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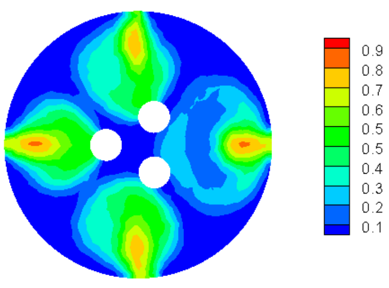

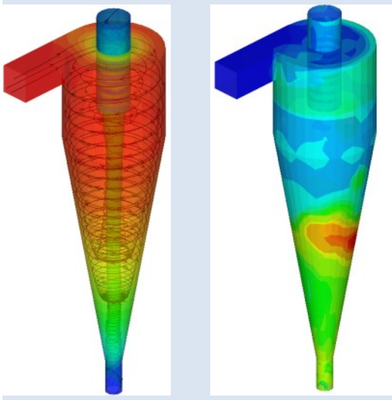

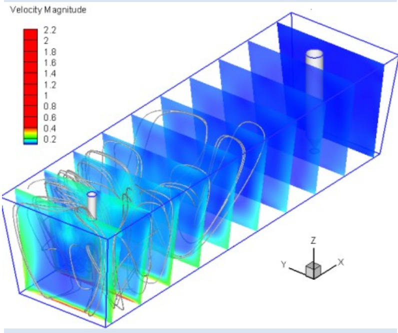

Report on Microwave for Leaching

Xiang-Qi Wang and Arun S. Mujumdar

Minerals, Metals and Materials Technology Centre (M3TC)
Faculty of Engineering, National University of Singapore

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MINERALS, METALS AND MATERIALS TECHNOLOGY CENTRE (M3TC)
NATIONAL UNIVERSITY OF SINGAPORE

Report on Microwave for Leaching

Abstract

Microwave applications in mining and process metallurgy have been the subject of many research studies over the past two decades. This paper reviews microwave-assisted leaching of copper, gold, nickel, cobalt, and manganese, lead and zinc and also coal desulphurization. It has been recognized that microwave technology has great potential to improve the extraction efficiency of metals in terms of both reduction in required leaching time and increased recovery of valuable metal. Despite a significant number of research studies in this area and potential for achieving highly attractive benefits, there is no agreement to the mechanism of interaction of microwaves with hydrometallurgical systems.

Introduction

Compared with pyrometallurgy, hydrometallurgical extraction of metals from their ores is potentially highly attractive. This attractiveness is attributed to economical, environmental, and technical reasons. It is often less costly and less harmful to the environment by avoidance of hazardous gases emissions such as SO_2. In addition, metals can be obtained directly in pure form from leach solution or recovered from impure leach solution. Factors such as the relatively mild corrosion issues compared to refractory lining consumption in smelting operations; low temperature processing; low handling cost of leaching products; possibility of treatment of low grade ores and the scale of operation make leaching more preferable than high temperature smelting.

However, some problems may arise during hydrometallurgical operations. These include: low recovery of extracted metal, difficulties in solid–liquid separation and effect of impurities on the ease of purification. The principal disadvantage of hydrometallurgical operations is probably the process times required to achieve high metal recovery since these processes are often carried out at low temperatures compared to pyrometallurgical processes.

Microwave-assisted leaching has been investigated in an attempt to improve the yield of extracted metal and to reduce process time, especially with the increasing demand for more environmental friendly processes. Unique microwave heating characteristics are the main driver for potential implementation in metal extraction. These include: **low processing time, direct, selective and volumetric heating, and a more controllable heating process.** It was indicated that microwave energy could have a potential application in comminution, drying, pre-treatment of refractory gold ores, coal desulphurisation, leaching, roasting, carbon reactivation, carbothermic reduction of oxides and waste and slag management [1].

Microwave energy is a form of electromagnetic energy, which travels in high frequency waves. The wavelengths are between 1 mm and 1 m with corresponding frequencies between 300 MHz and 300 GHz. Within this range, microwaves have extensive use in communication, especially in radar, cellular phones, television and satellite applications [2]. The most commonly used frequencies for heating purposes are 915 MHz and 2.45 GHz, which correspond to wavelengths of 33.5 and 12.2 cm, respectively. These frequencies were chosen by international agreement to minimize the interference with communication services [3].

Microwave heating is a process within a family of electro-heat techniques, such as induction, radio frequency, direct resistance, and infrared heating, which utilize specific parts of electromagnetic energy. Microwave heating of dielectric materials lies in the ability of the electric field to polarize the charge of the material where polarization cannot follow the rapid change of the electric field. The main types of dielectric polarization are:

- **Electron polarization** due to the change of electron position around the nucleus;
- **Atomic polarization** caused by positional shifts of the nucleus due to the non-uniform distribution of the charge within the molecule;

- **Orientation polarization** caused by the reorientation of the permanent dipoles due to the influences of electric field;
- **Spatial charge polarization** observed when material contains free electrons whose distribution is limited by the grain surface.

Orientation (dipole) polarization is the most important mechanism at the microwave frequencies because the energy required for electron and atomic polarization is much greater than can be produced by microwave frequencies. Therefore, these effects do not contribute to dielectric heating at microwave frequencies.

Ionic conduction is another important microwave heating mechanism. When a microwave field is applied to a solution containing ions, they move due to their inherent charge. As a result, ions collide and the collisions cause the conversion of kinetic energy to thermal energy. As the concentration of ions increases in solution, more collisions occur, causing the solution to heat faster.

Depending on the response to microwave heating, materials can be classified into three principal groups with respect to their interaction with a microwave field:

1. Transparent or low loss materials where microwaves pass through without any losses;
2. Conductors which reflect microwaves without any penetration;
3. Absorbing or high loss materials, which absorb microwaves and dissipate the electromagnetic energy as heat, depending on the value of the dielectric loss factor.
4. Materials containing two or more phases with different dielectric properties. Microwaves can selectively heat the high loss phase passing through the low loss one without significant absorption [4].

Microwave leaching

Microwave leaching of chalcopyrite

Chalcopyrite is the most important copper mineral in terms of scale of use and availability. This mineral is generally treated by pyrometallurgical processes either in reverberatory furnaces or by using flash smelting techniques. However, recently, there has been interest in hydrometallurgical leaching of sulphide minerals due to the requirement to avoid SO2 emission.

From an economic point of view, the most practical oxidants of chalcopyrite are ferric ions. However, the leaching rate of chalcopyrite is very slow when using ferric sulphate and is also slow in ferric chloride media. The slow reaction kinetics of chalcopyrite dissolution in these systems is due to the formation of sulphur layer around the particles preventing the oxidant from reaching unreacted mineral surface. Several techniques have been used to increase the reactivity of chalcopyrite, such as sulfidizing chalcopyrite activation, mechanical activation, organic extracting additions, the use of ozone as an oxidant, and the use of promoters (silver ions, surfactants, carbon particles, iron powder or hematite) [1].

The first attempt to use microwave energy to improve copper recovery from its ores was conducted by Kruesi and Frahm [5]. They obtained a US patent for the recovery of copper from its oxide and sulphide ores using microwaves. Various methods for different ores and concentrates were presented. More investigations can be found in Table 1.

Table 1 Previous study on microwave leaching of chalcopyrite.

References	Samples	Microwave	Results
Kruesi & Frahm [5]	1.6% copper 53% copper oxides 47% copper sulphide	600 W 2.45 GHz	86% of copper was found to be soluble.
Walkiewicz et al. [6]	24% copper with ferric chloride hexahydrate	1-kW 2.45 GHz	30% Cu was extracted after 10 min 224°C; 22% Cu was extracted after 10 min 255°C. Cu extraction is by non-thermal effect.
Worner [7]	85% copper (24%	650 W	Cu was found to completely dissolve with

	Cu, 29% Fe, 33% S, minor Pb, Zn, etc.) 15% ground peat		the resulting blue solution being separated from iron oxide residue.
Antonucci & Correa [8]	-	1 Kw 2.45 GHz	90% and 99% with high copper concentration in solution.
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Gold leaching

Hydrometallurgical extraction of gold from its ores by leaching with sodium cyanide proceeds according to the following reaction

$$4\mathrm{Au} + 8\mathrm{NaCN} + \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{NaAu(CN)}_2 + 4\mathrm{NaOH}$$

However, gold recovery from refractory gold ore is very low when conventional cyanide leaching is applied without pre-treatment. The main reason for refractoriness is the finely disseminated nature of gold in such ore. Therefore, high temperature oxidation, high pressure oxidation or biochemical oxidation pre-treatment have been investigated as a means of improving gold recovery. However, these methods are cost intensive, time consuming or impractical. One reason that microwave energy may have found successful application in gold extraction is that gold-bearing minerals tend to be good microwave absorbers, whereas gangue minerals commonly found in gold ores are microwave transparent.

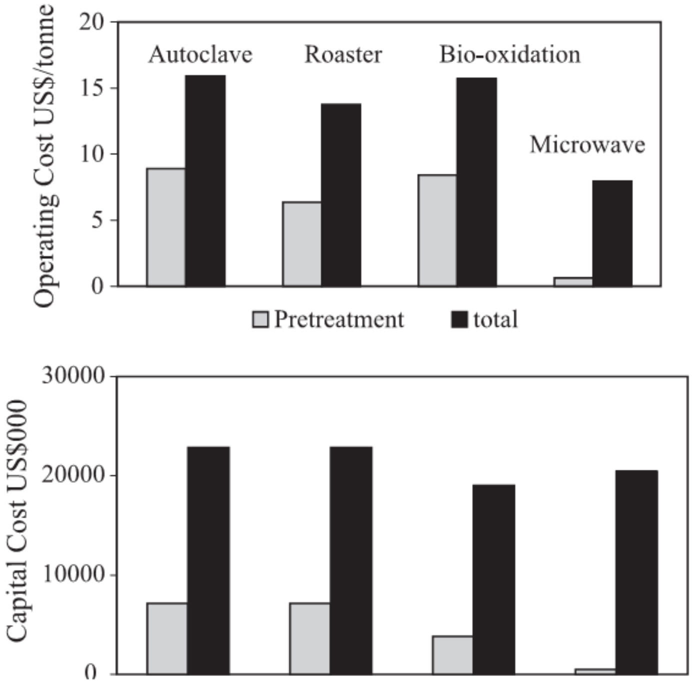

Figure 1 Comparative cost estimate for major gold ore pre-treatment technologies for a plant throughput of 200 tpd of concentrate [9].

Following Vaughan [10], the refractory gold has further categorized into two groups: (1) locked gold ore and (2) reactive gangue mineralogy. In the locked gold ore, the gold is either in solid solution or completely encased by the sulphidic matric mineral, such as pyrite and arsenopyrite. The reactive gangue ore type can be further classified as follows: (i) preg-robbing carbonaceous ores that absorb leached gold from the solution and (ii) ores in which the gold is associated with minerals that consume unacceptable quantities of leaching reagents. When both sulphides and carbonaceous matter are present then the ore is classified as a double refractory ore.

The microwave roasting of a double refractory gold ore was investigated by Nanthakumar et al. [11]. The results showed that the three major reactions involved in the roasting process were:

oxidation of pyrite, oxidation of the carbonaceous matter and the decomposition of carbonates. Both the real and the imaginary permittivities of the ore were relatively low but, in general, increased with increasing temperature. After roasting, the room temperature permittivities decreased to extremely low values and this was attributed to the removal of water, the carbonaceous matter and the conversion of pyrite to hematite. With direct microwave heating, the temperature of the ore increased with mass, time and energy input. However, because of the poor microwave absorption, large sample masses are required and this reduces the surface area to volume ratio and thus oxidation of the organic carbon was not possible. Therefore, direct microwave roasting was not feasible. Using magnetite as susceptor, indirect microwave roasting was tested, preg-robbing was eliminated and gold recoveries were over about 98%. In conventional roasting, the organic carbon could be eliminated at temperatures below that at which the carbonate carbon was removed. However, in the indirect microwave system, in contrast to conventional heating, the heating was not uniform and thus it was necessary to remove some carbon from the dolomite in order to eliminate all of the organic carbon. For microwave roasting, both the total carbon removal rate and the heating rate were higher and the specific energy consumptions were lower than the corresponding values for conventional roasting. For all the roasting processes, the sulphide sulphur was readily eliminated.

At EMR Technology, Canada, arsenopyrite gold ore was subjected to microwave pre-treatment under very low oxygen conditions at an energy level below 50 kJ/kg for very short time. The product contained pyrrhotite, elemental sulphur and arsenic, which was then acid washed to remove elemental suphur and arsenic then retreated again to oxidize pyrrhotite to magnetite [9]. The main advantages of this process were suggested to be low energy cost (about Cdn $0.5/tonne), the low SO_2 emission and the ore being processed at lower temperature than conventional roasting. An estimate of operational costs for a microwave treatment plant capable of processing 200 tonnes/day of ore concentrate compared to costs for roasters, autoclaves and bio-oxidation processes are shown in Figure 1. EMR put into operation a pilot plant for microwave pre-treatment of pyrite and arsenopyrite gold ores in 1997 which incorporated two microwave generators with a power level of 75 kW at a frequency of 915 MHz and a fluidized-bed-based cavity.

Coal desulphurization

The presence of sulphur in coal leads to SO_2 emission into the atmosphere during burning causing environmental problems. Generally, sulphur is present in coal in two forms: organic and pyritic. Conventionally, pyritic sulphur is removed by partial oxidation, chlorination, hydrodesulphurisation, and aqueous alkali leaching. However, organic sulphur can be removed only by molten caustic methods.

There have been several attempts to minimize sulphur content in coal using microwave energy to assist coal desulphurization.

Leaching of nickel, cobalt and manganese

Nickel and cobalt have been recovered from laterite ores by smelting operations to obtain ferronickel-cobalt, these are then selectively dissolved with ammonia-ammonium carbonate. This process is energy intensive. Alternatively, nickel and cobalt can be recovered by applying microwave radiation to the mixture of laterite, ferric chloride and sodium chloride. When the mixture was microwaved for 4 to 8 min, chlorides were formed which were subsequently leached in water. Manganese and cobalt can also be recovered in a similar way from deep-sea nodules. Microwave heating was applied directly to the leaching slurry containing sulphuric and hydrochloric acids. Metal extraction increased considerably compared with conventional leaching at temperature between 230 and 250 ^{o}C.

Extractions of lead and zinc from their ores and compounds

Microwave treatment was carried out in an adapted microwave oven with an energy output of 650 W at 2.45 GHz. In a similar study [12], it was found that microwave leaching kinetics of sphalerite in ferric sulphate were much faster than those produced by conventional leaching. The results showed that 92% of zinc was leached within 90 min when microwaves were applied compared to 41% total zinc recovery under conventional conditions. It has been suggested that, compared to other sulphide minerals, sphalerite is a poor absorber of microwave energy. In addition, it is likely that the heating rate of sphalerite in a microwave field is sensitive to the iron content of the mineral.

Another alternative source of zinc is from zinc silicate ores. However, when such ore is treated by hydrometallurgical processes, minimization of the dissolution of iron and silica and increased zinc recovery can be a problem. Using a quick leach method, the dissolution of silica could be reduced. However, iron dissolution increases which is not preferable. Hua et al. [13] applied microwave heating to quick leach zinc from silicate ores in diluted sulphuric acid. The zinc extraction increased with a combination of reduction in silica gel formation and iron dissolution. The authors obtained 99% zinc extraction after 15-min microwave leaching. The iron and silica in solution were as low as 0.3% and 0.1%, respectively.

Electric arc furnace (EAF) dust contains considerable amounts of lead and zinc and it is considered a hazardous waste. Zinc occurs in EAF dust mainly as zincite (ZnO) and magnetite-franclinite ($ZnFe_2O_4$). Lead occurs as lead oxide (PbO). It was observed that the leaching kinetics of zinc and lead in caustic solution were significantly improved when microwave energy was used as a heating source. The leaching efficiency was strongly dependent on the power, caustic concentration and solid/liquid ratio. According to the authors, this may be due to super heating of liquids, extremely violent behavior and interaction of the mcirowaves with the EAF dust solids in the solution (temperature of particles higher than would be achieved in conventional heating).

M3TC's potential projects

Possibility of mathematical modeling.

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Conclusion

The application of microwave energy in mining and metallurgy is in the early stages. The information presented in this review shows that microwaves have potential application in mineral processing and extraction of metals such as copper, gold, nickel, cobalt, lead, zinc and manganese. Also the use of microwave for coal desulphurization seems to be promising.

It has been shown that many research studies have been conducted to examine microwave-assisted leaching. However, there are no or limited industrial applications of the technology. This is may be due to a lack of understanding of the influence of microwaves on a particular leaching reaction system. The explanations that are used to justify the acceleration of the reaction rate under microwaves are:

- The existence of a non-thermal effect which reduces the activation energy of the reaction;
- The super heating effect occurring during dielectric heating making the temperature no longer representative of the reaction conditions;
- The large temperature gradient between solids and liquids assisting the mass transport from the reaction interface due to the generation of large thermal currents;
- The increase in surface area due to cracks initiated when solid particles contain more than one phase with different heating rates.

It is believed that the lack of reliable temperature measurement is the main reason behind the misunderstanding regarding the real microwave effect in any reaction system. Control and measurement of temperature in microwave fields is a major challenge because the electric field induced can cause serious errors or damage the thermocouples unless they have been carefully designed.

Non-thermal microwave effects are still under debate and not clearly proved. Non-thermal effects are not important if microwave irradiation is used as a convenient way to deliver heat. However, understanding of microwave interaction with materials and chemical systems is required to optimize the operation involved to achieve the best result with minimum energy consumption. This is because microwave energy is expensive in terms of capital cost and energy conversion factors. However, despite the debates that are ongoing, microwave energy has unique advantages that are waiting for greater exploitation.

References

1. Al-Harahsheh, M. and S.W. Kingman, *Microwave-assisted leaching--a review.* Hydrometallurgy, 2004. **73**(3-4): p. 189-203.
2. Thostenson, E.T. and T.W. Chou, *Microwave processing: fundamentals and applications.* Composites Part A: Applied Science and Manufacturing, 1999. **30**(9): p. 1055-1071.
3. Meredith, R.J., *Handbook of Industrial Microwave Heating*, ed. R. Meredith. 1998, London: Institution of Electrical Engineers.
4. Clark, D.E., D.C. Folz, and J.K. West, *Processing materials with microwave energy.* Materials Science and Engineering A, 2000. **287**(2): p. 153-158.
5. Kruesi, P.R. and J. Frahm, Veryl H., *Process for the recovery of nickel, cobalt and manganese from their oxides and silicates*, United States Patent 4311520, 1982.
6. Walkiewicz, J.W., G. Kazonich, and S.L. McGill, *Microwave heating characteristics of selected minerals and compounds.* Minerals and Metallurfical Processing, 1988. **5**(1): p. 39-42.
7. Worner, H.K., *Microwave irradiation of composites*, United States Patent 4906290, 1988.
8. Antonucci, V. and C. Correa. *Sulphuric acid leaching of chalcopyrite concentrate assisted by application of microwave energy*. in *Proceeding of COPPER 95-COPRE 95 International Conference. Electrorefining and Hydrometallurgy of Copper*. 1995. Santiago, Chile: The Metallurgical Society of CIM.
9. Tranquilla, J.M. *Mineral extraction and the use of microwave*. in *CIM Conference*. 1997. Vancouver, British Columbia, Canada.
10. Vaughan, J.P., *The process mineralogy of gold: The classification of ore types.* Journal of Metals, 2004. **56**(3): p. 46-48.
11. Nanthakumar, B., C.A. Pickles, and S. Kelebek, *Microwave pretreatment of a double refractory gold ore.* Minerals Engineering, 2007. **20**(11): p. 1109-1119.
12. Peng, J. and C. Liu, *Kinetics of leaching ofsphalerite with pyrolusite simultaneously by microwave irradiation.* Transaction of Nonferrous Metals Society of China, 1997. **7**(3): p. 152-154.
13. Hua, Y., Z. Lin, and Z. Yan, *Application of microwave irradiation to quick leach of zinc silicate ore.* Minerals and Metallurfical Processing, 2002. **15**: p. 451-456.