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A Systematic Investigation of Microwave Heating in Oxidised Platinum Group Metal Ores

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Systematic Investigation of Microwave Heating in Oxidised Platinum Group Metal Ores

Abstract

Extraction of valuable Platinum Group Metals (PGM) in oxidised ores has been fraught with challenges due to their physio-chemical properties that hinder high/economic extraction rates. The aim of this study was to understand the potential of microwave heating to enhance mineral liberation in oxidized PGM ores (assumed to be represented by their respective metals) in microwave heating are studied using COMSOL Multiphysics computer simulations.

The results showed that the ore constituents exhibited differential heating rates when mixed with a microwave absorbing additive, which is key to achieving thermal fracture within the ore to enhance mineral liberation. Also, an increase in microwave power resulted in an increase in the differential heating rate in the oxidized ores when an additive was present, suggesting that the presence of a microwave absorbing additive to the ores greatly improves the differential volumetric heating rate of oxidised ores. Of the elements tested, iron seems to have potential in increasing microwave heating in the oxidised ores when no additive is introduced. Copper was observed to be the one to first change state when heated thus giving a limit to the point at which the samples are heated.

These findings suggest that microwave heating has the potential to be a viable technology for enhancing mineral liberation in oxidized PGM ores. Further research, such as A more detailed understanding of the size range of ore particles that are susceptible to differential heating at the micro-scale, is needed to optimize the microwave heating process and to develop new mineral processing techniques based on microwave heating.

Overall, the study showed that microwave heating has the potential to be a versatile and effective technology for mineral liberation in oxidized PGM ores. Further research is needed to optimize the microwave heating process and to develop new mineral processing techniques based on microwave heating.

Introduction

The demand for precious minerals is set to rise owing to increased consumption by world-leading technological firms. Because of the ever-increasing demand for precious minerals, resources are dwindling. Therefore, there is a need to embrace the sustainable extraction of minerals in the mining industry. The sustainable extraction of minerals implies the efficient extraction and processing of minerals, leaving the least damage to the environment while ensuring the long-term viability of the mining industry.

Platinum Group Metals (PGM)s are a group of precious metals that are used in a wide range of applications, including catalysis, electronics, and jewellery. The world's largest producers of PGMs are South Africa, Russia, Zimbabwe, and Canada (Rafferty, 2013). In Zimbabwe, PGMs are mined from the Great Dyke, which is a geological feature that contains a wide range of minerals, including PGMs, chromium, and nickel. According to estimates, mining contributes eleven to twelve per cent of the country's export earnings (International Trade Administration, 2021); thus, the mining sector is a major economic player in Zimbabwe's economy.

The PGMs in the Great Dyke occur in both sulfidic and oxidized ores. The sulfidic ores are mined underground and processed using conventional methods. However, the oxidized ores are more difficult to process, and there is currently no economical method of extracting the PGMs from them. Sulphidic ores are associated with base metals such as copper, nickel, and iron, which are economical to exploit. The base metals can be recovered and sold in addition to the main minerals extracted. Other mineral orebodies occur near the surface, indicating the effects of weathering. Weathering alters the mineralogical composition of ores, depending on their constituents and locality. For example, mineral ores that occur in areas where perennial flooding may have hydroxyl groups attacking the base metals associated with ores, such as iron, to form hydroxides. Other ores may have been altered into carbonates owing to the effects of acid rain. These weather-altered minerals tend to be difficult to process, such that generic/conventional processes and equipment may not yield economic recovery rates. In addition to weathered ores, refractory ores contain minerals that are difficult to treat using conventional methods.

In Zimbabwe, there is enormous potential to increase mineral export revenue by processing oxidised ores to extracting valuable minerals ingrained within. This opportunity presents itself in the oxidic mineral reserves contained within the great dyke. Of particular interest are PGM oxidised ores that occur in both sulfidic (underground) and oxidised ores (near the surface). These oxidised ores are abundant along the length of the great dyke and are thus relatively inexpensive to extract compared to pristine sulfidic ores obtained via underground mining.

As of 2013, the Great Dyke alone was estimated to host about 160 to 250 Mt of oxidized PGM ore, with an estimated value of around US$200 billion. There is a great possibility that the value of the oxidised reserves has increased due to further explorative discoveries. The prospect of having more of these reserves and high commodity prices for PGMs makes the call to investigate ways of extracting them admissible. Unlocking the potential of oxidic ores can increase a country's gross domestic product (GDP).

Initial work to mine oxidized PGM ores via conventional metallurgical methods at the Old Wedza mine (close to Mimosa Mine) was unprofitable due to low PGM recovery (Oberthür *et.al..*, 2013). At present, the oxidised ores of the MSZ, are either left as is, are accumulated, or cast off as waste.

In the mining (extractive) sector, there is a constant battle to balance viability and mineral reserves. Mining industries are always seeking a perfect balance to achieve the highest possible mineral extraction rates from ores, while using minimum input resources and reducing the environmental impact footprint. To put it in context; if the cost of the resources required to achieve a high extraction rate is significantly less than the price obtained from that quantity of mineral, then the extraction route is said to be economically viable. However, the opposite is also true. Mineral processing encompasses the mineral extraction (from surface or underground), crushing/grinding, commutation, extraction/ separation, and refinery.

Mineral crushing and grinding are energy-intensive stages in mining operations. This energy challenge is the main reason mining industries invest in research and development to find ways of minimizing energy consumption and increasing recovery rates. This ensures sustainability of their operations. The main objectives of mineral processing are to liberate minerals from ores, upgrade mineral concentrations and refine minerals for market or other applications.

Microwave assisted extraction is a novel technology that has the potential to extract PGMs from oxidized ores. Microwaves are a form of electromagnetic radiation that can heat materials quickly and evenly. When microwaves are applied to ores, they can cause the minerals to break down and release the PGMs.

Over the years, research has been focused on flotation and leaching methods for the retrieval of PGMs from oxidic ores (Sefako et al., 2019). The presence of base metal oxides, which act as an impervious layer on mineral surfaces, makes the ore resistant to chemical attack, thus affecting the floatability of the oxidised ores(Sefako *et.al.*., 2019a). Pretreatment regimens marginally improved recoverability of the PGMs but are weighed down by the costs of the reagents, equipment, and process steps; thus, it remained uneconomical to extract the oxidised PGMs.

Microwave assisted extraction has several potential benefits over conventional mineral processing methods, including: improved efficiency, reduced environmental impact and, reduced costs.

Although microwave assisted extraction has the potential to revolutionize the mining industry, there is still a lot of research that needs to be done in this area. Some of the key research gaps include:

i. Developing a deeper understanding of the mechanisms by which microwaves interact with ores and minerals. This is essential for developing new and more efficient microwave heating systems and optimizing the microwave heating process for different types of ores and minerals.
ii. Developing new and more efficient microwave heating systems for mineral processing. Current microwave heating systems are often designed for other applications, such as food processing and industrial heating. New microwave heating systems need to be developed that are specifically designed for mineral processing.
iii. Optimizing the microwave heating process for different types of ores and minerals. The microwave heating process needs to be optimized for different types of ores and minerals to achieve the highest possible extraction rates and minimize energy consumption.

Microwave Heating Theory

Electromagnetic field

To understand how microwave radiation heats up materials, there is need to solve four mathematical equations that relate electric and magnetic fields. These equations are called Maxwell's equations of electromagnetism, and they describe how electric and magnetic fields interact with each other and matter. When heating an object in a microwave oven, the distribution of the electromagnetic field in the cavity can be described by Maxwell's equations.

$$\nabla \times \mu_r^{-1}(\nabla \times E) - k_0^2 \left(\varepsilon_r - \frac{j\sigma}{\omega\varepsilon_0}\right) E = 0 \qquad [1]$$

Where E is the electric field intensity, (V/m); μ_r is the relative permeability; k_0 is the free space wave number; ω is the angular frequency, (rad/s);σ is the conductivity, (S/m); ε_0 is the permittivity of vacuum, (F/m);ε_r is the relative permittivity (Hill & Jennings, 1993).

Heat transfer

During microwave propagation, part of the electromagnetic energy is converted to thermal energy of the heated object, which is a lossy dielectric (partially microwave absorbing material). In a lossy dielectric material, the microwave power is greatly reduced due to poor conduction. The energy dissipation of microwave P_v (Wm^{-3}) can be expressed as:

$$P_v = \pi f \varepsilon_0 \varepsilon'' |E|^2 \qquad [2]$$

Were ε'' is the dielectric loss factor, and f is microwave frequency.

The temperature distributions of the heated object can be simulated based on a three- dimensional heat transfer equation including the internal heat generation owing to microwave heating as shown in the equation [3]:

$$\rho C_P \frac{\partial T}{\partial t} = k\nabla^2 T + P_v \qquad [3]$$

Were ρ is the density, kg/m^3 ; C_p is the specific heat capacity at constant pressure, $J/(kg \cdot ℃)$; T is the temperature, $℃/K$; t is the heating time, s and k is the thermal conductivity $W/(m \cdot ℃)$.

The thermal convection between the heated object and the surrounding can be expressed as:

$$-k\nabla T = h_c(T - T_0) \qquad [4]$$

Were T_0 is the initial temperature,℃ ;h_c is the surface convective heat transfer coefficient, $W \cdot m^2/℃$ (Hill & Jennings, 1993).

Materials capable of absorbing microwave energy can be heated by irradiation, and according to their responses to microwave, the materials can be classified into three groups: transparent, conductor, and absorber (Li *et.al*, 2020). Only the absorber materials can be rapidly heated within a short duration of irradiation, which is known as heating of microwave (Haque, 1999).

Methodology

COMSOL Multiphysics software is used to design a virtual microwave.

The methodology is broken into three phases with the aim to ascertain **the following**:

1. How the mineral formations interact with the microwaves.
2. How the constituent minerals interact with the microwaves.
3. How a microwave absorbing material enhances microwaves heating of the constituent minerals.

Modelling Assumptions

Following the configuration of the microwave, the following assumptions were made.

1. The base metal oxides are treated as individual pure metals with their distinct characteristics.
2. Constituent materials that have unknown microwave properties were replaced with known alloys in which they are present and have similar or very close physical and chemical properties such as density, thermal conductivity, and specific heat capacity.
3. The ores exist as homogeneous layers above one another i.e., they are not engrained in one another in a complicated matrix.

The above assumptions make it easier to simulate the heating of the oxidised ore constituents. The permittivity of materials is dependent on their temperature and the microwave frequency (Mwase *et al.* 2020). Thus, the permittivity of materials varies differently when temperature is increased.

Phase 1

Known formations of oxidised PGMs are modelled into the software in layer form (homogenous layers).The formations are heated in the virtual microwave via simulation under three distinct regimes.

1. Microwave power regimes of 1kW,2kW and 3kW
2. Exposure time of 300 seconds.

Phase 2

The constituent minerals of oxidised PGMs are modelled into the software.The constituent minerals are heated in the virtual microwave via simulation under three distinct regimes.

1. Microwave power regimes of 1,2 and 3kW
2. Exposure time of 300 seconds.

Phase 3

A microwave absorbing material is introduced to the individual minerals are modelled into the software.The formations are heated in the virtual microwave via simulation under three distinct regimes.

1. Microwave power regimes of 1,2 and 3kW
2. Exposure time of 300 seconds.

The geometry and mesh of the microwave heating model are created starting from the microwave oven model available in the COMSOL Multiphysics application gallery, as illustrated in figure 1 and 2. The microwave oven includes a magnetron, waveguide, and a glass turntable. The port that provides microwave energy is located on the left side of the microwave oven cavity, as shown in figure 1. The microwave oven and waveguide were filled with air, and copper is used to cover the oven walls and the waveguide.

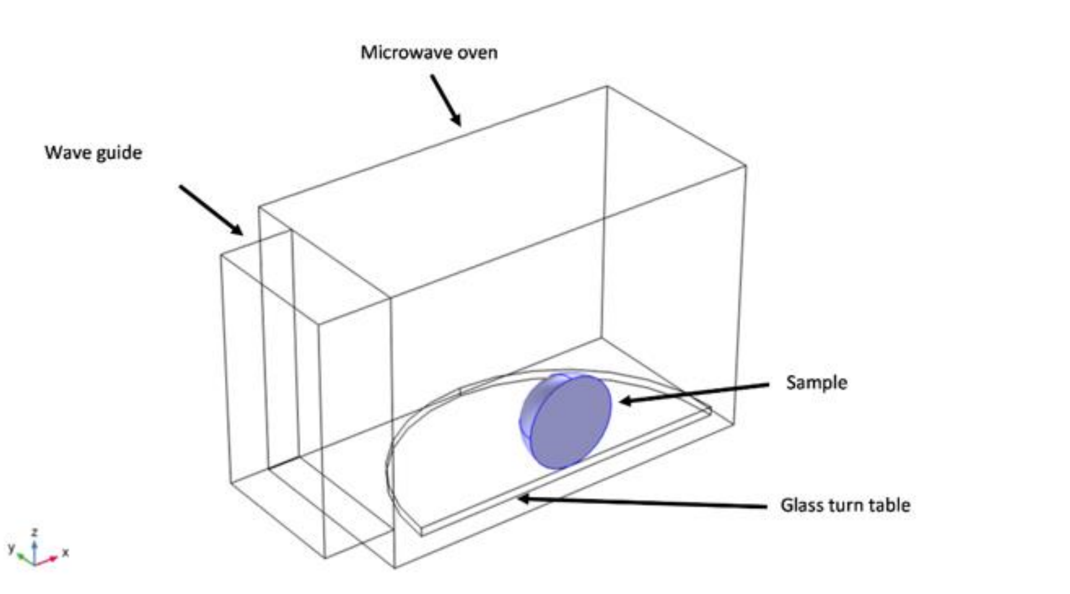

Figure 1: Geometry of sample

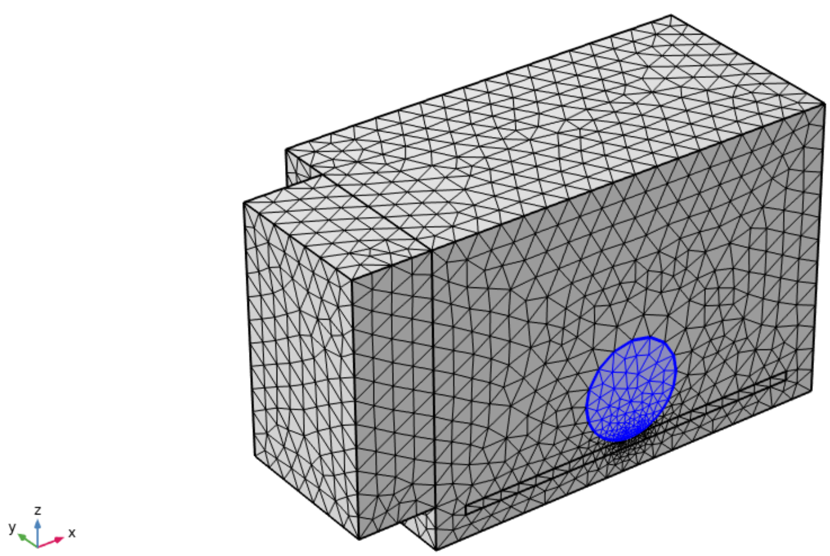

Figure 2 :Geometrical mesh of the sample

Results

When the quartz (SiO_2) was in contact with Silicon Carbide (SiC), an average heating profile was observed, as shown in the figure 3. When SiC is in contact with quartz, some of the heat is used to heat the quartz. The heating rate also increased as the microwave power increased from 1 kW to 3 kW.

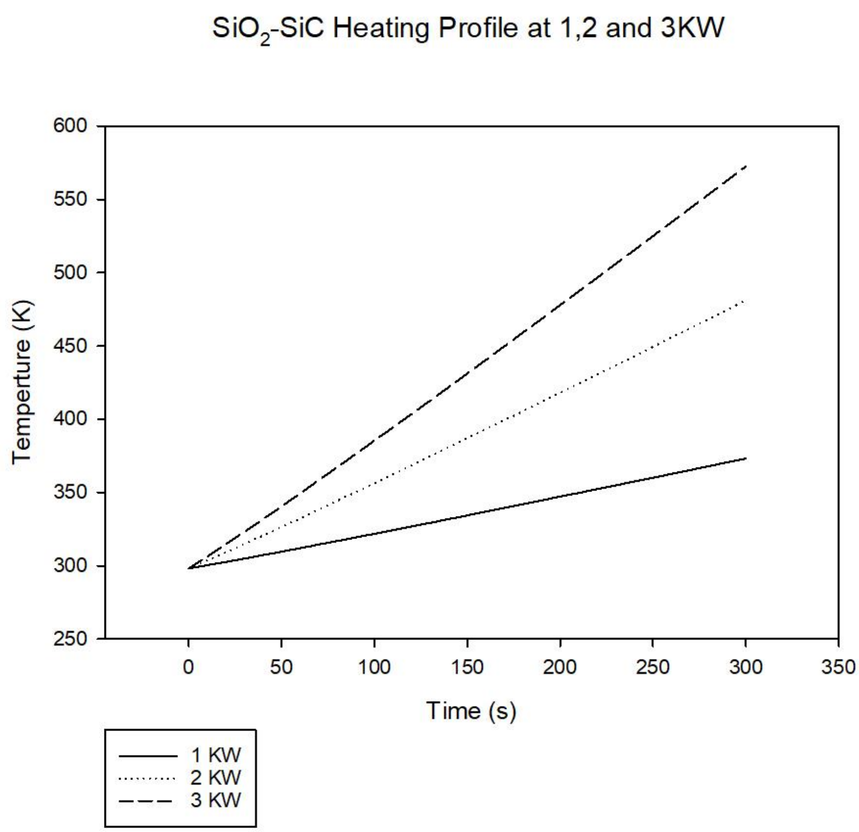

Figure3: Average heating profile of quartz and SiC.

Figure 4 shows the average heating profile of the Iron-SiC paired samples. This value is higher than that of the paired quartz- silicon carbide profile. The large temperature gain due to iron is attributed to its thermophysical properties such as heat capacity. The heating rate was proportional to the microwave power.

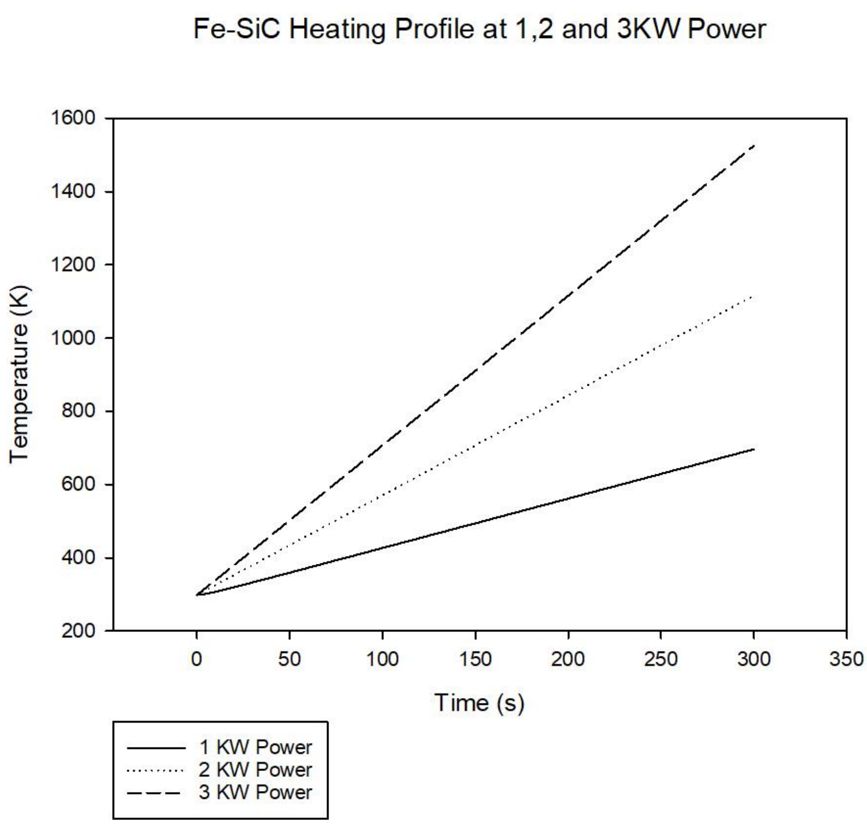

Figure 4: Heating profile of paired Fe-SiC

Figure 5 shows the average heating profiles of the Copper-Silicon carbid paired samples. This is slightly higher than that of the paired Fe-SiC profile. This is due to the differences in the physical properties of iron and copper (Cu), particularly the heat capacity, thermal conductivity, and density. Cu has a significantly higher density (8940[kg/m3] vs. 7860[kg/m3]) than iron and a higher thermal conductivity (400[W/ (m · K)] vs. 80.2[W/ (m · K)]) with a relatively lower heat capacity (385[J/ (kg · K)] vs. 449[J/ (kg · K)]) than iron. The higher thermal conductivity and lower heat capacity help offset the higher density and narrow the temperature difference with the iron.

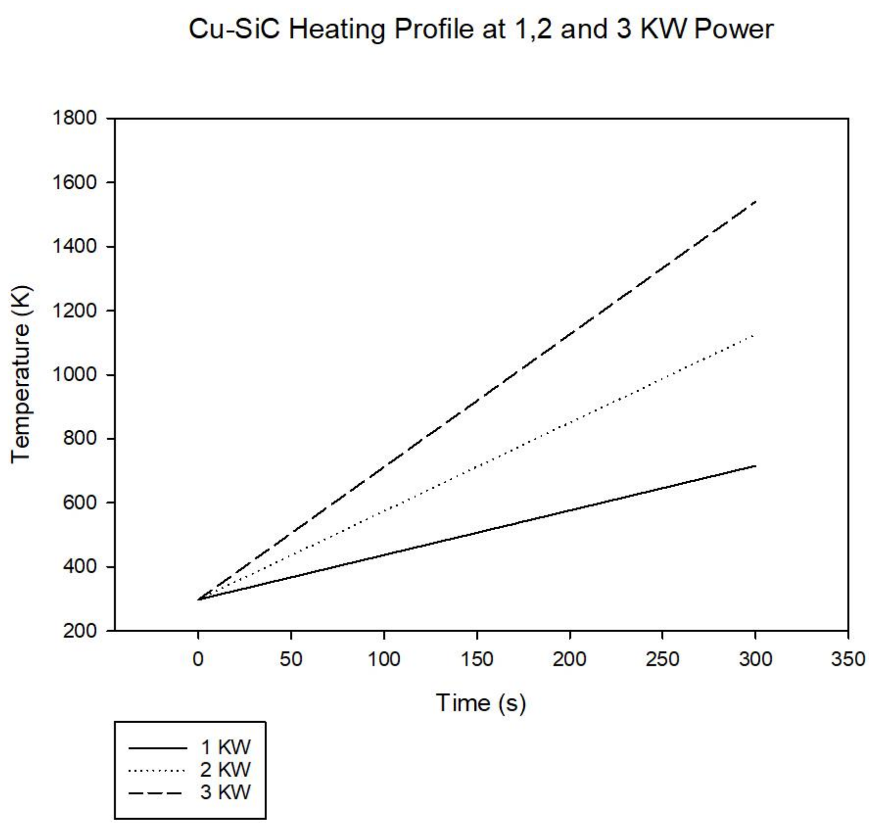

Figure 5: Heating profile of Cu-SiC

In figure 6, nickel (Ni) is not heated by the microwaves alone. However, when it is in contact with SiC, it has a high heating rate. This is because SiC transfers heat to Ni via conduction. The heating rate was also directly proportional to the microwave power.

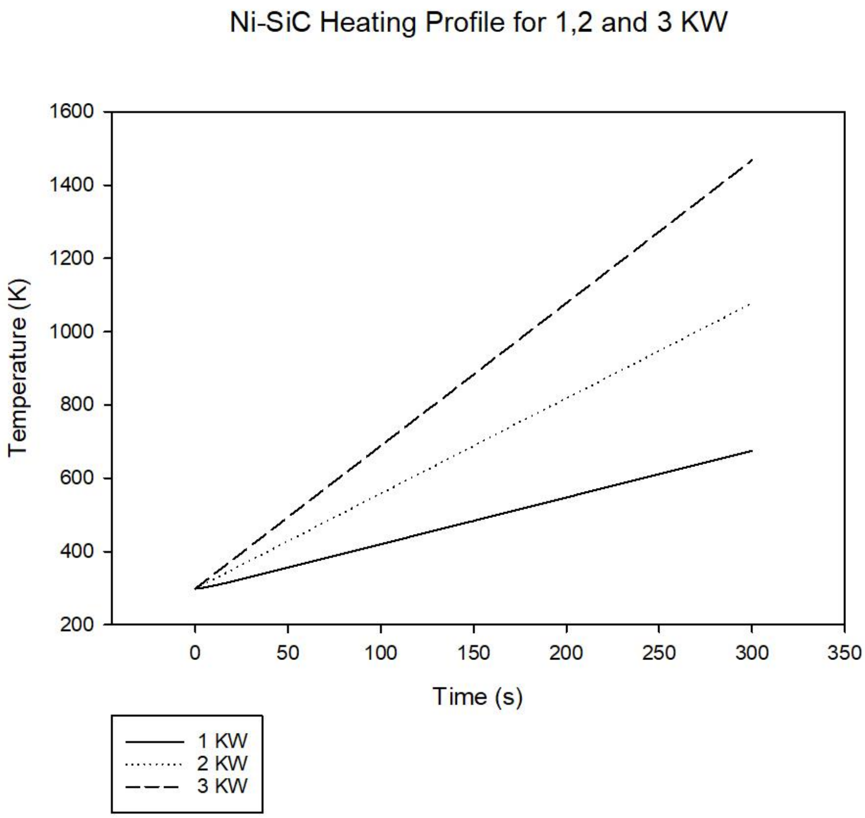

Figure 6: Heating profile of Ni-SiC

Figure 7 shows the average heating profile of the Platinum-Silicon Carbide (Pt-SiC) contact pair in different power modes. The highest temperature was obtained at a higher microwave power. A higher microwave power translates to a higher temperature of the SiC, which implies that there will be a greater thermal gradient within the sample and results in a higher average heating rate through the sample.

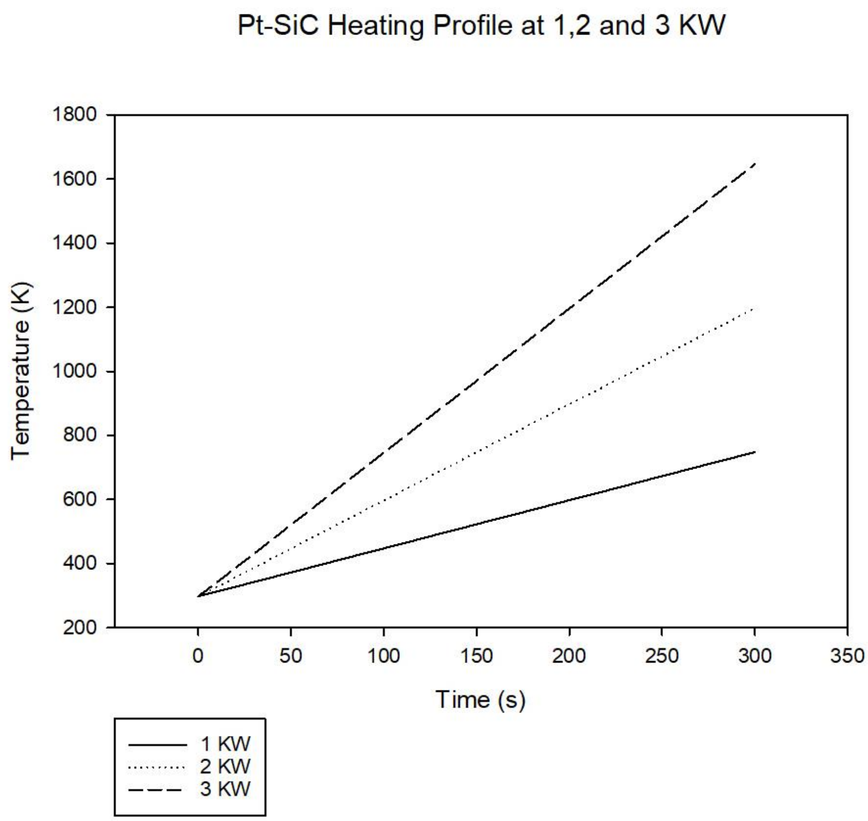

Figure 7: Heating profile of Pt-SiC

From the figures 8-10, quartz has a lower heating rate than the metals. This would likely lead to intergranular fractures within the sample because the quartz components would have a greater temperature difference with the base metals associated with the PGMs. There is less likelihood of observing a trans granular fracture because there is a slight difference in the temperature profiles of the metals.

During the simulation of microwave heating on SiO_2, the electric field passed through the sample. This means that quartz is transparent to microwaves and has no consequence when heating ores via microwaves. However, there was no change in the quartz temperature. This indicates that the quartz was not affected by microwaves.

From the results obtained from the simulation of microwave heating of metals, the electric fields could not penetrate the samples. This suggests that the metals were not transparent to microwave radiation. There was no notable change in the temperature profiles of the metals that were individually irradiated with microwaves. This suggests that the metals reflect the microwaves or are not receptive to them due to attenuation. Their permittivities and permeabilities do not affect their response to microwaves because they are heated via conduction. However, iron may show different results because it can be paramagnetic depending on its oxidation state in oxidized ores, as reported in the literature. There was no need to obtain other penetration depth graphs because the metals behaved the same, that is, they did not heat upon exposure to microwaves.

When samples are heated in contact with a microwave-absorbing material, they tend to heat rapidly. The results were then superimposed to obtain their individual behavior. This would provide a picture of how they would behave individually if they were in contact with a microwave-receptive material.

The presence of quartz within the mineral complex most likely aids in liberating metallic minerals. This is because it has a lower heating rate than metallic constituents.

It can be noted that at higher microwave powers, higher heating rates and higher temperatures were observed with an absorbing material. In addition, because of the higher heating rates and temperatures, there is a strong possibility of foaming alloys between metals.

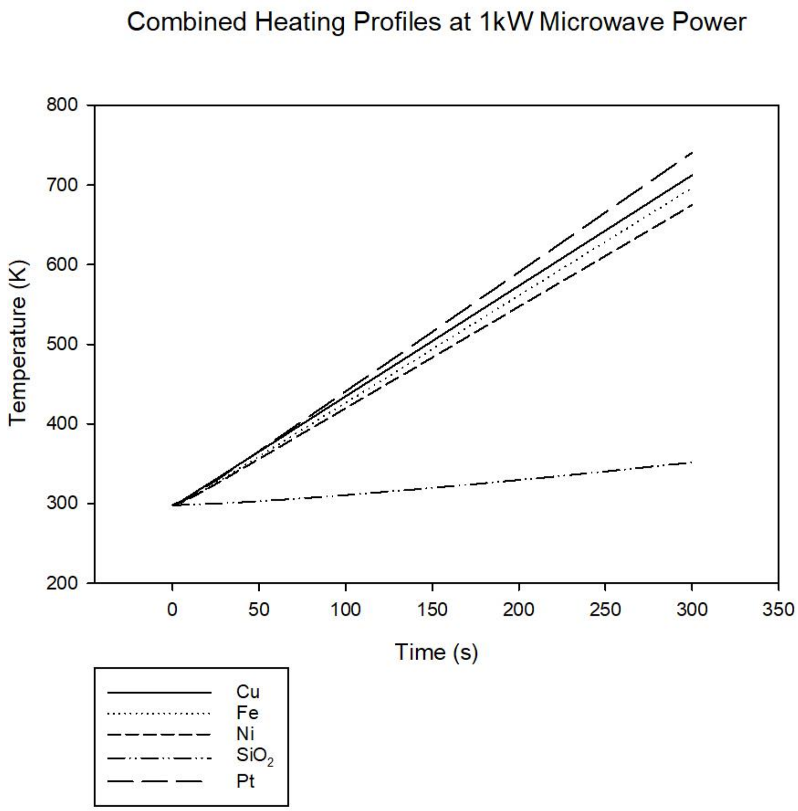

Figure 8: Graph showing the temperature profile of the constituents when heated in due to contact with SiC at 1kW microwave power.

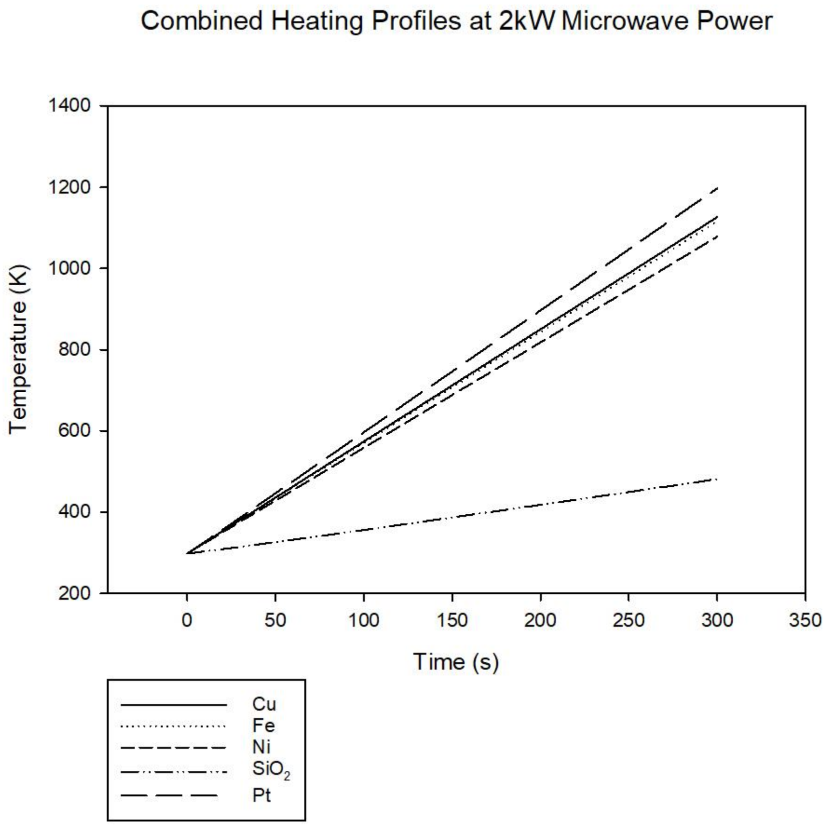

Figure 9: Graph showing the temperature profile of the constituents when heated in due to contact with SiC at 2kW microwave power.

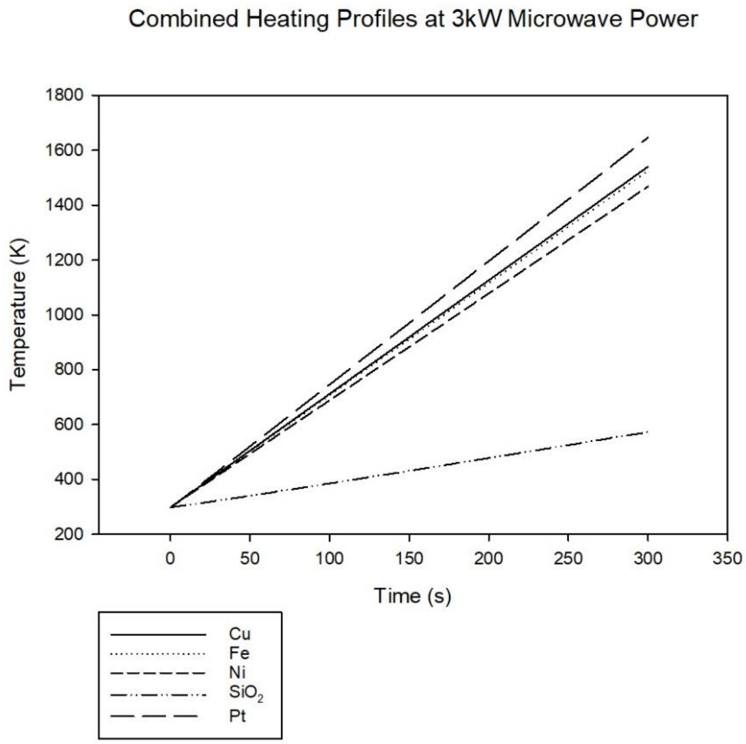

Figure 30: Graph showing the temperature profile of the constituents when heated in due to contact with SiC at 3kW microwave power.

From figure 11 , it can be noted that there is positive correlation between the microwave power and the heating rate of the materials. Seems Pt has a higher heating rate followed by Cu, Fe and Ni respectively. However, Cu has the lowest melting temperature of the above elements hence it is the first to change phase and melt.

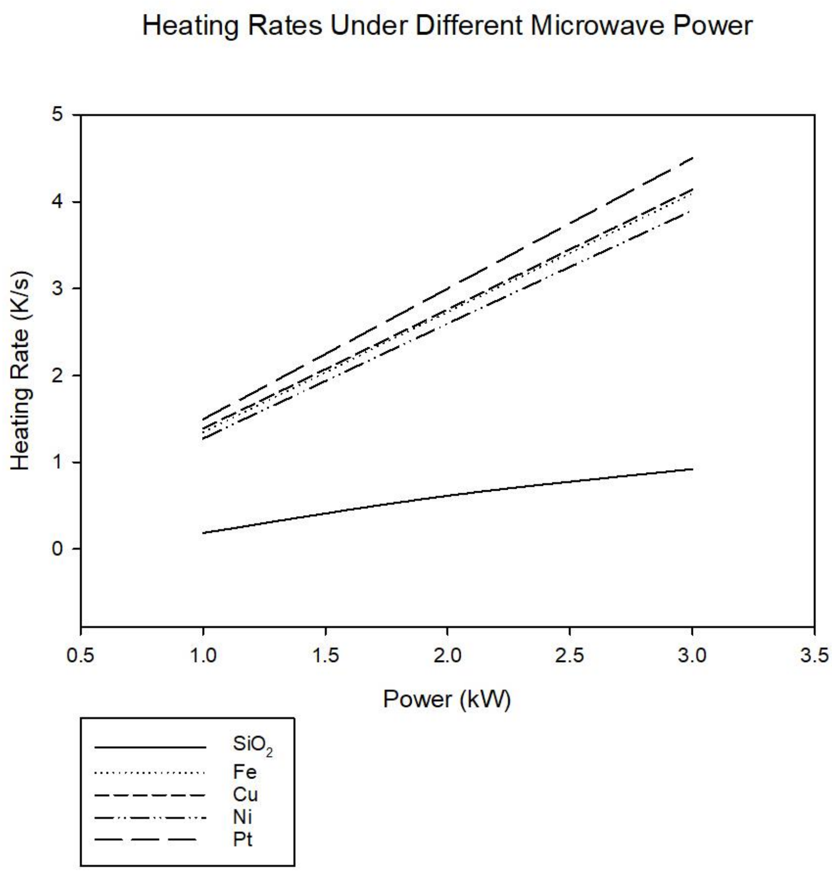

Figure 41: Heating rates under different microwave power.

The vertical axis of the graph (figures 12-14) shows the volumetric expansion coefficient, whereas the horizontal axis shows the time in seconds. The different lines represent different elements, including Cu, Ni, Fe, Pt, and quartz. From the above graphs, copper has a higher expansion factor and lower melting point than the other elements. It is an intrinsic property of every material, and it varies from one material to another. The initial conditions at time zero are that the elements are at room temperature.

From the above graphs, it was observed that there is a strong correlation between the microwave power and the volumetric expansion factors of the elements. The greater the microwave power, the greater the heating rate and volumetric expansion factor. The data obtained from the simulation suggests that there is differential expansion within the elements, and copper is the first constituent to change the phase.

Based on the above analysis, metals and quartz cannot be heated by microwaves at the designated power levels. They can only be heated when in contact with a microwave-absorbing material. When in contact with an absorbing material, heat is distributed from the absorber via conduction. The physical properties of the material, such as thermal conductivity, density, and heat capacity, play a pivotal role in heating the samples when in contact with an absorber. The constituent elements experience volume changes as they are heated. The change in volume differs from one constituent to another owing to the differences in their physical properties.

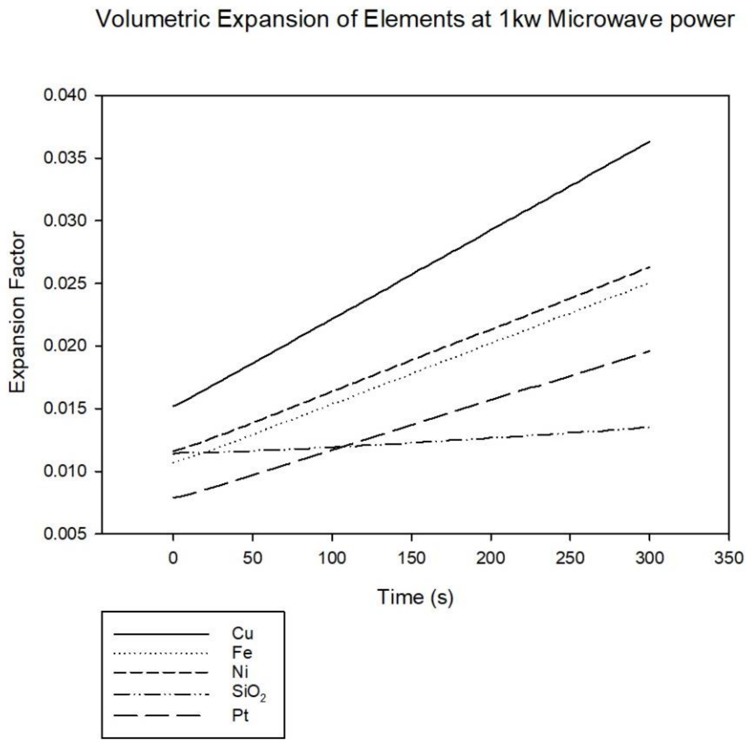

Figure 52: Volumetric expansion of elements at 1kw Microwave power

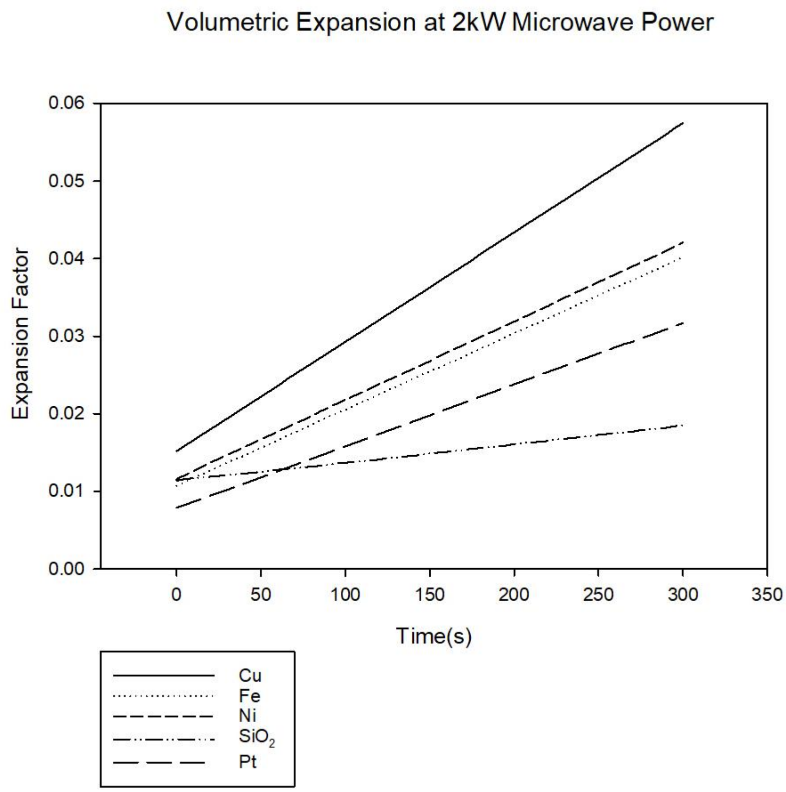

Figure 13: Volumetric expansion of elements at 2kw Microwave power

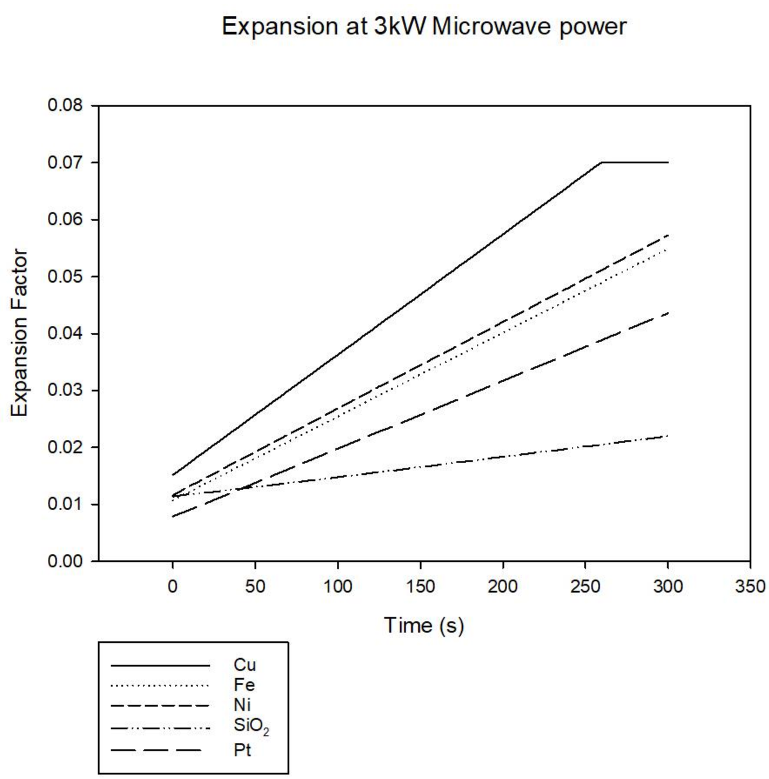

Figure 14: Volumetric expansion of elements at 2kw Microwave power

Discussions

Microwaves do not penetrate metal surfaces. They do however penetrate quartz but do not result in heating in the quartz. This implies that some metal oxides do not respond well to microwaves. The samples could not heat up when exposed to microwaves in the absence of a microwave-absorbing material.

SiC is a good microwave absorber, it heats well upon exposure. SiC can thus be used as a microwave absorber when treating materials that do not respond well to microwaves.

Also of importance are material's coefficient of thermal expansion and thermal conductivity. These two properties are related to a material's ability to expand when exposed to radiation, provided the material is receptive to the radiation or is in proximity with a material that is receptive to the microwaves. The difference in the thermal properties between the materials in contact contributes to trans-granular fracture within samples provided it is significantly different between the constituent materials.

The heating rate of the sample also plays a role in inducing thermal shock within the sample. From the results, it can be noted that one constituent heated rapidly when in contact with an absorbing material. This is attributed to the specific heat capacity of the samples and thermal expansion coefficients, if one constituent heats up more rapidly than the other different constituent, the resulting shear strain on their shared boundary usually results trans-granular fracture. If the lossy (microwave absorbing) material is engrained in the constituent of choice, its rapid heating and expansion may result in an intra-granular fracture within the heated sample.

High microwave power results in a high heating rate which is key in generating thermal fractures within the sample. However, long exposure times run the risk of altering the physio-chemical composition of the ore which may have some unexpected consequences or benefits.

Some oxidised PGM ores need to be in contact with materials that absorb microwaves to enable microwave heating. The study showed that microwave pretreatment of layered materials is feasible because of the different heating rates of their constituents when they are mixed with microwave-absorbing material. This difference is caused by their varying density and thermal properties. When their properties are different, it becomes easier to separate the PGMs. The heating rate and the fracture rate increase when the microwave power is increased. This lowers the extraction cost since no reagents are used to pre-treat the ores.

To commercialize this technology for treating mineral ores, it is important to first understand the nature of the materials and their constituents i.e., matrix structure. The nature of the constituents determines whether it is economically viable to fracture the materials with microwave radiation alone or whether they need to be combined with microwave-receptive materials. The size of the samples also matters because it affects how the expansion factor of the constituents influences the disintegration of the sample i.e., a mineral embedded in a quartz matrix structure may expand when heated but the extent of expansion that causes the ore to disintegrate is unknown.

Recommendations

The research findings indicate that it is important to test the practical effects of microwave irradiation on the characterised samples. This will help to determine if a microwave heating-enhancing material is required and what dimensions it should have. The piezoelectric effect of quartz may also be relevant, as some quartz phases exhibit this property and may increase the rate of mineral fracture. The optimal size of the ores for achieving adequate volumetric expansion and fracture within the ore body needs to be studied as well. Additionally, it is necessary to investigate.

i. Any phase change during the heating period and how that affects the separation process.
ii. Developing methods for pre-treating oxidized PGM ores to improve microwave heating efficiency.
iii. Designing and testing microwave heating systems that can be used for large-scale mineral processing operations.
iv. Developing methods for recovering PGMs from microwave-heated ores.

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Declaration of Competing Interests

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