

## **PARAMETERS INFLUENCING THE LEACHABILITY OF CALCINES EMANATING FROM MICROWAVE ROASTED SPHALERITE AND PYRITE CONCENTRATES**

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### **Abstract**

Microwave energy has been recently used in minerals processing to speed up the leaching process or to improve the liberation of targeted minerals (Al-Harahshed and Kingman, (2003); Bradshaw et al., (2001)). Applied to the roasting of sulphide minerals, microwaves allow the “tunning” of calcine types and products quality in addition to the energy savings as opposed to the conventional roasting (Mulaba, 2006). As more than 85% of world zinc is produced through the “roast-leach-electrowin” route, an attempt was made to optimize cost, energy and product quality for metal extraction process route. The use of microwaves was the alternative process route selected for the optimisation. Pyrite concentrate (0.17% Zn, 0.09% Cu, 35.71% Fe, 43.76% S) and sphalerite concentrate containing 43.81% Zn, 0.37% Cu, 3.86% Fe and 44.39% S were microwave roasted in a multimode cavity of 2.45 GHz with varying power levels and for different durations. The produced calcines were characterized using AAS, XRF, XRD and Mossbauer spectroscopy while the determination of residual Sulphur was used as products quality control tool to ascertain the degree of roasting achieved on the feed. The leachability of the produced calcines in HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> + HCl has been studied in terms of the best leaching yield, process kinetics economics and environmental aspect. With 800 W power for 30 minutes, ZnO and Fe<sub>2</sub>O<sub>3</sub> were formed corresponding to a 70% sulfur removed from sphalerite and 80% from pyrite concentrates respectively. While the roasting of the above concentrates appeared to be a first degree processes, it was noticed that the microwave assisted roasting of sphalerite and pyrite concentrates yielded lower sample surface temperature for a shorter time (i.e. less than 30 minutes) microwave exposition. Longer time (more than 30 minutes) microwave exposure showed a linear increase in temperature in function of power level used. While optimum roasting conditions were found at 800W, 30 minutes, a 10% increase of sulfur removal was noticed while pyrite concentrate was microwave roasted. Sulfuric acid was seen to give higher leaching yield than nitric acid. Zinc dissolution was hindered by the presence of franklinite.

## **Introduction**

Sulphide minerals are processed using conventional pyrometallurgical processes such as roasting, smelting and converting. These pyrometallurgical routes are known to be energy consuming, resulting in higher electricity costs (Bradshaw, Jones, Groves, Kingman, Lester, Whittles 2001). These challenges experienced while treating sulphide minerals with conventional pyrometallurgical processes resulted in hydrometallurgical processes such as leaching, solvent extraction and electro winning being introduced to the metallurgical industry as an alternative since they consume lesser energy and have environmental advantages of lesser SO<sub>2</sub> emission (Al-Harashsheh, Kingman 2003).

Although hydrometallurgy processes are favored recently to pyrometallurgy processes, there is a need to improve these processes and that resulted to the introduction of microwave technology to metallurgical processes. Recently there have been investigations on the use of microwaves in metallurgical processes, with the aim of having alternatives to processes such roasting, smelting and converting, since they consume a lot of energy and they have high SO<sub>2</sub> emissions. The possible use of microwaves in process industry has been investigated for comminution, drying, carbon regeneration, flotation, leaching and roasting (Bradshaw et al., 2001).

The work presented here aimed at investigating the acid leaching behavior of calcines of selected sulphide concentrates emanating from microwave assisted roasting. The sulphide concentrates were roasted at various temperatures, powers, times, and were acid leached with various acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> & HCl) at pH 2, temperature of 21°C and stirring rate of 300 rpm. The kinetics involved during roasting and acid leaching were investigated. At the end of the study conclusions about the effectiveness of microwave roasting will be made, with the main focus on the desired product being obtained (oxides), SO<sub>2</sub> emitted and energy consumption.

## **Experimental**

### **Materials and method**

Sphalerite concentrate received from Kumba Resources (Zincor, South Africa) and pyrite concentrate received from Ongopolo (Namibia) were the starting feed. XRD, AAS, XRF and Mossbauer spectroscopy were used in addition to the sulfur determination. The head feed was wet screened for the size distribution analysis requiring 80% passing 75 micron screen. Cone and quartered and spinned riffled were used to obtain representative samples for the roasting .

Microwave assisted roasting was conducted using a 1000W, 2.45GHz multimode cavity. 200W, 400W, 600W and 800W power levels and durations of 3s, 10s, 30s, 30min and 1hour were selected as experimental working conditions for the roasting process. 10 g of concentrate was spread evenly in the clay dish to ensure maximum exposure of the

materials to be roasted. The sample surface temperatures were measured using a non contact thermometer laser gun. It was naturally expected that the produced calcines were required to be from a dead roasting process to obtain ZnO (and iron oxide) since the next stage was leaching. The calcines obtained were characterized using XRD and were analyzed for sulphur content. The sulphur released was determined by combustion in a tube furnace. The air flow rate in the tube furnace was set at 0.2 l/min and the temperature inside the furnace was set at 850°C to ensure total combustion of sulphur. Mass of 0.2g sample was transferred to the combustion boat and 100 ml of neutral hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution was added to the receiving cylinder that was connected to the combustion tube. The combustion boat was then inserted in the heating zone of the combustion tube and was heated for 10 minutes. The sulphuric acid formed was measured by titration with 12,8 g/dm<sup>3</sup> of sodium tetraborate solution (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) to a blue grey end point.

Optimised calcines obtained from microwave assisted roasting were selected and acid leached with 70% HNO<sub>3</sub>, 35% HCl and 96% H<sub>2</sub>SO<sub>4</sub> at constant pH 2, temperatures of 21°C, stirring rate of 300 rpm and leach durations of 2 hours. 9 g of calcine was acid leached with a 250ml acid solution in a 500ml beaker and the stirring was carried out with a magnetic stirrer. The pH, temperature and volts were measured using a multimeter and samples were pipetted at time intervals of 10, 20, 30, 60, 90 and 120 minutes with a 20 ml pipette. Samples were then filtered and the filtrate analyzed with an Atomic Absorption Spectrometry for zinc, copper and iron.

## **Results and discussion**

The XRD mineralogical analysis of the as received feed indicated that the pyrite concentrate contained quartz (SiO<sub>2</sub>), pyrite (FeS<sub>2</sub>), covellite (CuS), bornite (Cu<sub>5.433</sub> Fe<sub>1.087</sub> S<sub>4</sub>) and zinc sulphide (ZnS) as shown in figure 1 (a) while the sphalerite concentrate contained sphalerite (ZnS), pyrite (FeS<sub>2</sub>), chalcopyrite (CuFeS<sub>2</sub>), chalcocite (Cu<sub>2</sub>S) and quartz (SiO<sub>2</sub>) as shown in figure 1 (b).

The AAS analysis of head grade for both concentrates indicated that the sphalerite concentrate had Zn 43.81%, Cu 0.37%, Fe 3.86% and S 44.39% while the pyrite concentrate contained Zn 0.17%, Cu 0.09%, Fe 35.71% and S 43.76%.

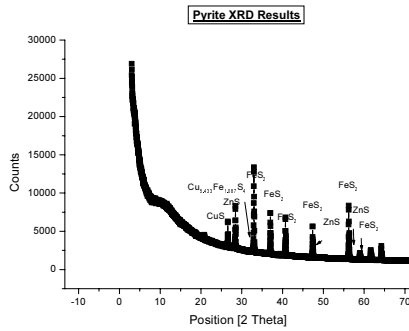


Figure 1 (a) : XRD pattern of the pyrite concentrate.

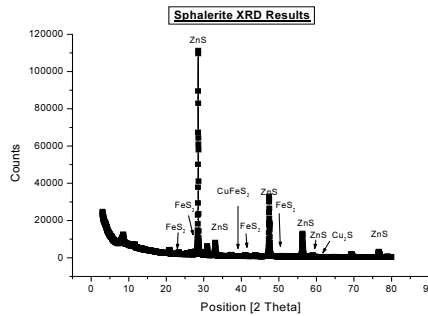


Figure 1 (b): XRD pattern of the sphalerite concentrate.

The wet screening of the as received sphalerite and pyrite concentrates was carried out at screen sizes of 500, 355, 212, 150, 106 and 75 microns. It yielded the mass distributions represented in figure 2 (a) and figure 2 (b) below.

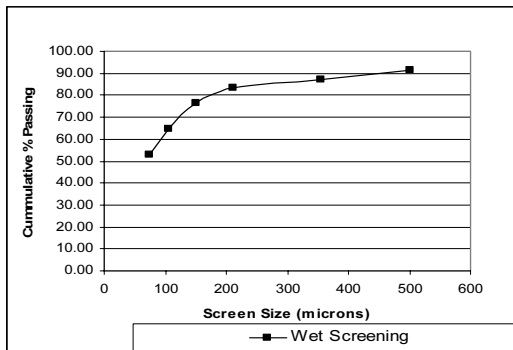


Figure 2 (a): Sphalerite Cumulative % passing against screen size

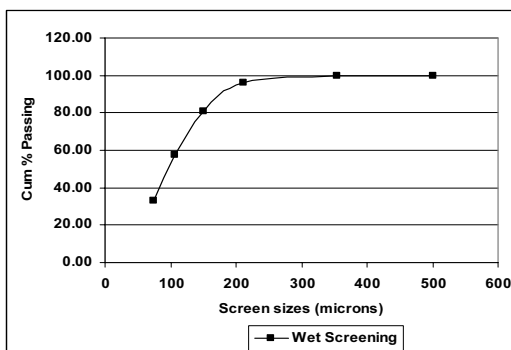


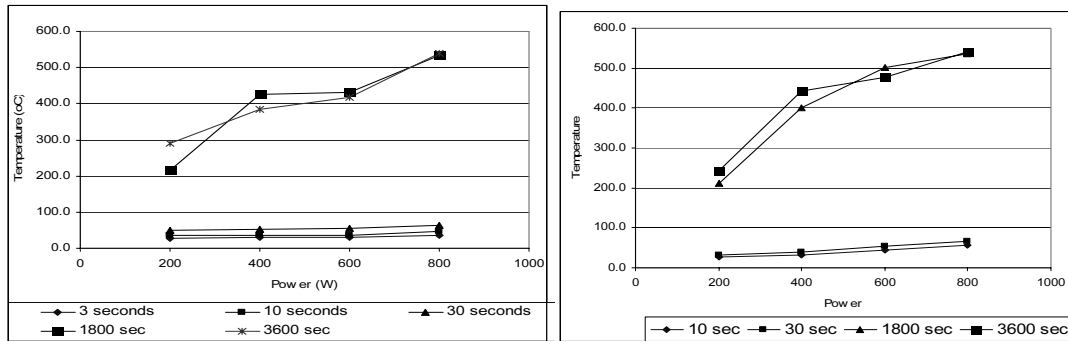
Figure 2(b): Pyrite Cumulative % passing against screen size

The results indicate that the sphalerite concentrate contained fine size fractions as 52.72% of the sphalerite passed the 75 microns screen. Figure 2(a) indicated that the cumulative % passing for screens sizes of 212, 355 and 500 microns were high at 83.57%, 87.73% and 91.34% respectively indicating that most size fractions were passing those screens. As shown in Figure 2(b) the pyrite concentrate used in this work contained fine size fractions, at screen sizes of 500, 355 and 212 microns, 99.96%, 99.78% and 96.18% of pyrite sample passed through respectively and at screen sizes of 150, 106 and 75 microns the pyrite was retained. At 75 microns screen about 33.09% of the fines passed through and that resulted to particle greater than 75 microns being combined, rod milled till 80% of the sample passed the 75 microns screen as required.

### Microwave Roasting

The surface temperature of the samples, figure 3 (a and b) were measured using a non contact laser gun thermometer.

The relationship between power applied during microwave roasting and the temperature obtained are indicated in figure 3 (a and b). In general, it is observed that the longer the duration of exposition to the microwaves the higher the temperature and the stronger the power the higher the surface temperature



**Figure 3(a):** Graph of surface temperature obtained during sphalerite concentrate roasting with microwaves

**Figure 3 (b):** Graph of surface temperature obtained during Pyrite concentrate roasting with microwaves

. The roasting of sphalerite at times of 3, 10 and 30 sec at all powers of the microwave resulted in low temperatures less than 100°C being obtained as shown in figure 3(a) indicating that roasting temperatures were not reached. The roasting duration was further increased to 30 minutes and 1 hour and the results showed a linear increase in temperature from 217 to 535°C for 30 minutes and 390 to 540°C for 1 hour at all powers used and thus resulting in roasting temperatures being reached. Figure 3(b) indicates that when radiating the pyrite with microwaves at times of 10 to 30 sec results in lower temperatures less than 100°C also being obtained which were insufficient to roast the pyrite. As the radiating times were increased to 30 min and 1 hour the temperatures obtained increases rapidly from 212 to 537°C for 30 minutes, and 244 to 540°C for 1 hour. The steady increase in temperatures would have been interpreted as due to the exothermic reactions which resulted in roasting of pyrite concentrate as it was visually observed by change into the reddish coloration of the calcine show a possible formation of hematite (Fe<sub>2</sub>O<sub>3</sub>).

**Table 1:** Phase produced from the microwave assisted roasting of sphalerite concentrate.

Power (W)	Exposure time				
	3s	10s	30s	30 min	1 hour
200	Zn S Si O <sub>2</sub> Fe S <sub>2</sub>	Zn S Fe S <sub>2</sub> Si O <sub>2</sub>	Si O <sub>2</sub> Fe S <sub>2</sub> Cu Fe <sub>2</sub> S <sub>3</sub> Zn S	Zn S Cu Fe S <sub>2</sub> Fe S <sub>2</sub> Si O <sub>2</sub>	Si O <sub>2</sub> Cu Fe S <sub>2</sub> Fe S <sub>2</sub>
400	Si O <sub>2</sub> Fe S <sub>2</sub> Zn S Cu Fe <sub>2</sub> S <sub>3</sub>	Zn S Si O <sub>2</sub> Fe S <sub>2</sub>	Zn S Fe S <sub>2</sub> Cu Fe <sub>2</sub> S <sub>3</sub> Cu <sub>2</sub> S	Zn S Si O <sub>2</sub> Cu <sub>2</sub> S Fe S <sub>2</sub>	Zn S Fe S <sub>2</sub> Si O <sub>2</sub>
600	Fe S <sub>2</sub> Cu <sub>2</sub> S Zn S Si O <sub>2</sub>	Zn S Cu Fe S <sub>2</sub> Si O <sub>2</sub> Fe S <sub>2</sub>	Zn S Fe S <sub>2</sub> Si O <sub>2</sub> Cu Fe <sub>2</sub> S <sub>3</sub>	Fe S <sub>2</sub> Si O <sub>2</sub>	Si O <sub>2</sub> Fe S <sub>2</sub> Zn S
800	Zn S Si O <sub>2</sub> Fe S <sub>2</sub>	Fe S <sub>2</sub> Zn S Si O <sub>2</sub>	Zn S Si O <sub>2</sub> Fe S <sub>2</sub>	Zn O Zn Fe <sub>2</sub> O <sub>4</sub> Fe S <sub>2</sub>	Zn O Zn S Zn Fe <sub>2</sub> O <sub>4</sub> Si O <sub>2</sub> Fe S <sub>2</sub> Fe <sub>2.937</sub> O <sub>4</sub>

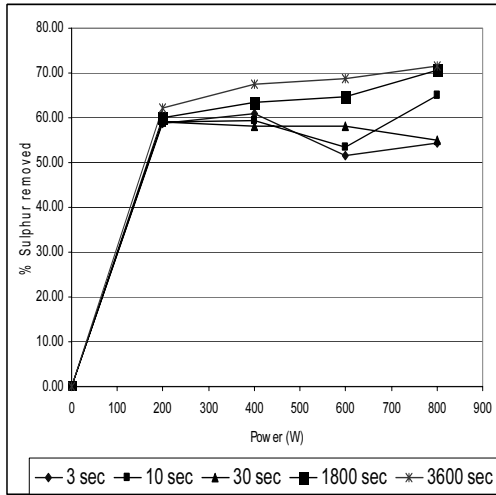
From the XRD results of microwave roasted sphalerite it was found that at powers of 200, 400, 600 and 800W and times of 3sec, 10sec and 30sec that the sphalerite was not roasted as shown by the presence of ZnS in table 1. After 30 min and 1hour of microwave roasting at powers of 200 and 400W there was still no roasting while at powers of 600W there was a formation of Zn<sub>0.825</sub>Fe<sub>0.175</sub>S and Zn<sub>0.776</sub>Fe<sub>0.224</sub>S respectively with no ZnO and at 800W power ZnO the desired product was obtained which was an indication that roasting did take place to a certain degree.

**Table 2:** Phase produced during the microwave assisted pyrite concentrate.

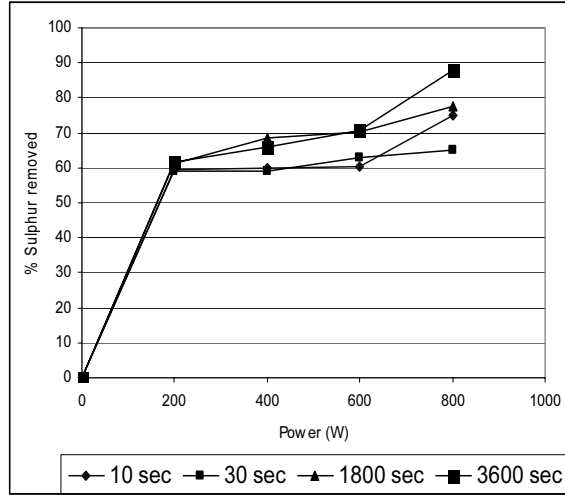
Power (W)	Exposure time			
	10s	30s	30 min	1 hour
<b>200</b>	Fe S <sub>2</sub> Si O <sub>2</sub> Zn S	Fe S <sub>2</sub> Si O <sub>2</sub> Cu <sub>2</sub> S Zn S	Fe S <sub>2</sub> Si O <sub>2</sub> Zn S	Fe S <sub>2</sub> Si O <sub>2</sub> Zn S
<b>400</b>	Fe S <sub>2</sub> Si O <sub>2</sub> Cu <sub>2</sub> S	Fe S <sub>2</sub> Si O <sub>2</sub> Cu <sub>2</sub> S Zn S	Fe <sub>2</sub> O <sub>3</sub> Fe S <sub>2</sub> Si O <sub>2</sub> Zn S Fe <sub>3</sub> O <sub>4</sub>	Fe S <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> Zn S
<b>600</b>	Fe S <sub>2</sub> Si O <sub>2</sub>	Fe S <sub>2</sub> Si O <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> Fe S <sub>2</sub> Si O <sub>2</sub> Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub> Fe S <sub>2</sub> Si O <sub>2</sub> Fe <sub>3</sub> O <sub>4</sub> Fe S <sub>2</sub>
<b>800</b>	Fe S <sub>2</sub> Si O <sub>2</sub> Cu <sub>2</sub> S Zn S	Fe S <sub>2</sub> Si O <sub>2</sub> Zn S	Fe <sub>2</sub> O <sub>3</sub> Si O <sub>2</sub> Fe S <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> Si O <sub>2</sub>

It was found that at the power of 200W, 400W and times of 10sec, 30sec, 30min and 1hour that there was no roasting taking place as only traces of ZnS were observed. At powers of 600W and 800W roasting was observed after 30min and 1 hour due to the presence of hematite (Fe<sub>2</sub>O<sub>3</sub>) reddish in colour and some traces of pyrite (FeS<sub>2</sub>). Therefore the optimum condition for pyrite roasting was at a power of 800W at times of 30minutes and 1 hour.

The sulphur removed during roasting with microwave was determined from the roasted calcines and the results are given in figure 4 (a) and figure 4 (b).



**Figure 4(a):** Graph of % Sulphur removed in Sphalerite after microwave roasting

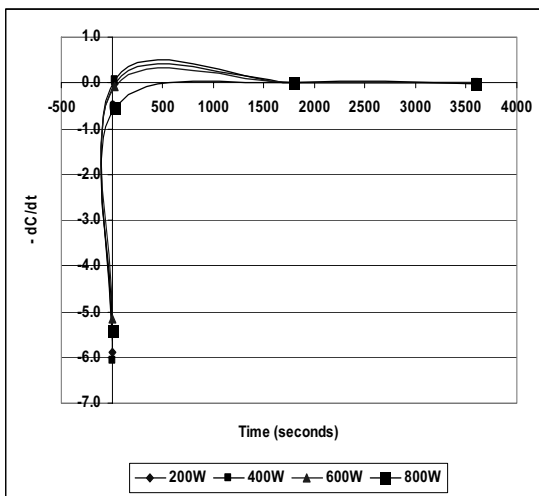


**Figure 4 (b):** Graph of % Sulphur removed from pyrite after microwave roasting

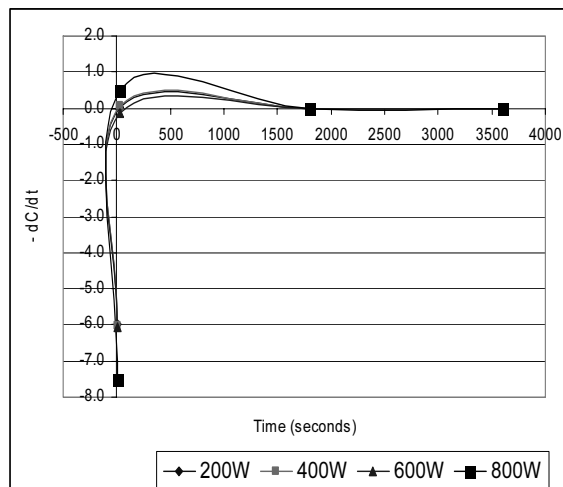
The roasting of sphalerite and pyrite concentrates with microwaves showed, figure 4 (a) and figure 4 (b), a quicker process at shorter durations 3, 10 and 30 seconds. A higher effectiveness (~ 10% more) of sulfur removal was observed in the case of roasting of pyrite concentrate, figure 4 (b).

**Kinetics of microwave assisted roasting of sphalerite and pyrite concentrate**

The kinetics involved in the microwave roasting of sphalerite and pyrite concentrates were investigated. The slope of % sulphur removed curves was used as assessing parameter.



**Figure 5(a):** Rate of sulphur removal from microwaved sphalerite concentrate

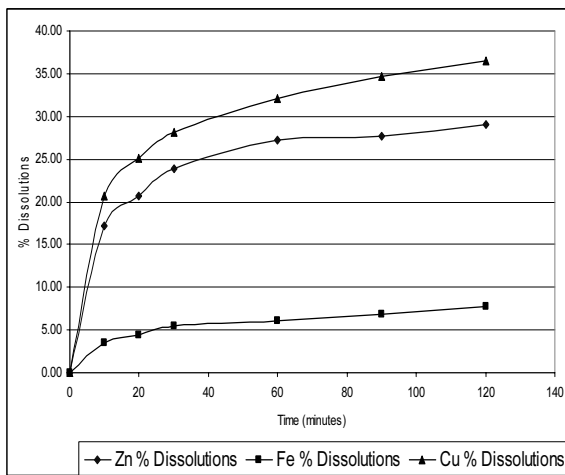


**Figure 5 (b):** Rate of sulphur removal from microwaved pyrite concentrate

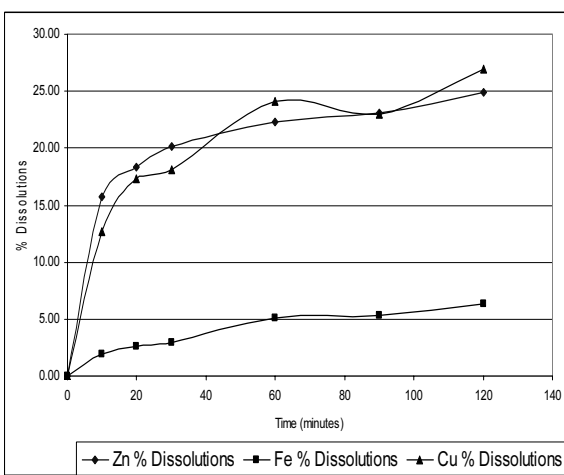


### Acid leaching

The calcines from the microwave roasting (800W, 30 minutes) of sphalerite concentrate were acid leached with 70% HNO<sub>3</sub>, 35% HCl and 96% H<sub>2</sub>SO<sub>4</sub> at a constant pH of 2, temperature of 21°C, stirring rate of 300 rpm and leach durations of 2 hours to investigate their leaching behaviour. While the conventional leaching behavior was observed, figure 6 (a and b) and figure 7), for all the mono acids (i.e. H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl), lower dissolutions of zinc 28.97%, slight increase for copper 36.52% and 7.74% for iron were noticed while leaching with sulfuric acid. The leaching in HNO<sub>3</sub> presented a relatively lower yield ( 24.86% zinc, 26.91% and 6.30% for iron).

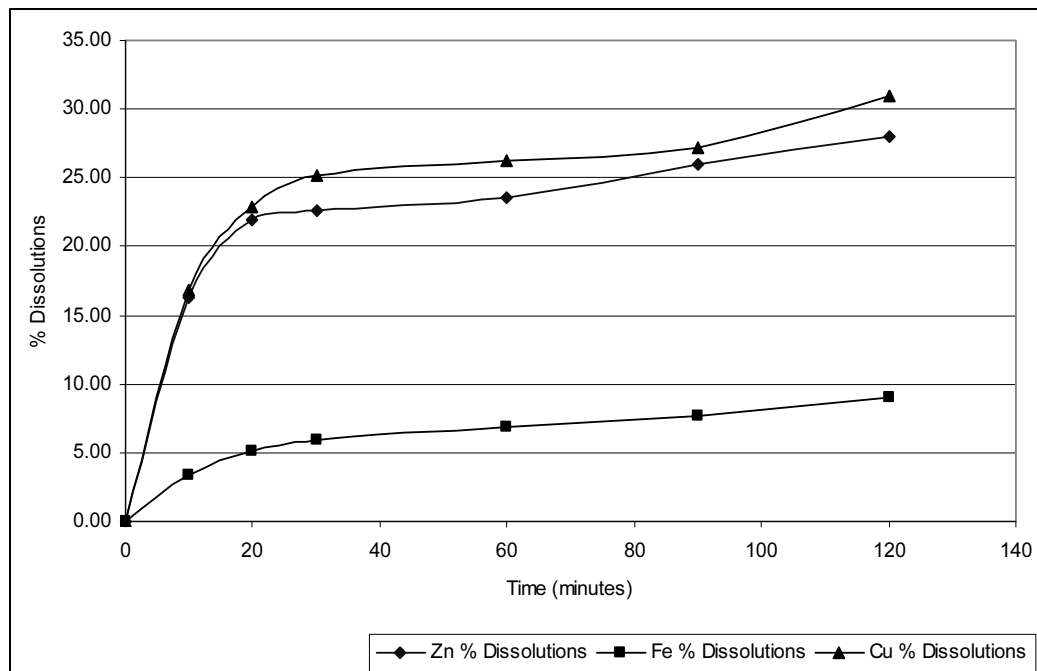


**Figure 6(a):** % dissolution in H<sub>2</sub>SO<sub>4</sub> of microwave roasted sphalerite concentrate



**Figure 6(b):** % dissolution in HCl of microwave roasted sphalerite concentrate

As the pH was kept constant at 2, the electropotentials maintained at about 300mV, it was expected from (pH- Eh diagrams) to have Zn<sup>+2</sup>, Cu<sup>+2</sup> and Fe<sup>+2</sup> in solution.



**Figure 7:** % dissolution in HNO<sub>3</sub> of the microwave roasted sphalerite concentrate against time.

1. It has been noticed that copper was easily dissolved (Cu, 31.01% ) followed by zinc (Zn, 28.00% ) and Iron (Fe, 9.06% ). The lower dissolution of zinc minerals could have been caused among other things by the franklinite (ZnFe<sub>2</sub>O<sub>4</sub>) present in the sample used .

## Conclusions

In conclusion it would be stated that the microwave assisted roasting of sphalerite and pyrite concentrates yield lower sample surface temperature for a shorter time (i.e.less than 30 minutes) microwave exposition. Longer time (more than 30 minutes) microwave exposure shows a linear increase in temperature in function of power level used.

While optimum roasting conditions were found at 800W, 30 minutes, 10% increase of sulfur removal was noticed while pyrite concentrate was microwave roasted.

## Acknowledgements

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## **References**

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