper oxide content. Total copper (% Cu) and copper oxide (% CuO) values were determined by a standard acid dissolution procedure and the atomic absorption spectroscopy.

TABLE-1
FLOATATION TEST CONDITIONS USED FOR COPPER ORES 1 AND 2

Conditions	Ore 1	Ore 2
Conditioning time (min)	2	2
Floatation time (min)	9	10
pH adjusted with lime	10.5	10.5
Cytec AP 6594 collector (g/t)	16	13
Cytec F-533 frother (g/t)	28	22
% Solids	30	35
Sample weight (g)	1000	1000
Denver cell impeller speed (rpm)	1200	1200

RESULTS AND DISCUSSION

The results of the floatation tests with the microwaved and untreated copper ore samples are summarized in Table-2, along with the irradiation times and temperatures. Ore 2 exhibited better microwave absorbing characteristics probably due to its more magnetite and pyrite content. The average surface temperature of ore 1 was measured 588 °C after 10 min of microwave irradiation, whereas with ore 2, it took 3 min to reach to an average surface temperature of 608 °C.

TABLE-2
FLOATATION TESTS RESULTS OF MICROWAVED AND
UNTREATED COPPER ORES 1 AND 2

Ores	Irradiation time (s)	Ave. surface temp. (°C)	Flot. feed grade (% Ox.Cu)	Conc. grade (% Cu)	Copper recovery (%)
Ore Type 1					
Untreated	–	Ambient*	0.045	11.3	85.2
Micowaved 1	12	58	0.045	10.9	85.1
Micowaved 2	30	87	0.045	10.6	86.2
Micowaved 3	180	321	0.051	11.6	81.4
Micowaved 4	360	420	0.049	10.7	81.5
Micowaved 5	600	588	0.052	9.8	70.3
Ore Type 2					
Untreated	–	Ambient*	0.014	14.4	90.2
Micowaved 1	30	163	0.016	14.6	89.8
Micowaved 2	120	356	0.018	16.3	90.4
Micowaved 3	180	608	0.043	18.2	85.7

*Ambient temperature: 25 °C.

As seen in Table-2, there is no indication of improved floatability for both the microwaved copper ore samples. The floatation test results with ore 1 samples indicated essentially the same recoveries up to the temperature of 87 °C and about 4 % decrease at 420 °C, but, a substantial decrease, about 15 %, when the samples were further heated up to 588 °C.

Floatation recoveries with the microwave treated ore 2 samples, on the other hand, are comparable to non-microwaved reference samples up to a higher temperature of 356 °C compared to ore 1 samples. Floatation recovery with the ore 2 decreased about 5 % when the sample heated to the temperature of 608 °C. It appears that the decrease in floatation recoveries may be caused by the oxidation of the copper minerals at elevated temperatures, as indicated by the higher copper oxide (% CuO) content present in the floatation feed for both the ore samples, reported in Table-2, column 4. The percentage of copper oxide (% CuO) values increased from 0.045 to 0.052 for ore 1 and from 0.014 to 0.043 for ore 2 at elevated temperatures at which the highest recovery losses were reported. The recovery loss at elevated temperatures was higher for ore 1 than for ore 2.

For ore 1 sample, the floatation concentrate copper grade decreased by 13 % at the temperature of 588 °C, but, for ore 2, it increased by 26 % at the temperature of 608 °C. This may be an indication of better liberation resulting from intergranular fracture during microwave irradiation of ore 2 than of ore 1.

To investigate the chemical alteration or oxidation of minerals that are possibly responsible for poor floatation results at higher irradiation temperatures, high-grade chalcopyrite specimens were obtained from Ward's Natural Science Establishment, Inc. (Rochester, NY, USA). The specimens consisted of fresh sulfide material with some traces of siliceous minerals, pyrite, sphalerite and iron oxides. Only minor

amounts (5-10 %) of natural surface oxidation were detected. The samples were irradiated at 1 kW power in the microwave oven for 30 s. An average bulk surface temperature of 240 °C for the samples was measured.

Several unique areas were defined on the irradiated chalcopyrite samples presented in Fig. 1. Substantial discolouration of the samples was observed, especially in certain areas that reached temperatures more than 1000 °C. First, dark blue to gray regions were observed on the surface. These were areas of heavy oxidation that penetrated 15 to 20 μ into the chalcopyrite matrix. In excessive heating areas, the surface exhibited fusion, as shown in Fig. 2. Surrounding this fused region is a brown material, it is thought to be a transition area of oxidized chalcopyrite. An earthy light brown area was also detected on the samples and resembled a heavily oxidized portion of gangue material mixed with iron oxides. Table-3 provides a semi-quantitative scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis of the various regions. It is evident from Table-3 that the dark blue and brown regions do indicate significant oxidation of the chalcopyrite. No formation of new copper sulfide minerals was detected.

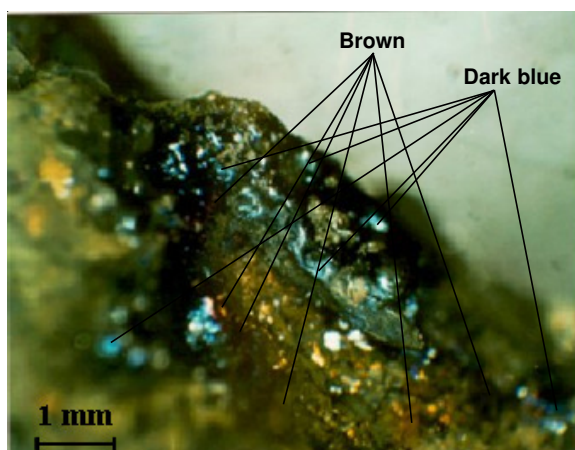


Fig. 1. Irradiated chalcopyrite mineral showing heavily oxidized dark blue and brown areas

TABLE-3
SEM-EDX ANALYSIS* OF REGIONS OBSERVED ON UNTREATED AND
MICROWAVED CHALCOPYRITE SAMPLES

Material	Cu (%)	Fe (%)	S (%)
Untreated samples	40	32	28
Microwaved samples			
Fused Area	38	40	20
Dark Blue	45	35	18
Brown	44	36	19
Light Brown	21	64	13

*Values are normalized to 100 % but may not add up to 100 % because of impurities.

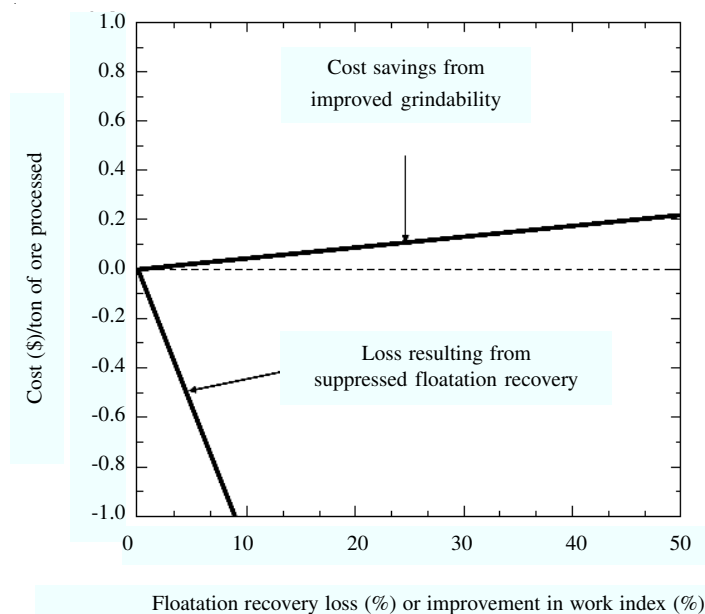


Fig. 2. Sensitivity of costs arising from a decreases in wok index (Wi) and floatation recovery

Although, the advantages in grinding may be realized as a decrease in grinding energy required or a subsequent increase in throughput, it was shown that any gains in comminution step can easily be lost with a deleterious change in downstream floatation recovery.

Using the assumptions of an ore feed grade of 0.7 % Cu, ore work index (Wi) of 11 kWh/t, floatation recover of 85 % and energy cost of \$ 0.04/kWh, the economic benefits of increasing grindability through microwave irradiation can be estimated. From the reported decreases in work index values in the literature for certain ores, an increase of 40 % in ore grindability would result in an ore work index of 6.6 kWh/ton. At the present cost of electrical energy, this pre-weakening of the ore would represent a cost savings of \$ 0.18 per ton of ore processed.

Similarly, any detrimental effects to concentrator production arising from floatation recovery loss due to microwaving can also be determined. Given the feed grade and recovery, *ca.* 5.95 kg of copper is extracted from each ton of ore processed. A decrease in recovery of 5 %, as obtained in this study, would result in only 5.60 kg of copper extracted. At a copper price of \$ 1.76 per kg (\$ 0.80/lb) a loss of \$ 0.6 per ton of ore processed would be realized.

It is clear from this example that the loss from a decrease in floatation recovery (5 % in this example) far outweighs any gain realized from an increase in grindability (40 % in this example), as seen in Fig. 2. It should be noted, however, that this example has been oversimplified by neglecting the cost savings of reduced liner

and grinding media wear. In addition, any advantage in work index reduction would most likely be realized by increased mill throughput.

Conclusion

The results have shown that differing ore mineralogy has been shown to affect the heating characteristics and the floatability of the ores treated with microwaves. The heating rate of porphyry copper ore (ore 1) was slower than that of vein type copper ore (ore 2). The batch floatation tests indicated no improvements with microwave pretreatment at low temperatures for both the microwave treated copper ores compared to untreated samples. High microwave irradiation temperatures, however, were detrimental to floatation recovery for both the copper ores due to oxidation of minerals at the surface. The recovery loss at elevated temperatures was 15 % for ore 1, but, 5 % for ore 2. The existence of significant oxidized areas on high grade chalcopyrite mineral surfaces has been shown with a semi-quantitative scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis of various regions exposed to microwave irradiation. No evidence of the formation of new copper minerals was observed. Microwave irradiation did not cause any significant mineral phase change. A simplified economic analysis was performed showing that the loss from a small decrease in floatation recovery due to microwaving far outweighs any gain realized from an increase in grindability.

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REFERENCES

1. J.D. Ford and D.C.T. Pei, *J. Microwave Power*, **2**, 61 (1967).
2. T.T. Chen, J.E. Dutrizac, K.E. Haque, W. Wyslouzil and S. Kashyap, *Can. Metall. Quart.*, **23**, 349 (1984).
3. J.W. Walkiewicz, G. Kazonich and S.L. McGill, *Miner. Metall. Proc.*, **39**, 39 (1988).
4. S.L. McGill and J.W. Walkiewicz, *J. Microwave Power, Symp. Summ.*, **22**, 175 (1987).
5. J.W. Walkiewicz, S. McGill and L. Moyer, in eds.: W.H. Sutton, M.H. Brooks and I.J. Chabinsky, *Microwave Processing of Materials*, Materials Research Society Symposium Proceedings, Materials Research Society, Vol. 124, p. 297 (1988).
6. J.W. Walkiewicz, A.E. Clark and S.L. McGill, *IEEE T Ind. Appl.*, **27**, 239 (1991).
7. L.M. Tavares and R.P. King, Application of Thermal Treatment to Improve Comminution, Presented at SME Annual Meeting, Denver, Colorado, USA (1995).
8. L.M. Tavares and R.P. King, In Proceedings of XIX International Mineral Processing Congress, San Francisco, CA, Vol. 1, pp. 203-208 (1995).
9. L.M. Tavares and R.P. King, Effect of Microwave-Induced Damage on Single Particle Comminution of Ores, presented at the SME Annual Meeting, Phoenix, Arizona, USA (1996).
10. P.C. Harrison and N.A. Rowson, Icheme Research Event-1st European Conference, p. 623 (1995).
11. P.C. Harrison and N.A. Rowson, Icheme Research Event-2nd European Conference, p. 271 (1996).
12. P.C. Harrison and N.A. Rowson, Icheme, Jubilee Research Event, p. 21 (1997).

13. S.W. Kingman and N.A. Rowson, *Miner. Eng.*, **11**, 1081 (1998).
14. S.W. Kingman, W. Vorster and N.A. Rowson, *Miner. Eng.*, **13**, 313 (2000).
15. S.W. Kingman, K. Jackson, A. Cumbane, S.M. Bradshaw, N.A. Rowson and R. Greenwood, *Int. J. Miner. Process.*, **74**, 71 (2004).
16. C. Sahyoun, S.W. Kingman and N.A. Rowson, *Eur. J. Miner. Process. Environ. Protect.*, **4**, 175 (2004).
17. S.W. Kingman, *Int. Mater. Rev.*, **51**, 1 (2006).
18. R. Okamoto, I. Hirano and H. Sugahara, In Proceedings of IV Congress International Association of Engineering Geology, New Delhi, India, Vol. 4, pp. 43-52 (1982).
19. A. Gungor and U. Atalay, Grindability of Microwave-Heated Ores, Presented at SME Annual Meeting, Denver, Colorado, USA, March (1999).
20. K.E. Fitzgibbon and T.J. Veasey, *Miner. Eng.*, **3**, 181 (1990).
21. G. Scott, S.M. Bradshaw and J.J. Eksteen, *Int. J. Miner. Process.*, **85**, 121 (2008).
22. Y. Wang, E. Forssberg and M. Svenson, Mineral Processing on the Verge of 21st Century, ed. Ozbayoglu, Balkema, Rotterdam, 3 (2000).
23. N.A. Rowson and N.M. Rice, *Miner. Eng.*, **3**, 363 (1990).
24. S. Marland, B. Han, N.A. Rowson and A.J. Merchant, *Acta Montanistica Slovaca Rocknik*, **3**, 351 (1998).
25. S.W. Kingman, G.M. Corfield and N.A. Rowson, *Magn. Elect. Sep.*, **9**, 131 (1999).
26. C. Sahyoun, S.W. Kingman and N.A. Rowson, *Phys. Sep. Sci. Eng.*, **12**, 23 (2003).
27. T. Uslu, U. Atalay and A.I. Arol, *Colloid Surface A: Physicochem. Eng. Aspects*, **225**, 161 (2003).
28. N.M. Can and I. Bayraktar, *Miner. Metall. Proc.*, **23**, 185 (2007).
29. P.R. Kruesi and V.H. Jr. Frahm, US Patent 4324582 (1982).
30. K.E. Haque, *Int. J. Min. Process.*, **57**, 1 (1999).
31. M. Al-Harahsheh and S.W. Kingman, *Hydrometallurgy*, **73**, 189 (2004).
32. P.A. Olubambi, J.H. Potgieter, J.Y. Hwang and S. Ndlovu, *Hydrometallurgy*, **89**, 127 (2007).
33. S.A. Shuey, *Eng. Min. J.*, 22 (2002).
34. D.H. Bradhurst and H.K. Worner, *Sprechsaal*, **123**, 194 (1990).
35. D.K. Xia and C.A. Pickles, *CIM Bull.*, **90**, 96 (1997).
36. X. Fan, R.M. Kelly and N.A. Rowson, *Can. Metall. Quart.*, **39**, 247 (2000).
37. G. Ozbayoglu, T. Depci and N. Ataman, *Energ. Source, Part A*, **31**, 492 (2009).
38. C. Sahyoun, N.A. Rowson, S.W. Kingman, L. Groves and S.M. Bradshaw, *J. South Afr. Inst. Min. Metall.*, 7 (Jan 2005).
39. W. Vorster, N.A. Rowson and S.W. Kingman, *Int. J. Min. Proc.*, **63**, 29 (2001).
40. S.W. Kingman, W. Vorster and N.A. Rowson, *J. South Afr. Inst. Min. Metall.*, **100**, 197 (2000).
41. A.O. Orumwense and T. Negeri, *Miner. Metall. Proc.*, **21**, 44 (2004).