Project FILER (Flexible Input Low Emission Reduction of Ore) Phase 2. Laboratory validation and rotary kiln seal design

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C-Tech Innovation Ltd

Capenhurst Technology Park

Capenhurst

Chester

CH1 6EH

Tel: +44 (0)151 347 2900

Website: www.ctechinnovation.com

Email: info@ctechinnovation.com

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01	23/01/2020	Yvonne Wharton	Rob Bell	Bob Crawford	For publication by BEIS

Table of Contents

1 Executive Summary

Project FILER (Flexible Input Low Emission Reduction of Ore) is concerned with the microwave assisted direct reduction of iron ore (DRI). This is proposed as an all-electric replacement of the conventional blast furnace process and offers the potential for renewable electricity use to replace fossil fuels. The work has been carried out with support from the Fuel Switching programme of the Department for Business, Energy and Industrial Strategy (BEIS).

Laboratory scale studies showed the potential for using hydrogen as the direct reducing agent for iron ore. Microwave heating in combination with radiant heating was shown to accelerate the reaction rate and allow the reduction to proceed at lower temperatures than when using conventional heating alone. It was possible to reduce iron oxide at 600°C and in less than 10 minutes. Microwave assistance gave a 50% increase in the reaction rate compared with not using microwave energy.

A microwave assisted continuous rotary kiln was modified as a test-bed for a new design of rotary seal that is a critical enabling component if the process is to be developed further. The rotary seal has to contain microwave radiation and hydrogen gas and operate at 650°C. The seals were designed and operated successfully.

Financial analysis of the microwave assisted process against a conventionally heated DRI process showed that the reduction of the operating temperature of the microwave process to 650°C from 950°C has the potential to make energy savings of up to 30% compared to the non-microwave DRI process. The payback time for the extra CAPEX for microwave equipment can be as short as 3 months.

The next stage is to optimise the conditions at laboratory scale and to design and build and operate a pilot plant.

2 Directly Reduced Iron

The principal source of emissions in steel making are in the primary iron production where iron ore is reduced in a blast furnace to produce molten iron. For conversion into steel liquid iron is transported to a basic oxygen convertor where oxygen is injected using a water cooled lance and the carbon content is reduced to below 2% and the iron becomes steel. The blast furnace production of steel is the largest route to the manufacture of primary steel.

The direct reduction of iron ore (DRI) offers an alternative route to iron production. In this process the iron ore is reduced to iron in solid form at lower temperatures and using either fossil fuels or hydrogen. The iron produced is subsequently melted and converted to steel using existing processes. The separation of the reduction and melting processes allows different energy sources to be used for the two steps. Several DRI process routes are used commercially and the total production globally is over 70 million tonnes. The primary reductants used are syngas, methane or coal and several process steps have been investigated to cut CO_2 emissions.

The FILER DRI process is intended to fit into a combined DRI+EAF process where DRI (directly reduced iron) is then converted to steel in an EAF (electric arc furnace). With the use of renewably generated hydrogen and electricity this DRI+EAF process will eliminate most of the carbon dioxide emission associated with steel production and the FILER technology is an enabler for that in reducing the cost of the DRI step.

The decarbonisation of steel production is key to modernising the industry and meeting climate obligations. Future BEIS R&D funding will target Clean Steel Production and Low Carbon Hydrogen Production. Other countries are addressing this challenge. One initiative is the HYBRIT project which was created in 2016 between a minerals company LKAB, energy producer Vatenfall, and steel producer SSAB, and aims to achieve fossil-free steel production by 2035. It features the use of renewably generated hydrogen. Another initiative is the SALCOS project developed by Salzgitter AG and Tenova and which targets a stepwise transition to a DRI-EAF process with the flexible incremental utilization of hydrogen.

Switching to hydrogen as the reducing agent in the iron ore refinery process has been proposed in a number of studies[1,2,3]. The direct reduction process can be carried out at operating temperatures below the melting point of iron (operating at approximately 900°C) and the process has the potential to give cost savings in terms of energy use due to the reduction in processing temperature with the added benefit of reducing the carbon footprint of the process.

Alexander Otto *et al* analysed the effect of replacing conventional processes with the use of renewable energy and hydrogen as a reductant. A number of cases were considered including the approach by ULCOS. The impacts on the total energy demand, fuel demand and CO_2 emissions were analysed and compared[4]. CO_2 reductions of up to 95% are possible when direct reduction technologies are applied with renewable energy sources. The energy requirement for the DRI process is similar to the energy requirement for the conventional blast furnace process. The primary advantage is the future potential to use renewable energy in place of fossil fuels in the most efficient and cost-effective way possible.

The transition from current blast furnace to basic oxygen furnace technology to DRI-EAF technology will take time. The FILER Development Plan will focus on working with partners who are actively engaged in building demonstrator systems and who can integrate FILER into prototype systems.

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[1] Vogl, Ahman & Nilsson. "*Assessment of hydrogen direct reduction for fossil-free steelmaking*". Journal of Cleaner Production 203 (2018) 736-745.

[2] Bilik, Pustejovska, Brozova & Jursova. "*Efficiency of hydrogen utilisation in reduction processes in ferrous metallurgy*". Scientia Iranica B (2013) 20 (2) 337-342.

[3] Rocha, Guilherme, Castro, Sazaki & Yagi. "*Analysis of synthetic natural gas injection into charcoal blast furnace*". J Mater Res Technol 2013 2(3) 255-262

[4] A.Otto *et al*. "*Power-to steel: Reducing CO2 through the integration of renewable energy and hydrogen into the German steel industry*". Energies (2017), 10(4), 451.

3 Microwave assisted DRI using hydrogen

C-Tech Innovation Ltd previously developed methods to increase the rate of reduction of ilmenite ore at lower temperatures and with significant energy savings compared to conventional processes by the application of microwave radiation. The process was demonstrated in the laboratory at 5 g scale and at a pilot scale of 300 kg/hour. The process achieved a greater degree of metallisation at a given temperature and also allowed for metallisation at lower temperatures than possible conventionally. The figure below shows the significant improvement in the kinetics and extent of metallisation at low temperatures compared with using conventional reduction processes. The most significant improvements were found at a temperature of 650°C which offers a significant energy saving.

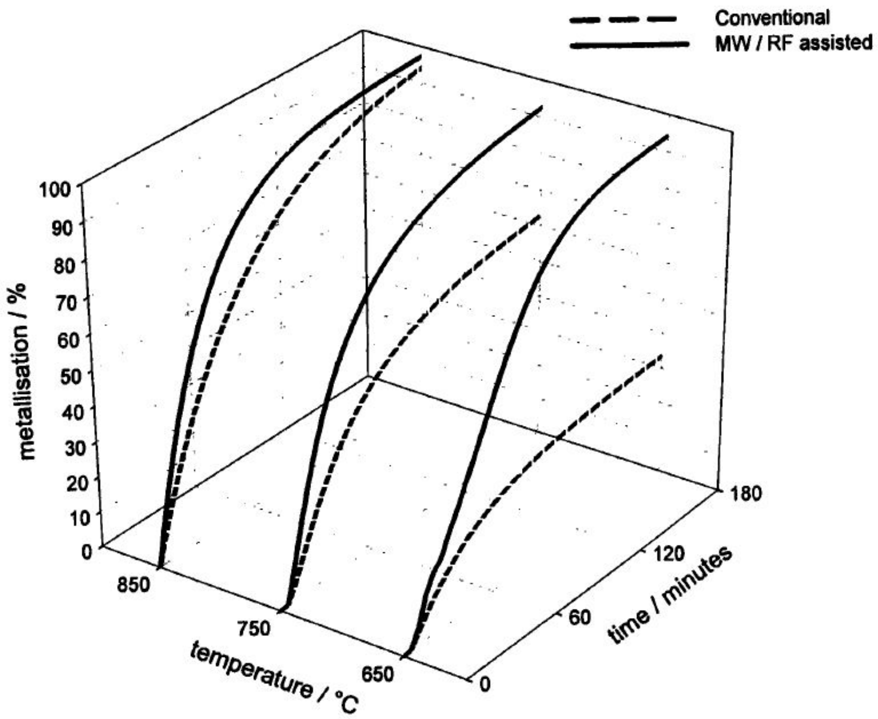


Figure showing the kinetics of the metallisation of ilmenite under hydrogen as a function of temperature

This novel process for the reduction of ilmenite gave an output equivalent to that of the conventional process but at an operating temperature of 650°C rather than 850°C. This lower temperature allows the use of electrical heat sources as opposed to fossil fuels for the pre-heating phase. The modified process provided cost savings from a reduction of heating energy (through electrification) and by using a more refined feedstock for the final processing stages.

4 Increased oxygen diffusion rates under microwave fields

Direct iron ore reduction with a solid ore involves two steps. First the reaction of oxygen with hydrogen at the surface of the solid, and second the diffusion of oxygen to the surface of the solid. Oxygen diffusion is usually the rate limiting step in the process and is therefore the focus of attention in this feasibility study. The process of this diffusion is complex and involves the diffusion of vacancies as the structure of the oxide moves from Fe_2O_3 to Fe_3O_4 and then to the less stable FeO structures. This conveyor of oxygen from the centre of the particle results in oxygen being removed at the surface where it reacts to form H_2O.

There is a body of empirical work that has looked at diffusion in solids under microwave fields. This has shown a variety of effects such as reduced sintering times, increased diffusion coefficients and changes in the structure of materials. These studies showed that solid the increased diffusion rates caused by the microwave fields meant that solid state reactions could be achieved more quickly and at lower temperatures.

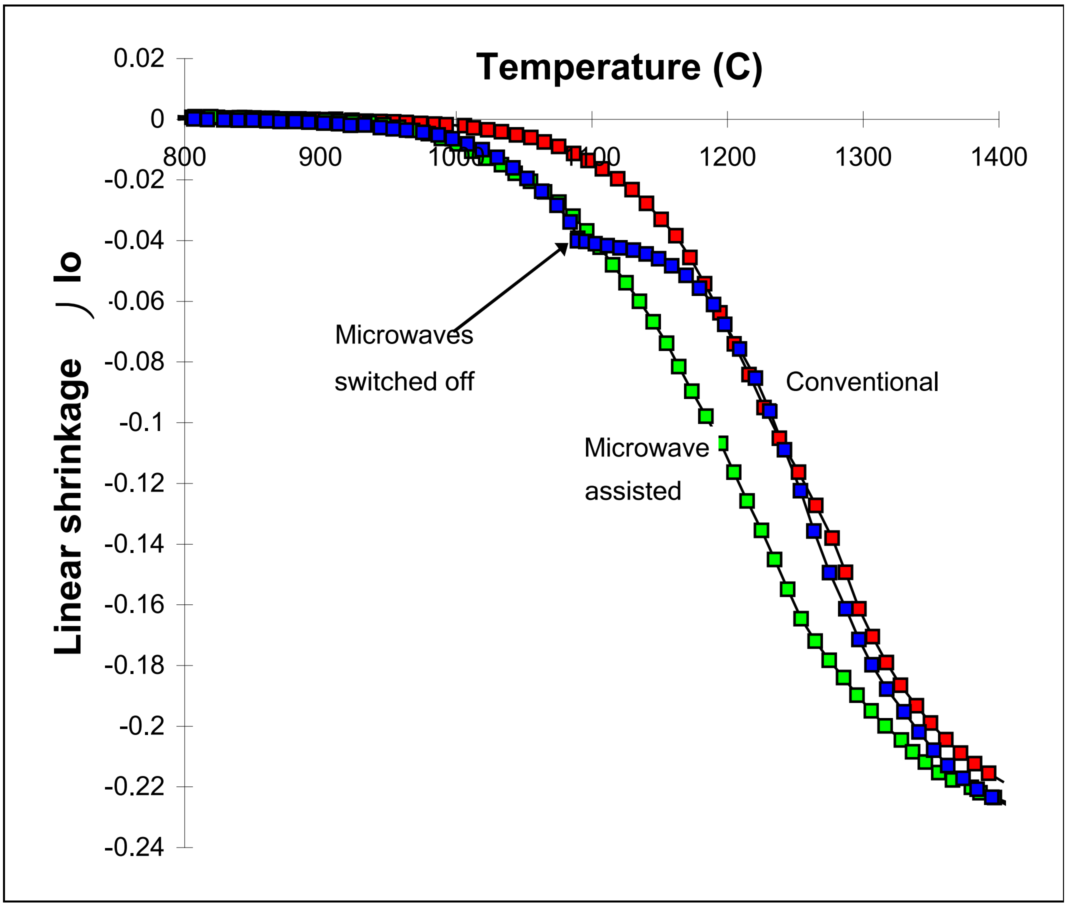
Second order effects such as sintering rate or grain growth have also been studied. Janney et al[5] considered diffusion coefficients in single crystals and showed that the volume diffusion of oxygen in sapphire was enhanced by heating in a 28 GHz microwave furnace. The apparent activation energy for volume diffusion was reduced by 40% from 650 to 390kJ mol^{-1} and the pre-exponential factor was reduced by five orders of magnitude from 9.7×10^{-2} to 3.8×10^{-7} ($m^2 s^{-1}$).

Sintering is the process of the densification of compacted powder bodies that occurs below the melting temperatures via shape accommodation of the powder particles. The main driving force for sintering is capillary stress, which acts to minimize the free energy associated with the surface area. The thermal sintering of a ceramic is a complex process with a number of diffusion mechanisms taking place which together produce the required increase in density and changes in mechanical properties of the material. Janney and Kimrey [6] studied the microwave sintering of alumina and showed that a 28 GHz microwave field enhanced densification of high-purity alumina proceeds as if the activation energy was reduced from 575 kJ mol$^{\sim1}$ to 160 kJ mol$^{\sim1}$. It was observed that the density of microwave sintered alumina increased more rapidly with temperature compared with the thermally processed alumina.

[5] Janney M and Kimrey H, *Diffusion-controlled processes in microwave-fired oxide ceramics*, in *Microwave processing of materials II, Materials Research Society symposium Proceedings* Snyder WB, et al., Editors. 1991, Materials Research Society: Pittsburgh. p. 215-227.

[6] Janney M and Kimrey H, *Diffusion-controlled processes in microwave-fired oxide ceramics*, in *Microwave processing of materials II, Materials Research Society symposium Proceedings* Snyder WB, et al., Editors. 1991, Materials Research Society: Pittsburgh. p. 215-227.

Wroe et al [7] showed that the sintering rates of zirconia were increased when microwave radiation was applied compared to the use of radiant heating. The densification rate at each temperature was found to be sensitive to the proportion of microwave power. With full microwave power, the densification curve was shifted towards lower temperatures by approximately 100°C, as compared to conventional heating. It was also observed that the removal of the microwave field during the densification process produced a slowing in the rate of densification until the temperature had increased sufficiently for densification to continue without microwave assistance, as shown in the graph below.



Graph showing the normalised linear shrinkage of zirconia as a function of sintering temperature for conventional and microwave assisted sintering. The effect of switching off the microwaves during processing at 1080°C is apparent.

[7] Wroe, R. and A.T. Rowley, *Evidence for a non-thermal microwave effect in the sintering of partially stabilized zirconia.* Journal of Materials Science, 1996. **31**(8): p. 2019-2026.

The sintering of NiCuZn ferrites was studied by Saita et al [8] in a microwave field of 2.45 GHz. It was established that densification of NiCuZn ferrites was significantly promoted by microwave processing and the effective activation energy for diffusion during microwave sintering was half the value of the conventional sintering case.

In a study of oxygen diffusion in sapphire Janney et al [9] it was found that the enhancement of oxygen diffusion in sapphire crystals heated in a 28 GHz microwave furnace equated with a 40% decrease in the apparent activation energy for bulk diffusion when compared to that of conventional heating. Rowley et al[10] obtained a similar result in a study of oxygen diffusion in YBCO superconducting material. The suggested mechanism for the phenomenon of microwave-enhanced oxygen diffusion in sapphire was an increase in the energy state of the vacancies giving rise to diffusion without a corresponding increase in the bulk temperature of the material.

Studies of the oxygen diffusion kinetics in YBCO was performed by Wittiker et al[11], who analysed the relative diffusion of ions as a function of the angle to the microwave field. A significant difference was observed in the oxygen diffusion coefficient when the material was subjected to polarized microwave irradiation, showing an angular dependence for the diffusion rate that is not observed in conventionally processed samples. The preferred diffusion direction was found to be parallel to the polarized microwave electric field vector with the apparent diffusion coefficient parallel with the field observed to be up to 10 times greater than that perpendicular to it.

The mechanism of interaction between microwaves and matter that causes these effects is the subject of ongoing research. One model that has been suggested to account for these phenomena is the solid state ponderomotive effect. This is a result of the nonlinear force that a charged particle experiences in an inhomogeneous oscillating electromagnetic field. It causes the particle to move towards the area of the weaker field strength, rather than oscillating around an initial point as happens in a homogeneous field. The result is an increase in vacancy diffusion is induced by the alternating electric field[12][13]. It is suggested that this can give rise to a concentration gradient that propagates into the bulk of the material.

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[8] AITA H, et al., *Microwave Sintering Study of NiCuZn Ferrite Ceramics and Devices.* Japanese journal of applied physics, 2002. **41**: p. 86-92.

[9] JANNEY M. A., et al., *Enhanced diffusion in sapphire during microwave heating.* JOURNAL OF MATERIALS SCIENCE 1997. **32** p. 1347-1355.

[10] Rowley, A.T., et al., *Microwave-assisted oxygenation of melt-processed bulk YBa2Cu3O7-delta ceramics.* Journal of Materials Science, 1997. **32**(17): p. 4541-4547

[11] Whittaker, A.G., *Diffusion in microwave-heated ceramics.* Chemistry of Materials, 2005. **17**(13): p. 3426-3432.

[12] Booske, J.H., et al., *Microwave ponderomotive forces in solid-state ionic plasmas.* PHYSICS OF PLASMAS, 1998. **5**(5): p. 1664-1670.

[13] Rybakov, K.I. and V.E. Semenov, *Mass transport in ionic crystals induced by the ponderomotive action of a high-frequency electric field.* Physical Review B, 1995. **52**(5): p. 3030.

5 Laboratory scale validation of microwave assisted DRI

A laboratory investigation of the direct reduction process was carried out using the C-Tech Innovation Hybrid Kiln. This unit combines radiant heating with microwave (MW) and radiofrequency (RF) heating. The aim was to evaluate hydrogen gas as the reducing agent with and without the use of microwave and radio frequency radiation. The rate of conversion of hematite (Fe_2O_3) to Fe_3O_4, FeO or Fe was measured.

The photograph shows the C-Tech Innovation Hybrid kiln which combines radiant, microwave and radiofrequency heating

This experimental program followed previous work on ilmenite reduction which showed that there was an increased rate of reduction when using microwave and radio-frequency radiation was used in combination with radiant heating. The greatest improvement was seen when RF and MW were used together in combination with radiant heating.

The aim of the experimental program was to determine how the following variable parameters affected the reduction of iron ore:

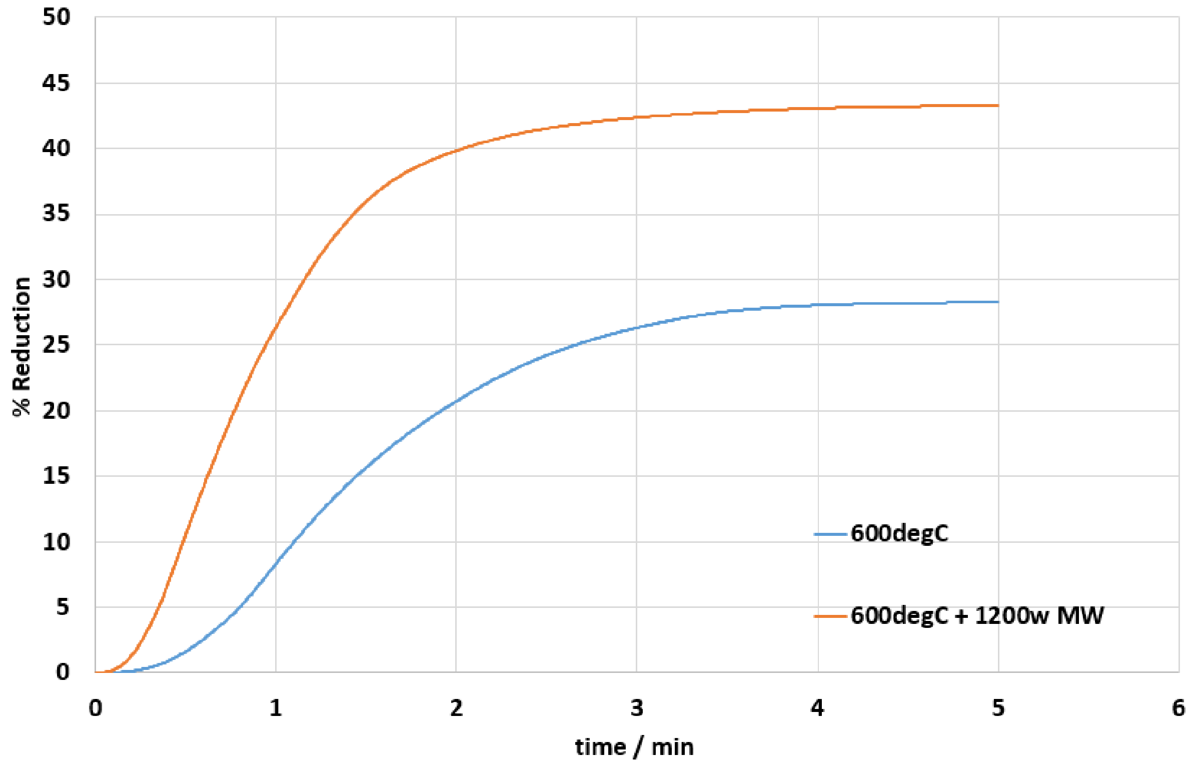
- temperature
- time
- MW power
- H_2 flow rate and concentration
- particle size

The reduction of iron oxide (hematite) to iron is according to the following reaction:

$$Fe_2O_3\,(s) + 3H_2\,(g) \rightarrow 2Fe\,(s) + 3H_2O\,(g)$$

The sample loses 28.20% of its mass when fully reduced and weight loss is used as a means of determining the extent of reduction.

Applying microwave energy it was possible to demonstrate a significant improvement in the reduction rate of the iron oxide. At low hydrogen flow rates the rate of reduction was increased by up to 53%. The graph below shows the effect of introducing microwave heating.



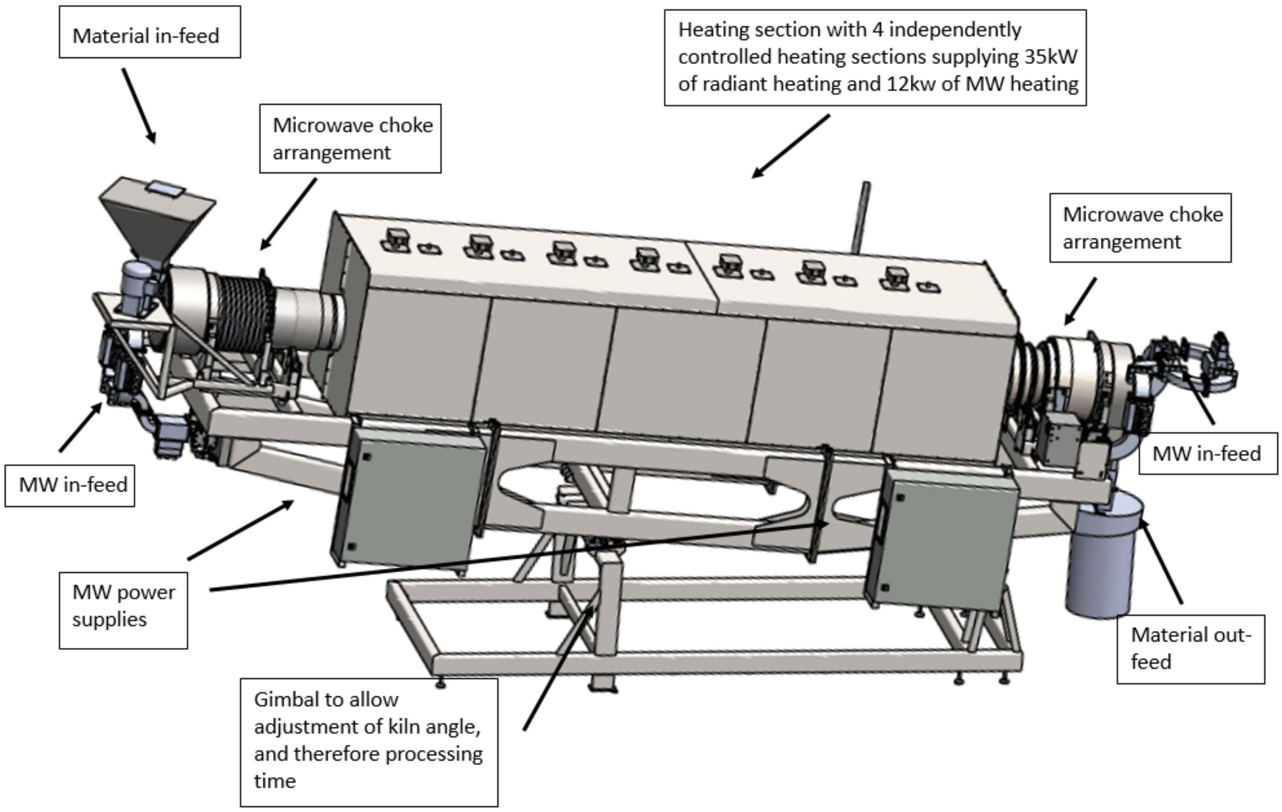
The trials validated that the direct reduction of iron ore is achievable using hydrogen gas and that the rate of reaction is significantly improved by the addition of MW heating and that the reaction can be carried out at a temperature of lower temperatures of 600°C.

Further work is needed to investigate the effect of different specifications of iron ore. The samples used in this work were synthetic materials of small particle size. Industrially representative samples will include contaminants and be of variable particle size.

6 Rotary kiln seal design

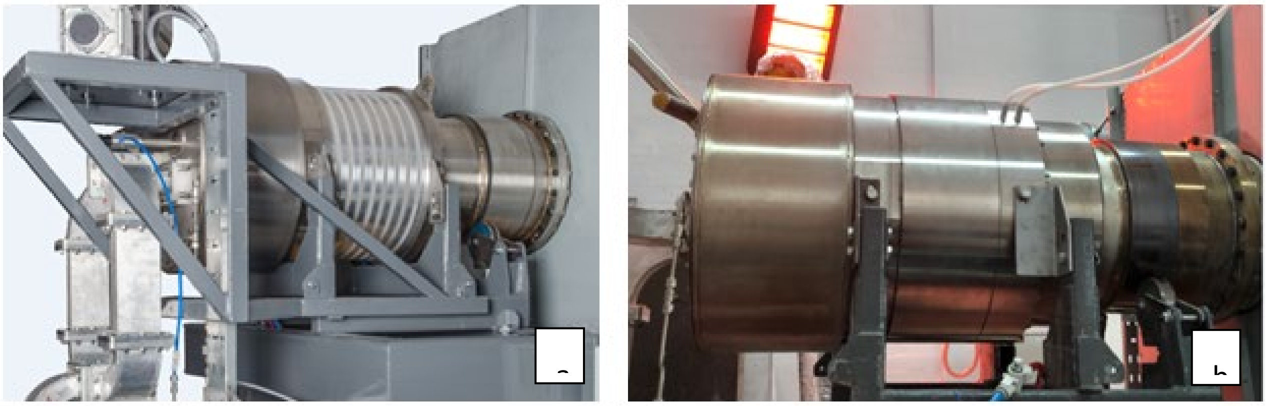
The company's microwave assisted rotary kiln was the basis for designing and testing new rotary seals that can be used to develop the process at pilot scale. The requirement is for a rotating gas-tight seal that will contain an explosive hydrogen containing gas, withstand extended operation at high temperatures, and be a microwave seal. Having such a seal is a requirement before further development of the process can take place at pilot scale and the design of the seal was the major engineering challenge for this phase of the project.

The rotary microwave assisted kiln has a 6 m long rotating drum with internal flights. It has 35 kW radiant heat in independently controllable zones and 12 kW of MW heating with microwave inlet ports at either end. It can operate at temperatures up to 1100°C. The kiln is mounted on a gimbal so that the angle of tilt can be adjusted. The residence time is determined by a combination of kiln angle, drum rotation speed, material properties, and fill level.



A gas tight seal was designed and built. It has the following features:

- accommodation for thermal expansion of the drum with changing temperatures
- able to operate at high temperatures
- a primary gas seal
- a secondary gas seal and gas capture arrangement
- multiple microwave choke rings



The photograph on the left shows the rotary kiln in its original configuration. The grooves are the external face of a set of microwave choke rings that serve as the microwave seal. The microwave injection port is at the left end under the triangular frame section. The seal is microwave-tight but not gas tight. The photograph on the right shows the installed new seal. A similar arrangement is provided at the other end of the kiln.

Other modifications to the kiln were made as a result of the risk assessment. It was necessary to eliminate any possibility of arcing at metallic joining points caused by the microwave field. This was achieved by fitting graphite seals between mating surfaces in the microwave waveguides and kiln, thereby ensuring a continuous electrical path between all components.

Microwave leakage was tested with a NARDA Field Meter, the maximum recorded leakage was 4 V/m which is well below the safety limit of 137 V/m.

Gas leak testing was carried out at a positive pressure of 200 mbar. The system held pressure when operating for one hour, within its design specification.

7 Competitive analysis against current technology

An analysis of the OPEX and CAPEX of the proposed process compared to a conventionally heated DRI process gives the following conclusions:

- A savings of 30% of the energy cost of operating the DRI process.
- Payback time for the microwave CAPEX of around 3 months

Basis of Comparison

- The microwave assisted DRI process operates at 650°C compared with 950°C for the conventional DRI process.
- 15% of the thermal energy requirement is provided as microwave energy. This is based on previous experience of sintering and reduction and remains to be confirmed at pilot scale for hematite.
- Estimated Plant Dimensions. For a throughput comparable to Port Talbot (3 million tonnes / year of steel) with 30-minute residence time and a 1 m fill depth (27% volume fill) two kilns of the following approximate dimensions are required:

Rotary Kiln		
Shaft Dia	m	3
Shaft Length	m	20
Empty Volume	m3	141.4
Fill Height, h	m	1.0
Angle, Theta	rad	2.391
Filled CSA	m2	1.9
Filled Volume	m3	38.4
Percentage Fill of Kiln		27.2%
Residence time	hrs	0.5
Throughput	m3/hr	76.88
No of Furnaces Required for Port Talbot Equivalent		2

- Residence times for microwave assisted and just thermal-only processing are the same but the reduction temperatures are 650°C and 950 °C respectively. 950 °C is a standard temperature for a DRI plant.
- Energy usage is based only on the maximum temperature, specific heat capacity and throughput. No account has been taken of the greater thermal losses expected for the conventional 950 °C DRI process.
- Gas supply requirements are the same for MW assist and thermal only DRI plant. This could be hydrogen, SynGas or a mixture of hydrogen and Syngas.
- The CAPEX for MW assist and conventional thermal DRI plants are assumed to be the same apart from the additional cost of microwave equipment (microwave generators and an allowance for application engineering). Common elements are furnace, solids feed, gas seals, gas supply, gas recirculation (including heat recovery and dehumidification), heat recovery and off gas management.
- Reducing gas (hydrogen) supply requirements are based on the stoichiometric iron oxide throughput for complete reduction to iron. It is assumed that the furnace operates with a

stoichiometric excess but the gas is recycled and dehumidified, hence only the hydrogen used for reduction is required.

- Industrial microwave generators have lifetimes of around 20 years. Magnetrons need to be replaced annually at around 8% of the purchase cost of the generator.

Comments

- Large rotary kilns are used at temperatures up to 1400°C and with throughputs up to 10,000 MT/days (3.5 MT/yr). A single cement kiln is comparable in size with the requirements of a large integrated steelworks, so that the sizes required are in line with current engineering practice.
- Microwave generators have been successfully industrially deployed at MW scale for drying and mineral processing, so the scale of operation has precedent.
- Microwave and RF generators are available in MW sized units from a number of suppliers worldwide, often as a common power supply unit feeding a number of magnetron heads to generate the MW power.
- Microwave and RF generators are a similar price per kW at large scale.
- Using multiple microwave generators or large generators with multiple heads allows magnetron replacement to be carried out while the plant is operating.
- Specific energy values (GJ/MT) are comparable with public data for direct reduction of Iron ore of 1 GJ/MT which gives us confidence in the analysis.
- The redeuced operating temperature will give rise to benefits that have not been factored in to the analysis including reduced energy losses and the option to use cheaper materials of construction including steel replacing refractory materials.

8 Conclusions

The conclusions of this work are:

1. The FILER DRI process is applicable to iron oxide. It was previously shown that microwave energy improved the reduction rate of ilmenite under hydrogen and it has now been shown that this is also the case for hematite.
2. The feasibility of a gas-tight microwave assisted rotary kiln has been demonstrated with the design and testing of a new seal design at pilot scale.
3. A saving of 30% in energy requirements for the FILER DRI process compared to the conventional DRI process is predicted. The payback time for the microwave CAPEX is estimated at around 3 months.

On the basis of these results the microwave-assisted DRI process has the potential to form a part of an all-electric and low-emission ore reduction process for iron and other metals.

9 Next Steps

The plan is to incorporate the FILER DRI technology as part of a demonstration facility for a low carbon steel making process. There are such facilities currently being planned and under construction. The next phase of this programme, FILER Phase 3, has the following objectives:

- Commission the FILER DRI pilot plant at 10 tonnes/day capacity
- Verification that the DRI process is effectively carried out at pilot scale
- Create an information pack for engagement with development partners

Work-packages for FLIER Phase 3 will include the following:

- Engagement with prospective end-user
- Materials Sourcing. Obtain relevant industrial grades of ores
- Laboratory validation of the process with industrial grades of ore
- Batch trials with representative ore samples on existing pilot plant. An upgrade to the exhaust gas system is required with the fitting of articulated ducting to cope with variable tilt angles at high exhaust temperature.
- Design upgrades to Pilot Plant. To include material handling for continuous operation at pilot scale and a gas recycling system that will remove water vapour and recycle hydrogen.
- Build kiln
- Commission kiln