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# Microwave Heating Applications in Mineral Processing

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# 1. Introduction

#### 1.1. History

The thermal treatment of ore to bring about thermal fracturing, and thereby a reduction in Ore strength is by no means a novel idea. The first century BC Greek historian, Diodorus Siculus, recorded in his Bibliotheca Historica the ancient practice of fire setting, verifying his work with that of another Greek historian, Agatharcides, who had visited the gold mines in Egypt around the second century BC (Meyer, 1997<sup>1</sup>).

Oldfather, 1967<sup>2</sup>, provides a translation of Diodorus's account of the practice: "The gold bearing earth which is hardest they first burn with a hot fire, and when they have crumbled it...they continue the working of it by hand; and the soft rock which can yield to moderate effort is crushed with a sledge".

The practice of fire setting basically consisted of constructing a large fire against the rock face to be mined. As the rock heated unevenly, it would fracture internally, severely weakening the rock. After the fires died down the rock face would be doused with water, though whether this rapid quenching was employed to further weaken the rock or to allow the miners to immediately continue working the rock face is not known (The Tech, 1886)<sup>3</sup>.

Using this process, it was possible to weaken the rock face to the depth of approximately a foot at a time, after which the soft ore was mined and when the harder rock face was again encountered, fire setting was again employed (Cowen, 1999)<sup>4</sup>.

Archeological evidence supports the notion that the practice of fire-setting was a worldwide phenomenon and may indeed be much older than those activities reported in the records of Diodorus Siculus, with ancient mining sites discovered at Rudna Glava in the Balkans suggesting the use of fire setting around 4500 to 4000 BC, at Ai Bunar in southern Bulgaria



also dated at several thousand years BC and from which it is estimated that between 20 000 and 30 000 tonnes of ore were mined while employing the method when required (Cowen, 1999), at the ancient mining sites around Isle Royale in the Lake Superior region in North America to mine copper and up until just a few centuries ago in Japan for creating long tunnels (The Tech, 1886)<sup>3</sup>.

In fact, it remained a vital part of the mining industry until the first use of gunpowder for blasting in 1613 (The Tech, 1886)3, after which the use of thermal treatment declined in favor of the quicker processes of drilling and blasting.

# 1.2. Initial studies on minerals breakage

It is reported in a review paper by Fitzgibbon and Veasey, 1990<sup>5</sup>, that work on the use of thermal treatment to aid in rock breakage during comminution processes began again early in the 20th century, with practical studies on Cornish tin ores (Yates, 1919) <sup>6</sup>and quartzites (Holman, 1927)<sup>7</sup>. Fitzgibbon and Veasey, 1990, report that this early work showed that the thermal pretreatment of ores before comminution resulted not only in a reduction in the strength of the ores studied, but also in fewer fines being produced. Work by Myer, 1925<sup>8</sup>, and Holman, 1927, also studied the dependence of the susceptibility of ores to heat treatment on particle size and concluded that the effectiveness of the treatment decreased with particle size (Fitzgibbon and Veasey, 1990).

#### **1.3. Economical evaluation**

In the second half of 20 century, many researchers studied on the economical aspect of conventional heat treatment. As early as 1962, it was known that the effect of thermal treatment on ore strength varies with ore mineralogy, and that fluorites and barites, in particular, are susceptible to this effect, but studies showed that the process of thermal treatment was uneconomical when compared to the use of conventional grinding alone (Prasher, 1987)<sup>9</sup>, due to the enormous energy requirements associated with heating the bulk ore to the required temperatures, where Wills et al., 1987<sup>10</sup>, report that other workers have calculated that the cost of heat treatment and subsequent grinding could be as high as 6 times that of conventional grinding alone (Scheding et al., 1981)<sup>11</sup>.

# 1.4. Water quenching after heat treatment

Some researchers studied on the effect of water quenching after heat treatment to reduce the economic costs of heat treatment process.

Kanellopoulos and Ball, 1975<sup>12</sup>, studied the effect of heat treatment on crushing and grinding of quartzite samples. Their investigations showed that heat treatment above 400°C improves the comminution of the ore, but that the best results are obtained after heating the quartzite to temperatures above the  $\alpha$ - $\beta$  phase transition temperature of quartz (i.e. 573°C), at which a sudden volumetric expansion (i.e. a volume increase of 0.86%) of quartz crystals occurs. Comparative testing of material which was slow cooled from 680°C to ambient, and material

which was shock cooled through water quenching, showed no difference in the product size distribution of the material after milling. Comparisons of results obtained from the same heat treatments after comminution by slow crushing, however, indicate that quenching the ore results in a change in the product particle size distribution, with significantly less material passing at larger sizes with the difference in passing size decreasing with particle size, thus resulting in a finer product without a significant increase in the production of very fine material. This was the first indication that the manner of the post-processing of the material may be as important as the thermal treatment itself.

Pocock et al., 1998<sup>13</sup>, investigated the use of various quenching solutions to ascertain whether any improvement could be seen from using acid, alkali or salt solutions instead of water. It was found that all of these showed improvements in grinding energy reduction over the use of water, and of these, it was found that the use of acid or alkali solutions provided the best results. At the same time, it was seen from UFLC tests that as comminution of the treated particles continued (i.e. as the particles become smaller), the observed effects of the thermal pretreatment are reduced. What this indicates is that as the easily exploited newly formed fractures are used up, the strength of the ore begins to once again approach that of the untreated ore.

#### 1.5. Minerals liberation and heat treatment

Wills et al., 1987<sup>10</sup>, investigated the thermally assisted liberation of cassiterite in an ore mined at South Crofty. Previous work on this ore (Sherring, 1981)<sup>14</sup> had shown a 55% reduction in grinding resistance when the ore was heated to 650°C and then rapidly cooled, however, this was greatly offset by the energy required to heat the material. It was suggested by Manser, 1983<sup>15</sup>, that an increase in tin recovery of 1% would offset this cost in the case of the South Crofty ore, due to the value of the recovered minerals. Employing similar conditions in their work, and heat treated polished sections of the ore which could be photographed before and after the treatment to look for any induced fractures which might indicate that this increase in liberation may be possible. Their results showed that while some intergranular fracturing was observed as a result of their heat treatment, in most of the cases extensive transgranular fracturing occurred, and later separation tests showed no enhanced liberation or recovery of this material with heat treatment.

# 2. Microwave treatment

# 2.1. Minerals in microwave field

Conventional heat treatment of minerals is a process with high-energy consumption and it is not economical. Hence, researchers, searched for processes that are more effective.

It is reported in a review paper by Xia and Pickles, 1997<sup>16</sup>, that the earliest work on the microwaving of minerals began with a study of the high temperature processing of certain oxides and sulfides using a resonant cavity operating at 2.45 GHz and variable power up to 1.6 kW (Ford and Pei, 1967)<sup>17</sup>. Table 1 shows the results. The results of this early work were

qualitative in nature, concluding that, in general, dark coloured compounds heated rapidly (reaching temperatures of up to 1000°C), while lighter coloured compounds heated slower but were capable of being heated to higher temperatures.

Compound	Heating time (min)	Max. Temp. (°C)
Al <sub>2</sub> O <sub>3</sub>	24	1900
С	0.2	1000
CaO	40	200
Co <sub>2</sub> O <sub>3</sub>	3	900
CuO	4	800
CuS	5	600
Fe <sub>2</sub> O <sub>3</sub>	6	1000
Fe <sub>3</sub> O <sub>4</sub>	0.5	500
FeS	6	800
MgO	40	1300
MoO <sub>3</sub>	0.46	750
MoS <sub>2</sub>	0.1	900
Ni <sub>2</sub> O <sub>3</sub>	3	1300
PbO	13	900
UO <sub>2</sub>	0.1	1100

**Table 1.** Microwave heating of some oxides and sulfide compounds

Further, Wong (1975) <sup>18</sup>and Tinga (1988<sup>19</sup>, 1989<sup>20</sup>) reported the microwave heating behavior of several metal oxides. These results were compared with published data; and classified based on heating rate into hyperactive, active, difficult-to-heat and inactive. Table 2 represents the compilation results. They demonstrated that microwave energy could be effective in the heating of minerals and inorganic compounds.

Material classification		Heating rate reported (°C/min)	Max. Temp. (°C)
Hyperactive Materials	UO <sub>2</sub>	200 (°C/s)	1100
	MoS <sub>2</sub>	150 (°C/s)	900
	C(charcoal)	100 (°C/s)	1000
	Fe <sub>3</sub> O <sub>4</sub>	20 (°C/s)	500-1000
	FeS2	20 (°C/ <i>s</i> )	500
	CuCl	20 (°C/s)	450

Material classification		Heating rate reported (°C/min)	Max. Temp. (°C)
Active	Ni <sub>2</sub> O <sub>3</sub>	400	1300
	CoO <sub>3</sub>	300	900
	CuO	200	800
	Fe <sub>2</sub> O <sub>3</sub>	170	1000
	FeS	135	800
	CuS	120	600
Difficult to Heat	Al <sub>2</sub> O <sub>3</sub>	80	1900
	PbO	70	900
	MgO	33	1300
	ZnO	25	1100
	MoO <sub>3</sub>	15	750
Inactive	CaO	5	200
	CaCO <sub>3</sub>	5	130
	SiO <sub>2</sub>	2-5	70

Table 2. Classification of some reagent grade materials based on microwave heating rate

Perhaps the most important of the early work was that of Chen et al., 1984,<sup>21</sup> who investigated the reaction of 40 minerals to microwave exposure in a waveguide applicator, which allowed the mineral samples to be inserted in an area of known high electric field strength. Though by this time, it was already known that microwaves would heat some minerals selectively; this work further showed that microwave heating is dependent on the composition of the mineral, and thus elemental substitutions would affect the behavior of a mineral in an electric field. An example of this was noted with sphalerite, where high iron sphalerite would eventually heat quite well after a period of slow heating at low temperatures, but that low iron sphalerite did not heat readily. From the large number of minerals tested, it was noted that most silicates, carbonates and sulfates, and some oxides and sulfarsenides, and some oxides, heat well when subjected to microwave irradiation.

More recently, the US Bureau of Mines reported test results of microwave heating a number of minerals and reagent grade inorganic compounds with 2450 MHz (McGill and Walkiewicz, 1987<sup>22</sup>, Walkiewicz et al., 1988<sup>23</sup>). The test results revealed that the highest temperatures were obtained with carbon and most of the metals oxides: NiO, MnO<sub>2</sub>, Fe<sub>3</sub> O<sub>4</sub>, Co<sub>2</sub>O<sub>3</sub>, CuO and WO<sub>3</sub>. Most metal sulphides heated well but without any consistent pattern. Metal powder and some heavy metal halides also heated well; gangue minerals such as quartz, calcite and feldspar did not heat. This study also revealed that rapid heating of ore minerals in a microwave transparent matrix generated thermal stress of sufficient

magnitude to create micro-cracks along mineral boundaries. This kind of micro-cracking has the potential to improve grinding efficiency as well as leaching efficiency.

Chunpeng et al. (1990)<sup>24</sup> conducted microwave heating tests on several oxide, sulfide and carbonate minerals. All tests were conducted on a 50.0 g powder (-200 mesh.) sample per batch with an input microwave power of 500 W of 2450 MHz frequency and constant exposure time (4 min). Test results are shown in Table 3. These results indicate that the majority of oxide and sulphide minerals heated well.

Minerals	Chemical composition	Temperature (°C)
Jamesoite	Pb2Sb2S5ZnS	>850
Titanomagnetite	xTiO2. yFe3O4	>1000
Galena	PbS	>650
Chalcopyrite	CuFeS <sub>2</sub>	>400
Pentlantite	(FeNi)(1-x)S8	>440
Nickel pyrrhotite	(FeNi)(1-x)S	>800
Cu–Co sulphide Concentrate	xCu <sub>2</sub> S. yCoS	>800
Sphalerite	ZnS	>160
Molybdenite	MoS <sub>2</sub>	>510
Stibnite	Sb <sub>2</sub> S <sub>3</sub>	Room temp
Pyrrhotite	Fe(1-x)S	>380
Bornite	Cu <sub>3</sub> FeS <sub>4</sub>	>700
Hematite	Fe <sub>2</sub> O <sub>3</sub>	>980
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	>700
Limonite	mFeO2.nH2O	>130
Cassiterite	SnO <sub>2</sub>	>900
Cobalt hydrate	CoO.nH2O	>800
Lead molybdenate	PbMoO <sub>4</sub>	>150
Iron titanite	FeTiO <sub>3</sub>	>1030
Rutile	TiO <sub>2</sub>	Room temp
Lead carbonate	PbCO <sub>3</sub>	>180
Zinespar	ZnCO <sub>3</sub>	>48
Siderite	FeCO <sub>3</sub>	>160
Serpentine	Mg(Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>3</sub>	>200
Melaconite	Cu2Al3(H(2-x)Si2O3)(OH)4	>150
Antimony oxide	Sb <sub>2</sub> O <sub>3</sub>	>150

**Table 3.** Effect of microwave heating on the temperature of various minerals (500 W, 2450 MHz, 4min radiation)

Interaction of microwave with minerals is poorly understood. Thus, a fundamental understanding of how microwave energy interacts with minerals is the key to unlocking the technology for use in mineral processing industries. To shed more light on the subject of the interaction of microwave with minerals, Barani et al., 2012,<sup>25</sup> studied the effect of sample factors, such as volume, surface area, size and shape, aspect ratio on the magnitude and uniformity of power absorption by iron ore and water samples and compared obtained data. The results showed that for water heating, with increasing in sample volume from 200 to 1000 cm<sup>3</sup> the microwave energy absorbed by water was increased from 71.27 to 100%, also with increasing in sample surface area from 50.24 to 78.50 cm<sup>2</sup> the microwave, energy absorbed by water was increasing in sample surface area, the microwave absorption was constant whereas with increasing in sample surface area from 50.24 to 126.6 cm<sup>2</sup>, the microwave energy absorbed by iron ore was increased from 36.6 to 61.82%. The maximum temperature for iron ore material was occurred at 5.7 cm distance from the center whereas the maximum temperature for water sample was occurred at 5cm distance from the center.

#### 2.2. Microwave assisted ore grinding

Walkiewicz et al. (1988<sup>23</sup>, 1991<sup>26</sup>) demonstrated that the rapid heating of ore containing microwave energy absorbing minerals in a non-absorbing gangue matrix generated thermal stress. This thermal stress caused micro fracturing along the mineral grain boundaries; as a result, such an ore sample becomes more amendable to grinding. According to these authors, the grinding operation (comminution) consumes 50%–70% of energy used in mineral processing operations. Again, the energy efficiency of a conventional grinding operation is approximately 1%. They demonstrated that microwave preheating of an iron ore improved grinding efficiency by 9.9% to 23.9%. However, this improvement was not enough to compensate for the energy consumption of the microwave preheating.

Walkiewicz et al., 1993,<sup>27</sup> investigating the effect of power level on Bond work index, found that the larger temperature gradients associated with the more rapid development of heat within the particle grains because of higher microwave powers, led to a larger decrease in ore strength than for exposure to lower microwave powers.

Tavares and King, March 1996,<sup>28</sup> investigating samples of specific iron, taconite and titanium ores in a multimode cavity using a low power input of between 0 and 1.2 kW, compared the strengths of untreated ore with that of ores treated both conventionally and with microwaves. It was observed that in all cases the thermal treatments affected the ore favourably in terms of both reductions in fracture energy and increased damage, however, there was very little difference between the results for the conventional and microwave treatments, with the exception of a greater reduction in fracture energy of the iron ore and greater damage to the titanium ore from microwave treatment. From examinations of the single particle breakage functions, it was further seen that the thermal pretreatments resulted in a shift in the top of the breakage function to smaller sizes without an increase in the production of very fine material, and also that the microwave treated ores tended to

produce a greater shift in the top of the breakage function than conventionally treated ores. It was concluded that this change in fragmentation pattern, together with observations from image analysis of a 50% increase in grain boundary fracture in the microwaved iron ore, might result in improved liberation. Later tests by the same authors (Tavares and King, August 1996)<sup>29</sup> on a copper ore showed no difference between the fracture energies of microwave pretreated and untreated material, though it was noted that there was a slight indication of grain boundary fracture around the sulfide grains. It is not stated what kind of microwave treatment was used, however, and thus these results are not comparable to those of other workers.

Work on the grind ability of coal by Marland et al., 2000<sup>30</sup>, indicated that reductions in work index of up to 50% occur after microwave pretreatment. The greatest strength reductions were obtained from lower ranked coals, and it was suggested that this was most likely due to the higher inherent moisture content of such coals, with gaseous evolutions of water and volatile matter the main causes of damage to the coal particles. It was also found that microwave radiation affected the calorific value to the same extent as would be expected from conventional drying procedure, and it was concluded that the application of microwave treatment did not alter the fuel potential of coal.

Kingman et al., 2000<sup>31</sup>, encompassing tests on several commercially exploited ores to investigate the influence of ore mineralogy on microwave assisted grinding showed that the most responsive ores were those with a consistent mineralogy, containing good absorbers in a transparent gangue, while those with small lossy particles that are finely disseminated in discrete elements were shown to have the worst response in terms of reduction in required grinding energy. One extremely important result from this paper was the suggestion that purpose built microwave cavities may be important in making the treatment of ores more economically viable.

Wang and Forssberg, 2000,<sup>32</sup> performed tests on three ores (i.e. limestone, dolomite and quartz) to investigate their microwave heating behavior and subsequent grindability during dry ball milling, after pretreatment. Each ore was crushed and sized into three fractions for testing, these being -9.75+5.75 mm, -4.7+1.6 mm and -1.6 mm. It was noted that the particle size of the material undergoing thermal pretreatment had a significant effect on the heating behavior and subsequent grindability of two of the ores, with tests on the quartz and limestone material showing that the microwave pretreatment was only effective for the -9.5+4.75 mm material, which then subsequently showed improved grindability. Below 4.75 mm, little or no effect was seen, and it was suggested that this was due to conductive heat transfer which plays a more important role in heat loss from smaller particles. It was also found that increasing the exposure time led to a further increase in the grindability of these two ores. Dolomite showed little reaction to microwave pretreatment during subsequent dry milling experiments. Tests were also performed to determine the degree of liberation of sulfide minerals in a low grade copper ore (0.22-0.4% Cu) from Aitik after crushing. SEM photomicrographs showed that thermal stress cracks occurred readily along the sulfide-gangue mineral grain boundaries, and image analysis software showed a substantial increase in the liberation of sulfide minerals in the ore matrix with microwave pretreatment prior to crushing.

Vorster et al, 2001<sup>33</sup>, performed several tests on a massive copper ore and a massive copperzinc ore, both from Neves Corvo in southern Portugal, using a 2.6 kW multimode cavity operating at 2.45 GHz. Quenching after 90 seconds of microwave exposure led to a 70% reduction in the work index of the massive copper ore. The effect of quenching was also illustrated with tests on the massive copper-zinc ore, where after 90 seconds of microwave exposure with no quenching, a reduction of 50% in the strength of the ore was obtained, while the addition of quenching directly after microwave treatment led to a further 15% reduction in work index. Copper flotation trials showed that no benefit in terms of improved copper recovery was seen after microwave treatment, and it was concluded that the improved liberation after microwave treatment which was noted from SEM analysis, was most likely offset by some surface oxidation of the recoverable sulfide minerals.

Kingman et al., 2004<sup>34</sup>, investigated the treatment of a copper carbonatite ore from a mine in South Africa using a single mode, high power applicator (i.e. a variable power input of up to 15 kW). Their results showed that a sort of threshold value existed for the power input into the system, which once passed, caused serious damage to the particle in a very short treatment time (< 0.5 seconds). The importance of this discovery is best seen when the values are turned into values of power densities within the valuable minerals, in which case these values are no longer specific to a certain microwave system, allowing the design of any system with the goal of obtaining these power densities. It was shown that reductions of up to 30% in grinding energy could be achieved with microwave energy inputs of less than 1 kWh/t. QEMSCAN analysis of the product of drop weight tests also showed a decrease in the amount of locked and middling copper sulfides in the +500  $\mu$  m size classes.

Amankwah et al., 2005<sup>35</sup>, performed tests on samples of a gold ore containing quartz, silicates and iron oxides with a head grade of 6.4 g/t of gold, using 2 kW of power in a multimode cavity. It was seen that the microwave treatment resulted in a maximum reduction of 31.2% in crushing strength and a reduction of 18.5% in work index. SEM analysis clearly showed that microwave induced fractures were occurring in the ore, and an improvement of 12% in gold recovery from gravity separation tests showed that this resulted in the liberation of the gold at coarser particles sizes during comminution.

Scott et al., 2007, studied the effects of microwave treatment on the liberation spectrum of a rod-milled South African carbonatite ore.The treated ore was processed for 0.5 s at 10.5 kW in a single mode microwave cavity in batches of 1 kg. The treated and untreated ore were subsequently grinded to 80%– $800 \mu$ m. The microwave treated ore showed a significant increase in the amount of liberated copper minerals in the relatively coarse particle size range (106 to 300 µm). Similar significant shifts in the liberation spectra were noted for all the minerals in the ore. It is inferred that microwave treatment induces changes in the fracture pattern, favoring liberation of microwave susceptible minerals at larger particle sizes.

Koleini et al., 2008<sup>36</sup>, investigated the effect of microwave radiation on the comminution of an iron ore. Iron ore material was preheated for different time at 1000W in a multi-mode microwave oven. Comparative bond rod mill work index was used to determine the effect of this process on the grinding energy required for size reduction of the material in a

laboratory rod mill. It is shown after 1, 3 and 5 minute radiation respectively, the amount of 12, 34 and 46% reduction in work index was achieved. Microwave exposure followed by water quenching is shown after 1, 3 and 5 minutes radiation respectively, the amount of 19, 38 and 50% reduction in work index was achieved.

Barani et al., 2010<sup>37</sup>, studied the influence of microwave pre-treatment on iron ore breakage. Drop weight tests were used to quantify the change in strength in terms of reduction in required comminution energy. The drop weight test parameters of untreated iron ore was compared to microwave-treated iron ore under the same experimental conditions and it was found that microwave-treated materials is softer than untreated in terms of the impact breakage parameter values and the abrasion breakage parameter values. After microwave treatment, about 100% increases in abrasion breakage parameter was achieved while maximum increasing in impact breakage parameter was 36%. It seems that microwave treatment is more effective for abrasion breakage mechanism; because abrasion is, a surface phenomenon and microwave treatment is more effective at surface heating

Koleini et al, 2012<sup>38</sup>, studied the effect of microwave treatment on the grinding kinetics of an iron, using mono-sized materials of -2.360+2.0 mm, -1.400+1.180 mm, -1.0+0.850 mm and -0.355+0.300 mm. Microwave-treated samples were treated in a multimode microwave oven with 1100 W input power. The grinding tests were conducted using a laboratory ball mill under identical conditions to allow a comparative analysis of the results. The specific rates of breakage (Si) and cumulative breakage distribution function (Bi,j) values, as grinding breakage parameters, were determined for those size fractions of untreated and microwave-treated feeds. It was determined that breakage of iron ore followed a first-order behavior for fine feed sizes and deviated from first order for coarse feed size. The specific rate of breakage parameters of untreated iron ore was compared with microwave-treated iron ore under the same experimental conditions and it was found that microwave-treated materials break faster than untreated in terms of the Si and A values. Breakage parameters showed that treated materials produce more coarse material than untreated material in terms of the  $\gamma$  value of Bi,j.

#### 2.3. Breakage mechanism

Walkiewicz et al., 1988<sup>23</sup>, showed that thermal stress fracturing along grain boundaries was induced in some samples after microwave heating, and suggested that this could significantly influence not only the grindability of microwave treated ores, but mineral liberation as well.

Work by Tinga, 1988<sup>19</sup>, in the field of microwave sintering suggested that preferential heating of grain boundaries occurs. This should be the case for any high loss dielectric grain of reasonable diameter embedded in a relatively low loss host material. Effects such as conduction losses and the rate of heating do play a role, however, and care should be taken before assuming this is true for any particular situation. Tinga, 1988<sup>19</sup>, also stated that the single most important factor when considering microwave heating was the design of the applicator, where choosing the wrong applicator for a task will mostly likely result in very few of the expected benefits of microwave processing being seen, and therefore very little improvement in results from the treatment versus those of conventional practices.

Salsman et al., 1996<sup>39</sup>, used a finite element numerical model of a single pyrite particle in a calcite matrix to further investigated the phenomenon of thermally assisted liberation using microwave energy. Using power densities, which are likely to be possible within the pyrite grains, it was seen that large tensile stresses, exceeding the tensile strengths of most common rock material, were generated along the pyrite-calcite interface. It was discovered that a decrease in either particle size or in the grain size of the microwave susceptible mineral inclusions, led to a decrease in the intergranular stresses developed within the particles. The influence of power density on the absorption of microwave energy by minerals was also investigated, and it was found that by using short concentrated microwave pulses to increase the power density within the material, substantially higher stresses could be generated within the particles at the same power inputs.

Whittles et al., 2003<sup>40</sup>, investigated the effect of power density on the microwave treatment of ores, using finite difference techniques to model microwave heating, thermal conduction, thermal expansion, thermally induced fracturing and strain softening of a particle containing dispersion of 2 mm square pyrite grains in a 15 mm by 30 mm calcite host matrix. Simulations were also performed to determine any change in the uniaxial compressive strength of the particle after microwave heating. It was shown that power density is an important factor in microwave treatment of ores, with the application of high power densities resulting in much greater damage to the particle. It was concluded that utilizing high power densities for shorter times could also drastically reduce the microwave treatment energy required to below 1 kWh/t.

Jones et al., 2005<sup>41</sup>, also investigated the effect of microwave treatment through numerical simulations of a system of microwave absorbing pyrite grains in a microwave transparent calcite host. An important result of this work was the verification and explanation of the observations of Wills et al., 1987<sup>10</sup>, who determined that regularly shaped mineral inclusions with smooth boundaries were much more likely to result in thermally induced intergranular fracture than irregular grains which tend to be damaged by transgranular fracturing as a direct result of thermal treatment. It was determined that for spherical absorbing grains the occurrence of transgranular fracture is highly unlikely as the symmetry of the grain ensures that the compressive stresses generated inside the microwave absorber are equal in all directions, thus reducing the likelihood of shear stresses developing within the grain. As grain shape deviates from spherical, the likelihood of transgranular fracture rises. It was also seen that as the grain size of the microwave absorber decreased, conduction losses resulted in lower temperatures being reached within the absorbing grain at the end of the same exposure time. This resulted in lower stresses being generated around the absorbing grain, with less damage to the host particle as a result.

#### 2.4. Microwave treatment and magnetic properties of minerals

Florek et al., 1996<sup>42</sup>, carried out a study of the effect of microwave treatment on the magnetization of iron ore minerals. It was concluded that the surface characteristics and magnetization of iron ore minerals alter after microwave radiation.

The effect of microwave radiation upon the mineralogy and magnetic processing of amassive Norwegian ilmenite ore was per- formed by Kingman et al. 1999<sup>43</sup>. It has been shown that short periods of exposure can cause fracture at grain boundaries, which leads to the formation of inter-granular fractures. This fracture coupled with an increase in remnant magnetization of the ilmenite mineral has been demonstrated to give rise to an increase in both concentrate grade and valuable mineral recovery. However, the study has also indicated that process efficiency can be effected with over exposure to microwave radiation.

Kingman and Rowson, 2000<sup>44</sup>, showed that a number of minerals, e.g. chalcopyrite, hematite and wolframite, not only heat readily during exposure to microwaves, but also exhibit a considerable increase in the magnetic susceptibility after being exposed to 650W microwave radiation.

Cui et al., 2002<sup>45</sup>, carried out an investigation to study the changes in magnetic properties after roasting to the different types of minerals contained in the oil sands tailings. It was observed that the magnetic susceptibility of ilmenite increased after either oxidation or reduction roasting. For hematite, reduction roasting increased its magnetic susceptibility and oxidation roasting did not seem to have any effect.

Sahyoun et al., 2003<sup>46</sup>, investigated the influence of conventional heat treatment and microwave radiation on chalcopyrite. There was a significant increase in the proportion of material recovered to magnetic fraction and magnetic susceptibility with conventional heating time. XRD analysis detected phase changes in conventional heat-treated chalcopyrite, which increases the magnetic susceptibility of the ore and enables its effective magnetic separation, which is impossible to achieve in its original state. With microwave treatment, the magnetic susceptibility increases and the proportion of material recovered to the magnetic fraction on the induced rolls is also increased. However, XRD analysis failed to detect any phase changes. A possible explanation for this observed behavior can be drawn that the more magnetic component has been formed by microwave treatment is below the threshold of detection of the XRD analyzer.

Uslu et al., 2003<sup>47</sup>, investigated the effect of microwave heating on magnetic processing of pyrite. The microwave treated pyrite samples of -0.420mm fraction were subjected to magnetic separation at magnetic field intensities of 0.1, 0.3 and 0.5T. It was found that pyrite was converted to such ferromagnetic minerals as pyrothite and  $\gamma$ -hematite, and magnetic separation recovery was improved after microwave treatment.

Znamenackova and Lovas., 2005<sup>48</sup>, showed that after 10 min pre- treatment of weakly paramagnetic ore in a microwave oven with maximum power of 900 W, essential change in the magnetic properties of the ore samples occurred and after 15 min, a rapid increase of magnetic susceptibility value was observed, showing the intensive decomposition of siderite. Finally, after 40 min of heating, a microwave sintering of powder grains in the form of agglomerates with molten mass was observed.

Waters et al., 2007<sup>49</sup>, investigated the effect of microwave radiation on the magnetic properties of pyrite. After treatment with a conventional multimodal reactor (2.45GHz and

1900W) for 120 s, the recovery of pyrite in the magnetic fraction after separation increased from 8% (wet) and 25% (dry) to greater than 80% for both process streams. The improvement in the magnetization of the sample has also been noted, determined using a vibrating sam- ple magnetometer (VSM). After exposure to microwave radiation, the magnetization of the mineral sample was increased.

Barani et al., 2011<sup>50</sup>, investigated the effect of microwave radiation on the magnetic properties of an iron ore. Four Iron ore samples were used in this research. Three samples were treated for 30, 60 and 120 S respectively, in a multi-mode microwave oven with a frequency of 2.45GHz and a maximum power of 1100 W. The magnetizations of non-treated and microwave-treated samples were determined using a vibrating sample magnetometer (VSM). With increasing in radiation time to 60 S, the total magnetism saturation and remnant magnetization of the samples were increased. The results show that with further increasing in microwave radiation time up to 120 S, localized sample melting was occurred and the total magnetism saturation and remnant magnetization were decreased. The results showed that the sample composes ferromagnetic and paramagnetic fractions. With increasing in microwave radiation time the magnetic susceptibility of the paramagnetic fraction was decreased from 0.0111 to zero whereas the magnetic susceptibility of the ferromagnetic fraction initially was increased from 0.0687 to 0.3879 then decreased to 0.1894 (at 120 S radiation time). It was confirmed that microwave radiation has a significant effect upon magnetic properties of iron ore. However, there is a limited condition, excessive radiation has a negative effect and reduces the magnetic susceptibility of iron ore.

# 2.5. Microwave assisted pretreatment of refractory gold concentrate

Gold is considered to be refractory when it cannot be easily recovered by alkaline cyanide leaching. The vast majority of refractory gold occurs in sulphidic minerals such as pyrite (FeS<sub>2</sub>), arsenopyrite (FeAsS) and pyrrhotite (FeS). Generally, refractory gold concentrate or ore is pretreated by roasting, O<sub>2</sub>-pressure leaching or bacterial leaching, to render it amenable to gold recovery by alkaline cyanide leaching (Haque, 1987a, b)<sup>51, 52</sup>. Because microwaves in general heat sulphidic minerals easily, it should be possible to pretreat sulphidic refractory gold concentrate by microwave energy. (Haque 1987a, b)<sup>51, 52</sup> conducted laboratory-scale microwave pretreatment tests in air on a typical arsenopyritic refractory gold concentrate. More than 80% of As and S were volatilized as As<sub>2</sub>O<sub>3</sub> and SO<sub>2</sub>, whereas iron was oxidized into hematite (Fe<sub>2</sub>O<sub>3</sub>) at 550°C (uncorrected). Alkaline cyanide leaching of the calcine yielded 98% Au and 60% Ag extractions.

To avoid the formation of As<sub>2</sub>O<sub>3</sub> and SO<sub>2</sub> this author conducted microwave calcination tests on the concentrate in a nitrogen atmosphere in a sealed silica tube. The major products were FeS, arsenious sulphide (As<sub>2</sub>S<sub>3</sub>) and sulphur (S). In addition, this author conducted microwave heating tests on a mixture of this concentrate and (NaOH), No SO<sub>2</sub> and As<sub>2</sub>O<sub>3</sub> evolved during microwave heating of this mixture; instead water soluble products such as; Na<sub>3</sub>AsO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub> were formed. The microwaved solids were leached with water at 75°C. After phase separation, the residue was leached with alkaline cyanide solution, and

yielded 99% Au and 79% Ag extractions. These results opened up a wide range of possibilities for investigation (Woodcock et al., 1989<sup>53</sup>). Non typical refractory gold ore, such as carbonaceous gold ore, some goethite bearing gold tailings, etc., have also been successfully pretreated by microwave heating (Author's unpublished results). Currently, EMR Microwave Technology, Fredericton, N.B., Canada is conducting pilot-scale microwave pretreatment tests on various kinds of refractory gold concentrates, ores and tailing.

Al-Harahsheh et al., 2005<sup>54</sup>, have investigated the leaching kinetics of chalcopyrite under the influence of microwave treatment. Comparison of the amount of copper recovered from chalcopyrite under conventional and microwave heat treatment show marginal, but consistent, improvements in copper recovery when using microwave treatment as opposed to conventional treatment. It was suggested that the increase in copper recovery with microwave leaching was due to localized higher temperatures around the outer shell of the leaching solution as a result of the high dielectric loss factor (and thus low penetration depth) of the solution, and also selective heating of the outer skin of the chalcopyrite particles due to the high conductivity of this material.

Amankwah et al., 2005<sup>55</sup>, performed tests on samples of a gold ore containing quartz, silicates and iron oxides with a head grade of 6.4 g/t of gold, using 2 kW of power in a multimode cavity. It was seen that the microwave treatment resulted in a maximum reduction of 31.2% in crushing strength and a reduction of 18.5% in work index. SEM analysis clearly showed that microwave induced fractures were occurring in the ore, and an improvement of 12% in gold recovery from gravity separation tests showed that this resulted in the liberation of the gold at coarser particles sizes during comminution.

Nanthakumar et al., 2007<sup>56</sup>, investigated microwave roasting of a double refractory gold ore as an alternative method and the results were compared to those obtained by conventional roasting. The compositional changes of the ore during roasting were determined by thermo gravimetric analysis (TGA). In addition, both the real and the imaginary permittivities, which determine the amount of energy absorbed by the ore and the heating rate of the ore respectively, were evaluated. In addition, the microwave heating behavior was studied. Conventional and both direct and indirect microwave roasting tests were performed and in all the cases, the pyrite was readily converted into hematite. Direct microwave roasting could not remove the organic carbon. Indirect microwave roasting was conducted using magnetite as a susceptor and preg-robbing was eliminated when about 94% of the organic carbon was removed. For both conventional and indirect microwave roasting, gold recoveries of over about 98% were achieved after cyanide leaching. For microwave roasting, both the total carbon removal rates and the heating rates were higher and the specific energy consumptions were lower than the corresponding values for conventional roasting.

Amankwah et al., 2008<sup>57</sup>, studied microwave roasting of a double refractory flotation concentrate to oxidize both the sulfides and the carbonaceous matter. The concentrate was characterized by thermo gravimetric and infrared analysis and the microwave absorption characteristics were quantified by determining the permittivities. The microwave heating

behavior studies showed that the sample temperature increased with increasing incident microwave power, processing time and sample mass. Due to the hyperactive response of the concentrate to the microwaves, a low incident power of 600 W was found to be suitable for roasting, as higher powers resulted in sintering and melting of the concentrate. The gold extraction values after cyanidation were over 96% and these were similar to those obtained by conventional roasting. The main advantages of microwave roasting were that both the total carbon removal rates and the heating rates were higher and the specific energy consumptions were lower.

Ma et al., 2008<sup>58</sup>, investigated removal of sulfur and arsenic from refractory flotation gold concentrates, bearing with 14.95% of As and 27.85% of S, by microwave roasting. Cooling patterns of the roasted products obviously affected the removal effects under oxygen-free roasting atmosphere. The highest removal occurred by crucible-uncapped cooling pattern, followed by the so-called half-open cooling pattern, and the crucible-capped cooling pattern attained the lowest removal. The mid pattern would be preferred because it could avoid spontaneous ignition compared to the crucible-uncapped cooling one. Roasting temperature showed obvious effect only above 450°C, increasing with the roasting temperature. However, desulfur was much more difficult than de-arsenic. Under oxygen-free roasting atmosphere, 95% of arsenic was removed when roasted for 40 minutes at 550°C, while the desulfur rate was only about 40%. Comparatively, the removal of sulfur dramatically reached above 90% in oxidizing atmosphere. Additionally the roasted products were analyzed by XRD.

#### 2.6. Dielectric properties of minerals in microwave fields

The nickeliferous laterite ores, in which the nickel occurs in oxide form, represent a significant potential resource of metallic nickel. However, in comparison to the nickel-containing sulfide ores, the extraction costs are relatively high and thus it will be necessary to develop new processing techniques, which are both technically and economically viable. Pickles et al., 2004<sup>59</sup>, investigated the potential application of microwaves for the heating of a nickeliferous limonitic laterite ore ((Fe,Ni)O(OH).nH2O) was investigated. Firstly, since the nickeliferous limonitic laterite ore contains considerable moisture, both free and combined, then thermogravimetric analysis (TGA) was performed in order to characterize the changes, which result from the dehydration processes. Derivative thermogravimetric analysis (DTGA) curves were calculated from the TGA data. Secondly, the real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) permittivities of the ore were measured at frequencies of 912 and 2460 MHz at temperatures up to about 1000 °C using the cavity perturbation technique and these results were related to the DTGA curves. Also, the loss tangent (  $\tan \delta = \frac{\varepsilon''}{\varepsilon'}$  ) was calculated from the permittivity data. Finally, the microwave heating behaviour of the nickeliferous limonitic laterite ore was determined at 2460 MHz. The results show that the both the real ( $\varepsilon'$ ) and imaginary permittivities ( $\varepsilon''$ ) and the loss tangent (  $\tan \delta = \frac{\varepsilon''}{c'}$  ) increase with temperature and change as both the free and the combined moisture are removed. The permittivities ( $\varepsilon'$  and  $\varepsilon''$ ) increased with increasing slope of the TGA curve and vice versa during the goethite to hematite dehydroxylation

reaction, where there was a maximum in the permittivities ( $\varepsilon'$  and  $\varepsilon''$ ). It is proposed that these changes, which occur during the dehydroxylation reaction, are a result of the liberation of hydroxyl units from the goethite structure.

Cumbane et al., 2008<sup>60</sup>, has been used a measurement system, comprising a circular cylindrical TM<sub>0n0</sub> cavity and based on a perturbation technique, for the determination of dielectric properties of five powdered sulphide minerals, which were measured at frequencies of 615MHz, 1410 MHz and 2210 MHz. The complex permittivity was measured from ambient temperature to 650 °C. The dielectric properties of galena and sphalerite exhibit little variation with temperature up to 500 °C. The dielectric properties of pyrite, chalcocite and chalcopyrite, show significant variation with temperature. These are related to composition and phase transformations during heating and were demonstrated by thermo-gravimetric analysis.

# 2.7. Microwave assisted carbothermic reduction of metal oxide

The vast majority of heavy metals oxides and carbon, as charcoal or coke, respond to microwave heating. Therefore, the microwave assisted carbothermic reduction of metal-oxides is possible. If the metal oxide is low lousy (i.e., poor receptor to microwave energy) then added carbon plays the role of microwave heating accelerator. Various researchers have demonstrated that iron oxides (hematite Fe<sub>2</sub> O<sub>3</sub>, magnetite Fe<sub>3</sub> O<sub>4</sub>) mixed with carbon (charcoal or coke) could be reduced to metallic iron (Standish and Worner, 1991<sup>61</sup>, Gomez and Aguilar, 1995<sup>62</sup>).

To compare conventional and microwave reduction, Standish et al. (1990, 1991)63, 61 conducted reduction tests on identical sample mixtures of hematite ore fines, coke and lime powder. A sample of each mixture was heated in an electrically heated muffle furnace at 1000°C, and in a 2450 MHz microwave oven at a power of 1.3 kW. The sample temperature was measured with a thermocouple inserted in the sample and the test was terminated when the temperature reached 1000°C. The results showed the microwave heating rate was much higher than the conventional heating rate. Some phase changes were observed and these might have enhanced the heating rate. Standish et al. (1991, 1990)<sup>61, 63</sup> concluded based on rational assumptions for capital and operating costs, that a microwave reduction process could save 15% to 50% over a conventional operation. Chunpeng et al., 1990<sup>64</sup>, also conducted microwave assisted carbothermic reduction on titanomagnetite concentrate. A powdered sample of titanomagnetite concentrate mixed with lignite powder and CaCO<sub>3</sub> was heated by microwave power of 500 W at 2450 3 MHz. These results, compared with those generated by conventional heating test, confirmed that the reduction rate of metal oxide by microwave heating was faster than by conventional heating. Beside the carbothermic reduction of iron oxides the researchers used microwaves to smelt rare earth magnet alloys, a high value product difficult to produce by conventional techniques. Although these alloys could be produced in a microwave furnace, the furnace needed design changes to eliminate the formation of gas plasma over the melt. Moreover, a suitable microwave transparent material was needed to contain the smelt at high temperature.

#### 2.8. Microwave assisted drying and anhydration

Materials and products such as agricultural, chemical and food product, textile, paper, lumber and many more (Cook, 1986<sup>65</sup>, Schiffmann, 1987<sup>66</sup>, Doelling et al., 1992<sup>67</sup>).Generally, drying refers to the removal of physically adsorbed solvent such as water, acid or high vapour pressure organic substance (e.g., alcohol, acetone, ether, halogenated hydrocarbons, aromatics, etc.). Anhydration refers to the removal of water chemically bound to a substance present intermolecularly as well as to the intramolecular elimination of water from hydroxy or carboxylic compounds. It was observed that the dielectric loss factor of a material to be dried often decreases with the loss of solvent (Schiffmann, 1987<sup>68</sup>). Unpublished results indicate that microwave heating can remove water from hydrated magnesium chloride (MgCl<sub>2</sub>.7H<sub>2</sub>O) and convert goethite (O=Fe–OH) into hematite (Fe<sub>2</sub>O<sub>3</sub>), (Haque, 1998<sup>68</sup>).

If both the solvent and the substance to be dried are transparent to microwaves (i.e., no heating by microwave energy), then a suitable microwave heat accelerator, such as carbon, magnetite or silicon carbide must be added to the system to heat the added material to volatilize the solvent. This heating concept may be applied in the removal of volatile contaminants from soil, or even ore material (George et al., 1994<sup>69</sup>).

#### 2.9. Microwave assisted minerals leaching

Analytical chemists have used microwave heating devices routinely for the dissolution of metals, minerals and various chemical products in chemical analysis (Matthes et al., 198370, Kingston and Jassie, 198571). As mentioned earlier, microwave heating is material specific, offers a faster heating rate and consequently a faster dissolution rate than conventional heating. In fact, the principle of the dissolution of analytical samples has been applied to the leaching of various minerals contained in an ore or concentrate sample. Kruesi and Frahm, 1982<sup>72</sup> and Kruesi,1986<sup>73</sup> conducted microwave assisted leaching of lateritic ores containing oxides of nickel, cobalt, and iron. The metals of these mineral components were converted into their chlorides by microwave heating (1200 W, 2450 MHz, N2 atmosphere) a mixture of the ore and ammonium chloride between 177°C and 312°C for 4-5 min, followed by water leaching at 80°C for 30 min. Nickel and cobalt extractions were 70% and 85%, respectively, and are comparable with roasting at 300°C in a conventional rotary kiln for 2 h. Similarly, copper ores or concentrates containing oxidic and/or sulphidic minerals were solubilized by microwave heating a mixture of the ore or concentrate and ferric or ferrous chloride between 350°C and 700°C, followed by hot brine leaching. Copper extraction was 96% (Kruesi and Frahm, 198274). To study nickel extraction, Chunpeng et al., 199024, conducted dry way chloridization of pentlandite concentrate with ferric chloride by microwave heating (500 W, 2450 MHz) in a chlorine atmosphere for 8–23 min, followed by aqueous leaching at pH 2 for 30 min. The maximum nickel recovery (~99%) was obtained from the sample heated for 14-17 min.

Peng and Liu, 1992a<sup>74</sup>, 1992b<sup>75</sup>, applied microwave energy in the leaching of sphalerite with acidic ferric chloride (FeCl<sub>3</sub> –HCl). Various leach parameters; such as 3 temperature, particle

size and ferric chloride concentration were studied. Test results demonstrated that the leaching rate of zinc increased with temperature in both microwave and conventional heating systems. They reported 90% zinc extraction when the leach conditions were at 0.1 M HCl, 1.0 M FeCl<sub>3</sub>, 60 min microwave heating at 95°C. Under similar conditions conventional leaching yielded only 50% zinc extraction. Weian, 1997<sup>74</sup>, conducted microwave assisted acidic ferric chloride leaching of a copper sulphide concentrate. The principal copper minerals in this concentrate were chalcocite (Cu<sub>2</sub> S) and chalcopyrite (CuFeS<sub>2</sub>). The leach slurry was heated directly by microwaves (700 W, 2450 MHz) for various lengths of time. Copper recovery reached 99% after 40–45 min of microwave heating whereas conventional heating required 2h to reach the same level of extraction. This author concluded that microwave assisted leaching provided a faster dissolution rate of copper and overcame the detrimental effect from elemental sulphur build-up on the mineral surface during the leaching of the copper sulphide concentrate.

In the recovery of copper from a chalcopyritic concentrate (30.1–30.3% copper) Antonucci and Correa,1995<sup>75</sup>, conducted a sulfation reaction by microwave heating (2450 MHz for laboratory tests and 915 MHz for semi pilot scale tests) a paste-like mixture of the concentrate and sulphuric acid followed by water leaching at 60°C and pH 1.6. Semi pilot scale tests were conducted in a 35 L capacity Teflon-lined cylindrical rotatory reactor. The whole setup was placed in a multimode applicator and microwaves (915 MHz) were applied. There was an opening on top of the reactor through which the charge (conc. + H<sub>2</sub> SO4) was fed and which also served as the outlet for the recovery of gas and elemental sulphur. The test results indicated that higher copper extraction could be achieved at higher sulphuric acid dosage. These authors concluded that copper extraction>96% could be achieved by microwaving a mixture containing 1.80 kg acid/kg conc. The process gave elemental sulphur and cupric sulphate. Antonucci and Correa, 1995<sup>79</sup>, also commented that although this process demanded more energy than the conventional smelting process the production of elemental sulphur was advantageous.

#### 2.10. Microwave assisted spent carbon regeneration

Currently, more and more gold ore processing industries are using activated carbon in CIP (carbon in pulp) or CIL (carbon in leach) operation. The carbon is regenerated after each cycle of adsorption and desorption of gold cyanocomplex. Usually, this spent carbon is regenerated by washing with a mineral acid followed by heating at high temperature (600°C to 750°C) in an externally heated rotary kiln (Avraamides et al., 1987<sup>76</sup>).

Haque et al., (1991<sup>77</sup>, 1993<sup>78</sup>), conducted laboratory scale carbon regeneration tests by microwave (2450 MHz) heating and confirmed the feasibility of spent carbon regeneration by microwave heating. Subsequent pilot scale carbon regeneration tests data (915 MHz) demonstrated that microwave regenerated carbon performed well or better than conventionally regenerated carbon (Bradshaw et al., 1997<sup>77</sup>). Currently, Ontario Hydro, Toronto, Ontario, Canada is marketing this technology.

#### 2.11. Microwave assisted waste management

Processing industries invariably generate waste material; mine-milling industries are no exception. To mitigate the danger presented by the constituents of the waste technologies are being investigated to minimize the waste generated and to provide safe handling, transportation, storage, destruction, removal or disposal of the hazardous waste. Currently, microwave energy is showing considerable potential in the management of a vast array of gaseous, liquid and solid wastes (Wicks et al., 1995<sup>78</sup>). Mine milling operations generate large volumes of solid waste with acid generation potential, liquid waste containing acid, toxic heavy metals and non-metals, cyanide, ammonia, organics etc., and gaseous wastes such as, sulphur dioxide (SO<sub>2</sub>), hydrogen sulphide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), oxides of nitrogen (NO<sub>x</sub>).

Cha (1993) demonstrated in laboratory scale tests that SO<sub>2</sub> and NO<sub>x</sub> in industrial off-gas can be decomposed into elemental nitrogen and sulphur, and a mixture of carbon dioxide and carbon monoxide. The first step of the process involves passing the off-gas stream containing SO<sub>2</sub> and/or NO<sub>x</sub> through a column packed with activated carbon to adsorb the toxic gases. The loaded carbon column is then heated by microwaves and the resulting CO, CO<sub>2</sub> and N<sub>2</sub> are released into atmosphere. Sulphur is cooled in a spray chamber and collected for sale.

H<sub>2</sub>S is a very toxic gas produced during refining crude petroleum. Generally, hydrogen sulphide waste gas streams are treated by the Claus process, which is based on partial oxidation of hydrogen sulphide into sulphur and water. The Claus oxidation process requires a suitable oxidant mixture. The Kurchatov Institute in Moscow, Russia, developed a process for the decomposition of hydrogen sulphide into hydrogen and sulphur by applying a microwave plasma (plasmatron). The Argon National Laboratory (ANL) of the USA developed a 'plasma-chemical waste treatment process' in which a hydrogen sulphide waste stream is passed through a microwave-generated plasma reactor where it decomposes into hydrogen and sulphur. ANL test results indicated that this decomposition ranged from 65% to 80% per single pass. Preliminary energy and economic analysis data suggest that the plasma-chemical waste treatment process has the potential for annual energy savings of 40 to 70 trillion Btu or \$500 to \$1000 million for the refining industries. Further details of the process are available from ANL (Harkness, 1994<sup>79</sup>).

Steel making furnaces generate metallic dust (Electric arc furnaces ,EAF), which use galvanized scrap metals, generate dust which often contains water leachable lead (Pb), cadmium (Cd), chromium (Cr) and zinc (Zn). This kind of dust is classified hazardous and needs to be treated prior to disposal. Currently, combined EAF dust production in Canada and the USA is 677,000 tons per year (Ionescu et al., 1997<sup>80</sup>). A current dust treatment process becomes economical if the treatment scale is 40,000 tons/year or above (Xia and Pickles, 1996<sup>16</sup>).

A large number of EAF mills are mini-mill type operations which need a treatment process that is a small scale, on-site and economic. Ghoreshy and Pickles, 1994<sup>81</sup>, Chose microwave

energy (900 W, 2450 MHz) for the heating a typical EAF dust mixed with powdered carbon for various length of time. Over 90% zinc was volatilized as ZnO (zinc oxide), which was condensed and collected on an alumina plate placed on top of the reaction crucible. The laboratory scale test results demonstrated that zinc removal was rapid and selective. The iron rich residue can be recycled in an iron or steel making furnace. Steel making slag usually contains 20 wt. % iron. To modify the physical characteristics of and to recover iron from the slag. Hatton and Pickles, 1994<sup>82</sup>, Conducted laboratory scale microwave heating tests (1000 W, 2450 MHz). The heating behavior of the steel making slag was investigated with and without the addition of carbon or magnetite. Test results demonstrated that both carbon and magnetite addition increased the heating rate of the slag; 1000°C with carbon, 800°C with magnetite, compared to 650°C without any addition. The amount of iron recovered increased with heating time and reached as high as 90%. Microwave heating altered the physical and chemical properties of the slag.

#### 2.12. Latest developments in microwave processing of minerals ores

The mechanical size reduction of solids is an energy intensive and highly inefficient process. Therefore, there is great incentive to improve the efficiency of size reduction and mineral separation processes. Over several decades, this has promoted significant amounts of research, unfortunately, this has only led to small, incremental improvements in efficiency. One area, which has shown significant promise for improving the efficiency of mineral comminution and separation processes, is microwave assisted grinding.

Until recently, the majority of test work carried out concerning microwave treatment of minerals utilized standard multi-mode cavities, similar to that found in a conventional kitchen microwave oven. The multimode cavity whilst mechanically simple suffers from poor efficiencies and low electric field strengths, vital to high power adsorption. Whilst the influence of microwave energy from this type of cavity has been shown to have a significant influence on ores and minerals, the inefficiencies of the application method have led to conclusions that at present, microwave treatment of minerals (despite the numerous process benefits) is not viable.

More recent studies have presented studies describing the influence of high electric field strength microwave energy on minerals and ores. It is well known that microwave power density in a material (or volumetric power absorption) is directly proportional to the square of the electric field strength within the material. Therefore, it was shown that if local electric field strength can be magnified energy adsorption or heating rate can be amplified many times without the use of further energy. In turn, this lead to reduced cavity residence times and reductions in the required microwave energy input per ton. Detailed tests at the University of Nottingham have shown that in cavities with high electric field strengths the microwave energy consumption to achieve a desired reduction in strength can be as little as 2% of that required in previous work.

Investigations have been carried out on several economically important ores utilizing a high electric field strength cavity for microwave treatment. A systematic approach was used in

order to establish the influence of applied power level and exposure duration on each ore sample. Assessment was made of the influence of particle size on heating rate (this will have an effect on the delivery and presentation methods). During sample treatment, assessment was made of electrical energy consumption, the efficiencies of the system being calculated by standard methods. To support the test programme, results of numerical finite difference simulations are presented which illustrate the importance of microwave and ore variables on post treatment ore properties. The results of the simulations showed that if the microwave energy can be supplied to the sample very rapidly (in order of microseconds) then thermal conduction from the heated phase into the bulk ore can be minimised and thermally induced stress is maximised.

In order to validate the simulation predictions a series of experiments are reported which utilise a pulsed microwave energy delivery system on several ore types. Samples were exposed in a multimode cavity connected to a high voltage solid state modulator and pulse generator. The experimental set up was able to deliver pulses at applied power levels of 1-5MW and pulse durations of 1-4µs at frequency of 2.8GHz.

Scanning electron microscopy and image analysis were used to map the pattern of induced fracture across the pulsed treated samples. It was shown that peak power level was the major influence on the degree of fracture with the highest powers giving greater effects. It was also shown that the fracture induced was predominately grain boundary related and the fractures did not seem to run into each other causing weakening of the bulk ore structure as found in samples treated in continuous wave microwave systems. Treated and untreated samples were then processed by appropriate separation techniques to determine if more valuable mineral could be recovered as a result of treatment. It is shown that pulsed treatment positively influences the recovery of valuable minerals from the different ore types investigated.

# 3. Summary and recommendations

The information compiled in this chapter demonstrates that microwave energy has the potential for application in mineral treatment and metal recovery processes such as heating, drying, grinding, leaching, roasting, smelting, carbothermic reduction of oxide minerals, pretreatment of refractory gold concentrate or ore, spent carbon regeneration and waste management. Usually, microwave energy is more expensive than electrical energy, mainly due to the low conversion efficiency from electrical energy (50% for 2450 MHz and 85% for 915 MHz). However, the efficiency of microwave heating is often much higher than conventional heating and overcomes the cost of the energy. Generally, mineral processing industries treat a large tonnage of ore or concentrate per day (several thousand to over 30,000 tonnes). Currently, the highest microwave power generator available is 75 kW at 915 MHz. To treat such a large tonnage of ore or concentrate a number of generators would have to be operated in parallel, which may not offer a cost advantage over the conventional process, for example,

pretreatment of refractory gold concentrate, regeneration of CIP spent carbon, roasting or smelting of ore or concentrate for smaller operations. Furthermore, it is possible to apply microwave energy to the leaching of ore or concentrate in slurry or semi-solid mixture (paste) at ambient pressure to yield a metal extraction comparable with pressure leaching. Today's processing industries, including mineral processing, are facing increasing global competition, more stringent environmental regulations, higher overhead costs and shrinking profit margins. The processing industries are addressing these problems in various ways, and their processes are approaching peak product yield as well as performance and productivity efficiency. In the foreseeable future processing industries will be looking for high performance conventional as well as nonconventional processing technology. This is the point at which processes based on microwave energy will get favorable consideration. The continued development of high power microwave generator and precision temperature measuring devices for high temperature operation should have positive impact in the acceptance of microwave assisted mineral treatment process. The current R&D status indicates that microwave energy has the potential to play an important and possibly crucial role in future mineral treatment processes. However, challenges remain to be overcome through a fundamental understanding of microwave interaction with minerals, innovation, R&D investigations and advanced engineering, especially in designing efficient applicators, processes and process control devices.

# Author details

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# 4. References

- Meyer, C., Umm Fawakhir, Bir., 1997, Insights into Ancient Egyptian Mining, JOM, 49 (3), 1997, pp. 64-68.
- [2] Oldfather, C.H., 1967, Diodorus of Sicily, Cambridge, Harvard U. Press.
- [3] The Tech., Vol. V, Massachusetts Institute of Technology, Boston, April 1, 1886, No. 12, pp. 179-180.
- [4] Cowen, R., Exploiting the Earth April, 1999, (online draft copy), http://www.geology.ucdavis.edu/~cowen/~GEL11.
- [5] Fitzgibbon, K.E. and Veasey, T.J., 1990, Thermally Assisted Liberation A Review, Minerals Engineering, vol 3, 1/2, pp 181-185.
- [6] Yates, A., Effect of Heating and Quenching Cornish Tin Ores before Crushing, Trans IMM, 28, 1918-1919, pp. 41.
- [7] Holman, B.W., 1926, Heat Treatment as an Agent in Rock Breaking, Trans IMM, 26, pp. 219.
- [8] Myers, W.M., 1925, Calcining as an Aid to Grinding, J. Am. Ceram. Soc., 8, pp. 839.

- [9] Prasher, C.L., 1987, Crushing and Grinding Process Handbook, John Wiley & Sons Limited, Chichester.
- [10] Wills, B.A.; Parker, R.H.; Binns, D.G., 1987, Thermally Assisted Liberation of Cassiterite, Minerals and Metallurgical Processing, pp 94-96.
- [11] Scheding, W.M., Sherring, A.J., Binns, D., Parker, R.H., Wills, B.A., 1981, The Effect of Thermal Pre-treatment on Grinding Characteristics, Camborne School of Mines Journal, vol 81, pp. 43-44.
- [12] Kanellopoulos, A.; Ball, A., The Fracture and Thermal Weakening of Quartzite in Relation to Comminution, Journal of the South African Institute of Mining and Metallurgy, pp 45-52.
- [13] Pocock, J., Veasey, T.J., Tavares, L.M., King, R.P.,1975, The Effect of Heating and Quenching on the Grinding Characteristics of Quartzite, Powder Technology, vol. 95, 1998, pp 137-142.
- [14] Sherring, A.J., 1981, The Effect of Thermal Pretreatment on Grinding Characteristics, Internal Report, Camborne School of Mines.
- [15] Manser, R.J., 1983, The Economics of Thermal Pretreatment, Internal Report, Camborne School of Mines.
- [16] Xia, K., Pickles, C.A., 1997, Applications of Microwave Energy in Extractive Metallurgy, a Review, CIM Bulletin, Vol. 90, No. 1011.
- [17] Ford, J.D., Pei, D.C.T., High Temperature Chemical Processing via Microwave Absorption, J. Microwave Power, Vol. 2, No. 2, pp. 61-64.
- [18] Wong, D., 1975, Microwave Dielectric Constants of Metal Oxides at High Temperature, MSc. Thesis, University of Alberta, Canada.
- [19] Tinga, W.R., 1988, Microwave dielectric constants of metal oxides, part 1 and part 2. Electromagnetic Energy Reviews 1 (5), 2–6.
- [20] Tinga, W.R., 1989, Microwave dielectric constants of metal oxides, part 1 and part 2. Electromagnetic Energy Reviews 2 (1), 349–351.
- [21] Chen, T.T., Dutrizac, J.E., Haque, K.E., Wyslouzil, W., Kashyap, S., 1984, The relative transparency of minerals to microwave radiation. Can. Metall. Quart. 23 (1), 349–351.
- [22] McGill, S.L., Walkiewicz, J.W., 1987, Applications of microwave energy in extractive metallurgy. J. Microwave Power and Electromagnetic energy, 22 (3), 175–177.
- [23] Walkiewicz, J.W., Kazonich, G., McGill, S.L., 1988, Microwave heating characteristics of selected minerals and compounds. Mineral and Metallurgical Processing, 5 (1), 39–42.
- [24] Chunpeng, L., Yousheng, X., Yixin, H., 1990, Application of microwave radiation to extractive metallurgy. Chin. J. Met. Sci. Technol. 6 (2), 121–124.
- [25] Barani, K., Koleini. S.M.J., 2012, Effect of sample Geometry and Placement on Iron Ore Processing by Microwave, ICKEM II, Singapore.
- [26] Walkiewicz, J.W., Clark, A.E., McGill, S.L., 1991, Microwave-assisted grinding. IEEE Transactions on industry applications 27 (2), 239.
- [27] Walkiewicz, J.W., Lindroth, D.P., Clarck, A.E., 1993, Grindability of Taconite Rod Mill Feed Enhanced by Microwave Induced Cracking, SME Annual Meeting, Reno, Nevada.
- [28] Tavares, L.M., King, R.P., 1996, Effect of Microwave-Induced Damage on Single-Particle Comminution of Ores, SME Annual Meeting, Phoenix, Arizona.
- [29] Tavares, L.M., King, R.P.,1996, Fracture Energies of Copper Ore Subject to Microwave Heating, Utah Comminution Center, University of Utah.

- 102 The Development and Application of Microwave Heating
  - [30] Marland, S., Han, B., Merchant, A., Rowson, N., 2000, The Effect of Microwave Radiation on Coal Grindability, Fuel, 79, pp. 1283-1288.
  - [31] Kingman, S.W.; Vorster, W.; Rowson, N.A., 2000, The Influence of Mineralogy on Microwave Assisted Grinding, Minerals Engineering, 13 (3), 313-327.
  - [32] Wang, Y., Forssberg, E., 2000, Microwave Assisted Comminution and Liberation of Minerals, Mineral Processing on the Verge of the 21st Century, Özbayoğlu et al. (eds), Balkema, Rotterdam.
  - [33] Vorster, W.; Rowson, N.A.; Kingman, S.W., 2001, The Effect of Microwave Radiation Upon the Processing of Neves Corvo Copper Ore, Int. J. Miner. Process., vol. 63, pp 29-44.
  - [34] Kingman, S.W., Jackson, K., Cumbane, A., Bradshaw, S.M., Rowson, N.A., Greenwood, R., 2004, Recent Developments in Microwave-Assisted Comminution, Int. J. Miner. Process, 74, pp. 71-83.
  - [35] Amankwah, R.K., Khan, A.U., Pickles, C.A., Yen, W.T., 2005, Improved Grindability and Gold Liberation by Microwave Pretreatment of a Free-milling Gold Ore, Trans. Inst. Min. Metall. C., Vol. 114, pp. C30-C36.
  - [36] Koleini, S.M.J., Barani, K., 2008, The effect of microwave radiation upon grinding energy of an iron ore, Microwave Technology Conference, Cape town, South Africa.
  - [37] Barani. K., Koleini., S.M.J., 2010, The effect of microwave treatment upon an iron Ore comminution, international mining congress, Tehran, Iran.
  - [38] Koleini, S.M.J., Barani, K., Rezaei, B., 2012, The effect of microwave treatment upon dry grinding kinetics of an iron ore, Mineral Processing and Extractive Metallurgy Review Journal, vol. 33 (2), pp.159-169.
  - [39] Salsman, J.B.; Williamson, R.L.; Tolley, W.K.; Rice, D.A., 1996, Short-Pulse Microwave Treatment of Disseminated Sulfide Ores, Minerals Engineering, vol 9, no.1, pp 43-54.
  - [40] Whittles, D.N., Kingman, S.W., Reddish, D.J., 2003, Application of Numerical Modelling for Prediction of the Influence of Power Density on Microwave Assisted Grinding, Int. J. Min. Proc., 68, pp. 71-91.
  - [41] Jones, D.A., Kingman, S.W., Whittles, D.N., Lowndes, I.S., 2005, Understanding Microwave Assisted Breakage, Minerals Engineering, 18, pp. 659-669.
  - [42] Florek, I., Lovas, M., Murova, I., 1996, The effect of microwave radiation on magnetic properties of grained iron containing minerals, in: Proceedings of the 31st International Microwave Power Symposium, Boston, USA.
  - [43] Kingman, S.W., Corfield, G.M., Rowson, N.A., 1999, Effect of microwave radiation upon the mineralogy and magnetic processing of amassive Norwegian ilmenite ore, Magn. Electrical, No. 9. pp.131–148.
  - [44] Kingman, S.W., Rowson, N.A., 2000, The effect of microwave radiation on the magnetic properties of minerals, J. Microwave Power Electromagn. Energy 35 () 144–150.
  - [45] Cui, Z., Liu, Q., Etsell, T.H., 2002, Magnetic properties of illmenite, hematite and oilsand mineral after roasting, Miner. Eng. Vol. 15 pp.1121–1129.
  - [46] Sahyoun, C., Kingman, S.W., Rowson, N.A., 2003, The effect of heat treatment on chalcopyrite, Phys. Sep. Sci. Eng. 12 pp.23–30.
  - [47] Uslu, T., Ataly, U., Arol, A.I., 2003, Effect of microwave heating on magnetic separa- tion of pyrite, Colloid Surf. A: Physicochem. Eng. Aspects 225, (2003), 161–167.

- [48] Znamenackova, I., Lovas, M., 2005, Modification of magnetic properties of siderite ore by microwave energy, Sep. Purif. Technol. 43 (2005), 169–174.
- [49] Waters, K.E., Rowson, N.A., Greenwood, R.W., Williams, A.J., 2007, Characterising the effect of microwave radiation on the magnetic properties of pyrite, Sep. Purif. Technol. 46(2007)9–17.
- [50] Barani. K., Koleini., S.M.J., Rezaei. B., 2011, Magnetic properties of an iron ore sample after microwave heating magnetic paper, Sep. Purif. Technol. 76 () 331-336.
- [51] Haque, K.E., 1987a. Gold leaching from refractory ores—literature survey. Min. Proc. Extv. Metall. Rev. 2, 235–253.
- [52] Haque, K.E., 1987b. Microwave irradiation pretreatment of a refractory gold concentrate. In: Salter, R.S., Wyslouzil, D.M., McDonald, G.W. \_Eds.., Proc. Int. Symp. on Gold Metallurgy. Winnipeg, Canada, pp.327–339.
- [53] Woodcock, J.T., Sparrow, G.J., Bradhurst, D.H., 1989, Possibilities for using microwave energy in the extraction of gold, Proc. 1st Australian Symp. on microwave power applications. Wollongong, Australia.
- [54] Al-Harahsheh, M., Kingman, S., Hankins, N., Somerfield, C., Bradshaw, S., Louw, W., 2005, The Influence of Microwaves on the Leaching Kinetics of Chalcopyrite, Minerals Engineering, 18(13-14), 1259-1268.
- [55] Amankwah, R.K., Khan, A.U., Pickles, C.A., Yen, W.T., 2005, Improved Grindability and Gold Liberation by Microwave Pretreatment of a Free-milling Gold Ore, Trans. Inst. Min. Metall. C., Vol. 114, March, pp. C30-C36.
- [56] Nanthakumar, B., Pickles, C.A., Kelebek, S., 2007, Microwave treatment a double refractory gold ore, Minerals Engeneering, Vol.120, pp.1109-1119
- [57] Amankwah, R.K., Pickles, C.A., 2008, Microwave roasting of a carbonaceous sulphidic gold, MEI Conference, Microwave Technology, Cape Town, South Africa
- [58] Ma,S., Luo, W., Mo, W., Su, X., Liu, P., Yang, J., 2008, Desulfur and de-arsenic of refractory gold concentrate by microwave roasting, MEI Conference, Microwave Technology, Cape Town, South Africa.
- [59] Pickles, C.A., 2004, Microwave heating behaviour of nickeliferrous limonitic laterite ores, Minerals Engineering, Vol.17, pp.775-784.
- [60] Cumbanea, A.J., Miles, N.J., Lester, E., Kingman, S.W., Bradshaw, S.M., 2008, Dielectric properties of sulphide minerals, MEI Conference, Microwave Technology, Cape Town, South Africa.
- [61] Standish, N., Worner, H., 1991, Microwave application in the reduction of metal oxides with carbon. Iron and Steel Maker 18 (5), 59–61.
- [62] Gomez, I., Aguilar, J.A., 1995, Microwave for reduction of iron ore pellet by carbon. Mat. Res. Soc. Proc. 366, 347–352.
- [63]Standish, N., Worner, H.K., Gupta, G., 1990, Temperature distribution in microwave heated iron ore–carbon composites. J. Microwave Power Electromagnet Energy 25 (2),75–80.
- [64] Chunpeng, L., Yousheng, X., Yixin, H., 1990, Application of microwave radiation to extractive metallurgy. Chin. J. Met. Sci. Technol. 6 (2), 121–124.
- [65] Cook, N.P., 1986, Microwave Principles and System, Chapter 1. Prentice Hall.
- [66] Schiffmann, R.F., 1987, Microwave and dielectric drying. In: Majumder, A.S. (Eds)., Handbook of Industrial Drying. Marcel Dekker, pp. 327–356.

- 104 The Development and Application of Microwave Heating
  - [67] Doelling, M.K., Jones, D.M., Smith, R.A., Nash, R.A., 1992, The development of a microwave fluid-bed processor: 1. Construction and qualification of a prototype laboratory unit, Pharmaceutical Research 9 (11), 1487–1501.
  - [68] Haque, K.E., 1998, Unpublished data, CANMET, 555 Booth St., Ottawa, ON, K1A 0G1, Canada.
  - [69] George, C.E., Rao, G.V.N., Thalakola, V., 1994, Thermal desorption of contaminants using microwave heated rotary mixture, Proceedings, 29th Microwave Power Symposium. Chicago, IL.
  - [70] Matthes, S.A., Farrell, R.F., MacKie, A.J., 1983, A microwave system for the acid dissolution of metal and mineral samples, US Bureau of Mines, TRP 120.
  - [71] Kingston, H.M., Jassie, L.B., 1985, Introduction to microwave sample preparation, theory and practice, Chapters 2 and 3, ACS professional reference book, Am. Chem. Soc.
  - [72] Kruesi, P.R., Frahm, V.H., 1982, Process for the recovery of nickel, cobalt and manganese from their oxides and silicates, Canadian patent 1,160,057, US patent 4,311,520 and 4,324,582.
  - [73] Kruesi, W.H., Kruesi, P.R., 1986, Microwave in laterite processing. Proceedings of CIM 25th Conf. of Metallurgists, Toronto.
  - [74] Weian, D., 1997, Leaching behaviour of complex sulphide concentrate with ferric chloride by microwave irradiation, Rare Metals 16 (2), 152–155.
  - [75] Antonucci, V., Correa, C., 1995, Sulphuric acid leaching of chalcopyrite concentrate assisted by application of microwave energy, Proc. of the Copper 95-Cobre 95, Int. Conf. Vol. 111, Santiago, Chile.
  - [76] Avraamides, J., Miovski, P., Van Hooft, P., 1987, Thermal reactivation of carbon used in the recovery of gold from cyanide pulps and solutions, Research and Development in Extractive Metallurgy, The Aus. I.M.M, Adelaide Branch.
  - [77] Bradshaw, S.M., Van Wyk, E.J., deSwardt, J.B., 1997, Preliminary economic assessment of microwave regeneration of activated carbon for the carbon in pulp process, J. Microwave Power and Electromagnetic Energy 32 (3), 131–144.
  - [78] Wicks, G.D., Clark, D.E., Schulz, R.L., Folz, D.C., 1995, Microwave technology for waste management applications including disposition of electronic circuitry, In: Clark, D.E., Folz, D.C., Oda, S.J., Silberglitt, R. (Eds)., Microwaves: theory and application in material processing. Vol. 111, pp. 79–89.
  - [79] Harkness, J.B.L., 1994, Plasma-chemical waste-treatment process for hydrogen sulphide. Proc. 29th Microwave Power Symposium, Chicago, IL.
  - [80] Ionescu, D., Meadowcraft, T.R., Barr, P.V., 1997, Classification of EAF dust and ZnO content and an assessment of leach performance, Can. Metall. Quart. 36 (4), 269–281.
  - [81] Ghoreshy, M., Pickles, C.A., 1994, Microwave processing of electric arc furnace dust, Proc. of 52nd Elect. Furn. Conf., Nashville, TN, pp. 187–195.
  - [82] Hatton, B.D., Pickles, C.A., 1994, Microwave treatment of ferrous slag. Proc. of Steel making Conf. ISS-AIME, Chicago, USA, Vol. 72, pp. 435–442.