Technical Note

# Microwave heating of ultramafic nickel ores and mineralogical effects

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## ARTICLE INFO

## ABSTRACT

Although mineral carbon sequestration (MCS) has several advantages over other carbon storage techniques, an economic process for MCS has not yet been developed. To reduce costs, it is suggested that MCS be combined with other processes and that waste products be used as feedstock. A process is proposed where ultramafic nickel ores are treated with microwave radiation to convert serpentine, the primary gangue mineral, to olivine. It is hypothesized the conversion of serpentine to olivine in ultramafic nickel ores may improve the mineral processing of these ores, and increase the carbon storage capacity of the flotation tailings. The microwave heating characteristics of ultramafic nickel ores, and the mineralogical changes that occur as a result of microwave treatment, are described in this paper. Ultramafic nickel ores were found to heat well in response to microwave radiation and the temperatures achieved were sufficient to convert serpentine to olivine. Microwave treatment was also found to convert pentlandite, the valuable nickel mineral, to other Fe–Ni–S minerals.

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## 1. Introduction

Mineral carbon sequestration (MCS) is a type of permanent and portable $CO_2$ storage based on rock weathering processes where $CO_2$ is reacted with alkaline minerals to form solid carbonates (Lackner et al., 1995). Although MCS has advantages over other carbon storage techniques, an economic process for MCS has not been developed, partly because significant energy is expended in preparation of the mineral feedstock. It is suggested that waste products be used as feedstock and that MCS be combined with other processes to reduce costs. Serpentine ($Mg_3Si_2O_5(OH)_4$) mine waste generated by ultramafic nickel ore processing operations has been identified as a potential MCS feedstock. Serpentine mine waste is abundant, already ground to a particle size appropriate for MCS (for the purpose of mineral benefaction) and contains the alkalinity required to store $CO_2$. Despite these advantages, serpentine is not overly reactive to $CO_2$, although pre-treatment can be used to improve the carbon storage capacity.

While useful as MCS feedstock, serpentine is undesirable in mineral processing operations. Serpentine has a negative effect on grinding and flotation, two techniques used in the upgrading of ultramafic nickel ores. Serpentine increases the viscosity of ore slurries due to its anisotropic nature and morphology (which can be fibrous) (Ndlovu et al., 2011), and slime-coats pentlandite (the

valuable nickel mineral) due to opposite surface charges (Edwards et al., 1980; Bremmel et al., 2005; Feng et al., 2012). Fibrous serpentine can also form fibre-bubble aggregates that report to the froth and dilute the concentrate (Xu et al., 2010).

A process is proposed where ultramafic nickel ores are treated with microwave radiation prior to grinding. Microwaves can be transmitted, reflected, or absorbed, and can efficiently and instantaneously generate heat in materials (Haque, 1999; Pickles, 2009). It is hypothesized that the microwave pre-treatment of ultramafic nickel ores should result in heating, serpentine dehydroxylation and the formation of olivine (reaction 1).

$$2Mg_3Si_2O_5(OH)_4 \rightarrow 3Mg_2SiO_4 + SiO_2 + 4H_2O \qquad (1)$$
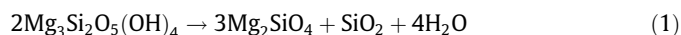
Olivine is not fibrous or anisotropic, has an isoelectric point close to that of pentlandite (Fuerstenau and Pradip, 2005), and is more reactive to $CO_2$ than serpentine (Bobicki et al., 2012). Hence, microwave pre-treatment should reduce or eliminate the negative effects of serpentine on mineral processing and increase the carbon storage capacity of the flotation tailings. The objective of this paper is to determine the microwave heating characteristics of ultramafic nickel ores and to determine if the microwave pre-treatment of these ores results in serpentine dehydroxylation.

## 2. Materials and methods

Two low-grade ultramafic nickel ores were used in this study: the "OK ore" (containing 0.26 wt.% Ni) from the Okanogan nickel

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deposit in Washington State, USA, and the "Pipe ore" (containing 0.23 wt.% Ni) from the Thomson Nickel Belt in Manitoba, Canada. The ores were crushed and sieved to produce 0.425–1 mm material, which was split into 100 g samples for microwave treatment. The mineral composition of the ores is given in Table 1.

Ore samples were treated in a quartz reactor inside a 1000 W, 2.45 GHz microwave oven (NN-SF550M Flat and Wide, Panasonic Corporation, Kadoma, Japan). The reactor was purged with 1 L/min of $N_2$ gas during treatment. The temperature achieved was determined by removing the sample from the microwave and inserting a type K thermocouple into the centre of the sample. Samples used for temperature measurement were discarded. Samples treated for mineralogical analysis were cooled for 2 h under nitrogen.

Quantitative X-ray diffraction (XRD) analysis was performed using the Reitveld refinement technique on powdered samples by PMET Inc. of New Brighton, Pennsylvania, USA

The composition of different mineral grains was determined by scanning electron microscopy (SEM, Hitachi S-2700 Scanning Electron Microscope) using an energy dispersive X-ray detector (EDX, PGT PRISM).

## 3. Results and discussion

### 3.1. Microwave heating

Temperature versus microwave heating time and heating rate versus temperature for the Pipe and OK ores are shown in Fig. 1. Both ores heated well in response to microwave treatment, although they demonstrated somewhat different microwave heating characteristics. The heating behaviour of the two ores can be explained by differences in their composition. The heating rate of a material as a result of exposure to microwave radiation (Eq. (2)) is directly proportional to power dissipation ($P(z)$), and inversely proportional to the material density ($\rho$) and specific heat capacity ($C_p$) (Pickles, 2009). The power dissipation of microwave energy for dielectric materials ($P(z)$) is a function of microwave frequency ($f$), the dielectric loss factor ($\varepsilon''$), the permittivity of free space ($\varepsilon_o$), and the electric field intensity ($E$) (Eq. (3)) (Pickles, 2009).

$$\frac{dT}{dt} = \frac{P(z)}{\rho C_p} \tag{2}$$

$$P(z) = 2\pi f \varepsilon_o \varepsilon'' E^2 \tag{3}$$

The OK ore heating curve was logarithmic in shape, with a high initial heating rate that declined with increasing microwave exposure time. The OK ore heating rate decreased with increasing temperature and was governed largely by the properties of serpentine (a plot of serpentine loss factor over heat capacity generates a curve nearly the same shape as the OK ore heating rate curve). The OK ore attained a maximum bulk temperature of 730 °C after 15 min heating time.

The Pipe ore heating and heating rate curves were somewhat different from those for the OK ore. Up until 8 min microwave heating time, the Pipe ore also demonstrated a high initial heating rate that declined with increasing microwave exposure time. However, after 8 min of microwave heating time, an increase in heating rate was observed. The increase in heating rate was accompanied by the appearance of a molten state in the centre of the Pipe ore sample which fused upon cooling. During the initial stage of heating (up to approximately 600 °C), the Pipe ore heating rate was dominated by the properties of serpentine. Above 600 °C, the Pipe ore heating rate was heavily influenced by the properties of magnetite (the second most abundant mineral in Pipe ore). At 600 °C, the heat capacity of magnetite decreases while the dielectric loss factor increases exponentially with increasing temperature (Robie and Hemingway, 1995; AECL and Voss Associates, 1990). Although magnetite is a magnetic material, and magnetic losses have been shown to dominate the heating of magnetite at low temperatures, magnetic absorption of microwave energy has been shown to be very small above the Curie point (585 °C) (Hotta et al., 2011; Peng, 2012). The formation of the molten phase may also have influenced the heating rate; however, the size of the molten material started out very small (<1 wt.% at 10 min microwave heating time) and did not represent a substantial portion of the sample until after 15 min microwave heating time, when the heating rate was decreasing. Thus, it is believed the combination of decreasing magnetite heat capacity and increasing magnetite dielectric loss factor at 600 °C led to the jump in the Pipe ore heating rate at this temperature. Overall, the Pipe ore attained a maximum bulk temperature of 1073 °C after 15 min heating time.

Microwave heating curves for comparable ores have not been found in the literature; however there is data on the microwave heating behaviour of the individual minerals (Haque, 1999; Hua and Lin, 1996; AECL and Voss Associates, 1990). In general, iron oxides and sulphides, such as magnetite, pyrrhotite and pentlandite, heat well in response to microwave radiation, while silicates,

**Table 1**
Mineral composition of untreated and microwave treated OK and Pipe ores as determined by quantitative XRD analysis.

| Composition of OK ore | | Microwave Treatment Time (min) | | | | |
|---|---|---|---|---|---|---|
| | | 0 | 2 | 4 | 8 | 15 |
| Serpentine (wt.%) | $Mg_3Si_2O_5(OH)_4$ | 84.0 | 85.0 | 86.6 | 54.5 | 15.8 |
| Olivine (wt.%) | $Mg_2SiO_4$ | 0.0 | 1.3 | 2.4 | 34.7 | 80.2 |
| Brucite (wt.%) | $Mg(OH)_2$ | 5.1 | 4.0 | 0.8 | 0.0 | 0.0 |
| Magnetite (wt.%) | $Fe_3O_4$ | 6.7 | 5.9 | 6.5 | 6.7 | 4.0 |
| Pyrrhotite (wt.%) | $Fe_{(1-x)}S$ | 0.0 | 0.0 | 0.0 | 1.8 | 0.0 |
| Pentlandite (wt.%) | $(Fe,Ni)_9S_8$ | 4.3 | 3.9 | 3.8 | 2.3 | 0.0 |
| Composition of Pipe ore | | Microwave Treatment Time (min) | | | | |
| | | 0 | 1 | 2 | 4 | 8 |
| Serpentine (wt.%) | $Mg_3Si_2O_5(OH)_4$ | 63.7 | 66.4 | 65.0 | 62.1 | 23.7 |
| Olivine (wt.%) | $Mg_2SiO_4$ | 7.7 | 5.5 | 5.3 | 9.6 | 51.1 |
| Cordierite (wt.%) | $Mg_2Al_4Si_5O_{18}$ | 1.0 | 1.0 | 1.4 | 1.9 | 1.0 |
| Vermiculite (wt.%) | $Mg_2Si_4O_{10}(OH)_2$ | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 |
| Dolomite (wt.%) | $CaMg(CO_3)_2$ | 5.5 | 5.3 | 5.6 | 3.5 | 1.4 |
| Magnetite (wt.%) | $Fe_3O_4$ | 12.3 | 12.1 | 12.5 | 12.7 | 14.1 |
| Pyrrhotite (wt.%) | $Fe_{(1-x)}S$ | 4.7 | 5.0 | 5.1 | 5.5 | 5.6 |
| Pentlandite (wt.%) | $(Fe,Ni)_9S_8$ | 2.8 | 2.6 | 2.7 | 1.9 | 0.8 |
| Quartz (wt.%) | $SiO_2$ | 1.6 | 2.1 | 2.4 | 2.8 | 2.3 |