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Mamdouh Omran

ACTA

# MICROWAVE DEPHOSPHORISATION OF HIGH PHOSPHORUS IRON ORES OF THE ASWAN REGION, EGYPT

DEVELOPING A NOVEL PROCESS FOR HIGH PHOSPHORUS IRON ORE UTILIZATION

UNIVERSITY OF OULU GRADUATE SCHOOL; UNIVERSITY OF OULU, FACULTY OF TECHNOLOGY



#### ACTA UNIVERSITATIS OULUENSIS C Technica 556

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### MICROWAVE DEPHOSPHORISATION OF HIGH PHOSPHORUS IRON ORES OF THE ASWAN REGION, EGYPT

Developing a novel process for high phosphorus iron ore utilization

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#### Abstract

There is a rapidly increasing demand for iron resources with the fast-paced development of the iron and steel industry. For this reason, the iron and steel industry is facing the risk of a raw material shortage. Deposits of high-phosphorus iron ores are widely spread worldwide, but the use of these deposits in industry is limited owing to the high phosphorus content, which affects the cost of the iron making process and the quality of the produced steel. For the utilization of high phosphorus oolitic iron ore, many hydrometallurgical and pyrometallurgical processes have been proposed. However, these methods have disadvantages, such as causing environmental pollution, not being cost-effective, being overly time consuming and having low iron recovery.

The aims of this present work are to study the possibility of the usage of microwave treatment to remove phosphorus from high phosphorus iron ore on a laboratory scale. This objective can be obtained through a combination of microwave pretreatment and physical separation methods.

The findings into the microwave treatment of high phosphorus iron ore are quite promising. The results have indicated that microwave heating increase liberation, improves magnetic properties and reduces the processing time of iron ore. The results of ultrasound treatment showed that a significant increase in iron grade and a reduction in phosphorus content of the product can be obtained. The results indicate that microwave pretreatment should be considered as a factor significantly affecting the result of ultrasonic treatment. Depending on the sample texture and degree of phosphorus liberation, more than 59 % phosphorus removal can be obtained.

Keywords: grindability, high phosphorus iron ore, liberation, magnetic properties, microwave heating, ultrasonic treatment

#### Omran, Mamdouh, Mikroaaltotekniikkaan perustuvan fosforinpoistomenetelmän kehittäminen korkeafosforiselle egyptiläiselle malmille. Uuden paljon fosforia sisältävän rautamalmin hyödyntämisprosessin kehittäminen

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#### Tiivistelmä

Raudan ja teräksen valmistusmäärien kasvaessa on tarve jalostaa aiemmin hyödyntämättömiä rautamalmeja ja ehkäistä siten mahdollinen raaka-ainepula tulevaisuudessa. Maailmalla on runsaasti rautamalmiesiintymiä, jotka sisältävät paljon fosforia. Näitä esiintymiä käytetään suuren fosforipitoisuuden vuoksi vain rajallisesti, koska fosfori heikentää raudan valmistusprosessin kustannustehokkuutta ja tuotetun teräksen laatua. Paljon fosforia sisältävän ooliittisen rautamalmin hyödyntämiseksi on ehdotettu monia erilaisia hydro- ja pyrometallurgisia prosesseja. Näihin menetelmiin liittyy kuitenkin haittapuolia, kuten huomattava ympäristörasitus, heikko kustannustehokkuus, prosessien hitaus ja alhainen raudan talteensaanti.

Tämän tutkimuksen tavoitteena oli tutkia laboratorio-olosuhteissa mahdollisuutta käyttää mikroaaltokäsittelyä fosforin poistamiseen paljon fosforia sisältävästä rautamalmista. Fosforinpoistoa tutkittiin mikroaaltoesikäsittelyn ja mekaanisten erottamisprosessien avulla.

Tutkimuksen perusteella mikroaaltokäsittely vaikuttaa olevan lupaava tapa poistaa fosforia paljon fosforia sisältävästä rautamalmista. Tutkimustulosten mukaan mikroaaltolämmitys parantaa erotustehokkuutta ja magneettisia ominaisuuksia sekä vähentää rautamalmin käsittelyyn kuluvaa aikaa. Ultraäänikäsittelyn tulokset osoittavat, että prosessin avulla voidaan parantaa merkittävästi rautarikasteen laatua ja pienentää rikastetuotteen fosforipitoisuutta. Tulokset viittaavat siihen, että mikroaaltoesikäsittelyllä voidaan merkittävästi vaikuttaa ultraäänikäsittelyn tehokkuuteen. Malmipartikkelien tekstuurista ja fosforin erottamisasteesta riippuen tutkitulla menetelmällä voidaan poistaa jopa 59 prosenttia fosforista.

*Asiasanat:* erottaminen, jauhautuvuus, magneettiset ominaisuudet, mikroaaltolämmitys, paljon fosforia sisältävä rautamalmi, ultraäänikäsittely

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Oulu, October 2015

Mamdouh Omran

# Abbreviations

B.E	Binding energy
Ch	Chamosite
EPMA	Electron Probe Microanalyses
EHF	Extremely high frequency
Emu	Electromagnetic unit
FWHM	Full Width at Half Maximum
FTIR	Fourier Transform Infrared
G1	High phosphorus content sample
G2	Low phosphorus content sample
G3	Intermediate phosphorus content sample
GHz	Gigahertz
Go	Goethite
Н	Applied magnetic field intensity
He	Hematite
Hr	Hour
kHz	Kilohertz
kWh	Kilowatt-hour
М	Magnetization
MHz	Megahertz
MS	Mass Spectroscopy
MWT	Microwave treatment
Oe	Orested
OM	Optical Microscope
Р	Fluoroapatite
Qz	Quartz
S	Second
SEM - EDS	Scanning Electron Microscope
SHF	Super-high frequency
Т	Tesla
TG-DSC	Thermogravimetry - Differential Scanning Calorimetry
TFe	Total iron
UHF	Ultra-high frequency
VSM	Vibrating Sample Magnetometer
W	Watt
WHIMS	Wet High Intensity Magnetic Separation

XRD X-ray Diffraction	
-----------------------	--

- XRF X-ray Fluorescence
- XPS X-ray Photoelectron Spectroscopy

# List of original publications

This thesis is based on the following publications, which are referred to throughout the text by their roman numerals.

- I Baioumy H, Omran M & Fabritius T (2015) Mineralogy, geochemistry and the origin of high-phosphorus oolitic iron ores from Aswan, Egypt. Manuscript.
- II Omran M, Fabritius T, Abdel-Khalek N, El-Aref M, Elmanawi AE.-H, Nasr M & Elmahdy A (2014) Microwave assisted liberation of high phosphorus oolitic iron ore. J Miner Mater Charact Eng 2: 414-427.
- III Omran M, Fabritius T, Elmahdy A, Abdel-Khalek N, El-Aref M & Elmanawi AE.-H (2014) Effect of microwave pre-treatment on the magnetic properties of iron ore and its implications on magnetic separation. Sep Purif Technol 136: 223-232.
- IV Omran M, Fabritius T, Elmahdy A, Abdel-Khalek N, El-Aref M & Elmanawi AE.-H (2015) XPS and FTIR spectroscopic study on microwave treated high phosphorus iron ore. App Surf Sci 345: 127 -140.
- V Omran M, Fabritius T & Mattila R (2015) Thermally assisted liberation of high phosphorus oolitic iron ore: A comparison between microwave and conventional furnaces. Powder Technol 269: 7–14.
- VI Omran M, Fabritius T, Elmahdy A, Abdel-Khalek N & Gornostayev S (2015) Improvement of phosphorus removal from iron ore using combined microwave pretreatment and ultrasonic treatment. Sep Purif Technol, doi: http://dx.doi.org/10.1016/j.seppur.2015.10.071

All of the above publications were written by the author of this thesis, whose main responsibilities were to carry out literature surveys, experimental work, analysis and writing.

# Contens

A	bstra	ct	
Ti	iviste	elmä	
A	cknov	wledgements	7
A	bbrev	viations	9
Li	st of	original publications	11
C	onten	15	13
1	Intr	oduction	15
	1.1	Objective and scope	16
2	Bac	kground	19
	2.1	Traditional methods	19
	2.2	Microwave treatment in mineral processing	21
	2.3	Fundamentals of microwave heating	22
3	Mat	terials and methods	25
	3.1	Materials	25
	3.2	Analytical techniques	27
	3.3	Experimental	30
		3.3.1 Microwave treatment	30
		3.3.2 Conventional Heating	31
		3.3.3 Magnetic separation	31
		3.3.4 Ultrasonic apparatus	32
4	Res	ults and discussion	35
	4.1	Material characterization	35
	4.2	Optimization of Microwave Heating	38
		4.2.1 Effect of sample particle size	38
		4.2.2 Effect of exposure time	39
		4.2.3 Effect of microwave power intensity	43
	4.3	Effect of microwave pretreatment on the liberation of high	
		phosphorous oolitic iron ore	43
	4.4	Effect of microwave pretreatment on the grindability of iron ore	47
	4.5	Effect of microwave pretreatment on the magnetic properties of	
		iron ore	48
	4.6	Effect of microwave pretreatment on the magnetic separation of	
		iron ore	51
	4.7	Comparison between microwave and conventional furnace	
		pretreatment of iron ore	53
			13

		4.7.1	Liberation	53
		4.7.2	Grindability	54
		4.7.3	Magnetic properties	55
		4.7.4	Energy consumption	56
	4.8	Ultras	sonic treatment of high phosphorus iron ore	57
		4.8.1	Effect of microwave pretreatment on the efficiency of	
			ultrasonic treatment of iron ores	58
		4.8.2	Effect of sonication time	
		4.8.3	Effect of particle size	61
		4.8.4	Effect of Pulp density	61
5	Sun	nmary	and conclusions	65
	5.1	Recor	nmendations for the future work	69
Re	efere	nces		71
O	rigin	al pub	lications	79

### 1 Introduction

In Egypt, iron-ore deposits occur in East Aswan, Eastern Desert, Bahariya Oasis, Western Desert and several localities near the Red Sea coast. Iron production in Egypt, which is mainly from El Gedida area, in Bahariya Oases, is decreasing today. The remaining minable reserves are just enough for about 15-20 years. The second important reserve of iron ores is present in East Aswan region. The problem with Aswan iron ore is its high phosphorus content, which affects the cost of the iron making process due to the high energy consumption during reduction, in addition to the low quality of the produced steel "brittle".

Deposits of high-phosphorus oolitic iron ores are widely spread worldwide (e.g. Abro et al. 2011, Champetier et al. 1987, El Aref et al. 1996, EL Sharkawi et al. 1996, Li et al. 2011, Manieh 1984, Ozdemir & Deutsch 1984), and some deposits contain huge reserves. The main obstacle associated with exploiting these deposits is the high contents of phosphorus in particular, mainly due to the poor liberation of iron minerals from phosphorus gangues. Song et al. (2013) observed that fine grinding (commonly 1-5 µm) is required to liberate iron minerals from associated phosphorus and gangue minerals. Such fine particles are very difficult to beneficiate via conventional mineral processing processes (e.g., flotation and magnetic separation). The two main challenges regarding the liberation of iron minerals from their associated phosphorus is high energy consumption during the very fine grinding required, and the efficiency of physical separation (Song et al. 2013). Approximately 1.5%-2% of industrial mining countries' total national energy consumption can be attributed to comminution (Tromans 2008). Wang et al. (2012) advocated two main reasons for investigating the improvement of liberation: first, the liberation of larger particles reduces the amount of energy consumed during grinding, and second, because a very fine grain size is extremely difficult to physically separate during separation processes, this results in increased energy consumption during grinding. Physical separation techniques, such as flotation or magnetic separation, are suitable for particle liberation at coarse grain size (> 10 µm) (Song et al. 2013). When discussing physical separation techniques, it is critical to focus on techniques that consume minimum amounts of power while still offering maximum particle size in relation to particle liberation.

Based on the above reasons, the use of these iron ores is limited in industry. Many attempts have been made to reduce phosphorus content to the accepted level, e.g. chemical leaching (Cheng *et al.* 1999, Xia *et al.* 2011), magnetization roasting and reduction (Tang *et al.* 2010, Yu *et al.* 2011), bioleaching (Delvasto *et al.* 2008,

Wang *et al.* 2010), but these methods still have disadvantages, such as causing environmental pollution, not being cost-effective, being time consuming and having low levels of iron recovery. Therefore, how to develop a novel method of removing phosphorus is the key factor for the rational use of high phosphorus iron ore resources, which is very important for the development of iron and steel industry.

#### 1.1 Objective and scope

The problem with the studied iron ore is its high phosphorus content, which affects the cost of the iron making process due to the high energy consumption during size reduction and low quality of the produced steel "brittle". The aims of the present research are to study the effect of a new technique (microwave heating) on the removal of phosphorus from high phosphorus iron ore. This objective can be obtained through a combination of microwave pre-treatment and physical separation. To achieve the aim of the thesis, the following objectives were set:

- 1. Mineralogical and geochemical investigations of representative iron ore samples using different techniques.
- 2. Optimization of microwave treatment through the study of the different microwave parameters.
- 3. To study the effect of microwave pre-treatment on the properties of iron ore including: grindability and liberation of the iron ore, magnetic properties of the iron ore and its implication on magnetic separation.
- 4. To study the mechanism of the effect of microwave radiation on the structure of iron bearing minerals by using different techniques.
- 5. Comparison between the microwave heating and conventional furnace heating on the characteristics of iron ore.
- 6. To study the possibility of phosphorus removal by the application of physical separation after microwave pretreatment. For example, using an ultrasonic technique.

As illustrated in Fig. 1, the relation of the original articles to the objective of the thesis can be presented as follows:

 Article I aims to highlight the texture, mineralogy and origin of P-bearing minerals in these ores. The paper also provides an opportunity to examine the distribution and mineralogy of trace and rare earth elements in these ores and discusses the possible source(s) of iron based on the geochemistry of these elements.

- Article II discusses the effect of microwave pretreatment on the grindability and liberation of iron ore, and optimization of microwave heating through studying the effect of different microwave parameters such as microwave power, exposure time and grain size of particles.
- Article III presents the effect of microwave radiation on the magnetic properties of iron ore by using a vibrating sample magnetometer and its implication on magnetic separation of iron minerals by using a wet high intensity magnetic separation technique.
- **Article IV** address the mechanism of the effect of microwave radiation on iron bearing and phosphorus bearing minerals by using different techniques.
- Article V provides a comparison between microwave and conventional furnace heating for the following items "liberation, grindability of iron ore and amounts of energy consumption during experiments."
- Article VI discusses the possibility of phosphorus removal by application of a physical separation method (e.g. ultrasonic treatment) after microwave pretreatment.



Fig. 1. Relation of the original articles to the objective of thesis.

## 2 Background

#### 2.1 Traditional methods

Phosphorus removal from the high-phosphorus oolitic iron ores has been investigated by several processes including:

- A) Hydrometallurgical methods (chemical leaching), (e.g. Cheng *et al.* 1999, Edwards *et al.* 2011, Fisher-White *et al.* 2009, Fisher-white *et al.* 2012, Ionkov *et al.* 2011, Ionkov *et al.* 2012, Ionkov *et al.* 2013, Patrick *et al.* 2001, Muhammed & Zang 1989, Yu *et al.* 2013 a&b, Xia *et al.* 2011, Zhu *et al.* 2010);
- B) Pyrometallurgical methods (magnetic roasting magnetic separation, direct reduction roasting -magnetic separation), (Bai *et al.* 2012, Li *et al.* 2011, Li *et al.* 2013, Li *et al.* 2014, Sun *et al.* 2012, Sun *et al.* 2013, Sun *et al.* 2015, Tang *et al.* 2010, Tang *et al.* 2014 a&b, Yu & Qi 2011, Yongli *et al.* 2012, Yin *et al.* 2012, Zhu *et al.* 2013);
- C) Microbiological method (bioleaching), (Delvasto *et al.* 2008, Delvasto *et al.* 2009, Wang *et al.* 2010), and
- D) Physical methods (selective flocculation-reverse flotation), (e.g. Ji 2003).

Fisher-White et al. (2012) studied the effects of heat treatment with sodium hydroxide followed by leaching with water, and a caustic leach of material heated without an additive, on the removal of phosphorus from goethitic iron ores. The results demonstrated that heating, followed by a caustic leach, reduced the phosphorus levels in the ore to below 0.075%. Although the phosphorus content reached an acceptable level, high levels of sodium in ores may be detrimental in a blast furnace feed. The results show the formation of water-insoluble sodium species during heat treatment with sodium hydroxide. Ionkov et al. (2011) & Ionkov et al. (2012) investigated the improvement of the leaching efficiency during phosphorous removal from high phosphorous gravity magnetic concentrate. The laboratory tests performed for dephosphorisation show that the combination of alkaline roasting followed by low intensity magnetic separation and acid leaching enables obtaining high-grade iron concentrate. Edwards et al. (2011) examined the leaching of Australian iron ores rich in phosphorus after roasting to 300°C. Zhu et al. (2010) studied the dephosphorisation of high P oolitic iron ore from Chinese deposits by roasting at 800°C, magnetic separation and leaching with sulfuric acid. Tang et al. (2010) proposed a new method (gas-based separation plus melt separation) to remove phosphorus from high phosphorus iron ore. Li et al. (2011)

studied how to extract iron from oolitic iron ore using a deep reduction and magnetic separation technique. Reduction roasting followed by magnetic separation has been applied to recover iron from oolitic hematite ore (Li *et al.* 2010, Matinde & Hino, 2011a&b). For magnetic roasting, the magnetic separation of magnetite from phosphorus is unsatisfactory because the typical structure of oolitic hematite remains approximately unchanged. Bai *et al.* (2012) studied the effect of sodium carbonate carbothermic reduction followed by magnetic separation on the dephosphorisation of limonitic iron ore. The results showed that the phosphorus content of the obtained magnetic concentrate is still high. Weissberger & Zimmels (1983) stated that Fe–P separation is more difficult to achieve from oolitic hematite ores with relatively more complex mineral compositions, textures and structures.

Although some of these methods achieve the purpose of phosphorus removal, they still have disadvantages, such as a low efficiency of dephosphorization, environmental pollution, relatively high cost, being overly time consuming, and low iron recovery. Bioleaching is usually very time consuming. The biological methods require a long processing duration. Leaching bacteria require collection, separation, culture and domestication, which all influence production efficiency (Xia *et al.* 2011).

Hydrometallurgical methods (acid leaching or caustic leaching), produce waste liquids and have negative impacts on the environment. Chemical leaching consumes a large amount of water for washing acids after the leaching process, and this represents the main problem in countries which have a shortage in water resources (like Egypt). In addition, inorganic acid may cause the loss of soluble iron (Li *et al.* 2013).

Pyrometallurgical methods are more attractive with respect to their processing scale and cost. However, due to the complex oolitic structure and fine dissemination of phosphorus, the reduction process improves the iron recovery rate, but it is very difficult to separate the ferrous phase from the P-containing gangue (Han *et al.* 2014). The apatite layers in the oolitic structure unit are extremely thin, and ultra-fine-grinding ( $< 10 \,\mu$ m) is required for the reduced composites. If this is carried out then a satisfactory phosphorus removal degree could be obtained (Yin *et al.* 2012, Elias & Mitsutaka 2011, Li *et al.* 2011), although this results in very high levels of energy consumption.

The objective of the present research is to study the effect of a novel technique (i.e., microwave heating) on the preparation of phosphorus-containing iron ores before conventional concentration processes. This study is a positive step towards the efficient and economical utilization of oolitic high-phosphorus hematite.

#### 2.2 Microwave treatment in mineral processing

Recently, a growing interest in microwave heating in mineral treatment has emerged, and a number of potential applications regarding microwave processing have been investigated. These include microwave assisted ore grinding, microwave assisted carbothermic reduction of metal oxides, microwave-assisted drying and anhydration, microwave-assisted mineral leaching, microwave-assisted roasting and smelting of sulfide concentrate, microwave-assisted pretreatment of refractory gold concentrate, microwave-assisted spent carbon regeneration and microwaveassisted waste management (Kingman & Rowson 1998, Barani *et al.* 2011). The previous studies with microwaves have been carried out with a laboratory scale microwave oven. In order to design an industrial pilot scale microwave applicator, more studies on the dielectric characterization of minerals are needed.

Microwave treatment has been proposed as a means of decreasing the costs associated with size reduction while simultaneously improving the physical separation process, and supporting the liberation of valuable minerals in ores. Microwave heating has the potential for speedy and efficient heating of minerals and in a commercial context may provide savings in both time and energy.

The findings of the literature review revealed that microwave heating can improve the liberation, grindability, and magnetic separation of valuable minerals from ores and has the potential to provide a new method for treating ores successfully (e.g. Ali & Bradshaw 2010, Amankwah *et al.* 2005, Chen *et al.* 1984, Chen *et al.* 2012a, Chen *et al.* 2012b, Chen *et al.* 2013, Fitzgibbon & Veasey 1990, Jones *et al.* 2005, Jones *et al.* 2007, Kingman & Rowson 1998, Kingman *et al.* 1999, Kingman *et al.* 2000, Kingman & Rowson 2000, Kingman *et al.* 2004a, Kingman *et al.* 2015b, Song *et al.* 2014a, Omran *et al.* 2014b, Omran *et al.* 2015a, Omran *et al.* 2015b, Song *et al.* 2013, Sahyoun *et al.* 2003, Tromans *et al.* 2008, Uslu *et al.* 2003, waters *et al.* 2007, Wang *et al.* 2012, Walkiewicz *et al.* 1991, Whittles *et al.* 2003, Zhao *et al.* 2014).

Microwave treatment improves the liberation of oolitic iron ores by generating intergranular fractures in the oolitic structure (Song *et al.* 2013). The difference in the absorption of microwave energy, thermal expansion and the dielectric properties of minerals leads to the generation of intergranular fractures between minerals (Fitzgibbon & Veasey 1990, Kingman & Rowson 1998, Jones *et al.* 2005, Whittles *et al.* 2003, Jones *et al.* 2007).

The effect of microwave radiation on the grindability of iron ore has been examined by Walkiewicz *et al.* (1991). In their study, iron ore was subjected to

microwave power intensity of 3kW, while raising the temperature between 840 and 940 °C. SEM photomicrographs were then used to confirm fractures along grain boundaries and throughout the gangue matrix. Standard Bond grindability tests showed that the microwave treatment reduced the work index of the iron ores by between 10 and 24%.

The magnetic properties of minerals can be improved by using microwave treatment (Barani *et al.* 2011, Kingman *et al.* 2000, Sahyoun *et al.* 2003, Uslu *et al.* 2003, Waters *et al.* 2007, Znamenackova *et al.* 2005). The effect of microwave radiation on a number of minerals, e.g., chalcopyrite, hematite and wolframite, exhibited a considerable increase in magnetic susceptibility after being exposed to 650 W of microwave radiation (Kingman *et al.* 2000). Barani *et al.* (2011) studied the effect of microwave radiation on the magnetic properties of iron ore and their results indicated that microwave radiation has significant effects on the magnetic properties.

#### 2.3 Fundamentals of microwave heating

Microwave energy is a non-ionizing form of electromagnetic radiation with frequencies in the range of 300 MHz to 300 GHz. Microwave frequencies include three bands: ultra-high frequency (UHF: 300 MHz to 3 GHz), super-high frequency (SHF: 3 GHz to 30 GHz) and extremely high frequency (EHF: 30 GHz to 300 GHz) (Haque 1999, Roussy & Pearce 1995). Microwave electromagnetic radiation consists of oscillating electric and magnetic fields that can propagate through empty space (Fig. 2).

![](_page_23_Figure_4.jpeg)

Fig. 2. Microwave electromagnetic radiation.

Microwaves cause molecular motion by migration of ionic species and /or rotation of dipolar species. Microwave heating a material depends to a great extent on its 'dissipation' factor, which is the ratio of dielectric loss or 'loss' factor to the dielectric constant of the material. The dielectric constant is a measure of the ability of the material to retard microwave energy as it passes through; the loss factor is a measure of the ability of the material to dissipate the energy (Haque 1999, Barani *et al.* 2011). Microwave heating utilizes the ability of some materials to absorb electromagnetic energy in the microwave energy can be classified into three groups (Haque 1999, Barani *et al.* 2011, Roussy 1995, Jones *et al.* 2002, Znamenàčkovà *et al.* 2005) (Fig. 3):

- 1. Materials can be transparent to microwaves (such as silica) are classed as insulators, meaning that microwaves pass through the substance. Insulators are often used in microwave ovens to support the material to be heated.
- 2. Reflective Materials (e.g., metals) are classed as conductors, meaning that microwaves are reflected from the surface and therefore do not heat metals. Conductors are often used as conduits (waveguides) for microwaves.
- 3. Materials which are excellent absorbers of microwave energy are classed as dielectrics (such as metal oxides i.e. hematite, magnetite and most sulphides).

![](_page_24_Figure_4.jpeg)

# Fig. 3. Interaction of materials with microwave energy (Haque 1999, reprinted by permission of international journal of mineral processing).

Microwave heating is fundamentally different from conventional heating because microwaves take the form of electromagnetic energy and can penetrate deep into a sample. This allows sample heating to be initiated volumetrically, as opposed to conventional thermal processing, which heats the sample from the outside inwards via standard heat transfer mechanisms, i.e., convection, conduction, and radiation (Jones *et al.* 2002).

Compared with conventional heating techniques, the main advantages of microwave heating in terms of mineral processes are (Haque 1999, Jones *et al.* 2002):

- Non-contact heating;
- Energy transfer, rather than heat transfer;
- Rapid heating;
- Material selective heating;
- Volumetric heating;
- Lower power consumption;
- Heating starts from interior of the material body;
- Automation (operation and shutdown).

### 3 Materials and methods

#### 3.1 Materials

The iron ore samples used in this study were collected from the Aswan region, Egypt. The Eastern Aswan area represents the main occurrence of Cretaceous ironstone bands in South Egypt, which are confined to clastic successions belonging to the "Nubian" sandstones or "Nubia facies" (El Aref *et al.* 1996, EL Sharkawi *et al.* 1996). Three representative samples were obtained from the Aswan region taking into consideration the high-phosphorus intervals of the ore successions from the study areas. Fig. 4 shows the location of the different sample groups. Different size fractions of iron ore samples were prepared by crushing and sieving. The chemical and mineralogical analysis of the three representative samples are listed in Tables 1 and 2, respectively.

![](_page_26_Figure_3.jpeg)

Fig. 4. Simplified geographic map showing the location of the study iron ores.

Sample		TFe	P <sub>2</sub> O <sub>5</sub> (%)	CaO (%)	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	MgO (%)	F
code		(%)						(%)
G1	Bulk sample	48,33	5,64	7,59	15,03	3,37	1,23	0,37
	+125 -250 µm	48,57	3,48	5,36	17,70	3,70	1,25	0,21
	+250 -500 μm	47,97	3,17	4,83	20,07	3,40	1,14	0,22
	+500 – 1000 μm	51,11	3,09	4,70	17,25	3,10	1,03	0,19
	+10000 -2000 µm	49.78	3.42	5.33	16.98	3.65	1.12	0.19
G2	Bulk sample	46,08	2,25	2,67	29,54	3,27	0,27	0,32
	+125 -250 µm	46,96	1,89	2,44	30,32	2,58	0,36	0,28
	+250 -500 μm	45,35	1,45	1,75	33,26	2,41	0,45	0,29
	+500 – 1000 μm	44,23	1,33	1,59	34,61	2,24	0,26	0,3
	+10000 -2000 µm	45,33	1,42	1,82	33,62	2,35	0,25	0,28
G3	Bulk sample	58,27	3,24	5,44	7,48	4,47	1,26	0,19
	+125 -250 µm	59,61	2,50	4,67	8,16	3,99	0,92	0,07
	+250 -500 μm	58,50	2,79	4,97	8,66	4,12	0,99	0,09
	+500 – 1000 μm	62,30	2,28	4,10	6,84	3,40	0,74	0,05
	+10000 -2000 µm	58,82	2,45	4,78	7,89	3,88	0,88	0,21

Table 1. Chemical analyses (wt. %) for the three iron ore samples and different size fractions from each sample. (Paper VI, reprinted by permission of the Separation and Purification Journal).

(G1) High phosphorus sample, (G2) Low phosphorus sample, (G3) Intermediate phosphorus sample.

Table 2. Mineralogical composition (wt. %) for the three iron ore samples and different size fractions from each sample. (Paper VI, reprinted by permission of the Separation and Purification Journal).

Sample		Hematite	Goethite	Chamosite	Fluorapatite	Quartz
code		(%)	(%)	(%)	(%)	(%)
G1	Bulk sample	60,52	5,46	8,42	13,28	12,32
	+125 -250 µm	59,21	6,78	9,25	9,38	15,38
	+250 -500 µm	58,79	6,32	8,50	8,45	17,94
	+500 – 1000 μm	62,84	5,88	7,75	8,22	15,31
	+10000 -2000 μm	60,38	6,52	8,50	9,50	15,10
G2	Bulk sample	60,67		8,17	4,67	26,49
	+125 -250 µm	60,83		7,45	4,27	27,45
	+250 -500 µm	59,17		6,02	3,06	31,75
	+500 – 1000 μm	58,41		5,60	2,78	33,21

Sample		Hematite	Goethite	Chamosite	Fluorapatite	Quartz
code		(%)	(%)	(%)	(%)	(%)
	+10000 -2000 μm	58,30		6,58	3,28	31,84
G3	Bulk sample	74,63		11,17	9,52	4,68
	+125 -250 μm	76,20		9,97	8,17	5,66
	+250 -500 μm	74,93		10,30	8,69	6,08
	+500 – 1000 μm	79,62		8,50	7,17	4,71
	+10000 -2000 μm	76,48		9,58	7,88	6,06

<sup>(G1)</sup> High phosphorus sample, <sup>(G2)</sup> Low phosphorus sample, <sup>(G3)</sup> Intermediate phosphorus sample.

#### 3.2 Analytical techniques

Three iron ores samples were collected from the study area and investigated through a variety of mineralogical, chemical, and spectroscopic techniques. Table (3) presents the different analytical methods used and the purpose of each technique. Fig. 5 gives a simplified flow sheet which explains the different analytical and experimental methods used in the present study.

Analytical techniques	Instrumental model	Analysis measured
X-ray diffraction (XRD)	Siemens D5000 XRD powder	Bulk mineralogical composition of
	diffractometer	the iron ore
X-ray fluorescence (XRF)	Bruker AXS S4 Pioneer	Whole rock chemical analyses
Optical Microscope (OM)	Olympus BX51	Mineralogy and textures of the
		iron ores
		(paper I)
Scanning electron microscope	Zeiss ULTRA plus FESEM	Micro-morphological
(SEM - EDS)		characteristics of the iron ores
		(papers I - VI)
Electron Probe Microanalyses	Jeol JXA-8200 device with	Mineral chemistry of the iron
(EPMA)	WDS/EDS microanalyzer	minerals and element distribution
		maps within oolites and interstitial
		spaces between oolites (papers II
		& V)
Thermoanalyses (TG-DSC) &	Netzsch STA409 PC Luxx	The thermal behavior of iron ore
Mass spectroscopy (MS)		(papers III & IV)

#### Table 3. List of the different analytical methods.

Analytical techniques	Instrumental model	Analysis measured
Fourier Transform Infrared (FTIR) spectroscopy	Bruker Vertex V 80 vacuum FT-IR spectrometer	Surface chemistry of microwave treated and untreated samples
		Provides information about crystal morphology, degree of crystallization of iron oxide. (paper IV)
X-ray photoelectron spectroscopy (XPS)	ESCALAB 250Xi instrument	Provides information about the oxidation and structural state of the iron oxides
		(paper IV)
The vibrating sample magnetometer (VSM)	VSM (7410 Lakeshore, USA)	The magnetic properties of iron ore
		(paper III)

![](_page_30_Figure_0.jpeg)

Fig. 5. Analytical and experimental Flow sheet.

#### 3.3 Experimental

#### 3.3.1 Microwave treatment

A multimode microwave oven (sandstorm, model S25CSS11E and cavity dimension 513 mm (D)  $\times$  482 mm (W)  $\times$  310 mm (H)) with a maximum output power of 900 W was used in the treated iron ore samples at varying power levels (power varied by duty cycle) and exposure times. Samples were treated under normal atmospheric conditions and directly used without any pretreatment. 100 g of the representative samples were placed in the microwave oven in crucibles made of pure alumina. The temperature of the test samples was measured by quickly inserting a thermocouple into the middle of sample after the power was turned off, and was monitored via a digital display temperature controller (Aguilar-Garib 2011). The measured temperatures are the bulk temperatures of the samples. The samples were then allowed to cool in the microwave oven to room temperature. The amounts of energy consumed during the tests was measured using a CLM1000 Professional (Plus) energy meter, which was connected directly to the microwave power cable, shown in Fig. 6.

![](_page_31_Figure_3.jpeg)

Fig. 6. Schematic diagram of the microwave experimental apparatus.

#### 3.3.2 Conventional Heating

Representative samples of iron ore were placed in a furnace and heated at 400, 500 and 600 °C for a period of one hour. The amounts of energy consumed during these experiments were measured using a wireless electricity monitor (RCS-S22A). This wireless monitoring system (RCS-S22A) consists of three sensor clamps which are connected to a transmitter, these sensor clamps are then attached to the live wires of the furnace. The sensor clamps immediately begin to monitor the current and the energy monitoring system begins to work, while the LCD screen of the display unit displays the power consumption of the monitored object in real time. The use of an RJ45-USB data cable and SEMS software facilitated the viewing of energy consumption data on a standard computer, Fig. 7.

![](_page_32_Figure_2.jpeg)

Fig. 7. Schematic diagram of the conventional furnace experimental and wireless electricity monitor RCS-S22A.

#### 3.3.3 Magnetic separation

Wet high-intensity magnetic separation (Carpco wet high intensity magnetic separator, MWL3465 - 121) was applied to the microwave treated sample to investigate the effect of microwave radiation on the magnetic separation of iron minerals. A simplified schematic representation for the WHIMS is shown in Fig. 8. Samples of fractions – 0.125 mm were subjected to microwave radiation at 900 W power for 20 s, 40 s, 60 s and 90 s exposure times. The samples were then subjected

to wet magnetic separation at 0.5 T, 0.7 T and 1 T magnetic field intensities. The recovery ratio was calculated based on the following equation (Chen *et al.* 2012b):

Recovery ratio  $\% = m/m_0 \times 100$  (1)

Where m and m<sub>0</sub> are the magnetic fraction and total weight, respectively.

![](_page_33_Figure_3.jpeg)

Stage I. Separation with magnetic field Stage II. washing without magnetic field

Fig. 8. Sketch of a wet high-intensity magnetic separator.

#### 3.3.4 Ultrasonic apparatus

An ultrasonic cleaning vessel (Elmasonic P30H) with an ultrasonic frequency of 37 kHz and ultrasonic power of 350 W was used to perform the experiments. The experimental setup is shown in Fig. (9). Pulp was placed in the experimental vessel together with an impeller (for stirring) in the ultrasonic bath.

Experiments were performed with different pulp densities (15%, 30% and 45%) and different ultrasonic treatment times to see the effect of the sonication time and pulp density on the performance of ultrasonic disintegration and the removal of gangues materials. The mass of the samples used in the experiments depended on the slurry density, most of experiments were carried out at a pulp density of 15% (50 g of sample). Samples with different grain sizes were used in the experiments to see the effect of particle size on the efficiency of the ultrasonic treatment. After the experiments, the pulp was de-slimed through a – 63  $\mu$ m sieve and the de-slimed and product fractions were dried, weighed and chemically analyzed for total Fe grade and impurities, phosphorous, alumina and silica. The amounts of de-slimed materials (- 63  $\mu$ m) represent the percentages of disintegration materials.

![](_page_34_Figure_0.jpeg)

Fig. 9. Experimental setup for ultrasound experiments. (Paper VI, reprinted by permission of the Separation and Purification Journal).
### 4 Results and discussion

#### 4.1 Material characterization

Three representative samples were obtained from the Aswan region. Fig. 10 and Tables 1 and 2 give the XRD patterns and chemical analysis, respectively, of the iron ore samples. Hematite was found to be a major mineral in all samples. The other minerals that were also observed in the ores were quartz, fluoroapatite and chamosite. These samples have different mineralogical texture,  $Fe_2O_3$  and  $P_2O_5$  percentage. Based on the chemical compositions and sample texture, the iron ore samples are classified into three types:

1. Sample G1 (TFe, 48.33 % and P<sub>2</sub>O<sub>5</sub>, 5.64 %), (high phosphorus content).

SEM images show that Fe-bearing minerals occur mainly as fine-grained cementlike materials mixed with phosphorus bearing minerals and detrital quartz (Figs. 11A - 11D). The phosphorus and hematite particles range in size from 5 to less than 10  $\mu$ m. Also hematite occurs as small ooid grains (< 100  $\mu$ m in diameter) (Fig. 11A). The EDX analyses indicated that phosphorus occurs as a very fine grain disseminated in fine mineral iron (Fig. 11B and 11D). The SEM analyses indicated that the sample texture is composed of sandy and silty ironstones (ferruginous sandstone and siltstone).

2. Sample G2 (TFe, 46.04 % and  $P_2O_5$ , 2.25 %), (low phosphorus content).

The SEM images show that the sample is composed mainly from ooiltic hematite and detrital quartz (Fig. 12A and 12B). The ooids range in size from 300 to 500  $\mu$ m in diameter. Chamosite and Fluoroapatite occur mainly as cement-like materials mixed with quartz and iron filling the spaces between ooid grains (Fig. 12A - 12D). SEM and EDX analyses indicated that the sample texture occur as oolitic ironstones (< 50% ooids), and most gangues minerals (quartz, chamosite and fluoroapatite) were concentrated in the spaces between the ooids.



Fig. 10. X–ray diffraction pattern for iron ore samples. He, hematite; Go, goethite; P, fluorapatite; Qz, quartz; and Ch, chamosite. (Paper IV, reprinted by permission of applied surface science journal).



Fig. 11. Sample G1, (A) SEM image shows that sample occurs as fine-grained cementlike materials of hematite (He) and phosphorus (P), (B) EDX analyses of the squared area in (A), (C) Higher magnification image of fine grained material, (D) EDX analysis of the square area (C).



Fig. 12. ample G2, (A) and (B) SEM images show that the sample is composed mainly from oolitic hematite (He) and detrital quartz (Qz), with minor chamosite (Ch), (C) and (D) EDX analysis of the square areas (i) and (ii) in (B). (Paper VI, reprinted by permission of the Separation and Purification Journal).



Fig. 13. Sample G3, (A) SEM image shows that hematite (He) occurs as oolitic, (B) Enlargement of squared area in (A), (C) and (D) EDX analysis of the square areas (i) and (ii) in (B). (Paper V, reprinted by permission of powder technology journal).

3- Sample G3 (TFe, 58.27 % and P<sub>2</sub>O<sub>5</sub>, 3.24 %), (intermediate phosphorus content).

SEM images show that Fe-bearing minerals occur as oolitic hematite, shown in Fig. 13A, with less abundant phosphates and ferruginous clayey materials "chamosite" (<5%). The ooids are generally rounded to subrounded, moderately to well sorted and range in size from 500 to 1000  $\mu$ m in diameter. Fluoroapatite (phosphorus bearing mineral) occurs mainly as a fine-grained material (< 5  $\mu$ m) and fills the spaces between ooid grains (Figs. 13B - 13D). Chamosite occurs as a rim surrounding (coating) the ooid grains (Fig. 13B and 13D). EDX analyses indicated that phosphorus was concentrated mainly in the interstitial spaces between ooids (Figs. 13B and 13C). SEM analyses showed that the sample has a true oolitic (>95 % ooids) ironstone texture.

#### 4.2 Optimization of Microwave Heating

The effect of power intensity, exposure time and particle size on the heating rate of the iron ore with microwave was studied. Figs. 14 - 19 show the measured temperature for the samples exposed to microwave radiation for different exposure times and power intensities. Table 4 lists the heating properties of hematite and gangues minerals under microwave treatment (Chen *et al.* 1984, Kobusheshe 2010).

#### 4.2.1 Effect of sample particle size

Figs. 14 - 16 show the effect of particle size on the heating rate of the samples. For the three samples, the sample temperature increases with an increase of the particle size of the samples. For example, sample G 3 of particle size -9.5 +8 mm exposed to a microwave power intensity of 900 W for 60 s resulted in the sample temperature of 546 °C, while that for sample G3 of particle size of +0.5 -1 mm under the same conditions resulted in a temperature of 485 °C. These results indicate that microwave treatment is more effective at coarser size fractions compared to finer fractions, and the stress generated on coarser grain size will be more significant than on finer grain size. This result may be explained by the fact that larger particles will retain heat longer than small particles; therefore, the rate of heating will be more significant for particles of a coarser size (Kingman *et al.* 2000).

#### 4.2.2 Effect of exposure time

The effects of exposure time on the temperature of the samples are shown in Figs. 14 - 16. For the three samples, the measured sample temperature increases with increasing exposure time. The temperature increased very rapidly at first and then slowly at higher exposure time (> 80 s). Figs. 14 - 16 show that under the same conditions, the acquired temperature for sample G3 is higher than samples G1 & G2. This is because sample G3 contains a higher iron content than sample G1 & G2. Iron minerals have a higher microwave absorption capability than fluoroapatite and chamosite gangue minerals (Zhao *et al.* 2014). For example, sample G 3 with a particle size -9.5 +8 mm exposed to a microwave power intensity of 900 W for 60 s resulted in a sample temperature of 546 °C, while for sample G1 with a particle size of -9.5 +8 mm under the same conditions the result was a temperature of 490 °C. For all samples, by increasing the exposure time up to 150 s, the sample melted completely.

Mineral	Formula	Microwave Heating		
Hematite	Fe <sub>2</sub> O <sub>3</sub>	Heats readily, but no mineral phase		
Quartz	SiO <sub>2</sub>	Does not heat (inactive)		
Fluroapatite	Ca <sub>5</sub> (PO <sub>4</sub> ,CO <sub>3</sub> ) <sub>3</sub> F	Very little or no heat generated		
Chamosite	$(Fe^{++},Mg,Fe^{+++})_{5}AI(Si_{3}AI)O10(OH,O)_{8}$	Very little or no heat generated		

Table 4. Heati	ng properties	of minerals	with microwave	radiation.
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Fig. 14. Effect of the microwave exposure time on the measured mineral temperature at different particle sizes (sample G1).



Fig. 15. Effect of the microwave exposure time on the measured mineral temperature at different particle sizes (sample G2).



Fig. 16. Effect of the microwave exposure time on the measured mineral temperature at different particle sizes (sample G3). (Paper III, reprinted by permission of the Separation and Purification Journal).



Fig. 17. Effect of microwave power density on the measured mineral temperature (exposure time of 50 s), (sample G1).



Fig. 18. Effect of microwave power density on the measured mineral temperature (exposure time of 50 s), (sample G2).



Fig. 19. Effect of microwave power density on the measured mineral temperature (exposure time of 50 s), (sample G3). (Paper III, reprinted by permission of the Separation and Purification Journal).

#### 4.2.3 Effect of microwave power intensity

The effect of power intensity on the sample temperatures is indicated in Figs. 17 - 19. For the three samples, with increasing power intensity, the measured sample temperature was observed to increase. For example, sample G 3 with a particle size of -9.5 + 8 mm exposed to 900 W of microwave power at an exposure time of 50 s attained a temperature of 420 °C, while sample G3 of the same particle size exposed to 450 W of microwave power for the same exposure time attained a temperature of 258 °C. The increase of the sample temperatures with increasing microwave power results from the increase in the absorption of microwave energy (Uslu *et al.* 2003). Figs. 17 – 19 indicate that the increasing power intensity is more significant for samples of coarser particle sizes than for finer size fractions. Fig. 19 shows that, a sample of particle size -9.5 + 8 mm exposed to a microwave power intensity of 450 W and 900 W for 50 s resulted in an increased sample temperature from 250 °C to 430 °C respectively, while for a sample of particle size +0.125 - 0.250 mm under the same conditions there were increases in temperature from 190 °C to 330 °C, respectively.

# 4.3 Effect of microwave pretreatment on the liberation of high phosphorous oolitic iron ore

The influence of microwave power intensity, exposure time and grain size on the generation of intergranular fractures between oolitic iron ore and gangue minerals, and its effect on the liberation of iron ore were investigated in papers II & V (Omran *et al.* 2014a & Omran *et al.* 2015b).

As in the previous theoretical studies concerning the microwave treatment of ore, the main reason for the damage after microwave treatment is the thermallyinduced tensile stress, which occurred during the thermal expansion of the absorbent phases, exceeding the tensile strength of the material (Ali & Bradshaw 2009, Ali & Bradshaw 2010, Barani *et al.* 2011, Haque 1999, Jones *et al.* 2005, Jones *et al.* 2007, Salsman *et al.* 1996). During microwave heating hematite is an active material, while gangue minerals (fluoroapatite, chamosite and quartz) are inactive materials. When iron ore was exposed to microwave radiation, the hematite expanded more than the gangue. This difference in the expansion resulted in the formation of intergranular fractures (Song *et al.* 2013). Table 3 shows the microwave heating properties of hematite and gangue minerals (Chen *et al.* 1984, Kobusheshe 2010). Table 5 gives the thermal expansion coefficient of hematite and quartz as a function of temperature (Clark *et al.* 1966).

At the optimum microwave heating conditions (Omran *et al.* 2014a & Omran *et al.* 2015b), at a microwave exposure time of 60 s and a microwave power of 900 W, intergranular fractures formed between the gangue (fluoroapatite, quartz and chamosite) and oolitic hematite and almost no damage in the oolites grains Fig. 20. At this stage, oolites are mostly liberated from the matrix which means that most of phosphorus can be removed Fig. 20D. This localized damage effectively facilitates the liberation of oolites at coarser sizes and reduces over-grinding and slime losses. This result indicated that the issue of ultrafine grinding (<5  $\mu$ m) required to liberate iron minerals from associated phosphorus (Song *et al.* 2013), can be overcome by using microwave heating. The coarse liberation of the ooids following intergranular cracking would allow P rejection at coarse sizes. With an increased exposure time of up to 150 s at the same microwave power, the sample completely melted Fig. 21.

Omran *et al.* (2014a & 2015b) concluded that, as the exposure time increases the fractures increase. Micro-fractures firstly occur in the matrix (Fig. 20C), and then by increasing the exposure time; intergranular oolite/matrix (Fig. 20D) and transgranular fractures in the oolitic structures occurred.

Mineral	Thermal expansion coefficient (1/K) (10 <sup>-6</sup> )					
	373K	473K	673K			
Hematite	25.2	26.9	30.9			
Quartz	45.0	43.3	49.7			

Table 5. Thermal expansion coefficient as a function of temperature (Clark et al. 1966).



Fig. 20. BSE images for sample G3 (A) Before and (B) After microwave treatment, (C) Intergranular fractures between oolitic iron ore and gangue, (D) Liberated ooid grain. (Paper VI, reprinted by permission of the Separation and Purification Journal).



Fig. 21. SEM image of the melting iron ore.

In the case of sample (G2), fractures are formed on the boundaries between the gangue and oolitic hematite after microwave treatment (Fig. 22). Also fractures appeared in the matrix between ooids (Fig. 22B). These intergranular fractures facilitate phosphorus separation at a coarser grain size. On the other hand, in sample G1, a few micro-cracks were observed in the fine grained materials and between the small dispersed oolites and the matrix (Fig. 23).

Omran *et al.* (2014a & 2015b) concluded that the behavior of samples during microwave heating was different in terms of the generation of intergranular fractures. The sample mineralogical texture affected the degree of liberation of iron minerals from the associated phosphorus. Samples (G2 and G3) were affected significantly by microwave heating more than sample (G1). Samples (G2 and G3) have a coarse grained (oolitic ironstones) texture, while sample (G1) has fine-grained texture. It was observed that the effect of microwave heating increased with increasing grain size (Kingman & Rowson 1998, Jones *et al.* 2002, Jones *et al.* 2005, Whittles *et al.* 2003, Jones *et al.* 2007).



Fig. 22. BSE images for sample G2. (A) and (B) Intergranular fracture between oolitic hematite and gangue and Matrix micro-fractures. (Paper VI, reprinted by permission of the Separation and Purification Journal).



Fig. 23. BSE images for sample G1. (A) Micro-cracks in the fine grained materials. (B) Enlargement of squared area in (A) indicated that micro-fractures formed between iron and gangue. (Paper VI, reprinted by permission of the Separation and Purification Journal).

In the next sections, the results for sample G3 is only presented in the thesis, while the results for samples G1 & G2 are presented in papers IV & VI.

#### 4.4 Effect of microwave pretreatment on the grindability of iron ore

To measure the effect of microwave pretreatment on the grindability of iron ore, the microwave treated and untreated samples were ground for 30 s. The sample was first treated in the microwave oven for different exposure times of 30, 40, 50 and 60 s at a microwave power of 900 W. After grinding, the fraction of less than 0.125 mm of the ground specimen was determined by sieve analysis for both untreated and microwave-treated iron ore samples.

Then calculate grindability % = wt of undersize fraction (0.125) / total wt before grinding  $\times 100$ .

The weight percentage of untreated and microwave treated samples for -0.125 mm size fractions are shown in Fig. 24. It is clear from Fig. 24 that after 60 s of microwave pretreatment, the weight percentages for microwave treated iron ore for -0.125 mm particle sizes increased to 59.76%, while the weight percent for the untreated sample is 46.6%. This result indicated that the grindability of iron minerals can be improved, and a reduction in comminution energy is possible after microwave treatment.



Fig. 24. The weight percentages of untreated and microwave treated samples for – 0.125 mm size fractions. (Paper V, reprinted by permission of the Powder Technology Journal).

#### 4.5 Effect of microwave pretreatment on the magnetic properties of iron ore

The effect of microwave radiation on the magnetic properties of iron minerals was extensively studied in papers III & IV (Omran *et al.* 2014b & Omran *et al.* 2015a). The magnetic properties of iron ore are revealed by a hysteresis loop in the plot of the magnetization (M, electromagnetic unit, emu) versus the applied magnetic field intensity (H, Orested, Oe). Fig. 25 shows hysteresis loops for an untreated sample and for a microwave-treated sample for 90 s exposure time and 900 W of microwave power.

The magnetization curve for an untreated sample (Fig. 25) shows a tendency towards a linear relationship between the magnetization and the field strength. This result indicates that the sample behaves like paramagnetic materials. After microwave treatment for 90 s, the magnetization curve shows a tendency to level off and achieve saturation, which indicates a degree of ferromagnetism in the sample (Fig. 25). This ferromagnetism occurs because microwave heating induces phase changes at the grain boundaries of the mineral, inducing the formation of a new magnetic phase ( $\gamma$ -hematite), which can alter the magnetic properties of the sample (Florek *et al.* 1996, Waters *et al.* 2007, Omran *et al.* 2014b, Omran *et al.* 2015a).

This result is supported by high resolution of XPS spectra of Fe 2p (Fig. 26). X-ray photoelectron spectroscopy is used to provide information about the oxidation and structural state of the iron oxides (Biesinger *et al.* 2011). Fig. 26 shows the Fe 2p XPS spectra of an untreated and microwave treated sample. For

the untreated sample (Fig. 26), the Fe 2p spectrum contains two peaks of Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  at binding energy (B.E.) positions of ~710.48 eV and ~723.88 eV, respectively. The observed signals at these B.E. positions correspond to the formation of an iron oxide phase, i.e., Fe<sup>3+</sup> in Fe<sub>2</sub>O<sub>3</sub> (hematite) phase (Hawn & DeKoven 1987, Graat & Somers 1996, Muhler *et al.* 1992, Mills & Sullivan 1983, Roosendaal *et al.* 1999, Wagner *et al.* 1979). The Fe  $2p_{3/2}$  peak has an associated satellite peak at ~ 718.48 eV. Researchers have found that the satellite peak of Fe  $2p_{3/2}$  for Fe<sub>2</sub>O<sub>3</sub> is located approximately 8 eV higher than the main Fe  $2p_{3/2}$  peak (Aronniemi *et al.* 2004, Aronniemi *et al.* 2005, Barbieri *et al.* 1994, Descostes *et al.* 2000, Frost *et al.* 1972, Frost *et al.* 1974, Jain *et al.* 2004, Mills & Sullivan 1983, Nasibulin *et al.* 2009, Yuan *et al.* 2012).



### Fig. 25. Comparison of the hysteresis loops for untreated iron ore and iron ore treated with microwaves for 90 s exposure time.

For the microwave treated sample (Fig. 26), there is a significant shift in the position of an Fe 2p doublet, and the B.E. positions are observed at ~709.68 eV (for Fe 2p3/2) and ~723.08 eV (for Fe 2p1/2), which is shifted to a lower B.E. side compared to the untreated samples. The satellite peak which was associated with the Fe  $2p_{3/2}$  peak disappeared in the microwave treated sample. This means that the oxidation state of the iron oxide has been changed (Grosvenor *et al.* 2004).

The Fe  $2p_{3/2}$  spectra for the untreated iron ore shows relatively narrow peaks (FWHM) of Ca. (3.8) with a small broad satellite peak centered around ~718.48

eV, which is typical of the Fe(III) oxidation state (Brundle *et al.* 1977, McIntyre & Zetaruk 1977). When the sample treated with microwaves, there was a significant broadening of the Fe  $2p_{3/2}$  peak (FWHM) of Ca. (4.9) and it shifted to a lower BE. This finding indicates the presence of a mixture of Fe(II) and Fe(III) oxides, both of which contribute to the Fe  $2p_{2/3}$ . This means some reduction of the Fe<sup>3+</sup> state to Fe<sup>2+</sup>, has taken place. This means that after microwave radiation the iron oxide (hematite, Fe<sup>3+</sup>) transformed into a more magnetic phase as observed due to reduction of some Fe<sup>3+</sup> to Fe<sup>2+</sup>. This finding has been confirmed by other researchers (Allen *et al.* 1974, Brundle *et al.* 1977, Ingo *et al.* 1996, Ingo *et al.* 1994).



Fig. 26. Fe 2p spectra for; (a) untreated, (b) microwave treated iron ore. (Paper IV, reprinted by permission of the Applied Surface Science Journal).

Fig. 27 shows the O 1s spectra for untreated and microwave treated samples. Two main components are observed at ~529.78 eV and ~531.58 eV. The lower binding peak is due to the oxide (Brundle *et al.* 1977, McIntyre & Zetaruk 1977, Mills & Sullivan 1983, Wandelt 1982). The second peak which occurs at a higher binding energy is due to the presence of hydroxyl species as a result of the chemisorption of water on the air-exposed surfaces (Brundle *et al.* 1977, McIntyre & Zetaruk 1977,

Pratt *et al.* 1994). After microwave treatment, it can be seen that the high energy peak has completely gone and a broad peak at ~530.38 eV is observed, which is mainly due to the oxide phase of iron (Fe<sup>+2</sup> and Fe<sup>+3</sup>). It can be seen that the shift in O 1s peaks to a lower binding energy is associated with the shift in Fe 2p peaks, due to the reduction of some Fe<sup>+3</sup> that transformed to Fe<sup>+2</sup>.



Fig. 27. XPS spectra of O 1s for; (a) untreated, (b) microwave treated iron ore. (Paper IV, reprinted by permission of the Applied Surface Science Journal).

## 4.6 Effect of microwave pretreatment on the magnetic separation of iron ore

To investigate the effect of the changes in the magnetic properties of the microwave treated iron ore on magnetic separation, a series of magnetic separation tests were conducted on untreated and microwave treated samples for different exposure times, shown in paper III (Omran *et al.* 2014b).

It can be seen that after microwave heating, the iron recovery was observed to increase (Fig. 28). It is clear from the amount of material recovered as a magnetic fraction that by increasing the microwave exposure time, the magnetic recovery ratio increases. Fig. 28 shows that the maximum recovery of untreated iron ore is

ca. 39.54%, which was obtained at a magnetic field intensity of 1 T. This low recovery ratio is to be expected because hematite is considered as a weak magnetic mineral (paramagnetic). The maximum recovery ratio obtained was 97.95% after 90 s of exposure time at 900W of microwave power and at a magnetic field intensity of 1 T (Fig. 28). The results showed that the phosphorus content decreased from 2.50% in the feed sample to 1.33% in the obtained magnetic concentrate. Although about 50% of the phosphorus was removed the phosphorus content is still unsatisfactory (Table 6). The improvement in the iron recovery is attributed to the improvement of the magnetic properties of the weakly magnetic hematite via the absorption of microwave radiation (Waters *et al.* 2007).

	TFe	P <sub>2</sub> O <sub>5</sub>	P <sub>2</sub> O <sub>5</sub>	Fe
	%	%	removal %	Recovery %
Feed sample (+32-125µm)	59.61	2.50		
Product (magnetic fraction)	61.88	1.33	50 %	97 %

Table 6. Product grade, recoveries of Fe, P<sub>2</sub>O<sub>5</sub> after magnetic separation (HIMS).



Fig. 28. Magnetic recovery ratio for untreated and microwave-treated iron ore at 900W for different exposure times. (Paper III, reprinted by permission of the Separation and Purification Journal).

## 4.7 Comparison between microwave and conventional furnace pretreatment of iron ore

#### 4.7.1 Liberation

To investigate the effects of microwave, and conventional heating pretreatment on the liberation of iron bearing minerals from the associated gangue, the percentages of intergranular fractures generated between the oolitic/matrix and in the oolitic layers were determined for each sample.

Fig. 29 shows oolitic iron ore exposed to 900 W of microwave power at 60 s exposure time, and oolitic iron ore heated in a conventional furnace at 600 °C for 1 h. Significant damage was observed for the microwave treated sample, shown in Fig. 29. Regarding intergranular fractures between the oolites and the matrix, the cracks were more localized around the oolites' boundaries (Fig. 29).

With conventional heating at 600 °C for 1 h (Fig. 29), few micro-cracks and fractures were observed between the oolites/matrix and in the oolitic layers. The percentages of intergranular fractures generated in oolitic iron ore treated with microwave for 60 s were in excess of 80%. Approximately 30% of intergranular fractures were found to have been generated in oolitic iron ore after being conventional heated at 600 °C for 1 h.

The reasons why microwave treatment improves the liberation of high phosphorus oolitic iron ore over conventional heat treatments are:

- Microwave heated only the responsive phase. Hematite is an active material during microwave heating, while gangues are inactive. When iron ore is exposed to microwave radiation, the hematite expands more than the gangues, and the difference caused by this expansion results in the formation of intergranular fractures (Song *et al.* 2013).
- Microwaves heat faster than conventional heating methods. The speed at which the materials heat up is important in both conventional and microwave thermally assisted liberation. In the case of microwave heating, the transfer to the absorbing grain is very rapid, as microwave energy is delivered directly to the materials through molecular interaction with the electromagnetic field. In contrast, in conventional thermal processing, energy is transferred to the material through convection at the particle surface and conduction through the particle, with convective heat also drawn from the surface. Clearly this relatively slower and more uniform

heat transfer process will generate smaller temperature gradients and lower thermal stresses (Ali & Bradshaw 2010).



Fig. 29. BSE images of oolitic iron ore (A) exposed to 900 W microwave power for 60 s (B) heated in a conventional furnace at 600  $^{\circ}$ C for 1 h.

#### 4.7.2 Grindability

For comparison grindability tests were conducted for treated and untreated samples to identify the changes in the grindability of iron ore after both microwave and conventional heating, (see section 4.4).

Fig. 24 shows the weight percentages of untreated and microwave-treated samples for -0.125 mm size fractions. It is clear from Fig. 24 that the weight percentages of -0.125 mm increased from 46.6% for the untreated sample to 59.76% for the 60 s microwave treated sample (28.30% increase in grindability). The weight percentages of untreated and conventional furnace heated samples for -

0.125 mm size fractions are shown in Fig. 30. The weight percentages for -0.125 mm samples increased to 50.80 % for the microwave treated sample after being heated at 600°C for one hour, compared to 46.6 % for the untreated sample (9% increase in grindability). Grindability tests indicated that microwave treated iron ore could be more easily ground compared with iron ore treated in a conventional furnace. This improved grindability is attributable to the large number of intergranular fractures which formed in the oolitic iron ore after treatment with microwave radiation. This suggests that a reduction in comminution energy is possible after microwave treatment.



Fig. 30. The weight percentages of untreated and conventional furnace heated samples for – 0.125 mm size fractions. (Paper V, reprinted by permission of the Powder Technology Journal).

#### 4.7.3 Magnetic properties

The hysteresis loops for an untreated sample and conventional heating sample for 1 hr at 600 °C are shown in Fig. 31. There is no difference between the hysteresis loops for the untreated and conventional heating sample (Fig. 31). The magnetization curves show a tendency towards a linear relationship between the magnetization and the field strength. This result indicates that the samples behave like paramagnetic materials; the absence of any degree of ferromagnetism indicates that conventional heating has an insignificant effect on the sample magnetic properties. The hysteresis loops for the untreated sample and for microwave-treated sample for 90 s exposure time and 900 W of microwave power (Fig. 25) show that there is a significant difference between the hysteresis loops for the untreated

sample and for the microwave treated sample. The magnetization of the samples increased with increasing microwave exposure time. With an increase in microwave exposure time from zero to 90 s, the saturation magnetism was increased from 0.50 to 2.48 emu/g, which may be attributed to the phase changes on the surface of the mineral particles (Florek *et al.* 1996, Waters *et al.* 2007).



Fig. 31. Hysteresis loops for untreated iron ore and iron ore conventionally heated at 600 °C for 1 hr.

#### 4.7.4 Energy consumption

The amounts of energy consumed during the microwave tests were measured using a CLM1000 Professional (Plus) energy meter connected directly to the microwave. The amounts of energy consumed during the conventional furnace experiments were measured using a wireless electricity monitor (RCS-S22A).

Energy consumption measurements revealed that microwave treatment consumes much smaller quantities of energy compared to conventional heating ovens. For example, during conventional heating at 600 °C for one hour, approximately 5.33 kWh of electric energy was required to increase the grindability of iron ore from 46.60 % to 50.80 %. While in microwave treatment, approximately 0.0237 kWh of electric energy was required to increase the grindability from 46.60 % to 59.76 % (microwave power uses 224 times less power than a conventional oven). This large difference in the amount of electric energy consumption between the

microwave and the conventional furnace was due to the microwave heating only the "responsive" or "active" phases; therefore, no energy is wasted in heating the entire sample (Kingman *et al.* 2000). Another important factor is the time spent on the experiments. Microwave treatment takes only a few seconds, whereas conventional heating takes hours. Rapid heating by microwave leads to greater savings in time (time = money).

The major disadvantage of using microwave assisted comminution is the amount of energy required to achieve the desired effects compared to the potential savings (Kingman *et al.* 2004a). Although the benefits of microwave assisted comminution compared to conventional furnaces are technically attractive, the economics are poor. In the example given above, microwave heating at 900 W for 60 s with a 100 g sample gives a specific energy consumption of 144 kWh/t. It could be expected that the reduction in grindability due to the microwave heating would be less than the specific energy consumption 144 kWh/t. The reasons for high energy consumption are due to the low energy efficiency of multimode microwave, which is typical 60% at 2.45 GHz.

The performance of a multimode cavity depends on many variables including the shape, dimensions, configuration of microwave feeds, as well as the dimensions and properties of the load. A small change in any of these variables can significantly affect the heating performance (Kingman *et al.* 2004a&b). For this reason, it is very difficult to optimize heating in multimode cavities. With further microwave cavity development (single-mode cavity) and by increasing the power density, a significant improvement in grindability can be achieved at low microwave energy inputs. This suggests that a scale-up is potentially feasible in terms of energy added to the process (Kingman *et al.* 2004a&b).

The aims of calculating energy consumption during this work is to provide an indication that microwaves consume less energy than conventional furnaces, but for integral comparison between conventional heating and microwave heating further optimization is needed and the specific energy consumption should be calculated.

#### 4.8 Ultrasonic treatment of high phosphorus iron ore

Ultrasonic treatment was applied to the microwave treated samples, with the aim of investigating the effect of microwave pretreatment on the efficiency of ultrasonic separation of phosphorus and other gangue minerals from iron ore. Different parameters (sample grain size, sonication time and pulp density) were applied to achieve the best results, shown in paper VI (Omran et al. 2015c).

#### 4.8.1 Effect of microwave pretreatment on the efficiency of ultrasonic treatment of iron ores

The difference in the effect of ultrasound on iron ore pretreated with microwaves and on iron ore without microwave pretreatment is quite obvious, see (Fig. 32). The amounts of disintegration materials (- 63  $\mu$ m) generated for iron ore samples without microwave pretreatment is significantly lower than (12.22 %) for iron ore samples pretreated with microwaves (14.44 %). These results are due to the fact that the microwave pretreatment generated intergranular fractures between the gangues (fluoroapatite, quartz and chamosite) and oolitic hematite (Omran *et al.* 2014a & 2015b). These intergranular fractures improved the liberation of the iron ore, and facilitated ultrasonic disintegration and removal of phosphorus and gangue minerals from the surface of oolitic iron ore. It is clear from these results that, microwave pretreatment increases the efficiency of ultrasonic disintegration and removal of particles by about 20 % higher than in untreated samples. These observations indicated that microwave pretreatment should be considered as a factor significantly affecting the result of ultrasonic treatment.

#### 4.8.2 Effect of sonication time

The influence of ultrasonic treatment times on the disintegration and removal of fine materials was studied for different treatment times (Fig. 33). According to Fig. (33), increasing the ultrasonic exposure times resulted in increasing the amounts of disintegration materials (-  $63\mu$ m), it is also worth noting that the efficiency of ultrasonic disintegration decreases with increasing ultrasonic time (Donskoi *et al.* 2012, Donskoi *et al.* 2007, Donskoi *et al.* 2006, Donskoi *et al.* 2008, Pandy *et al.* 2010). For example, the amount of fine materials generated for a sample with a particle size of +125 -250 µm after ultrasonic treatment for a duration of 10 and 30 minutes was 15 % and 24 %, respectively (Fig. 33). Although the difference in treatment time is a factor of three, the difference in the increase of disintegration materials is 59 %.



Fig. 32. Effect of microwave pretreatment on the percentages of disintegration materials after ultrasound treatment. (15% pulp density, 10 min ultrasound time).



Fig. 33. Effect of sonication time on the percentages of disintegration materials, (15% pulp density). (Paper VI, reprinted by permission of the Separation and Purification Journal).



Fig. 34. Effect of different ultrasonic treatment times on Fe grade and impurities (phosphorous and alumina). (Paper VI, reprinted by permission of the Separation and Purification Journal).

Fig. (34) shows the effect of different ultrasonic treatment times on the total iron grade and on decreasing the impurities such as phosphorous and alumina. From all these graphs it is clear that the iron grade increases and the gangue decreases at the optimum ultrasonic treatment time. This is due to the disintegration and removal of fine materials (which are lower in iron grades and higher in phosphorus and gangue contents) from the coarser fractions. Researchers (Donskoi *et al.* 2007, Donskoi *et al.* 2012, Pandy *et al.* 2010) found that longer ultrasonic treatment times resulted in the hematite starting to disintegrate, which resulted in a decrease in the iron grade.

Tables (6 and 7) presented the chemical and mineralogical analyses at optimum ultrasonic treatment times. It can be seen from Fig. (34) that the most significant increase in iron grade and reduction in phosphorus and alumina content occurs after 10 min of ultrasonic treatment. With longer ultrasonic treatment times, the iron grade is decreased. The chemical compositions show that the iron grade has increased from 58.50 % to 60.58 %. Phosphorus decreased from 2.79 % to 1.88% (32 % reduction, 42% reduction from initial sample). Alumina decreased from 4.12 % to 2.86 % (30 % reduction, 36% reduction from initial sample). Silica decreased from 8.66 % to 7.22 %. The total reduction of phosphorus compared to the initial ore is 42%. The reduction in silica product grade is less significant than for phosphorus and alumina. The mineralogical analysis for the products (Table 7) shows that the percentage of hematite has increased after ultrasonic treatment (from 74 % to 82 %). The amounts of fluoroapatite and chamosite (iron clay) have

significantly decreased (from 8.69 % to 5.91 % and from 10.30 % to 7.21 % respectively).

#### 4.8.3 Effect of particle size

The effect of particle size on the quantity of disintegration material is show in Fig. (33). The effect of ultrasonic treatment on larger particles is significantly lower than smaller particles. For example, under the same experimental conditions (5 min of ultrasonic treatment, 15% pulp density), the amount of disintegration material generated using a sample with a particle size of +125 -250 µm was 11.54 % (Fig. 33), significantly higher than that generated using the same sample with a larger particle size of +250 -500 µm, where amount of material generated came to 9.34% (Fig. 33). The reason for the decreasing the amount of disintegration material with larger particle sizes has been explained by other researchers (Donskoi *et al.* 2012, Donskoi *et al.* 2008). They demonstrated that the larger the size of the particles the lower their surface area so the effect of ultrasound is also expected to be less (Donskoi *et al.* 2012).

It is noted that the effectiveness of disintegration and fines removal was much lower with samples with larger particle sizes ( $+500 - 1000 \mu m$ ). The percentage of disintegration materials generated using samples with a particle size of  $+500 - 1000 \mu m$  was 2.66 %, which was significantly lower than that generated using the same sample with a smaller particle size  $+125 - 250 \mu m$ , where 11.54% of disintegration material was generated (Fig.33), under the same conditions. The large particles ( $+500 - 1000 \mu m$ ) partially settled at the bottom of the cell, resulting in low permeability for the ultrasonic waves. This causes a low level of cavitations and a significant reduction in the ultrasonic effect (Donskoi *et al.* 2012).

#### 4.8.4 Effect of Pulp density

The effect of ultrasonic treatment at various concentrations of solids (pulps density) was investigated (Fig. 35). The amount of disintegration material generated is higher for low pulp density than high pulp density, but this difference was not very much. Donskoi *et al.* (2008 & 2012) found that the effect of ultrasound on lower density pulps was to be slightly more effective than on high density pulps.

At the same duration of ultrasonic treatment (10 min) but with the density of the pulp increased three times, the amount of material generated in the sample of  $(+125 - 250 \mu m)$  at (15% pulp density) was 14.62% higher than in the same sample with (45% pulp density), where 10.44% of fine materials were generated (Fig. 35).

Exp.		Fe	P <sub>2</sub> O <sub>5</sub> %	SiO <sub>2</sub>	$AI_2O_3$	Fe Recovery	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>
conditions		%		%	%	(%)	Removal	Removal
							(%)	(%)
Particle size	Product	60.85	1.88	7.22	2.86	91.61	32.61 % (F)	30.58% (F)
(+250 -500							41.97 % (I)	36.02% (I)
μm), sonication	Feed sample	58.50	2.79	8.66	4.12			
time (10 min), pulp density (15%).	Initial sample	58.27	3.24	7.48	4.47			

Table 7. Products grades and recoveries of Fe,  $P_2O_5$ ,  $Al_2O_3$  and  $SiO_2$  after ultrasonic treatment followed by de-sliming.

 $^{(F)}$  Feed sample with grain size (+250 -500  $\mu m$ ),  $^{(I)}$  Initial sample G3.

 Table 8. Products mineralogical composition (wt. %) after ultrasonic treatment followed by de-sliming.

Exp. conditions		Hematite	Chamosite	Fluorapatite	Quartz
		%	%	%	%
Particle size	Product	82.04	7.21	5.91	4.84
(+250					
-500 µm),	Feed	74.93	10.30	8.69	6.08
sonication time	sample				
(10 min), pulp	Initial	74.63	11.17	9.52	4.68
density (15%).	sample				



Fig. 35. Effect of pulp density on the percentages of disintegration materials.

### 5 Summary and conclusions

The main problem associated with exploiting high phosphorus iron ore is the very fine dissemination and high levels of phosphorus content. These very fine phosphate particles (commonly  $1-5 \mu m$ ) are very difficult to separate with conventional mineral processing (e.g., by using flotation and magnetic separation). For the utilization of high phosphorus oolitic iron ore, many hydrometallurgical and pyrometallurgical processes have been proposed.

The present work describes a new method to remove phosphorus from high phosphorus iron ore through a combination of microwave pre-treatment and physical separation. Fig. 36 shows a schematic flow sheet for the experimental procedures and the results. The following is a summary of the results achieved:

Mineralogical and chemical characterization of the three representative iron ore samples showed that hematite is the main mineral in all samples. In addition to quartz, fluoroapatite and chamosite are found as gangue minerals. Based on the chemical compositions (TFe and  $P_2O_5$ ) and sample mineralogical texture, the iron ore samples are classified into three types:

- 1. A high phosphorus sample (G1), TFe (48.33 %) and P<sub>2</sub>O<sub>5</sub> (5.64 %). Sample texture occurs mainly as fine-grained cement-like materials mixed with phosphorus.
- 2. A low phosphorus sample (G2), TFe (46.08 %) and  $P_2O_5$  (2.25 %). Sample texture occurs as oolitic ironstones (< 50 % ooids).
- 3. An intermediate phosphorus sample (G3), TFe (58.27 %) and P<sub>2</sub>O<sub>5</sub> (3.24 %). Sample texture occurs as oolitic ironstones (> 95 % ooids).

The heating rate of iron ore with microwaves showed that the sample temperature increases with an increase in the particle size of the samples. The optimization of microwave heating indicated that microwave heating is more effective at coarser grain sizes and higher microwave power intensity.



Fig. 36. Flow sheet for the experimental procedures and results.

The influence of microwave power intensity, exposure time and particle size on the generation of intergranular fractures between oolitic iron ore and gangue minerals, and its effect on the liberation of iron ore indicated that significant damage was formed at higher microwave power and coarser grain size. At the optimum microwave heating conditions, (microwave exposure time of 60 s and microwave power of 900 W), intergranular fractures formed between the gangues (fluoroapatite and chamosite) and oolitic hematite after microwave treatment, leading to improved liberation of the iron ore. The grindability tests indicated that microwave treated iron ore could be more easily ground compared with untreated iron ore. This improved grindability is attributable to the large amount of intergranular fractures which are formed on the oolitic iron ore after treatment with microwave radiation.

The effect of microwave pre-treatment on the magnetic properties of iron ore showed that after microwave heating for 90 s exposure time and 900 W of microwave power, the magnetism saturation of the hematite increased from 0.50 to 2.48 emu/g, and a degree of ferromagnetic phase formed. This may be attributed to the phase changes on the surface of the mineral particles. High resolution XPS analyses of Fe 2p peaks, O 1s peaks, Fe 2p shake up satellite peak values for untreated and microwave treated samples showed that after microwave radiation a portion of Fe (+III) was reduced to Fe (+II). This means that after microwave radiation iron oxide (hematite, Fe<sup>3+</sup>) transformed into a more magnetic phase (Fe<sup>2+</sup>). These results indicated that microwave radiation had a positive effect on the magnetic properties of iron oxide, through the formation of ferromagnetic phases.

Wet high intensity magnetic separation (WHIMS) tests were conducted on untreated and microwave treated samples, to investigate the effect of the changes in the magnetic properties of the microwave treated iron ore on magnetic separation. The magnetic separation (1 T of magnetic field intensity) indicated that the magnetic recovery ratio increased from 34% to 98% after microwave treatment for 90 s exposure time and 900 W microwave power. The improvement in the recovery is attributed to microwave radiation enhancement of the magnetic properties of weak magnetic minerals through the altering of the mineral surface and resulting in more magnetic phases.

The comparison between the effect of microwave heating and a conventional heating furnace on the liberation, grindability, and magnetic properties of iron ore showed that:

- The liberation analysis for iron ore exposed to 900 W and 60 s, and iron ore heated in a conventional furnace at 600 °C for 1 h showed that the percentages of intergranular fractures generated in oolitic iron ore treated with microwaves for 60 s were in excess of 80%. While approximately 30% intergranular fractures were generated in oolitic iron ore after being conventionally heated at 600 °C for 1 h.
- Grindability tests indicated that microwave treated iron ore could be more easily ground compared with iron ore treated in a conventional furnace. The grindability test for the microwave treated sample at 60 s and 900 W showed about a 28.30% increase in grindability after microwave treatment. There was only a 9% increase in grindability after conventional heating at 600 °C for 1 h. This improved grindability is attributable to the large number of intergranular fractures which are formed on the oolitic iron ore after treatment with microwave radiation.
- The magnetic properties for conventionally heating a sample for 1 hr at 600 °C indicated that there is no difference between the magnetic properties of an untreated and conventionally heated sample. The hysteresis loops showed that the samples behaved as paramagnetic materials after conventional heating; the absence of any degree of ferromagnetism indicated that conventional heating has an insignificant effect on the sample magnetic properties. The magnetic properties for the microwave-treated sample for 90 s and 900 W indicated that there was a significant difference between the magnetic properties for untreated the sample and for the microwave treated sample. The hysteresis loops showed that the magnetization of the sample increased with increasing microwave exposure time, and that a ferromagnetic phase formed.
- In summary, the findings indicate that microwave treatment possesses multiple advantages over conventional thermal treatment. When compared with conventional thermal treatment, microwave treatment improves liberation and magnetic properties, and reduces the processing time.

Ultrasonic treatment (37 kHz and 350 W) was applied to the microwave treated samples, to investigate the effect of microwave pretreatment on the efficiency of ultrasonic separation of phosphorus and other gangue minerals from iron ore. The results indicated that microwave pretreatment significantly increases the efficiency of ultrasonic disintegration and the removal of gangues. The improvement in the Fe grade and the decrease in impurities after ultrasonic treatment is attributed to the disintegration and removal of fine gangue components. The experiments

indicated that the disintegration of fine gangue mineral particles decreases with increasing sample particle size and pulp density under similar sonication conditions. The mineralogical texture and the degree of phosphorus liberation affect the efficiency of phosphorus removal. With the optimum ultrasonic treatment (15% pulp density and 5 - 10 mins), the total iron grade of the products can be higher than that for untreated ore by 2 to 3%. The amount of phosphorus and alumina with ultrasonic treatment can be up to 59 - 33% and 51 - 30% respectively, less than without treatment.

#### 5.1 Recommendations for the future work.

The presented work reports new methods which have resulted in significant phosphorous removal, through a combination of microwave pre-treatment and physical separation (ultrasonic treatment). Even though the results are quite promising, further research is needed to study the possibility of phosphorus removal by using other physical techniques (such as attrition scrubbing and flotation) in combination with microwave pre-treatment. Although the results of ultrasonic treatment are quite promising, more extensive study of other ultrasonic parameters (such as ultrasonic power and ultrasonic frequency) may yield good results.

All of these experiments and previous works have been carried out with a laboratory scale microwave oven. In order to design an industrial pilot scale microwave applicator, more fundamental studies are needed. The proposed investigations may include, for example, the dielectric characterization of the different minerals' phases. This will let us understand the behavior of the materials undergoing microwave treatment (e.g. whether the material will reflect / absorb microwaves) and will give us the electrical permittivity (dielectric constant + loss factor) values and the magnetic permeability for electromagnetic simulation software.
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# **Original publications**

- I Baioumy H, Omran M & Fabritius T (2015) Mineralogy, geochemistry and the origin of high-phosphorus oolitic iron ores from Aswan, Egypt. Manuscript.
- II Omran M, Fabritius T, Abdel-Khalek N, El-Aref M, Elmanawi AE.-H, Nasr M & Elmahdy A (2014) Microwave assisted liberation of high Phosphorus oolitic iron ore. J Miner Mater Charact Eng 2: 414-427.
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- V Omran M, Fabritius T & Mattila R (2015) Thermally assisted liberation of high phosphorus oolitic iron ore: A comparison between microwave and conventional furnaces. Powder Technol 269: 7–14.
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