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MICROWAVE ASSISTED BREAKAGE OF METALLIC SULFIDE BEARING ORE

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Abstract

A refractory ore body located in Michigan's Upper Peninsula contains high concentrations of nickel and copper chiefly occurring in the minerals pyrrhotite, chalcopyrite, and pentlandite. Refractory ore bodies are difficult to treat by conventional mineral processing methods so microwave pre-treatment of the ore is employed to increase metallic-particle/host rock liberation by making use the differential thermal expansion properties of the mineral phases that absorb microwave energy. The Curie temperature measurement of metallic-bearing particles is in agreement with the known value for pyrrhotite occurring at 325°C. A nickel-rich iron sulfide mineral is found to be in occurrence and also appears to be magnetic under BSE imaging. It is shown the ore particles heat rapidly when exposed to microwave radiation for short durations of time mainly due to the high concentration of ferromagnetic mineral phases. Rapid heating causes thermal expansion of constituent mineral phases that produce cracks within ore particles. SEM imaging shows fracture occurring along grain boundaries and throughout host rock matrix. Ball milling experiments show an increased grindability of the ore resulting in a decrease in work index values.

Introduction

Crushing and grinding operations consume 50-70% amount of energy used in mineral processing operations [1]. All these processes involve high energy impact of surfaces to develop compressive stresses that produce cracks to initiate breakage of particles. Microwave pre-treatment of certain types of ore might provide an energy savings to these type grinding processes by taking advantage of the tensional forces produced by selectively heating microwave absorbing type mineral phases. The heating of ore particles produces cracking by thermal expansion of the constituent mineral phases. Conventional heating has been investigated and shown to positively aid in grinding processes but determined energy inefficient to be used commercially.

Minerals that absorb microwave energy and rapidly heat are termed high loss. Not all minerals present within an ore particle will absorb microwave energy but will heat as a result of thermal conduction from neighboring high loss minerals. All minerals are subjected to heating but selectively heating high loss minerals causes different rates of thermal expansion between mineral grains. Thus, it is the difference that minerals expand and contract during heating and cooling processes that cause cracking.

By selectively heating high loss minerals contained within the ore, crack formation can be produced in short durations of time with high power density. If the power density of ore particles under microwave irradiation is better understood, pre-treatment of ore can potentially result in a large energy savings in the crushing and grinding process. Though microwave heating of refractory ore particles is not well understood, the breakage characteristics after exposure are shown to increase with microwave energy exposure time. It is observed though that increasing exposure time can result in localized melting of mineral phases.

The amount of thermal energy generated by an electromagnetic field within a particle exposed microwave radiation is known as the power absorption density [2]. It is dependent on the internal electric field strength within the minerals, the frequency of the microwave radiation, and on the dielectric and magnetic properties of mineral phases. If the electromagnetic field strength is known, the power absorption density per unit volume of a mineral can be approximated by the equation:

$$P = 2\pi f_0 \left(\varepsilon_0 \varepsilon'' E^2 + \mu_0 \mu'' H^2\right)$$

Where P_d is power density (W/m³), f is the frequency of the electromagnetic radiation (Hz) ε_0 is the permittivity of free space (8.845×10^{-12} F/m), ε_r'' is the relative permittivity of the mineral phase, E_0 is the magnitude of the electric field, μ_0 is the permeability of free space, and μ_r'' is the relative permeability of the mineral phase, all of which are proportional to the microwave energy (V/m) propagating thru the mineral.

Future work will investigate the effect of different microwave power and frequency but current work is performed with a conventional multimode 1000W, 2.45GHz microwave applicator. Understanding operating frequency and power levels insures optimum processing controls. Figure 1 displays the interrelated processing parameters that affect the power absorption density of ore particles when exposed to microwave radiation.

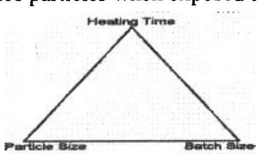

Fig.1. Relation of heating time, particle size and batch size during microwave treatment of ore particles

The minerals contained in the ore body exhibit different magnetic and electrical properties. A mineral that absorbs microwaves due to its electronic structure heats by loss caused by its relative permittivity. Conversely, a mineral heating by absorption and loss due to its magnetic structure heats by its relative permeability. As many minerals display a wide variety of ionic character and all minerals are classified according to their magnetic properties it is not always clear as to the mechanism of microwave absorption. Also, grain size, impurities and defects all contribute to the microwave absorption properties of a mineral.

Experimental

Magnetic Measurements

Magnetic susceptibility investigations were carried out at IIT Kanpur, India. The equipment made available is used mainly for metals and ceramics to generate hysteresis loops and Curie temperature measurements, so it is only possible to test small sample sizes (>2g). Large ore particles were crushed into smaller pieces and particles with metallic appearance were hand-picked for testing. The Curie temperature measurement was made up to 400°C using conventional heating, which was high enough temperature to cause a rapid decrease in the magnetic susceptibility of samples.

Microwave Treatment

The microwave used to obtain materiel for grinding tests was a conventional multi-mode 1000W oven with a 1.1 ft^3 cavity and glass turntable. Core samples were jaw crushed then later gyratory and roll crushed to obtain particles of various sizes for classification. After classifying a specific size range for a bulk sample of crushed ore product, the material is sent through a particle splitter to achieve homogenous bulk samples for grinding experiments. Samples were microwave treated as follows: For the gyratory -6+8 sample, 100 gram samples were treated in an alumina crucible placed in the center of the cavity. For jaw crushed -6+10 and -8+12, 500 gram samples were distributed evenly, single layered on the rotating glass tray of the microwave applicator. All samples were heated for the indicated times, removed from the applicator and cooled on a ceramic plate. A portion of microwave treated ore was then mounted in epoxy, polished to 0.05 µm, and examined under the optical and SEM microscope to better understand morphology of the ore after being heated with microwaves. At various times throughout testing, water in a 100 ml beaker was heated for 30 sec to test if the magnetron was still functioning properly.

Grinding Experiments

Laboratory work index measurements are often time consuming with significant amounts of material needed for completion when using F. Bonds grinding procedures [3]. About 3-4kg is needed for completion and only one sieve size is used for testing for oversize and undersize material. Ore particles passing the 6 mesh sieve (3327µm) were run through a particle splitter a dozen times to ensure homogeneity of the particles. A portion of the sample was then treated with microwave energy. The ball mill was fitted with the 285 balls following Fred Bond's procedure for measurement of work index.

Treated and untreated particles are ball milled following Fred Bonds procedure for grinding and crushing calculations. For determination of the work index (kW·h per ton ore), the following equation was used:

$$W_i = \frac{44.5}{P_i^{0.23} Gbp^{0.82}\left(\frac{10}{\sqrt{P_{80}}} - \frac{10}{\sqrt{F_{80}}}\right)}$$

Where P_i is the test sieve size in microns, *Gbp* is the grindability of the ore, *P* is the size in microns of 80 percent of the last cycle sieve undersize product passes, and *F* is the size in microns of 80 percent of the new feed passes.

Results and Discussion

Curie Temperature

The strong magnetic property of the ore particles indicates that rapid heating will occur by microwave irradiation. Strong absorption of microwave energy within ore particles can be strongly attributed to the main metallic host mineral pyrrhotite ($Fe_{1-x}S$). When occurring with the 4C superstructure and stoichiometric composition of Fe_7S_8 the structure is ferromagnetic [4]. As other strongly ferromagnetic minerals are an occurrence within the ore, ferromagnetic spinel minerals, Curie temperature measurements were made on samples with metallic appearance. The samples shown in Figure 2 have magnetic moment measurements measured in electromagnetic units, emu, (0.001A·m²) plotted as a function of temperature (°C). Though the plots have very different magnetic moment measurements, the shapes of the plots are in agreement and at roughly 300°C, randomly arrangement of magnetic dipoles rapidly decreases the measured magnetic moment. If ferromagnetic pyrrhotite is thermodynamically stable past 325°C, it is likely to have the effect of thermal runaway and high amounts of localized heating will occur in ore particles.

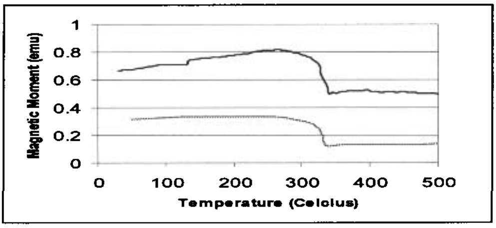

Fig. 2. Curie temperature measurements of metallic ore particles.

The rapid decline of magnetization in metallic particles occurs at roughly 300° C. This is within 25°C of the known pyrrhotite Curie temperature measurement of 325°C [5]. The Curie temperature measurement is within a close approximation of the measured value for a pure pyrrhotite mineral. The slight difference in Curie temperature measurements could possibly be due to the high amount of nickel-rich pyrrhotite (Ni-Po) formed as a derivative superstructure of the pyrrhotite (Po). Rather than characteristic exsolution of the mineral pentlandite ($FeNiS_2$) during cooling [6], nickel was able to be incorporated into the vacant hexagonal structure of the Po. An example of these minerals disseminated within an ore particle can be seen in the backscattered electron image in Figure 3. The Ni-Po is magnetic, as it appears grey in the BSE image due to an incomplete signal from the BSE detector with random scatter of electrons emitted from the beam.

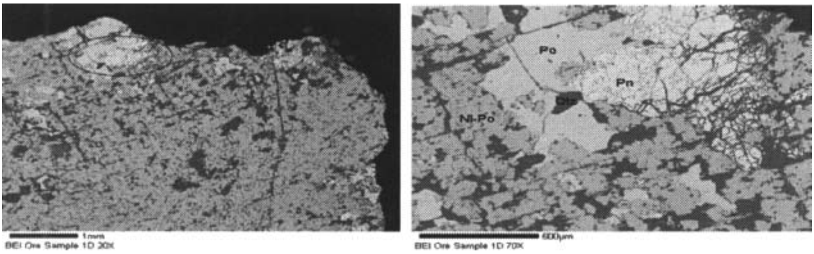

Fig. 3. BSE image of dissemenated sulfide minerals pyrrhotite (Po), pentlandite (Pn) and nickel-rich pyrrhotite (Ni-Po) occuring with quartz (Qtz)

<u>Microwave Induced Cracking of Sulfide Ore Particles</u>

The images in Figure 4 are before and after optical images of the same polished surface of a jaw crushed +1/2" piece of ore before and after microwave radiation. The surface was re-polished to remove the partial oxidation that had occurred after microwave exposure for 30s. The mineral grains are seen in Figure 4b but with a cracking propagating thru the gangue between them with another crack propagating out of the field of view.

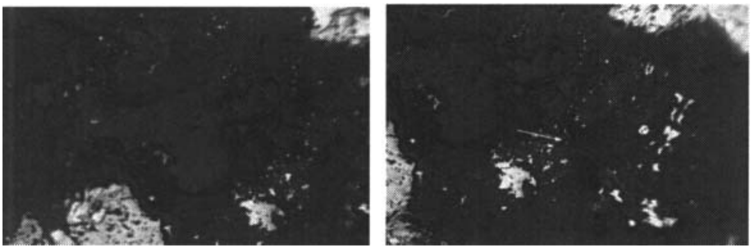

Fig. 4. Optical image of **a.)** Metallic sulfide grains **b.)** Same grains as in image **a** but microwave exposure for 30 seconds. (*Scale bar not shown*)

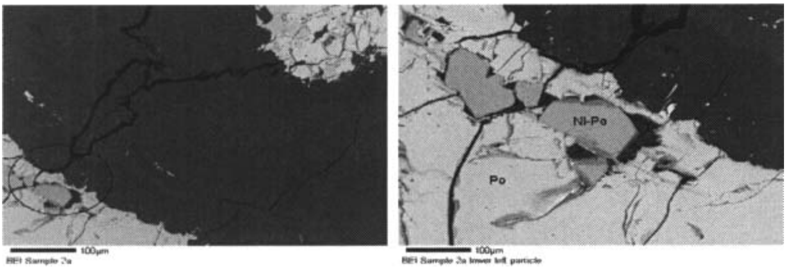

Fig. 5 BSE image of cracking between pyrrhotite (Po), Ni-rich pyrrhotite and the pyroxene host matrix.

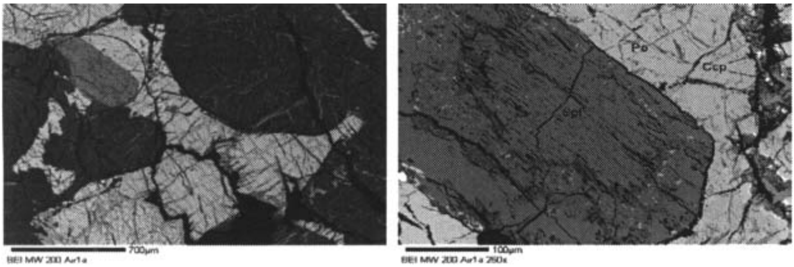

Fig. 6. BSE image of a spinel mineral grain exposed to microwave radiation.

Similar type cracking is seen in Figure 5 showing cracking between sulfide grains and Px gangue. Smaller grains of Ni-Po cause intergranular cracking of the iron sulfide surrondings. These particles hold value and should be magnetically washed during processing for the small percentage of nickel value they hold. In Figure 6, a Cr-bearing spinel mineral in liberated from its sulfide mineral neighbors also forming cracks within itself. Spinels are considered a refractory ore in mineral processing and difficult treat conventionally. Here it is seen completely liberated from its surrondings. Thus, physically seperating minerals at various sieve sizes might prove sucessful for recovery of metallic bearing minerals from gangue waste rock.

Crushing and Grinding Experiments

Grinding and sieve testing was performed on ore particles to better understand size classification of particles before and after treatment. These experiments are performed to predict the test sieve size that shows a decreased grindability during ball milling. Particles microwave pre-treated for shorter durations of time would consume less energy but may not heat to temperatures high enough to introduce significant amounts of stress within particles to induce cracks and increase the grindability of the ore. It is of interest to microwave samples for short time durations because of less energy consumption of microwave pre-treating material. It can be seen in Figure 8 that particles microwave treated for 30s and 60s time duration show an increase in the cumulative percent passing for all particle size tested. The sample MW treated for 60s has a marked effect on the cumulative percent passing for all particle sizes seen in Figure 8.

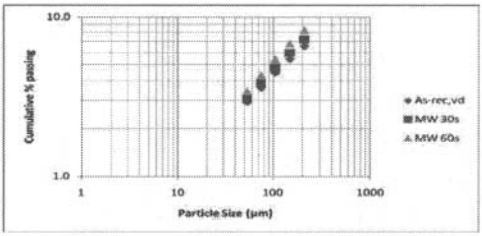

Fig. 8. Cumulative percent passing for particles ball milled 100 revolutions

The results of the grinding experiments are displayed in Table 1. The grindability is increased for all microwave treated ore particles compared to untreated ore particles resulting in a reduction of the ball mill work index. The largest particles, gyro -6+10, had the largest work index calculated for any of the samples. Conversly, the smallest particle size, jaw-8+12, with the microwave exposure time of 30s had the lowest calculated work index. As the feed particle size is increased, the reduction of size largly occurs by abrasion to the mineral surface rather then breakage at mineral grain boundaries. This is seen by lower grindability, or amount of undersize produced per mill revolution. The jaw particles have close values of work index specifically because of the way they were treated. Larger samples treated consequently absorb more microwave energy reducing the average power input for each particle. Heat tranfer between particles is also greatly reduced when placed on the glass tray rather than in the crucible.

Table 1. Effect of Microwave Heating on Grindability and Work Index of Sulfide Ore.

Feed Material	Test Sieve Size (µm)	Grindability, grams per mill revolution	Work Index, kW·h per ton ore
Gyro -6+10			
As-received	147	0.79	20.81
MW 30s	147	0.82	20.52
MW 60s	147	0.86	19.87
Jaw -6+10			
As-received	417	1.83	17.16
MW 60s	417	1.97	17

Jaw -8+12			
As -received	208	1.57	16.10
MW 30s	208	1.58	15.78

Conclusion

The measured Curie temperture, 300°C, is in agreement with the known measured value for pyrrhotite, 325°C. The ore is heated by microwave radiation largely due to the high amount of ferromagnetic pyrrhotite present within the ore. BSE imaging of the nickel-rich pyrrhotite shows it as another dissemenated magnetic mineral phase within the ore. The spinel minerals occuring within the ore are strong absorbers of microwave energy. Mineral grains heated under microwave energy produce cracks along mineral grain boudaries and across the host rock matrix in ore particles. An improvement in grinding characteristics is seen with longer heating intervals resulting in a reduction of work index values. When the liberated particles are of fine sizes compared to the feed material, it can be assumed that size reduction is taking place largely by abrasion. Abrasive wear to accomplish size reduction is ineffective because a high amount of energy is wasted mainly in the form of heat created by friction from collisions of balls and particles. Thus, it may prove better to "stamp" the ore particles after microwave treatment for liberation of metallic-bearing mineral phases.

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