

Non-isothermal reaction of iron ore-coal mixtures

by

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S.D.G.

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ABSTRACT

Extensive work is reported in literature on the reduction of iron oxides with carbonaceous reductants. Most of this work considered isothermal reaction of the material mixture, although as shown in some studies, isothermal reaction conditions are not often the norm because of sample size and heating arrangement in the experiment. In industrial processes, such as the rotary hearth type processes and the IFCON[®] process for iron ore reduction, the norm is non-isothermal reaction. Simulation of industrial processes should take non-isothermal reaction into account if the heat transfer effects within the process are to be investigated. To avoid the complications of coal volatiles in the experimental set-up, few studies were done with coal as reductant. The primary aim of the work presented here is to quantify radiation heat transfer to the surface of an iron ore and coal mixture heated uni-directionally from the sample surface to show the importance of heat transfer in the IFCON[®] process. Secondary aim of this work are to show the effects of layer thickness, coal volatiles, phase chemistry and particle size in this reaction system. The experimental set-up consists of a tube furnace modified to transport the sample into and out of the experimental tube furnace heating zone under a protected atmosphere, whilst the product gas is analysed throughout the experiment by quadropole mass spectrometer. The sample surface temperature, heating zone temperatures and material bed temperatures were measured throughout the experiment. A sample cutter-splitter was developed to divide the reacted sample into three horizontal segments for chemical analyses. The sample surface temperature and the heating zone temperatures were used as inputs to a radiation network calculation to quantify radiation heat transferred to the sample surface. The radiation network calculation was calibrated against heat-mass balance calculations for pre-reduced ore and graphite samples reacted at furnace temperatures of 1300, 1400 and 1500°C. The results show that radiative and conduction heat transfer control prevails for 16 mm to 40 mm material layers heated uni-directionally from the material layer surface. It is shown that coal volatiles contribute to reduction in the stagnant material layer. Also, smaller particle sizes result in increased reaction rates because of a decrease in the diffusion limited effects which were seen in reaction of the base size of coal and ore particles.

Keywords: heat transfer, uni-directionally, radiation network, radiation, conduction, coal, iron ore, temperature, furnace, material layer

Nie-isotermiese reaksie van ystererts-steenkool mengsels
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OPSOMMING

‘n Groot aantal studies in die literatuur handel oor die reduksie van ysteroksied met koolstof. In die meeste studies word verhitting van die mengsel beskou as isotermies. Sommige studies toon egter dat isotermiese verhitting selde plaasvind as gevolg van monstergrootte en verhittingsmetode soos aangewend in die eksperimentele opstelling. In industriële prosesse waarin ystererts gereduseer word, soos die roterende herd tipe prosesse en die IFCON[®] prosesse is nie-isotermiese reaksie die norm. In die simulatie van industriële prosesse behoort nie-isotermiese reaksie in oorweging geneem te word om die effek van hitteoordrag te ondersoek. Min studies is gedoen waarin steenkool as reduktant aangewend is omdat die teenwoordigheid van steenkoolvlugstowwe ’n komplekse opstelling vereis. Die primêre doelwit van hierdie studie is om stralingshitteoordrag na die monsteroppervlak van ‘n ystererts-steenkool mengsel, eendimensioneel verhit vanaf die monsteroppervlak, te kwantifiseer om daardeur aan te toon dat hitteoordrag belangrik is in die IFCON[®] prosesse. Die sekondêre doelwit van die studie is om die invloed van laagdikte, steenkoolvlugstowwe, fasechemie en partikelgrootte in hierdie reaksiesisteen aan te toon. Die eksperimentele opstelling bestaan uit ‘n buisond wat aangepas is om die monster onder ‘n beskermende atmosfeer in en uit die warm sone van die oond te verplaas met deurlopende produkgasanalises deur middel van ‘n massaspektrometer. Die monsteroppervlak-temperatuur, verhittings sone temperature en temperatuur in die materiaal is deurlopend in die eksperiment gemeet. ‘n Monster snyer-verdeler is ontwikkel om die gereageerde monster in drie horisontale segmente te verdeel vir chemiese analises. Die monsteroppervlak-temperatuur en die verhittings sone temperature dien as insetparameters tot ‘n stralingsnetwerk berekening waarmee hitteoordrag na die monsteroppervlak bereken word. Die stralingsnetwerk berekening is gekalibreer teenoor die massa-hitte balans berekening vir voorgereduseerde ystererts-grafiet monsters gereageer teen 1300, 1400 en 1500°C. Die resultate toon dat stralings- en geleidings hitteoordragbeheer plaasvind vir materiaal laagdiktes van 16 mm tot 40 mm. Die resultate toon dat steenkoolvlugstowwe bydra tot reduksie in ‘n stagnante ystererts-steenkool materiaal laag. Reaksie van kleiner partikels toon verhoogte reaksietempo as gevolg van ‘n afname in diffusie beperkende effekte, soos waargeneem in reaksie van die basis partikelgrootte vir steenkool en ystererts.

Sleutelwoorde: Hitteoordrag, eendimensioneel, stralingsnetwerk, straling, geleiding, steenkool, ystererts, temperatuur, oond, materiaal laag



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INTRODUCTION

The use of coal instead of coke as reductant in the iron and steel industry has become more important because this industry realised that coking coal supply could soon be less than demand (Nashan *et al.*, 2000). Furthermore, the future trend is expected to tend toward process consolidation by reducing the number of reactors needed to produce steel from raw material (Wiesinger, 2000). Accompanied with the trend in coal usage has emerged several processes that use iron ore fines, which are not compatible with older iron making technologies when not agglomerated or pelletised (Sarma and Fruehan, 1998). Most of these processes use natural gas to reduce fine iron ore to directly reduced iron (DRI). A few processes that use coal as reductant to produce DRI have been developed. These are the rotary kiln type processes: SL/RN (Bornman and Ackerman, 1993), Accar (Rierson, 1993), Davy DRC (Haworth *et al.*, 1995) and rotary hearth based processes: Fastmet (Hoffman and Harada, 1997) and Comet (Borlée *et al.*, 1999) processes. Of these processes, only the rotary kiln type processes have been commercialised on a large scale. The only commercially established coal based process to produce hot metal is the Corex process (Flickenschild *et al.*, 1996). Other hot metal processes have been developed: AISI (Aukrust, 1992), Hismelt[®] (Cusack *et al.*, 1995), Dios (Saito, 1992), Romelt (Romenets *et al.*, 1999), Ausmelt (Floyd, 2000) and Technored (Contrucci, 2000). The first commercial Hismelt[®] plant has been successfully hot commissioned in October 2005 in Kwinana, Western Australia and production will be ramped up to full capacity over three years to 800 000 t/year (Rio Tinto News Release, 2006).

Thus, it is evident from the development of the above mentioned processes that the use of coal and iron ore fines is becoming more important as traditionally used feed stocks of iron ore and coal are depleted. Only the Comet (Borlée *et al.*, 1999) process uses coal and iron ore fines in a fixed material bed, although in alternate layers, to produce DRI. The hot metal production processes do use coal and iron ore fines, but these raw materials are reacted through bath smelting.

The IFCON[®] process is a direct steelmaking process reacting iron ore fines and coal in a single vessel to produce crude liquid steel. Material mixture of ore fines, coal and fluxes of -10 mm is fed onto the liquid metal bath to form heaps floating on the metal bath. The freeboard is heated by combustion of natural gas and an air and oxygen blast blown into the freeboard via burners. In addition to the natural gas that is combusted in the freeboard, the coal volatiles and reduction product gas from the heaps are combusted to generate heat in the freeboard. The upper portion of the heap where solid state reduction takes place is heated by fossil fuel energy generated in the freeboard. The bottom ends of the heaps are heated from the metal bath, which is in turn heated by inductors.

As identified by Pistorius (2005) ore-carbon/coal reaction systems form the third type of heat transfer control in which there is a band of reaction temperatures in which the process can take place, if no bulk melting of reactants and products takes place. Most of the work done on mixtures of carbon/coal and iron ore (as reported in the literature) was done with the intent of isothermal reaction, but the use of relatively large sample sizes and/or heat transfer hampering sample containment arrangements resulted in non-isothermal reaction. Therefore, the non-isothermal treatment of the samples was not taken into account, and reaction data from the experiments was used to calculate apparent activation energies at the furnace temperatures. From the magnitude of the apparent activation energies conclusions were made as to the rate controlling mechanism in the experiment. Seaton *et al.* (1983) were the first to highlight the problem of using chemical kinetics alone to make conclusions on the rate controlling step when the mixed ore-carbon/coal sample is reacted non-isothermally.

As pointed out by Vankateswaran and Brimacombe (1977) a lot of work is required to obtain all the necessary detailed fundamental information to describe the process progress in a mixed bed system so that an empirical approach to reaction rate measurements is more effective. Therefore a realistic simulation experiment is required in which the heat transfer rate is quantified from measurement of temperature and reaction extent as functions of reaction time and position within the sample material. Here the development of such a simulation experiment for the solid state reduction under unidirectional radiative heating is described, and results reported and interpreted. The information gained from such an experiment should provide enough information to use in validation of mathematical models that can then be used for process design and testing process sensitivities.

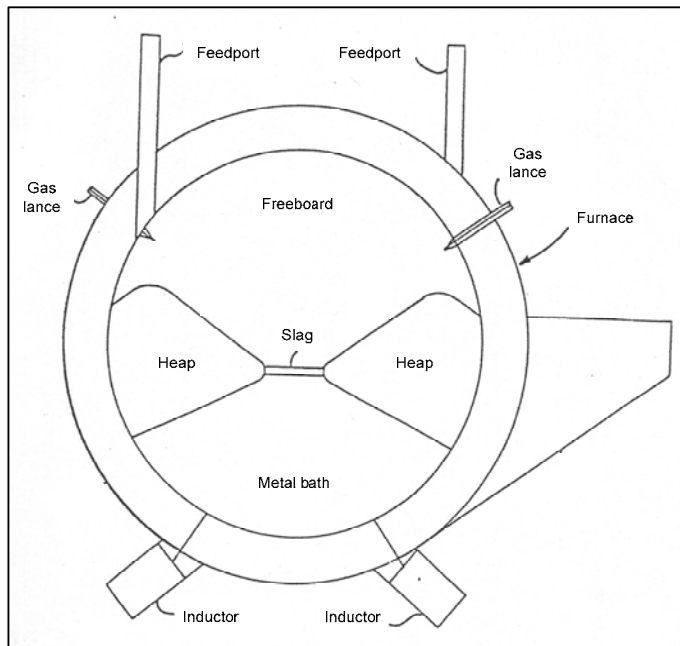
CHAPTER I

LITERATURE SURVEY

1.1. Background

The IFCON[®] process (U.S. Patents 5411570, 6146437, 6537342) is a direct steelmaking process reacting iron ore fines, coal and fluxes in a single vessel to produce crude liquid steel of ~0.1%C. The furnace cross section is shown diagrammatically in **Fig. 1**, and indicates the three main phase volumes: freeboard, heaps, and metal bath. The material mixture of ore fines, coal and fluxes of -10 mm is fed onto the liquid metal bath to form heaps floating on the metal bath. The freeboard is heated by combustion of natural gas and an air and oxygen blast blown into the freeboard via burners. In addition to the natural gas combusted in the freeboard, coal volatiles and reduction product gas from the heaps are combusted to generate heat in the freeboard, which in turn heats the heap surface. This upper section of the heap, where solid state reduction takes place, is heated by fossil fuel energy. Solid state reduction of the iron ore takes place at the heap surface, within the top 20-25 mm layer of material mixture. The material at the heap surface can be heated to temperatures the order of 1400°C, or higher, provided the furnace refractories are not damaged and the iron product remains in the solid state to be melted at the interface between the heap bottom and the metal bath.

Fig. 1: IFCON[®] furnace cross section



The bottom portions of the heaps are heated from the metal bath, which is in turn heated by inductors. The energy input to the metal bath is regulated to maintain the desired metal bath temperature whilst providing sufficient energy for final reduction and melting of the heaps into metal and slag. For steel production the metal bath is operated 50°C to 100°C above the liquidus temperature of the steel.

It is important to quantify and understand ore reduction extent, coal devolatilisation and carbon consumption occurring simultaneously at the heap surface. The carbon content of metallised product formed at the heap surface is also important in development of process understanding because the aim is to make crude steel, not hot metal.

1.2. Iron Ore Reduction with Coal/Carbon

The reduction of iron oxide with carbon is endothermic. For this reason, heat transfer to a mixture of iron oxide and carbon is essential, and in many cases temperature differences can arise within the mixture of solids. In some studies the intention was for a non-isothermal experiment in order to simulate reaction conditions specific to a process e.g. Dutta and Gosh (1994), Wang *et al.* (1997, 1998) and Fortini and Fruehan (2005) reacted composite pellets to simulate conditions in industrial rotary hearth furnace reactors such as Inmetco (Gou and Lu, 1998) and Fastmet (Hoffman and Harada, 1997). Mookherjee *et al.* (1985b) reacted a core of iron ore, surrounded by a cylinder of coal char, non-isothermally to simulate reaction conditions in the Hoggan process in which the oxide and coal are not mixed. Abraham and Gosh (1979) used an experimental set-up in which the electrode graphite powder and the hematite pellet were contained in the same crucible, but physically separated at various distances. The aim was to simulate reaction conditions in the rotary kiln process. Prakash (1994), Prakash and Ray (1990, 1991) and Prakash *et al.* (1986) reacted a mixed bed of coal and ore in the MBR (Moving Bed Reactor) to simulate a vertical retort process for DRI (Directly Reduced Iron) production. Shivaramakrishna *et al.* (1996) reacted coal-ore composite pellets with external coal in an electrically heated rotary tube furnace to simulate DRI production in a rotary kiln furnace. Roman-Moguel and Brimacombe (1988) used a bench scale batch rotary kiln to study the use of unagglomerated iron ore as feed material.

In many cases, it appears that experiments performed on mixtures of carbon/coal and iron ore were intended to yield isothermal reactions, but in most instances the experiment turned out to be non-isothermal because of relatively large sample sizes and/or sample containment arrangements which hampered heat transfer. This unintended outcome is usually ignored and the experimental results are reported as isothermal, and usually the furnace temperature is taken as the experimental temperature.

Isothermal reaction is only obtained when small masses of material, of the order of one gram, is used—as in the work of Otsuka and Kunii (1969), Rao (1971), Fruehan (1977) and Mookherjee *et al.*

(1985a). Even in a relatively small mixed bed sample the difference between the furnace temperature and the material mixture can be significant as shown by Haque *et al.* (1993) for reaction of $-2 +1$ mm iron ore – coal mixture at furnace temperatures of 900-1050°C in a mild steel crucible of 30 mm diameter and 50 mm height for 100-200 minutes total reaction time. The sample temperature reached the furnace temperature after 19-22 minutes of heating time. Mookherjee *et al.* (1986) reacted 45 g samples of coal and ore arranged as separate cylindrical shapes in mild steel crucibles, of 33 mm i.d. and 50 mm height, at furnace temperatures of 850 to 1050°C. The sample temperature was measured, starting when the sample was introduced into the furnace. The sample temperature reached the furnace temperature after 20-30 minutes reaction time. The total reaction time was 150-180 minutes.

Seaton *et al.* (1983) showed that the heating conditions were non-isothermal in 14 mm diameter magnetite and hematite containing composite pellets. In magnetite composite pellets the measured temperature profiles at the pellet centre and pellet surface showed that these two temperatures equalised after 10, 15, and 27 minutes at furnace temperatures of 1200°C, 1000°C and 1100°C, when reduction was complete or ceased. According to Seaton *et al.* (1983) the maximum temperature differential between the pellet centre and pellet surface occurs when the gasification (Boudouard) reaction is predominant. The surface temperatures reached values close to the furnace temperature after 7.5, 16 and 4 minutes for furnace temperatures of 1200°C, 1000°C and 1100°C, respectively. Seaton *et al.* (1983) calculated apparent activation energies, but also did heat transfer calculations for one experiment to show the importance of heat transfer. The heat transfer calculations showed that heat flux to the sample surface becomes insufficient to drive the gasification reaction in the latter part of the reaction period, as the pellet core and surface temperatures reach the furnace temperature. Seaton *et al.* (1983) were the first to highlight the problem of using chemical kinetics, and not taking heat transfer limitations into account. They showed that although chemical kinetic analysis of the results indicated the gasification reaction to be rate limiting, heat transfer calculations indicated heat transfer to the sample to be rate limiting, after the initial period of reaction. Recent work by Fortini and Fruehan (2005) confirms the importance of heat transfer in reaction of composite pellets reacted at 900-1280°C furnace temperatures. Fortini and Fruehan (2005) show that heat transfer control alone prevailed in composite pellets that contained highly reactive carbon in the form of wood charcoal, whilst chemical rate control prevailed in coal char containing pellets.

The only other laboratory scale study to consider heat transfer in reaction of iron ore and coal/carbon material mixtures is that of Huang and Lu (1993), and Sun and Lu (1996) who improved on the experimental set-up used by Huang and Lu (1993). A mixed bed of iron ore and coal, of 81% -75 μ m and 88% -149 μ m respectively, was reacted in a hollow cylindrical stainless steel crucible of 118 mm diameter and 150 mm height. The crucible was placed in a muffle furnace at 1200°C. Huang and Lu (1993) concluded from their results that heat transfer in the mixture was rate limiting. The

experimental set-up used by Huang and Lu (1993) was three-dimensional, or by approximation two-dimensional, although the intention was for it to give one-dimensional heating in the radial direction. The mathematical model, for this experimental set-up, was developed for a one-dimensional configuration. From the model predictions it was concluded that heat transfer within the material mixture is the rate-limiting step due to the endothermic reactions taking place, and the low thermal conductivity of the material mixture (Sun and Lu, 1992, 1993). Sun and Lu (1996) improved on the experimental set-up used by Huang and Lu (1993) by insulating the crucible sidewalls, and heating only the crucible bottom. This approach ensured that heat transfer was one-dimensional, or as close to it as experimentally possible. A mathematical model was developed to simulate the experiment (Sun and Lu, 1996, 1999a, 1999b). It was found that convection and radiation heat transfer within the mixed bed was negligible in comparison to conduction heat transfer, for furnace temperatures smaller than 1300°C. Heat flux to the sample, and within the sample was calculated in the model. From sensitivity analyses done on the model, it was concluded that conduction heat transfer within the material is rate-limiting to the reduction process.

A summary of the different studies in which apparent activation energies were calculated is shown in **Table 1** for coal containing samples and in **Table 2** for carbon containing samples. In the tables an opinion is given on which reaction systems can be considered to be reacted isothermally. In most of the studies apparent activation energies were calculated from the experimental data assuming isothermal reaction.

Depending on the amount of information obtained from the experimental measurements, the reaction extent for the individual reactions of reduction and gasification can be calculated. In absence of detailed information the reaction extent was expressed in terms of the sample mass loss measured, as a fraction of the maximum possible mass loss attainable. Kinetic parameters were then calculated in terms of the overall reaction extent. The resultant magnitude of the activation energy was then used to make conclusions as to the prevailing rate limiting step in the overall reaction sequence. As indicated by Seaton *et al.* (1983) this is questionable if non-isothermal conditions prevail because heat transfer may be the rate-limiting factor, but cannot be identified through chemical kinetic studies alone.

As seen from **Table 1 and 2** few studies were done with coal as reductant. Even when processes with coal as feed material are simulated, coal char is used rather than coal. This is done to avoid experimental difficulties in handling and analysing of coal product gases, and to simplify the reaction system so that conclusions can be made more easily from results. In most studies the contribution of coal volatiles to reduction has been ignored, and in some studies this contribution was inferred e.g. Mookherjee *et al.* (1986) and Haque *et al.* (1993) concluded reduction by volatiles based on the absence of an incubation period in the reduction kinetic plot for the initial reaction period when the

sample was still heating up to the furnace temperature. Dey *et al* (1993) viewed reacted composite pellet microstructures and concluded from these observations that reduction by volatiles took place along “favourable diffusional paths” and that volatiles release was too fast, at reaction temperatures above 1000°C, to contribute to reduction. Wang *et al.*(1997) showed that significant reduction by volatiles took place at temperatures above 700°C. The contribution of volatiles to reduction was calculated from mass loss information from isothermal reaction of a coal sample, an ore/alumina/coal layered sample and an ore/coal mixture, respectively. Sohn and Fruehan (2006a) followed a similar procedure to show that up to 56% reduction by volatiles occurred in a layered Fe₂O₃/coal sample heated from the top surface 1000°C. Sohn and Fruehan (2006b) showed that reduction by volatiles in a single layer of composite pellets was negligible, but in a three layer bed of pellets volatiles from the bottom pellet layer reduced the top pellet layer. The work by Wang *et al.* (1997) and Sohn and Fruehan (2006a, 2006b) were concentrated on composite pellets and not on the uni-directional heating of a packed bed of coal and ore. Therefore, the contribution of volatiles to reduction in a packed bed heated uni-directionally must be simulated in an experimental set-up that is representative of the material and heat transfer arrangement of the process under study to obtain quantified experimental evidence of volatile contribution to reduction for the particular process.



Table 1: Activation Energy calculated in Previous Studies on Ore Reduction with Coal

Authors	P/MB/FB ^a	*	FT ² (°C)	Rate Equation ¹	Activation Energy (kJ/mol)	Particle Size (µm)
Mookherjee <i>et al.</i> (1986)	Ore column surrounded by coal	N	850 900 980 1050	$G(\alpha) = 1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = kt$	Reduction: 156.2 Differential method: 130.7 at $\alpha=0.2$, 152.1 at $\alpha=0.3$, 144.7 at $\alpha=0.6$ and 146.3 at $\alpha=0.70$	-500 +250
Mookherjee <i>et al.</i> (1985a)	Ore column surrounded by coal	I	850 920 1000	$G(f) = 1 - \frac{2}{3}f - (1-f)^{2/3} = kt$	Reaction: 210	-500 +250
Mookherjee <i>et al.</i> (1985b)	Ore column surrounded by coal	N	1.7- 2.4°C/ min to 1100°C	$G(\alpha) = 1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = kt$	Reduction from Coats & Redfern equation: 111.7	-500 +250
Haque <i>et al.</i> (1993)	MB	N	900 950 1000 1050	$G(\alpha) = -\ln(1-\alpha) = kt$	Reduction: Integral method: 159 Reduction: Differential method: 153 at $\alpha=0.20$ and 160 at $\alpha=0.60$	-2000 +1000
Haque <i>et al.</i> (1993)	FB	N	900 950 1000	$G(\alpha) = -\ln(1-\alpha) = kt$	Reduction: Integral method: 155 Reduction: Differential method: 152 at $\alpha=0.60$ and 159 at $\alpha=0.50$	Ore: -250 +180 Coal: -500 +353
Haque <i>et al.</i> (1992a)	MB	N	950 1000 1050	None	Reduction: Differential method: 148-151.4 at $\alpha=0.6-0.9$	-2000 +1000
Prakash and Ray (1990)	MB	I	800 900 1000	$G(\alpha) = 1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = kt$	Reduction: 111.2 Reaction: 90.9	-6000 +3000
Prakash <i>et al.</i> (2000)	P	I	800 900 1000 1050	$G(\alpha) = -\ln(1-\alpha) = kt$	Reduction: 49-50 (Pellet basicity=0.82); 47-52 (Pellet basicity=1.33)	-75 (Pellet ϕ = 10-12.5 mm)
Wang <i>et al.</i> (1998)	P	N	1050 1200 1250	$G(\alpha) = -\ln(1-\alpha) = kt$	Reduction: Soft coal pellet: 82.61; Hard coal pellet: 68.95	(Pellet ϕ = 16-18 mm)
Reddy <i>et al.</i> (1991)	P	N	900 950 1000 1050 1100	$\frac{1}{C_{A0}(1.5-M)} \ln \frac{M(1-X_A)}{(M-1.5X_A)} = kt$ $M = C_{A0}/C_{B0}$ C_{A0} =initial concentration Fe_2O_3 [g./mol] C_{B0} =initial concentration C [g./mol] X_A =fraction conversion of Fe_2O_3 to Fe	Reaction: Initial stage: 108.15; Latter stage: 93.16	-150 (Pellet ϕ = 14 mm)
Dey <i>et al.</i> (1993)	P	N	900 950 1000 1025 1050	None	Reaction: At different fraction reaction: 0.1: 35.0, 0.2: 30.3, 0.3: 40.5 and 30.3, 0.4: 44.2 and 30.3, 0.5: 44.2 and 30.3, 0.6: 44.2	-85 +53 (Pellet ϕ = 10 mm)
Shivarama- krishna <i>et al.</i> (1996)	P	N	950 1000 1050	$G(f) = -\ln(1-f) = kt$	Reaction: Char: 138; Coal: 92	Ore: fine Coal: -500 +50 or -50 (Pellet ϕ = 10-12 mm)

*Isothermal = I; Non-isothermal = N

¹ α or f_r = reduction extent; f = reaction extent; f_c = gasification extent

^a P = pellet; MB = mixed bed; FB = Fluidised bed

² FT = Furnace temperature



Table 2: Activation Energy calculated in Carbon Reduction Studies

Authors	P/MB ^a	*	Carbon Type	FT ² (°C)	Rate Equation ¹	Activation Energy (kJ/mol)	#	Particle Size (µm)
Otsuka and Kunii (1969)	MB	I	Graphite	1050 1100 1150	None	At 20% R: 230 (C fine), 259 (C coarse), 272 (Both ore & C fine) At 60% R: 63 (both ore & C fine), 98 (fine ore, coarse C)	R	Ore mean size: fine = 20; coarse = 124 Graphite mean size: fine = 67; coarse = 190
Rao (1971)	MB	I	Amorphous carbon	957 987 1007 1037 1087	$G(f) = \ln(1.743 - f) = -kt + \ln(1.743)$	301	O	Oxide: -4 Carbon: -49
Gosh and Tiwari (1970)	P	N	Lignite Coke	900 950 1000 1050 1100	None	At %R > 50%: 78	R	-250; (Pellet ϕ = 19 mm)
Srinivasan and Lahiri (1977)	P	N	Graphite	927 1022 1060 977	None	At 20% R: 418; At 60% R: 286; At 80% R: 56	R	-53; (Pellet ϕ = 9.7-12 mm)
Fruehan (1977)	MB, P	I	Coconut Charcoal, Coal Char, Metallurgical Coke	900 950 1000 1050 1100 1200	$G(f_c) = -\ln(1 - f_c) = k_c t$	$\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$ and $\text{FeO} \rightarrow \text{Fe}$: 293-335	G	-75; (Pellet ϕ = 6-14 mm cylinder)
Abraham and Gosh (1979)	MB, OP-GP ^d	N	Electrode Graphite	880- 1042	None	At %R < 20: MB: 305; MB (pressed): 296 At %R > 20: MB: 230; MB (pressed): 140 At 35-60%R: OP-GP: 314	G	Oxide: -49; Graphite: -75 +49; (Pellet ϕ = 15.2-17.2 mm, height = 2.8-6.6 mm)
Wright <i>et al.</i> (1981)	P (Iron Ore) in char	I	Char	900 950 1000 1075 1150 1200	$G(\alpha) = -\ln(1 - \alpha) = kt$	290-335	R	(Ore Pellet ϕ = 12 mm) Char: -8 +1 mm
Seaton <i>et al.</i> (1983)	P	N	Coal Char	900 1000 1100 1150	$G(\alpha) = \ln(1 - 0.98f) = -kt$ $G(\alpha) = \ln(1 - 1.037f) = -kt$	Haematite: 126, 239 Magnetite: 159	O	Ore: ? Char: -49 (Pellet ϕ = 14 mm)
Roman-Moguel and Brimacombe (1988)	MB	N	Coal Char	800 850 900 950	Gasification: $G(f_c) = -\ln(1 - f_c) = k_c t$ Reduction: $G(f_r) = 1 - (1 - f_r)^{1/3} = k_r t$	Gasification: Coal char: 224; Lignite: 264 Reduction: 116.4	R & G	Ore: -420 +300 Coal char: -210 +150
Mookherjee <i>et al.</i> (1985a)	Ore column in char	I	Coal Char	850 920 1000	$G(f) = 1 - \frac{2}{3}f - (1 - f)^{2/3} = kt$	195.8; 168.8 (5% Na ₂ CO ₃ added to char) Differential: 188.1 at f=0.3; 144.2 at f=0.4 Na ₂ CO ₃ added to char: 179.9 at f=0.3; 152.0 at f=0.4	O	-500 +250
Mookherjee <i>et al.</i> (1985b)	MB	N	Coal Char	10°C/m in; 20°C/m in to 1100°C	$G(f) = -\ln(1 - f) = kt$	Last segment of Non-isothermal kinetic plots: Coats-Redfern equation = 99; Dixit-Ray equation = 114	O	-90 +63
Mookherjee <i>et al.</i> (1985b)	Ore column in char	N	Coal Char	10°C/m in to 1100°C	None	119	O	-500 +250
Mookherjee <i>et al.</i> (1986)	Ore column in char	I	Coal Char	850 900 950 1000	$G(\alpha) = 1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = kt$ $G(f_c) = 1 - \frac{2}{3}f_c - (1 - f_c)^{2/3} = kt$	Reduction: 168.4 Gasification: 176.6	R & G	-500 +250



Authors	P/MB ^a	*	Carbon Type	FT ² (°C)	Rate Equation ¹	Activation Energy (kJ/mol)	#	Particle Size (µm)
Ajersch (1987)	P	N	Electrode Graphite	837 1127 1027	None	Fe ₂ O ₃ → FeO: 169 (initial), 182 (steady) FeO → Fe: 647	R	Oxide: -57 +44; Graphite: - 105 +74; (Pellet φ = 10 mm = height)
Nasr <i>et al.</i> (1994)	P	N	Coke	950 1000 1050 1100	$\ln(A - R) = -kt + \ln(A)$ $R = AC_u + B$ $R = \% \text{Reduction}$; $C_u =$ $\% \text{Carbon utilisation}$; A, B are constants	5% Coke in mix: 231; 10% Coke in mix : 179; 15% Coke in mix: 159; 20% Coke in mix: 123	R	-75 (Pellet φ = 7.5 mm, height = 10 mm)

*Isothermal = I; Non-isothermal = N; ^a P = pellet; MB = mixed bed; ⁴ OP-GP = Oxide pellet – graphite powder, 1.6 cm apart
¹ α or f_r = reduction extent; f = reaction extent; f_g = gasification extent. %R=%Reduction; # Reaction measured in study: R = reduction; G = Gasification; O = Overall reaction; N = None

Studies on coal devolatilisation as applicable to ore reduction are limited. Sampaio *et al.* (1992) experimentally simulated coal devolatilisation of 3-9 mm particles in slag at 1325, 1435, 1520°C at heating rates of 5640, 7020, 10140°C/min applicable to bath smelting processes, and Patisson *et al.* (2000) simulated devolatilisation of 10 mm coal particles in a rotary kiln at 8, 14, 30 °C/min up to 850°C.

The heating rates used by Patisson *et al.* (2000) are rather low but this work does give valuable information on the expected devolatilisation products: C₂H₄, C₂H₆, C₂H₂, CO₂, CO, H₂, H₂O and tar. Increased heating rates resulted in more light gases and less tar being formed. The studies on the mechanism and reaction sequences in coal pyrolysis indicate the rate and extent of coal devolatilisation to be dependent on the heating rate of the coal (Tomeczek and Kowol, 1991; Goyal and Rehmat, 1993; Devanathan and Sexena, 1987; Jones and Schmid, 1964; Arendt and van Heek, 1981; Peters and Bertling, 1965; Jüntgen and van Heek, 1979). At high heating rates secondary reactions occur, in which coal tar (forming in the devolatilisation process) is further cracked to simple components such as H₂, char and gas (Devanathan and Sexena, 1987). Generally, for a coal, an increased heating rate results in a higher devolatilisation temperature, and an extended temperature range of devolatilisation (Pattison *et al.*, 2000). Coal heated to high temperatures at high heating rates can evolve more volatile matter than that found in the proximate analysis (Desypris *et al.*, 1982). Primary devolatilisation of coal starts at 300-400°C, and continues at higher temperatures up to 1000°C for high heating rates (Stubington and Sumaryonon, 1984; Arendt and van Heek, 1981).

Information on the extent of carburisation of the iron formed in the solid state reduction product at the heap surface is important because the final product aim is making crude steel. If the product from the solid state reduction zone is high in carbon, refining must be done in the rest of the process. Few studies were done to investigate carburisation of iron by coal in mixed ore-coal reaction. Haque *et al.* (1992b, 1993) measured carburisation of iron in reaction of coal-ore packed beds and found increased carbon deposition at lower temperatures. Haque *et al.* (1992b, 1993) explain this to be the result of

slow devolatilisation and slow dissociation of volatiles at low temperatures, enhancing formation of deposited carbon. Formation of combined carbon is enhanced by increased reaction time and temperature. In the case of char as reductant only small amounts of free carbon is formed, and according to Haque *et al.* (1992b, 1993) this carbon deposition took place on sample cooling. The combined carbon content of DRI, when char was used as reductant, is similar to that formed when coal was used as reductant. Additions of Na_2CO_3 or CaCO_3 resulted in increased combined carbon contents. Haque *et al.* (1992b, 1993) ascribed this to early formation of iron in the presence of the carbonates, so increasing the contact time between carbon and iron for diffusion of carbon into iron.

Towhidi and Szekely (1983) performed reduction experiments on Fe_2O_3 pellets in $\text{CO-H}_2\text{-N}_2$ gas mixtures at 600-1234°C and found that the maximum rate of carbon deposition occurred at 500-600°C. Carbon deposition only occurred at temperatures below 900°C and formed a layer of carbon on the pellet surface that prevented access of reducing gas to the pellet, resulting in decreased reduction rates. The gas mixtures used in experiments varied from CO and H_2 , to mixtures of CO and H_2 of 25%CO-75% H_2 , 50%CO-50% H_2 and 75%CO-25% H_2 . The maximum rate of carbon deposition was observed in a 75%CO-25% H_2 gas mixture. At constant partial pressure of CO, carbon deposition was enhanced by H_2 and hindered by N_2 . Deposited carbon was elemental carbon, not cementite. Carbon deposition is not only dependent on thermodynamics as it was found that carbon deposition does not take place to a significant extent in the initial stages of reduction, but once iron had formed from reduction, the iron served as a catalyst for carbon deposition.

The catalytic effect of iron on CO decomposition means that the pore surface area of the iron formed in the reduction process directly influenced the carbon deposition rate (Turkdogan and Vinters, 1974). The product iron surface area formed in reduction of hematite in turn depends on the pore surface area of the source material as shown by Turkdogan and Vinters (1972); a small iron oxide surface area (porosity) results in a small iron surface area. Turkdogan and Vinters (1972) also determined that the coarseness of the iron pore structure formed from hematite reduction increases with increased reduction temperatures, and the iron pore surface area decreases. Also, a more coarse iron pore structure is formed from reduction by CO than that formed by H_2 reduction.

1.3. Indicators for Heat Transfer Control

Pistorius (2005) identified heat transfer control of three different types: (1) thermodynamically constrained processes such as calcination of limestone which takes place at a specific temperature where increased heat input results in increased reaction rate at the specific reaction temperature, (2) processes in which the process temperature is limited by the slag liquidus temperature so that increased heat input results in increased reaction rate, but process temperatures remain similar to that at lower heat input as is the case in ferromanganese and ferrochromium production, (3) reaction of

ore-carbon/coal systems in which there is a band of reaction temperatures in which the process can function, given no bulk melting of reactants and products takes place. As shown by Pistorius (2005) mixed control between heat transfer control and chemical reaction control can prevail in ore-carbon/coal reaction systems, and heat transfer control can be in the form of radiation heat transfer control, that is heat transfer from the heat source to the heated surface is controlling, or heat transfer control can be in the form of conduction heat transfer (where heat transfer from the sample surface to the sample interior is limiting).

The main indicator for heat transfer control is the presence of a persistent temperature differential between the heat source and the heated surface. This was shown by Venkateswaran and Brimacombe (1977) to be the case in the SL/RN direct reduction kiln process. The authors developed a model for the process and compared the model outputs with solids bed temperature measurements from a pilot SL/RN kiln of 35 m length and 2.1 m ID. The temperature differential between the solids bed and the gas varied from a maximum of 597°C closest to the charge end, in the reduction zone of the kiln, to a minimum of 165°C towards the discharge end of the kiln. At the same physical positions in the kiln, the temperature differential between the solids bed and the kiln wall varied from 247°C to 41°C. Venkateswaran and Brimacombe (1977) conclude that heat transfer control prevails in the reduction zone of the kiln because the air profile in the kiln is an important variable, and that high energy requirement for the gasification reaction explains heat transfer control in the reduction zone. Heat transfer control in the SL/RN process is also indicated by the effect of more reactive reductant on the bed temperature. This is shown in graphical format by Cunningham and Stephenson (1980): for lignite as reductant the bed temperature is 900°C, increasing to 1000°C for gas-flame coal, and a further increase to 1140°C for coke breeze as reductant. In the work presented here the sample is heated unidirectionally from the sample surface to test the effect of heat transfer control within the material bed. Therefore, in the experimental work presented here a significant temperature differential, at least 100°C, between the sample surface and the heat source is expected.

Besides the observation of a persistent temperature differential between the heat source and the heated surface, the second indication of heat transfer control in a reaction system is that increased reaction rates result from increased heat transfer to the reacting material. The latter statement sounds obvious for an endothermic reaction system but can be better explained from the work of Seaton *et al.* (1983) in which the reaction of char-hematite composite pellets almost ceases for reaction at 900°C when the pellet surface and centre temperatures levelled off with the onset of the gasification reaction. For reaction of the pellets at 1000°C and 1100°C furnace temperatures, instead, the similar eventual levelling off of pellet surface and centre temperatures is seen, but the reaction extent was much larger before reactions ceased. Therefore, as pointed out by Seaton *et al.* (1983), not enough heat is transferred to the pellet at 900°C to overcome the heat demand of the gasification reaction at this

temperature, whilst heat supply to the pellet at 1000°C and 1100°C furnace temperature was higher to at least enable significant gasification reaction progress to supply CO for the reduction of FeO. The latter observation does not mean the absence of heat transfer control at 1000°C and 1100°C furnace temperatures, only that the effect of heat transfer control was more pronounced at 900°C.

Another indicator of heat transfer control is the observation of apparent activation energy values which are much lower than that for chemical reaction control. In some studies a possible explanation put forward for the lower apparent activation energy was catalysis of the gasification reaction, Seaton *et al.* (1983), Abraham and Gosh (1979). The other explanation often put forward is mixed control because the activation energy is close to half that reported by Walker *et al.* (1959) of 360 kJ/mol for chemical reaction control.

1.4. Chemical Reaction Rates

1.4.1. Reduction

Usually the aim of rate chemical studies of reduction/gasification is to determine the intrinsic reaction rate for a particular material. To measure the intrinsic reduction/gasification rate the experiment must be set up in such a way that effects of film mass transfer and diffusion are eliminated. Reacting small samples at low temperatures and under sufficient gas flow rates ensure that only the chemical reaction rate is measured. This information provides the absolute maximum rate at which reduction/gasification can take place. However, rates in industrial processes are usually not under chemical reaction control only, since high reaction temperatures are employed. Relevant reduction rate studies are summarised in **Table 3**. Comparison of the rate data from these studies is shown in graphical format in Coetsee *et al.* (2002).



Table 3: Studies on Reduction Rates

Authors	Year	Activation Energy (J/mol)	Reaction Step*	Reduction Temperature (°C)	Gas	Start Material	Particle Diameter/ Thickness (mm)	A/N/ D/C/ S/PB
McKewan	1960	64 015	W/F	600-1050	H ₂	Ore fines	5-18; 6-25 (Hard Taconite)	P
McKewan	1960	62 342	M/F	400-550	H ₂	Ore fines	5-18; 6-25 (Hard Taconite)	P
McKewan	1961	56 902	M/F	400-500	H ₂ -H ₂ O-N ₂	Reagent Grade Fe ₂ O ₃	9	P
McKewan	1962a	57 739	H/F	700-1000	H ₂ -H ₂ O-N ₂	Reagent Grade Fe ₂ O ₃	9	P
McKewan	1962b	56 484	M/F	350-500	H ₂	Reagent Grade Fe ₂ O ₃	9	P
Trushenski <i>et al.</i>	1974	99 998 64 434 [105 397?]	H/M M/W	750, 775, 800	CO-CO ₂	Pure Fe ₂ O ₃ Powder	13.5	P
Trushenski <i>et al.</i>	1974	69 036 78 241 116 131	H/M M/W W/F	750, 775, 800	CO	Pure Fe ₂ O ₃ Powder	13.5	P
Turkdogan & Vinters	1972	191 409	W/F	600-1100	H ₂	Hematite Ore	0.4-3.6	A
Turkdogan & Vinters	1972	125 614	W/F	700-1200	CO-CO ₂	Hematite Ore	0.4-3.6	A
Turkdogan & Vinters	1972	137 439	W/F	800, 1050, 1200	CO-CO ₂	Oxidised Fe Strip	1 x (4-11 cm ²)	S
Nabi & Lu	1968	92 048	H/M	811-1011	H ₂ -H ₂ O	Hematite Ore	9.3 x 27 length	C
Quets <i>et al.</i>	1960	61 505	M/F	400-590	H ₂ -N ₂	Reagent Grade Fe ₂ O ₃ & Fe Strip	15.6 (C) 20 x 15 x 0.1 (S)	C, S
Quets <i>et al.</i>	1960	13 389	M/W	590-1000	H ₂ -N ₂	Reagent Grade Fe ₂ O ₃ & Fe Strip	15.6 (C) 20 x 15 x 0.1 (S)	C, S
El-Geassy <i>et al.</i>	1977	53 555 (Dense) 21 506 (Porous)	H/F	800-1100	H ₂	Chemically Pure Fe ₂ O ₃	Dense: 9.8 x 11.1 height Porous: 10.8 x 12.2 height	C
El-Geassy <i>et al.</i>	1977	31 589 (Dense) 9 540 (Porous)	H/F	800-1100	CO	Chemically Pure Fe ₂ O ₃	Dense: 9.8 x 11.1 height Porous: 10.8 x 12.2 height	C
Murayama <i>et al.</i>	1978	79 161 120 499 125 143	H/M M/W W/F	800-1050	CO-CO ₂	Pyrite Cinder	10	P
El-Rahaiby & Rao	1979	71 550	W/F	238-417	H ₂	Fe Strip	0.0508 x (2.40-5.28 cm ²)	S
Al-Kahtany & Rao	1980	77 739	M/F	234-620	H ₂	Fe Strip	0.089 x (1.12-9.88 cm ²)	S
Sun and Lu	1999b	65 689 69 454 73 638	M/W W/F M/F	1200	CO (Coal)	Fe ₃ O ₄	Fines	PB
Sun and Lu	1999b	61 505 63 597 68 618	M/W W/F M/F	1200	H ₂ (Coal)	Fe ₃ O ₄	Fines	PB
Rao & Moinpour	1983	65 325	H/F	245-482	H ₂	Fe Strip	0.136x (6.40-6.56 cm ²)	S
Towhidi Szekely and	1981	52 300	H/M	600-1234	CO	Fe ₂ O ₃	4-20	P
Towhidi Szekely and	1981	60 668	H/M	600-1234	H ₂	Fe ₂ O ₃	4-20	P



Authors	Year	Activation Energy (J/mol)	Reaction Step*	Reduction Temperature (°C)	Gas	Start Material	Particle Diameter/ Thickness (mm)	A/N/D/C/S/PB
Warner	1964	63 597	W/F	650-950	H ₂	Fe ₂ O ₃	10 x 10 height	C
Meraikib & Friedrichs	1987	63 100	H/F	800-1000	CO	Hematite Ore	13	P
Meraikib & Friedrichs	1987	51 700	H/F	750-1000	H ₂	Hematite Ore	13	P
Tsay <i>et al.</i>	1976	92 048 [Nabi & Lu] 71 128 63 579 [Warner]	H/M M/W W/F	800, 850, 900	H ₂	Fe ₂ O ₃	28.6 x 10 height	P
Tsay <i>et al.</i>	1976	113 805 73 638 69 454	H/M M/W W/F	800, 850, 900	CO	Fe ₂ O ₃	28.6 x 10 height	P

* Pellet (P) or Particle (A) or Disk (D), or Cylinder (C), Packed Bed of Coal and Oxide (PB), Strip (S)

* Fe₂O₃=H; Fe₃O₄=M; FeO=W; Fe=F

1.4.2. Gasification

Gasification of carbon occurs via a surface reaction on the carbon pore surface. Therefore, as in the case of iron oxide reduction with CO, experimental measurement of fundamental kinetics requires prevention of diffusion control, by using small particles. The pore surface area and pore size distribution are different for different types of carbon. Also, as the carbon is gasified the pore structure changes: the pores increase in size when carbon is carried away in the gas phase as CO.

Global kinetic parameters were determined in most of the gasification studies, but some authors determined the kinetic parameters for the elementary steps in the gasification process, as presented in the Langmuir-Hinshelwood (LH) expression. The latter approach involves the reaction of carbon under different CO₂-CO gas mixtures, at different temperatures, whilst the former may be calculated from gasification experiments under CO₂ gas only. As it is well known from experimental evidence that the gasification rate is retarded by CO and H₂ in the reactant gas it would seem appropriate to measure gasification rates in the presence of these retarding gases, since they will be present in significant quantities in metallurgical processes.

However, there still remains much uncertainty as to the applicability of the LH expression, and the meaning of the constants in the expression. Wu *et al.* (1988) questioned the interpretation of the constants in the LH expression and Bandyopadhyay and Ghosh (1996) questioned the applicability of the expression for CO-CO₂ gases containing large amounts of CO.

The LH equation is:

$$rate = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}} \quad (1)$$

The widely accepted mechanism as represented in the LH expression is that proposed by Reif (1952):



$$K_1 = k_1; K_2 = k_2 / k_3; K_3 = k_1 / k_3$$

(O) = carbon-oxygen complex formed by adsorption of oxygen onto the carbon surface

As discussed by Von Fredersdorff and Elliott (1963), the LH expression can be simplified for extreme reaction conditions of temperature and partial pressures of CO and CO₂, for total pressures up to 1 atm. If gasification occurs at low temperature and high P_{CO_2} , the P_{CO} will be low and the simplified LH expression will be zero order with respect to P_{CO_2} as $K_2 P_{CO} \ll 1$ and $K_3 P_{CO_2} \gg 1$. Most of the active carbon sites are then filled by adsorbed oxygen and the gasification rate is that of the gasification step, reaction (3), and the activation energy, E_{k_3} . Dutta *et al.* (1977) found that the gasification rate is independent of P_{CO_2} at CO₂ pressures in excess of 15 atm., and therefore zero order with respect to P_{CO_2} .

At low P_{CO_2} and low temperatures, when P_{CO} is low, the LH expression simplifies to express the rate of the oxygen adsorption reaction step, reaction (2), as $K_2 P_{CO} \ll 1$ and $K_3 P_{CO_2} \ll 1$. The reaction order with respect to P_{CO_2} is then one. This is also the case when gasification takes place at high temperature and P_{CO_2} , because the K_2 and K_3 become small under these conditions. That is, the gasification reaction rate constant (k_3) is large compared to the oxygen adsorption and desorption reaction rate constants, k_1 and k_2 so that most of the active carbon sites are free carbon sites. The gasification rate expressed is that of the oxygen adsorption rate, reaction (2) forward, and the activation energy is E_{k_1} .

The extreme reaction conditions that allow simplification of the LH equation are usually absent in ore-carbon reduction. Then the reaction order with respect to P_{CO_2} falls between one and zero. As indicated by Von Fredersdorff and Elliott (1963), the LH expression does not allow for zero gasification rates at equilibrium conditions when high P_{CO} prevails at ore-carbon reduction temperatures. Rao and Jalan (1972) show that incorporation of the reverse reaction (3) results in a modified LH expression that does eliminate the above problem. Reaction (3) (reverse) was not taken into account in the past as the argument was that carbon transfer from gas to solid carbon would occur if this reaction takes place, and this was not seen in previous studies, Ergun (1956). The contrary was concluded by Kapteijn *et al.* (1994).

The gasification mechanism under water vapour may be considered to be analogous to that of gasification under CO₂:



$$K_1 = k_1; K_2 = k_2 / k_3; K_3 = k_1 / k_3$$

(O) = carbon-oxygen complex formed by adsorption of oxygen onto the carbon surface

The LH equation for steam gasification of carbon:

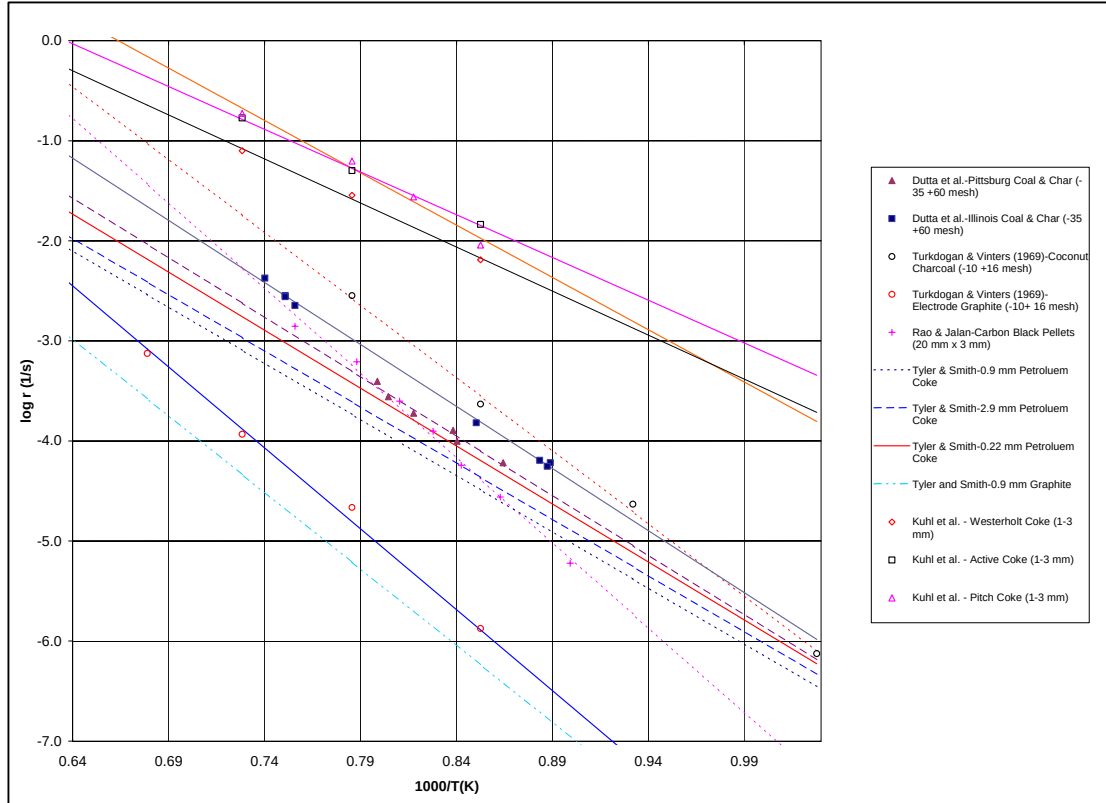
$$rate = \frac{K_1 P_{H_2O}}{1 + K_2 P_{H_2} + K_3 P_{H_2O}} \quad (6)$$

In most instances the gasification rate is determined under CO₂ (or H₂O) gas only, and the apparent activation energy is calculated from the first order reaction rate expression. In some instances the reaction order with respect to P_{CO_2} is checked, but in most cases it is assumed. Also, the initial reaction rates are used so that the carbon pore surface area used in rate calculations can then be assumed to be the same as that measured in the unreacted carbon. The rates are compared in units of per time here for easy comparison as the internal pore surface area has not been measured in all the studies. The use of small particles is very important in gasification rate measurements as the internal surface area is large so that diffusion control can easily set in when large particles are used. Turkdogan *et al.* (1968) determined that the carbon particles should be smaller than 6 mm at 900°C and 2 mm at 1100°C to ensure reaction control under CO₂.

In **Fig. 2** the reaction rates from various studies, at 1 atm. total pressure CO₂, are shown. Where points are indicated in the graphs these points were calculated from individual data points in the reported study, whilst lines without points indicate extrapolation of data measured at low temperatures or a rate expression determined by the authors and then only converted to the required units for this study. Where a data series consists of both points and a line, the line represents a linear fit determined in this study, and the kinetic parameters from this straight line may not be exactly that reported in the particular study.

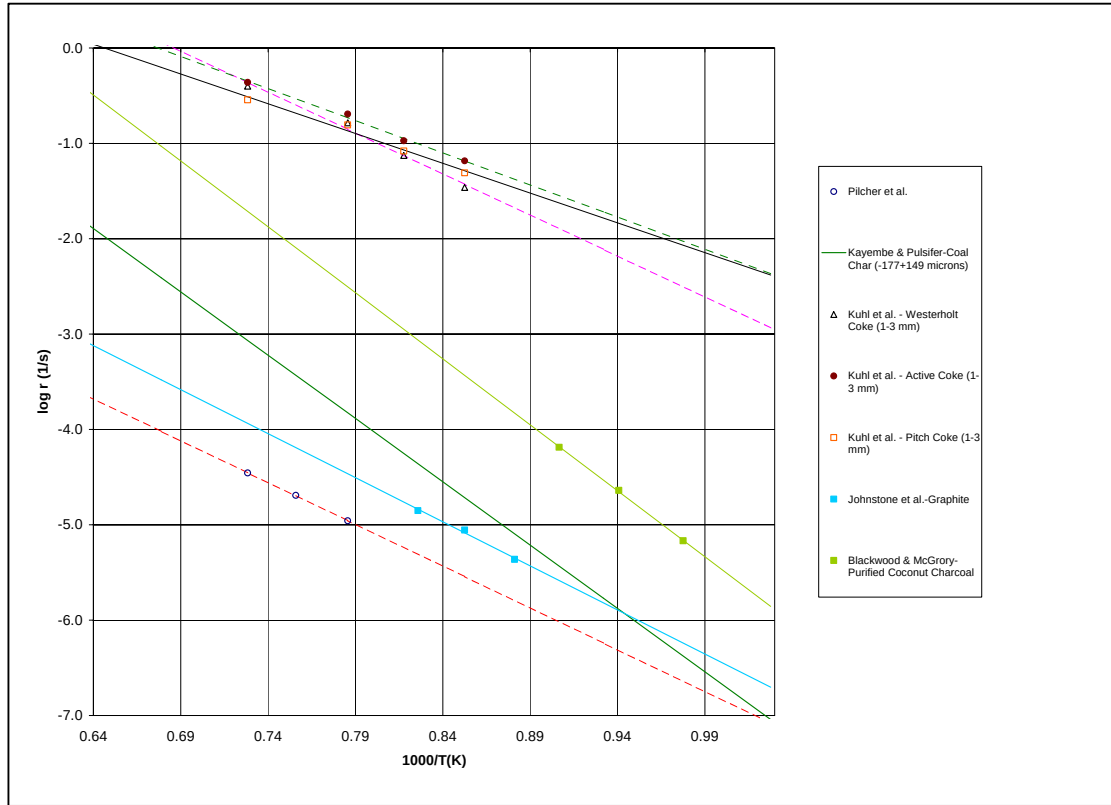
It is seen that the reaction rates range from lowest rates for unreactive graphite, to petroleum coke, coal char and most reactive coconut charcoal. The activation energies range from 164 kJ/mol for Pitch coke by Kühl *et al.* (1992) to 325 kJ/mol for Carbon Black by Rao and Jalan (1972). The reaction rates measured by Kühl *et al.* (1992) for different coke samples are higher than the rest. This may be due to the rates being measured at 40% carbon reaction, when the pore surface area should be close to its maximum value, Wu *et al.* (1988).

Fig. 2: Initial Gasification Rates under CO₂



A limited number of studies have been done on steam gasification of carbon. **Fig. 3** shows some of the initial reaction rates from these studies under 1 atm. H₂O. The values reported for Johnstone *et al.* (1952) and Blackwood and McGrory (1958) were calculated from the LH-expression parameters determined in those studies. Kayembe and Pulsifer (1976) calculated an activation energy of 254 kJ/mol for coal char gasification under steam. This value is much higher than that determined in the other studies done by Pilcher *et al.* (1955), Johnstone *et al.* (1952) and K hl *et al.* (1992) ranging from 120-177 kJ/mol. The gasification rates measured by K hl *et al.* (1992) for different coke types are also higher than that measured in the other studies, but this may be due to the rates being measured at 40% reaction, when the carbon surface area is close or at its maximum, Wu *et al.* (1988).

Fig. 3: Initial Gasification Rates under H_2O



1.5. Conclusion

Chemical reaction rates of reduction and gasification indicates the maximum possible process production rates for mixed bed systems, but do not necessarily provide realistic process production rate predictions because the real process is usually not under chemical reaction control. Apparent activation energy values calculated from experiments on composite pellets and mixed bed materials can not be used alone to make conclusions on heat transfer control, as pointed out by Seaton *et al.* (1983). As pointed out by Vankateswaran and Brimacombe (1977) a lot of work is required to obtain all the necessary detailed fundamental information to describe the process progress in a mixed bed system so that an empirical approach to reaction rate measurements is more effective. Therefore, the primary aim of the work presented here is to construct a realistic simulation experiment to quantify radiation heat transfer from measurement of temperature and reaction extent as functions of reaction time and position within the sample material. These results will show the importance of heat transfer in the IFCON[®] process. Secondary aims of this work are to show the effects of layer thickness, coal volatiles, phase chemistry and particle size in this reaction system. The information gained from such an experiment should provide enough information to use in validation of mathematical models that can then be used for process design and testing process sensitivities.

CHAPTER II

EXPERIMENTAL

As discussed in the literature study in Chapter I, one needs an experimental set-up that will simulate uni-directional heating conditions typical of the industrial process under study. To simulate uni-directional heating in a tube furnace a unique experimental set-up was developed that allows the sample to be transported into and out of the experimental tube furnace heating zone, under a protected atmosphere. This set-up also allows for product gas analyses to be done throughout the experiment. Furthermore the experimental set-up was used to quantify the heat transferred to the sample over the experimental time period.

A standard tube furnace was adapted to connect a sample lifting tube to the bottom lid, attached to the furnace tube. The sample lifting tube contained a pedestal holder that lifted the pedestal into the furnace through a piston action. Radiation shields were positioned inside the top and bottom end of the furnace tube to direct radiation heat to the sample surface, and away from the sample sides. The top lid contained a view port for sample surface temperature measurement. The pedestal contained thermocouples to measure the sample temperature at different positions within the sample. The furnace tube surface, used as radiation heat source to heat the sample surface, was conceptually divided into three heating surfaces. Radiation heat transfer input to the sample surface was increased by increased heat input to the heating surfaces via the furnace heating elements. The furnace temperature control thermocouple was positioned outside the furnace tube, close to the middle of the furnace element heating zone. Increased heat transfer to the sample surface was established by increased furnace control thermocouple set points of 1300°C, 1400°C and 1500°C, respectively. The heating surface temperatures were measured throughout each experiment.

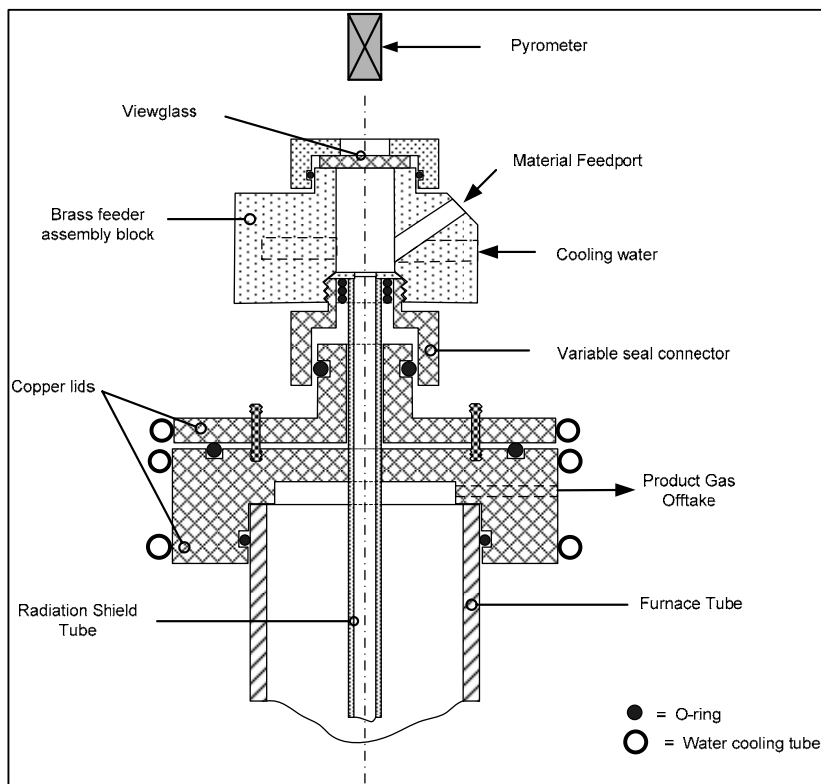
2.1. Experimental Set-up

2.1.1. Furnace

The furnace set-up consisted of an alumina furnace tube, 99.8% purity, 88.9 mm O.D. x 79.4 mm I.D. x 1200 mm, positioned vertically inside a circle of six lanthanum chromite (LaCrO_3) heating elements which were placed on a circle radius of 57.5 mm from the furnace tube centre. The top and bottom ends of the alumina tube were sealed gas tight via O-rings contained within each brass lid. The furnace tube was supported via the bottom brass lid, resting on a steel bracket bolted onto the furnace frame. The top lid on the furnace connected to another lid to serve as a reducer and variable seal. Because of thermal expansion of the ceramic furnace tube a variable seal was made between the bolt-on top lid and the rest of the top assembly. The top assembly rested on a bracket bolted onto the tube furnace

frame, as not to rest on the ceramic tube. The position of the top assembly was high enough to accommodate the alumina tube expansion at 1600°C hot zone temperature, but low enough to seal the furnace tube off at room temperature. **Fig. 4** shows the top assembly schematically.

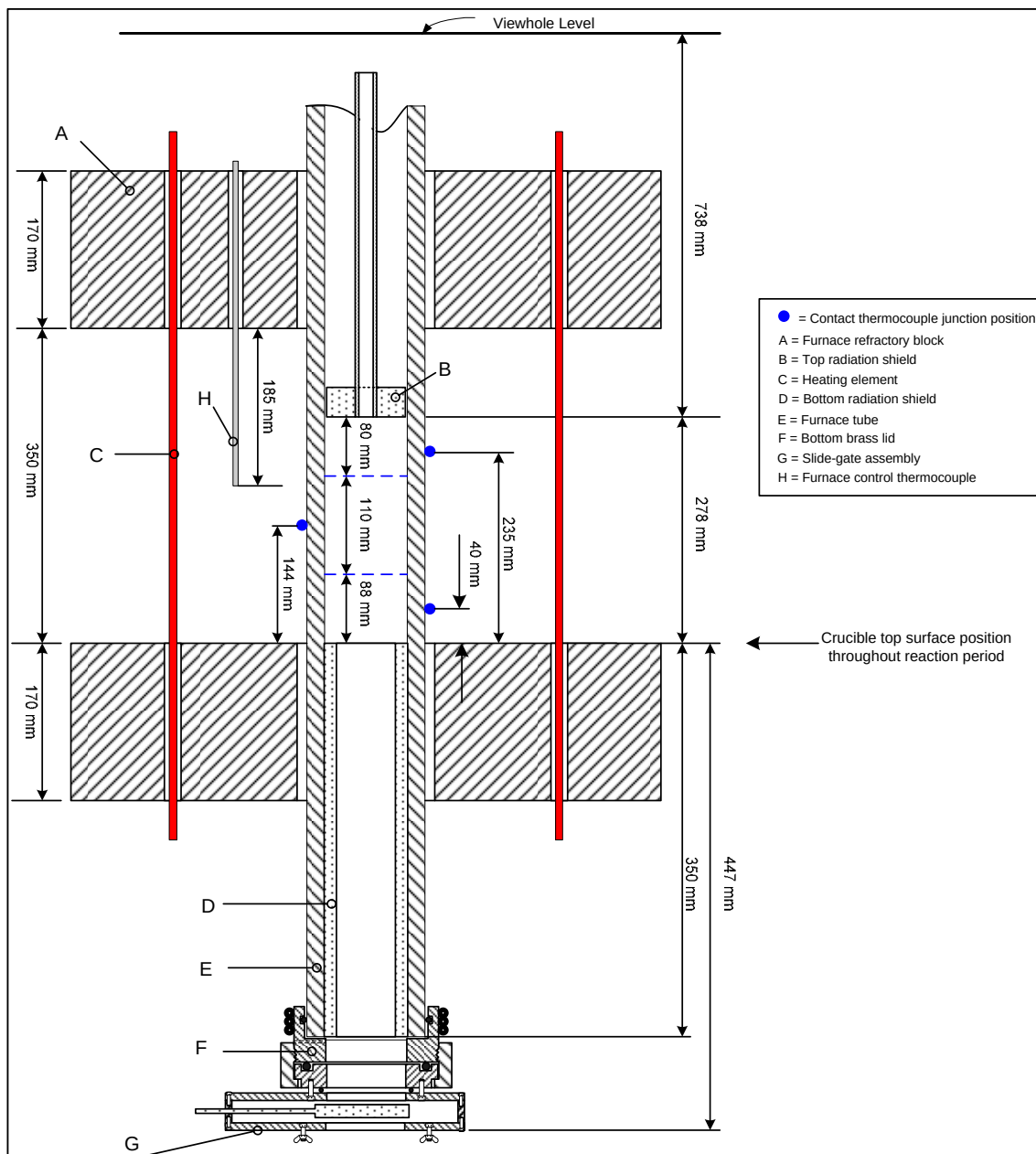
Fig. 4: Top Assembly



The top radiation shield consisted of a fibreboard disk pasted onto the end of a 20 mm o.d. x 15 mm i.d. mullite tube. The top end of the radiation shield tube was gripped by O-rings contained within the top assembly to keep it in position. The tube also served as the view hole guide. The positioning of the radiation shields relative to the tube furnace refractories is shown in **Fig. 5**. A slide-gate assembly was attached to the bottom lid of the furnace tube, **Fig. 6**. The sample lifting tube in turn was attached onto the bottom end of the slide gate, **Fig. 7**. The sample lifting tube contained a ceramic fibreboard pedestal mounted in an aluminium holder. Four type-K thermocouples were placed within the pedestal on a 5 mm radius, **Fig. 9**. The thermocouple wires, of ~ 0.4 mm diameter housed in twin bore alumina tubes of 2.2 mm o.d., exited the pedestal at the bottom end of the aluminium pedestal holder. The wires were coiled within the free space below the aluminium pedestal holder so that they may uncoil as the pedestal holder is lifted up inside the aluminium tube by Ar gas. The aluminium pedestal holder functioned as a piston inside the aluminium tube by sliding on two o-rings contained in radial grooves at the bottom and top ends of the aluminium pedestal holder. A stopper ring at the top of the aluminium tube stopped the aluminium pedestal holder at the predetermined travel distance. The

sample was lifted into the furnace by letting Ar gas flow into the bottom end of the sample tube, via a control valve set at 50 kPa gauge pressure. When the sample reached the top of the travel position into the furnace, the sample surface level was flush with the bottom radiation shields' top surface. To lower the sample into the sample tube the Ar gas was pumped out of the tube by a vacuum pump.

Fig. 5: Furnace layout



The wires exited the sample tube via a sealed fitting and the thermocouple outputs were logged with a dataTaker DT500 logger at one-second intervals. The sample crucible, shown in **Fig. 8**, was made from ceramic fibreboard and sat on top of the pedestal, with type-K thermocouples entering the sample

through the crucible bottom. The crucible dimensions were 30 mm i.d., 50 mm o.d. and the crucible bottom was either 10 or 24 mm thick. The crucible was filled with material mixture so that the sample surface and the crucible top surface were level. The sample tube contained two fibreboard insulation rings, within its wider top section, to protect the aluminium when the hot sample was lowered into the sample tube. The sample tube assembly could be flushed via an Ar gas inlet and outlet on the sample tube, each line fitted with a ball valve. The furnace was flushed with Ar gas entering through the bottom brass lid, and exiting through the top brass lid. The furnace tube contained a cylindrical fibreboard radiation shield made from individual fibreboard rings cemented onto each other. This radiation shield rested on the bottom brass lid.

Fig. 6: Furnace Tube Bottom Assembly (Bottom lid & slide gate)

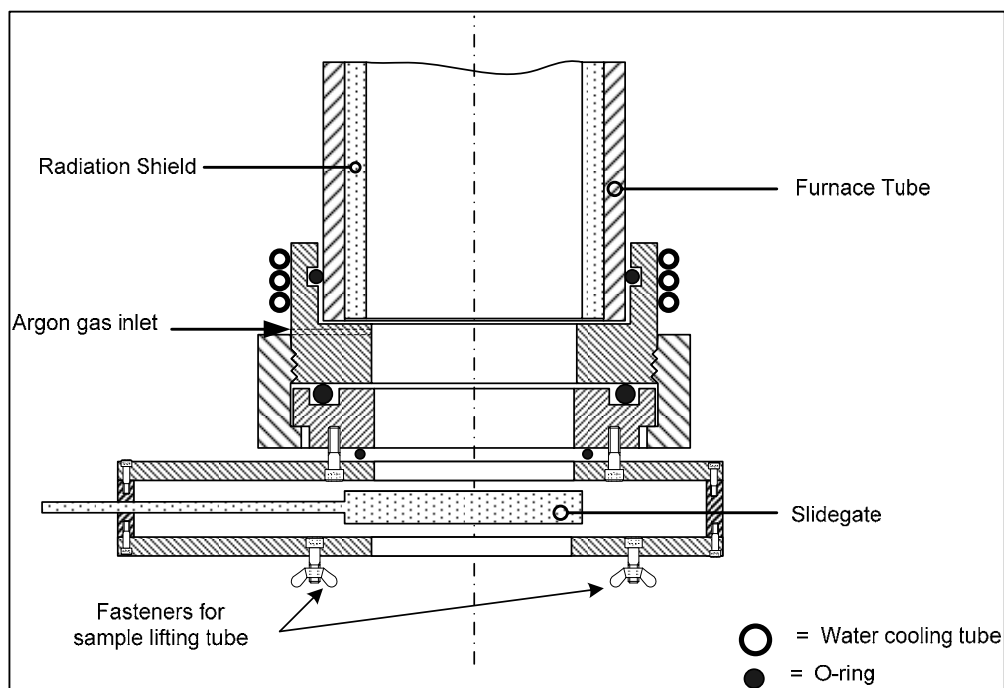


Fig 7: Sample Tube with Pedestal

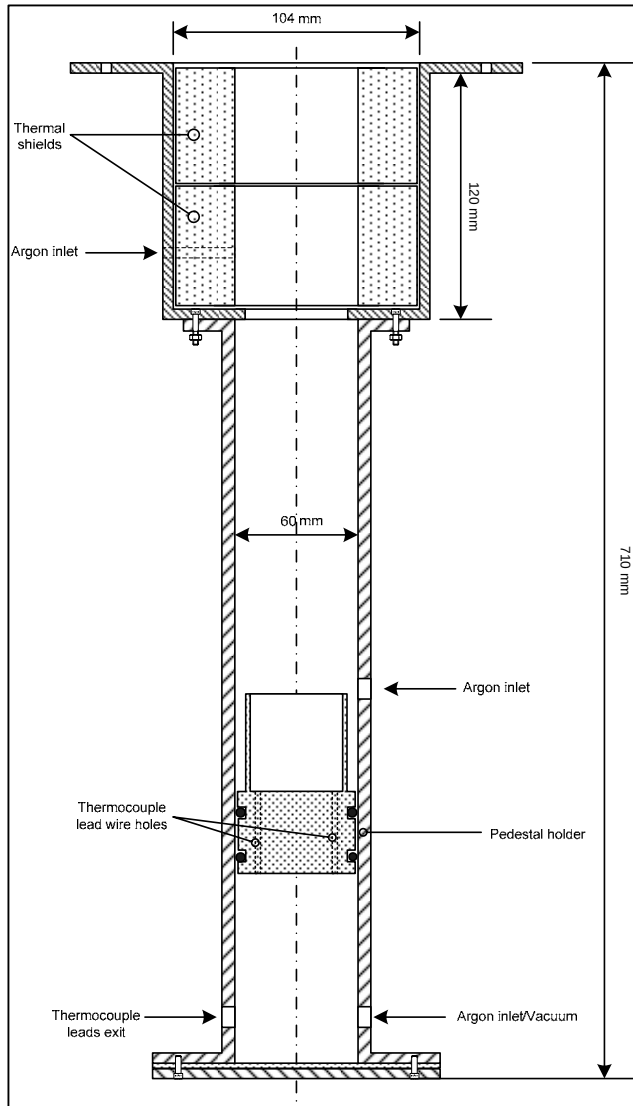
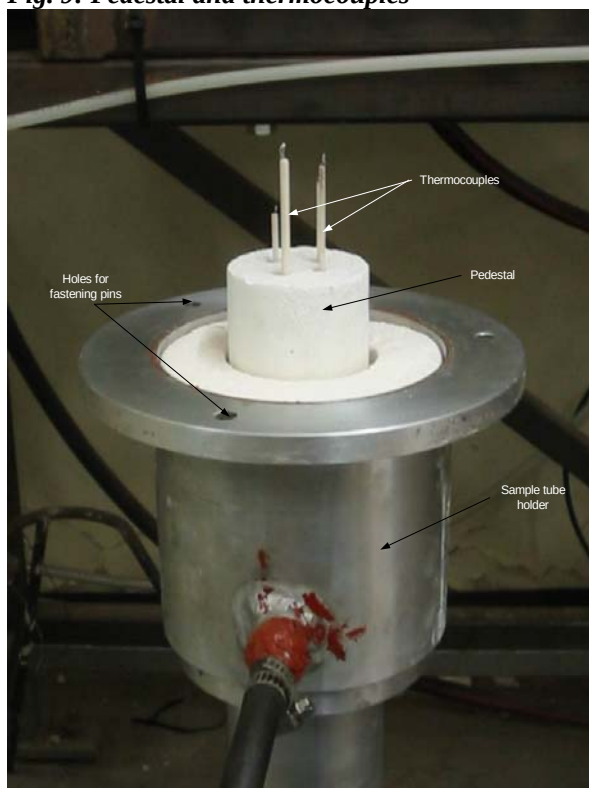


Fig. 8: Crucible

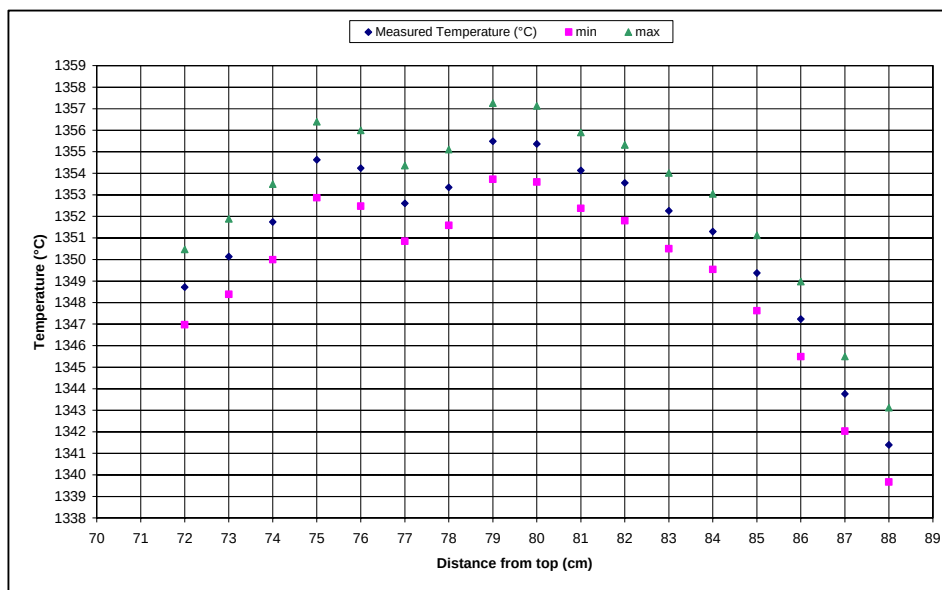


Fig. 9: Pedestal and thermocouples



The furnace temperature was controlled by a PID controller/programmer using a type-B thermocouple positioned next to the furnace tube, radially close to the hot zone, and vertically close to the middle of the furnace element heating zone. The hot zone position was measured by placing a hand held type-S thermocouple at various depths into the furnace tube. The thermocouple was kept at one position for two minutes, and then moved to the next position. The measurements are shown **Fig. 10**, with the certified standard deviation range for the thermocouple wire. The 0 cm reference point was the top surface of the top assembly when the view glass holder was removed.

Fig. 10: Hot zone measurements



Initial efforts to use a 87 mm heating zone around the hot zone centre, at 784 mm from 0 reference level, was not successful as the bottom radiation shield could not shield the sample sides sufficiently from radiation heat from the furnace tube. This was because the total heating length of the furnace is 350 mm in length, see **Fig. 5**. Thus, the heating zone was enlarged to include the section of furnace tube extending from the bottom of the hot zone to the top of the external furnace refractory. This second heating zone was conceptionally divided into two sections. The heating zone thus consists of three sections, the furnace tube length of 80 mm around the furnace hot zone, and the second and third sections of 110 mm and 88 mm length, respectively, extending below the first heating zone. The heating surface temperatures of each of the three heating sections were measured throughout each experiment by type-S contact thermocouples placed on the furnace tube exterior surface, as shown in **Fig. 5**. Uni-directional heat transfer along the vertical axis of the crucible and contents was confirmed by viewing polished sections of reacted samples under reflected light, which showed that no reaction fronts existed across the horizontal axis of the crucible contents.

2.1.2. Gas Lines

The supply lines to the furnace and the gas off-take lines from the furnace to the quadrupole mass spectrometer (Gaslab) are shown diagrammatically in **Fig. 11**. Argon gas of 99.999% purity was used as carrier gas. The Ar gas was cleaned by passing through anhydrous CaSO_4 to remove water (“Drierite”), and through an “Oxyzorb” cartridge to remove oxygen. The carrier gas was passed through the experimental set-up at $\sim 1500 \text{ Ncm}^3/\text{min}$. The Ar flow rate was measured before each experiment sequence using a bubble meter, and the flow was controlled by a Rotameter fed from the Ar bottle via a pressure regulator.

The product gas was passed through a Balston filter (050-11 DX) to remove small solid particles from the gas. The gas flowed past a draw off point for the mass spectrometer (Gaslab), and then through a bubbler to the vent. The gas system was also used to calibrate the mass spectrometer for Ar, CO₂, CO, CH₄ and H₂ by connecting the particular calibration gas supply to the one-way inlet valve connection shown in **Fig. 11**. The calibration gases used were 100%CO, 5%CH₄-Ar, 5%H₂-Ar, 100%Ar and 10%CO₂-Ar, respectively. Calibration for Ar and CO₂ was done by using the furnace gas supply lines up to the one way inlet valve connection, **Fig. 11**.

The product gas water content was measured by a Dewmet cooled mirror dewpoint meter. The product gas off-take lines, 6 mm o.d. copper tubing, were heated by trace heating to prevent condensation of water from the product gas. A type-K thermocouple was placed in the heated line to monitor the gas temperature. These temperature values were typically between 120-135°C. This K-type thermocouple measurement was pre-calibrated to the gas temperature measured with a thermometer at the dewpointmeter chamber gas inlet. At 1300°C furnace temperature the gas temperature measured at the dewpoint chamber inlet was 76°C for type-K thermocouple measurement of 133°C. The type-K thermocouple was used as an indicator temperature to prevent overheating the Dewmet sensor.

The Ar gas used for initial flushing of the sample holder, to displace the bulk of air in the sample holder and furnace tube, was also 99.999% pure Ar taken from a separate cylinder, and passed through “Drierite”. The gas sampling response time could best be determined from devolatilisation experiments. This is because devolatilisation starts at a few hundred degrees so that sample gas evolution is immediate when the sample is lifted into the furnace tube, and so provided a definitive start time for gas evolution against which the response time to the first analyses of the devolatilisation product gas could be measured. The sampling delay time at ~1500 Ncm³/min was found to be 11-12 seconds from zero time. Zero time is the time at which the sample has reached the top of the travel position into the furnace tube. The 11-12 seconds is the fastest analysis interval time achieved by the mass spectrometer for the analyses set-up selected on the mass spectrometer. For the Dewmet the sampling response time was 22-24 seconds. The time to lift the sample up into the furnace, or lower the sample into the sample holder, was approximately 5 seconds. The flow rate of product gas components was calculated by scaling relative to the input Ar flow rate, as shown in **Appendix I**.

The maximum gas retention time in the furnace tube open volume was calculated to be 159 seconds for a volume of 3892 cm³ and Ar gas flow rate of 1500 Ncm³/min. The minimum gas retention time in the furnace tube was calculated as ~ 30 seconds, assuming the gas was heated to the sample surface temperature. The time period required for the product gas analysis to return to that before the sample was lifted into the furnace tube, was noted from the product gas analyses. This data is expressed, for each product gas component, as a multiple of the gas retention time in the furnace tube open volume.

$$t_m = \frac{(t_s - t_l)}{t_r} \quad (7)$$

t_m = Time multiple for product gas to return to product gas composition at start of experiment [seconds]

t_s = Time when product gas analysis return to product gas composition at start of experiment [seconds]

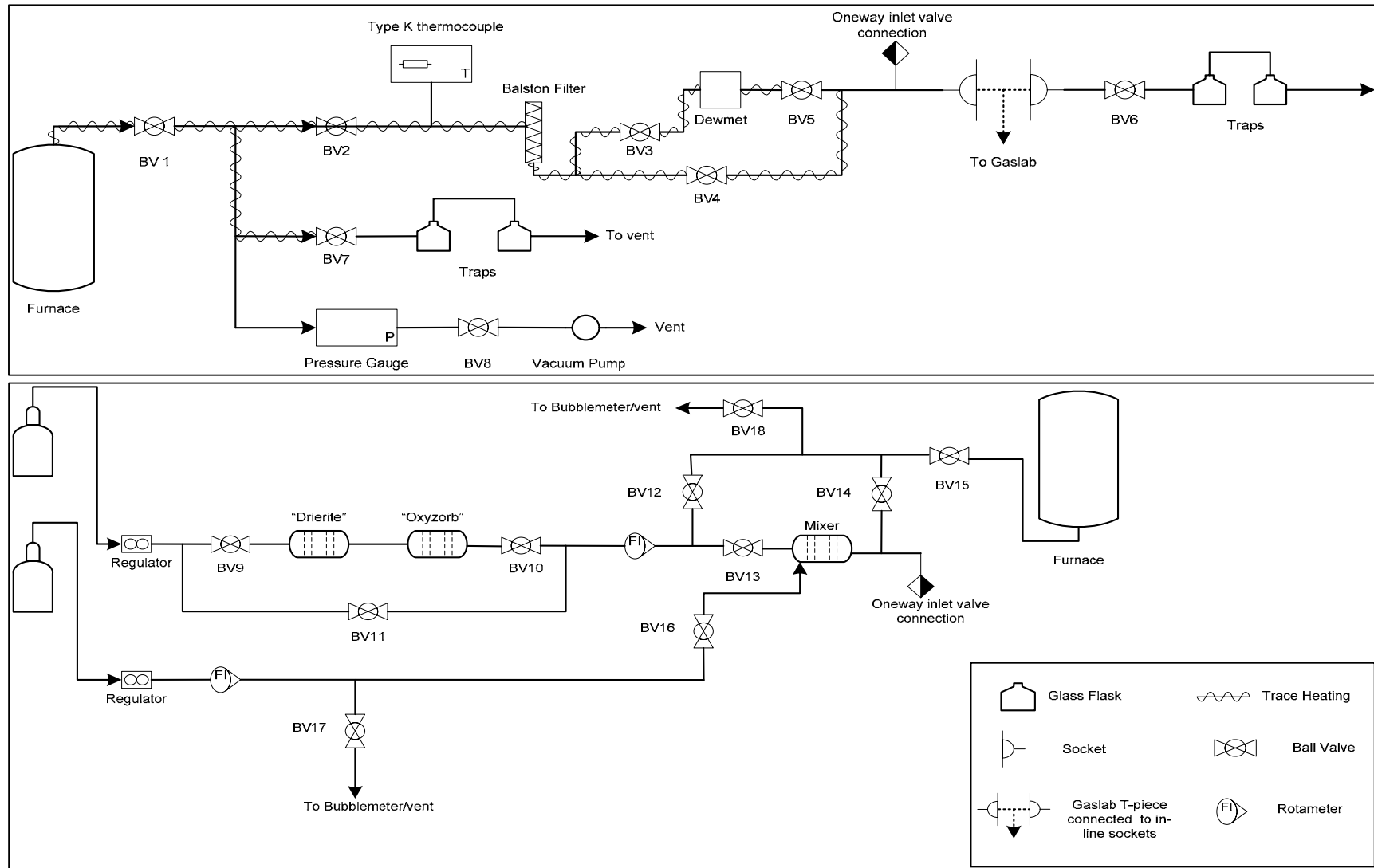
t_l = Time when sample was lowered from furnace tube [seconds]

t_r = Maximum gas retention time in the furnace tube open volume [seconds]

For the samples of graphite and pre-reduced Sishen iron ore the time multiples varied from -8 to +5. The negative values are possible when the component in the product gas return to the initial levels before the sample is lowered from the furnace tube. For the ore-coal samples the time multiples varied from -1 to 8, and in two experiments the CO analyses did not return to the initial level. The data for calculation of the time multiple is summarized in **Appendix I**.

The furnace assembly was checked for gas leaks by drawing vacuum of 80 kPa on the assembly, if this vacuum was maintained, the assembly was considered gas tight. The sample holder was checked for gas leaks by passing gas through the assembly, and using soap water to identify leaks.

Fig. 11: Gas supply and off-take lines to/from furnace



2.2. Calibration

2.2.1. Radiation Network

The radiation heat transfer set-up in the tube furnace is shown in **Fig. 12**. The heat transferred to the sample surface can be calculated from a radiation network representing the heat flows in the experimental set-up. The network is shown in **Fig. 13** and was developed according to the formalism set out in Holman (1992), p. 410-413. Calculation of the view factors is summarised in **Appendix II**. The calculations are outlined below. In **Fig. 12** two imaginary surfaces 8 and 7 are used to calculate the shape factors for use in the radiation network calculations. The symbols shown in **Fig. 13** are defined as follows: J_i = radiosity of surface i = total radiation that leaves surface i per unit time per unit area [kW/m^2]; R_i = Resistance i in radiation network [m^2]; $E_{bi} = \sigma T^4$ = blackbody emissive power of surface i [kW/m^2]; σ = Stefan-Boltzmann constant = $5.669 \times 10^{-8} \text{ W/m}^2\text{K}^4$.

Fig. 12: Radiation Configuration

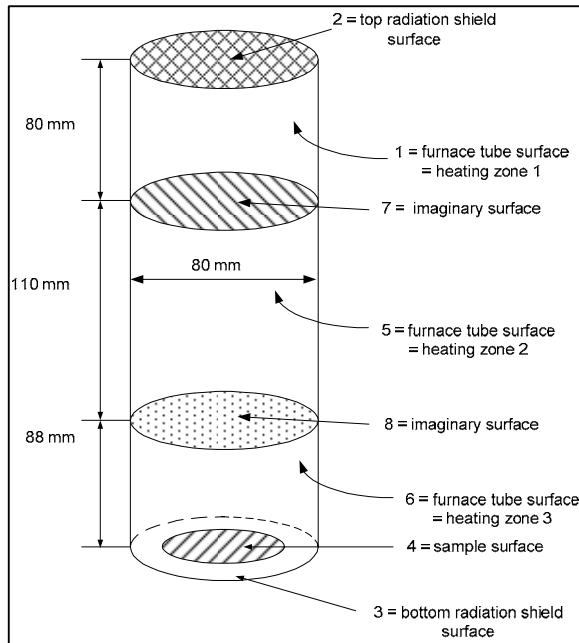
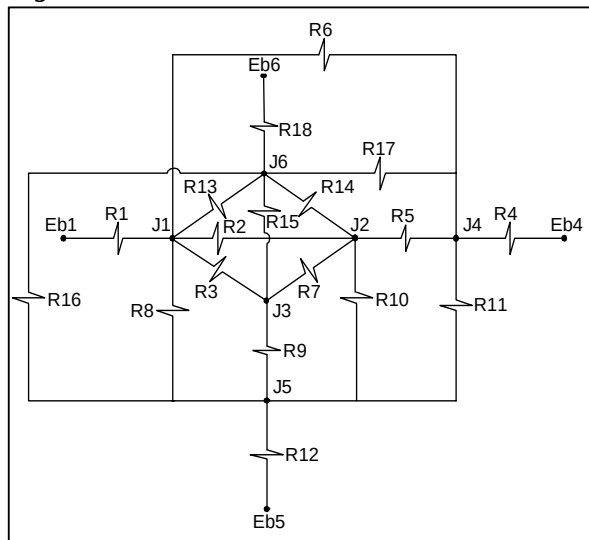


Fig. 13: Radiation Network



2.2.1.1. Resistances

The radiation network resistances in **Fig. 13** were calculated as follows:

For the surface resistances of surfaces 1, 4, 5 and 6:

$$R_1, R_4, R_{12}, R_{18}: R_i = \frac{1 - \varepsilon_j}{\varepsilon_j A_j} \quad (8)$$

R_i = Resistance i in radiation network

ε_j = Emissivity of surface j in radiation network

A_j = Area of surface j

For the space resistances:

$$R_2, R_3, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}: R_n = \frac{1}{A_i F_{ij}} \quad (9)$$

F_{ij} = View factor for radiation from surface i to surface j

A_i = Area of surface i

2.2.1.2. Node Equations

The temperatures for surfaces 1, 4, 5 and 6 are known and the radiosity of the six nodes must be calculated from the node equations. The following node equations were generated according Kirchhoff's rule. The equations are solved numerically for the radiosities (J_i).

Node 1:

$$\frac{E_{b1} - J_1}{R_1} + \frac{J_2 - J_1}{R_2} + \frac{J_3 - J_1}{R_3} + \frac{J_4 - J_1}{R_6} + \frac{J_5 - J_1}{R_8} + \frac{J_6 - J_1}{R_{13}} = 0 \quad (10)$$

Node 2:

$$\frac{J_1 - J_2}{R_2} + \frac{J_3 - J_2}{R_7} + \frac{J_4 - J_2}{R_5} + \frac{J_5 - J_2}{R_{10}} + \frac{J_6 - J_2}{R_{14}} = 0 \quad (11)$$

Node 3:

$$\frac{J_1 - J_3}{R_3} + \frac{J_2 - J_3}{R_7} + \frac{J_5 - J_3}{R_9} + \frac{J_6 - J_3}{R_{15}} = 0 \quad (12)$$

Node 4:

$$\frac{E_{b4} - J_4}{R_4} + \frac{J_1 - J_4}{R_6} + \frac{J_2 - J_4}{R_5} + \frac{J_5 - J_4}{R_{11}} + \frac{J_6 - J_4}{R_{17}} = 0 \quad (13)$$

Node 5:

$$\frac{E_{b5} - J_5}{R_{12}} + \frac{J_1 - J_5}{R_8} + \frac{J_2 - J_5}{R_{10}} + \frac{J_3 - J_5}{R_9} + \frac{J_4 - J_5}{R_{11}} + \frac{J_6 - J_5}{R_{16}} = 0 \quad (14)$$

Node 6:

$$\frac{E_{b6} - J_6}{R_{18}} + \frac{J_1 - J_6}{R_{13}} + \frac{J_2 - J_6}{R_{14}} + \frac{J_3 - J_6}{R_{15}} + \frac{J_4 - J_6}{R_{17}} + \frac{J_5 - J_6}{R_{16}} = 0 \quad (15)$$

The heat transferred to the sample surface is then calculated:

$$q_4 = \frac{E_{b4} - J_4}{R_4 A_4} \text{ [kW/m}^2\text{]} \quad (16)$$

2.2.2. Emissivity Measurements

The emissivities of alumina powder, alumina furnace tube material, fibre board and fibre board coated with alumina paste were measured by placing the materials in a muffle furnace to heat up with the furnace to 999, 1104, 1208 and 1306°C, respectively. A hand held type-S thermocouple was used to check that the furnace temperature is at the furnace temperature set on the furnace PID controller. The different material temperatures were measured by opening up the muffle furnace door and measuring the sample temperature with an optical pyrometer, Minolta/Land Cyclops 152A infrared thermometer, with the emissivity on the pyrometer set at 1.00. The measurements were logged with a dataTaker DT500 logger at one-second intervals. After a measurement was made on one of the four materials, the muffle furnace was closed to allow it to attain the set temperature again, before the next material sample temperature was measured. The main assumption is that the material samples in the muffle furnace are at the furnace temperature when the pyrometer temperature measurement is made. Equation 17, the Planck blackbody radiation law, was used to back calculate the sample material emissivity required to set the material sample surface temperature equal to the furnace temperature (T_r). The other variable in the calculation is the spectral response of the Minolta/Land Cyclops 152A infrared thermometer at 0.8-1.1µm. Calculations were done for both the upper and lower limit wavelength of the pyrometer spectral response, but the emissivity values calculated for 0.95µm at 1306°C furnace temperature were used in further calculations. The temperature measurements are summarised in **Table 4**. The emissivities calculated at different wave lengths are summarised in **Table 5**.

Table 4: Temperature measurements with pyrometer emissivity set to 1.00

Furnace Temperature (°C)	Alumina powder	Alumina furnace tube	Fibre board	Fibre board coated with alumina paste
999	946.3	946.0	960.3	942.1
1104	1032.1	1047.0	1036.6	1032.1
1208	1126.8	1146.0	1131.3	1121.1
1306	1204.8	1244.8	1208.2	1210.8

Table 5: Emissivities calculated at different wavelengths

Furnace Temperature (°C)	Alumina powder			Alumina furnace tube			Fibre board			Fibre board coated with alumina paste		
Wavelength (μm) →	0.80	0.95	1.10	0.80	0.95	1.10	0.80	0.95	1.10	0.80	0.95	1.10
999°C	0.54	0.60	0.64	0.54	0.59	0.64	0.64	0.69	0.72	0.51	0.57	0.61
1104°C	0.49	0.55	0.59	0.57	0.62	0.66	0.51	0.57	0.61	0.51	0.55	0.59
1208°C	0.49	0.55	0.60	0.59	0.64	0.68	0.52	0.57	0.62	0.47	0.53	0.58
1306°C	0.46	0.52	0.57	0.63	0.68	0.72	0.48	0.53	0.59	0.48	0.54	0.59

2.2.3. Sample Surface Temperature Measurement

One of the main input parameters into the radiation network calculation is the sample surface temperature. In the experiments the sample surface temperature was measured with a Minolta/Land Cyclops 152A infrared thermometer with spectral response of 0.8-1.1μm. The measurement was made through a view glass, along a 15 mm i.d. tube, 738 mm in length. The view glass consisted of 4mm thick Robax[®] glass with transmissivity of 0.88 at 1.1μm and 0.91 at 0.8μm. To check the accuracy of the sample surface temperature measurement made with the pyrometer, the actual surface temperature of an inert alumina powder sample was measured with a type-S thermocouple positioned 5 mm from the sample surface. The sample was introduced into the furnace, and once the sample temperature stabilised, sample surface temperature measurements were made simultaneously using the type-S thermocouple and the pyrometer.

The pyrometer emissivity was set at 1.00 for the pyrometer sample surface temperature measurement. This measured temperature value (T_m) was then corrected for the actual alumina powder emissivity of 0.52 reported in **Table 5**, and glass transmissivity if applicable, using equation 17. Initial measurements were made with and without the view glass, and with and without Ar purging gas, at 1300, 1400 and 1500°C furnace hot zone temperatures, respectively. Measurement with Ar purging gas flow through the furnace tube resulted in a maximum decrease of 5°C in sample surface temperature, at 1500°C furnace hot zone temperature. Comparisons were made for measurements through the view glass with Ar gas flow through the furnace. The same alumina sample mass was used in each experiment. The measurement for 1300°C furnace temperature was repeated. The change in

sample and surface temperatures for the two tests at 1300°C furnace temperature, as well as for 1400°C and 1500°C furnace temperatures are shown in the graphs in **Appendix III**. It is seen that the sample was positioned in the furnace for 50 minutes, or more, to stabilise the sample temperatures. For measurements made at 1500°C furnace temperatures some interference with the thermocouple measurements was experienced. The filtered values are shown in the first graph, for measurements at 1500°C, in **Appendix III** and both the filtered and original data are shown in the following graph. It was determined that the interference occurred with the heating cycles of the furnace elements, therefore only the values at the end-point were checked by switching the furnace off. The end-point temperatures measured by the type-S thermocouple and the pyrometer, respectively, are shown in **Table 6**. The sample surface temperatures as adjusted for the emissivity setting on the pyrometer and the view glass transmissivity are also shown in **Table 6**. The pyrometer sample surface temperature measurement over reads the sample surface temperature by 6°C at 1300°C furnace temperature, and under reads 14°C at 1500°C furnace temperature. The effect of the pyrometer over and under reading of the alumina sample surface temperature on heat transferred to the sample surface is shown by comparison of the kW/m² transferred to the alumina sample surface, calculated using the radiation network set out in 2.2.1., using as input the sample surface temperature measured with the type-S thermocouple vs. the sample surface temperature measured with the pyrometer. In the radiation network calculation the sample surface temperatures shown in **Table 6** were used with the associated heating zone temperature values at the end of the heating period. The resultant differences in radiation heat transfer calculation values are summarised in **Table 6**. Heat transfer calculation values vary from under calculation of 4kW/m² at 1300°C furnace temperature to over calculation of 13kW/m² at 1500°C furnace temperature.

Table 6: Sample surface measurements

Furnace Hot Zone Temperature (°C)	Pyrometer measurement (°C); $\varepsilon = 1.00$	S-type thermocouple measurement (°C)	Adjusted Pyrometer measurement (°C) @ 0.95 μm	ΔT^a	*kW/m ² into alumina sample	$\Delta \text{kW/m}^2$ for alumina sample ^b
1300a	1076	1172	1177	-6	-61	-3
1300b	1082	1178	1184	-6	-59	-4
1400	1172	1290	1288	2	-73	2
1500	1250	1394	1380	14	-93	13

^a (S-type thermocouple measurement) – (Adjusted Pyrometer measurement)

* kW/m² calculated from S-type thermocouple surface temperature measurement

^b (kW/m² calculated using the S-type thermocouple measurement as sample surface temperature) – (kW/m² calculated using the adjusted Pyrometer measurement used as sample surface temperature).

$$T_r = \frac{C_2}{\lambda} \cdot \frac{1}{\ln\left(\frac{C_1}{\lambda^5 E_b} + 1\right)} - 273 \quad (^\circ\text{C}) \quad (17)$$

$$E_b = \frac{E_{app}}{\varepsilon \tau} \quad (18)$$

$$E_{app} = \frac{C_1}{\lambda^5} \cdot \frac{1}{e^{\frac{C_2}{\lambda T_m}} - 1} \quad (19)$$

$$C_1 = 3.743 \times 10^5 \text{ kW } \mu\text{m}^4/\text{m}^2$$

$$C_2 = 1.4387 \times 10^4 \text{ } \mu\text{m K}$$

λ = wavelength (μm)

ε = emissivity

τ = transmissivity

T_m = Temperature measured by pyrometer (K)

T_r = Real Temperature ($^{\circ}\text{C}$)

E_b = Black body emissive power per unit wavelength [$\text{kW}/\mu\text{m m}^2$]

E_{app} = Apparent body emissive power per unit wavelength [$\text{kW}/\mu\text{m m}^2$]

2.2.4. Calibration of Radiation Network Calculation

To calculate the heat transferred to the sample one must know the relevant surface temperatures, that is the average furnace tube temperature for each heating zone and the sample surface temperature. As shown in the furnace layout diagram in **Fig. 5**, the section of the furnace tube used as heating surface is 278 mm in length, compared with the typical tube furnace hot zone length of ~ 80 mm. Therefore, the heating surface is not at one temperature and the variation in temperature over the total 278 mm length of heating surface is required as input to the radiation calculation. Consequently the heating surface was divided conceptionally into three heating zone sections to add resolution to the radiation network calculation. The temperature at the vertical centre of each heating zone was measured by placing a contact thermocouple at the outside surface of the furnace tube at a position 5 mm below the heating zone centre. The 5 mm allowance was made to account for the furnace tube expansion.

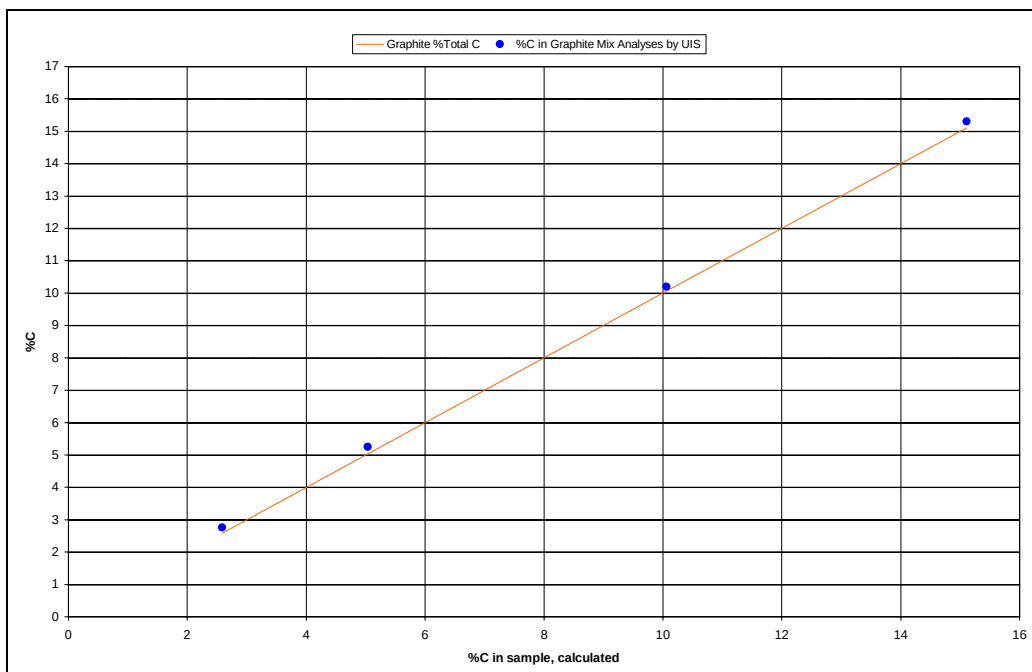
In addition to the three heating zone surface temperatures, the sample surface temperature was measured by pyrometer, through the view glass at the top of the experimental assembly. These temperatures were used as inputs to the radiation network calculation. The sample surface temperature was measured with the pyrometer emissivity setting at 1.00, and the measurements were then corrected for view glass transmissivity of 0.88 and sample material emissivity of 0.90 at $0.95\mu\text{m}$ wavelength, using equation 17.

To calibrate the radiation network samples of pre-reduced Sishen ore and graphite were reacted at 1300, 1400 and 1500°C , respectively. This selection of materials was made to simplify the possible reactions, as compared to coal and unreduced Sishen fines. The graphite and pre-reduced Sishen ore were of $-850 +425\mu\text{m}$ size fraction. Chemical analyses for these materials and XRD (X-ray diffraction) analysis for the pre-reduced ore are shown in **Appendix IV**. After the runs the reacted samples were sectioned horizontally into three portions, and analysed for forms of Fe, %C by Leco

method, and main components by ICP (Inductively coupled plasma) method. As a check on the chemical analyses control samples were prepared from pre-reduced ore and graphite at different carbon contents. These samples were submitted for analyses, and the resultant analyses compared with the calculated %C and forms of Fe from the input material analyses. Control samples were also prepared from coal and pre-reduced ore. The comparison for %C in the sample mixtures is shown in **Fig. 14 (a)** for graphite and **Fig. 14 (b)** for coal. It is seen that the %C analysed for the mixtures containing graphite corresponds well. For the coal containing samples it is seen that the total carbon content is analysed, that is fixed carbon and carbon in the volatiles. The analyses and calculated total carbon values differ by a maximum of 1.5%. The forms of Fe analyses are summarised in **Table 7**.

Fig. 14: Comparison of %C in control sample and %C analyses

(a) Graphite



(b) Coal

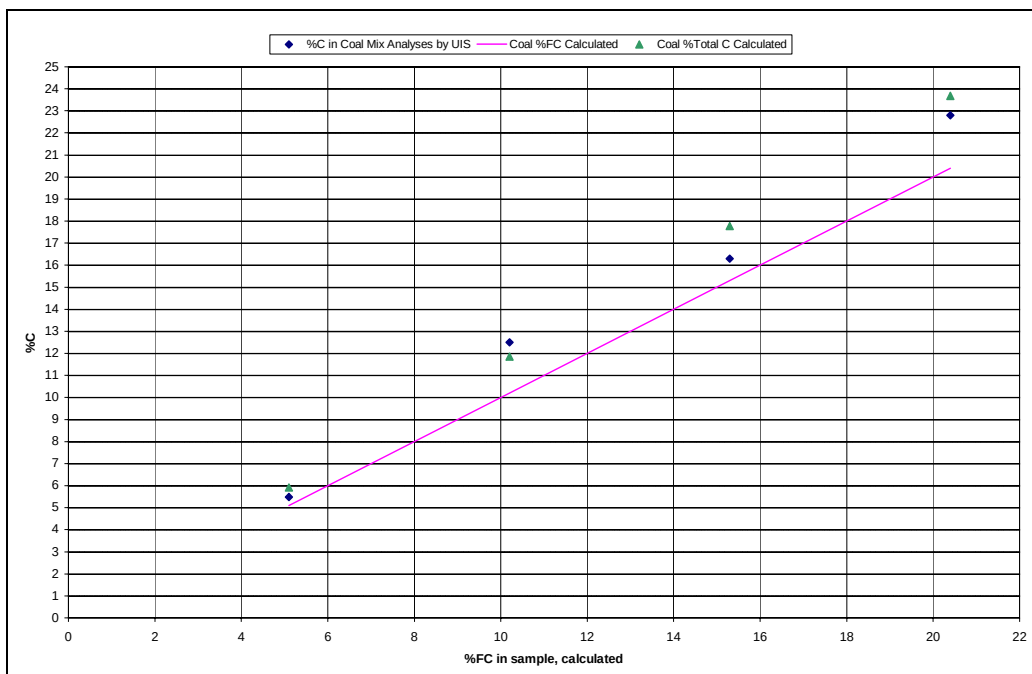


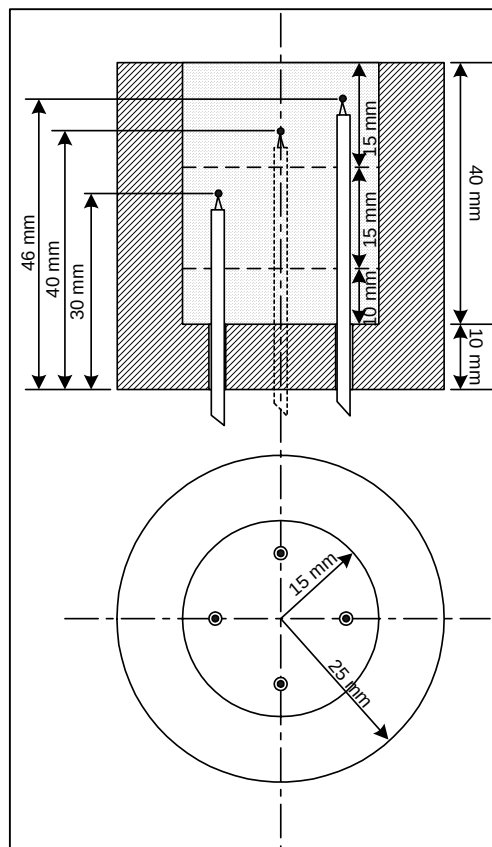
Table 7: Comparison of Forms of Fe from analyses of control samples and input materials.

%C in Graphite-Pre-reduced ore mixture	Fe(total)	Fe ⁰	FeO	Fe ₂ O ₃
2.5	70.3 / 70.4*	0.24 / 0.18	73.6 / 74.0	19.0 / 18.0
5.0	68.5 / 68.7	0.24 / 0.23	71.7 / 71.9	18.5 / 18.0
10.0	64.8 / 64.9	0.23 / 0.24	67.8 / 68.0	17.5 / 16.8
15.0	61.2 / 60.9	0.21 / 0.28	64.0 / 63.6	16.5 / 15.9
%Fixed Carbon in Coal-Pre-reduced ore mixture	Fe(total)	Fe ⁰	FeO	Fe ₂ O ₃
5.0	66.5 / 67.7	0.23 / 0.25	69.6 / 71.6	18.0 / 16.8
10.0	60.9 / 62.4	0.21 / 0.29	63.6 / 62.4	16.5 / 19.4
15.0	55.2 / 55.3	0.19 / 0.42	57.6 / 57.8	15.1 / 14.2
20.0	49.6 / 49.6	0.17 / 0.45	51.7 / 52.9	13.6 / 11.4

* Input value/Analysed value

In the reacted sample each of the three horizontal portions can be associated with temperature data measured throughout the experiment by the type-K thermocouples embedded within the sample, at different heights. From the end-point analyses and temperatures a mass balance calculation is made for each horizontal section of the sample (node). Summation of the heat transferred into the sample, as calculated from the heat-mass balance, must correspond to the radiation network calculation that uses only the sample surface temperature, and furnace tube heating zone temperatures as inputs. A schematic representation of the sample nodes and thermocouple positions is shown in **Fig. 15**.

Fig. 15: Crucible, thermocouple positions and node divisions



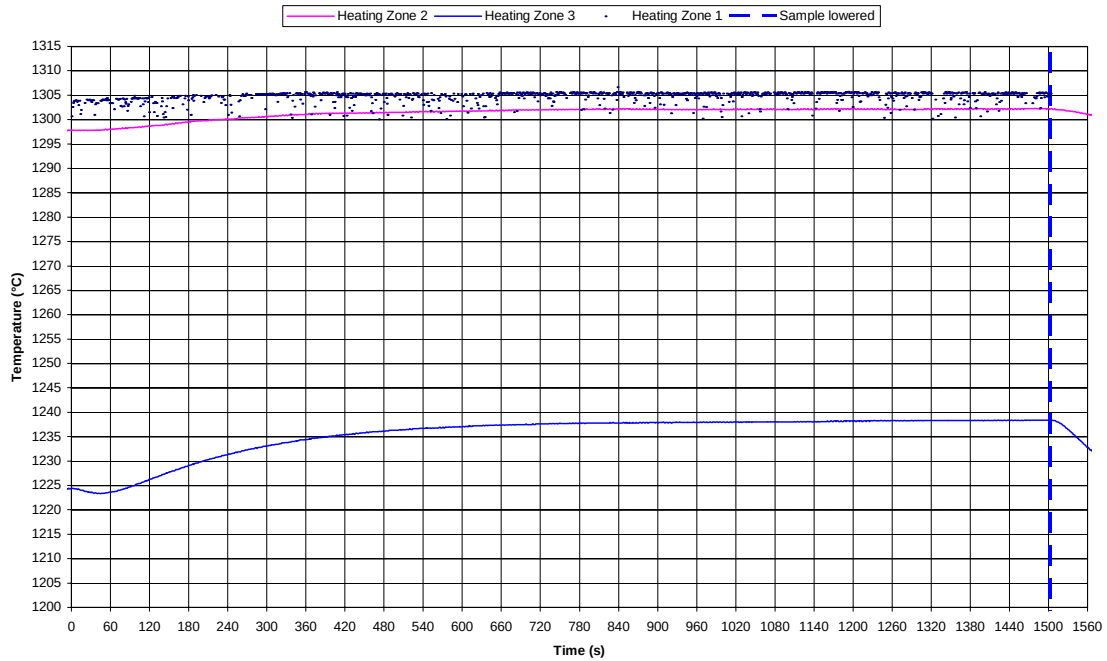
To ensure that all the samples were consistently separated into the three horizontal portions, a sample cutter-splitter was developed as shown in **Fig. 16**. This equipment enables the sample to be separated into the required three portions even if the thermocouples are sintered into the sample, thus cutting through the thermocouple sheath. To test repeatability of the sample cutting method, ten samples of sand were divided into three nodes each and the resultant portions of silica sand nodes and fibre board crucible were then weighed. The detailed mass measurements are summarised in **Appendix V**. The crucible was vertically positioned in the sample cutter to attain the sample divisions so that the top two nodes would respectively take up more of the total sample mass than the bottom node, as the bottom node will be least reacted, and thus of less importance in chemical analyses. Also, the sample material contracts as the sample reacts so that the sample division results in the top node material mass being proportionately less of the total sample mass with increased sample reaction extent. The maximum sample bed height contraction observed visually was 2 mm for coal-ore, coal-char and graphite-ore samples, and maximum 5 mm contraction for coal-alumina samples. The average mass% distribution for the top, middle and bottom nodes is 46, 33 and 21% with 95% confidence limits of 1.0, 0.3 and 0.9%.

as inputs to the radiation network. The weighted average radiation heat transfer value over the experimental period was then used for comparison with the weighted average energy input to the sample as calculated from the incremental heat-mass balance. Because of the one second interval logging of temperature values, the weighted average radiation heat transfer value and the average radiation heat transfer value is the same.

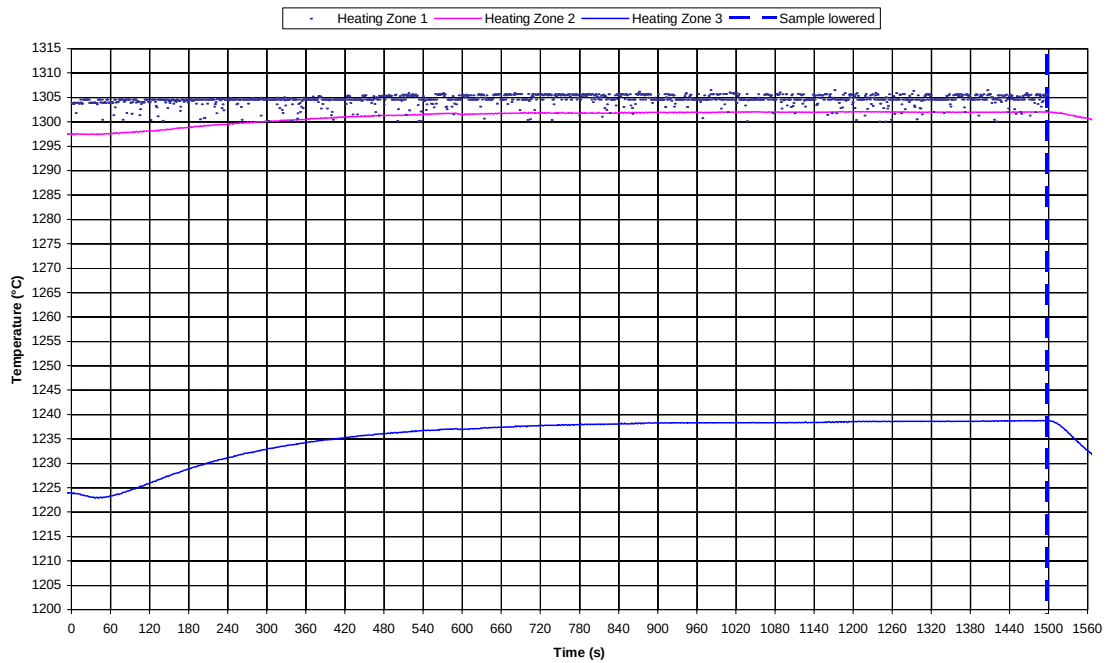
For samples 1300A and 1300B the heating zone 1 temperature values were scattered due to a loose connection to the logger. This temperature corresponds to the hot zone temperature of the furnace, and is therefore close to the controller set point, as is seen for the 1400C, 1400D, 1500E and 1500F samples in **Fig. 18 (a) and 19 (a)**. The scatter values below 1300°C were filtered out, and the removed scatter values were then replaced with the average of the values that remained after the filtering step. These values are shown in **Fig. 17 (a)**.

Fig. 17: Calibration Measurements at 1300°C Hot Zone Temperature

(a) Heating Zone Temperatures (1300A)

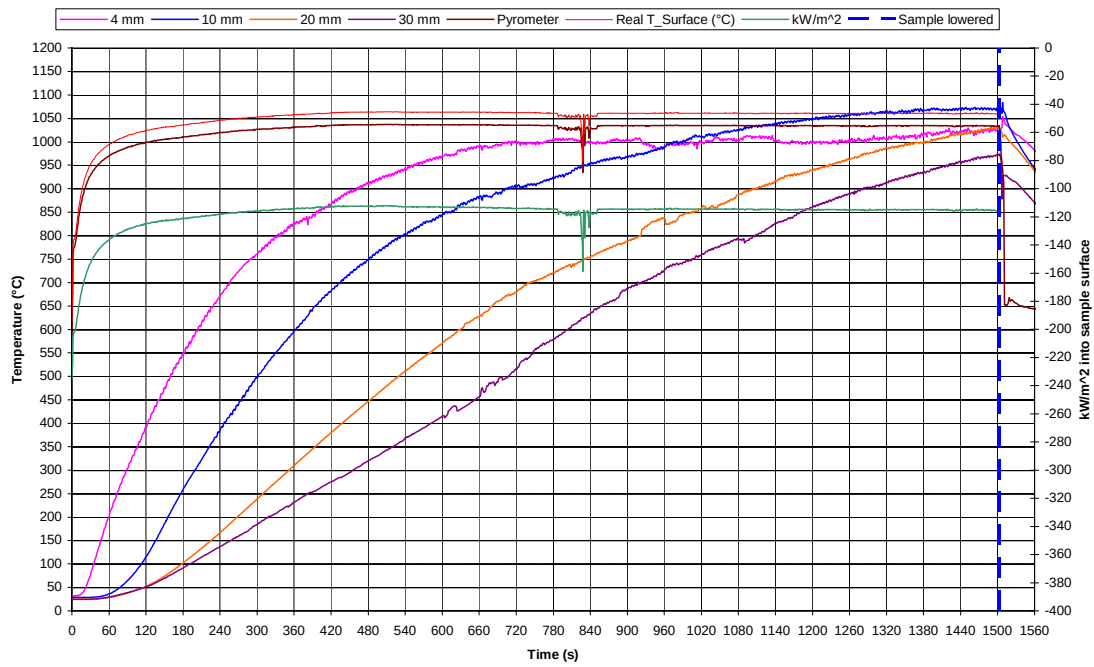


(a) Heating Zone Temperatures (1300B)

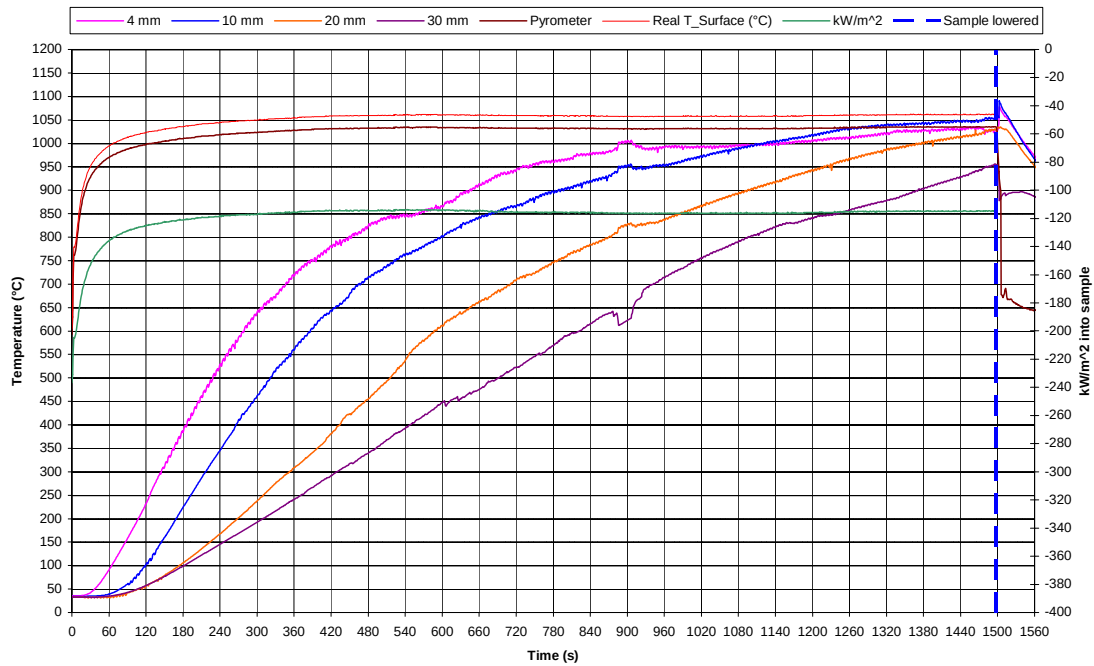




(b) Sample Temperatures (1300A)

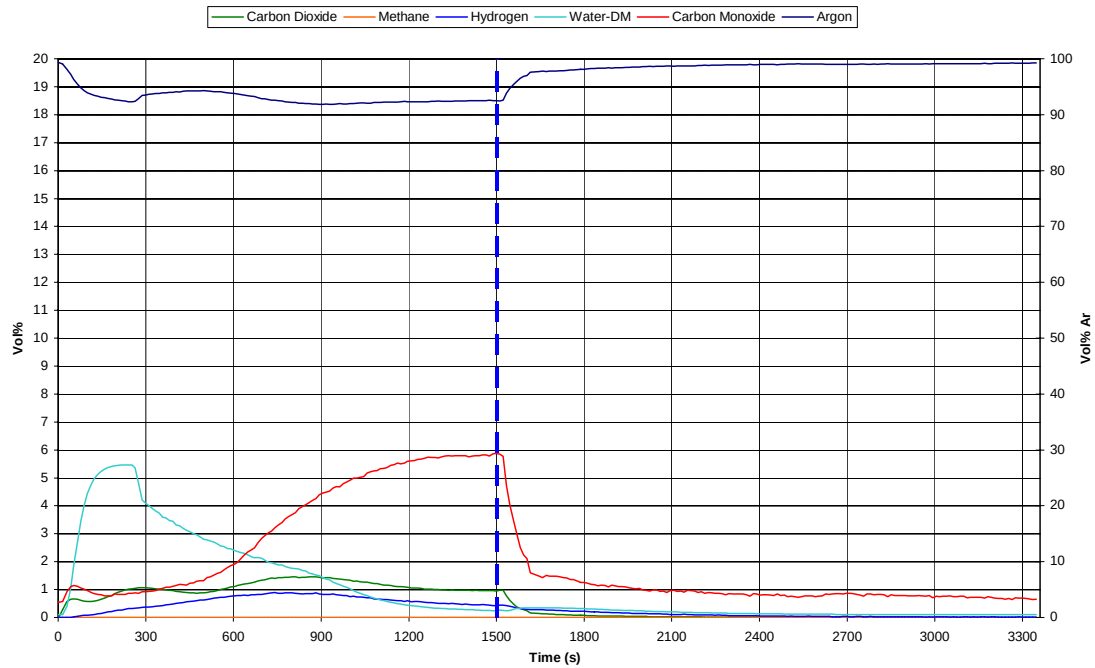


(b) Sample Temperatures (1300B)





(c) Product Gas Analyses (1300A)



(c) Product Gas Analyses (1300B)

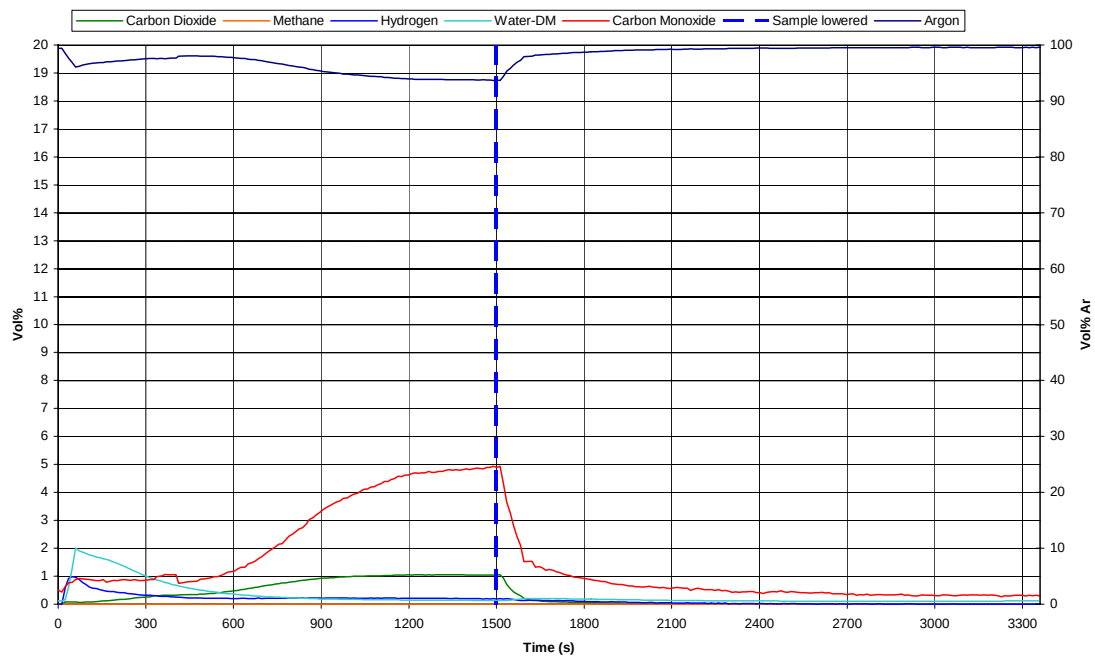
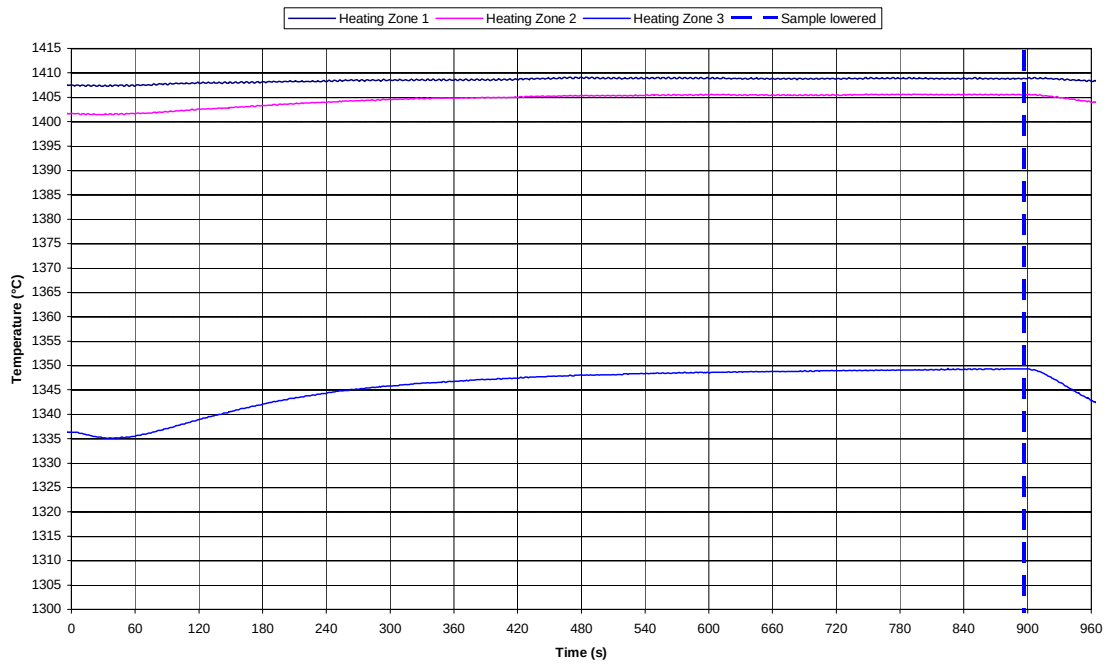
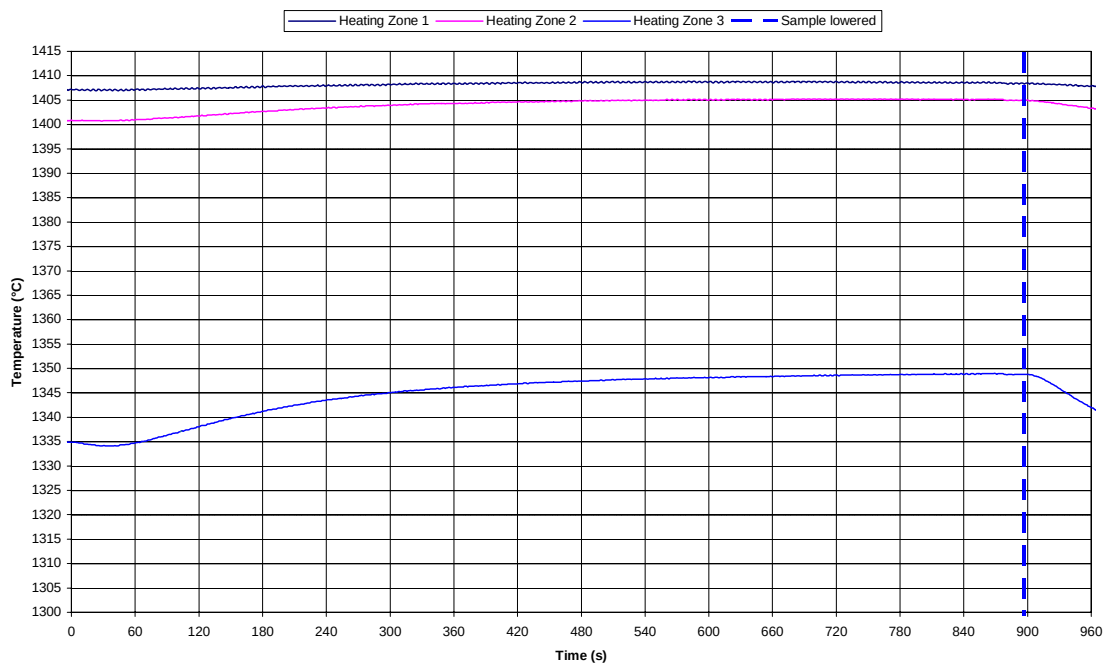


Fig. 18: Calibration Measurements at 1400°C Hot Zone Temperature

(a) Heating Zone Temperatures (1400C)

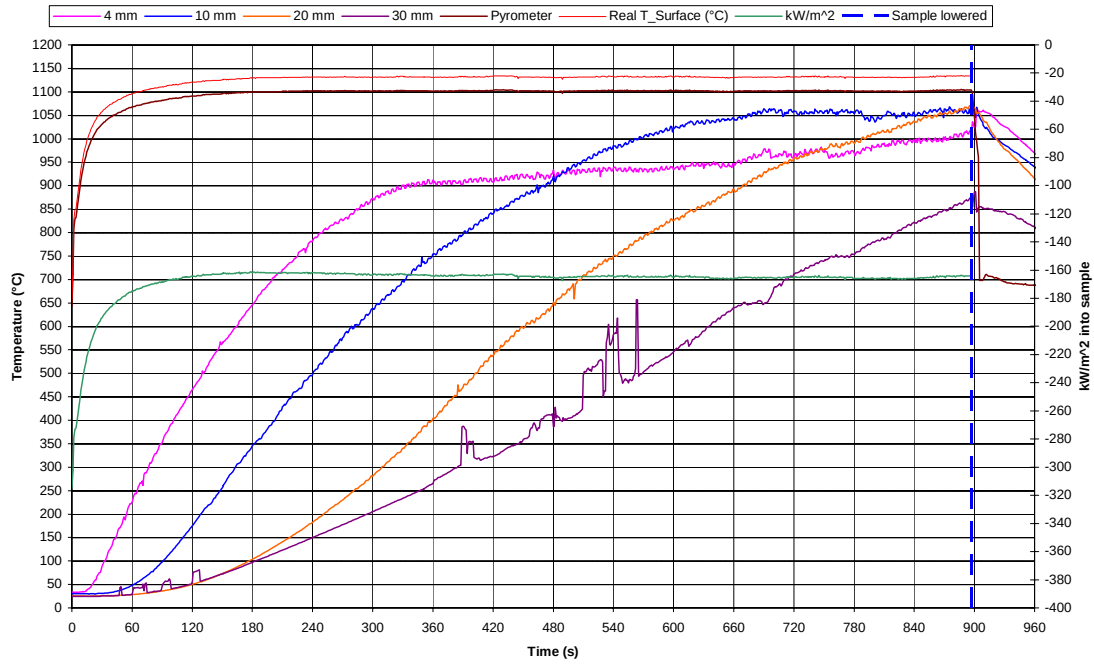


(a) Heating Zone Temperatures (1400D)

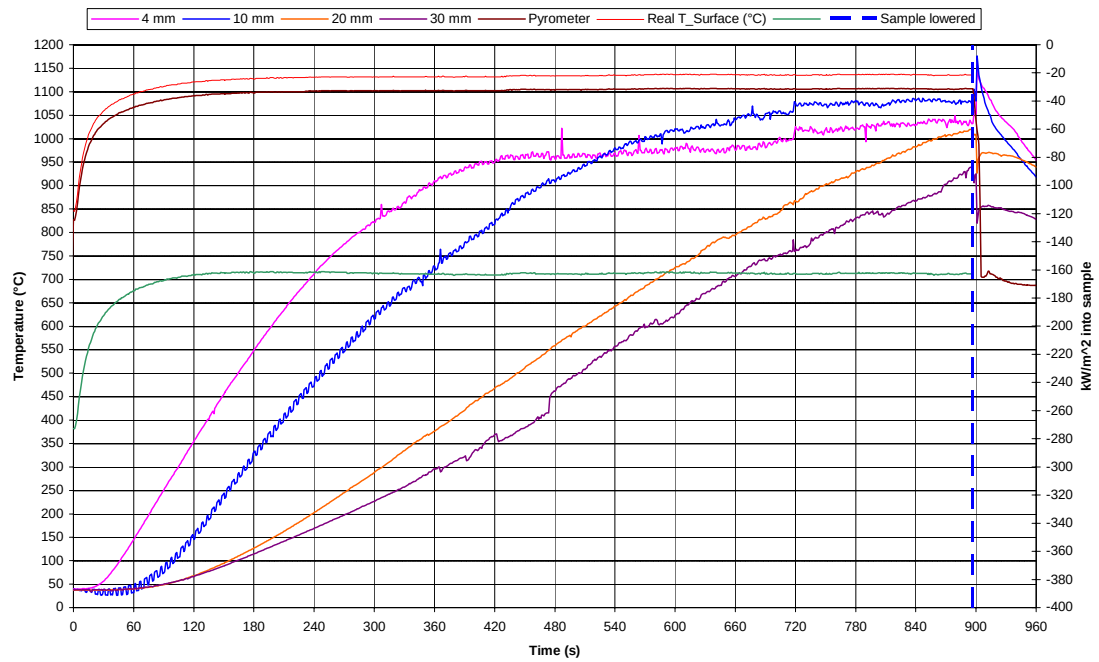




(b) Sample Temperatures (1400C)

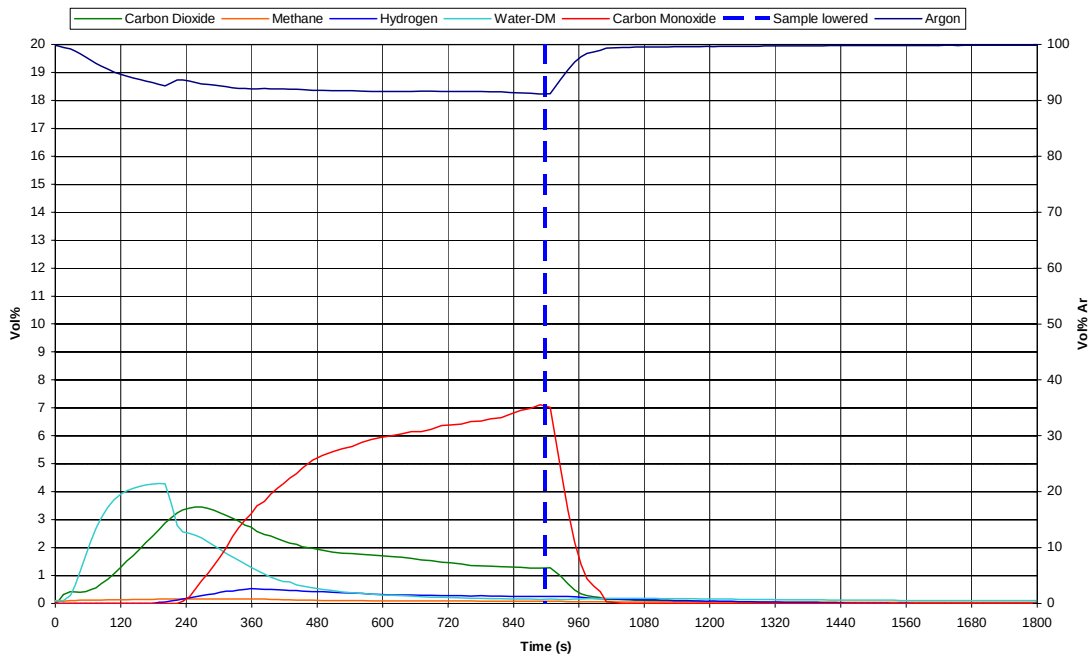


(b) Sample Temperatures (1400D)





(c) Product Gas Analyses (1400C)



(c) Product Gas Analyses (1400D)

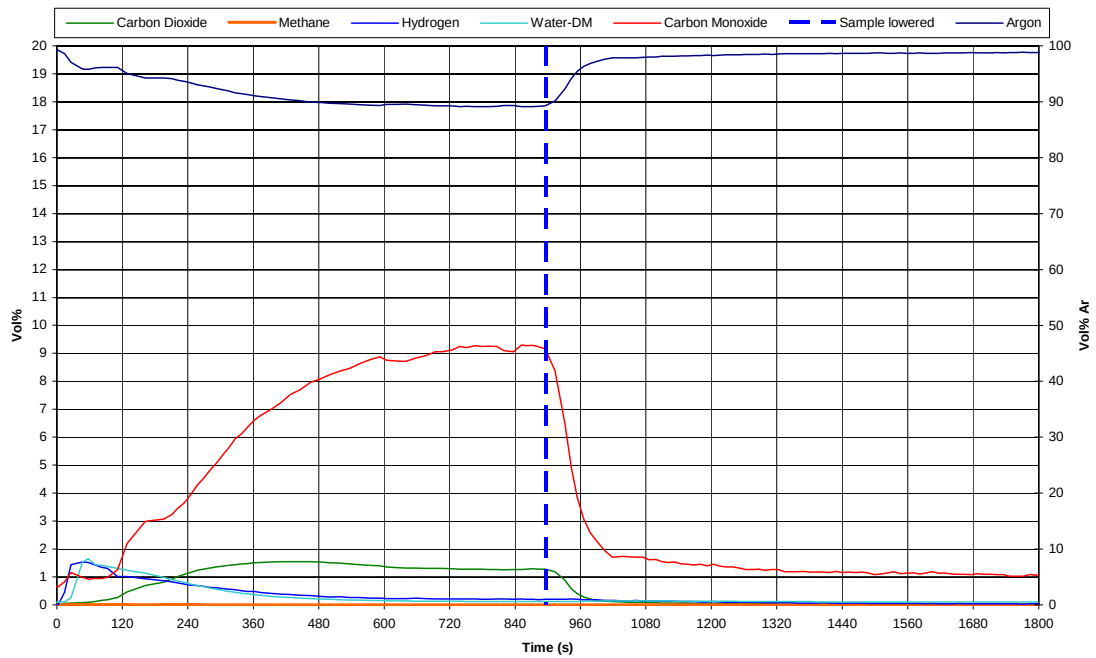
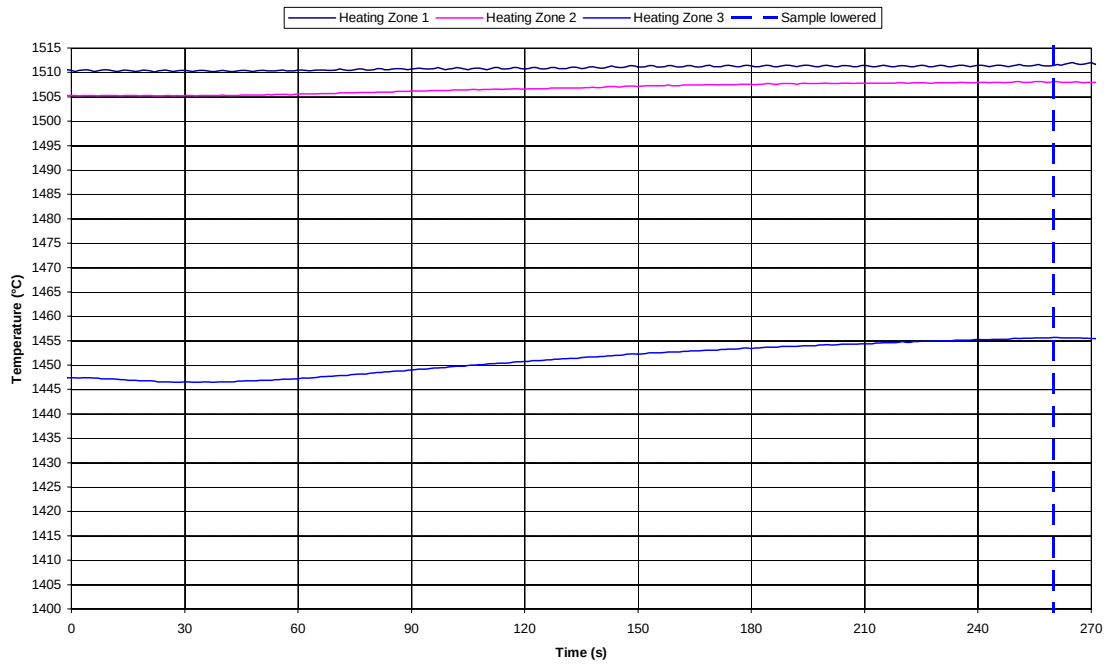
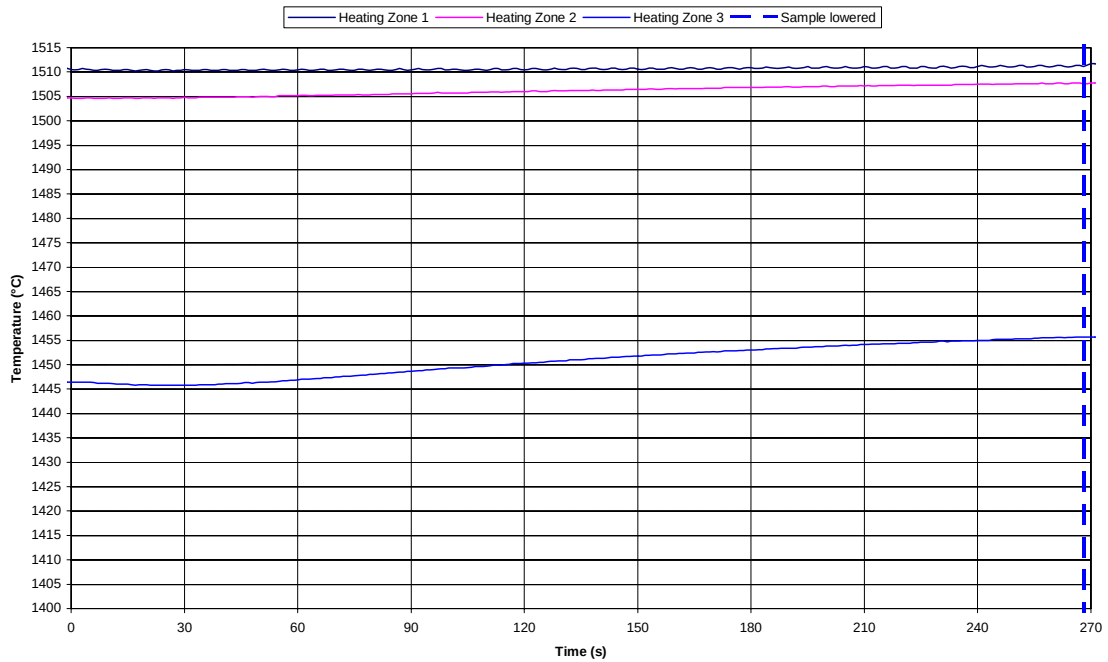


Fig. 19: Calibration Measurements at 1500°C Hot Zone Temperature

(a) Heating Zone Temperatures (1500E)

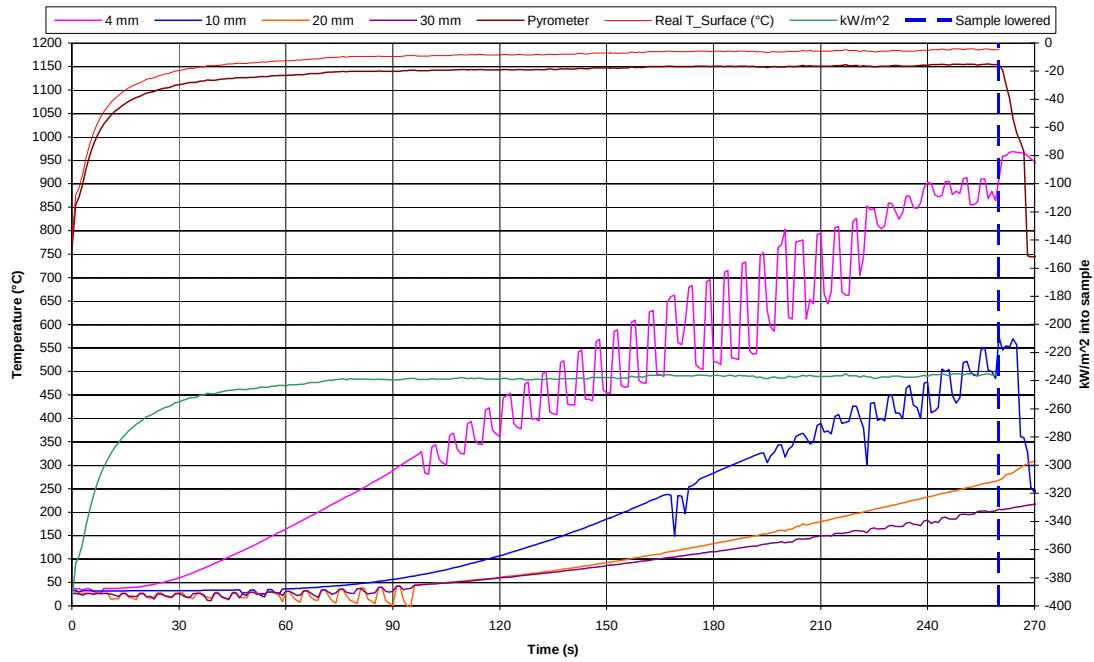


(a) Heating Zone Temperatures (1500F)

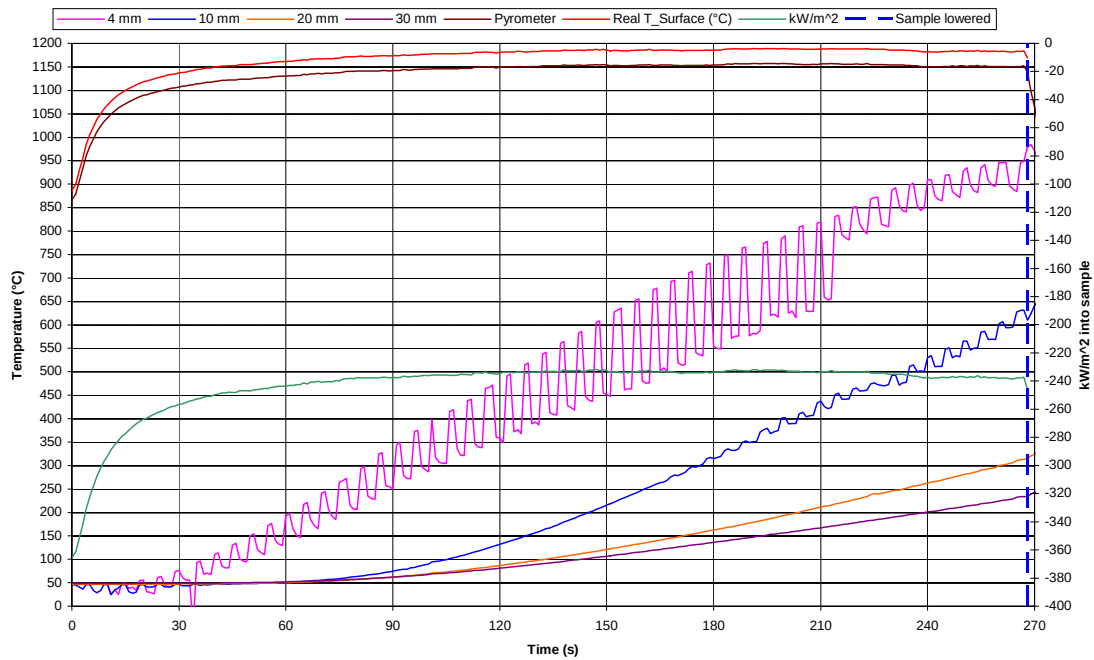




(b) Sample Temperatures (1500E)

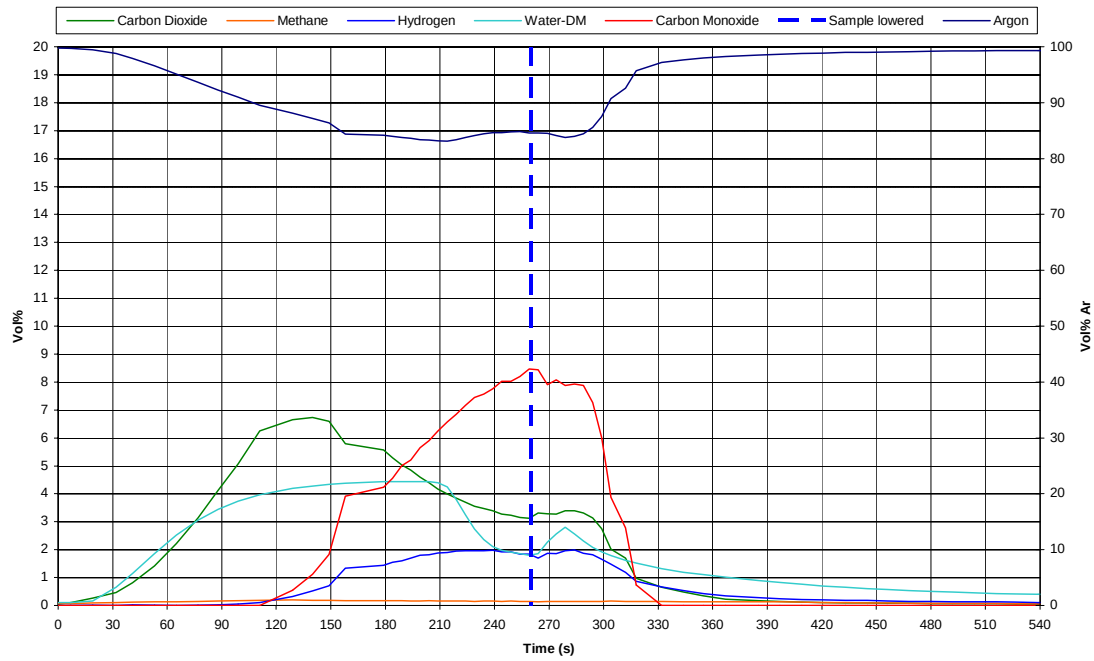


(b) Sample Temperatures (1500F)

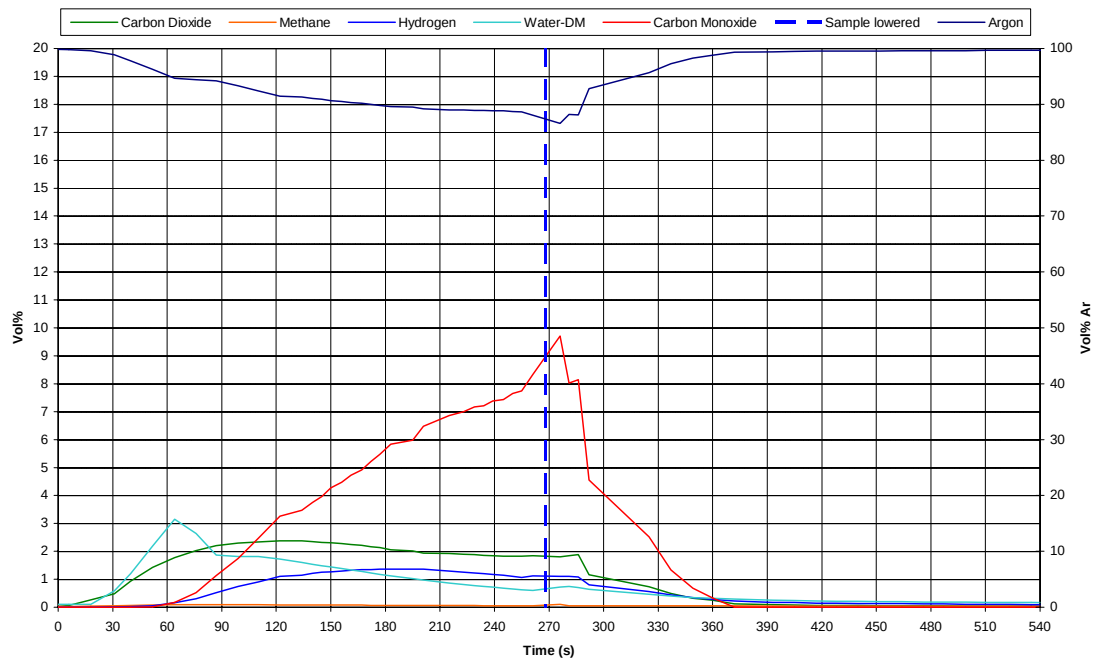




(c) Product Gas Analyses (1500E)



(c) Product Gas Analyses (1500F)



To indicate the sensitivity of the radiation network calculation (of heat transfer to the sample surface), to changes in conditions, the individual measurement parameters were changed and the effect noted. This is shown in **Table 8**. The measurements for the calibration sample 1400C, reacted at 1400°C furnace temperature, were used as basis for the sensitivity calculations. It is seen from **Table 8** that the sample surface emissivity used in the calculation has the biggest influence on the radiation network calculation. For the measured parameters the sample surface temperature and the heating zone 3 temperatures have the biggest effect on the calculated heat transferred to the sample surface. If the correct emissivity value of 0.90 is used for the sample surface, the remaining effect of possible errors in the temperature measurements provides an estimated maximum error of $\pm 19 \text{ kW/m}^2$ for the heat transfer calculation.

Table 8: Radiation network calculation sensitivities

Parameter	Parameter Value Change	Parameter Basis Value	kW/m ²	*ΔkW/m ²
Basis	----	----	-167	0
Measured sample surface temperature (surface 4)	+15°C	1093°C	-159	-8
Measured sample surface temperature (surface 4)	-15°C	1093°C	-176	9
Heating zone No. 1 temperature (surface 1)	+15°C	1409°C	-168	+1
Heating zone No. 1 temperature (surface 1)	-15°C	1409°C	-167	0
Heating zone No. 2 temperature (surface 5)	+15°C	1405°C	-170	+3
Heating zone No. 2 temperature (surface 5)	-15°C	1405°C	-165	-2
Heating zone No. 3 temperature (surface 6)	+15°C	1346°C	-177	+10
Heating zone No. 3 temperature (surface 6)	-15°C	1346°C	-158	-9
Furnace tube emissivity: $\epsilon_1, \epsilon_5, \epsilon_6$	+0.10	0.68	-167	0
Furnace tube emissivity: $\epsilon_1, \epsilon_5, \epsilon_6$	-0.10	0.68	-168	+1
Sample surface emissivity ϵ_4	+0.09	0.90	-191	+24
Sample surface emissivity ϵ_4	-0.10	0.90	-141	-26
Bottom radiation shield emissivity ϵ_3	+0.10	0.53	-167	0
Bottom radiation shield emissivity ϵ_3	-0.10	0.53	-167	0
Top radiation shield emissivity ϵ_2	+0.10	0.54	-167	0
Top radiation shield emissivity ϵ_2	-0.10	0.54	-167	0

$$*\Delta \text{kW/m}^2 = (\text{Basis kW/m}^2) - (\text{New kW/m}^2)$$

When the sample was cut into the three node sections some fibre board material carry over occurred. The sample masses were corrected for this fibre board carry over by mass balance of the SiO₂ and Al₂O₃ in the sample, using the analyses of %SiO₂ and %Al₂O₃ in the reacted samples, and consequently the sample analyses were corrected for the fibreboard carry over as well. The details of

this calculation are shown in **Appendix VII**. The masses and analyses before and after the correction are shown in **Appendix VI**. The end-point chemical analyses for the calibration samples, the corrected sample node masses out and the end-point temperatures are summarised in **Table 9**.

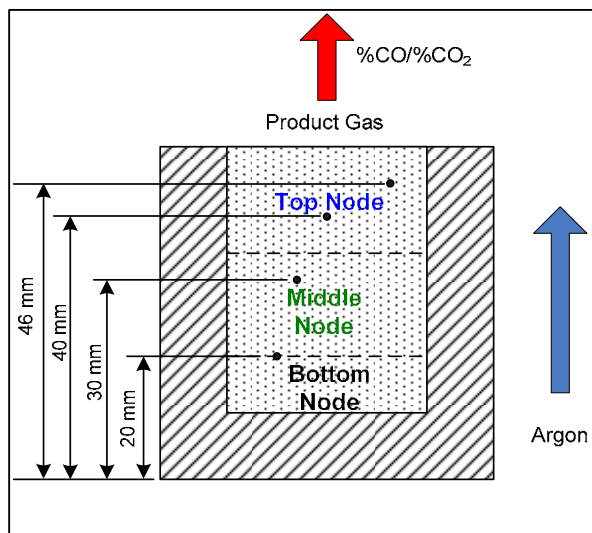
Table 9: End-point data for calibration samples

Furnace Temperature (°C)	Sample Number	Sample Position	Node End Temperature (°C)	*Node mass out (g.)	*Fibre board mass out (g.)	*%C	%Reduction
1300	1300A	Top	1071	15.4	14.5	12.9	45.4
		Middle	1030	15.4	4.2	13.2	25.5
		Bottom	974	10.7	12.9	15.1	23.9
1300	1300B	Top	1051	18.2	11.2	12.4	38.8
		Middle	1027	14.6	6.9	12.7	25.2
		Bottom	954	8.6	12.9	18.7	24.5
1400	1400C	Top	1054	16.0	11.7	10.5	46.6
		Middle	1071	15.1	7.3	13.5	25.6
		Bottom	874	9.5	13.4	18.0	24.7
1400	1400D	Top	1077	15.1	12.1	12.2	54.8
		Middle	1014	14.8	7.0	11.1	26.1
		Bottom	922	9.7	13.2	16.2	25.2
1500	1500E	Top	909	18.7	11.8	16.8	31.4
		Middle	268	15.4	6.9	12.2	21.2
		Bottom	206	9.1	13.6	13.9	23.3
1500	1500F	Top	981	11.5	5.8	14.6	36.5
		Middle	316	14.5	7.7	14.3	23.0
		Bottom	234	16.9	17.3	13.6	22.9

*Corrected for fibreboard carry-over

The assumptions made in the incremental mass-energy balance calculations are discussed below with reference to **Fig. 20** in which the reaction products are shown. For each time interval the reaction extent and temperature of the solid material and gas products in each node are required.

Fig. 20: Crucible and sample material



- The sample mass out (on completion of reaction) and the mass Fe out were used in the mass balance calculations. This is acceptable because the mass Fe in to mass Fe out ratio is close to one, as expected and is shown in **Appendix VI**.
- The reduction extent over reaction time is stepwise linear. This linear trend is used to interpolate the reduction extent between the initial input material reduction extent and the reduction extent as analysed in the sample material after total reaction. The reduction extent at the end of each time interval was calculated by re-proportioning of the forms of iron analysis of the input pre-reduced ore material.
- The oxygen removed from the sample must be present in the product gas as CO or CO₂. This assumption is made based on no volatile content in the graphite used as reductant, and little H₂ and H₂O present in the product gas. The carbon balance must be closed by using a CO-CO₂ gas composition from each node to attain the %C calculated equal to that analysed in the reacted node sample. Forms of Fe analyses of the reacted samples show the reduction extent in each node, and from this information it is seen that the middle and bottom nodes do not show further reduction progress from the initial reduction extent. Therefore, the CO and CO₂ in the product gas are generated from the top node only, and are taken to exit the sample at the top node temperature. The mass of oxygen released to the product gas is calculated from the reduction extent in the top node. The product gas %CO/(%CO+%CO₂) ratio is then specified in the heat-mass balance as equal to that at the end of each time interval in the total product gas analysis. The %C remaining in the sample is then a result of the heat-mass balance calculation, and can be compared with that analysed in the reacted sample.
- The total water measured in the product gas analysis is taken as part of the sample and released with the rest of the product gas from the sample at the top node temperature. This assumption is based on the chemical analyses done on the reacted material, which shows that most of the reduction takes place in the top node. Water release from the sample over time was proportioned according to the water content analysed in the product gas.
- The temperatures measured by the four thermocouples positioned in the material layer are assigned to the three node segments as follows: the top node is at the end-point temperature measured by the thermocouple positioned 10 mm from the sample surface; the middle node is at the end-point temperature of the thermocouple which is 20 mm from the sample surface; and the bottom node is at the end-point temperature of the thermocouple which is 30 mm from the sample surface. It is seen from the sample temperature graphs in **Fig. 17-19 (b)** that the thermocouple positioned 4 mm from the sample surface, for longer experiment times at 1300°C

and 1400°C, levels off and the thermocouple values are lower than that for the thermocouple at 10 mm and/or 20 mm from the sample surface. The material bed level lowers throughout the experiment, so that the top thermocouple may not be covered by material at the end of the experiment, and thus temperature values from the top thermocouple are not reliable towards the end of the experiment. For the tests done at 1500°C a short reaction time was used because of slag formation. For these two tests, the thermocouple positioned 10 mm from the sample surface is much lower than the thermocouple positioned 4 mm from the sample surface. Therefore, the latter temperature is used for the top node for these two samples reacted at 1500°C furnace temperature.

- In the mass and energy balance several factors must be taken into account, besides the end-point material temperatures discussed above. The heat transferred to the sample also heats up the thermocouples embedded in the sample, as well as the crucible material. The masses for the crucible material can be proportioned between the three nodes, using the mass measurements made when the sample was cut into the three node portions. The thermocouple material must be roughly estimated from mass measurements of alumina sheaths cut to the length of the thermocouples embedded into the sample. The latter masses are small compared to that of the crucible material, and were therefore not considered in the heat-mass balance. The crucible material consists of 65% Al_2O_3 and 35% SiO_2 , and was considered to be mullite in the heat-mass balance calculations.
- The other factor to take into account for the heat mass balance is the heat transferred to the Ar carrier gas used. This is factored into the heat-mass balance by assuming that the Ar is heated to the top node temperature. The Ar gas flow rate for each time increment was calculated by proportioning the total Ar flow rate for each time increment.

The incremental heat-mass balance calculation sheets for sample 1400C are shown in **Appendix VI**. The sensitivities of the above assumptions for sample 1400C are summarised in **Table 10**. Comparison of the heat transfer values calculated from the heat-mass balance to that calculated in the radiation network is shown in **Table 11** and **Fig. 21**. Reduction extent for the top segment is shown in **Fig. 22**. Comparison of the %C in the reacted sample with that analysed is shown in **Fig. 23 a-c**. The data values in the figures are shown at the furnace temperatures offset by 5°C to facilitate clarity of the graphs. It is seen that for the experiments at 1300°C and 1400°C furnace temperature the calculated mass-heat balance kW/m^2 values and those calculated from the radiation network correspond well. However, for the experiment 1500F reacted at 1500°C there is a difference of 22% of the value calculated from the incremental heat-mass balance. From **Fig. 23 a-c** it is seen that the calculated and

analysed %C remaining in the sample differ by a maximum of 7% for the top node of sample 1500F. In terms of the total initial mass carbon input of 3.0 g into the sample top node, 7% is 0.2 g.

Table 10: Heat-mass balance sensitivities for sample 1400C

Condition	kW/m ² calculated from heat-mass balance	kW/m ² calculated from radiation network
+Ar; +FB, +H ₂ O	-163	-167
+Ar; +FB, -H ₂ O	-158	---
+Ar; -FB, +H ₂ O	-109	---
-Ar; +FB, +H ₂ O	-131	---
+Ar at 500°C; +FB, +H ₂ O	-146	---
+Ar; +FB, +H ₂ O, 100%CO in CO-CO ₂ product gas	-167	---
+Ar; +FB, +H ₂ O, 100%CO ₂ in CO-CO ₂ product gas	-159	---
+Ar; +FB, +H ₂ O, sample solids temperatures +50°C	-171	---
+Ar; +FB, +H ₂ O, sample solids temperatures -50°C	-155	---

+Ar = Argon carrier gas included in heat-mass balance

+FB = Fibreboard crucible material included in heat-mass balance

+H₂O = Water in product gas analysis included in heat-mass balance

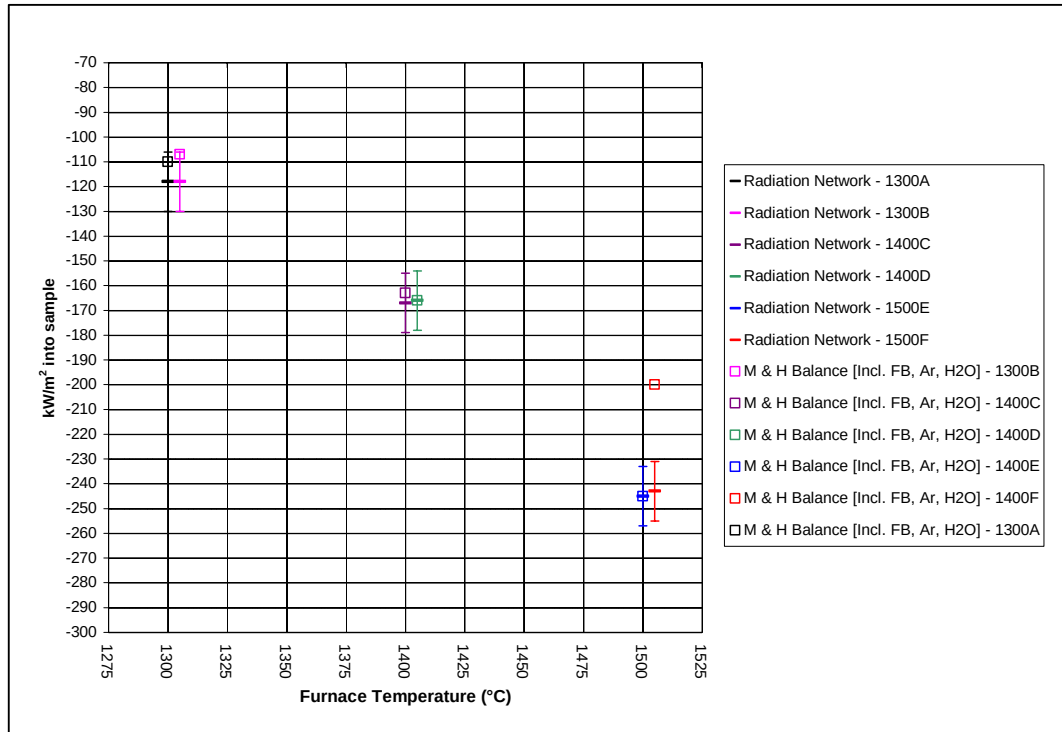
Table 11: Heat transfer values comparison

Sample No.	kW/m ² calculated from incremental heat-mass balance	kW/m ² calculated from radiation network	*Difference in kW/m ²	Difference as % of kW/m ² calculated from incremental heat-mass balance
1300A	-110	-118	8	7
1300B	-107	-118	11	10
1400C	-163	-167	4	2
1400D	-166	-166	0	0
1500E	-245	-245	0	0
1500F	-200	-243	43	22

*Difference in kW/m² = (kW/m² calculated from incremental heat-mass balance) - (kW/m² calculated from radiation network)

Fig. 21: Heat transferred to sample

(Experimental period at 1500°C furnace temperature is 4.5 minutes only)



Radiation Network = weighted average kW/m^2 heat transferred to sample as calculated from radiation network

M & H Balance = weighted average kW/m^2 heat transferred to sample as calculated from incremental heat – mass balance

Fig. 22: %Reduction in top segment

(Experimental period at 1500°C furnace temperature is 4.5 minutes only)

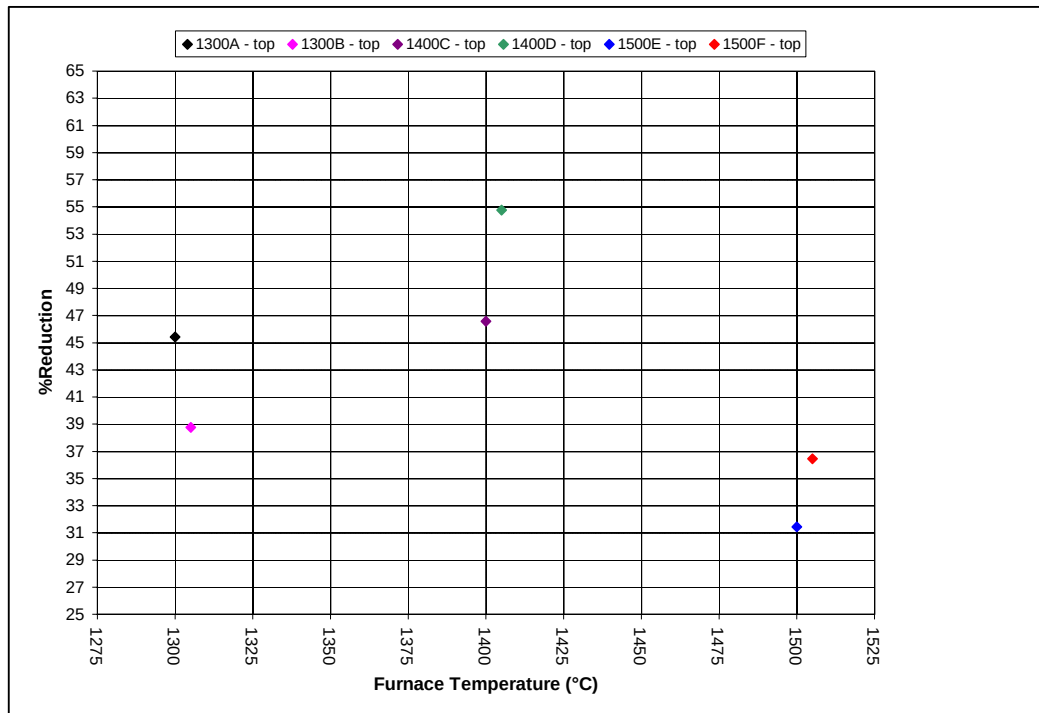
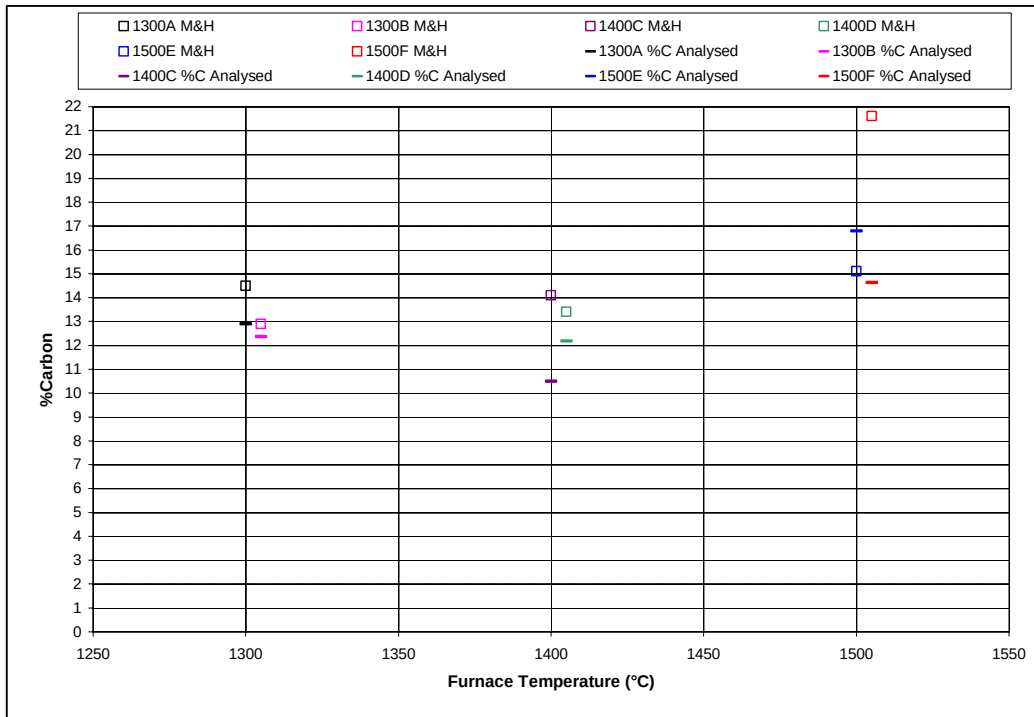
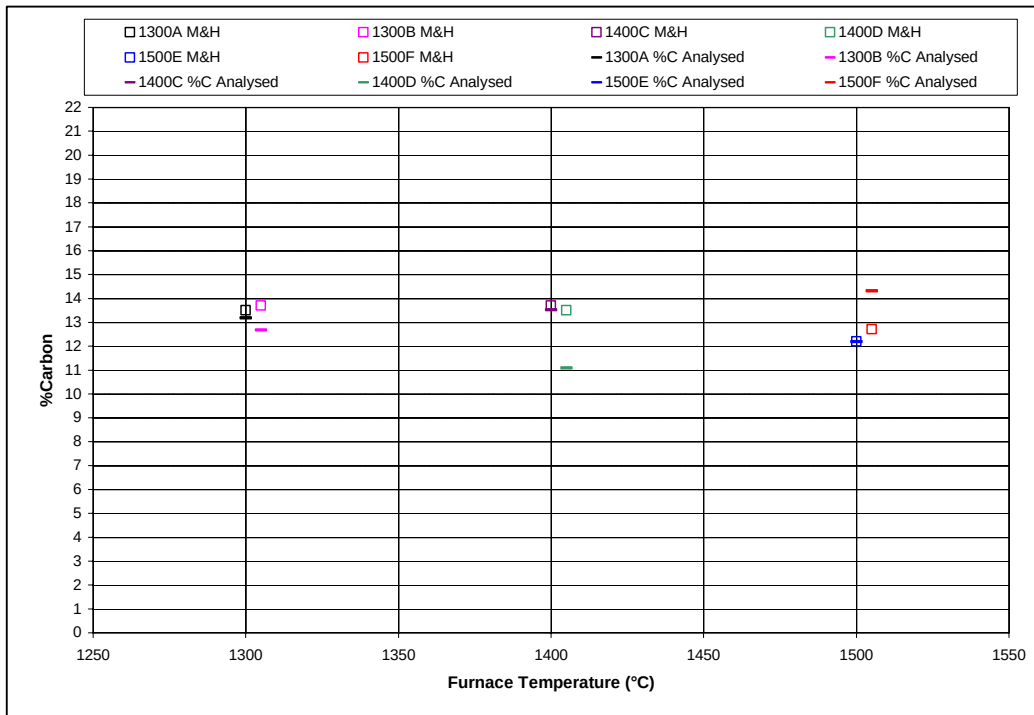


Fig. 23: %C analysed vs. calculated from heat-mass balance

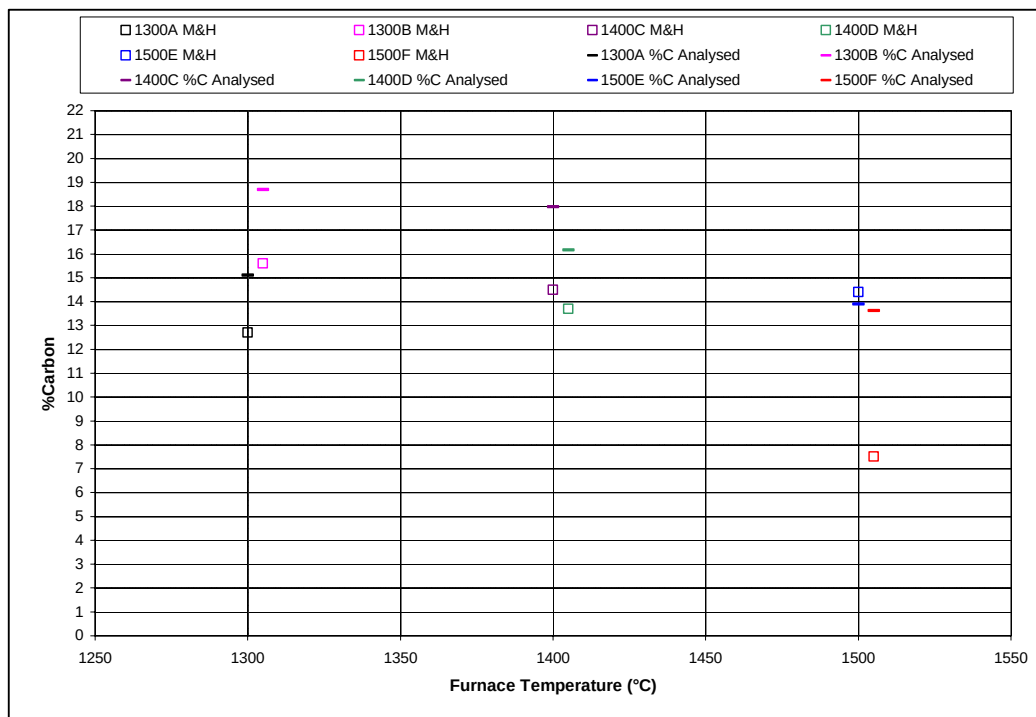
(a) Top node



(b) Middle node



(c) Bottom node



2.3. Conclusion

The experimental set-up is appropriate for quantifying radiation heat transfer to samples reacted non-isothermally in this set-up. The heat-mass balance calculations and the radiation heat transfer to the sample, as calculated from the radiation network, correspond within the radiation network calculation uncertainty for samples reacted at 1300°C and 1400°C furnace temperatures. For samples reacted at 1500°C furnace temperature, the difference is larger due to the short reaction time and resultant small reaction extent achieved in these samples. The sample cutter-splitter allows for the repeatable division of the reacted sample into three node portions for further chemical analysis.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Introduction

An experimental set-up was constructed to heat a material layer sample uni-directionally from the sample surface, to study heat transfer to and within the layer. Large differentials between the sample surface temperature and bed temperatures, at increasing depth from the sample surface, show conduction heat transfer control within the layer of material. Increased reduction extent for decreased material layer thickness would also confirm conduction heat transfer control within the material layer. Large temperature differentials between the sample surface and the furnace heating surfaces would indicate radiation heat transfer control. Also, increased reduction extent achieved for increased heat transfer rate would confirm radiation heat transfer control. These ideas were tested experimentally, and the results are reported below.

Mixtures of coal and ore were reacted at heating zone 1 temperatures of 1300°C, 1400°C and 1500°C to measure the extent of reaction at increased heat input into the sample. Sishen fines and Eikeboom coal of -850 +425 µm were used as input materials for the bulk of the experiments. A molar ratio of fixed carbon to reducible oxygen in ore of 0.97 was used. The input material chemical compositions are shown in **Appendix IV**. To test the effect of different particle sizes, ore and coal fractions of -425 +300 µm and -2000 +1400 µm were also used. The material layer thickness of 40 mm was used as basis, and a series of 16 mm material layer thickness was tested for comparison. To determine the devolatilisation components of the coal, the ore portion in the sample mixture was replaced by alumina particles of the same particle size as the ore. The coal-alumina samples were then reacted to complete devolatilisation. The radiation network calculation from Chapter II was used to calculate radiation heat transfer to the sample surface at one second intervals. The reacted samples were sectioned into three parts, as shown in Chapter II, and analysed for reduction extent and carbon content.

The product gas was analysed by mass spectrometer. As an example the data set of sample temperatures, furnace heating zone temperatures and product gas analyses measured in each experiment is shown in **Fig. 24** for the 40 mm layer thickness sample, of coal-ore mixture, reacted for 15 minutes at 1400°C heating zone 1 temperature. Similar sets of data for all the samples reacted are shown in **Appendix VIII** in graphical form. The iron balance for the samples was calculated and the

*Reducible oxygen is the oxygen bound to the total Fe analysed in the iron ore, expressed as Fe₂O₃

ratio of iron into the sample to iron out of the reacted sample varied from 0.99 to 1.08. These values are summarised in **Appendix XI**, as are sample analyses and total product gas analyses.

The total mass loss according to the product gas analyses was compared to the sample mass weighed after the sample was split into three sections, and these measurements corrected for fiberboard crucible material carry over. The values are summarised in **Appendix XI**, and graphs are shown in **Appendix X**. In most instances the difference in mass loss as percentage of the mass loss calculated from the weighed sample mass of the reacted sample is within 30% of the sample mass loss calculated from the product gas analysis. The biggest difference of 100% was for the 40 mm sample layer with fine ore fraction reacted for 9 minutes at 3.13 g mass loss.

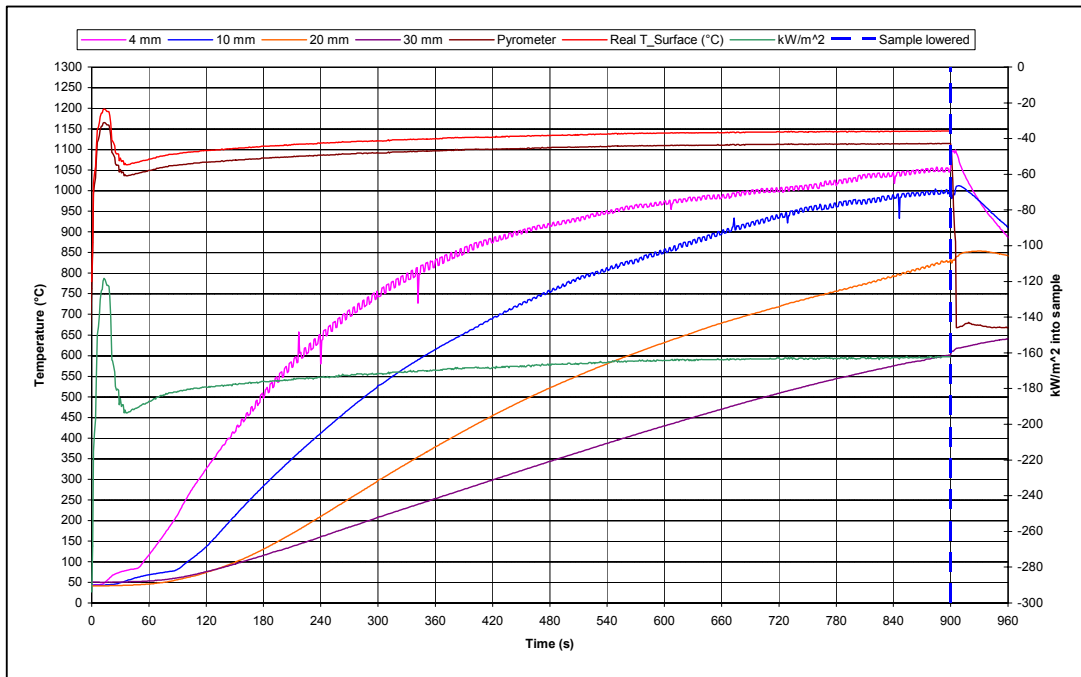
The mass of carbon reacted, as calculated from %C analyses of the reacted material, was similarly compared to that calculated from the product gas analyses. Graphs of mass carbon remaining as calculated from these two information sources are shown in graphs in **Appendix X**. The analysis uncertainty for total carbon analysis in the reacted ore-coal mixture, $\pm 1.5\%C$ as shown in **Fig. 14 (b)**, is indicated by error bars in the graphs. With the exception of the 16 mm sample layer reacted for 15 minutes the difference in mass carbon remaining in the reacted sample, expressed as percentage of the mass of carbon remaining as calculated from the reacted sample carbon analysis, is within 20% of the mass carbon remaining calculated from the product gas analysis. The 57% percentage difference for the 16 mm sample layer reacted for 15 minutes was 0.70 g carbon of 1.20 g carbon calculated from the carbon analysis on the reacted sample.

Similarly the mass oxygen released in the product gas analyses was compared to the mass oxygen reduced from the ore as calculated from the forms of Fe analyses. The uncertainty in the mass oxygen release calculation from the forms of Fe analyses is that the oxygen released from coal is not included in the calculation. This uncertainty is shown as error bars in the graphs in **Appendix X**. Without taking the error estimation into account the maximum difference in mass oxygen released from the sample, as percentage of the mass oxygen released as calculated from the forms of Fe analyses, is 78%. This percentage difference is 0.55 g oxygen of 0.70 g oxygen released into the product gas for a 16 mm sample layer reacted for 3 minutes, and 1.64 g oxygen of 2.09 g oxygen released into the product gas for a 40 mm sample layer with fine ore fraction reacted for 9 minutes.

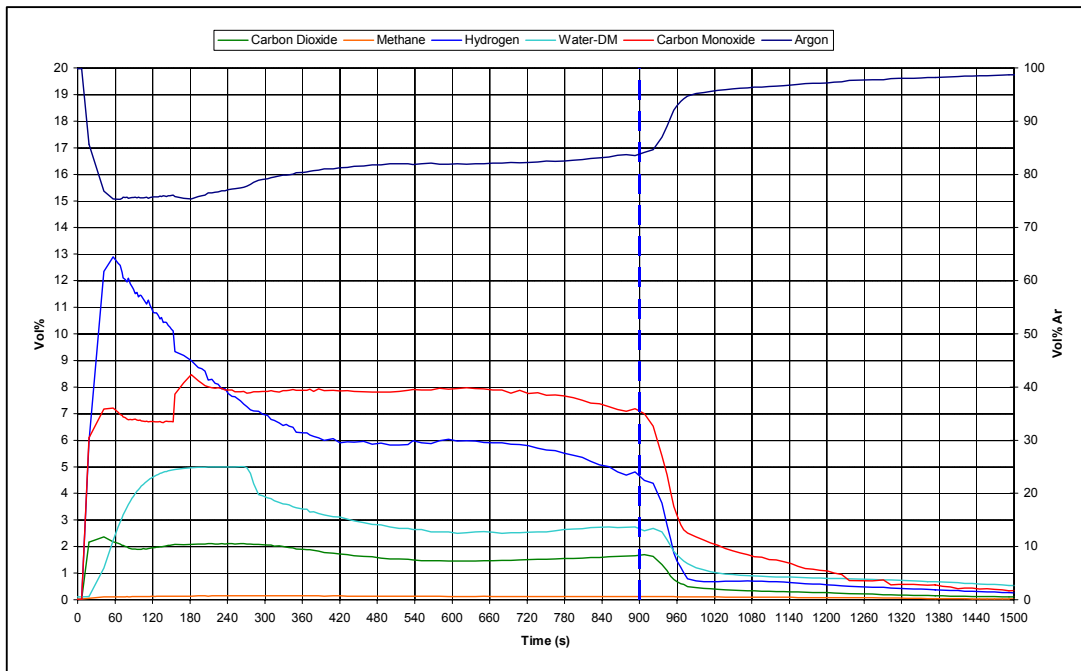
The product gas analyses were used to calculate the CO/CO₂ ratios in the product gas. These values were compared to the equilibrium gas ratios for the FeO/Fe and the C/CO₂ equilibrium to indicate which reaction was more important in the reaction system. The %C and forms of Fe analyses in the reacted samples were used in reaction extent calculations.

Fig. 24: Temperatures and product gas analyses for 40 mm layer thickness of coal-ore mixture reacted at 1400°C for 15 minutes.

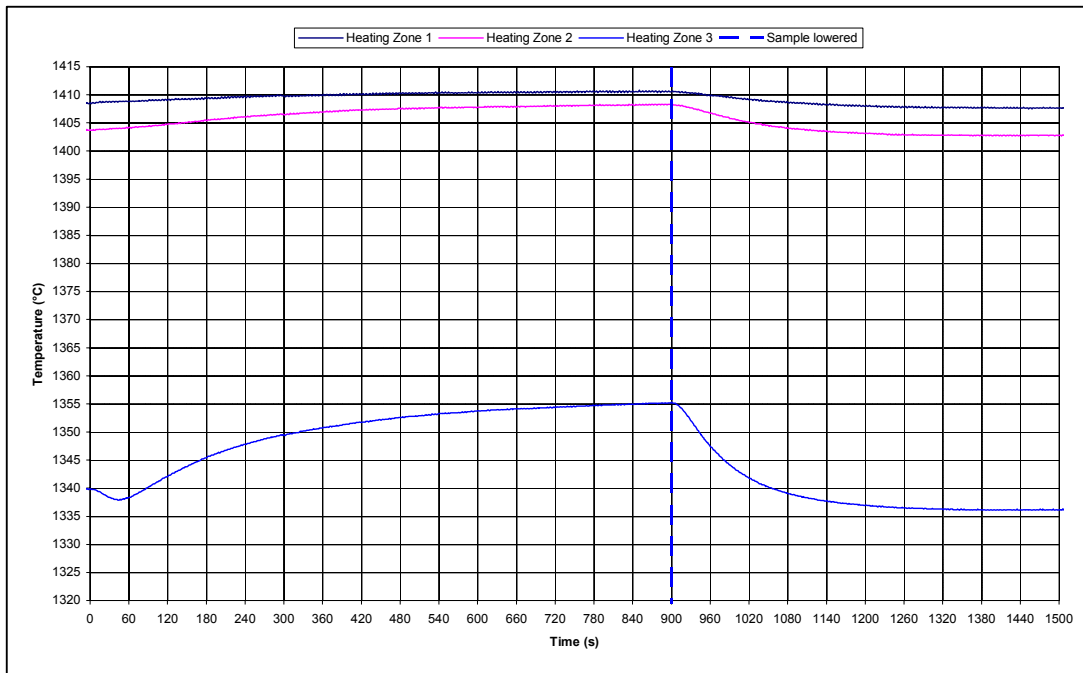
(a) Sample Temperatures



(b) Product gas analyses



(c) Furnace heating zone temperatures



3.2. Effect of Increased Heat Transfer

Radiation heat transfer to the sample surface was calculated from the radiation network using the sample surface temperature and the furnace heating zone temperatures as inputs, at one second intervals. As a comparative example of increased heat transfer achieved with increased furnace temperature, the data for 40 mm sample layers reacted for 15 minutes at furnace heating zone 1 temperatures of 1300, 1400 and 1500°C is shown here. The sample surface temperatures, corrected for pyrometer emissivity setting and view glass transmissivity, are shown in **Fig. 25**. The incremental radiation heat transfer values calculated for each second of temperature data logged are shown in **Fig. 26**. The heating zone temperatures for these three experiments are shown in **Fig. 27 (a)-(c)**. Increased furnace temperatures result in increased radiation heat transfer to the sample surface and the heat transfer rate plot follows the sample surface temperature plot closely, indicating the strong interrelation between sample surface temperature and heat transferred. The average radiation heat transfer values over the reaction period for each sample are shown in **Table 12**. These values are equivalent to weighted average heat transfer values because the incremental radiation heat transfer values were calculated at one second intervals.

Comparison of the heap surface temperatures shown in **Fig. 25** with the heating zone temperatures shown in **Fig. 27** shows that a large temperature differential persists between the sample surface temperature and each of the heating zone temperatures.

Table 12: Average radiation heat transfer to sample surface of 40 mm layer coal-ore samples

Reaction Time (minutes)	Average kW/ m ² at Furnace Heating Zone 1 Temperature (°C)			*ΔkW/m ² (a)	*ΔkW/m ² (b)
	1300°C	1400°C	1500°C		
3	-120	-181	-259	61	78
6	-127	-180	-250	53	70
9	-125	-178	-254	53	76
12	-109	-175	-211	66	36
15	-108	-169	-208	61	39

*ΔkW/m² (a) = (Average kW/m² at 1400°C furnace heating zone 1 temperature) - (Average kW/m² at 1300°C furnace heating zone 1 temperature)

*ΔkW/m² (b) = (Average kW/m² at 1500°C furnace heating zone 1 temperature) - (Average kW/m² at 1400°C furnace heating zone 1 temperature)

From **Fig. 25 and 27** the temperature differentials between the sample surface temperatures and the heating zone 1 temperatures are of the order of 200-250°C, and that between the sample surface temperatures and the heating zone 3 temperatures are 150-200°C. The temperature differentials between the heating zone 1 temperatures and the sample surface temperatures for the rest of the 40 mm layer samples are shown in **Table 13**. Also, as shown in **Fig. 24 (a)**, the initial temperature differentials in the material bed when the material layer is heated uni-directionally from the sample surface, persist when the surface temperature levels off towards a steady state value. The temperature differentials between the sample surface temperatures and the material layer bottom segment temperatures for the rest of the 40 mm layer samples are shown in **Table 13**. Hence both radiative heat transfer and conduction were limiting factors under these conditions.

Table 13: Temperature differentials for 40 mm material layers

Reaction Time (minutes)	ΔT _{Top} * at 1300°C	ΔT _{Top} * at 1400°C	ΔT _{Top} * at 1500°C	ΔT _{Bed} * at 1300°C	ΔT _{Bed} * at 1400°C	ΔT _{Bed} * at 1500°C
3	277	302	338	907	995	1053
6	259	292	312	785	888	870
9	272	303	310	677	735	700
12	229	283	262	641	639	615
15	224	266	257	537	543	421

ΔT_{Top}* at the furnace heating zone 1 temperature = Furnace heating zone 1 temperature – Sample surface temperature

ΔT_{Bed}* at the furnace heating zone 1 temperature = Sample surface temperature – Sample bottom segment temperature (30 mm from sample surface)

The difference between average radiation heat transfer values calculated for samples reacted for different periods at 1300°C and 1400°C furnace heating zone 1 temperature are similar, as shown in **Table 12**. However, for samples reacted at 1400°C and 1500°C furnace heating zone 1 temperature the difference in average radiation heat transfer values are lower at 12 and 15 minute reaction times. This is due to increased heap surface temperatures measured in the samples reacted at 1500°C furnace heating zone 1 temperature for 12 and 15 minutes, respectively. The increased surface temperatures at

12 and 15 minutes reaction time can be explained by decreased reduction rate at increased reduction extent in the top node, 70% reduction at 12 minutes reaction time and 76% reduction at 15 minutes reaction time, resulting in decreased energy utilisation for reduction and consequently increased energy utilisation for heating the material bed.

Fig. 25: Sample Surface Temperatures at different furnace heating zone temperatures for 40 mm coal-ore samples reacted for 15 minutes

(Corrected for pyrometer emissivity setting and view glass transmissivity)

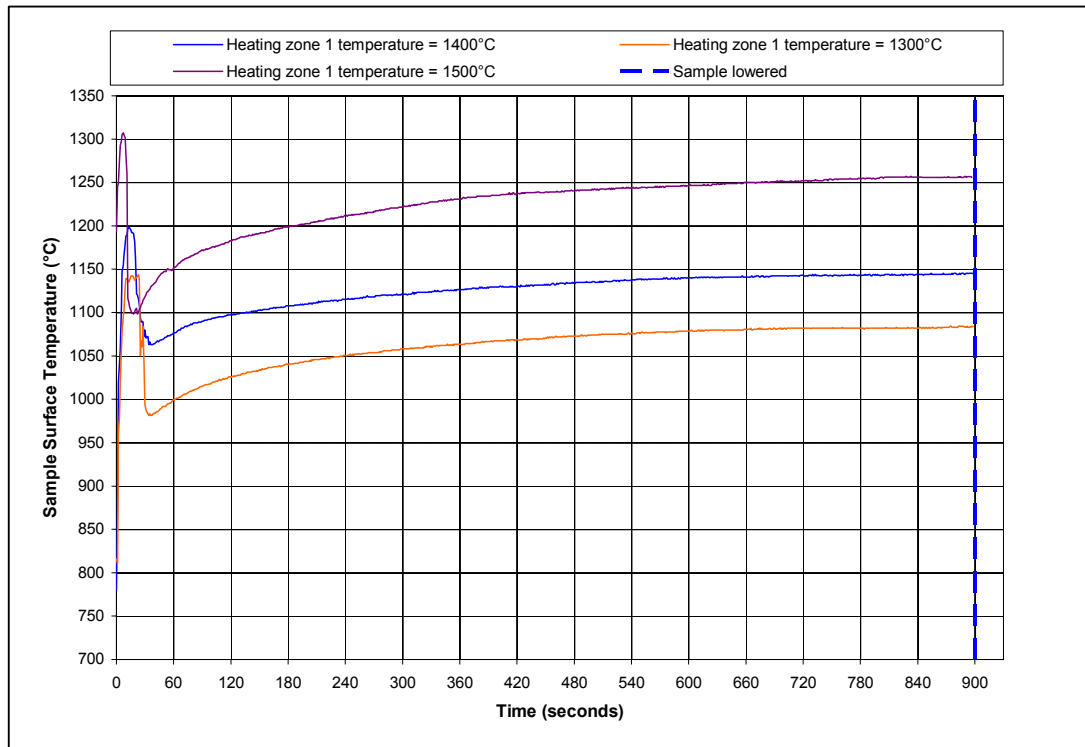


Fig. 26: Radiation heat transfer to sample surface at different furnace heating zone 1 temperatures for 40 mm coal-ore samples reacted for 15 minutes

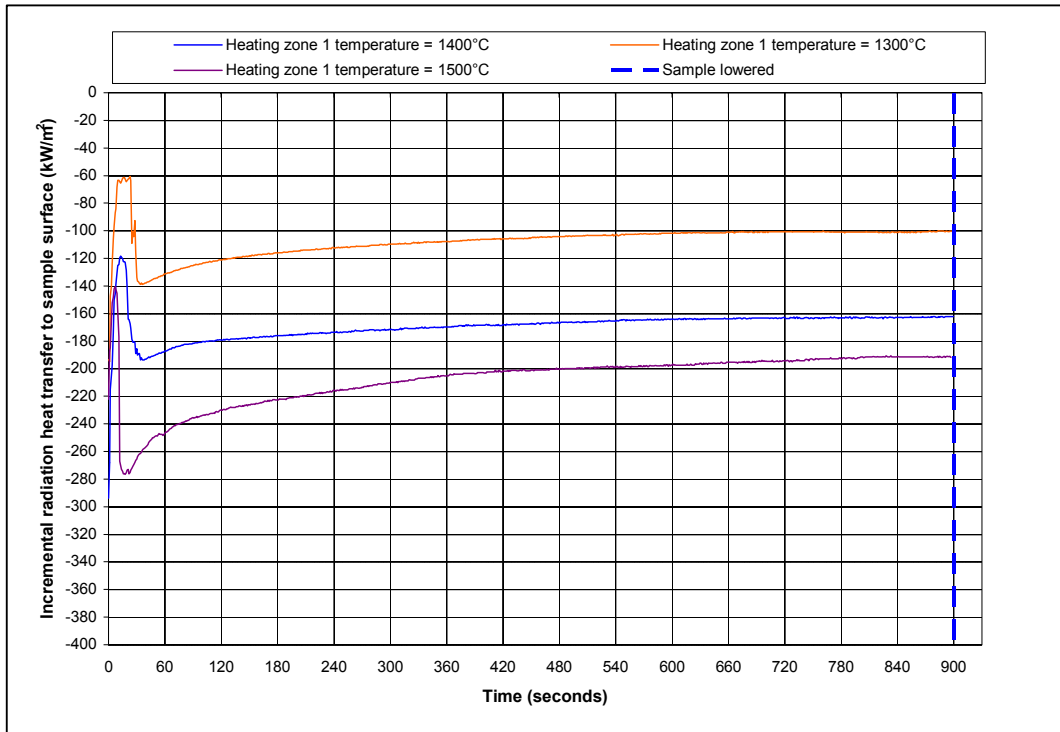
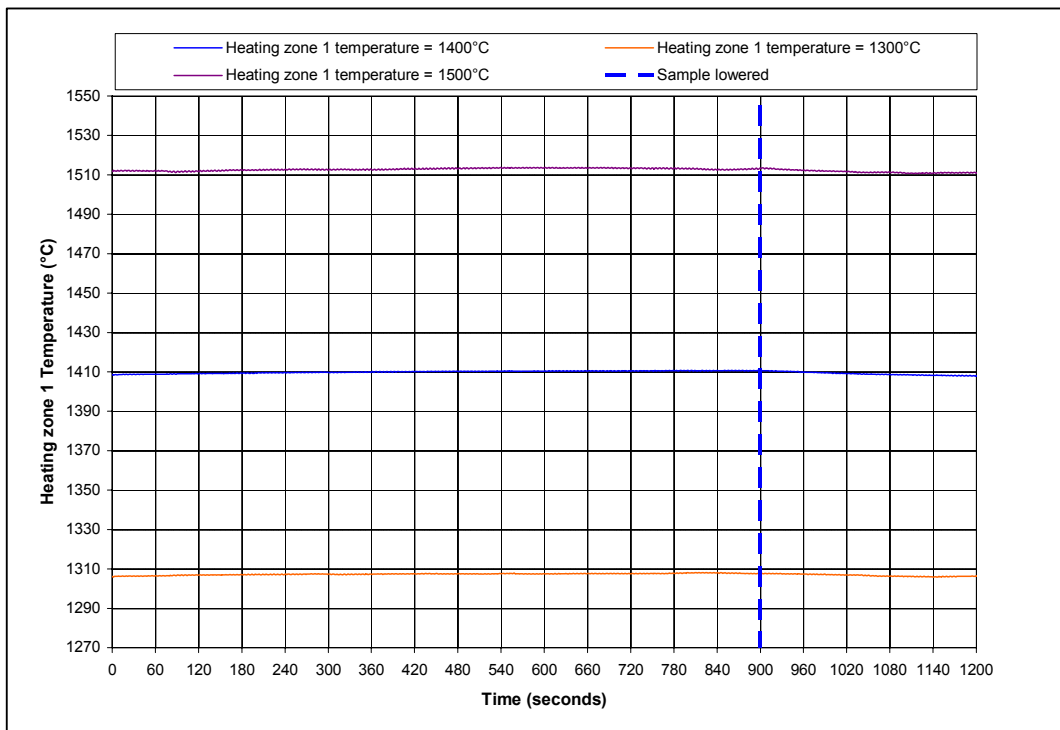
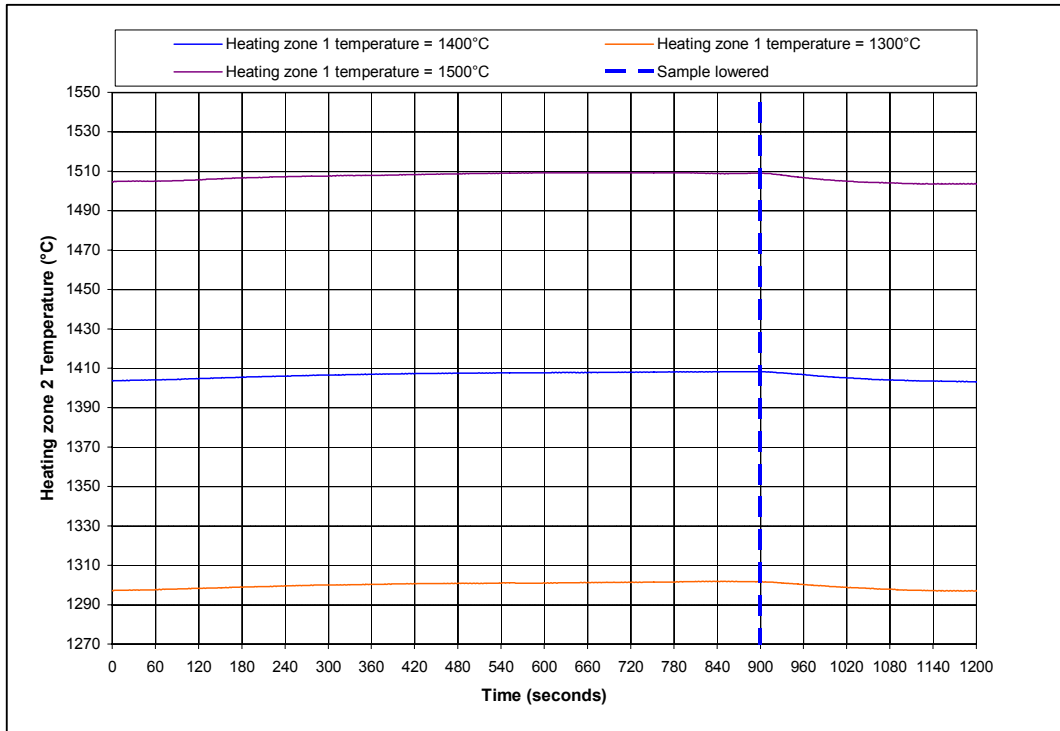


Fig. 27: Heating zone temperatures at different furnace heating zone 1 temperatures for 40 mm coal-ore samples reacted for 15 minutes

(a) Heating zone 1 temperatures



(b) Heating zone 2 temperatures



(c) Heating zone 3 temperatures

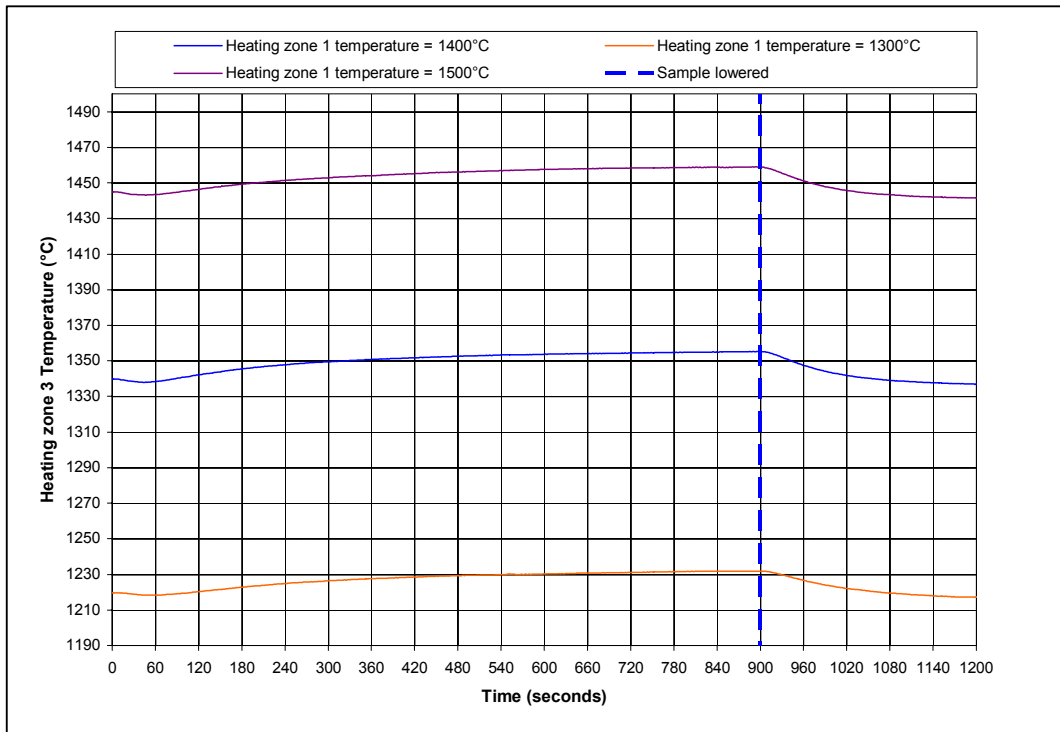


Fig. 28 (a) and (b) show the reduction extent and carbon consumption for the whole sample. Carbon consumption and reduction extent per sample segment, in **Fig. 29** and **Fig. 30**, indicate that very little reduction takes place in the middle and bottom segments of the sample. The reduction extent for each sample segment was calculated from the forms of iron analyses of the reacted material of the particular segment. Because little reduction took place in the middle and bottom segments the carbon consumption values in these segments are erratic, compared to that in the top segment. For ten of the segment analyses the carbon consumption values for the middle and bottom segments are negative by 0.03 to 0.27 g carbon, compared with 1.6 and 1.8 g C input to the middle and bottom segments.

Fig. 28 (a): Composite reduction extent

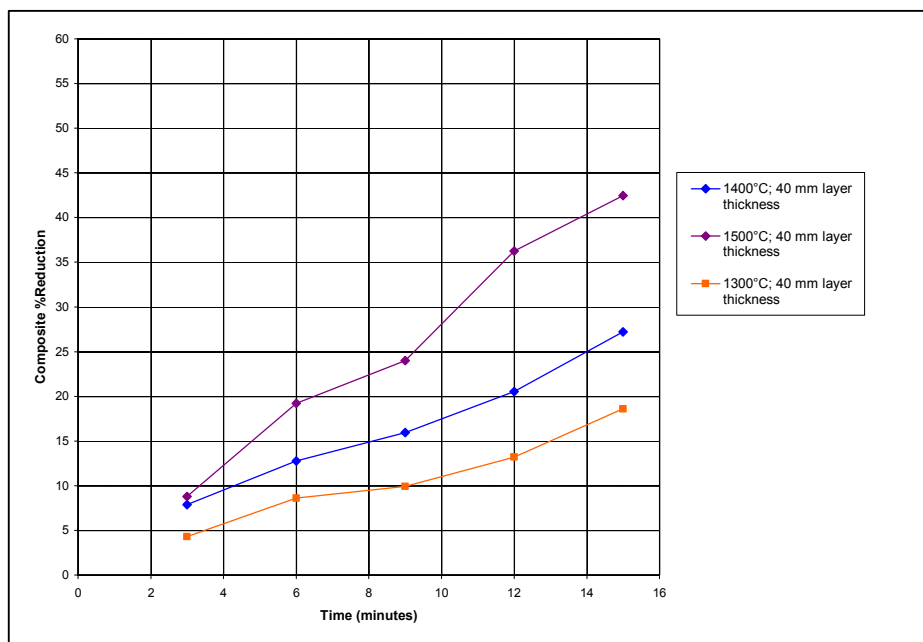


Fig. 28 (b): Composite carbon consumption

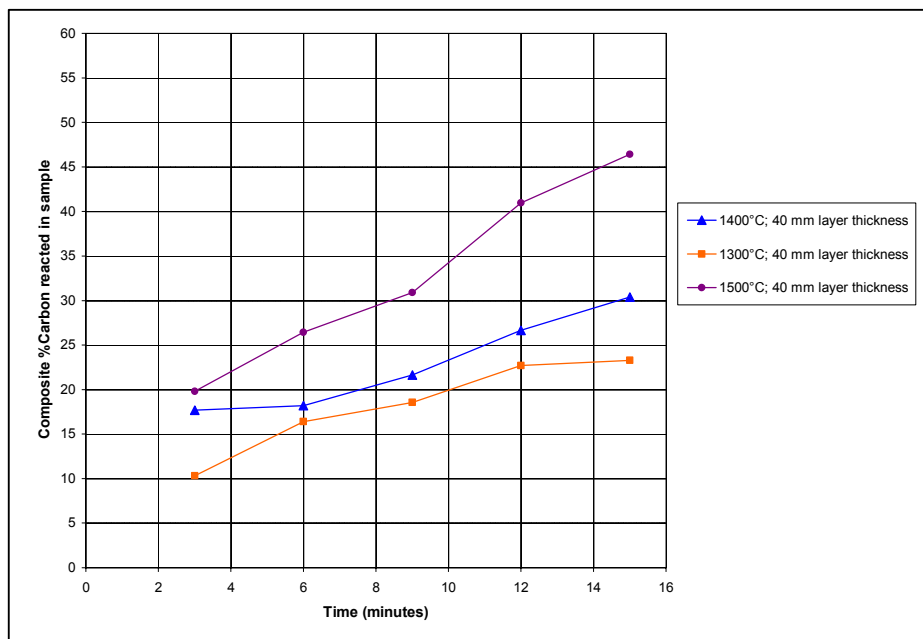


Fig. 29: Reduction extent for each material layer segment

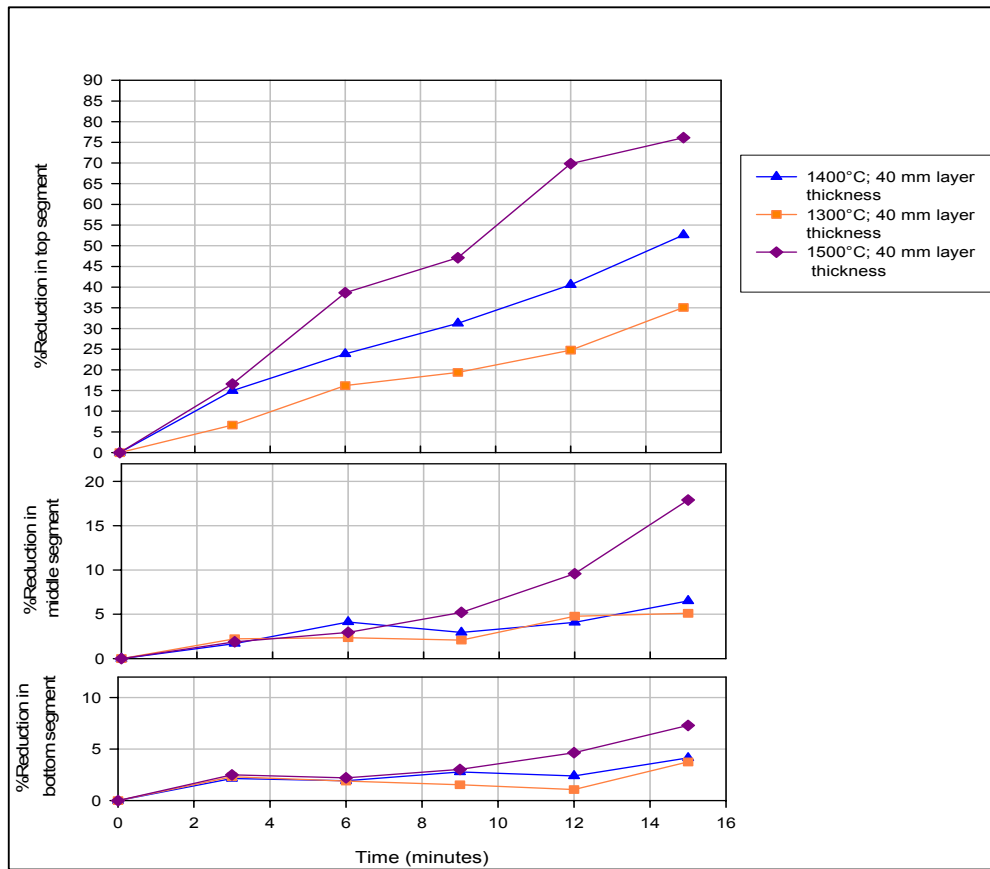
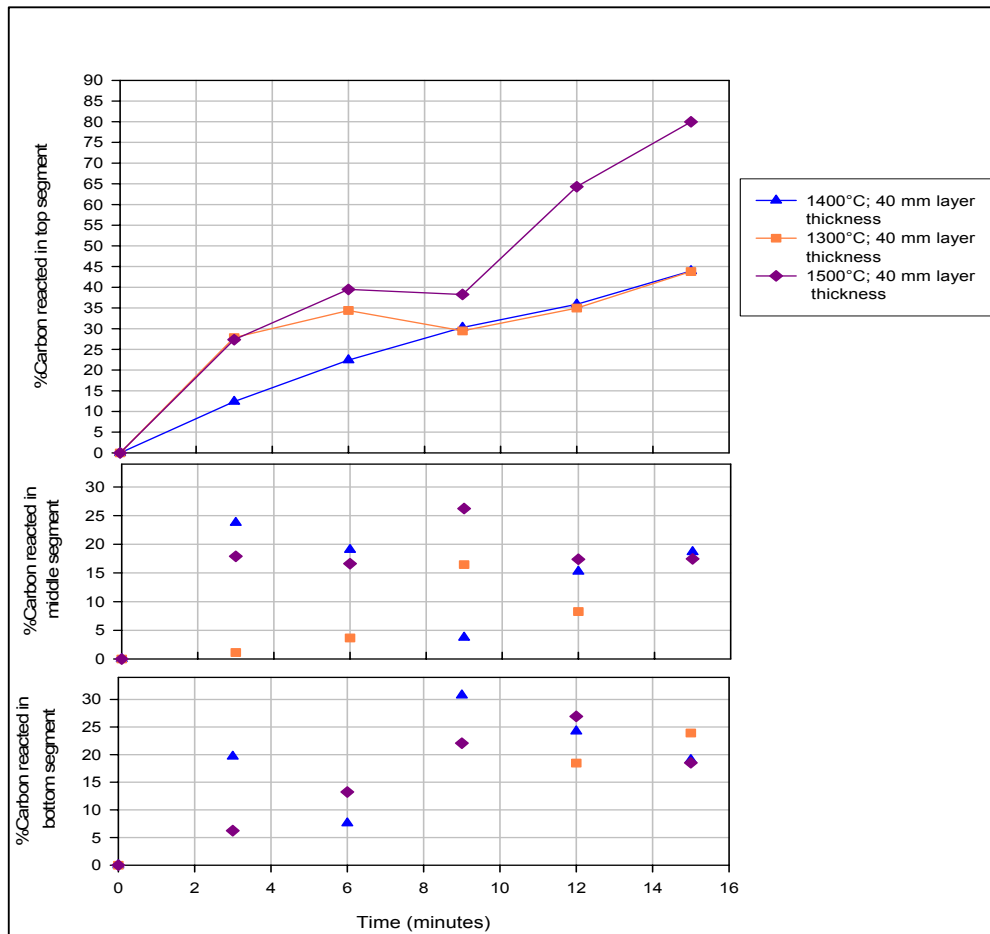
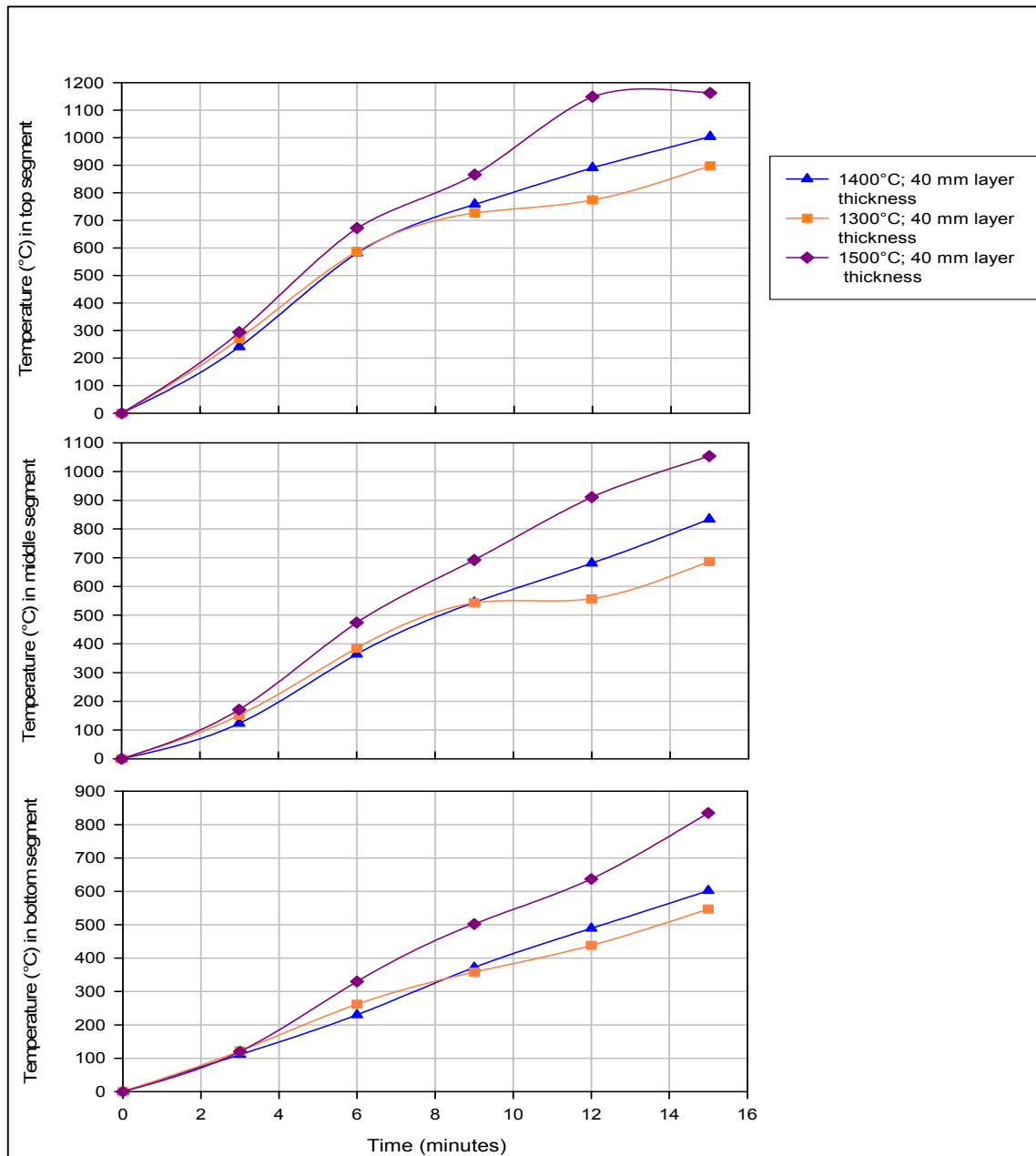


Fig. 30: Carbon consumption for each material layer segment



The temperature in each material layer segment at the end of the reaction period is shown in **Fig. 31**. At three minutes reaction time the material segment temperatures are similar, and up to nine minutes reaction time the material segment temperatures at 1300°C and 1400°C heating zone one temperatures are similar. Beyond three minutes reaction time material segment temperatures at 1500°C heating zone one temperature are distinctly higher compared to the rest of the segment temperatures, for the same reaction time.

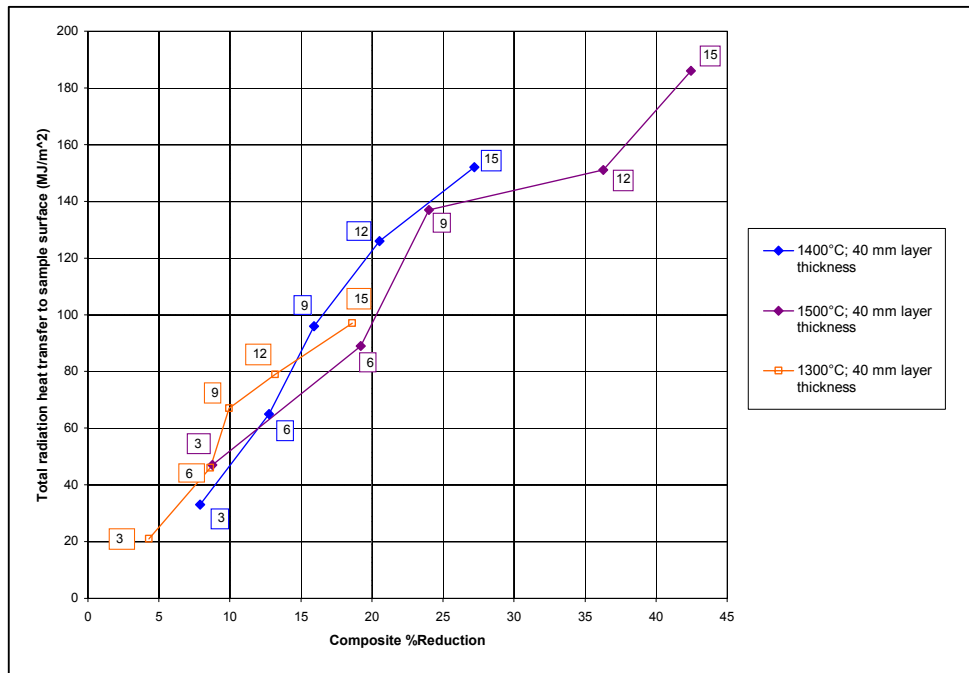
Fig. 31: Temperature for each material layer segment at the end of the reaction time



In addition to the presence of large persistent temperature differentials between the sample surface and the heating zones, as well as temperature differentials within the material layer, another indicator of heat transfer control is increased reaction rate attained at increased heat transfer rate. This is shown in **Fig. 32** below.

Fig. 32: Total radiation heat transferred vs. Composite %Reduction

(Number inside square frame shows reaction time in minutes)



3.3. Effect of Layer Thickness

At 1400°C heating zone 1 temperature material layer thickness samples of both 40 mm and 16 mm were reacted. Increased reaction extent in 16 mm material layers, as compared to that in 40 mm material layers, for the same heat input conditions shows conduction heat transfer control. The sample temperature profiles for 15 minutes reaction time of a 40 mm and 16 mm material layer, respectively, are shown in **Fig. 33 (a) and (b)**. The associated heating zone temperatures are compared in **Fig. 34 (a) and (b)**. The steady state surface temperature for the 16 mm layer material is 26°C higher than that of the 40 mm layer material. The bed temperatures in the 16 mm layer at 4 mm and 10 mm from the sample surface are higher than those in the 40 mm layer.

The product gas profiles for 40 mm material layers and 16 mm material layers were similar. The difference is that product gas of higher reducing potential was produced in the 16 mm layers, as compared to that from the 40 mm layers. This is shown in **Fig. 35 (a) and (b)** where the $\%CO/(\%CO+\%CO_2)$ ratio in the product gas, for each experiment, is compared to the equilibrium ratio for reduction of FeO by CO, reaction (20), and the equilibrium ratio for gasification, reaction (21). The equilibrium $\%CO/(\%CO+\%CO_2)$ values were calculated at the material bed temperatures measured over the 15 minute reaction time. The calculations were done for the longest reaction time of 15 minutes only because the temperature profiles for reaction times smaller than 15 minutes are represented by the 15 minute reaction time temperature profiles as well. The heat capacity values,

standard enthalpy and entropy values used to calculate the enthalpy and entropy of reactions (20) and (21) are shown in **Appendix XII**. A linear fit of the free energy values was made for each reaction as shown in **Appendix XII**.



At the sample surface temperature the product gas %CO/(%CO+%CO₂) ratio for the 16 mm and 40 mm layers experiments plot in-between the equilibrium ratios of reactions (20) and (21). If the reduction reaction, reaction (20), was slowest the product gas CO content would be at the gasification reaction equilibrium which is 100%CO at the sample surface temperatures. If the gasification reaction was slowest the product gas CO content would be at the equilibrium %CO/(%CO+%CO₂) ratio of the reduction reaction, reaction (20). The product gas composition does not follow either equilibrium %CO/(%CO+%CO₂) ratio exclusively, indicating the interdependence of reactions (20) and (21) at the sample surface.

Fig. 36 shows the comparative reduction extent. The reduction extent for the 16 mm layer is 8% higher than that of the top layer for the 40 mm layer material sample for reaction times 9, 12 and 15 minutes. At reaction times below 6 minutes the reduction extent is similar. **Fig. 37 (a) and (b)** shows the %Carbon and mass carbon reacted in the top node in the 40 mm material layer, compared to that in the 16 mm layer. The top node comprises 46% of the 40 mm sample height, that is 18 mm. It is seen that the rate of carbon consumption is similar, but the carbon consumption is higher in the 16 mm material layer in accordance with the increased reduction extent achieved in the 16 mm layer. Heat transfer rates to the 16 mm material layer were lower compared to the 40 mm layer material, due to the slightly higher sample surface temperature and 10°C lower heating zone 3 temperatures. **Fig. 38** shows the average heat transferred to the sample for a 40 mm layer as compared to that for a 16 mm layer.

Fig. 33 (a): Temperatures of 40 mm layer thickness of coal-ore mixture reacted at 1400°C for 15 minutes.

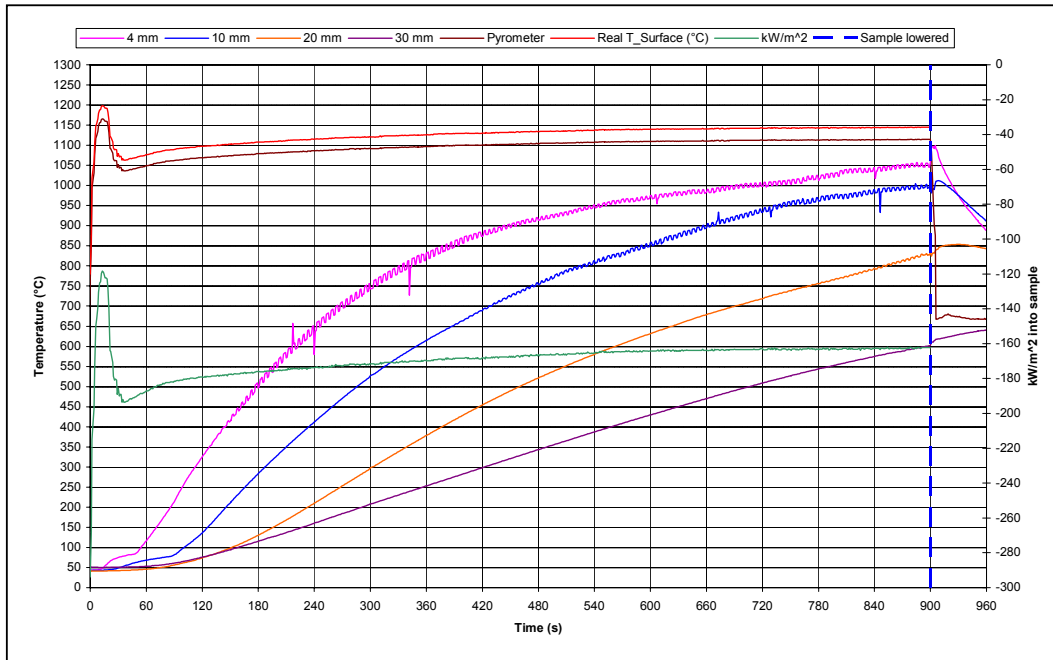


Fig. 33 (b): Temperatures of 16 mm layer thickness of coal-ore mixture reacted at 1400°C for 15 minutes.

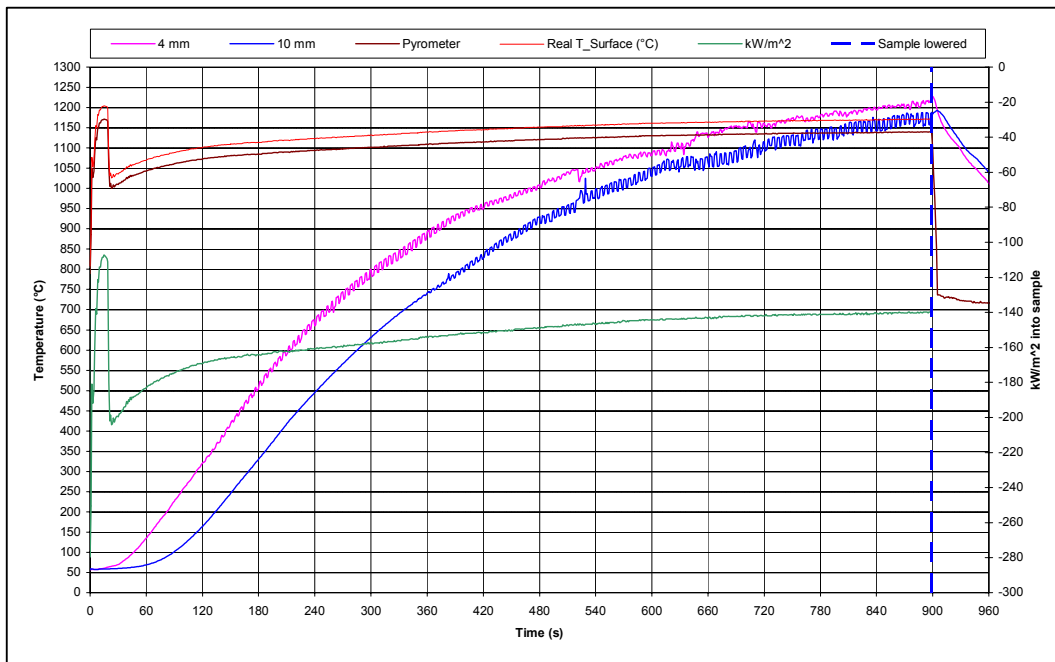




Fig. 34 (a): Comparison of furnace tube temperatures for 40 mm vs. 16 mm

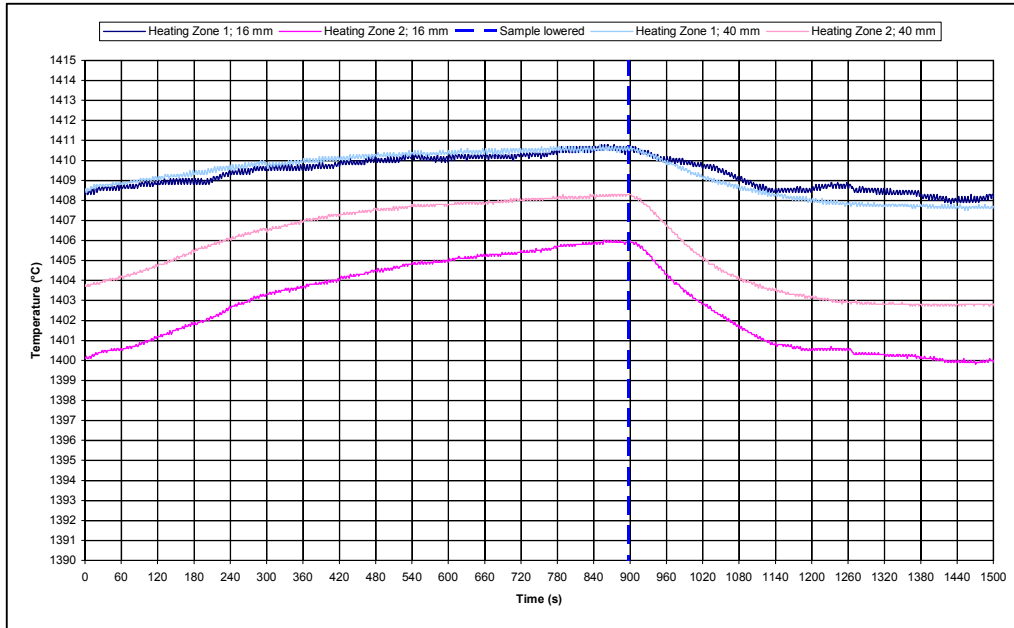


Fig. 34 (b): Comparison of furnace tube temperatures for 40 mm vs. 16 mm (Heating zone 3)

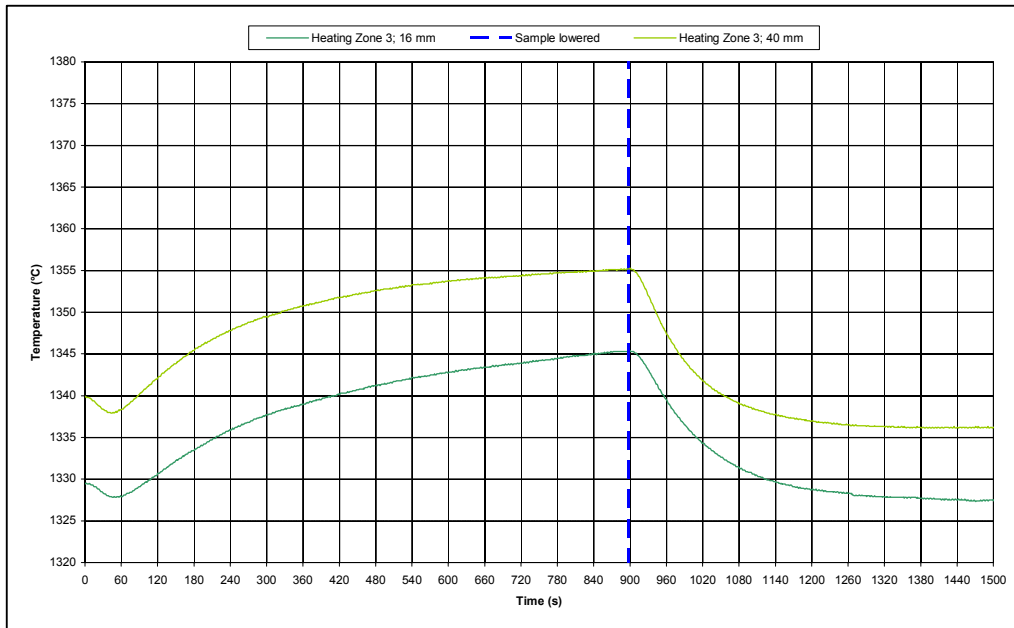


Fig. 35 (a): %CO/(%CO+CO₂) in product gas: 15 minute reaction time at 1400°C furnace temperature for 40 mm material layer

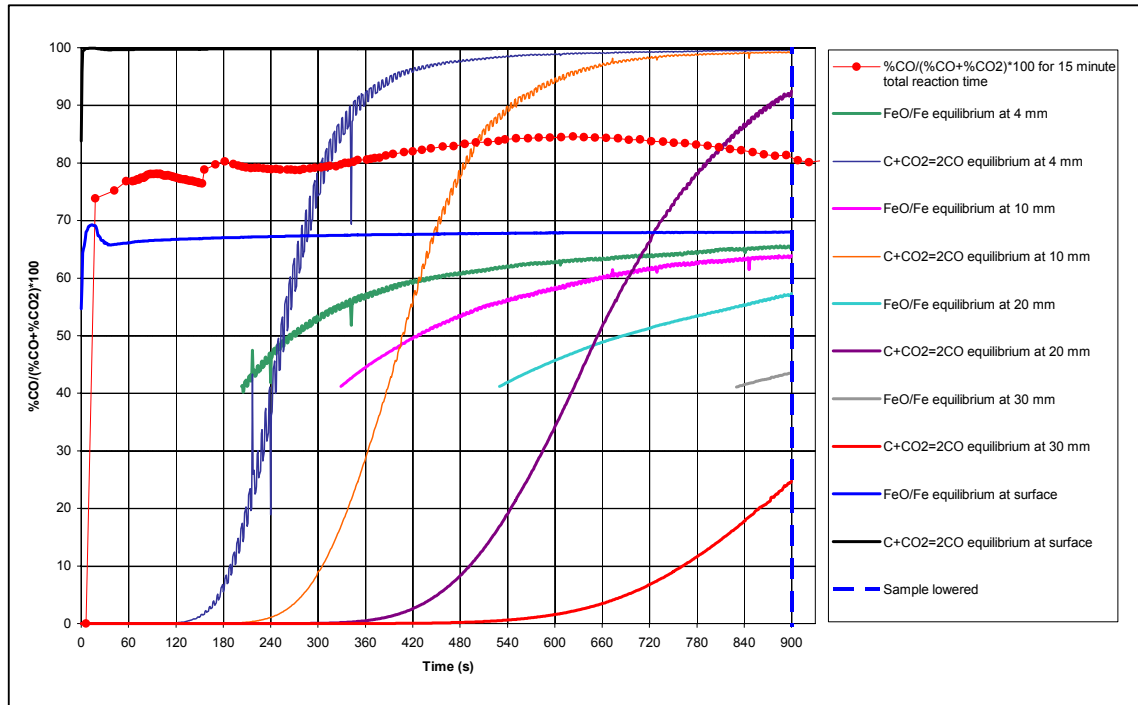


Fig. 35 (b): %CO/(%CO+CO₂) in product gas: 15 minute reaction time at 1400°C furnace temperature for 16 mm material layer

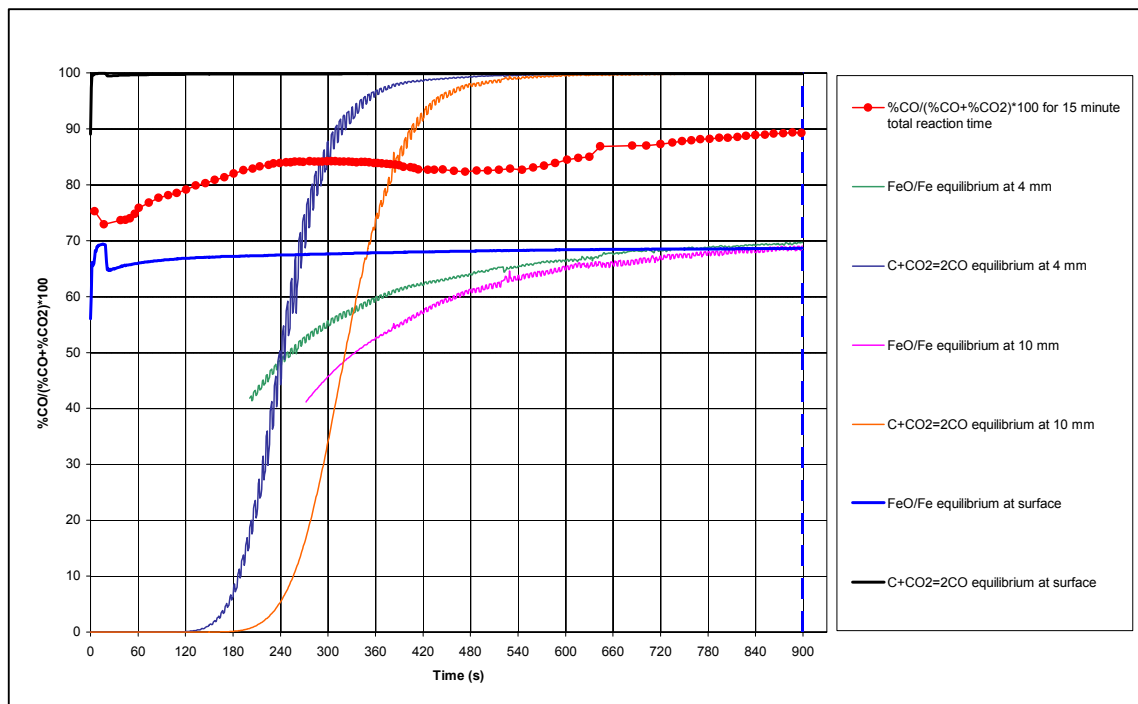


Fig. 36: Comparison %Reduction in top segment of 40 mm material layer vs. 16 mm material layer
(Top segment of 40 mm material layer is 18 mm)

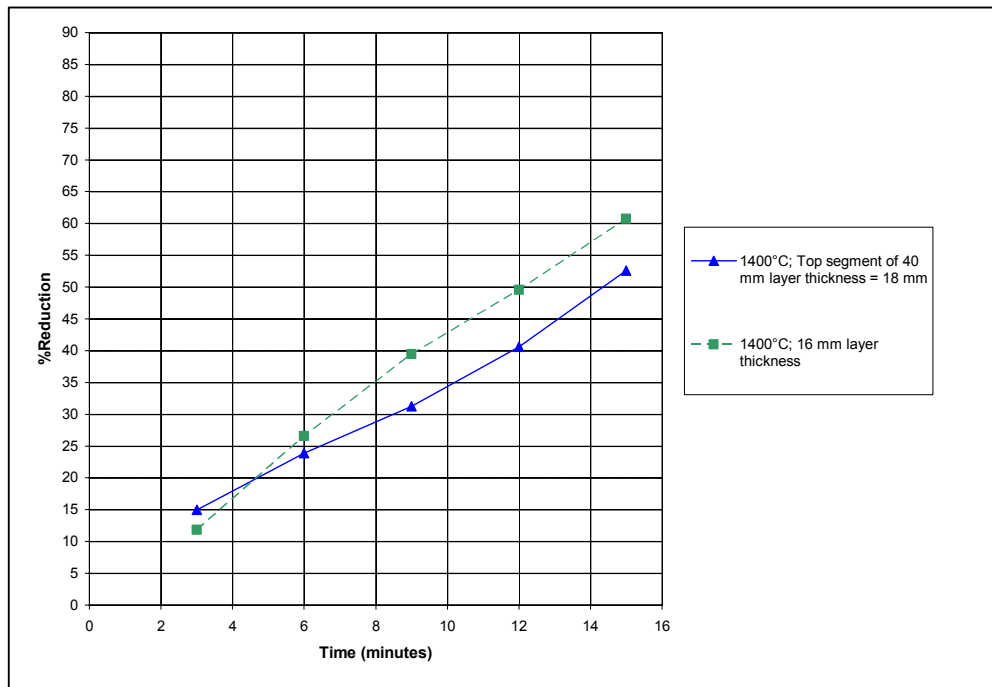


Fig. 37 (a): Comparison %Carbon for top segment of 40 mm to 16 mm material layer thickness

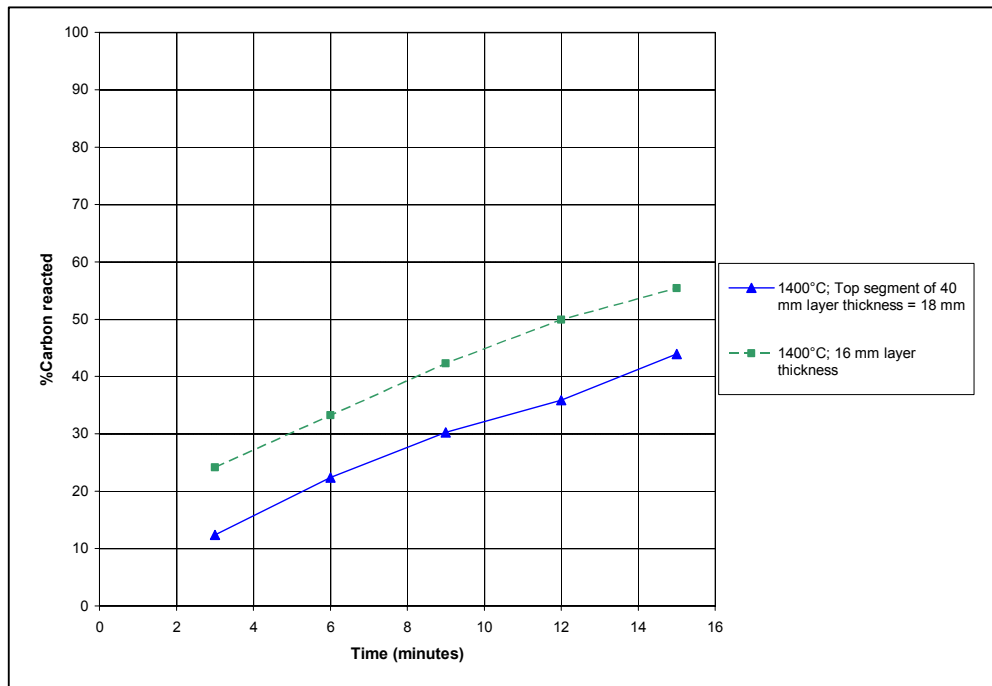


Fig. 37 (b): Comparison mass carbon for top segment of 40 mm to 16 mm material layer thickness

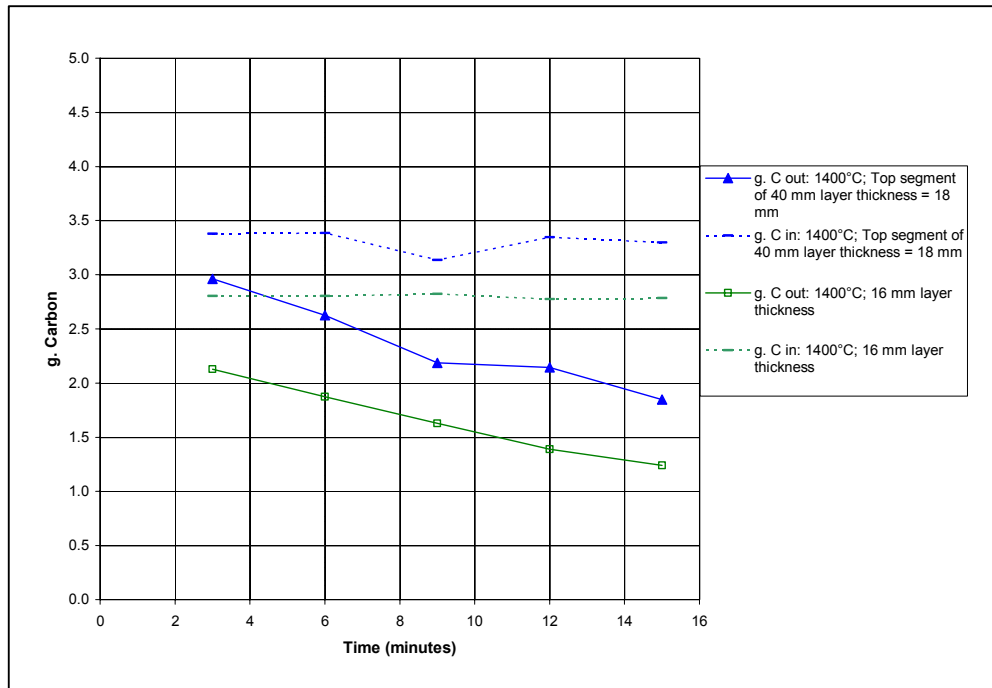
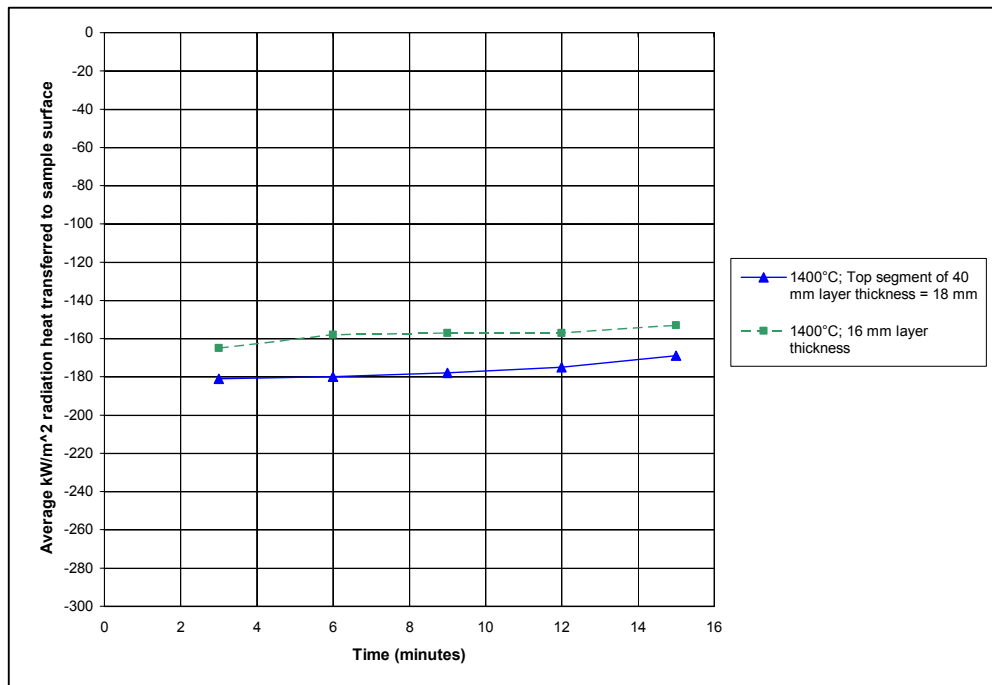


Fig. 38: Average radiation heat transfer to sample surface: Top segment of 40 mm material layer vs. 16 mm material layer



3.4. Effect of Volatiles in Coal

The composition and flow rate of the gas product released from the heap surface are important input information for the process energy balance. The contribution of coal devolatilisation to the product gas was isolated by heating coal-alumina samples instead of coal-ore samples. This approach has been used by Dey *et al.* (1993), Wang *et al.* (1997, 1998), Dutta and Gosh (1994), Sohn and Fruehan (2006a). The coal-alumina samples were heated until negligible volatile content was observed in the product gas analyses. The volatile components in the product gas for coal reacted at different furnace temperatures are shown in **Fig. 44-46**, with the associated material bed temperatures. Although the product gas analyses show that the coal volatiles consisted largely of hydrogen on volume basis, the hydrogen portion decreases from 26 mass% at 1300°C furnace temperature to 12 mass% and 13 mass% at 1400°C and 1500°C furnace temperature as the mass of CO and CO₂ increased with increasing furnace temperature. Negligible methane was measured in the product gas. This does not mean that methane is not one of the devolatilisation products as carbon deposition onto the crucible walls was observed whenever coal was reacted. An example of carbon deposition is shown in **Fig. 39**, compared to samples of char-ore mixtures reacted under the same conditions, shown in **Fig. 40**.

The molar quantities of product gas for the total reaction time, at each heating zone temperature, are shown in **Fig. 41**, indicating increased H₂, H₂O and CO release with increased reaction temperature. The endpoint reaction temperatures in the coal-alumina material layer, shown in **Fig. 44-46**, is in excess of 900°C, indicating that devolatilisation should be complete in the samples. The total mass of carbon reporting to the product gas is shown in **Fig. 42**, as calculated from the product gas analyses and the carbon analyses of the devolatilised sample. The mass carbon to gas for devolatilisation, shown in **Fig. 42**, corresponds well for 1500°C, and not well for 1300°C and 1400°C. The calculations of mass loss to the gas, as shown in **Fig. 43**, correspond better for reaction at 1300°C and 1400°C, but not for 1500°C. Coal volatile content values calculated from the mass loss measured are 24%, 31% and 28% at 1300°C, 1400°C and 1500°C vs. 14%, 32% and 64% calculated from the product gas analyses. The increased volatile gas release with increased reaction temperature and increased heating rates has been reported in literature (Desypris *et al.*, 1982).

Fig. 39: Carbon deposition on crucible walls for coal-ore samples



Fig. 40: No carbon deposition on crucible walls for char-ore samples



Fig. 41: mol to gas in coal devolatilisation

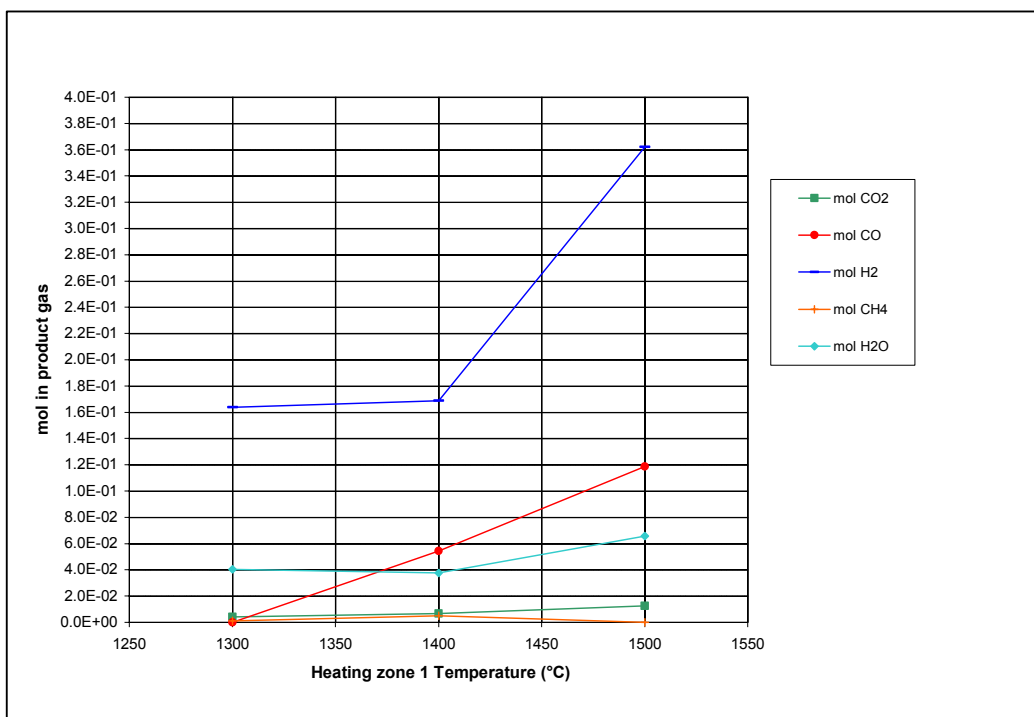


Fig. 42: Mass carbon to product gas in coal devolatilisation

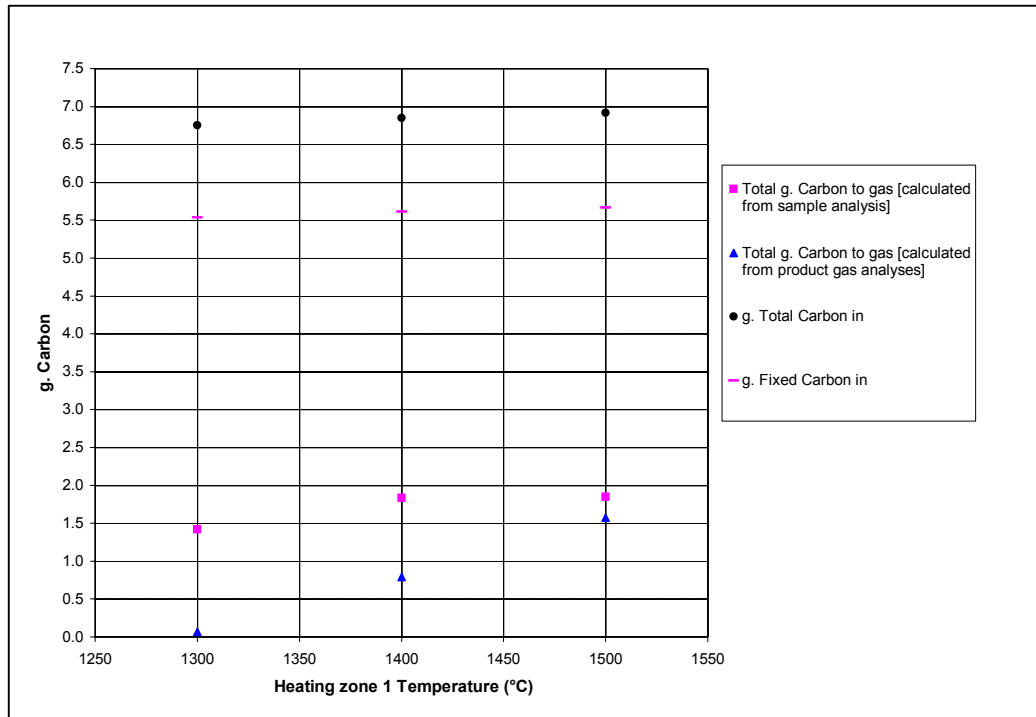
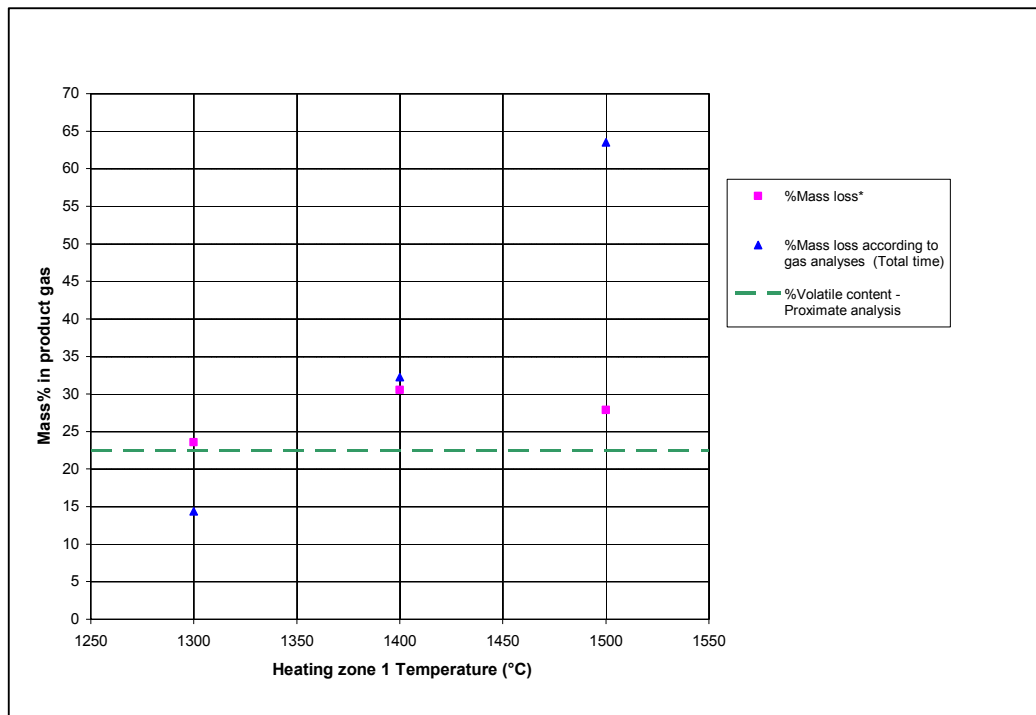
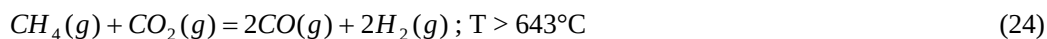
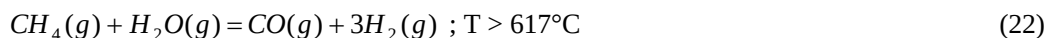


Fig. 43: Mass% of initial mass coal to product gas in coal devolatilisation



*Mass loss = (mass in) – (mass out); (mass in) calculated from alumina mass balance; (mass out) calculated from sample mass measured after sample split and then corrected for fibreboard carry over.

The following reactions are possible reactions of devolatilisation in the absence of oxygen. The temperatures at which the forward reaction can take place according to thermodynamics are indicated below; the thermodynamic calculation data is shown in **Appendix XII**.



(s) = solid material

(g) = gas phase material

The picture in **Fig. 39** shows that the carbon deposition profile along the height of the crucible extended further down the crucible with increased reaction time. This indicates that carbon deposition is associated with increased temperature via reaction (23) and (26) not via reaction (27). Further indication that carbon deposition is not due to reaction (27), as the sample was cooled, is that the picture in **Fig. 40** for ore-char samples shows no deposited carbon.

For devolatilisation at 1300°C heating zone 1 temperature, as shown in **Fig. 44**, the absence of CO and/or CH₄ in the product gas indicates that the only reactions that proceeded significantly are H₂ formation from reaction (23) forward and/or direct H₂ release from coal. The small quantities of CO₂ formed indicate that reaction (25) did not proceed to a significant extent. Devolatilisation at 1400°C and 1500°C is more complex because CO is present in the product gas. As is the case for devolatilisation at 1300°C, no significant quantity of CH₄ is present in the product gas.

The CO can be the product of reactions (22), (24), (26) and (27) at temperatures below 848°C. **Fig. 45** and **Fig. 46** show the H₂/CO ratio in the product gas, and the time at which changes in the H₂/CO ratio took place are indicated by vertical broken lines. The corresponding time markings are indicated on the material temperature graphs, adjusted for the residence time of gas in the furnace set-up. For reaction at 1400°C this ratio is initially higher than four, and then levels off to a value of three until a dip in the ratio at 799 seconds, indicated by the vertical broken green line in the product gas composition graph. The ratio of three indicates that reaction (22) is the dominant reaction. At 927 seconds, indicated by the vertical broken pink line, the H₂/CO ratio recovers to 3 and continues to increase beyond this value to the end of the devolatilisation.

For devolatilisation at 1500°C furnace temperature the H_2/CO ratio is close to three from the beginning of reaction. Three changes in the H_2/CO ratio are indicated by the time markings on the gas composition and bed temperature graphs. The first change is a slight increase in the H_2/CO ratio at 720 seconds on the product gas composition graph, indicated by the vertical broken red line, and can be explained by the bottom segment temperature reaching 551°C to release H_2 from the decomposition of CH_4 , reaction (23). Then the H_2/CO ratio increases to four, and suddenly drops back to three at 912 seconds, indicated by the vertical broken green line. At 1011 seconds the H_2/CO ratio increases as the product gas CO content decrease more quickly than the H_2 product gas content. The latter effect can only be explained from reaction (23) because this is the only reaction to form H_2 alone.

From the above the conclusion is that significant H_2 is released in coal devolatilisation over 3-15 minute reaction periods of coal containing material layers of 40 mm reacted at 1300, 1400 and 1500°C furnace temperatures. The release of H_2 is due to decomposition of CH_4 and/or direct release of H_2 from the coal.

Fig. 44 (a): Coal devolatilisation in coal-alumina sample reacted at 1300°C: Temperatures
 (Horizontal temperature lines for reactions (22) to (27) indicates the equilibrium temperatures)

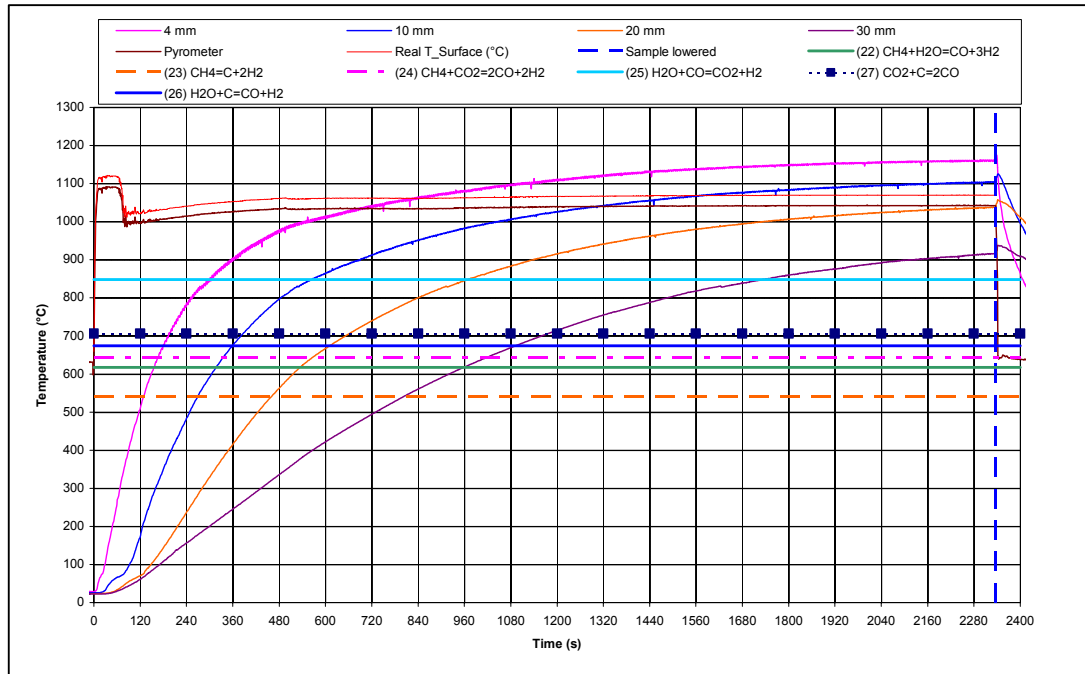


Fig. 44 (b): Coal devolatilisation in coal-alumina sample reacted at 1300°C: Product gas

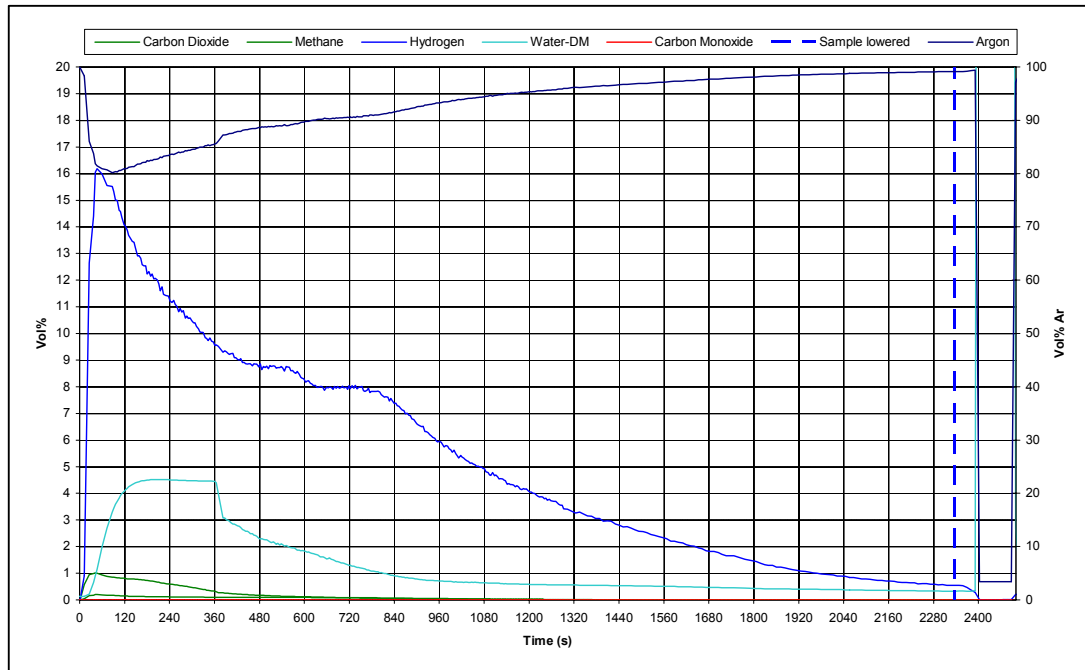


Fig. 45 (a): Coal devolatilisation in coal-alumina sample reacted at 1400°C: Temperatures
 (Horizontal temperature lines for reactions (22) to (27) indicates the equilibrium temperatures)

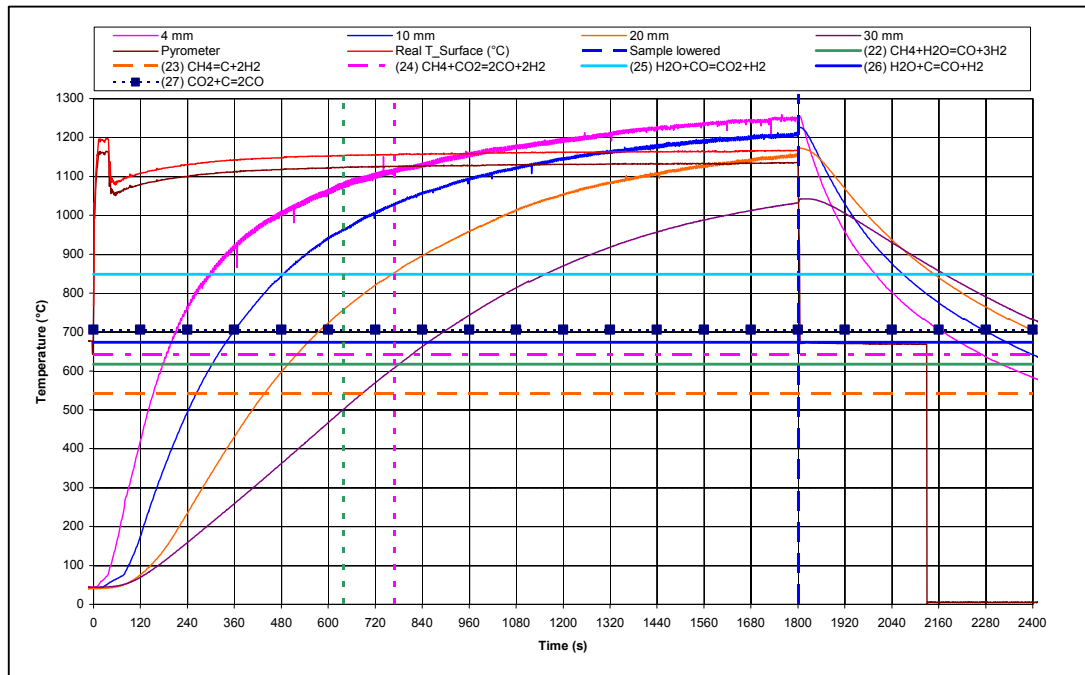


Fig. 45 (b): Coal devolatilisation in coal-alumina sample reacted at 1400°C: Product gas

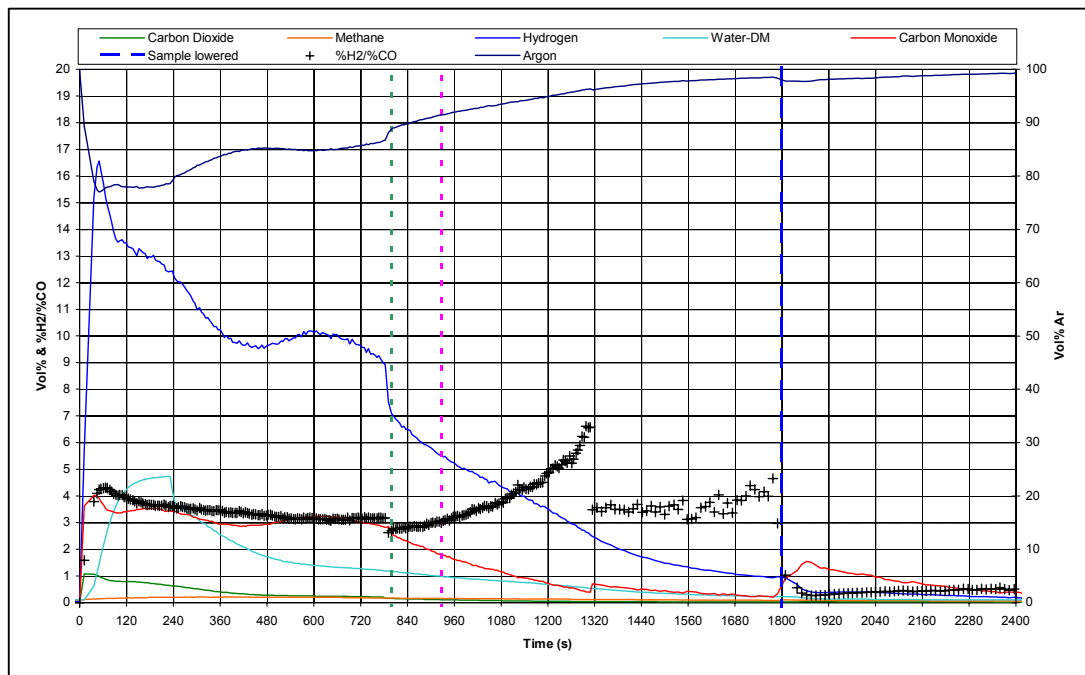


Fig. 46 (a): Coal devolatilisation in coal-alumina sample reacted at 1500°C: Temperatures
 (Horizontal temperature lines for reactions (22) to (27) indicates the equilibrium temperatures)

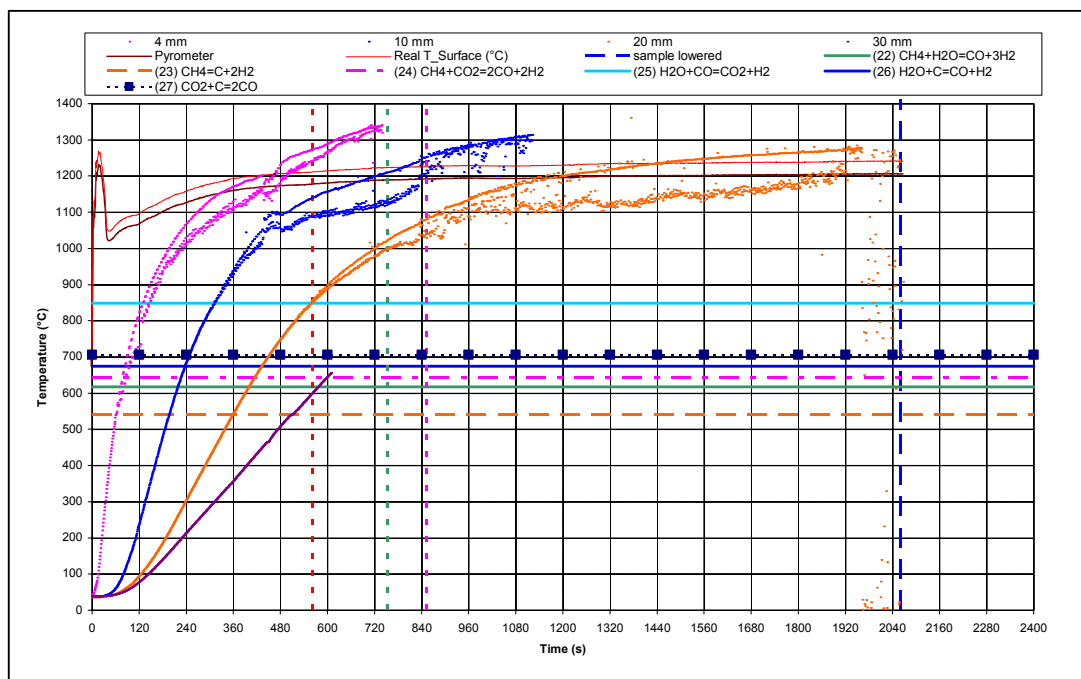
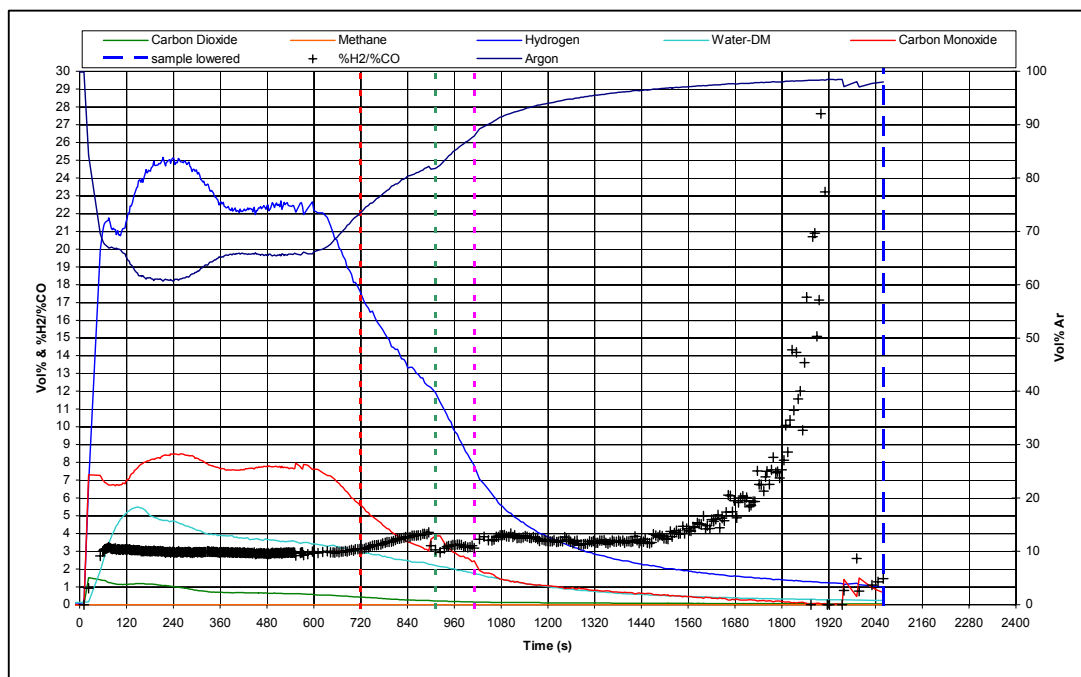


Fig. 46 (b): Coal devolatilisation in coal-alumina sample reacted at 1500°C: Product gas



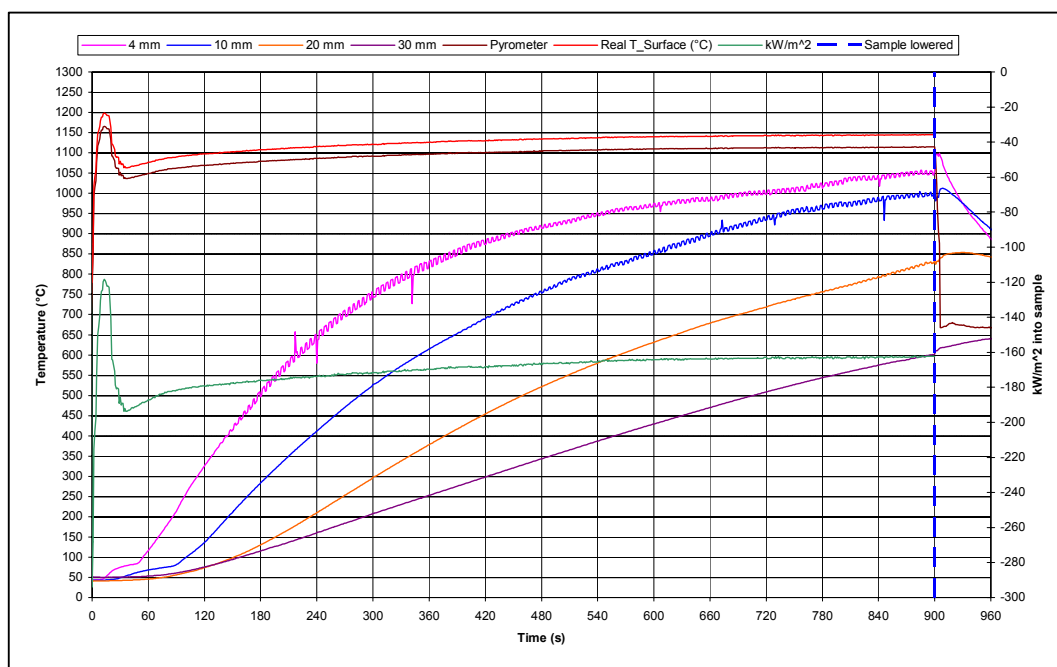
The effect of volatiles on reduction extent has been tested by reaction of char instead of coal as reductant. Comparative sample bed temperatures and product gas analyses are shown for 15 minutes reaction time in **Fig. 47 and 48**. Material bed temperatures in the char containing sample are higher than that for the coal containing sample. The temperature difference can not be uniquely ascribed to the effect of the heat of devolatilisation because the heat of devolatilisation has been found to vary from endothermic to exothermic by 200 kJ/kg parent coal, even for coal of similar composition (Tomeczek and Palugniok, 1996). The difference in material bed temperatures is because of more heat used in reduction work and less heat used to heat up the material layer in the coal containing sample, as compared to a reversal of this heat proportioning in the char containing sample.

The sample surface temperatures for coal containing samples show an apparent increase within the first minute of reaction. This effect is absent when char is used instead of coal. The increased measured temperature is a result of the initial release of volatiles, forming a gas cloud which shielded the radiation seen by the pyrometer, from the sample surface. This was confirmed by video material recorded through an enlarged view hole when a sample of -2000 +1400 μm ore and coal was reacted at 1400°C heating zone one temperature. Snapshots taken from the video material are shown in **Fig. 49**.

Reduction extent for each sample segment is shown in **Fig. 50**, showing that reduction by volatiles does take place for a stagnant bed of material mixture. The composite carbon consumption and reduction levels are shown in **Fig. 51 (a) and (b)**.

Fig. 47: Sample temperatures of Coal vs. Char as reductant

(a) Coal-Ore reacted at 1400°C furnace temperature





(b) Char-Ore reacted at 1400°C furnace temperature

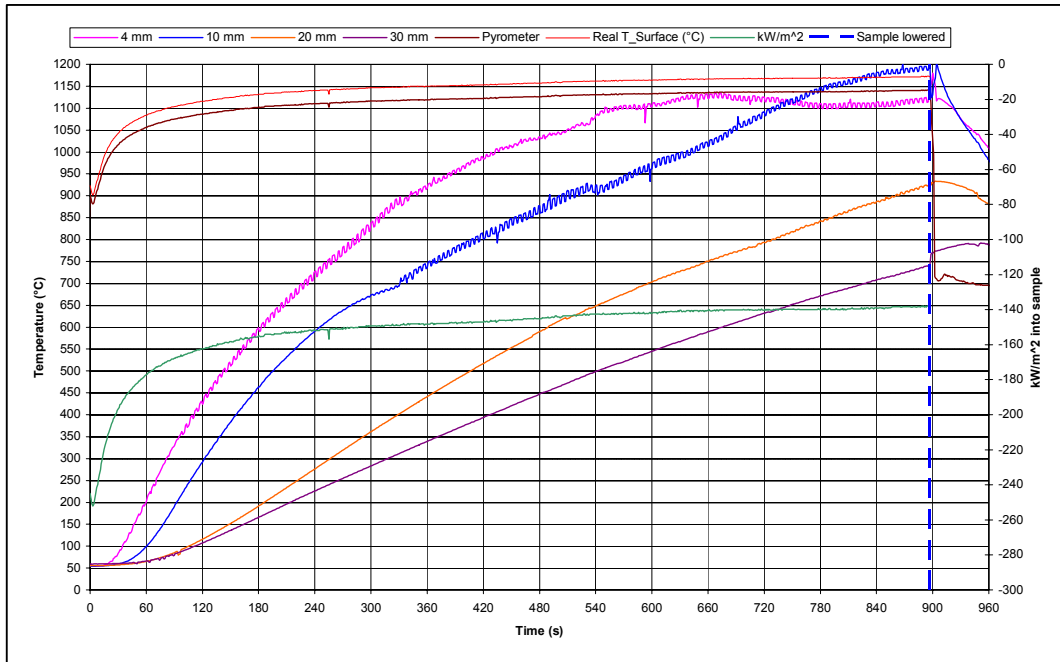
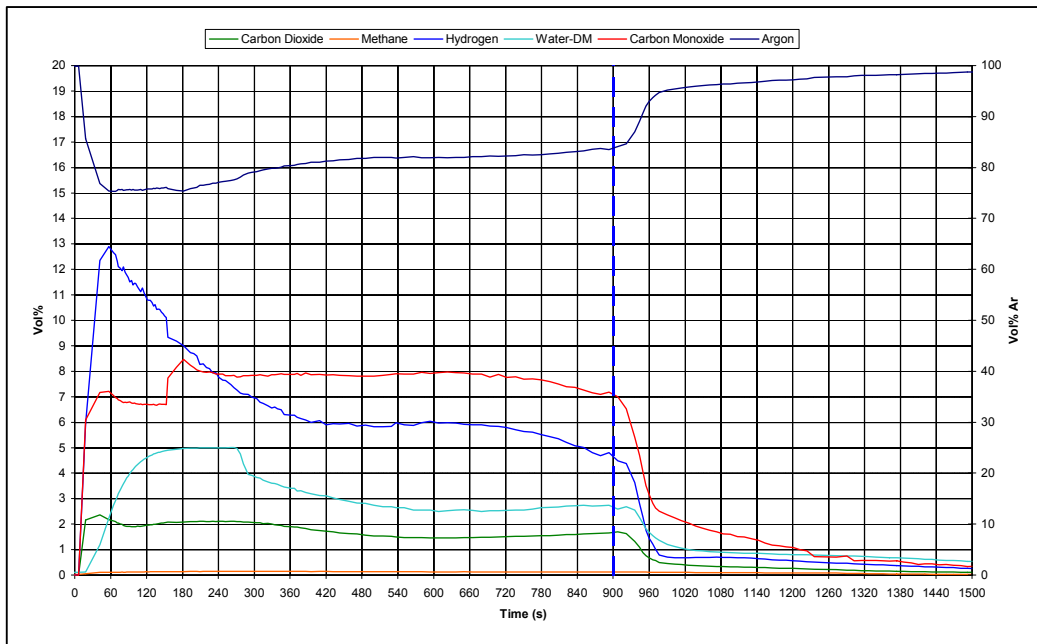


Fig. 48: Product gas for Coal vs. Char as reductant

(a) Coal-Ore reacted at 1400°C furnace temperature



(b) Char-Ore reacted at 1400°C furnace temperature

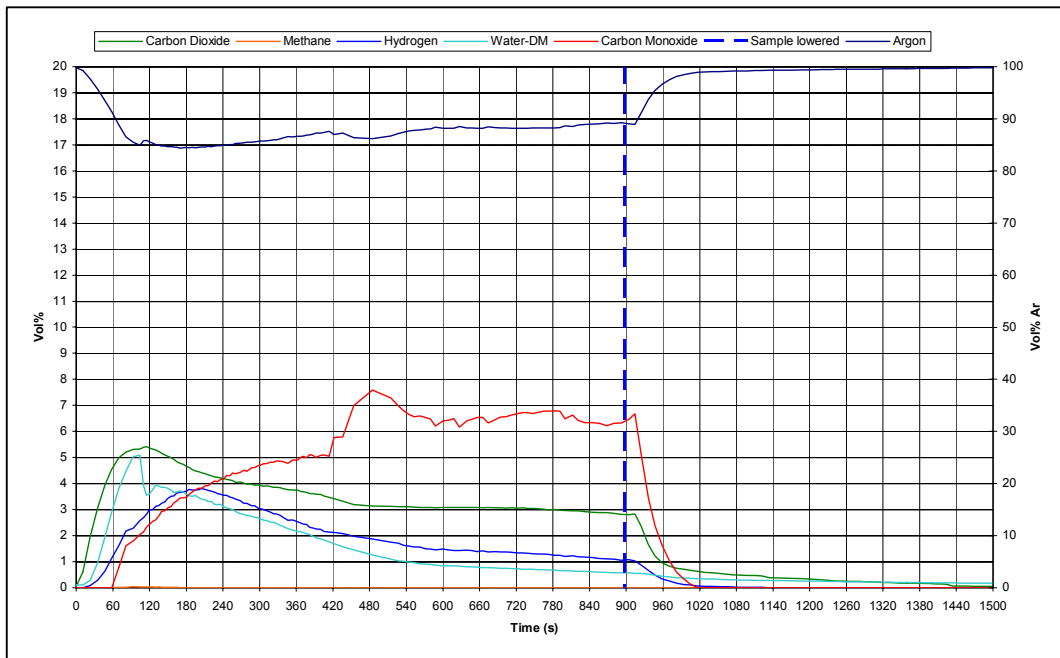
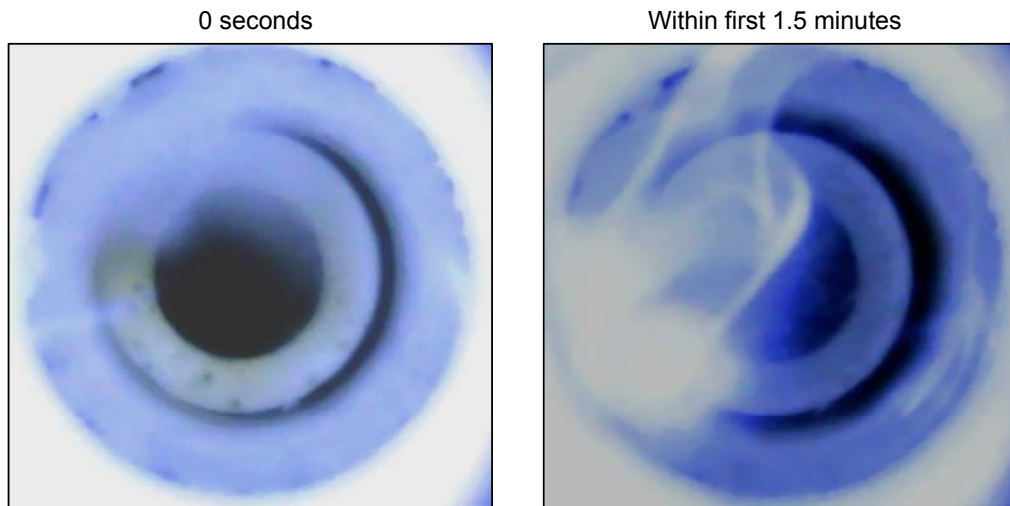
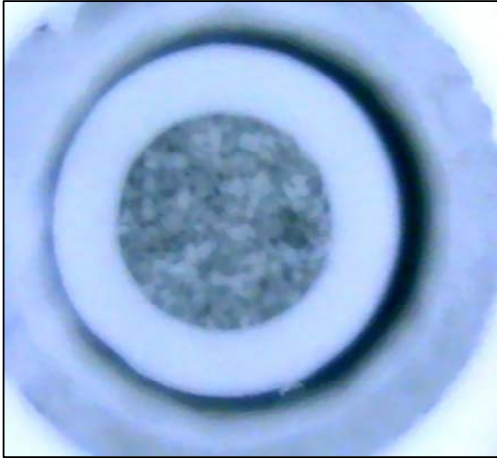


Fig. 49: Snapshots from video material for -2000 +1400 μm ore and coal reacted at 1400°C heating zone1 temperature



1.5 minutes



9.5 minutes



Fig. 50: %Reduction for Coal vs. Char as reductant

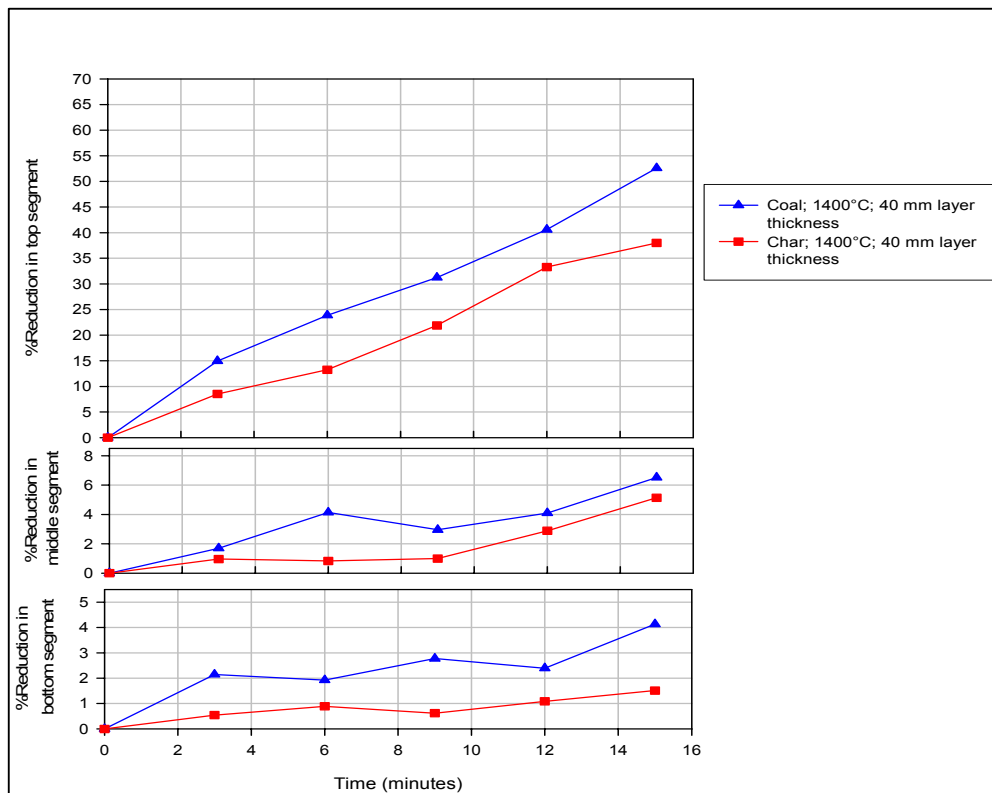


Fig. 51 (a): Composite %Carbon consumption for Coal vs. Char as reductant

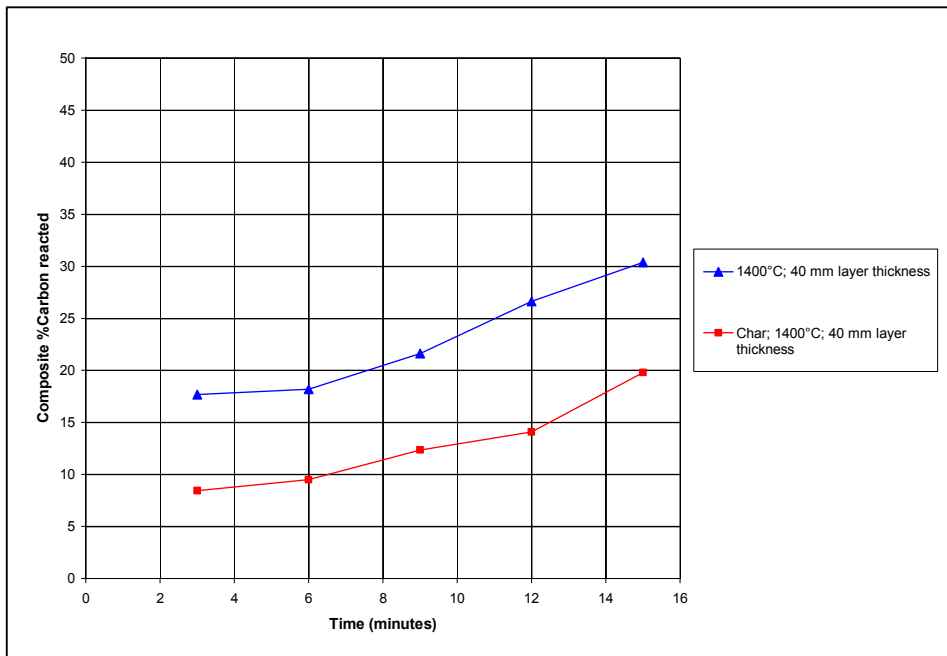
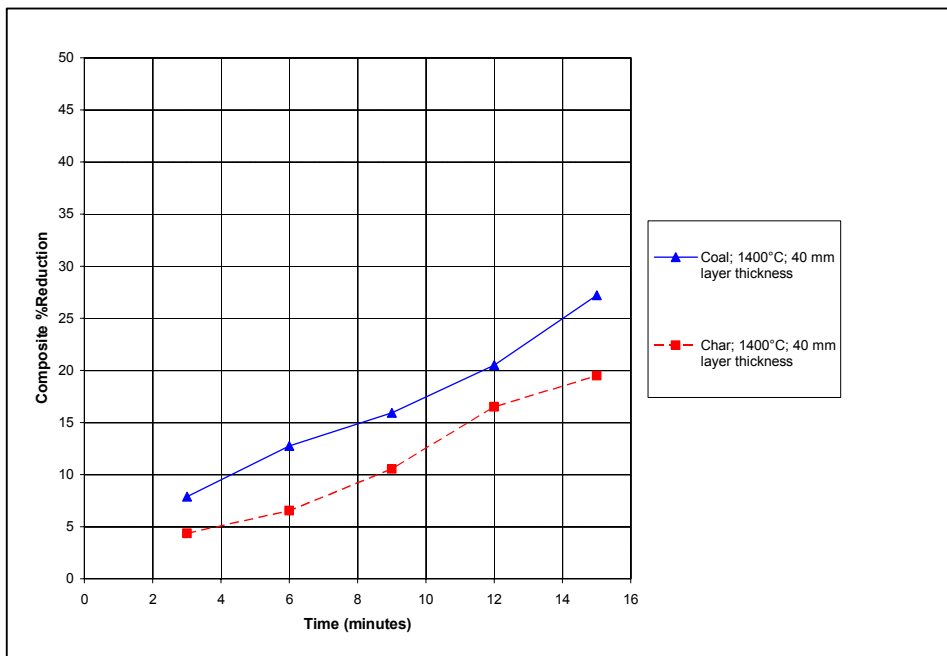


Fig. 51 (b): Composite %Reduction for Coal vs. Char as reductant

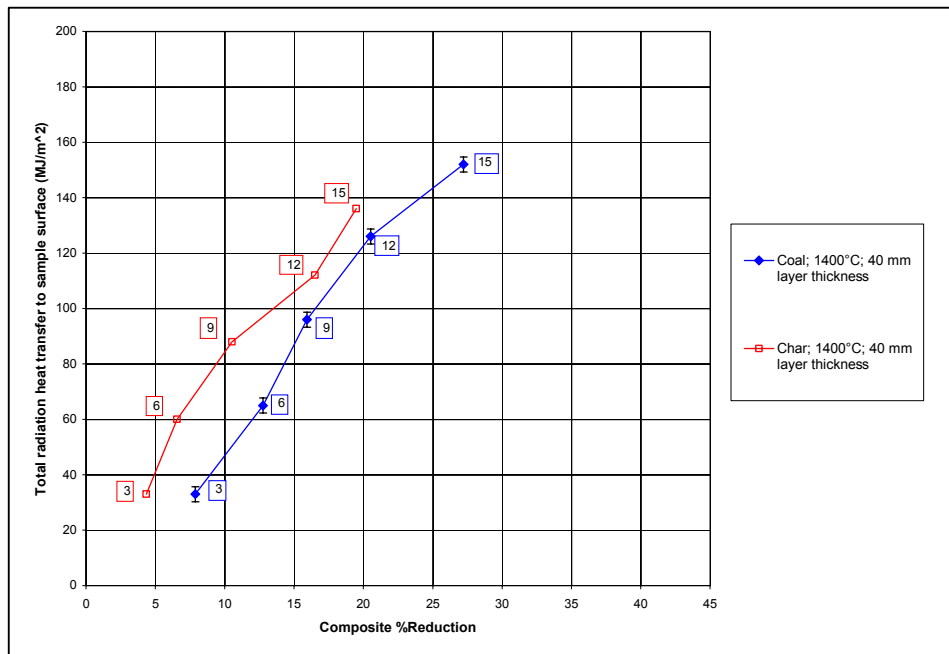


In **Fig. 52** data of the total heat transferred to the sample vs. composite reduction extent is shown. Heat transferred to the coal-ore sample is higher than heat transferred to the char-ore sample, for the same reaction time because the coal-ore sample surface temperatures were lower than that of the char-ore sample surface. The total heat demand in reaction of a coal-ore sample did not exceed the total heat demand for reaction of a char-ore sample to attain the same level of composite reduction. The possible effect of exothermic or endothermic heat of coal devolatilisation on heat transferred to the sample surface is shown as error bars in **Fig. 52**, 200 kJ/kg parent coal (Tomeczek and Palugniok, 1996). The higher reduction extent achieved in the coal-ore samples at equivalent energy input to the sample is most probably because the release of coal volatiles results in more reducing conditions beyond reduction to magnetite in the material layer at lower temperatures, as compared to $\sim 700^{\circ}\text{C}$ required in the char-ore samples to generate reducing conditions with CO from the gasification reaction. This is in agreement with the work of Sohn and Fruehan (2006b), for a bed of three layers of composite pellets reacted at 1000°C bed surface temperature, which showed significant reduction of the top pellet layer from coal volatiles released from the bottom layer of pellets.

In this study the reduction work done by coal volatiles, primarily hydrogen, released at low material layer temperatures resulted in higher reduction rates in coal-ore samples as compared to char-ore samples. The percentage reduction gain of 4% to 8% for 3 to 15 minutes reaction time was achieved in a stagnant material layer. However, the extent to which this advantage is realised in practice would depend on the process details. For example, if the material is fed through the hot furnace freeboard the coal will devolatilise at least in part and the percentage reduction gain from coal volatiles will be partially reduced, or eliminated. Alternatively the material mixture can be fed to through the furnace sidewalls to gain maximum contribution of coal volatiles in reduction. From the results it is clear that significant reduction by coal volatiles takes place in a mixed coal-ore bed heated uni-directionally from the sample surface. As discussed previously with reference the SL/RN process, in Chapter I, the effect of lowered bed temperature with more reactive reductant used is also observed here for coal vs. char as reductant.

Fig. 52: Total radiation heat transferred vs. Composite %Reduction

(Number inside square frame shows reaction time in minutes)



3.5. Phase chemistry of Metal and Oxide Phases

Duplicate samples were reacted for 15 minutes reaction time at 1300°C, 1400°C and 1500°C furnace temperatures and set in epoxy, polished and viewed under reflected light. The photomicrographs taken under reflected light are shown in **Fig. 53 to 55**, and clearly show the variability of reaction of the ore in the top and middle segments. Because the ore contained variable amounts of gangue, and was of variable porosity, ore particles exposed to the same conditions of temperature and reducing atmosphere, showed different degrees of reduction and metallisation. These observations show that this ore does not reduce according to a single rate mechanism. In **Fig. 54 (a)** and **Fig. 55 (a)** extensive metal rim formation is seen around the edge of the reduced ore particle, and the interior is filled with slag and rounded wustite grains. Therefore, the top segment material of the samples reacted for 15 minutes at 1400°C and 1500°C no longer follow exclusively solid state reduction, but are in a semi-molten state. The coal particles also show variable extent of devolatilisation. In **Fig. 55 (b)** some of the coal still has an even texture, whilst the largest coal particle has already reacted somewhat. In the top segment of a sample that has significant metallisation, **Fig. 55 (a)**, the coal has been totally devolatilised, and the carbon skeleton consumed extensively in reduction reactions. The reacted ore and coal features in these photomicrographs clearly show the variability in reaction mechanism for both ore and coal.

The metal product carbon content is important where the aim is to make steel, not hot metal. If the carbon content in the metal product at the heap surface is high, metal refinement is required in the rest of the process zones. The polished sections shown in **Fig. 53-54** were etched with 2% Nital solution to show up the presence of pearlite, indicating carbon content in excess of 0.025%C solubility limit in ferrite. The polished sections were viewed and analysed using a JSM-6300 SEM (Scanning Electron Microscope) at 15 kV and 200 second counting interval. The analysed areas are shown in **Fig. 56-58**. It is seen from the images that no second phase is present in the metal product, indicating that the metal product is ferrite. This is possible because the proximity of carbon to the metal product is not close in the packed bed as seen in **Fig. 53-55**, and there is no carbon deposition onto the metal product. The other interesting observation from the metal analyses is the absence of sulphur, indicating that sulphur pick-up must take place elsewhere in the process.

As is seen from **Fig. 53 (a) and (b)** much variability in reduction is seen for the sample reacted at 1300°C furnace temperature and only a few ore particles were reduced to metal. The metallised ore particles were not restricted to the top segment in the sample. Here two areas with metallised ore particles, in the sample reacted at 1300°C, were analysed for comparison with the analyses of the samples reacted at 1400°C and 1500°C. The ore particle in **Fig. 56 (a)** contained little gangue material and the ore particle is of high porosity so that metallisation occurs throughout the particle and little or no glass phase is formed. In contrast **Fig. 56 (b)** shows metallisation at the ore particle edge and glass phase at the ore particle interior due to high gangue content in the ore particle initially and associated low initial ore particle porosity. Wüstite grains (light grey rounded grains) are embedded in the glass phase. The phase morphology seen in **Fig. 56 (b)** is also seen extensively in the top segments of the samples reacted at 1400°C and 1500°C heating zone 1 temperatures as shown in **Fig. 57** and **Fig. 58**.

Fig. 53 (a): 1300°C furnace temperature; 15 minutes; 40 mm layer, top segment
(C=Coal; O=Ore)

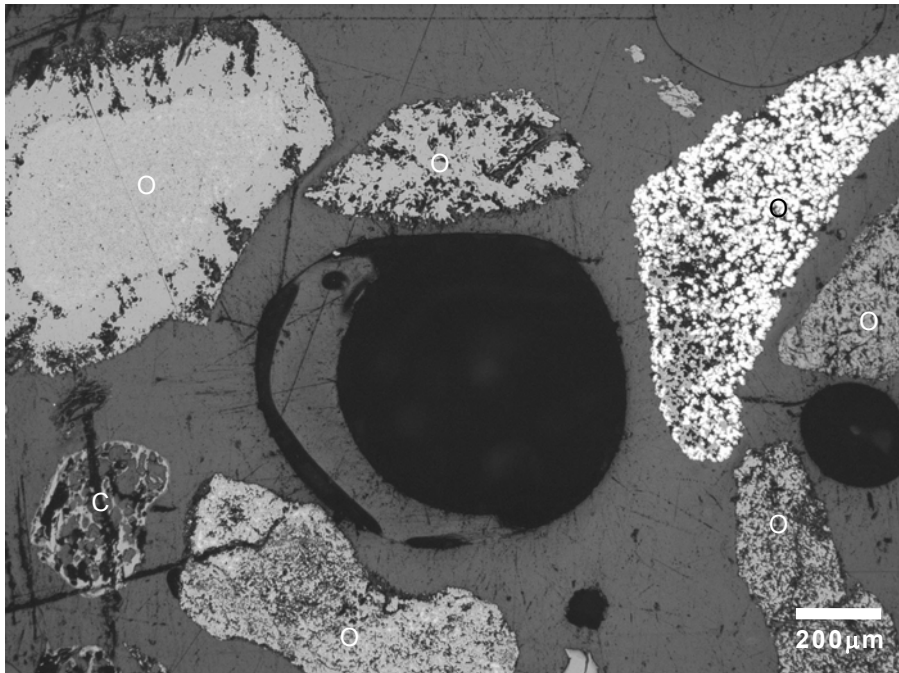


Fig. 53 (b): 1300°C furnace temperature; 15 minutes; 40 mm layer, middle segment
(C=Coal; O=Ore)

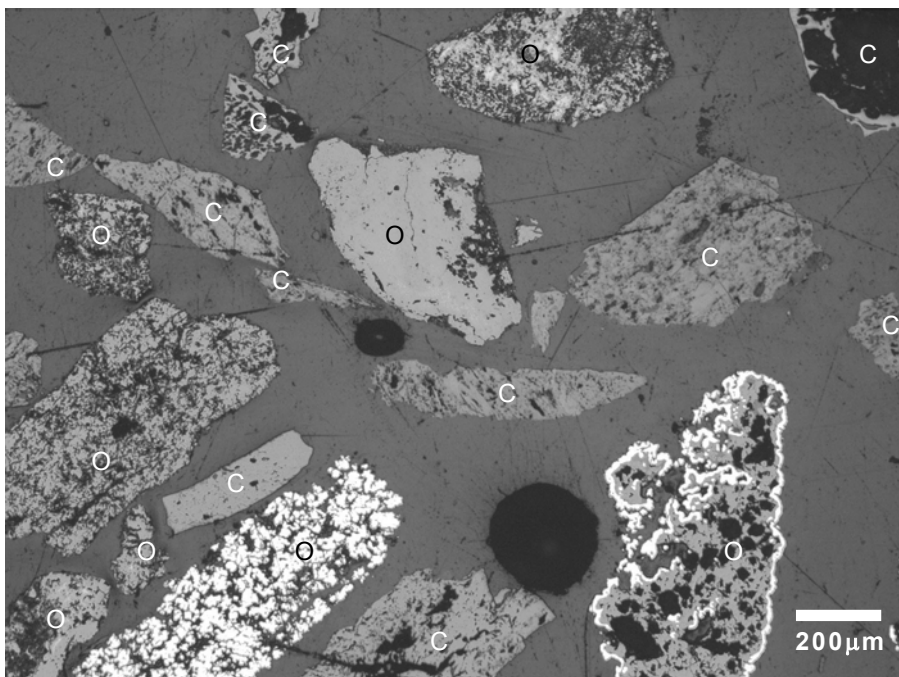


Fig. 54 (a): 1400°C furnace temperature; 15 minutes; 40 mm layer, top segment
(C=Coal; O=Ore)

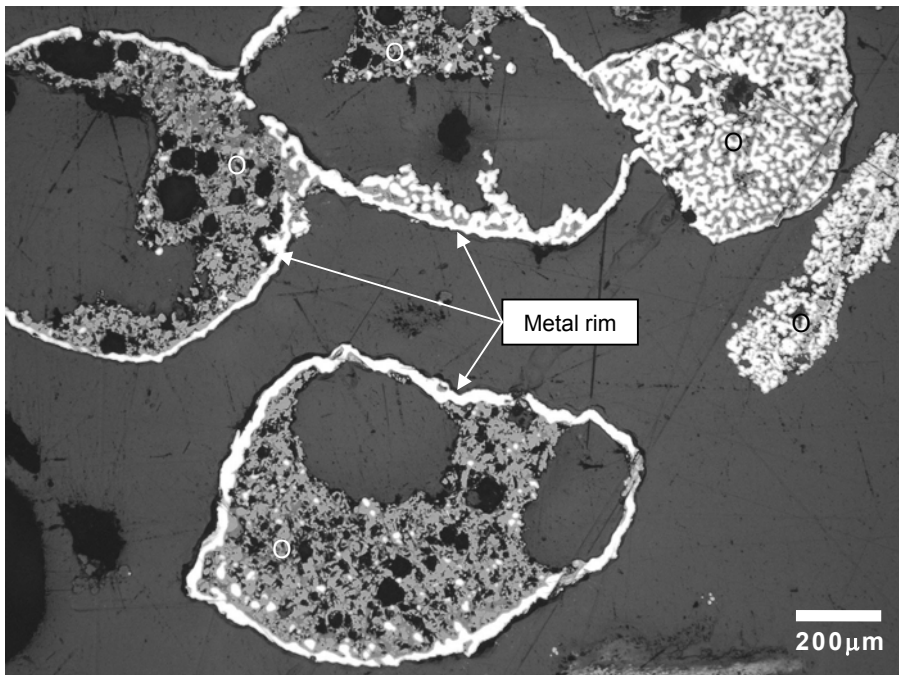


Fig. 54 (b): 1400°C furnace temperature; 15 minutes; 40 mm layer, middle segment
(C=Coal; O=Ore)

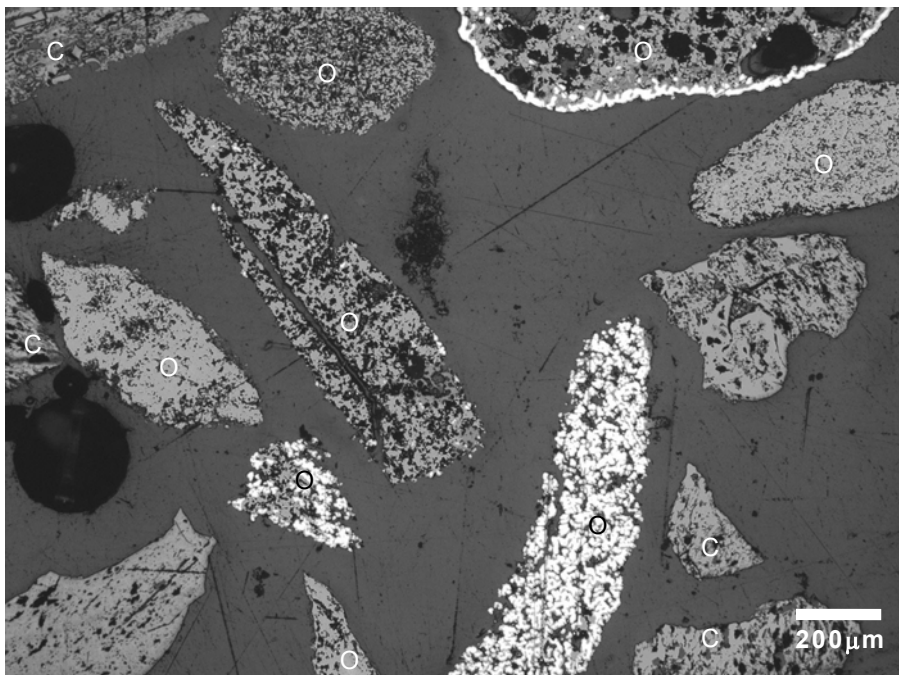


Fig. 55 (a): 1500°C furnace temperature; 15 minutes; 40 mm layer, top segment
(C=Coal; O=Ore)

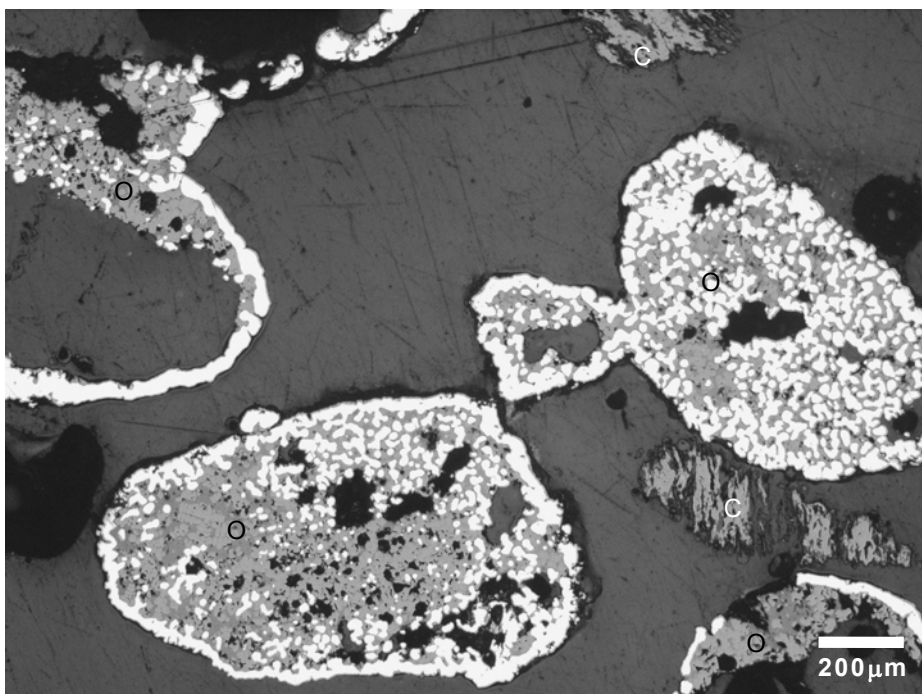
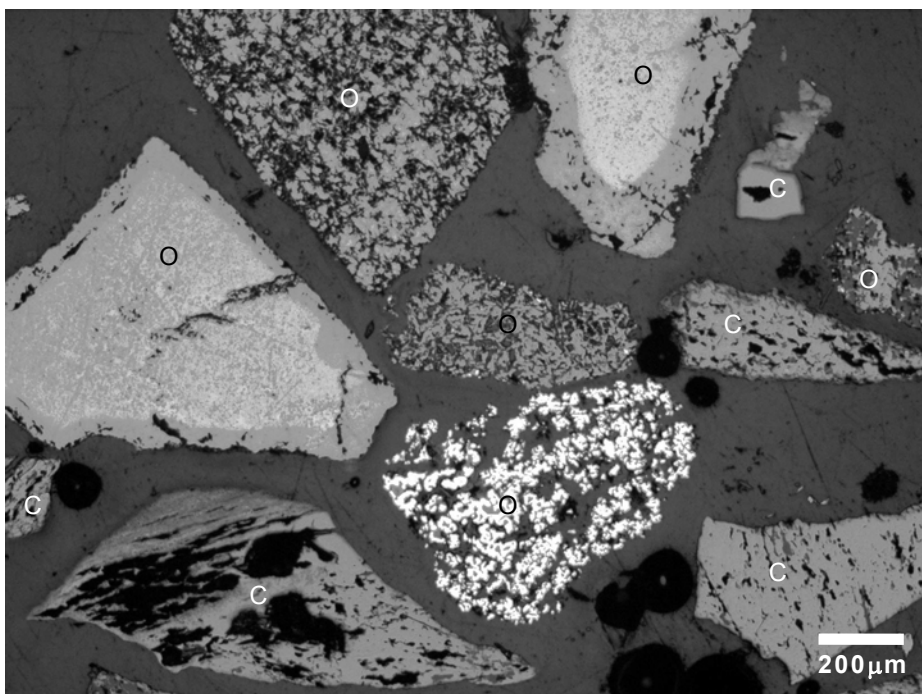
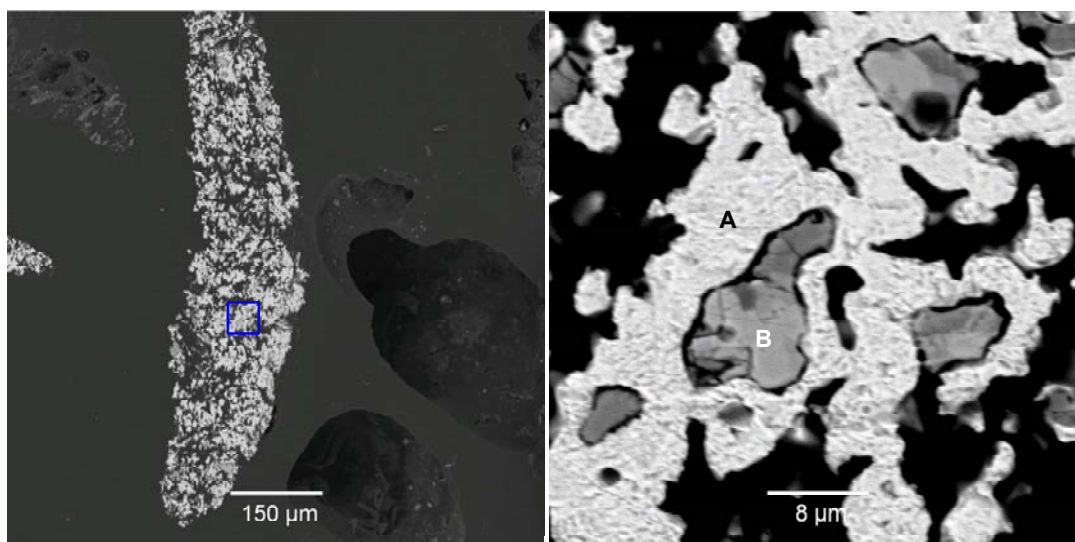


Fig. 55 (b): 1500°C furnace temperature; 15 minutes; 40 mm layer, middle segment
(C=Coal; O=Ore)



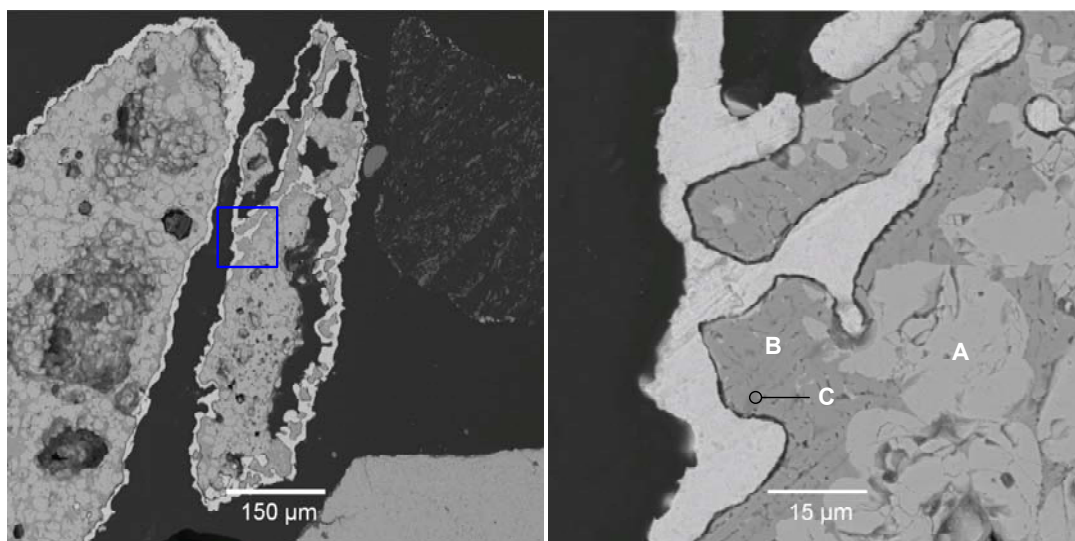
The analyses from **Fig. 58 (a)** show that the oxide phases consist of FeO (light grey rounded grains) and silicate needles initially. The composition of the needles corresponds to the stoichiometry for Fayalite, $2\text{FeO} \cdot \text{SiO}_2$, with a liquidus temperature of 1208°C and solidus temperatures of 1175°C associated with FeO, and 1180°C associated with silica. The sample surface temperature is $\sim 1250^\circ\text{C}$ whilst the sample bed temperature 10 mm from the sample surface is $\sim 1160^\circ\text{C}$. Therefore, the silicate phase could have been liquid at the sample temperatures, but not the FeO areas because the lowest solidus temperature for FeO is 1371°C . This is important because the lowered oxide liquidus temperature limits the maximum temperature to which the heap surface can be heated without bulk melting. This is a function of the gangue component in the ore so that use of a higher quality ore will allow for higher heap surface temperatures. The silicate glass composition changes from higher FeO content initially to lower FeO content as the FeO grains are reduced. The lower FeO content in the silicate glass is seen from **Fig. 58 (b)**. As shown in **Fig. 57 (a) and (b)**, similar phase morphology is seen in the top segment of the sample reacted for 15 minutes at 1400°C . The glass phase analyses shown in **Fig. 56 (b)**, **Fig. 57 (a) and (b)** and **Fig. 58 (b)** are all similar in composition to the silicate needles' composition in **Fig. 58 (a)** with the stoichiometry of Fayalite, $2\text{FeO} \cdot \text{SiO}_2$. However, the material layer surface temperatures were 1084°C , 1145°C and 1256°C for the samples reacted at heating zone 1 temperatures of 1300°C , 1400°C and 1500°C . The liquidus temperature of Fayalite is 1208°C and the solidus 1175°C . Melting of Fayalite could only take place at 1084°C and 1145°C because of the presence of Fe^{3+} in the Fayalite and/or substitution of minor elements such as K, Na, P into the glass phase to reduce the liquidus and solidus temperature. The partial oxygen pressures for the CO/CO₂ values were calculated at the sample surface temperatures of 1084°C , 1145°C and 1256°C to be 4×10^{-12} , 3×10^{-11} and 2×10^{-9} atm. At these partial oxygen pressures Fe^{3+} should be present in the glass phase. Glass phase formation within ore particles should be avoided as it results in decreased porosity resulting in metallisation restricted to the glass phase boundary, as seen above. Furthermore, bulk melting of ore should be avoided because energy utilisation is shifted toward melting rather than reduction and metallisation at the heap surface.

Fig. 56 (a): Phases in Top segment of coal-ore sample reacted at 1300°C for 15 minutes
 (Right hand image is area in blue block enlarged)



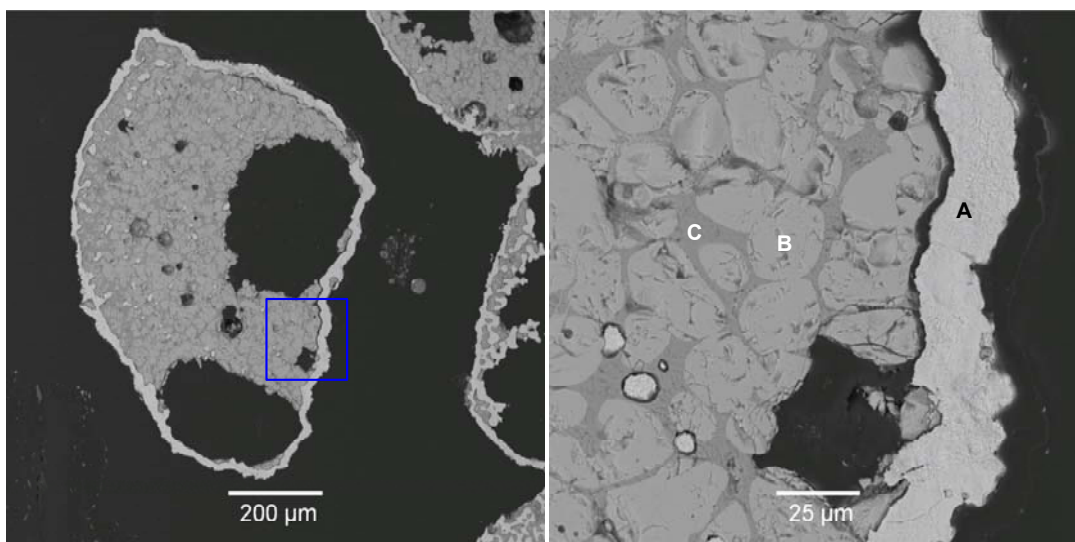
Element	Fe	Si	Al	Ca	K	Ba	Ti	Mg	Mn	S	P	Na	Total
A: Metal (mass%)	99.6	0.0	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.0	100
B: FeO grains (mass%)	95.6	0.7	3.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.1	100

Fig. 56 (b): Phases in Top segment of coal-ore sample reacted at 1300°C for 15 minutes
 (Right hand image is area in blue block enlarged)



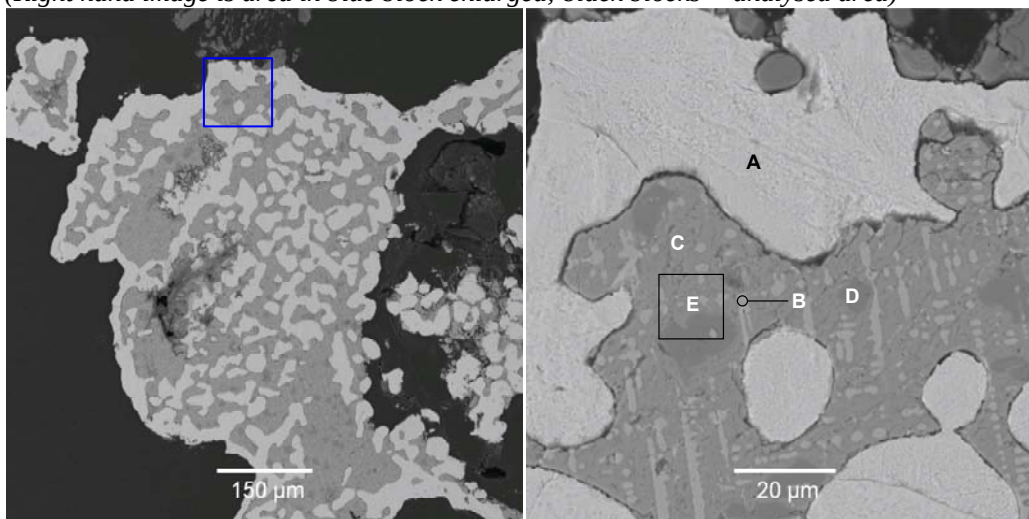
Element	Fe	Si	Al	Ca	K	Ba	Ti	Mg	Mn	S	P	Na	Total
A: FeO grains (mass%)	98.6	0.3	0.7	0.0	0.0	0.0	0.0	0.2	0.0	0.1	0.0	0.0	100
B: Glass (mass%)	75.5	16.9	3.3	1.6	0.2	0.6	0.0	0.1	0.3	0.7	0.8	0.0	100
B: Glass (mol fraction)	0.62	0.28	0.06	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	1.00
C: Dark phase (mass%)	70.4	10.9	17.0	0.4	0.1	0.0	0.2	0.0	0.3	0.1	0.5	0.2	100

Fig. 57 (a): Phases in Top segment of coal-ore sample reacted at 1400°C for 15 minutes
 (Right hand image is area in blue block enlarged)



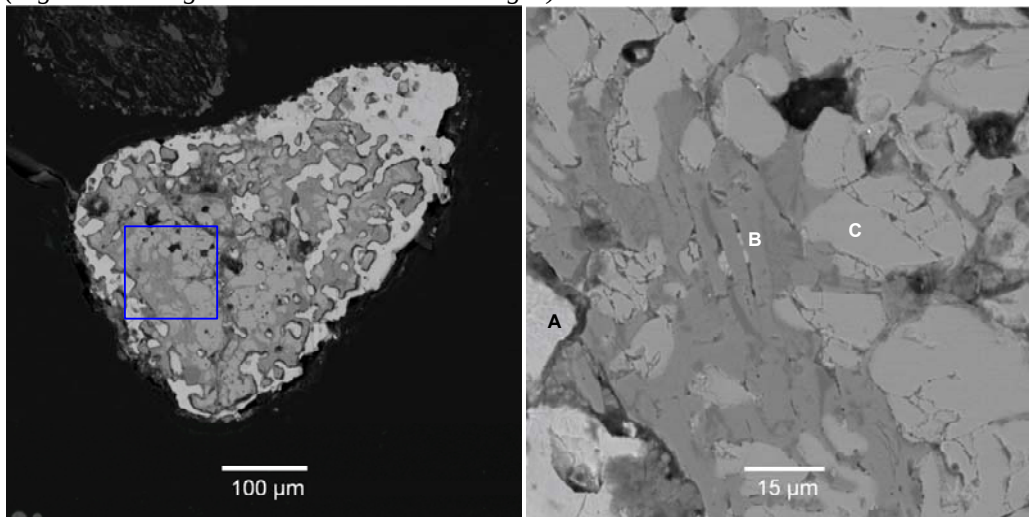
Element	Fe	Si	Al	Ca	K	Ba	Ti	Mg	Mn	S	P	Na	Total
A: Metal (mass%)	99.4	0.2	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	100
B: FeO grains (mass%)	98.0	0.3	1.0	0.1	0.0	0.0	0.2	0.1	0.2	0.0	0.0	0.1	100
C: Glass (mass%)	77.9	13.4	6.0	0.4	0.2	0.3	0	0.2	0.1	0.7	0.6	0.1	100
C: Glass (mol fraction)	0.64	0.22	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	1.00

Fig. 57 (b): Phases in Top segment of coal-ore sample reacted at 1400°C for 15 minutes
 (Right hand image is area in blue block enlarged; black blocks = analysed area)



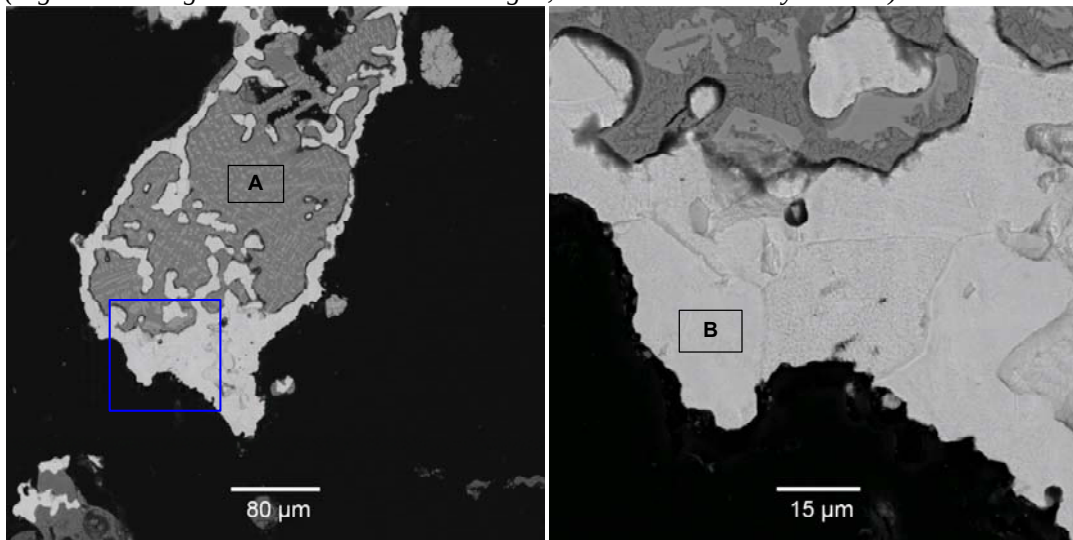
Element	Fe	Si	Al	Ca	K	Ba	Ti	Mg	Mn	S	P	Na	Total
A: Metal (mass%)	99.6	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	100
B: FeO dendrites (mass%)	94.1	2.4	2.4	0.1	0.0	0.2	0.2	0.0	0.0	0.5	0.0	0.2	100
C: Glass (mass%)	77.0	17.2	3.3	0.5	0.1	0.2	0.2	0.1	0.0	0.8	0.5	0.0	100
C: Glass (mol fraction)	0.63	0.28	0.06	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	1.00
D: Dark phase (mass%)	64.9	4.7	28.5	0.1	0.1	0.4	1.1	0.0	0.0	0.2	0.0	0.0	100
E: Oxide area analysis (mass%)	79.1	12.8	4.9	0.4	0.2	0.0	0.3	0.0	0.0	1.6	0.3	0.2	100

Fig. 58 (a): Phases in Top segment of coal-ore sample reacted at 1500°C for 15 minutes
 (Right hand image is area in blue block enlarged)



Element	Fe	Si	Al	Ca	K	Ba	Ti	Mg	Mn	S	P	Na	Total
A: Metal (mass%)	99.8	0.1	0.1	0	0	0	0	0	0	0	0	0	100
B: Needles (mass%)	79.0	18.9	0.5	0.8	0.1	0	0	0	0.1	0	0.4	0.1	100
C: FeO grains (mass%)	98.2	0.3	0.9	0	0	0	0.1	0	0.2	0	0	0.2	100
B: Needles (mol fraction)	0.66	0.31	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	1.00

Fig. 58 (b): Phases in Top segment of coal-ore sample reacted at 1500°C for 15 minutes
 (Right hand image is area in blue block enlarged; black blocks = analysed area)



Element	Fe	Si	Al	Ca	K	Ba	Ti	Mg	Mn	S	P	Na	Total
A: Glass (mass%)	61.8	19.9	5.8	0.8	0.3	0.0	8.8	0.7	0.5	1.1	0.2	0.2	100
A: Glass (mol fraction)	0.48	0.30	0.09	0.01	0.00	0.00	0.08	0.01	0.00	0.01	0.00	0.00	1.00
B: Metal (mass%)	99.2	0.3	0.2	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.0	100

3.6. Effect of particle size

The effect of particle size fraction was tested to gauge the relative importance of the reduction reaction and the gasification reaction, respectively. The basis size fraction of -850 +425 μm was used for ore and coal particles. For particle size fraction testing the coal in the mixture was changed to a smaller size fraction of -425 +300 μm and a larger size fraction of -2000 +1400 μm , respectively whilst using the ore of the basis size. The same variation in ore particle size was used in combination with the basis size fraction coal. The samples were reacted at 1400°C furnace temperature for 9 minutes reaction time. The variation in reduction extent and carbon consumption are summarised in **Table 14**.

Table 14: Effect of particle size variation at 1400°C and 9 minutes for 40 mm layer material

Sample Change	Ore size fraction (μm)	Coal size fraction (μm)	Composite %R*	Top Segment %R*	%C consumption	Top Segment %C consumption	Average kW/ m ²
Coarse Ore	-2000 +1400	-850 +425	17	33	27	36	-152
Coarse Coal	-850 +425	-2000 +1400	15	25	22	41	-146
Fine Coal	-850 +425	-425 +300	21	40	28	53	-153
Fine Ore	-425 +300	-850 +425	23	44	23	39	-153
Basis	-850 +425	-850 +425	16	31	22	30	-178

%R = %Reduction

The product gas reducing potential is shown in **Fig. 59**. Heat transferred to the sample as a function of composite reduction extent is shown in **Fig. 60**. The energy input into the samples with larger and smaller particles are similar in magnitude, and the energy input values of this group is lower than that of the basis case. Although the energy input among the particle size variation samples is similar the reduction extent in the top node of these samples differs significantly. Different product gas temperature may result from different particle size material reacted (for example, if the mixture is more reactive, reaction can occur at a lower temperature, leading to a lower bed temperature and hence a lower off-gas temperature). To quantify the possible effect of different product gas temperature on the total heat transfer to the sample (as required for reduction), a simple heat-mass balance was used to calculate the heat input to the sample with product gas temperature variation of $\pm 100^\circ\text{C}$. The resultant variation in total heat transfer was $\pm 3 \text{ MJ/m}^2$. This is small compared with the differences in heat transferred (for similar degrees of reduction) for the beds of different particle sizes (see **Fig. 60**).

A clear increase in reduction extent is seen when smaller ore or coal particles are reacted, as compared to reaction of larger ore and coal particles. Increased reduction extent achieved for decreased particle size is most likely due to decreased diffusion barriers to reacting gases in the case of reduction and gasification. Alternatively, reduced particle sizes may reduce the effect of diffusion barriers as a result of increased surface area of reacting particles. The presence of diffusional barriers to reduction gasses as a result of glass phase formation was shown in **Fig. 54** and **Fig. 57**. Variable gasification extent of

char particles in close proximity is also seen in **Fig. 54 (b)**; compare the char particle in top left hand corner with the char particle in bottom left hand corner. Increased reduction rates for smaller coal and ore particles indicate that the reduction reaction and the gasification reaction in combination are important. The increased reduction extent for fine coal and fine ore is confirmed from the higher reducing potential in the product gas as shown in **Fig. 59**. Carbon consumption differences are significant in the top node, but explanation of the relative differences is complicated by the effect of devolatilisation gases in reduction on the overall carbon consumption. Increased ore particle size does not result in significant change in reduction extent, whilst increased coal particle size results in decreased reduction extent, confirming the importance of diffusion effects on the reduction reaction.

Fig. 59: %CO/(%CO+CO₂) in product gas: 9 minute reaction time at 1400°C furnace temperature for 40 mm material layer and different particle sizes

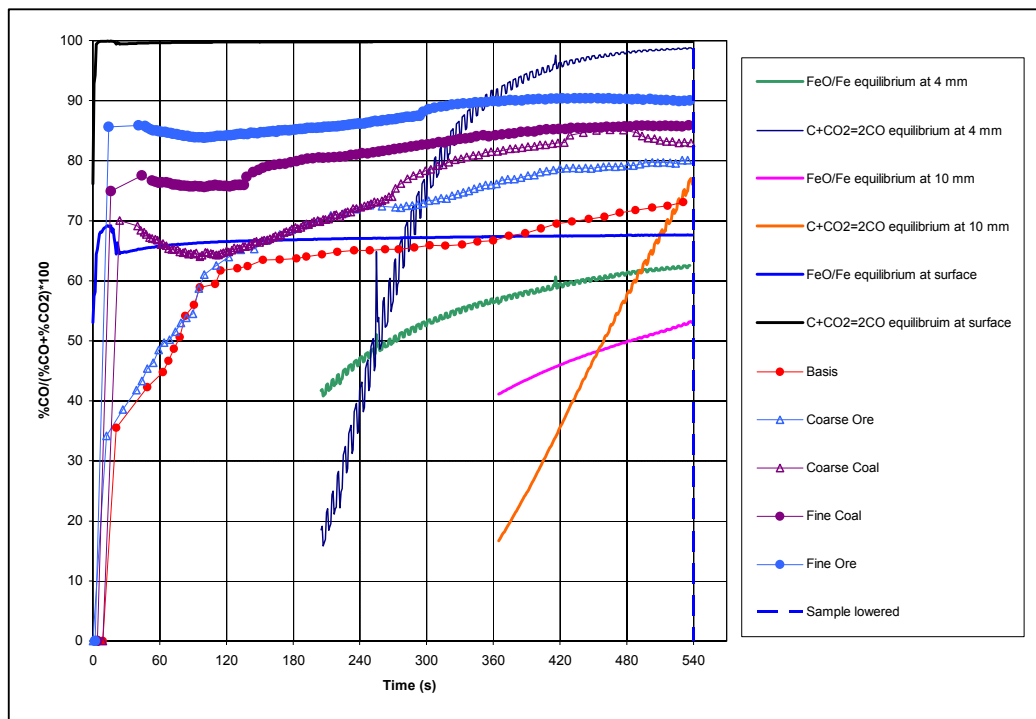
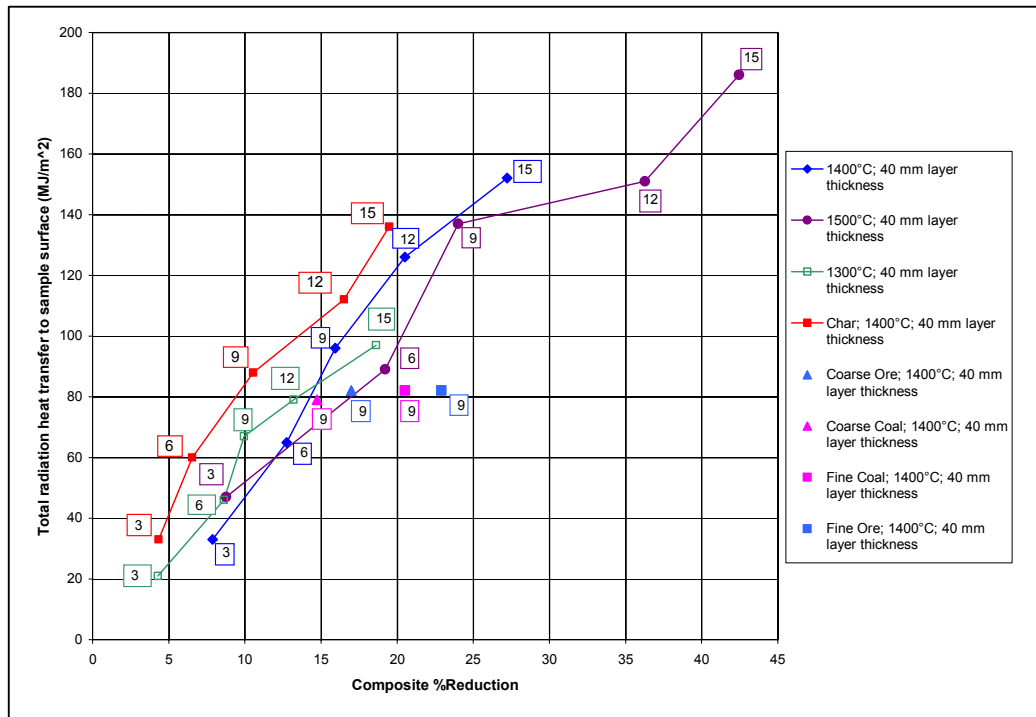


Fig. 60: Total radiation heat transferred vs. Composite %Reduction

(Number inside square frame shows reaction time in minutes)



Comparison for material layer temperatures for fine and coarse ore and coal particle sizes is shown in **Fig. 61 (a) and (b)**. Except for the material layer temperatures at 10 mm from the sample surface, the temperatures for fine and coarse ore particle sizes in the samples are similar. For variation in coal particle size it is clear from **Fig. 61 (b)** that material layer temperatures are lower in the case of fine coal as compared to coarse coal. This temperature difference indicates increased energy use for reaction of the sample rather than heating the sample, in agreement with higher reaction extents for smaller sized particles as shown in **Table 14**.

Fig. 61 (a): Material layer temperatures for fine and coarse ore particles

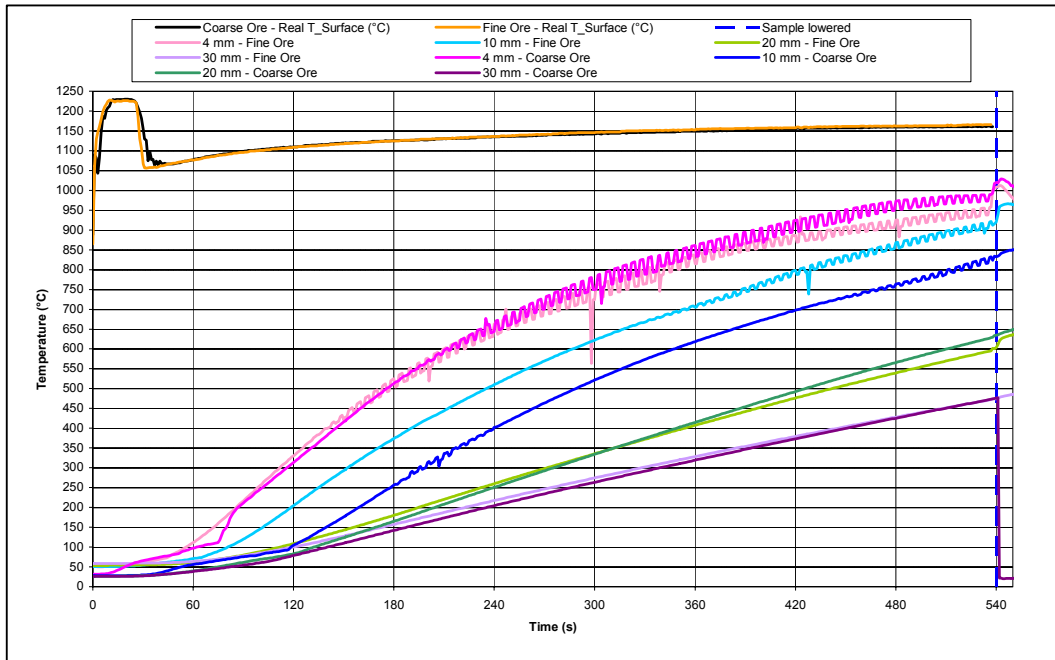
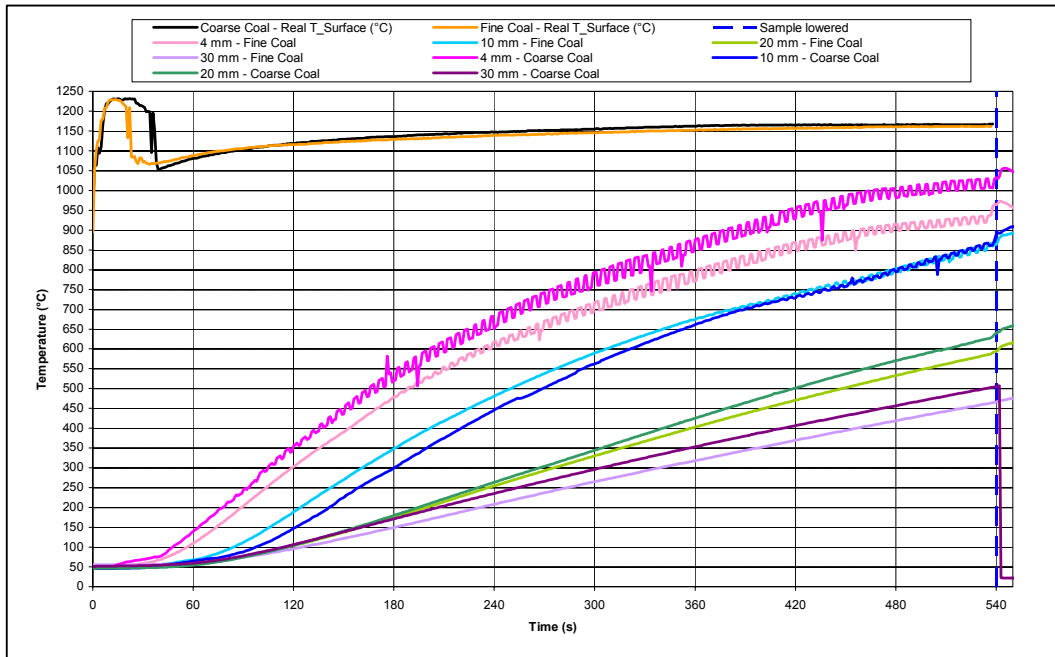


Fig. 61 (b): Material layer temperatures for fine and coarse coal particles



The input sample bulk densities were of similar magnitude (1391-1423 kg/m³), indicating that initial particle packing density could not influence heat transfer within the sample by changing the material bed conductivity. Some bed compaction should take place as a result of reduction to improve the conductivity of the material bed. In addition metallisation in the top segment can also increase conductivity in the material bed. Differences between the endpoint temperatures measured at respective positions in the material layer are shown in **Table 15**. The difference in material layer temperatures for fine ore and fine coal are of similar magnitude, and that for coarse ore and coarse coal is similar. This indicates similarities in heat transfer effects within the material layer when mixtures of fine ore and coal, respectively, were reacted. The latter effect may be due to similar extent of reduction and metallisation for fine ore and coal to improve material bed conductivity.

Table 15: Material bed temperatures for coarse and fine ore/coal particle size material reacted at 1400°C and 9 minutes, 40 mm material layer

Sample Change	*Surface	*4 mm	*10 mm	*20 mm	*30 mm	² Surface – 4 mm	² 4 mm – 10 mm	² 10 mm – 20 mm	² 20 mm – 30 mm
Coarse Ore	1161	992	823	629	474	169	169	194	155
Coarse Coal	1167	1006	862	631	503	161	144	231	128
Fine Coal	1161	937	866	588	464	224	71	278	124
Fine Ore	1166	958	921	596	472	208	37	325	124

*Temperature at indicated material layer position. ² Temperature difference between material layer temperatures measured at indicated positions.

3.7. Conclusions and Future Work

- The simulation experiment developed in this work adequately quantifies radiation heat transfer to a material layer heated uni-directionally from the sample surface. These results show the importance of heat transfer in the IFCON[®] process.
- Radiative and conduction heat transfer control prevails for 16 mm to 40 mm material layers heated uni-directionally from the material layer surface. Radiative heat transfer control is indicated by the persistent temperature differential measured between the sample surface and the furnace heating zone temperatures and increased reaction extent achieved with increased radiation heat transfer to the sample surface. At 1400°C furnace temperature the temperature differentials between the main radiation heat source, heating zone at 1410°C, and the sample surface temperatures were 266-303°C for 40 mm material layers, and 240-287°C for 16 mm material layers. Conduction heat transfer control is indicated by the persistent temperature differentials within the material layer measured after initial heating of the material layer. Increased reaction extent for decreased material layer thickness confirms conduction heat transfer control in the material layer. At 1400°C furnace temperature the temperature differentials between the material layer surface temperature and the material layer bottom temperatures were 543-995°C for 40 mm material layers, and 914-105°C for 16 mm material layers. At 15 minutes reaction time of a 16 mm layer the temperature differentials within the material layer were eliminated.
- Coal volatiles contribute to reduction in a 40 mm layer material bed, mainly in the form of hydrogen. Some CO and CO₂ are also released as volatile material at higher material bed temperatures.
- The product gas for the coal-ore material layers reacted non-isothermally in this work is of sufficiently high reducing potential to reduce FeO to Fe, even from the start of reaction when only the sample surface is at high temperature. The product gas analyses follow a reducing potential between that of the FeO/Fe and the C/CO₂ equilibrium values.
- Reduction of Sishen fine ore does not follow a single reaction mechanism because of variability of gangue content and porosity in the ore grains. The metal product formed is ferrite. Glass phase of Fayalite (2FeO.SiO₂) stoichiometry was formed. Therefore reduction did not follow exclusively solid state reduction, but reduction occurred in a semi-molten state. The lowered oxide liquidus temperature, compared to that of FeO, limits the maximum temperature to which the heap surface can be heated without bulk melting, and so sets a limit to radiation heat transfer rates which are practically attainable.

- Increased ore size fraction from -850 +425 μm to -2000 +1400 μm , did not result in significant change in reduction extent and carbon consumption. However a clear increase in reduction extent and carbon consumption was seen when a reduced ore size fraction of -425 +300 μm was reacted. Increased reduction extent and increased carbon consumption were observed when a reduced coal size fraction of -425 +300 μm (from -850 +425 μm) was reacted. For increased coal size fraction to -2000 +1400 μm reduction extent decreased and carbon consumption increased. Increased reaction rates for smaller coal and ore particles are most likely due to decreased diffusion barriers in smaller particles.
- Increased reduction extent is achieved with increased radiation heat transfer to the sample surface, irrespective of factors such as reductant reactivity and material layer thickness.
- Future work should include a mathematical model of the reaction system presented in this work. Such a model will provide a method to test the effect of individual possible rate controlling parameters independently from each other: radiation heat transfer, conduction heat transfer within the material layer, gasification rate, reduction rate and devolatilisation rate. The effect of each of these parameters on the overall reaction system productivity can be tested individually in the model by adjusting the model parameters that determine each of these parameters: furnace heating surface temperatures to simulate radiation heat transfer effects, material bed thermal conductivity to simulate conduction heat transfer effects within the material layer, reaction rate constants to simulate the effects of reaction rates for reduction, gasification and devolatilisation.

CHAPTER IV: REFERENCES

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CHAPTER V: APPENDICES

Appendix I

Gas retention times for samples & Product gas calculations

Time multiple data for graphite and pre-reduced Sishen ore sample mixtures

Sample Reference No.	Sample lowered time [seconds]	Re-zero time - %H ₂ [seconds]	Re-zero time - %CO ₂ [seconds]	Re-zero time - %CO [seconds]	Re-zero time - %H ₂ O [seconds]	Re-zero time - %CH ₄ [seconds]	Sample removal time [seconds]	Gas retention time in furnace tube volume [seconds]	Re-zero time/gas retention time - %H ₂ [seconds]	Re-zero time/gas retention time - %CO ₂ [seconds]	Re-zero time/gas retention time - %CO [seconds]	Re-zero time/gas retention time - %H ₂ O [seconds]
1300A	1503	1359	1558	1682	1161	n.p.	3347	159	-1	0	1	-2
1300B	1498	154	1559	2271	499	n.p.	3417	159	-8	0	5	-6
1400C	897	n.p.	952	999	508	n.p.	2701	159	n.p.	0	1	-2
1400D	897	350	954	1145	315	n.p.	2821	159	-3	0	2	-4
1500E	260	355	344	332	482	n.p.	1388	159	1	1	0	1
1500F	268	337	337	360	325	n.p.	1503	159	0	0	1	0

n.p. = component not present in product gas

Time multiple data for coal-ore sample mixtures

Furnace Temperature (°C)	Coal/Char	Coal/Char Size*	Ore Size*	Reaction Time [min.]	Sample Layer Thickness [mm]	Sample lowered time [seconds]	Re-zero time - %H ₂ [seconds]	Re-zero time - %CO ₂ [seconds]	Re-zero time - %CO [seconds]	Re-zero time - %H ₂ O [seconds]	Re-zero time - %CH ₄ [seconds]	Sample removal time [seconds]	Gas retention time in furnace tube volume [seconds]	Re-zero time/gas retention time - %H ₂ [seconds]	Re-zero time/gas retention time - %CO ₂ [seconds]	Re-zero time/gas retention time - %CO [seconds]	Re-zero time/gas retention time - %H ₂ O [seconds]
1300	Coal	2	2	3	40	177	342	246	no	1045	n.a.	2179	159	1	0	no	5
1300	Coal	2	2	6	40	360	631	442	no	934	n.a.	2037	159	2	1	no	4
1300	Coal	2	2	9	40	537	789	606	595	1395	n.a.	1806	159	2	0	0	5
1300	Coal	2	2	15	40	898	1207	965	1388	1553	n.a.	2698	159	2	0	3	4
1300	Coal	2	2	12	40	720	1173	789	1244	1563	n.a.	2224	159	3	0	3	5
1400	Coal	2	2	3	40	179	514	261	293	928	n.a.	1424	159	2	1	1	5
1400	Coal	2	2	6	40	359	769	455	444	1111	n.a.	1556	159	3	1	1	5
1400	Coal	2	2	9	40	540	1020	626	595	1350	n.a.	1917	159	3	1	0	5
1400	Coal	2	2	12	40	718	1164	779	885	1117	n.a.	2226	159	3	0	1	3
1400	Coal	2	2	15	40	900	1273	977	1398	1540	n.a.	2768	159	2	0	3	4
1500	Coal	2	2	3	40	180	526	311	257	1482	n.a.	2108	159	2	1	0	8
1500	Coal	2	2	6	40	357	966	487	444	1105	n.a.	1790	159	4	1	1	5
1500	Coal	2	2	9	40	536	1061	669	648	1309	n.a.	2183	159	3	1	1	5
1500	Coal	2	2	12	40	718	1155	881	1255	1491	n.a.	2530	159	3	1	3	5
1500	Coal	2	2	15	40	897	1184	1033	1434	1345	n.a.	2708	159	2	1	3	3
1400	Coal	2	2	3	16	177	292	280	280	915	n.a.	1317	159	1	1	1	5
1400	Coal	2	2	6	16	355	487	441	415	786	n.a.	1537	159	1	1	0	3
1400	Coal	2	2	9	16	537	612	612	929	682	n.a.	2162	159	0	0	2	1
1400	Coal	2	2	12	16	717	783	795	1074	947	n.a.	2035	159	0	0	2	1
1400	Coal	2	2	15	16	899	863	933	1772	702	n.a.	4299	159	0	0	5	-1
1400	Coal	2	1	9	40	538	1188	700	603	1530	n.a.	1980	159	4	1	0	6
1400	Coal	1	2	9	40	538	1111	621	627	1218	n.a.	2147	159	4	1	1	4
1400	Coal	3	2	9	40	537	1220	625	1043	1114	n.a.	2011	159	4	1	3	4
1400	Coal	2	3	9	40	537	1215	625	1297	990	n.a.	2083	159	4	1	5	3
1400	Char	2	2	3	40	190	293	293	225	1184	n.a.	1877	159	1	1	0	6
1400	Char	2	2	6	40	358	441	452	429	623	n.a.	1758	159	1	1	0	2
1400	Char	2	2	9	40	539	627	627	603	828	n.a.	2241	159	1	1	0	2
1400	Char	2	2	12	40	717	791	885	756	953	n.a.	2479	159	0	1	0	1
1400	Char	2	2	15	40	897	947	1075	994	947	n.a.	2868	159	0	1	1	0

n.p. = component not present in product gas

no = component concentration did not return to initial level

* 1 = -2000 +1400 µm; 2 = -850 +425 µm; 3 = -425 +300 µm

Product gas composition calculation

Data for the pressure of water vapour over water, in mm Hg, for temperatures of -16 to 30 was taken from CRC Handbook of Chemistry and Physics, 86th Edition, 2005-2006. An equation fit for the data was made and this equation used to calculate the %H₂O in the product gas.

$$P_{H_2O} = 2.896 \cdot 10^{-6} \cdot T_{dp}^4 + 1.986 \cdot 10^{-4} \cdot T_{dp}^3 + 1.058 \cdot 10^{-2} \cdot T_{dp}^2 + 3.332 \cdot 10^{-1} \cdot T_{dp} + 4.587$$

$$\%H_2O = P_{H_2O} / 760 \cdot P_{atm.}$$

P_{H_2O} = Water vapour pressure (mm Hg)

$P_{atm.}$ = atmospheric pressure (Bar)



T_{dp} = water dewpoint (°C)

$$\%g_n = \frac{\%g_a}{\sum_0^i \%g_a + \%H_2O} \cdot 100$$

$$Q_g = Q_{Ar} \frac{\%g_n}{\%Ar_n} \cdot \frac{t_p}{60}$$

$$n_g = Q_g / 22400$$

$\%g_n$ = % of component g in gas

$\%g_a$ = % of component analysed by mass spectrometer

$\sum_0^i \%g_a$ = sum of % of components 0 to i analysed by mass spectrometer

Q_{Ar} = Ar flow rate into experiment [Ncm³/min.]

Q_g = flow rate of gas g in product gas [Ncm³/min.]

t_p = time interval [seconds]

n_g = mol gas g in product gas for time interval t_p

Appendix II

View factor calculations for radiation network

The view factors were calculated as follows.

From parallel disk geometry (Wong, 1977):

$$F_{24} = \frac{1}{2B^2} (X - \sqrt{X^2 - 4B^2C^2})$$

$$B = \frac{r_2}{h}$$

$$C = \frac{r_4}{h}$$

$$X = (1 + B^2 + C^2)$$

F_{ij} = view factor from area i to j

r_i = radius of disk [m]

h = separation distance between disks [m]

A_i = area of surface i [m²]

Similarly the following view factors were calculated: $F_{27}, F_{2(3+4)}, F_{28}, F_{(3+4)7}, F_{47}, F_{48}, F_{(3+4)8}, F_{87}$.

$$F_{21} = 1 - F_{27}$$

$$F_{22} = 0$$

$$F_{23} = F_{2(3+4)} - F_{24}$$

$$F_{25} = F_{27} - F_{28}$$

$$F_{26} = F_{28} - F_{2(3+4)}$$

$$F_{11} = 1 - 2F_{12}; F_{12} = F_{17}$$

$$F_{12} = F_{21} \frac{A_2}{A_1}$$

$$F_{(3+4)1} = F_{(3+4)7} - F_{(3+4)2}$$

$$F_{(3+4)2} = F_{2(3+4)} \frac{A_2}{A_{(3+4)}}$$

$$F_{1(3+4)} = F_{(3+4)1} \frac{A_{(3+4)}}{A_1}$$



$$F_{13} = F_{1(3+4)} - F_{14}$$

$$F_{14} = F_{41} \frac{A_4}{A_1}$$

$$F_{41} = F_{47} - F_{42}$$

$$F_{15} = F_{51} \frac{A_5}{A_1}$$

$$F_{16} = 1 - (F_{11} + F_{12} + F_{13} + F_{14} + F_{15})$$

$$F_{41} = F_{47} - F_{42}$$

$$F_{43} = 0; F_{44} = 0$$

$$F_{45} = F_{48} - F_{47}$$

$$F_{46} = 1 - (F_{41} + F_{42} + F_{45})$$

$$F_{51} = F_{57} - F_{52}$$

$$F_{57} = F_{58}$$

$$F_{85} = 1 - F_{87}$$

$$F_{58} = F_{85} \frac{A_8}{A_5}$$

$$F_{52} = F_{25} \frac{A_2}{A_5}$$

$$F_{53} = F_{5(3+4)} - F_{54}$$

$$F_{5(3+4)} = F_{(3+4)5} \frac{A_3 + A_4}{A_5}$$

$$F_{(3+4)5} = F_{(3+4)8} - F_{(3+4)7}$$

$$F_{54} = F_{45} \frac{A_4}{A_5}$$

$$F_{55} = 1 - 2F_{58}$$

$$F_{56} = 1 - (F_{51} + F_{52} + F_{53} + F_{54} + F_{55})$$

$$F_{31} = F_{13} \frac{A_1}{A_3}$$



$$F_{32} = F_{23} \frac{A_2}{A_3}$$

$$F_{34} = 0; F_{33} = 0$$

$$F_{35} = F_{53} \frac{A_5}{A_3}$$

$$F_{36} = F_{63} \frac{A_6}{A_3}$$

$$F_{61} = F_{16} \frac{A_1}{A_6}$$

$$F_{62} = F_{26} \frac{A_2}{A_6}$$

$$F_{63} = F_{6(3+4)} - F_{64}$$

$$F_{6(3+4)} = F_{68}; F_{(3+4)6} = 1 - F_{(3+4)8}$$

$$F_{64} = F_{46} \frac{A_4}{A_6}$$

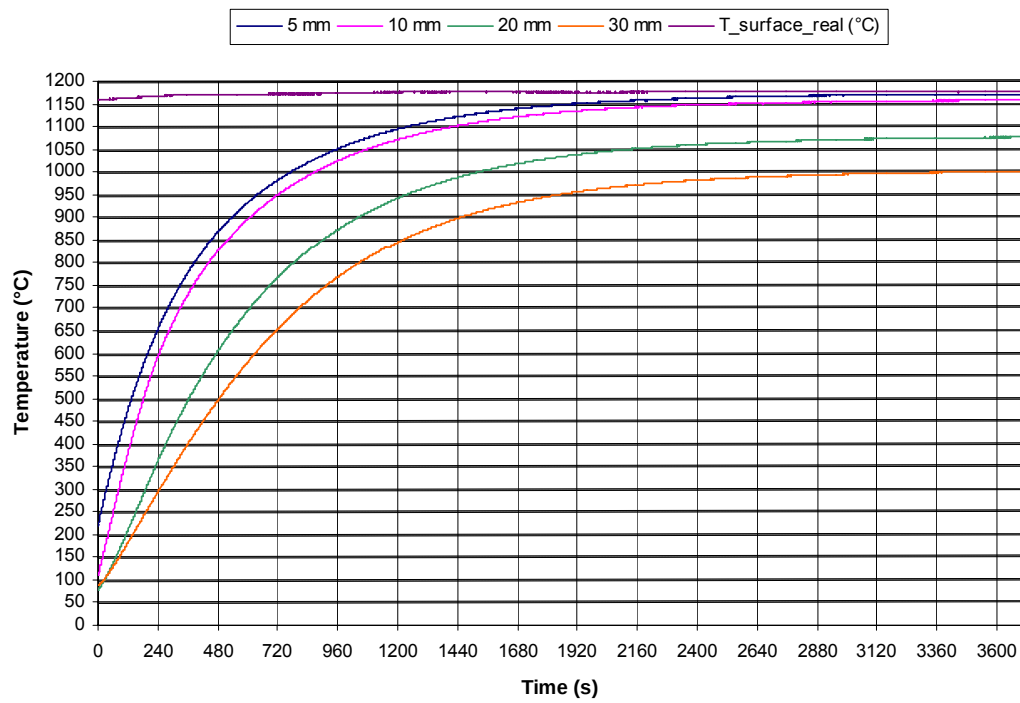
$$F_{66} = 1 - 2F_{68}; F_{68} = F_{6(3+4)}$$

$$F_{65} = 1 - (F_{61} + F_{62} + F_{63} + F_{64} + F_{66})$$

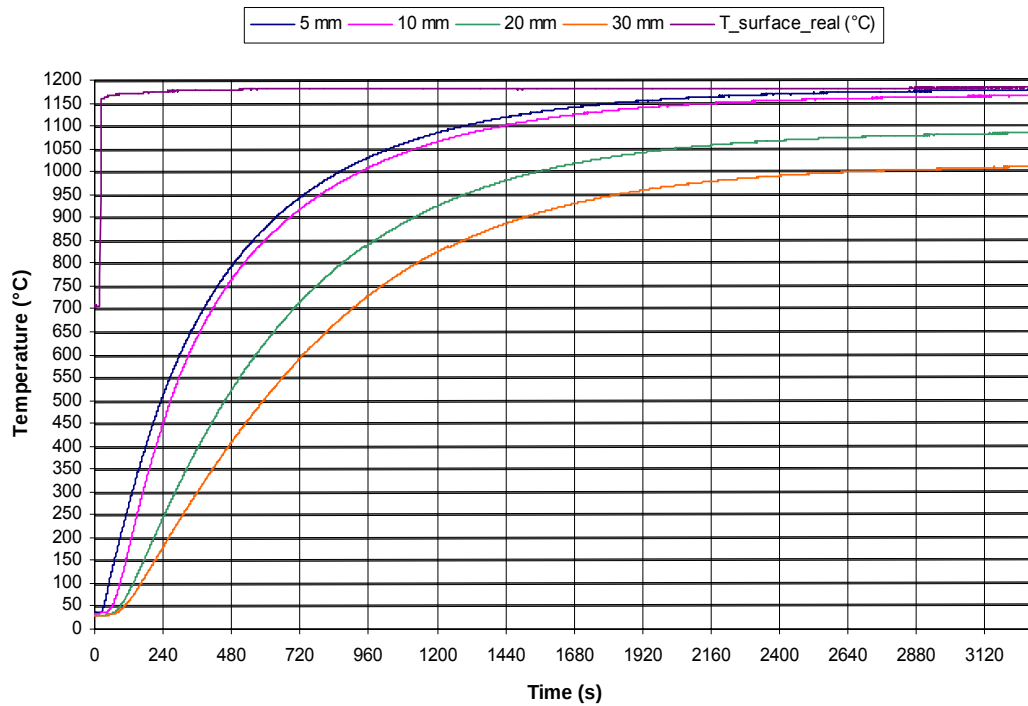


Appendix III

Surface temperature measurement for alumina sample (1300°C a)

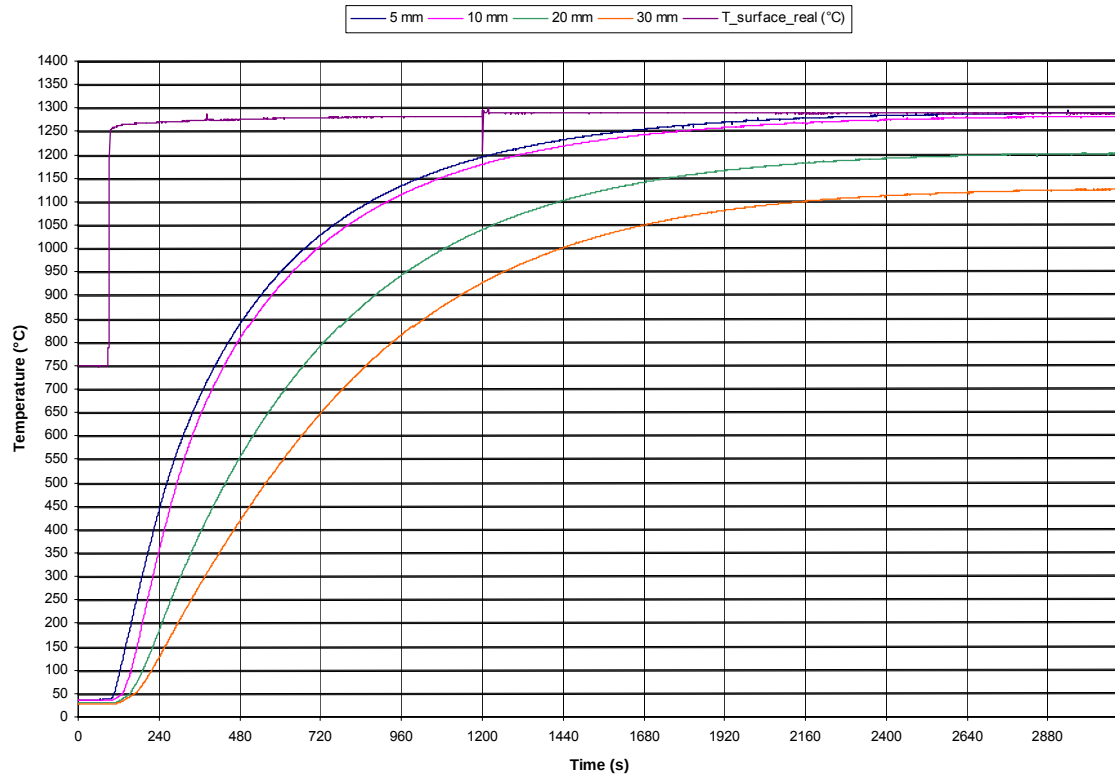


Surface temperature measurement for alumina sample (1300°C b)

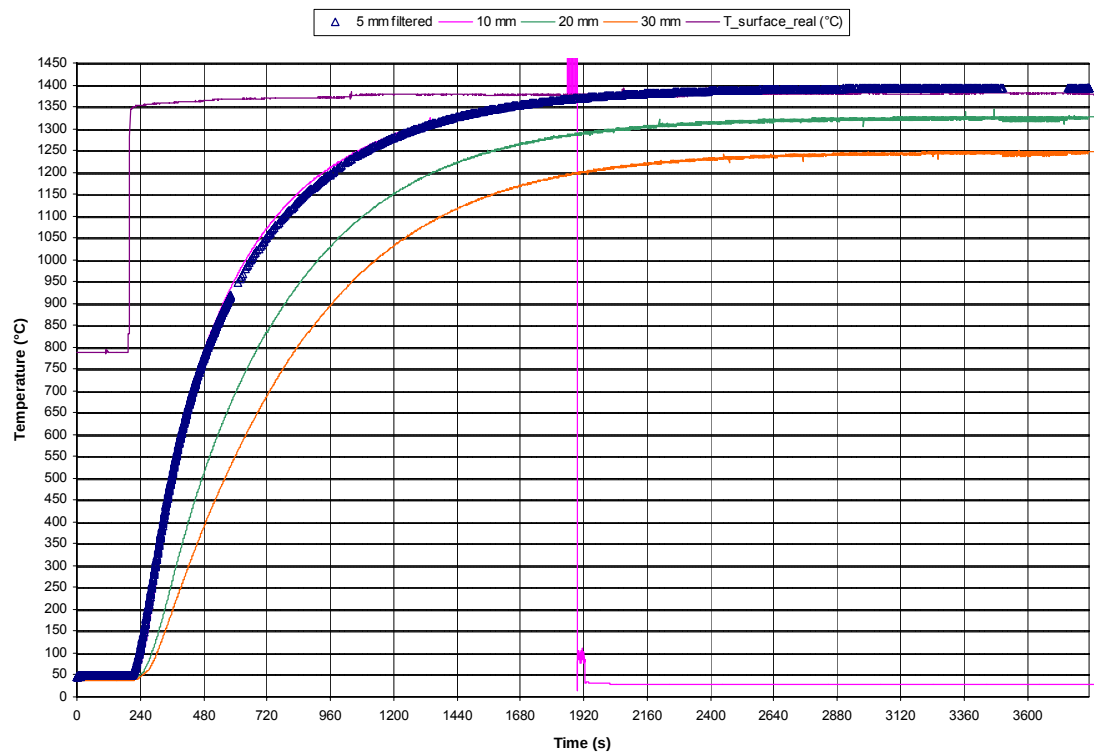




Surface temperature measurement for alumina sample (1400°C)

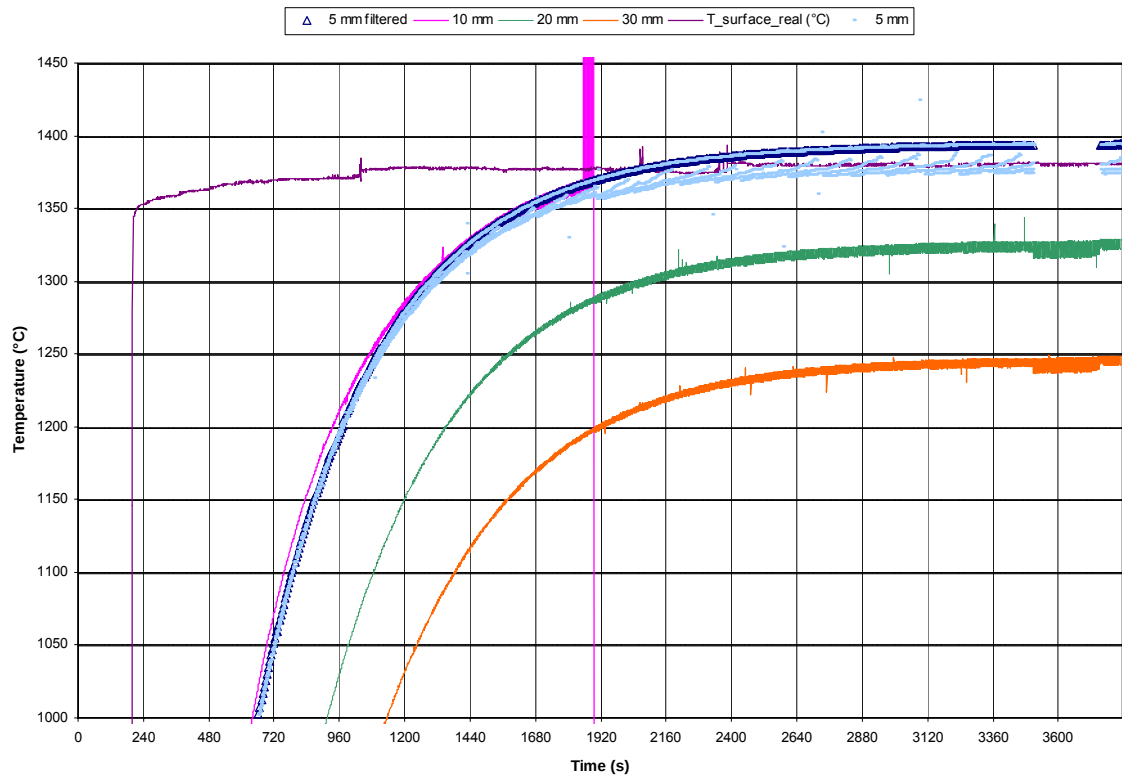


Surface temperature measurement for alumina sample (1500°C) (Filtered data for thermocouple placed 5 mm from sample surface shown)





Surface temperature measurement for alumina sample (1500°C)
(Both filtered and original data for thermocouple placed 5 mm from sample surface shown)





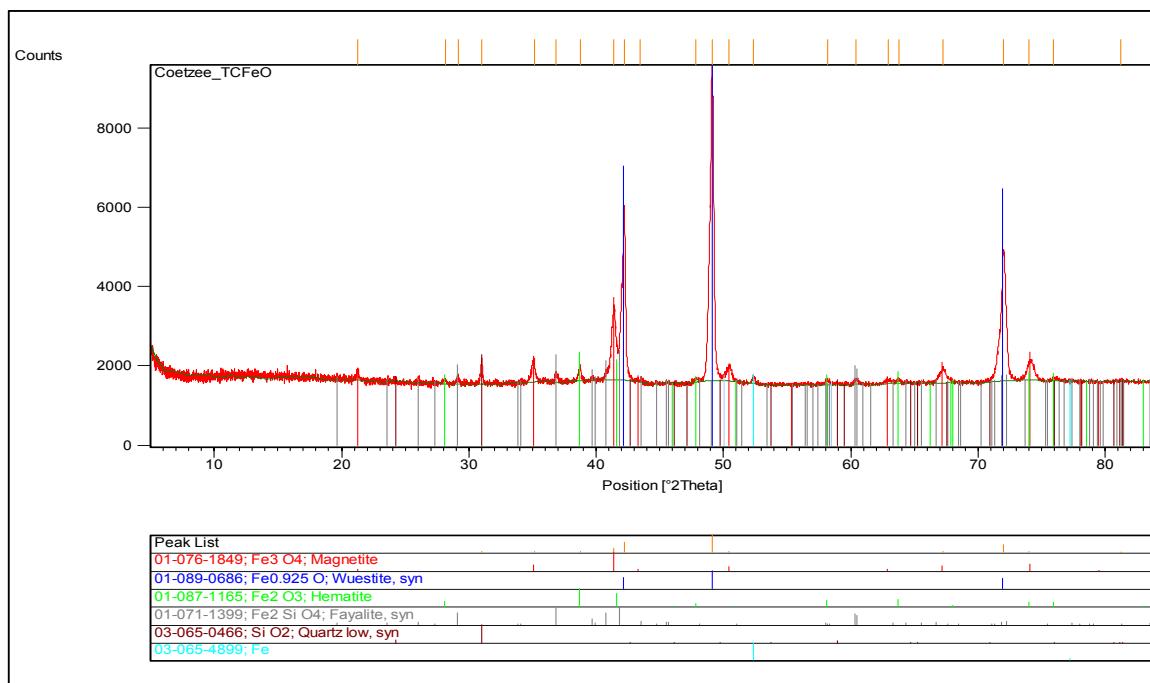
Appendix IV

Chemical Analyses of Input Materials

Ore Analyses

	Sishen Fines: -425 +300 μm	Sishen Fines: -850 +425 μm	Sishen Fines: -2000 +1400 μm	Pre-Reduced Sishen Fines
Al_2O_3	1.35	1.64	1.35	1.81
CaO	0.25	0.19	0.25	0.10
Cr	<0.05	<0.05	<0.05	n.d.
Fe(total)	63.5	63.0	63.5	71.1
Fe^0	n.d.	n.d.	n.d.	0.64
FeO	n.d.	n.d.	n.d.	68.1
Fe_2O_3	n.d.	n.d.	n.d.	25.0
K_2O	0.20	0.23	0.20	0.23
MgO	0.08	0.05	0.08	0.04
MnO	0.03	0.04	0.03	0.04
Ni	<0.05	<0.05	<0.05	n.d.
P	0.05	0.05	0.05	0.05
SiO_2	3.43	3.95	3.43	3.84
C	0.03	0.01	0.03	n.d.
S	0.01	0.02	0.01	n.d.
Ba	<0.05	0.49	<0.05	n.d.
TiO_2	0.06	0.10	0.06	0.08
Moisture	0.02	0.01	0.02	n.d.

XRD analysis of pre-reduced Sishen fines



Hand milled, top loading onto zero-background holder due to small sample size
Analysed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-K α radiation
Phases identified using X'Pert Highscore plus software



Coal, Char and Electrode Graphite Analyses

Ultimate Analyses (Dry basis)

%	Eikeboom Coal: -425 +300 μm	Eikeboom Coal: -850 +425 μm	Eikeboom Coal: -2000 +1400 μm	Eikeboom Char: -850 +425 μm	Electrode Graphite
C	76.0	75.9	76.0	78.9	98.7
H	3.60	3.53	3.60	0.26	0.01
N	1.80	1.81	1.80	0.60	<0.01
O	5.72	6.03	5.72	2.64	---

Proximate Analyses

%	Eikeboom Coal: -425 +300 μm	Eikeboom Coal: -850 +425 μm	Eikeboom Coal: -2000 +1400 μm	Eikeboom Char: -850 +425 μm
Moisture content (air dried)	3.2	3.3	3.2	4.0
Ash content (air dried)	12.0	12.0	12.0	17.3
Volatile matter content (air dried)	22.8	22.5	22.8	1.9
Fixed Carbon (air dried)	62.0	62.2	62.0	77.5
Total Sulphur	0.36	0.36	0.36	0.31

Ash Composition

%	Eikeboom Coal: -425 +300 μm	Eikeboom Coal: -850 +425 μm	Eikeboom Coal: -2000 +1400 μm	Eikeboom Char: -850 +425 μm
Al_2O_3	39.37	38.72	39.37	32.75
CaO	2.81	2.42	2.81	0.96
Cr_2O_3	0.04	0.05	0.04	0.17
Fe_2O_3	1.32	1.65	1.32	5.42
K_2O	0.50	0.50	0.50	0.66
MgO	0.68	0.67	0.68	0.51
MnO	0.02	0.02	0.02	0.67
Na_2O	0.27	0.30	0.27	0.02
P_2O_5	1.25	1.17	1.25	0.14
SiO_2	49.10	50.62	49.10	55.90
TiO_2	2.11	2.13	2.11	1.86
V_2O_5	0.04	0.05	0.04	0.05
ZrO_2	0.14	0.12	0.14	0.08
Ba	0.25	0.24	0.25	0.10
Sr	0.20	0.18	0.20	0.05
SO_3	1.26	0.81	1.26	0.55
Total	98.77	99.68	98.77	99.89

Appendix V

Mass measurements of sand samples divided in Sample Cutter-Splitter

Crucible Number	Fibre Board Crucible Mass In (g.)	Sand Mass In (g.)	g. Sand - Top Node	g. Sand - Middle Node	g. Sand - Bottom Node	g. Fibre Board - Top Node	g. Fibre Board - Middle Node	g. Fibre Board - Bottom Node	Mass Sand out (g.)	Mass Fibre board out (g.)	Mass%Top Node	Mass% Middle Node	Mass% Bottom Node	Mass%Top Node	Mass% Middle Node	Mass% Bottom Node	Mass Sand In - Mass Sand Out (g.)	Mass Fibre Board In - Mass Fibre Board Out (g.)	Sum of Sand and FB Mass Differences (g)
1	21.05	36.52	17.3	12.4	7.9	6.6	4.3	8.6	37.65	19.48	46	33	21	34	22	44	1.13	-1.57	-0.44
2	20.93	36.52	18.3	12.4	7.0	6.7	4.2	8.4	37.70	19.39	48	33	19	35	22	44	1.18	-1.55	-0.37
3	21.56	36.53	18.1	12.3	7.4	6.7	4.4	8.9	37.83	19.98	48	33	20	34	22	45	1.30	-1.58	-0.28
4	20.45	36.52	18.2	12.7	6.8	6.6	4.2	8.3	37.63	19.10	48	34	18	35	22	43	1.11	-1.34	-0.23
5	20.23	36.52	16.9	12.8	8.1	5.9	4.3	8.3	37.84	18.58	45	34	21	32	23	45	1.31	-1.66	-0.34
6	20.24	36.52	16.4	12.9	8.1	5.5	4.1	8.4	37.41	17.96	44	34	22	31	23	47	0.88	-2.28	-1.40
7	21.02	36.52	17.8	12.7	7.4	6.5	4.3	8.5	37.94	19.34	47	33	20	34	22	44	1.42	-1.68	-0.26
8	19.90	36.52	17.2	12.7	8.0	6.0	4.2	8.2	37.86	18.34	45	34	21	33	23	45	1.34	-1.57	-0.22
9	21.10	36.52	16.9	12.8	8.4	5.4	4.4	9.5	38.03	19.34	44	34	22	28	23	49	1.51	-1.76	-0.25
10	21.16	36.53	16.8	12.6	8.5	6.6	4.5	8.4	37.93	19.47	44	33	22	34	23	43	1.41	-1.69	-0.28
Average	20.76	36.52	17.4	12.6	7.8	6.3	4.3	8.6	37.8	19.1	46	33	21	33	22	45			
Population Standard Deviation			0.6	0.2	0.5	0.5	0.1	0.4			1.7	0.5	1.4	2.0	0.5	1.7			
95% Confidence Limit			0.4	0.1	0.3	0.3	0.1	0.2			1.0	0.3	0.9	1.2	0.3	1.0			

Appendix VI

Calibration sample masses and analyses

Sample Name	Sample Reference No.	Reaction Time (minutes)	Sample Mix Out			Fibreboard			Thermocouples			Totals Out			In			
			g. sample mix - top	g. sample mix - middle	g. sample mix - bottom	g. Fibreboard - top	g. Fibreboard -middle	g. Fibreboard -bottom	g. thermocouple - top	g. thermocouple - middle	g. thermocouple -bottom	Total g. sample mix out	Total g. Fibreboard out	Total g. Thermocouples out	g. Fibreboard in	g. Mix in	mass% "FeO" in	mass% Graphite in
19_09_2006_1300_A_25	1300A	25	15.981	16.182	11.261	13.906	3.371	12.299	0.16	0.098	0.328	43.424	29.576	0.586	31.854	43.787	85.4	14.6
19_09_2006_1300_B_25	1300B	25	18.615	15.453	8.847	10.798	6.092	12.643	0	0	0	42.915	29.533	0	31.264	43.218	85.4	14.6
20_09_2006_1400_C_15	1400C	15	16.283	16.030	9.815	11.435	6.303	13.048	0.234	0.217	0.193	42.128	30.786	0.644	32.365	44.023	85.4	14.6
20_09_2006_1400_D_15	1400D	15	15.534	15.739	10.043	11.572	5.972	12.867	0.346	0.337	0.534	41.316	30.411	1.217	32.096	43.017	85.4	14.6
21_09_2006_1500_E_4.5	1500E	4.3	18.954	16.168	9.610	11.560	6.162	13.160	0	0	0	44.732	30.882	0	32.395	44.519	85.4	14.6
21_09_2006_1500_F_4.5	1500F	4.5	11.482	15.372	18.011	5.814	6.784	16.174	0	0	0	44.865	28.772	0	30.868	43.968	85.4	14.6

Sample Reference No.	Sample out Fe analyses											Sample out Fe analyses - Corrected*																								
	% Fe(met) - Top	% Fe(met) - Middle	% Fe(met) - Bottom	% FeO - Top	% FeO - Middle	% FeO - Bottom	% Fe2O3 - Top	% Fe2O3 - Middle	% Fe2O3 - Bottom	% Fe(total) - Top	% Fe(total) - Middle	% Fe(total) - Bottom	% Fe(met) - Top (Corrected)*	% Fe(met) - Middle (Corrected)*	% Fe(met) - Bottom (Corrected)*	% FeO - Top (Corrected)*	% FeO - Middle (Corrected)*	% FeO - Bottom (Corrected)*	% Fe2O3 - Top (Corrected)*	% Fe2O3 - Middle (Corrected)*	% Fe2O3 - Bottom (Corrected)*	% Fe(+2) - Top (Corrected)*	% Fe(+2) - Middle (Corrected)*	% Fe(+2) - Bottom (Corrected)*	% Fe(+3) - Top (Corrected)*	% Fe(+3) - Middle (Corrected)*	% Fe(+3) - Bottom (Corrected)*	% Fe(total) - Top (Corrected)*	% Fe(total) - Middle (Corrected)*	% Fe(total) - Bottom (Corrected)*	g. Fe in/ g. Fe out					
1300A	15.6	0.2	0.2	51.5	57.2	52.6	11.6	20.5	24.0	63.8	59.1	57.9	16.2	0.3	0.2	53.6	60.3	55.5	12.06	21.61	25.34	41.6	46.8	43.1	8.4	15.1	17.7	66.3	62.2	61.1	1.01					
1300B	11.4	0.1	0.1	52.5	57.7	52.7	17.6	20.9	21.6	64.5	59.5	56.2	11.6	0.1	0.1	53.6	61.0	54.1	17.98	22.08	22.19	41.6	47.3	42.1	12.6	15.4	15.5	65.9	62.9	57.7	1.00					
1400C	17.3	0.1	0.2	53.4	57.5	53.1	11.5	19.7	21.3	66.9	58.6	56.4	17.6	0.1	0.2	54.4	61.2	55.1	11.72	20.96	22.12	42.3	47.5	42.8	8.2	14.7	15.5	68.1	62.3	58.5	1.04					
1400D	23.0	0.1	0.1	47.5	59.8	55.8	6.5	18.8	20.7	64.5	59.8	58.0	23.7	0.1	0.1	49.0	63.8	57.8	6.71	20.05	21.45	38.1	49.5	44.9	4.7	14.0	15.0	66.5	63.7	60.1	1.04					
1500E	4.3	0.4	0.4	56.4	46.9	51.2	17.2	31.9	26.2	60.2	59.2	58.5	4.4	0.4	0.4	57.1	49.3	53.9	17.41	33.53	27.57	44.3	38.3	41.8	12.2	23.5	19.3	60.9	62.1	61.5	1.02					
1500F	7.1	0.2	0.4	58.0	50.2	50.8	12.1	26.2	27.3	60.7	57.6	58.9	7.1	0.2	0.4	58.1	53.2	54.0	12.13	27.77	29.04	45.2	41.3	42.0	8.5	19.4	20.3	60.7	61.0	62.7	1.01					

Sample Reference No.	Product gas analysed					%C calculated vs. Analysed							Mass C in and out										g. Mass loss		g. O to gas			
	Total g. CO2 in Product Gas	Total g. CH4 in Product Gas	Total g. CO in Product Gas	Total g. H2 in Product Gas	Total g. H2O in Product Gas	%C out analysed - top (Corrected)*	%C out calculated from incremental Mass & Energy Balance - Top	%C out analysed - middle (Corrected)*	%C out calculated from incremental Mass & Energy Balance - Middle	%C out analysed - bottom (Corrected)*	%C out calculated from incremental Mass & Energy Balance - Bottom	%Fixed Carbon in start mixture	Total g. C in	g. C in - top	g. C in - middle	g. C in - bottom	Total g. C remaining in sample	Total g. C consumption according to % C chemical ana	g. C to gas - Product gas analysis	g. C to gas according to incremental Mass & Energy Balance	g. C to gas according to chemical ANALYSIS - top	g. C to gas according to chemical ANALYSIS - middle	g. C to gas according to chemical ANALYSIS - bottom	Massa Loss according to Product gas [Total Time]	Mass loss calculated in incremental mass & energy balance	g. O in CO & CO2 Product gas [Total Time]	g. O From Reduction to gas according to incremental Mass & Energy Balance	g. O From Reduction to gas according to incremental Mass & Energy Balance
1300A	0.92	0.00	2.34	0.03	0.75	12.9	14.5	13.2	13.5	15.1	12.7	14.4	6.4	2.9	2.1	1.3	5.6	0.77	1.25	0.58	0.96	0.09	-0.27	4.0	2.2	2.0	0.9	0.9
1300B	0.56	0.00	1.71	0.01	0.21	12.4	12.9	12.7	13.7	18.7	15.6	14.4	6.3	2.9	2.1	1.3	5.7	0.59	0.89	0.45	0.65	0.23	-0.29	2.5	1.3	1.4	0.7	0.7
1400C	0.99	0.03	1.30	0.01	0.30	10.5	14.1	13.5	13.7	18.0	14.5	14.4	6.4	3.0	2.1	1.3	5.4	1.01	0.83	0.54	1.28	0.08	-0.35	2.6	1.8	1.5	1.0	1.0
1400D	0.63	0.00	2.96	0.01	0.14	12.2	13.4	11.1	13.5	16.2	13.7	14.4	6.3	2.9	2.1	1.3	5.0	1.24	1.44	0.83	1.05	0.43	-0.25	3.7	2.2	2.2	1.3	1.3
1500E	0.72	0.02	0.41	0.01	0.29	16.8	15.1	12.2	12.2	13.9	14.4	14.4	6.5	3.0	2.1	1.4	6.3	0.21	0.37	0.13	-0.16	0.27	0.10	1.5	0.7	0.8	0.3	0.3
1500F	0.33	0.01	0.47	0.01	0.12	14.6	21.6	14.3	12.7	13.6	7.5	14.4	6.4	3.0	2.1	1.3	6.1	0.36	0.29	0.17	1.28	0.04	-0.96	0.9	0.6	0.5	0.3	0.3

*Corrected for Fibreboard carry over

Sample Reference No.	g. Al ₂ O ₃ In	g. Al ₂ O ₃ out	g. SiO ₂ In	g. SiO ₂ out	Total g. Al ₂ O ₃ pick-up	Total g. SiO ₂ pick-up	g. Al ₂ O ₃ pick-up			g. SiO ₂ pick-up			%Al ₂ O ₃ - Out			%SiO ₂ - Out			Corrected masses out			Corrected Fibreboard masses		
							g. Al ₂ O ₃ pick-up - top	g. Al ₂ O ₃ pick-up - middle	g. Al ₂ O ₃ pick-up - bottom	g. SiO ₂ pick-up - top	g. SiO ₂ pick-up - middle	g. SiO ₂ pick-up - bottom	%Al ₂ O ₃ Analysed - Top	%Al ₂ O ₃ Analysed -Middle	%Al ₂ O ₃ Analysed -Bottom	%SiO ₂ Analysed -Top	%SiO ₂ Analysed -Middle	%SiO ₂ Analysed -Bottom	g. sample mix out - Top (Corrected)*	g. sample mix out - Middle (Corrected)*	g. sample mix out - Bottom (Corrected)*	g. Fibreboard out - Top (Corrected)*	g. Fibreboard out - Middle (Corrected)*	g. Fibreboard out - Bottom (Corrected)*
1300A	0.68	1.91	1.44	2.24	1.24	0.81	0.42	0.51	0.31	0.19	0.32	0.29	4.59	4.52	3.99	5.35	4.92	5.26	15.4	15.4	10.7	14.5	4.2	12.9
1300B	0.67	1.54	1.42	2.00	0.87	0.58	0.23	0.50	0.14	0.16	0.32	0.10	2.88	4.68	3.15	4.37	5.12	4.47	18.2	14.6	8.6	11.2	6.9	12.9
1400C	0.68	1.71	1.45	2.05	1.03	0.61	0.20	0.61	0.21	0.11	0.35	0.15	3.17	5.22	3.64	4.74	5.18	4.61	16.0	15.1	9.5	11.7	7.3	13.4
1400D	0.67	1.74	1.41	2.15	1.08	0.74	0.31	0.59	0.18	0.18	0.39	0.17	3.95	5.15	3.17	5.31	5.43	4.69	15.1	14.8	9.7	12.1	7.0	13.2
1500E	0.69	1.65	1.46	1.99	0.96	0.53	0.17	0.50	0.29	0.05	0.29	0.19	2.58	4.48	4.52	3.82	4.77	5.15	18.7	15.4	9.1	11.8	6.9	13.6
1500F	0.68	1.89	1.44	2.21	1.21	0.77	0.15	0.54	0.52	-0.12	0.33	0.56	3.99	4.97	3.69	4.77	5.24	4.78	11.5	14.5	16.9	5.8	7.7	17.3

*Corrected for Fibreboard carry over

Top Node heat balance

Top Node kJ IN																
Time (s)	Fe (met)	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	MgO	MnO	P ₂ O ₅	SiO ₂	TiO ₂	C	Mullite	H ₂ O	Ar	kJ IN
0	0.0	-38.2	-19.7	-5.1	-0.2	-0.2	-0.1	0.0	-0.2	-10.0	-0.2	0.0	-192.9	-4.8	0.0	-271.6
120	0.0	-38.2	-19.7	-5.1	-0.2	-0.2	-0.1	0.0	-0.2	-10.0	-0.2	0.0	-192.9	-4.8	0.8	-270.8
240	0.0	-42.6	-11.4	-5.1	-0.2	-0.1	-0.1	0.0	-0.2	-10.0	-0.2	0.4	-191.3	-2.0	0.8	-261.9
360	0.1	-39.5	-8.9	-5.0	-0.2	-0.1	-0.1	0.0	-0.2	-9.7	-0.2	1.7	-187.1	-0.1	0.8	-248.7
480	0.4	-35.2	-8.4	-4.9	-0.2	-0.1	-0.1	0.0	-0.2	-9.5	-0.2	2.8	-183.5	0.0	0.8	-238.3
600	0.8	-32.0	-8.2	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.4	-0.2	3.6	-181.0	0.0	0.8	-231.0
720	1.2	-29.4	-8.0	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.3	-0.2	4.0	-179.5	0.0	0.8	-225.8
840	1.5	-27.4	-7.9	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.3	-0.2	4.0	-178.9	0.0	0.8	-222.7
897	1.9	-25.7	-7.9	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.3	-0.2	3.9	-179.0	0.0	0.4	-221.4

Top Node kJ OUT																		
Time (s)	Fe (met)	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	MgO	MnO	P ₂ O ₅	SiO ₂	TiO ₂	C	Mullite	H ₂ O	Ar	CO	CO ₂	kJ OUT
0	0.0	-39.5	-18.4	-5.1	-0.2	-0.2	-0.1	0.0	-0.2	-10.0	-0.2	0.0	-192.9	0.0	0.0	0.0	0.0	-266.8
120	0.0	-42.6	-11.4	-5.1	-0.2	-0.1	-0.1	0.0	-0.2	-10.0	-0.2	0.4	-191.3	-2.0	3.5	0.0	-1.6	-260.8
240	0.1	-39.5	-8.9	-5.0	-0.2	-0.1	-0.1	0.0	-0.2	-9.7	-0.2	1.7	-187.1	-0.9	3.5	-0.1	-1.3	-248.1
360	0.4	-35.2	-8.4	-4.9	-0.2	-0.1	-0.1	0.0	-0.2	-9.5	-0.2	2.8	-183.5	-0.4	3.5	-0.2	-1.0	-237.3
480	0.8	-32.0	-8.2	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.4	-0.2	3.6	-181.0	-0.4	3.5	-0.4	-0.6	-229.7
600	1.2	-29.4	-8.0	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.3	-0.2	4.0	-179.5	0.0	3.5	-0.4	-0.6	-224.0
720	1.5	-27.4	-7.9	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.3	-0.2	4.0	-178.9	0.0	3.5	-0.5	-0.3	-220.8
840	1.9	-25.7	-7.9	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.3	-0.2	3.9	-179.0	0.0	3.5	-0.5	-0.3	-219.0
897	2.0	-25.0	-7.9	-4.8	-0.2	-0.1	-0.1	0.0	-0.2	-9.3	-0.2	3.8	-179.0	0.0	1.7	-0.2	-0.1	-219.6
																		(kJ OUT) - (kJ IN)
																		5
																		10
																		14
																		11
																		9
																		7
																		5
																		4
																		2

Middle Node mass balance

Middle Node Mass IN								Mass in (g.)																
Time (s)	Middle Node %	T (°C)	%Reduction	%Fe(total)	%Fe(met)	%Fe(+2)	%Fe(+3)	g. Fe (total)	g. Fe (met)	g. FeO	g. Fe2O3	g. Al2O3	g. CaO	g. K2O	g. MgO	g. MnO	g. P2O5	g. SiO2	g. TiO2	g. C	g. Mullite	g. H2O	g. Ar	Total g. in
0	33	25	25.6	62.3	0.10	47.5	14.70	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
120		25	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
240		50	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
360		182	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
480		404	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
600		652	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
720		826	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
840		958	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2
960		1038	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	22.2

Middle Node Mass OUT		Mass Out:	15.1	g. Fe out:	9.4		Mass out (g.)																		
Time (s)	T (°C)	%Reduction	%Fe(total)	%Fe(met)	%Fe(+2)	%Fe(+3)	g. Fe (total)	g. Fe (met)	g. FeO	g. Fe2O3	g. Al2O3	g. CaO	g. K2O	g. MgO	g. MnO	g. P2O5	g. SiO2	g. TiO2	g. C	g. Mullite	g. H2O	g. Ar	g. CO	g. CO2	Total g. Out
0	25.0	25.6	62.3	0.10	47.5	14.70	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
120	50	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
240	182	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
360	404	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
480	652	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
600	826	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
720	958	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
840	1038	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2
960	1071	25.6	62.3	0.1	47.5	14.7	9.4	0.0	9.2	3.2	0.2	0.0	0.0	0.0	0.0	0.0	0.5	0.0	2.1	7.0	0.0	0.0	0	0	22.2

Middle Node heat balance

Middle Node kJ IN																
Time (s)	Fe (met)	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	MgO	MnO	P ₂ O ₅	SiO ₂	TiO ₂	C	Mullite	H ₂ O	Ar	Total kJ IN
0	0.0	-33.7	-16.3	-3.7	-0.1	-0.1	-0.1	0.0	-0.2	-7.2	-0.1	0.0	-111.3	0.0	0.0	-172.8
120	0.0	-33.7	-16.3	-3.7	-0.1	-0.1	-0.1	0.0	-0.2	-7.2	-0.1	0.0	-111.3	0.0	0.0	-172.8
240	0.0	-33.5	-16.3	-3.7	-0.1	-0.1	-0.1	0.0	-0.1	-7.2	-0.1	0.0	-111.1	0.0	0.0	-172.4
360	0.0	-32.7	-16.0	-3.7	-0.1	-0.1	-0.1	0.0	-0.1	-7.1	-0.1	0.3	-110.3	0.0	0.0	-170.1
480	0.0	-31.2	-15.4	-3.6	-0.1	-0.1	-0.1	0.0	-0.1	-7.0	-0.1	0.9	-108.7	0.0	0.0	-165.5
600	0.0	-29.4	-14.6	-3.5	-0.1	-0.1	-0.1	0.0	-0.1	-6.9	-0.1	1.8	-106.7	0.0	0.0	-159.9
720	0.0	-28.2	-14.1	-3.5	-0.1	-0.1	-0.1	0.0	-0.1	-6.8	-0.1	2.4	-105.2	0.0	0.0	-155.9
840	0.0	-27.2	-13.7	-3.5	-0.1	-0.1	-0.1	0.0	-0.1	-6.7	-0.1	3.0	-104.1	0.0	0.0	-152.7
960	0.0	-26.6	-13.5	-3.4	-0.1	-0.1	-0.1	0.0	-0.1	-6.7	-0.1	3.3	-103.4	0.0	0.0	-150.8

Middle Node kJ OUT																			
Time (s)	Fe (met)	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	MgO	MnO	P ₂ O ₅	SiO ₂	TiO ₂	C	Mullite	H ₂ O	Ar	CO	CO ₂	Total kJ OUT	(kJ OUT) - (kJ IN)
0	0.0	-33.7	-16.3	-3.7	-0.1	-0.1	-0.1	0.0	-0.2	-7.2	-0.1	0.0	-111.3	0.0	0.0	0.0	0.0	-172.8	0.0
120	0.0	-33.5	-16.3	-3.7	-0.1	-0.1	-0.1	0.0	-0.1	-7.2	-0.1	0.0	-111.1	0.0	0.0	0.0	0.0	-172.4	0.4
240	0.0	-32.7	-16.0	-3.7	-0.1	-0.1	-0.1	0.0	-0.1	-7.1	-0.1	0.3	-110.3	0.0	0.0	0.0	0.0	-170.1	2.3
360	0.0	-31.2	-15.4	-3.6	-0.1	-0.1	-0.1	0.0	-0.1	-7.0	-0.1	0.9	-108.7	0.0	0.0	0.0	0.0	-165.5	4.5
480	0.0	-29.4	-14.6	-3.5	-0.1	-0.1	-0.1	0.0	-0.1	-6.9	-0.1	1.8	-106.7	0.0	0.0	0.0	0.0	-159.9	5.6
600	0.0	-28.2	-14.1	-3.5	-0.1	-0.1	-0.1	0.0	-0.1	-6.8	-0.1	2.4	-105.2	0.0	0.0	0.0	0.0	-155.9	4.1
720	0.0	-27.2	-13.7	-3.5	-0.1	-0.1	-0.1	0.0	-0.1	-6.7	-0.1	3.0	-104.1	0.0	0.0	0.0	0.0	-152.7	3.1
840	0.0	-26.6	-13.5	-3.4	-0.1	-0.1	-0.1	0.0	-0.1	-6.7	-0.1	3.3	-103.4	0.0	0.0	0.0	0.0	-150.8	1.9
960	0.0	-26.3	-13.4	-3.4	-0.1	-0.1	-0.1	0.0	-0.1	-6.7	-0.1	3.4	-103.1	0.0	0.0	0.0	0.0	-150.0	0.8

Bottom Node mass balance

Bottom Node Mass IN								Mass in (g.)																
Time (s)	Bottom Node %	T (°C)	%Reduction	%Fe(total)	%Fe(met)	%Fe(+2)	%Fe(+3)	g. Fe (total)	g. Fe (met)	g. FeO	g. Fe2O3	g. Al2O3	g. CaO	g. K2O	g. MgO	g. MnO	g. P2O5	g. SiO2	g. TiO2	g. C	g. Mullite	g. H2O	g. Ar	Total g. in
0	21	25	24.7	58.5	0.20	42.8	15.50	5.5	0.0	5.2	2.1	0.1	0.01	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
57		25	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
146		56	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
241		150	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
340		265	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
448		386	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
522		546	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
616		711	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4
713		822	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	22.4

Bottom Node Mass OUT		Mass Out:	9.5	g. Fe out:	5.5		Mass out (g.)																		
Time (s)	T (°C)	%Reduction	%Fe(total)	%Fe(met)	%Fe(+2)	%Fe(+3)	g. Fe (total)	g. Fe (met)	g. FeO	g. Fe2O3	g. Al2O3	g. CaO	g. K2O	g. MgO	g. MnO	g. P2O5	g. SiO2	g. TiO2	g. C	g. Mullite	g. H2O	g. Ar	g. CO	g. CO2	Total g. Out
0	25.0	24.7	58.5	0.20	42.8	15.50	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
57	56	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
146	150	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
241	265	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
340	386	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
448	546	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
522	711	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
616	822	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4
713	874	24.7	58.5	0.2	42.8	15.5	5.5	0.0	5.2	2.1	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.3	13.2	0.0	0.0	0	0	22.4

Bottom Node heat balance

Bottom Node kJ IN																
Time (s)	Fe (met)	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	MgO	MnO	P ₂ O ₅	SiO ₂	TiO ₂	C	Mullite	H ₂ O	Ar	kJ IN
0	0.0	-19.1	-10.8	-2.4	-0.1	-0.1	0.0	0.0	-0.1	-4.6	-0.1	0.0	-211.6	0.0	0.0	-248.8
57	0.0	-19.1	-10.8	-2.4	-0.1	-0.1	0.0	0.0	-0.1	-4.6	-0.1	0.0	-211.6	0.0	0.0	-248.8
146	0.0	-18.9	-10.8	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.6	-0.1	0.0	-211.3	0.0	0.0	-248.3
241	0.0	-18.6	-10.6	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.6	-0.1	0.1	-210.2	0.0	0.0	-246.5
340	0.0	-18.2	-10.4	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.5	-0.1	0.3	-208.7	0.0	0.0	-244.2
448	0.0	-17.7	-10.2	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.5	-0.1	0.6	-207.0	0.0	0.0	-241.5
522	0.0	-17.1	-9.9	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.4	-0.1	0.9	-204.5	0.0	0.0	-237.7
616	0.0	-16.4	-9.5	-2.2	-0.1	-0.1	0.0	0.0	-0.1	-4.4	-0.1	1.3	-202.0	0.0	0.0	-233.6
713	0.0	-15.9	-9.3	-2.2	-0.1	-0.1	0.0	0.0	-0.1	-4.3	-0.1	1.5	-200.2	0.0	0.0	-230.8

Bottom Node kJ OUT																			
Time (s)	Fe (met)	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	MgO	MnO	P ₂ O ₅	SiO ₂	TiO ₂	C	Mullite	H ₂ O	Ar	CO	CO ₂	kJ OUT	(kJ OUT) - (kJ IN)
0	0.0	-19.1	-10.8	-2.4	-0.1	-0.1	0.0	0.0	-0.1	-4.6	-0.1	0.0	-211.6	0.0	0.0	0.0	0.0	-248.8	0.0
57	0.0	-18.9	-10.8	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.6	-0.1	0.0	-211.3	0.0	0.0	0.0	0.0	-248.3	0.5
146	0.0	-18.6	-10.6	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.6	-0.1	0.1	-210.2	0.0	0.0	0.0	0.0	-246.5	1.7
241	0.0	-18.2	-10.4	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.5	-0.1	0.3	-208.7	0.0	0.0	0.0	0.0	-244.2	2.4
340	0.0	-17.7	-10.2	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.5	-0.1	0.6	-207.0	0.0	0.0	0.0	0.0	-241.5	2.7
448	0.0	-17.1	-9.9	-2.3	-0.1	-0.1	0.0	0.0	-0.1	-4.4	-0.1	0.9	-204.5	0.0	0.0	0.0	0.0	-237.7	3.8
522	0.0	-16.4	-9.5	-2.2	-0.1	-0.1	0.0	0.0	-0.1	-4.4	-0.1	1.3	-202.0	0.0	0.0	0.0	0.0	-233.6	4.1
616	0.0	-15.9	-9.3	-2.2	-0.1	-0.1	0.0	0.0	-0.1	-4.3	-0.1	1.5	-200.2	0.0	0.0	0.0	0.0	-230.8	2.8
713	0.0	-15.7	-9.2	-2.2	-0.1	-0.1	0.0	0.0	-0.1	-4.3	-0.1	1.7	-199.3	0.0	0.0	0.0	0.0	-229.5	1.3

Time (s)	kJ Out - kJ In Top	kJ Out - kJ In Middle	kJ Out - kJ In Bottom	Incremental kJ
120	10	0	1	11
240	14	2	2	18
360	11	5	2	18
480	9	6	3	17
600	7	4	4	15
720	5	3	4	12
840	4	2	3	8
897	2	1	1	4
Total Incremental kJ:				103
Weighted Average kW/m ² :				163

Appendix VII

Mass and Heat Balance equations

(a) Mass balance equations

m_j^{i-in} = mass of component j in node i of unreacted sample

m_j^{i-out} = mass of component j in node i of reacted sample

m_{j-corr}^{i-out} = corrected mass of component j in node i of reacted sample

m_{total}^{in} = total g. unreacted sample mix in crucible

$\%Y^{i-in}$ = mass% of component Y in node i of unreacted sample

$\%Y^{i-out}$ = mass% of component Y in node i of reacted sample

$\%Y_{corr}^{i-out}$ = corrected mass% of component Y in node i of reacted sample

mm_k = molar mass of component k

X_i = mass fraction of sample material mix in node i , i = top, mid, bot for top, middle or bottom node

i = top, mid, bot for top, middle or bottom node

$n_{j-phase}^{i-out}$ = mol of component j in node i of reacted sample in a phase

Correction of reacted mass out for fibreboard carry over to top node reacted sample

mix:

$$m_{total}^{top-in} = m_{total}^{in} \cdot X_{top}$$

$$m_{Al_2O_3}^{carry-over} = m_{total}^{top-out} \cdot \frac{\%Al_2O_3^{top-out}}{100} - m_{total}^{top-in} \cdot \frac{\%Al_2O_3^{top-in}}{100}$$

$$m_{SiO_2}^{carry-over} = m_{total}^{top-out} \cdot \frac{\%SiO_2^{top-out}}{100} - m_{total}^{top-in} \cdot \frac{\%SiO_2^{top-in}}{100}$$

$$m_{Al_2O_3-corr}^{top-out} = m_{total}^{top-in} - m_{Al_2O_3}^{carry-over} - m_{SiO_2}^{carry-over}$$

$m_{Al_2O_3}^{carry-over}$ = g. Al_2O_3 carry-over from fibreboard to reacted sample mix in top node

$m_{SiO_2}^{carry-over}$ = g. SiO_2 carry-over from fibreboard to reacted sample mix in top node

m_{total}^{in} = total g. unreacted sample mix in crucible

The fibreboard carry-over calculations for the middle and bottom node are done in the same manner.

Correction of fibreboard crucible mass, in top node section, for fibreboard carry-over to top node reacted sample mix:

$$m_{FB_corr}^{top_out} = m_{FB}^{top_out} + m_{Al_2O_3}^{carry-over} + m_{SiO_2}^{carry-over}$$

$$m_{Al_2O_3}^{carry-over} = g. Al_2O_3 \text{ carry-over from fibreboard to reacted sample mix in top node}$$

$$m_{SiO_2}^{carry-over} = g. SiO_2 \text{ carry-over from fibreboard to reacted sample mix in top node}$$

The fibreboard mass correction calculations for the middle and bottom node are done in the same manner.

Correction of FeO analyses for top node for fibreboard carry-over to top node reacted sample mix:

$$m_{FeO}^{top_out} = m_{total}^{top_out} \cdot \frac{\%FeO^{top_out}}{100}$$

$$\%FeO_{corr}^{top_out} = \frac{m_{FeO}^{top_out}}{m_{total_corr}^{top_out}} \cdot 100$$

$$\%Fe(+2)_{corr}^{top_out} = \frac{m_{FeO}^{top_out}}{m_{total_corr}^{top_out}} \cdot 100 / mm_{FeO} \cdot mm_{Fe}$$

Similarly the corrected mass% of C, Fe₂O₃, Fe metal, Fe(total) can be calculated. The calculations are done for the top, middle and bottom nodes.

Calculation of mass FeO into top node material mix

$$m_{FeO}^{top_in} = m_{total_corr}^{top_out} \cdot \frac{\%Fe(+2)_{corr}^{top_out}}{Fe(total)_{top_in}} \cdot \frac{\%Fe(total)_{corr}^{top_out}}{100} / mm_{Fe} \cdot mm_{FeO}$$

$$m_{FeO}^{top_out} = m_{total_corr}^{top_out} \cdot \frac{\%Fe(+2)_{corr}^{top_out}}{100} / mm_{Fe} \cdot mm_{FeO}$$



Calculation of CaO into top node material mix

$$m_{CaO}^{top_out} = m_{CaO}^{top_in} = m_{total}^{top_in} \cdot \frac{\%CaO^{top_in}}{100}$$

$$m_{total}^{top_in} = m_{total}^{in} \cdot X_{top}$$

Fe balance calculation to check Fe mass accounting

$$m_{Fe}^{total_in} = m_{total}^{in} \cdot \frac{\%FeO^{total_in}}{100} \cdot \frac{\%Fe(total)^{total_in}}{100}$$

$\%FeO$ = mass% pre-reduced ore in sample mix

$$m_{Fe}^{total_out} = m_{corr}^{top_out} \cdot \frac{\%Fe(total)_{corr}^{top_out}}{100} + m_{corr}^{mid_out} \cdot \frac{\%Fe(total)_{corr}^{mid_out}}{100} + m_{corr}^{bot_out} \cdot \frac{\%Fe(total)_{corr}^{bot_out}}{100}$$

$$\frac{m_{Fe}^{total_in}}{m_{Fe}^{total_out}} \approx 1$$

C balance

$$m_C^{top_in} = m_{total}^{top_in} \cdot \frac{\%Graphite^{total_in}}{100} \cdot \frac{\%C^{total_in}}{100}$$

$$m_{total}^{top_in} = m_{total}^{in} \cdot X_{top}$$

$$m_C^{top_out} = m_C^{top_in} - (n_{CO_gas}^{top_out} + n_{CO_2_gas}^{top_out}) \cdot mm_C$$

$\%Graphite^{total_in}$ = mass% graphite in sample mix

$\%C^{total_in}$ = %C in graphite



O balance

$$n_{O_gas}^{top_out} = m_{FeO}^{top_in} / mm_{FeO} + m_{Fe_2O_3}^{top_in} / mm_{Fe_2O_3} \cdot 3 - m_{FeO}^{top_out} / mm_{FeO} - m_{Fe_2O_3}^{top_out} / mm_{Fe_2O_3} \cdot 3$$

$$\frac{n_{CO_gas}^{top_out}}{n_{CO_gas}^{top_out} + n_{CO_2_gas}^{top_out}} = r / 100$$

$$n_{CO_gas}^{top_out} + 2 \cdot n_{CO_2_gas}^{top_out} = n_{O_gas}^{top_out}$$

$$n_{CO_2_gas}^{top_out} = n_{O_gas}^{top_out} \cdot (1 - r) / (2 - r)$$

$$r = \frac{\%CO}{\%CO + \%CO_2} \text{ in product gas analysis}$$

(b) Heat balance equations

$$C_p(T) = A + BT + C/T^2 + DT^2 \text{ [J/mol K]}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT + \Delta H_{T_1} = A \cdot (T_2 - T_1) + B/2 \cdot (T_2^2 - T_1^2) - C/(T_2 - T_1) + D/3 \cdot (T_2^3 - T_1^3)$$

The $C_p(T)$ equations were obtained from Kubashewski *et al.* (1993).

$$\Delta J_{total}^{top} = \sum \Delta H_j^{top} \cdot n_j^{top_out} - \sum \Delta H_j^{top} \cdot n_j^{top_in} \text{ [J]}$$

$$\Delta J_{total} = \Delta J_{total}^{top} + \Delta J_{total}^{mid} + \Delta J_{total}^{bot} \text{ [J]}$$

$$\Delta W_{total} = \Delta J_{total} / 6000 \cdot t \text{ [kW]}$$

$$q_{HM} = \frac{\Delta W_{total}}{A_4} \text{ [kW/m}^2\text{]}$$

$C_p(T)$ = heat capacity of component at constant pressure

ΔH = change in enthalpy of component material when heated from T_1 to T_2

t = total reaction time in minutes

q_{HM} = heat transfer to sample as calculated in heat-mass balance

The enthalpy equation parameters used are shown below:



Component	$\Delta H_f [J/mol]$	$T_1 [K]$	$T_2 [K]$	[J/deg mol]			
				A	$B \cdot 10^3$	$C \cdot 10^{-5}$	$D \cdot 10^6$
Fe ₂ O ₃	-823400	298	950	98.28	77.82	-14.85	---
	-731081	950	1050	150.62	---	---	---
	-716019	>=1050		132.67	7.36	---	---
Fe ₃ O ₄	-1108800	298	900	91.55	202	---	---
	-980846	>=900		213.4	---	---	---
FeO	-263000	>=298		48.79	8.37	-2.8	---
Fe	0	298	800	28.18	-7.32	-2.9	---
	15571	800	1000	-263.45	255.81	619.23	---
	24408	1000	1042	-641.91	696.34	---	---
	27308	1042	1060	1946.25	-1787.5	---	---
	28525	1060	1184	-561.95	334.13	2912.11	---
	35002	1184	1665	23.99	8.36	---	---
	53069	1665	1809	24.64	9.9	---	---
	72893	1809	2000	46.02	---	---	---
SiO ₂	-908300	298	540	46.9	31.51	-10.08	---
	-893971	540	2000	71.63	1.88	-39.06	---
	-781586	>=2000		86.19	---	---	---
Al ₂ O ₃	-1675700	298	2325	117.49	10.38	-37.11	---
CaO	-634900	298	2900	50.42	4.18	-8.49	---
MgO	-601600	298	3105	48.99	3.43	11.34	---
CO	-110500	>=298		28.41	4.1	-0.46	---
CO ₂	-393500	>=298		44.14	9.04	-8.54	---
C(graphite)	0	298	1100	0.11	38.94	-1.48	---
	13998	>=1100		24.43	0.44	-31.63	---
MnO	-384900	298	2058	46.48	8.12	-3.68	---
H ₂	0	298		27.37	3.33	---	---
H ₂ O (liquid)	-285800	>=298		75.44	---	---	---
H ₂ O (gas)	-241800	>=298		30	10.71	0.33	---
TiO ₂	-944000	>=298		73.35	3.05	-17.03	---
Na ₂ O	-415100	298	1023	55.48	70.21	-4.14	-30.54
	-351070	1023	1243	82.3	12.76	---	---
	-317883	1243	1405	84.85	10.71	---	---
	-254140	>=1405		104.6	---	---	---
K ₂ O	-363200	>=298		95.65	-4.94	-11.05	23.68
P ₂ O ₅	-1505000	>=298		74.89	162.34	-15.61	---
Mullite (3Al ₂ O ₃ .2SiO ₂)	-6820800	298	600	233.59	633.88	-55.86	385.77
	-6698110	600		503.46	35.1	-230.12	-2.51

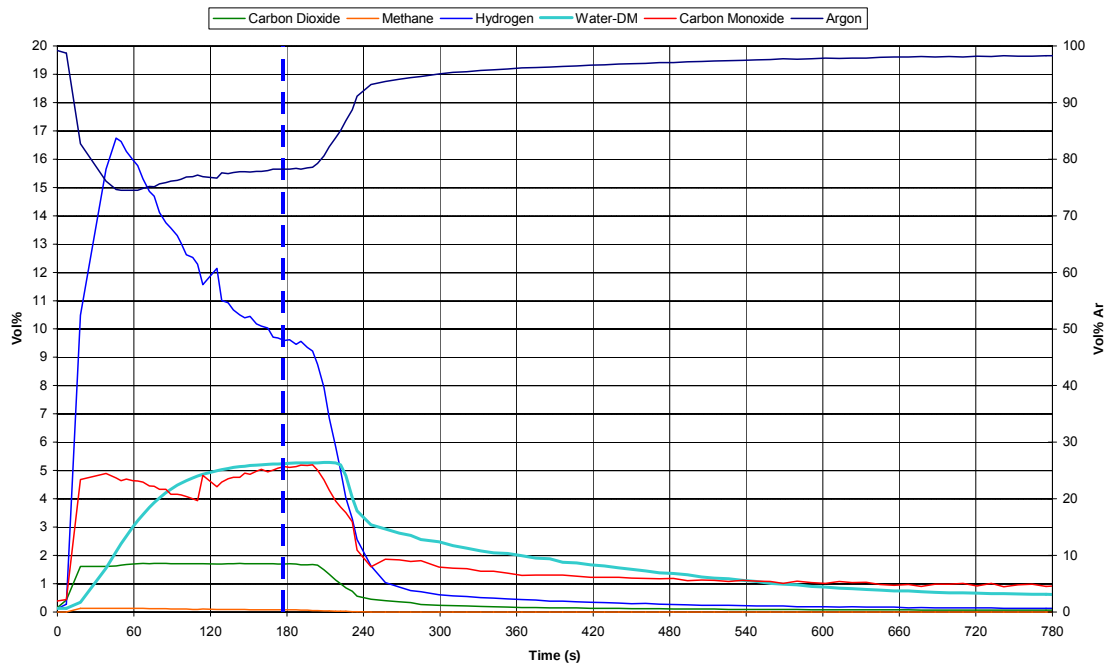
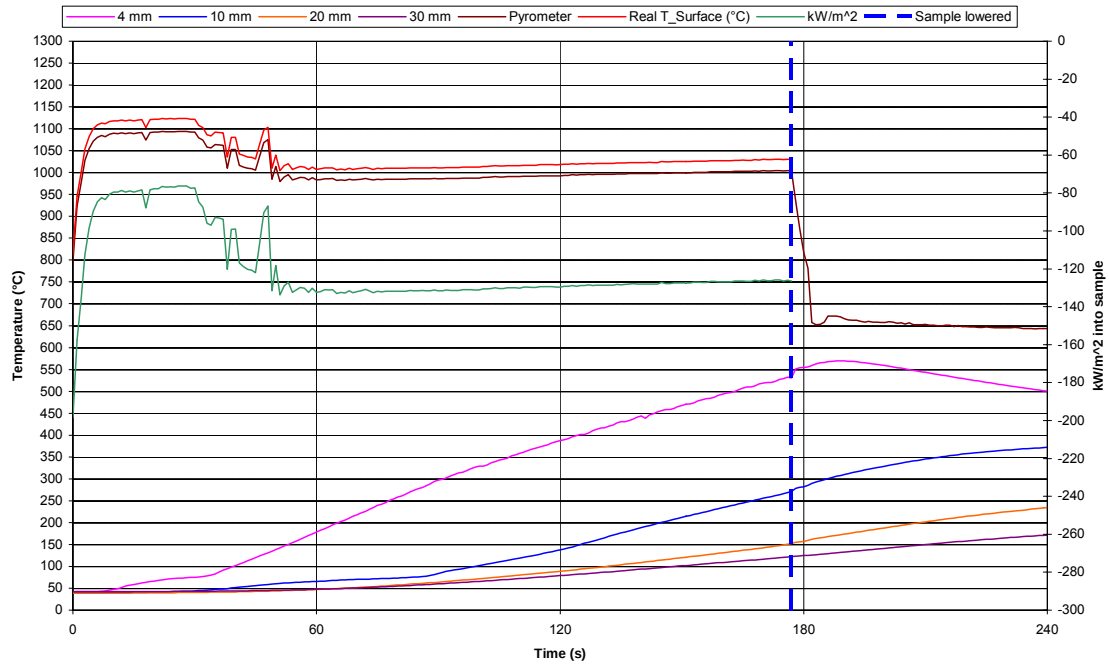
$C_p(T)$ of Argon taken as 20.786 J/mol K from Chase, M.W., Jr., *NIST-JANAF*

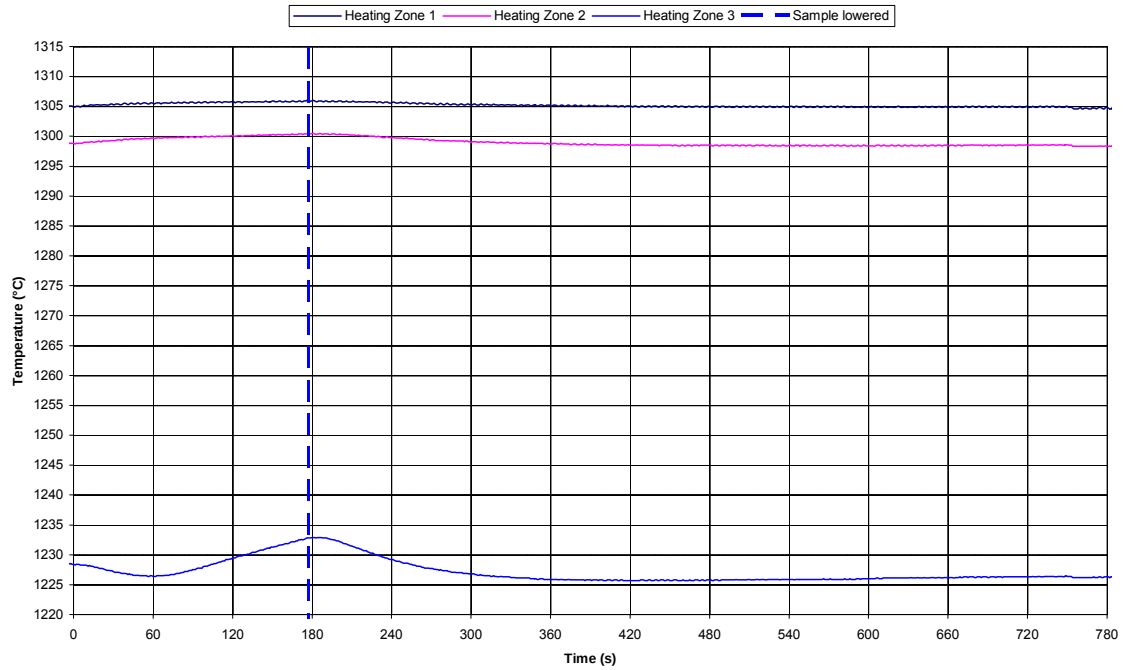
Thermochemical Tables, Fourth Edition, 1998. American Institute of Physics, Woodbury, New York.



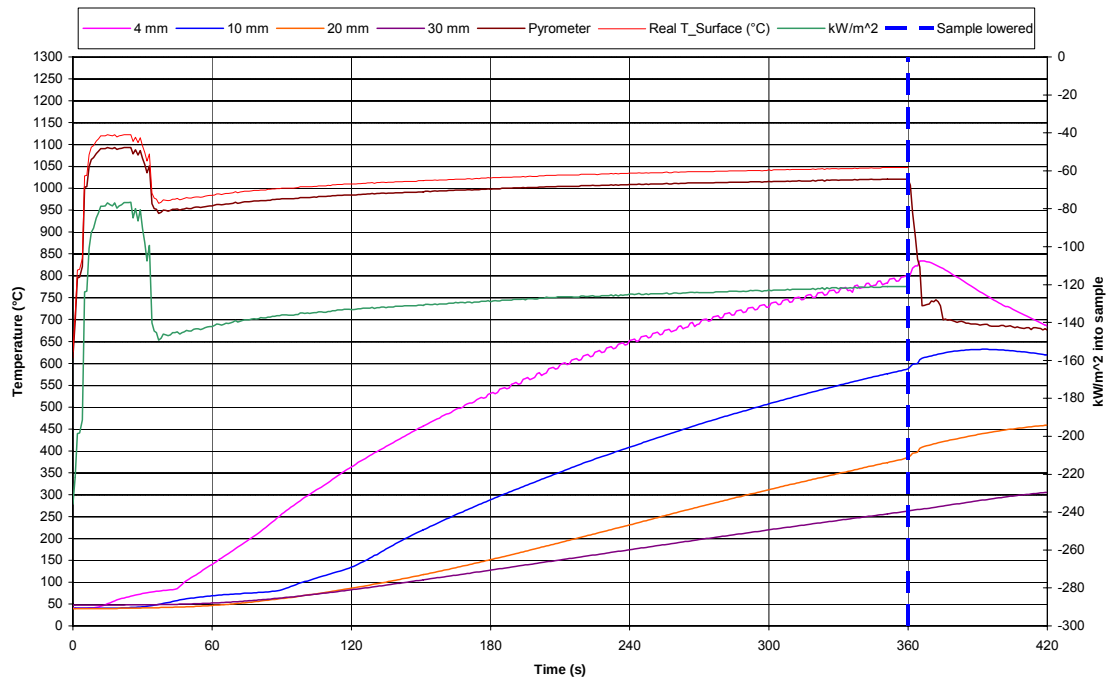
Appendix VIII: Experimental data graphs

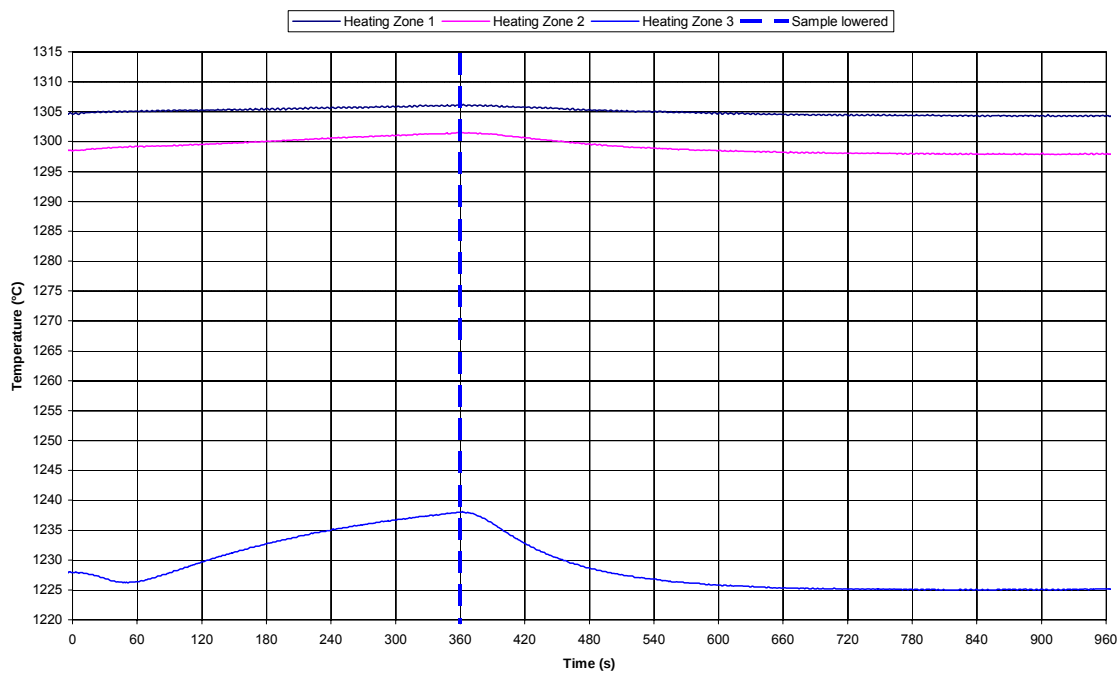
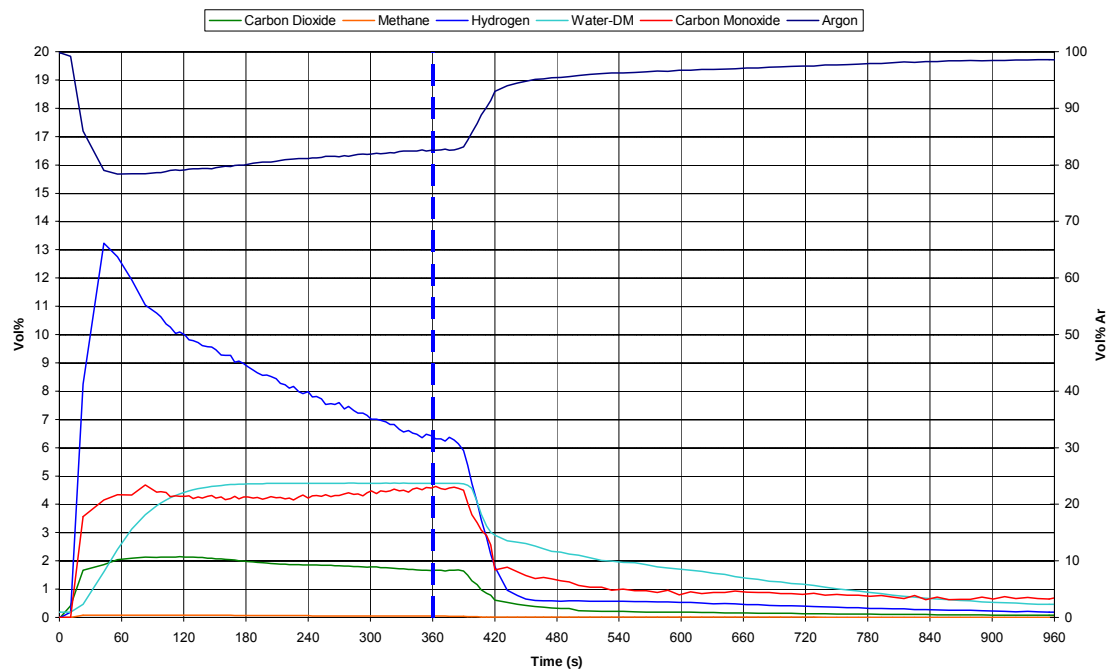
Coal-Ore; 40mm layer, 1300°C, 3minutes





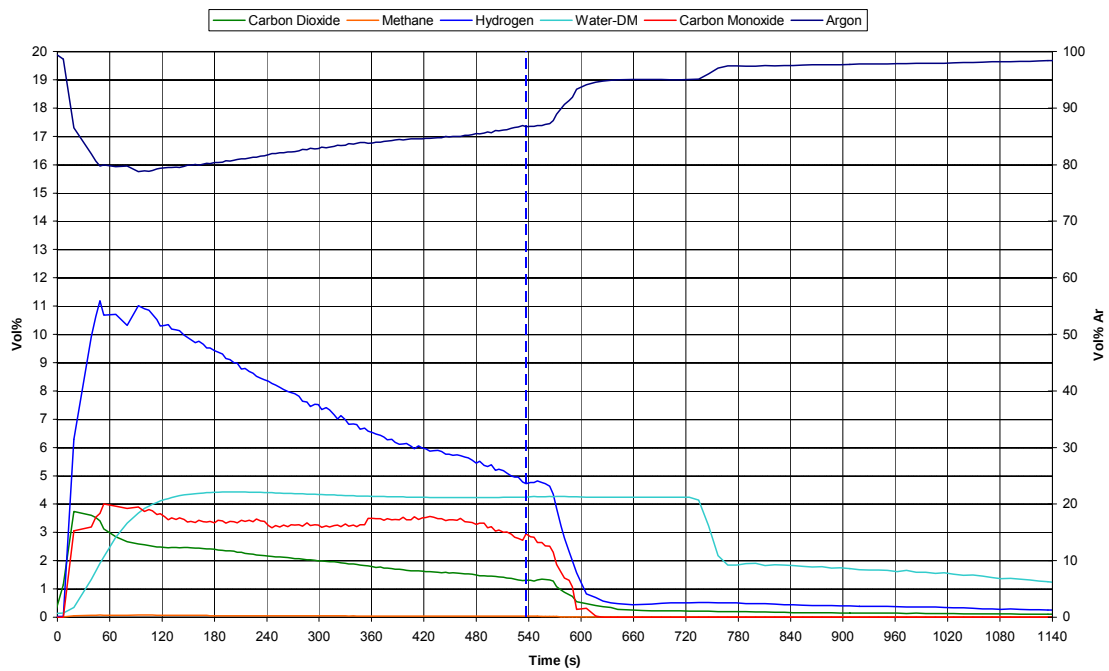
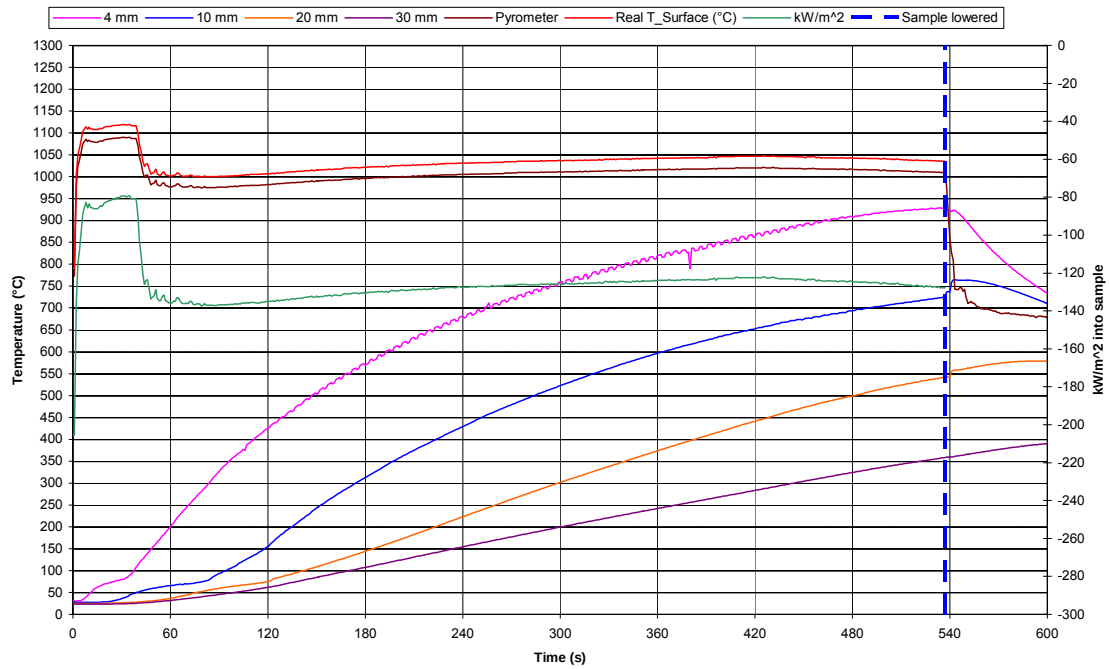
Coal-Ore; 40mm layer, 1300°C, 6minutes

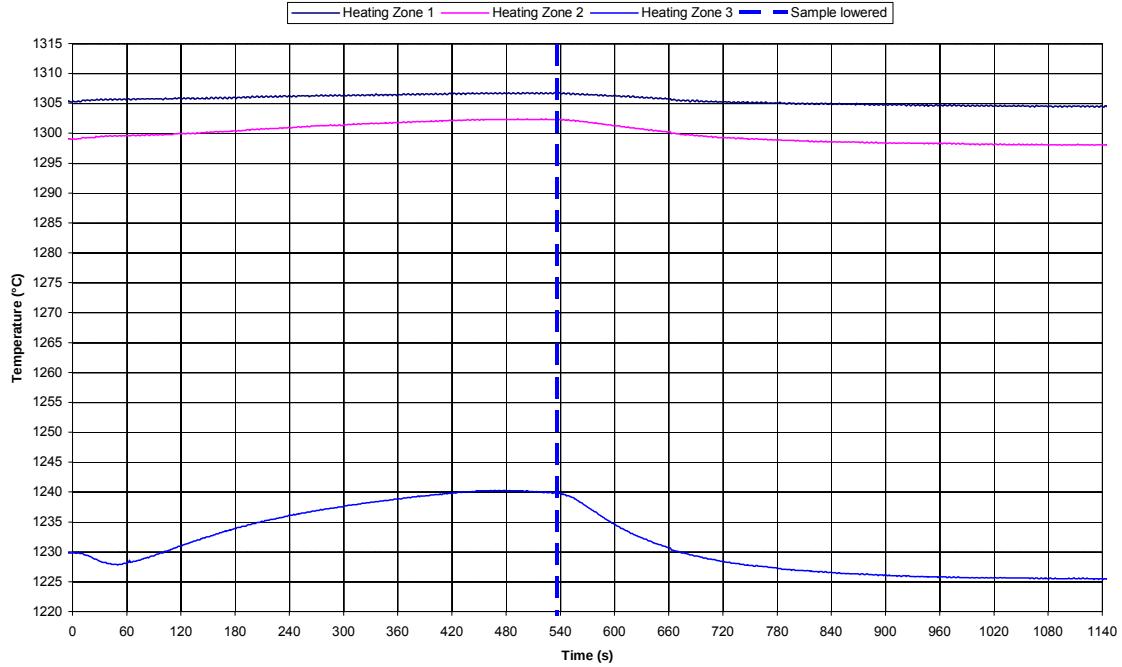




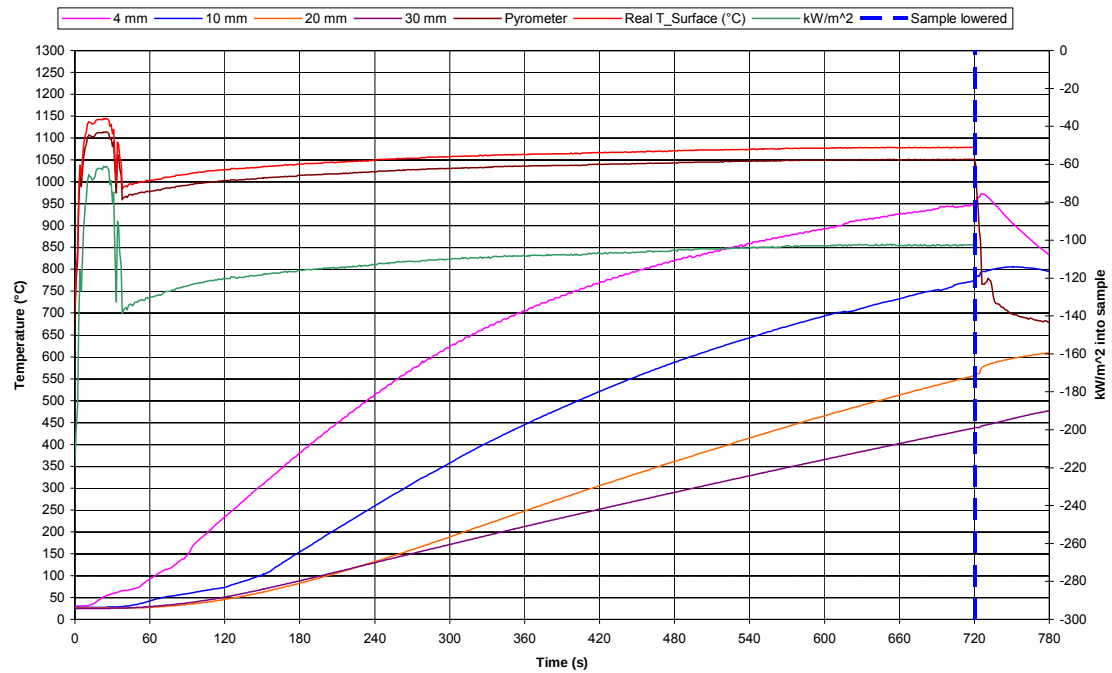


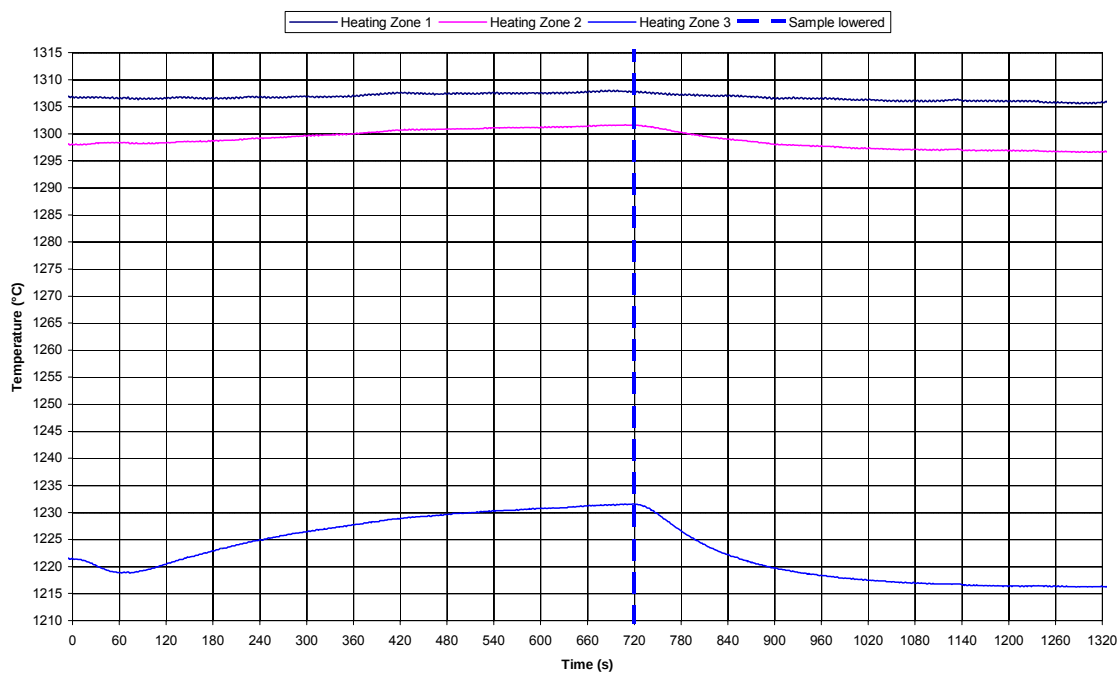
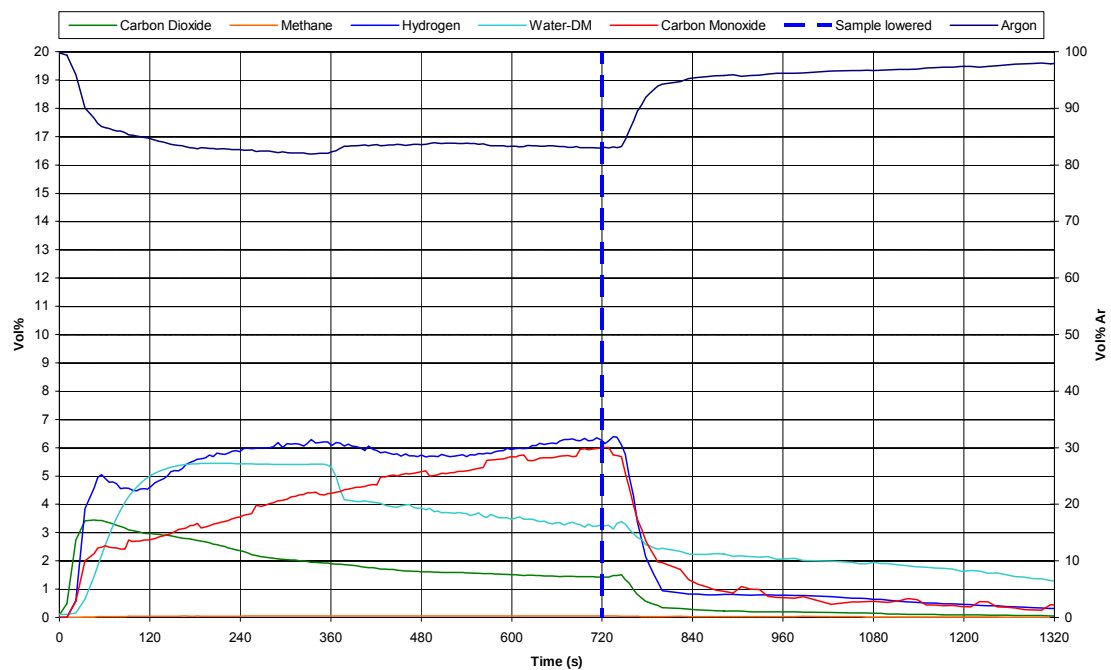
Coal-Ore; 40mm layer, 1300°C, 9minutes





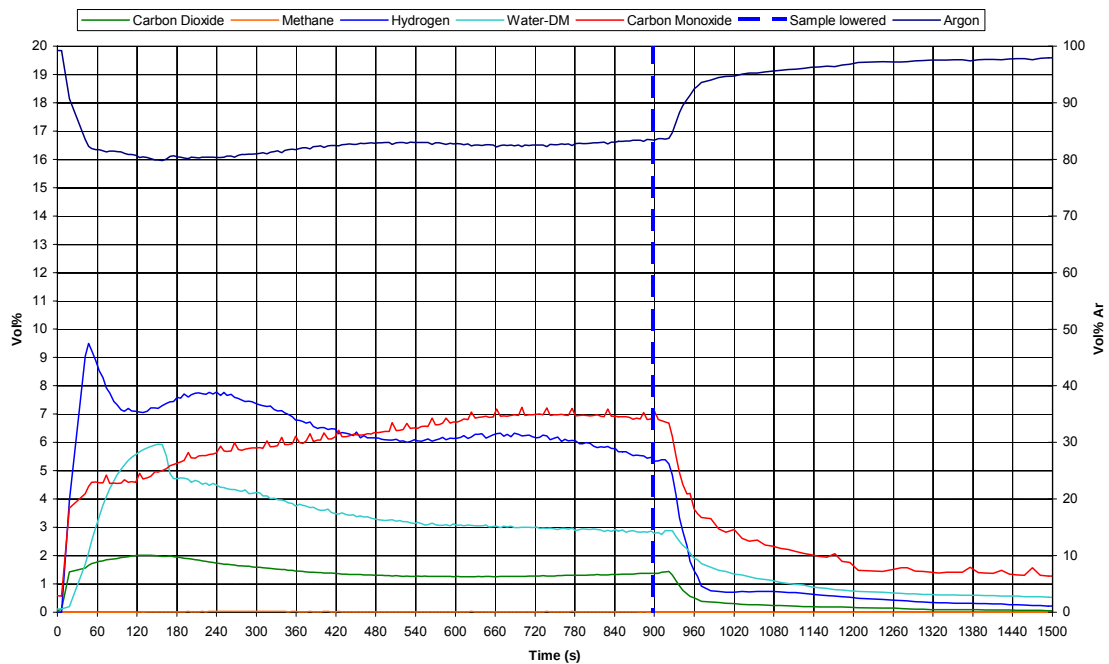
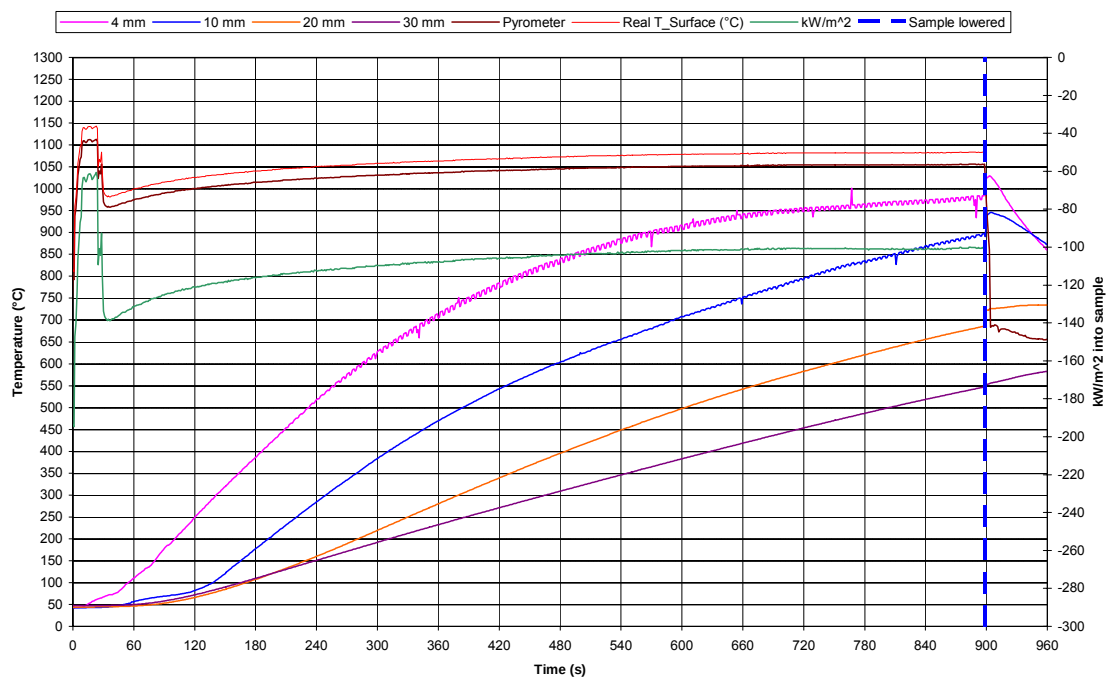
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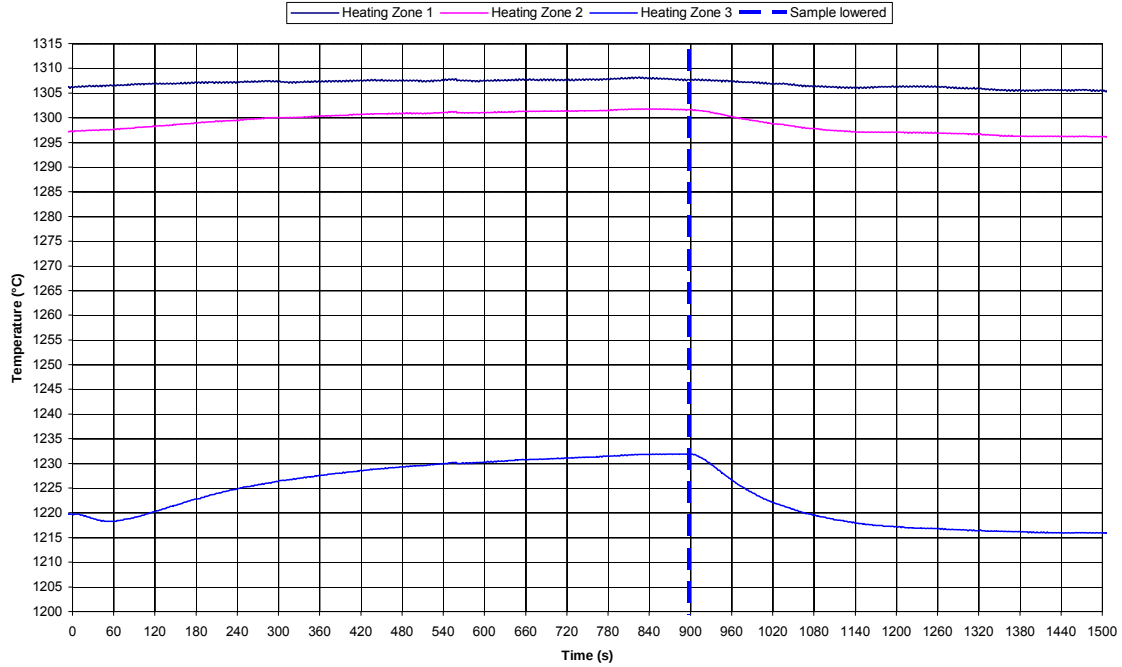




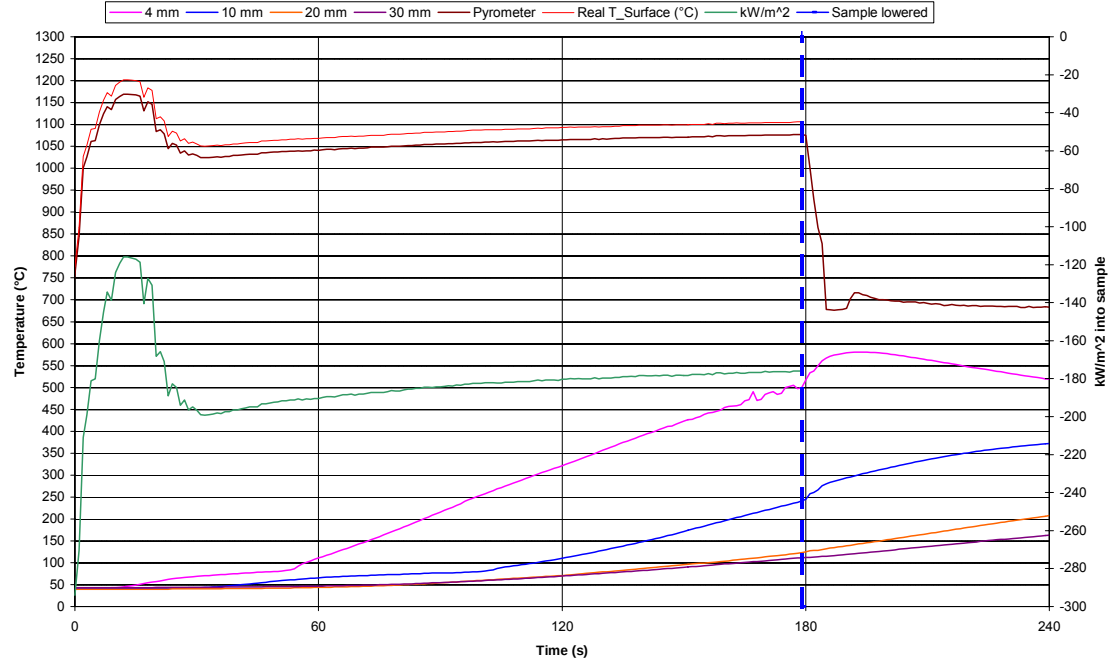


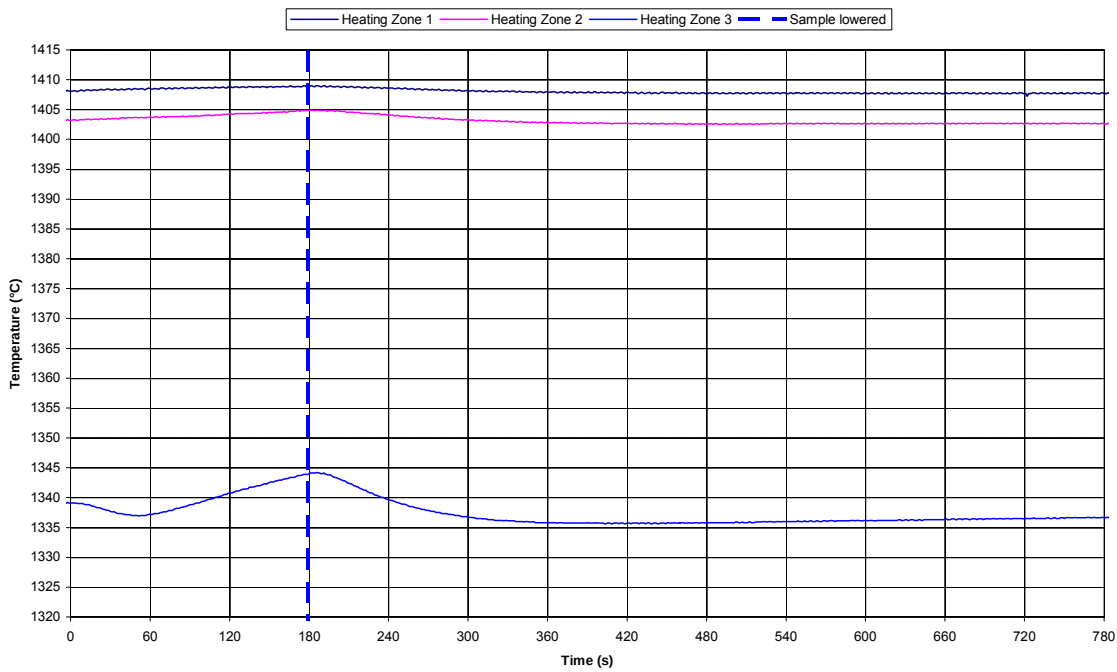
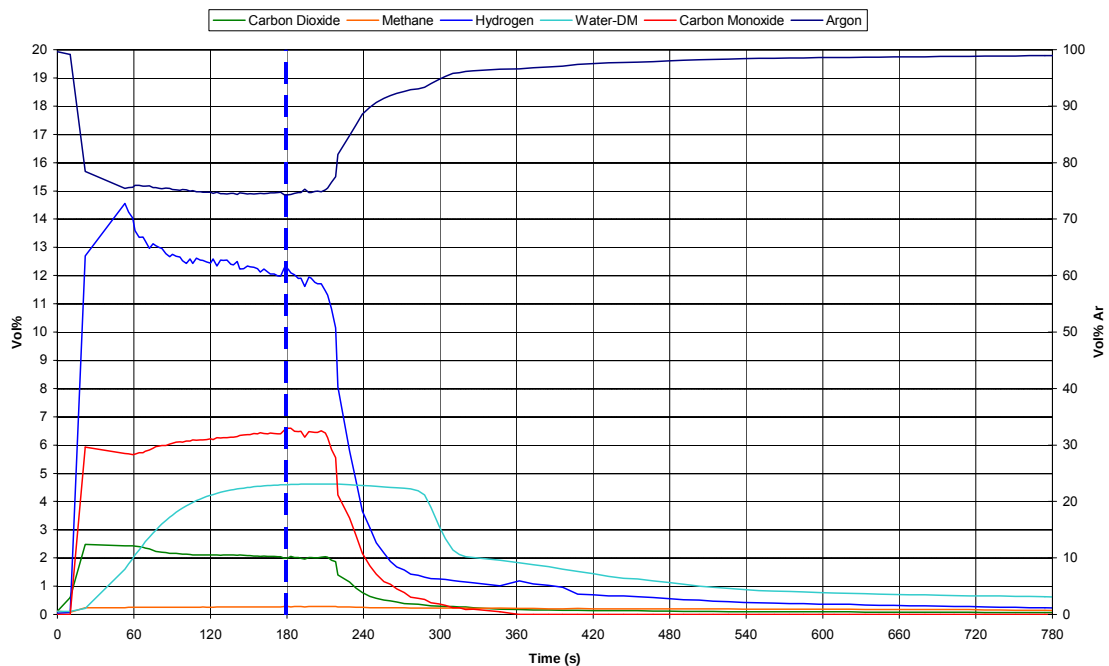
Coal-Ore; 40mm layer, 1300°C, 15minutes





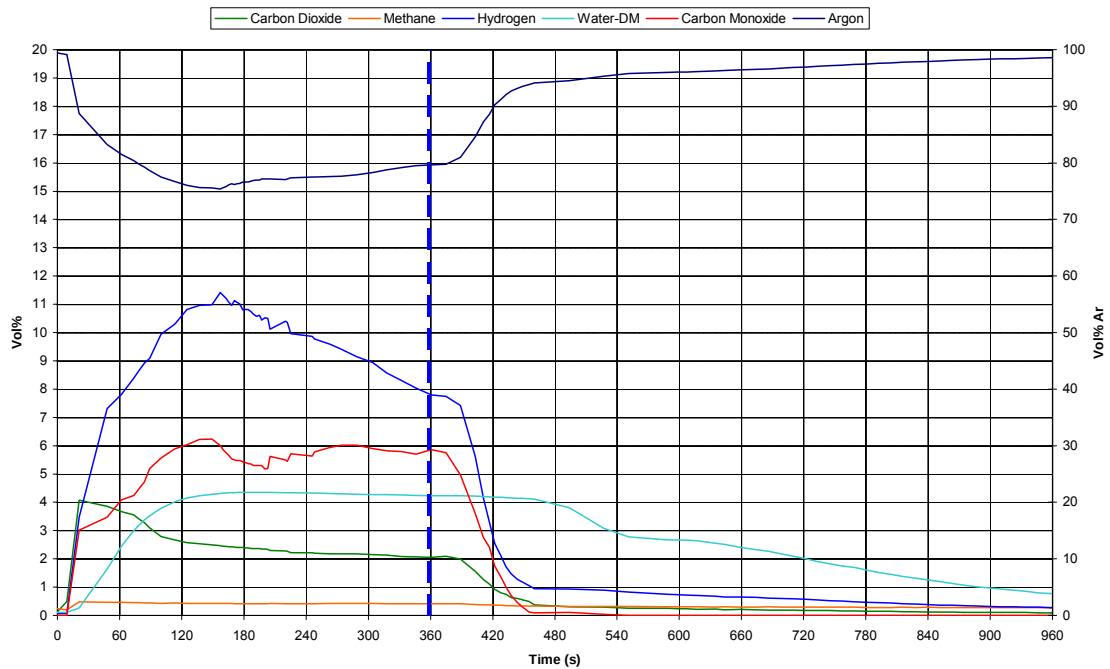
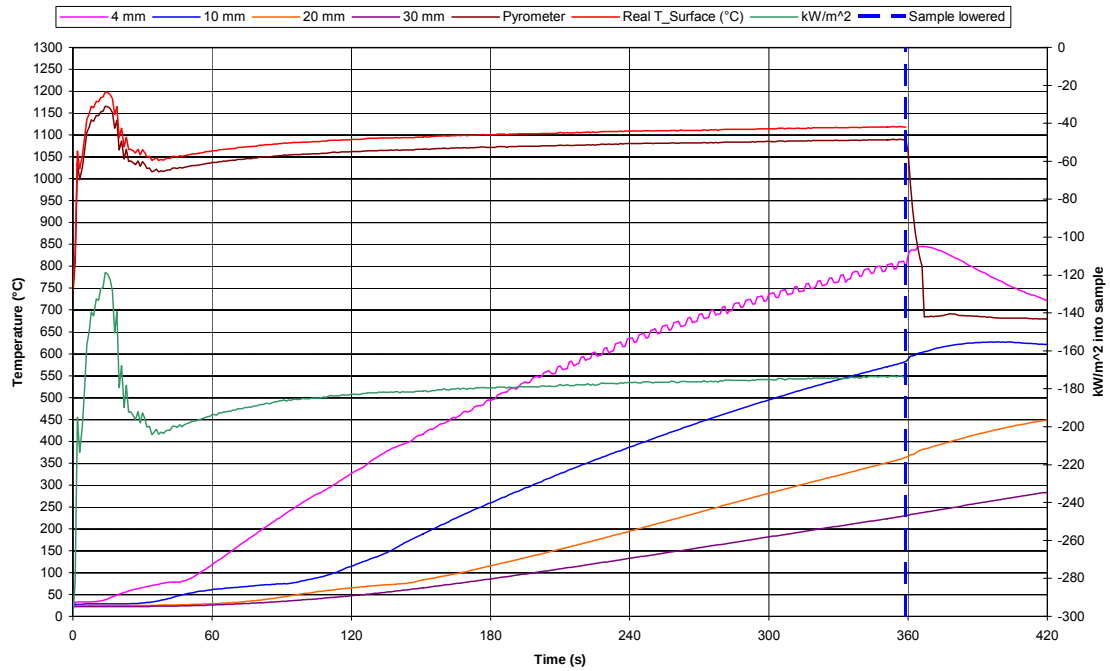
Coal-Ore; 40mm layer, 1400°C, 3minutes

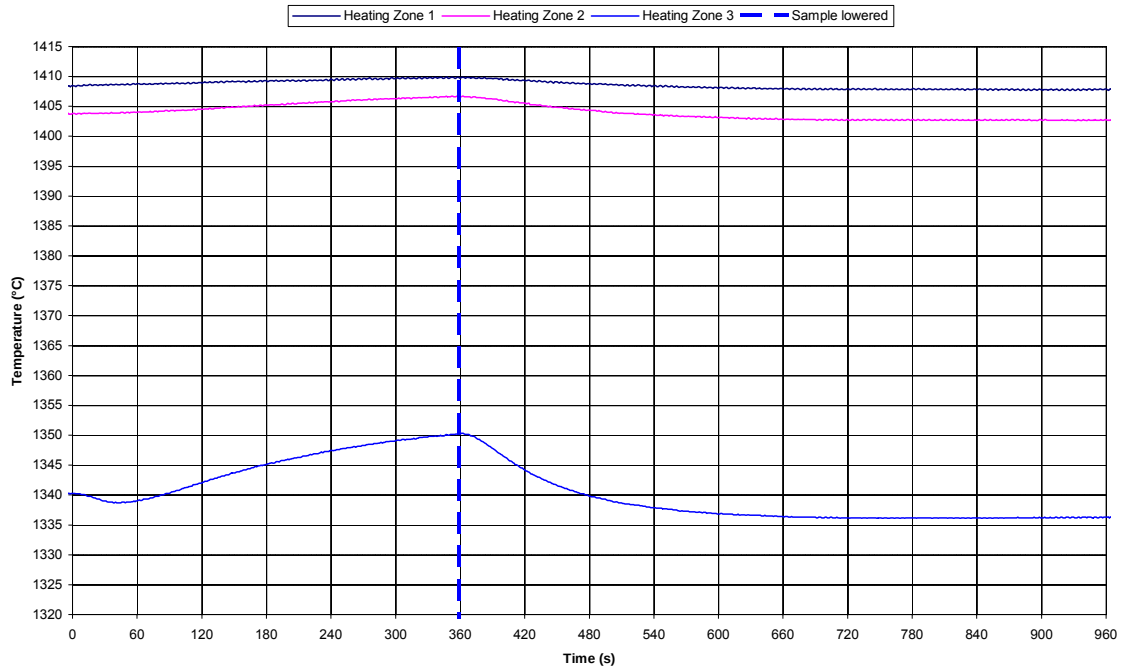




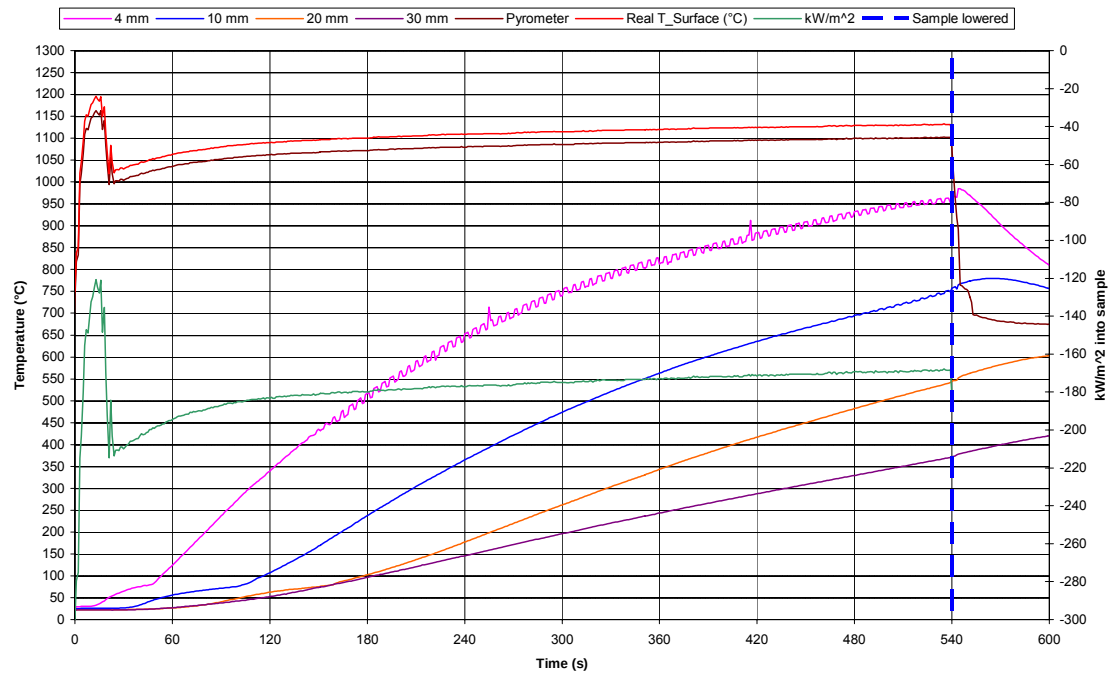


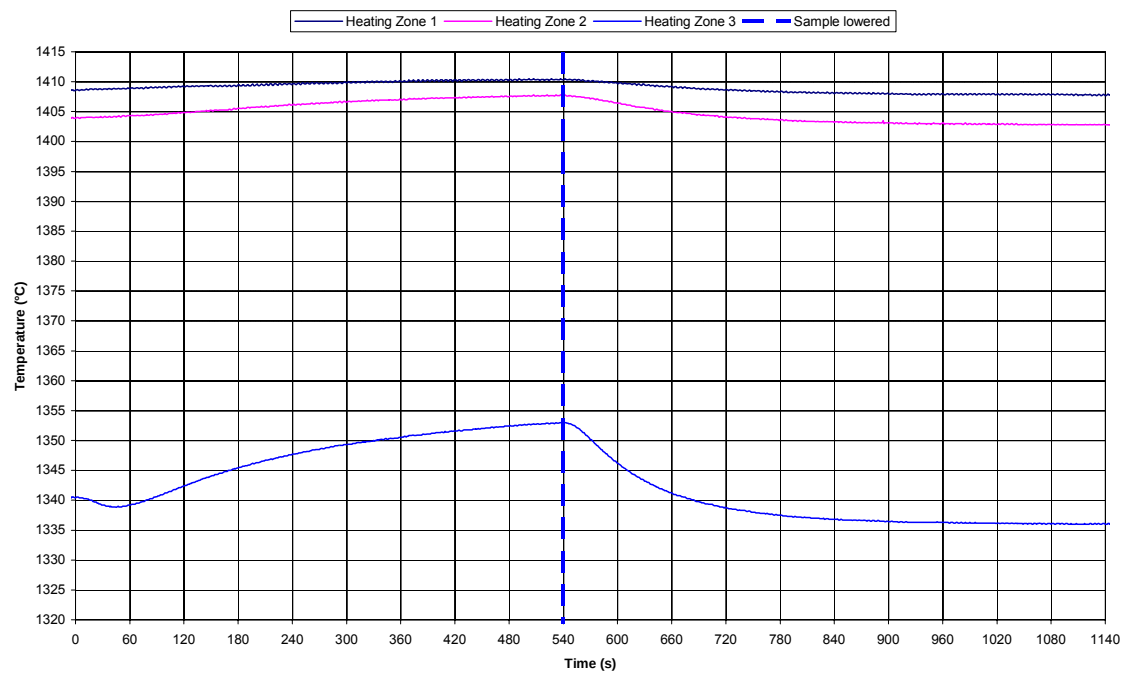
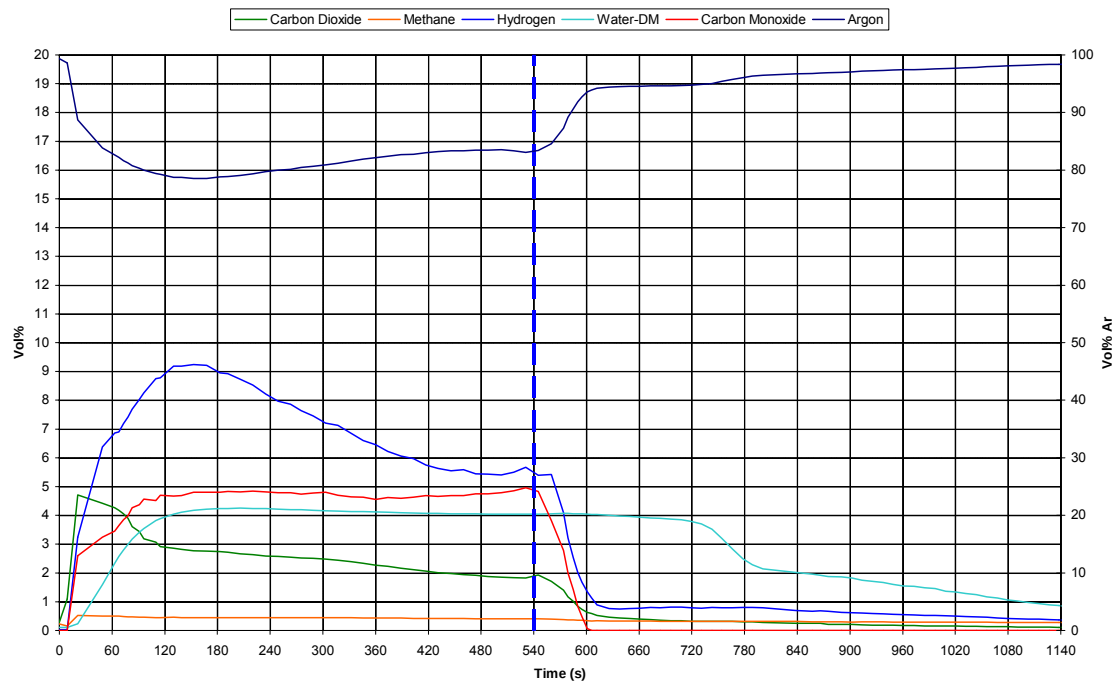
Coal-Ore; 40mm layer, 1400°C, 6minutes





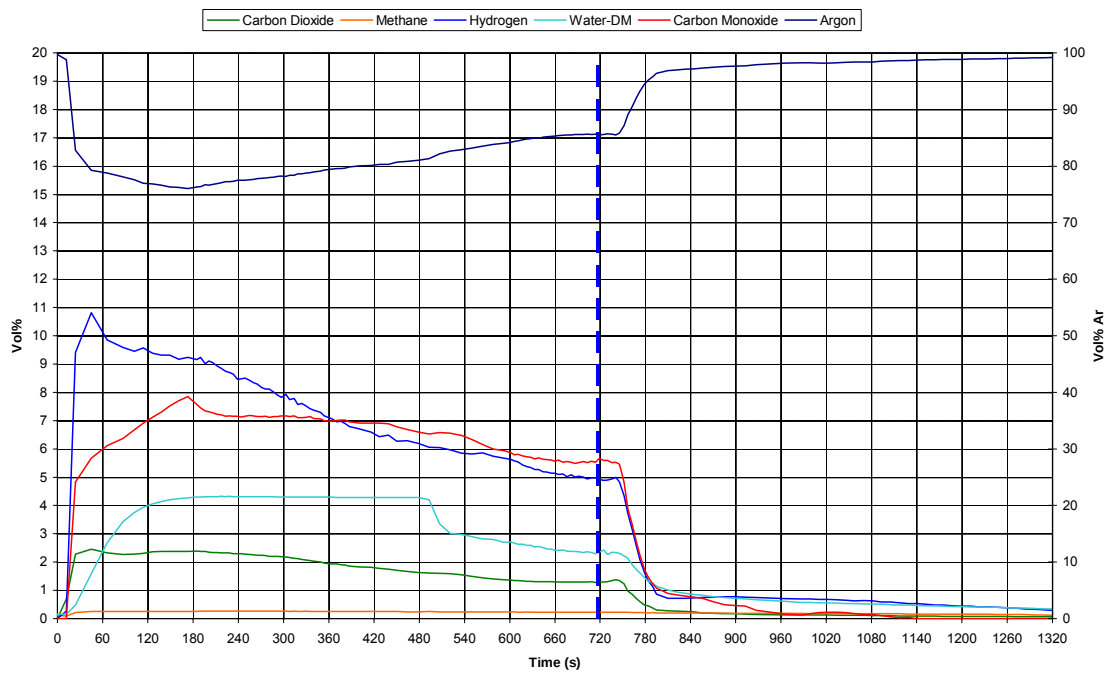
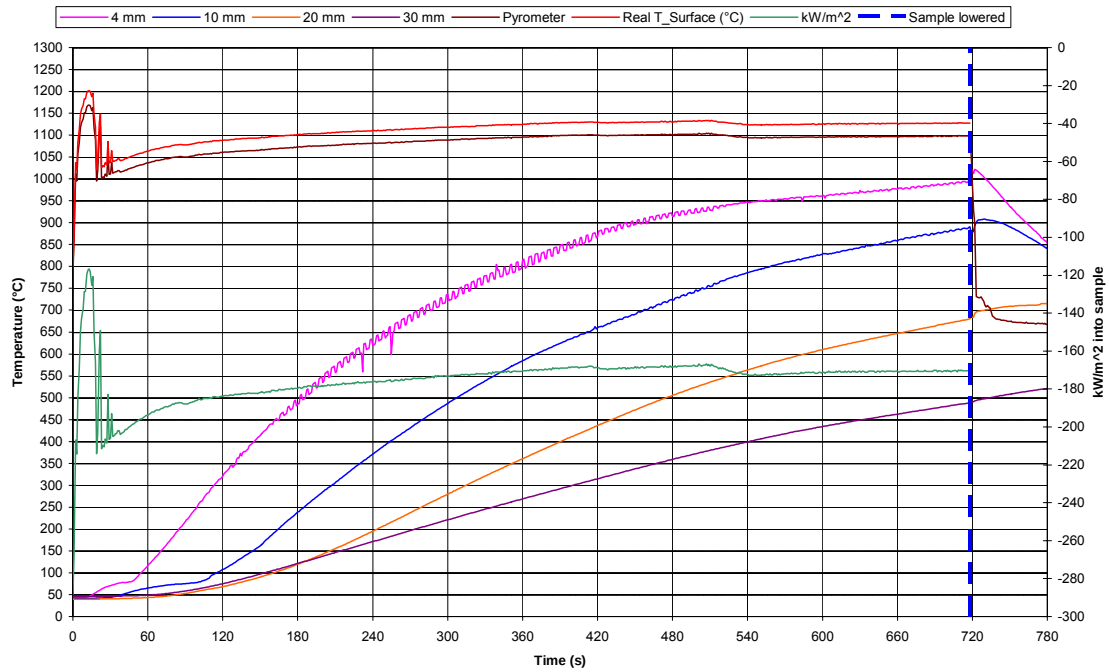
Coal-Ore; 40mm layer, 1400°C, 9minutes

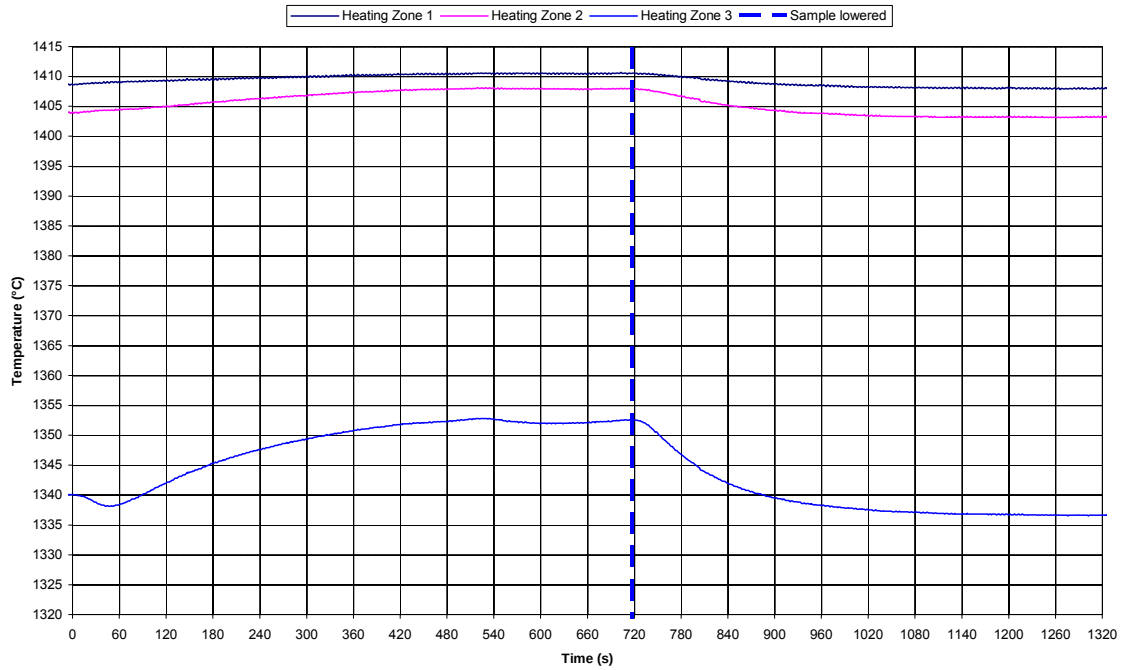




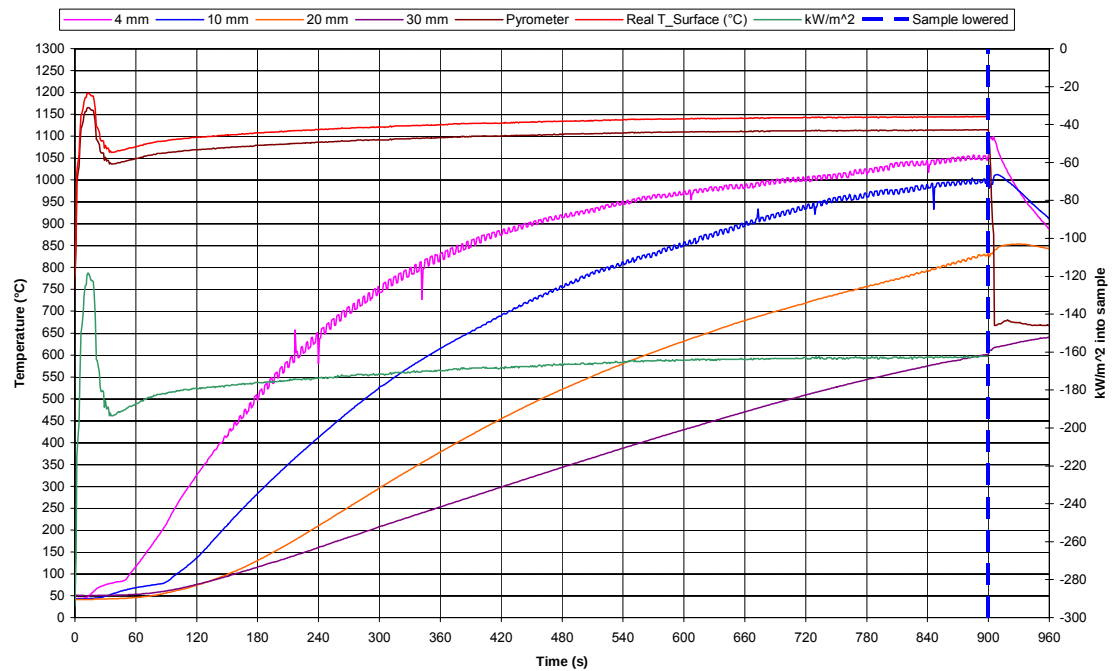


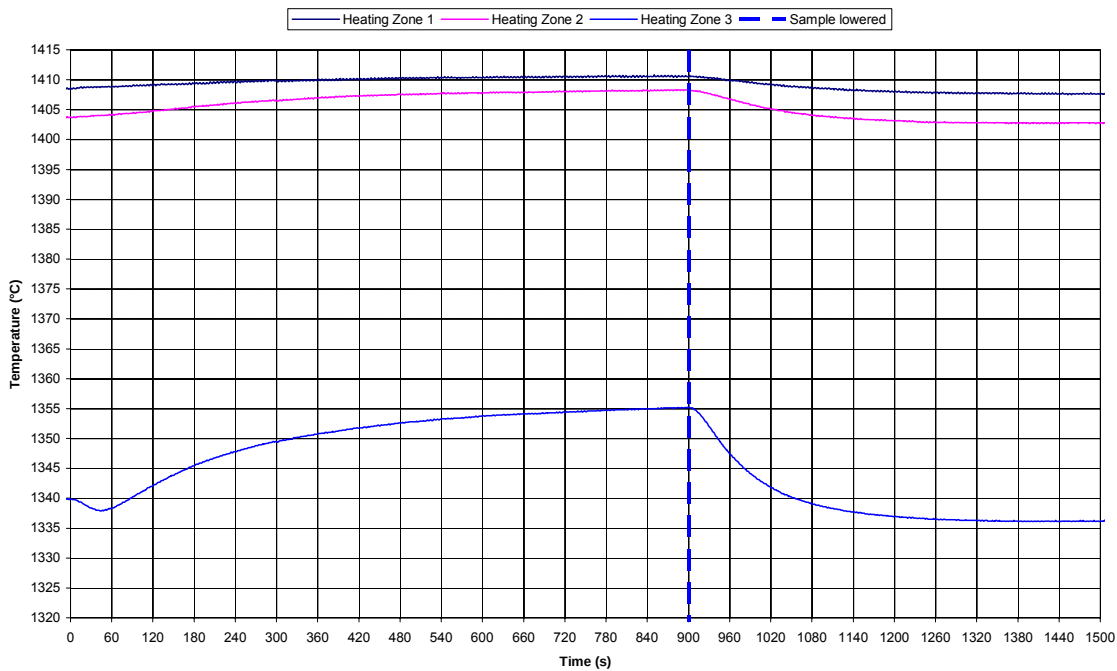
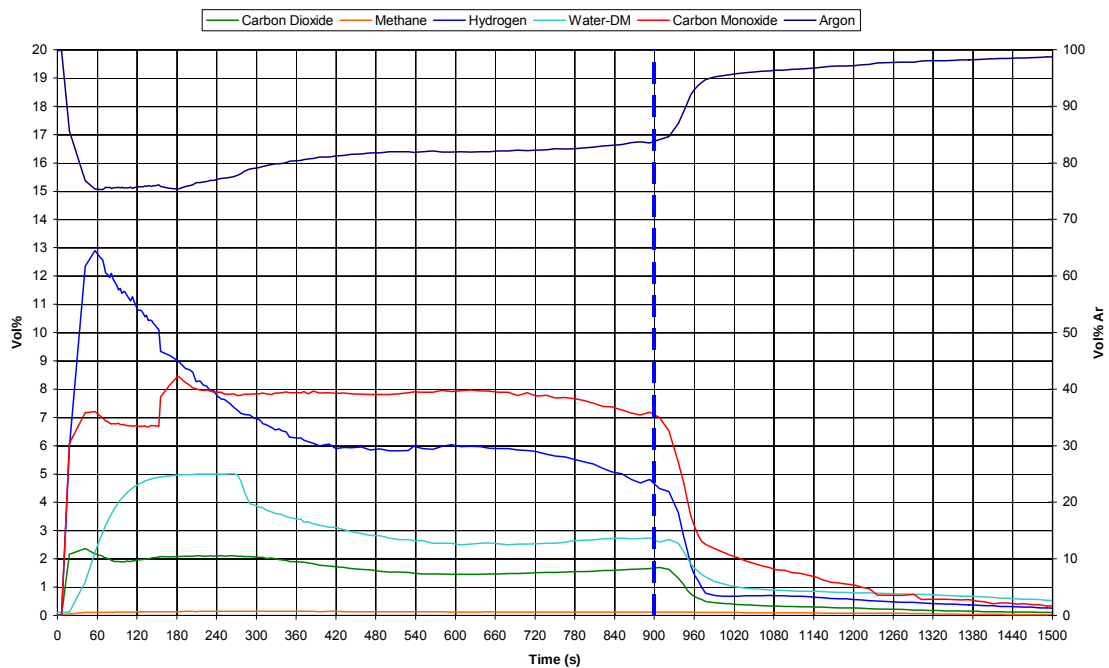
Coal-Ore; 40mm layer, 1400°C, 12minutes





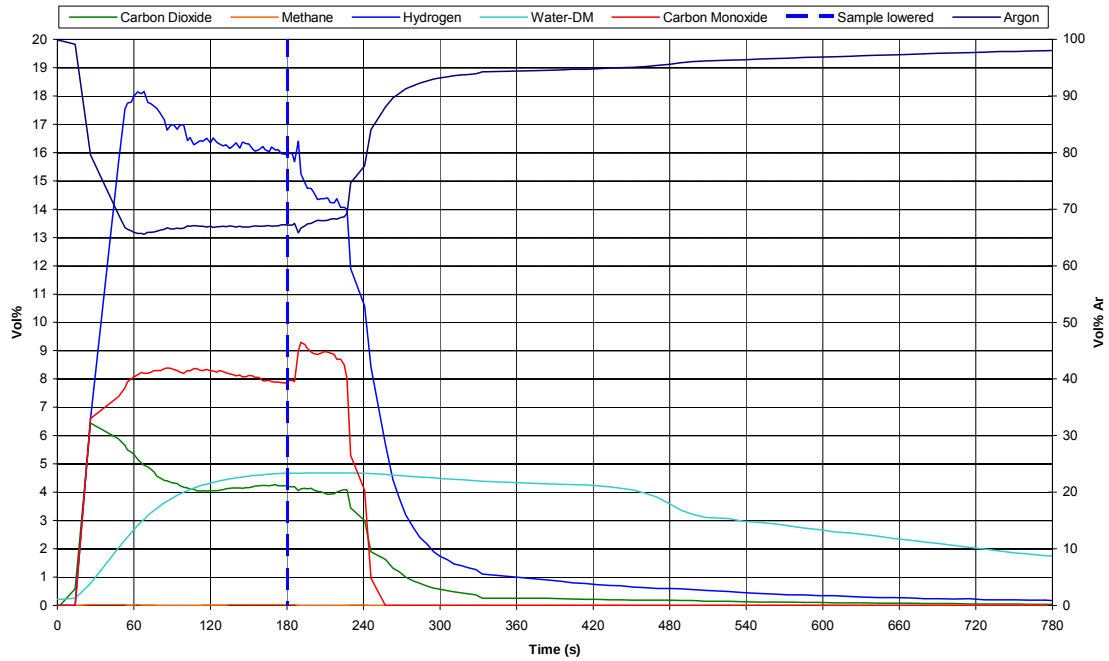
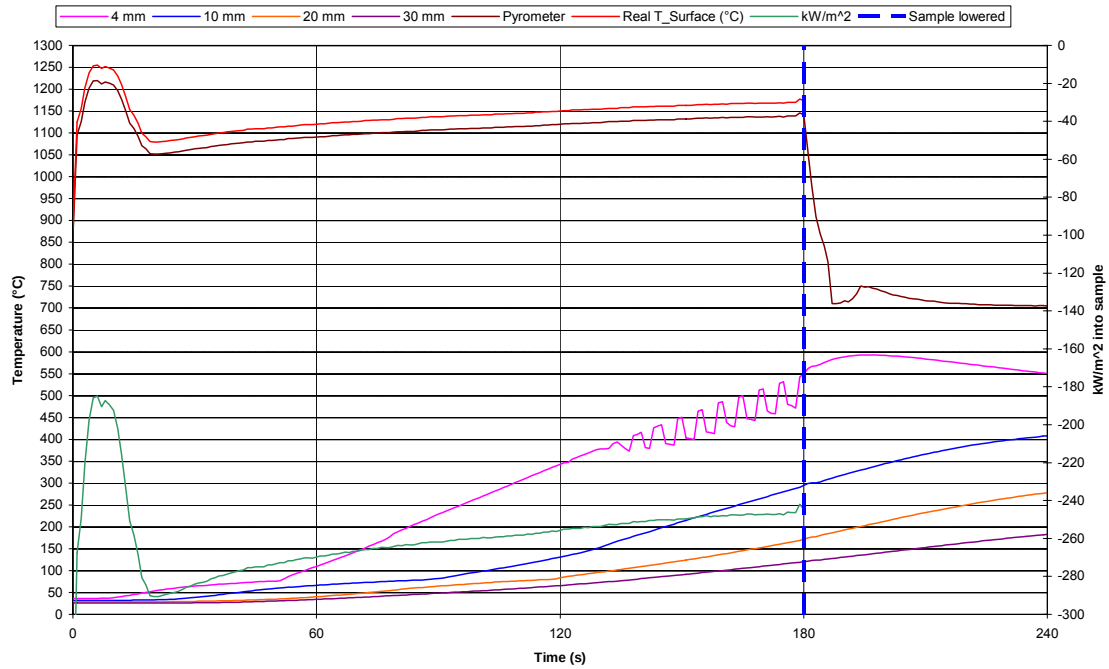
Coal-Ore; 40mm layer, 1400°C, 15minutes

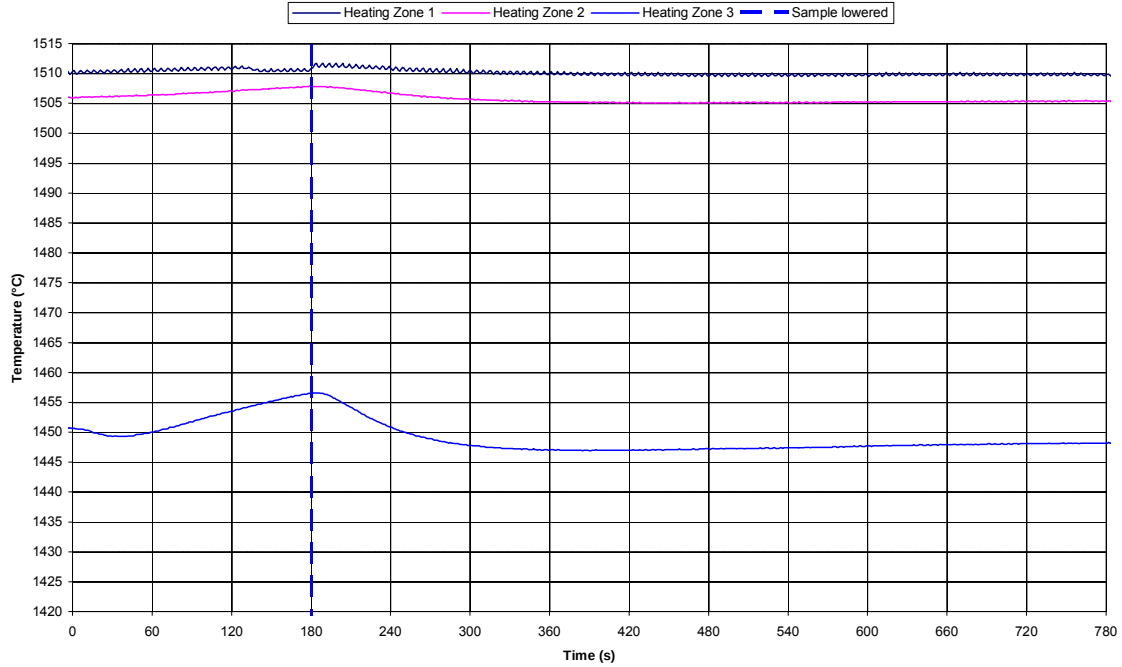




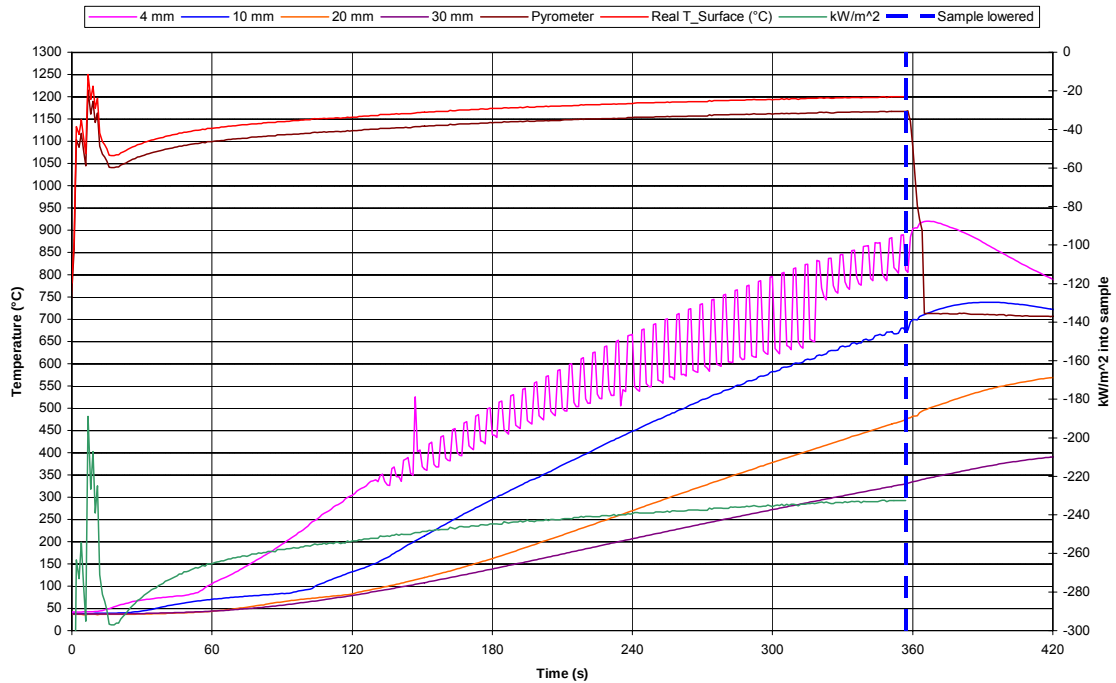


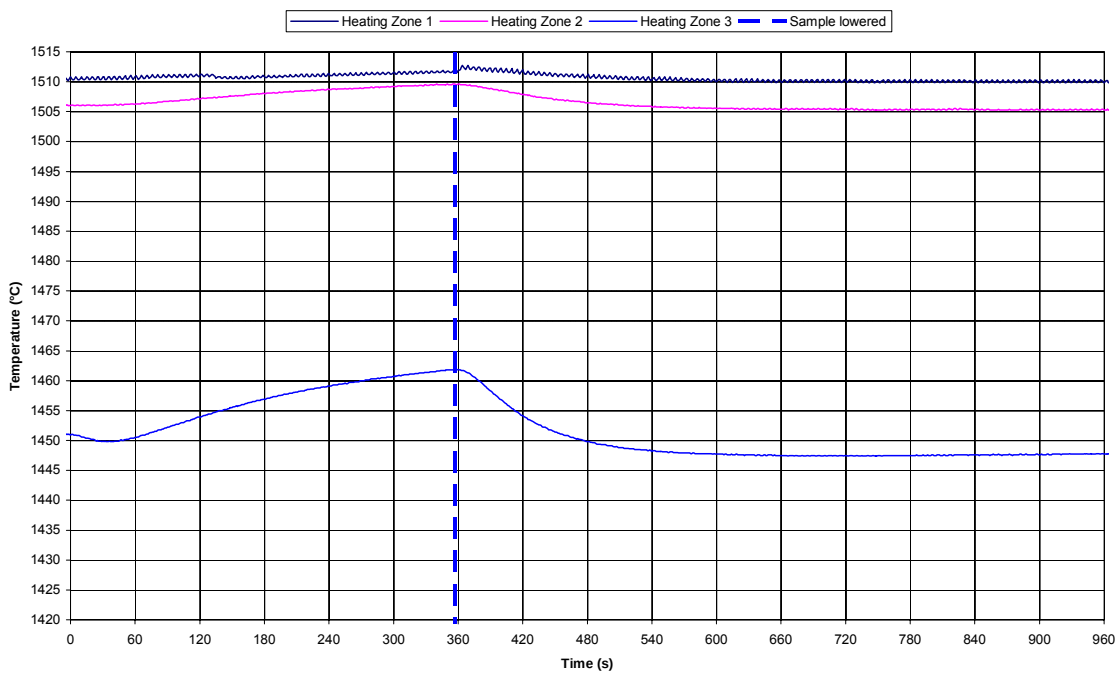
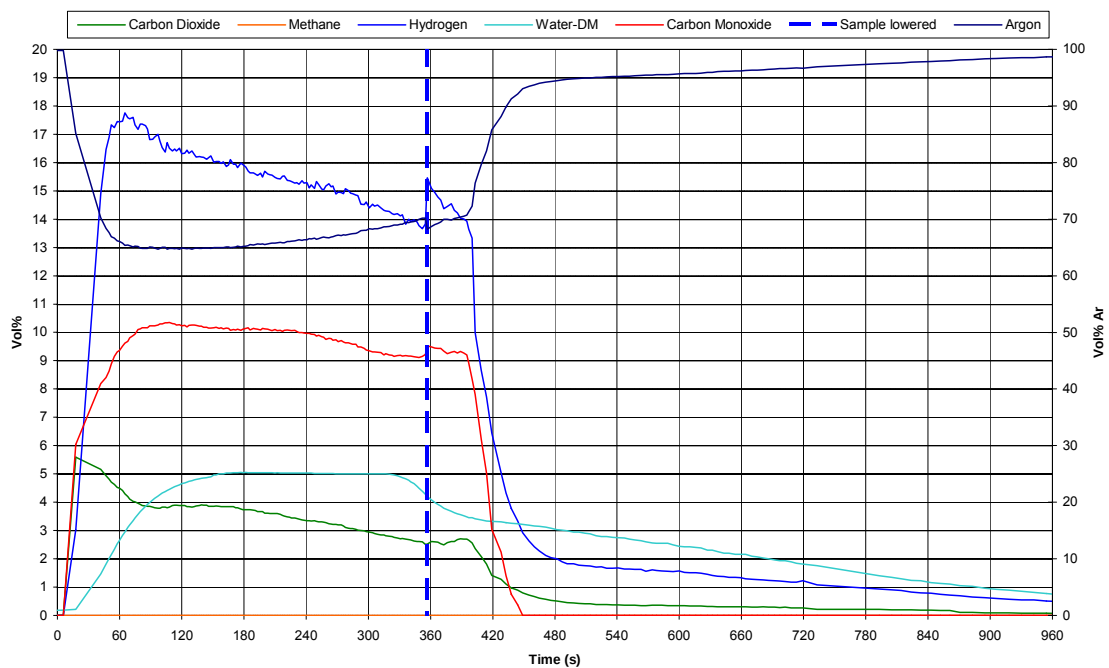
Coal-Ore; 40mm layer, 1500°C, 3minutes





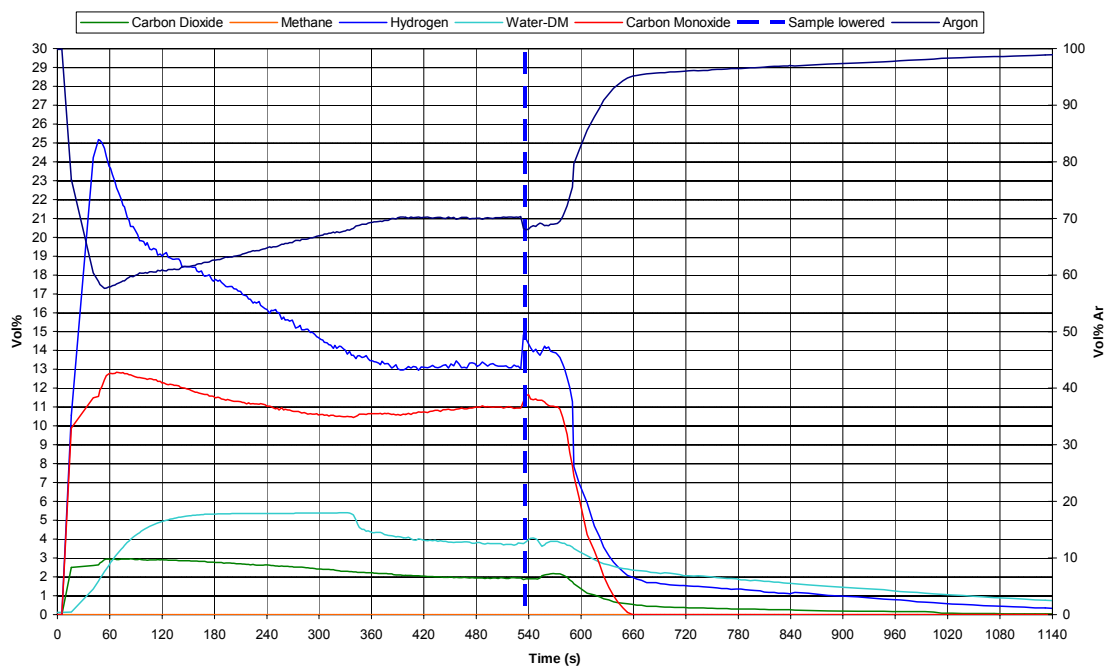
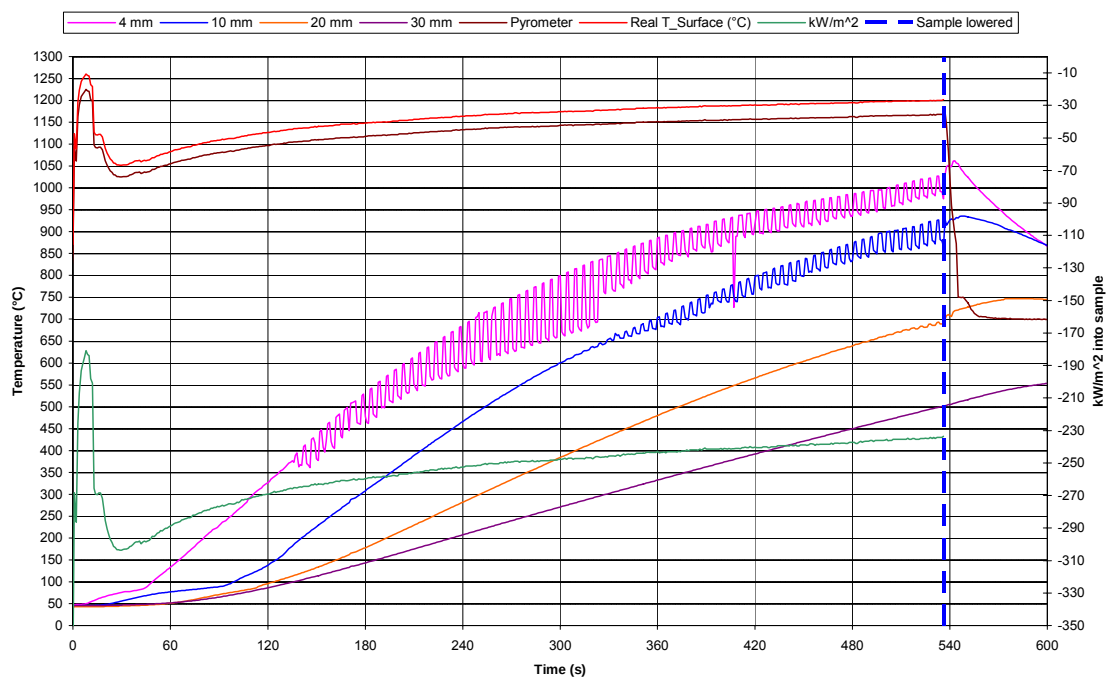
Coal-Ore; 40mm layer, 1500°C, 6minutes

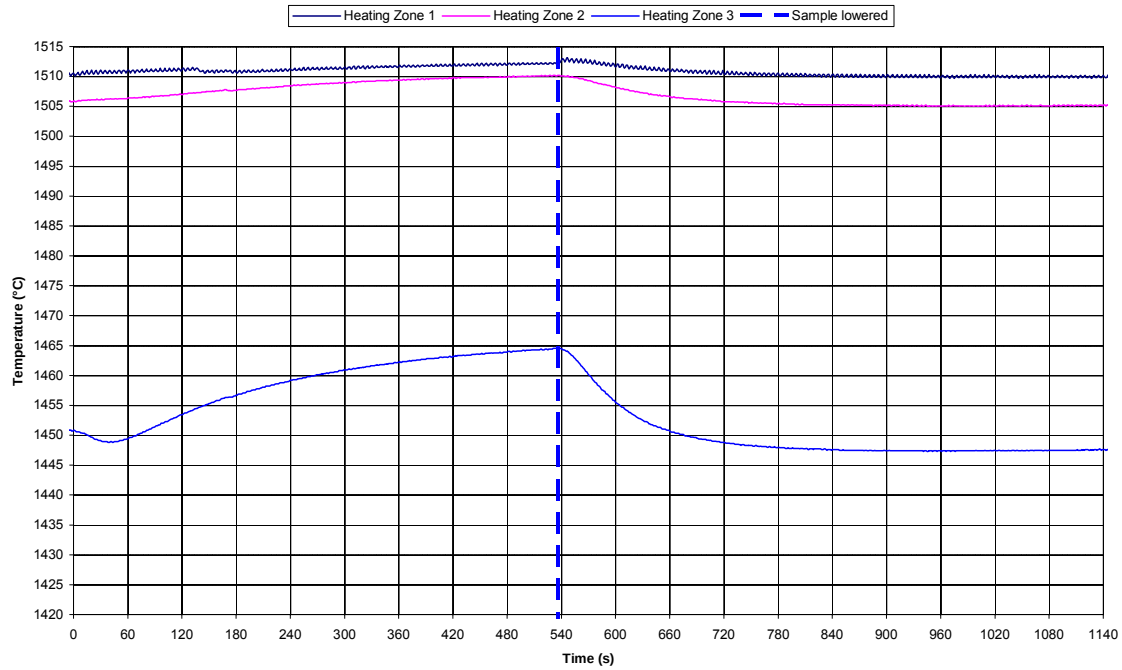




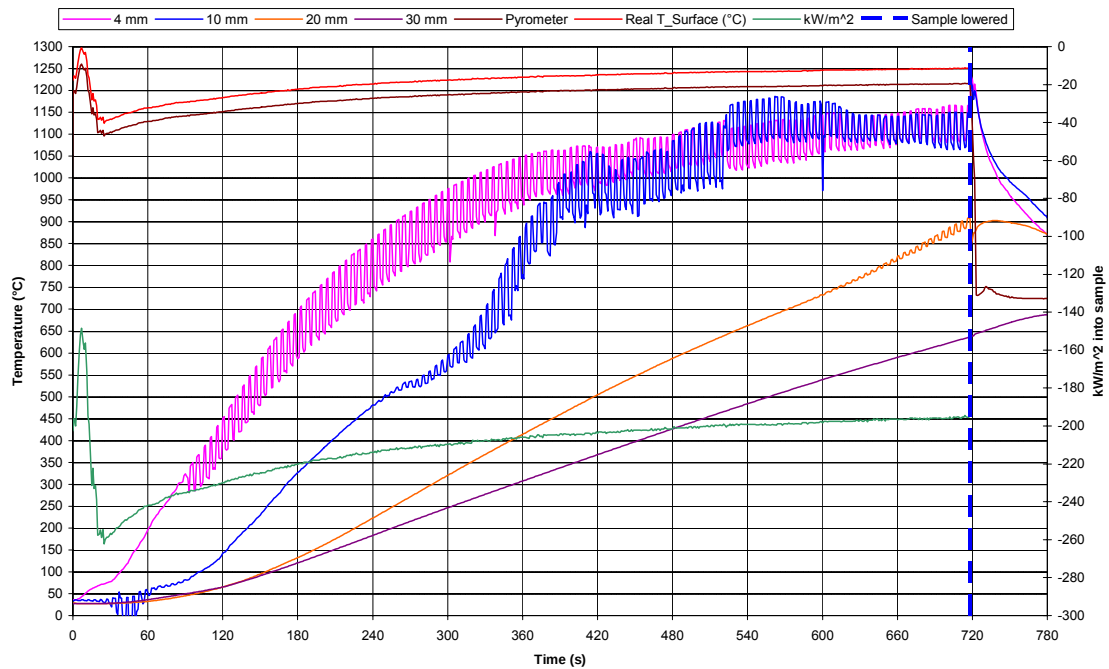


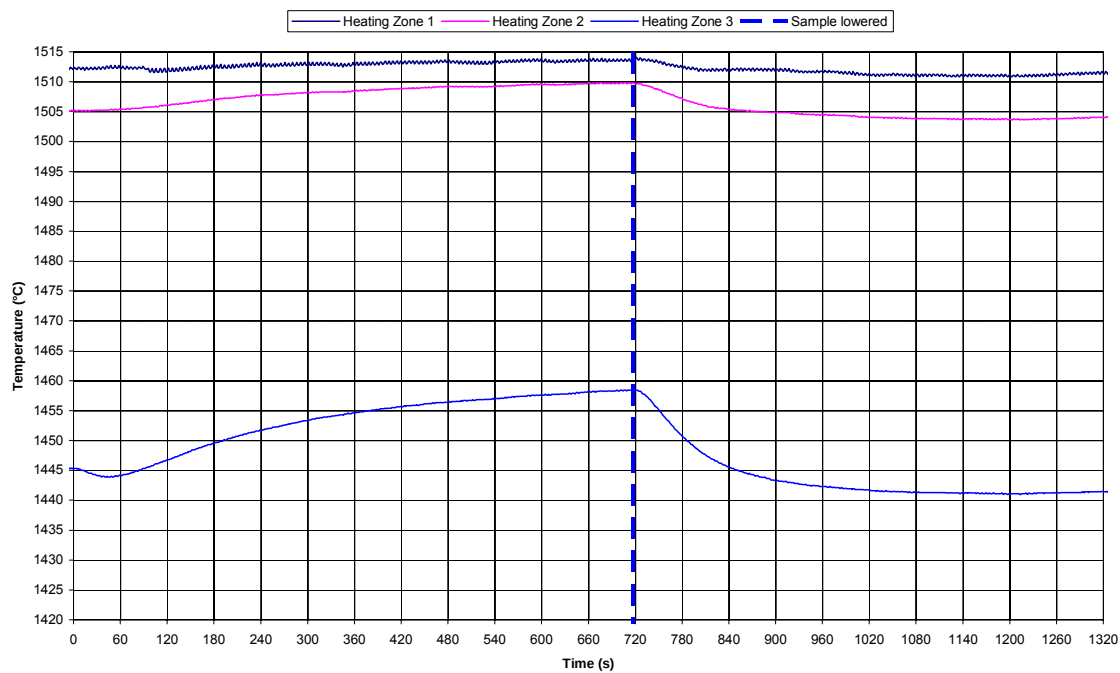
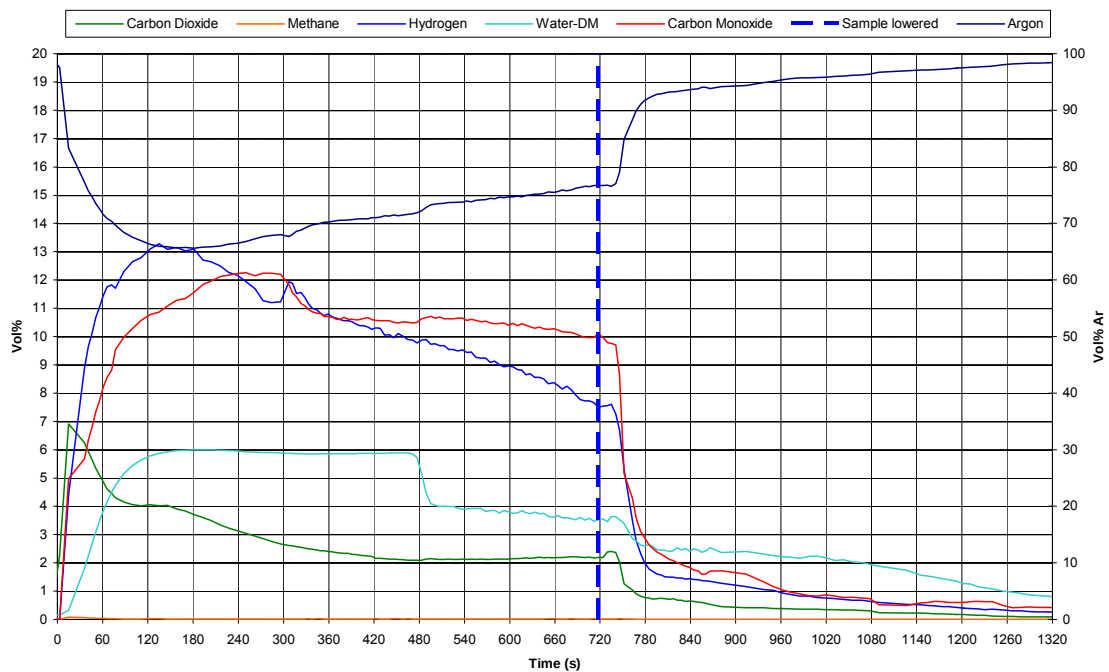
Coal-Ore; 40mm layer, 1500°C, 9minutes





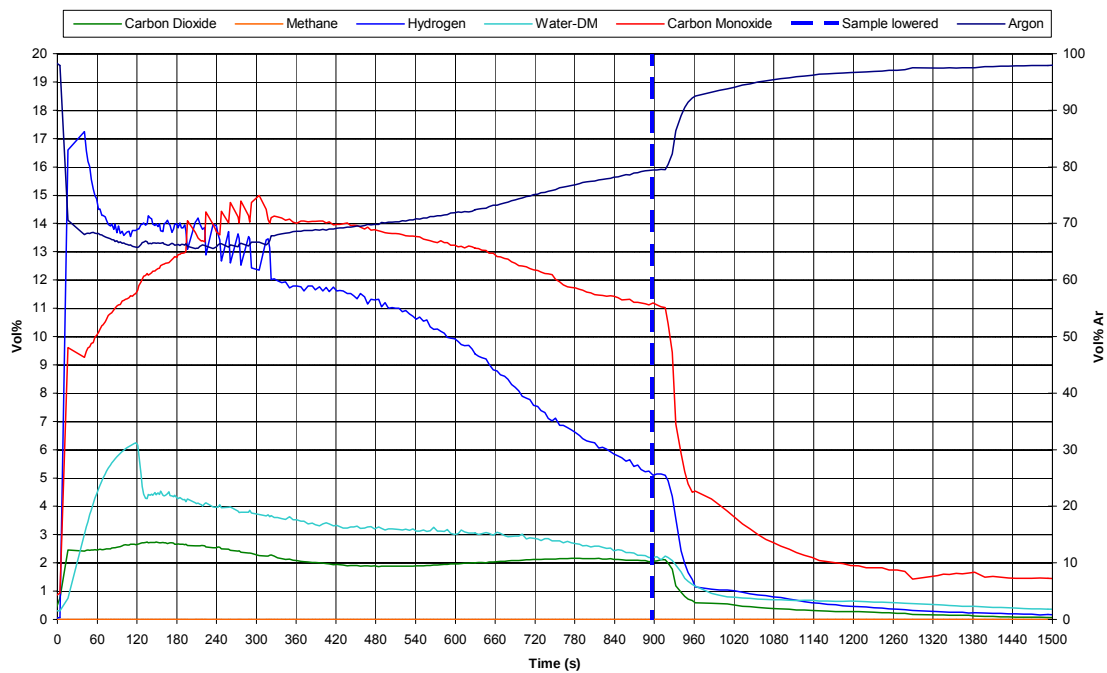
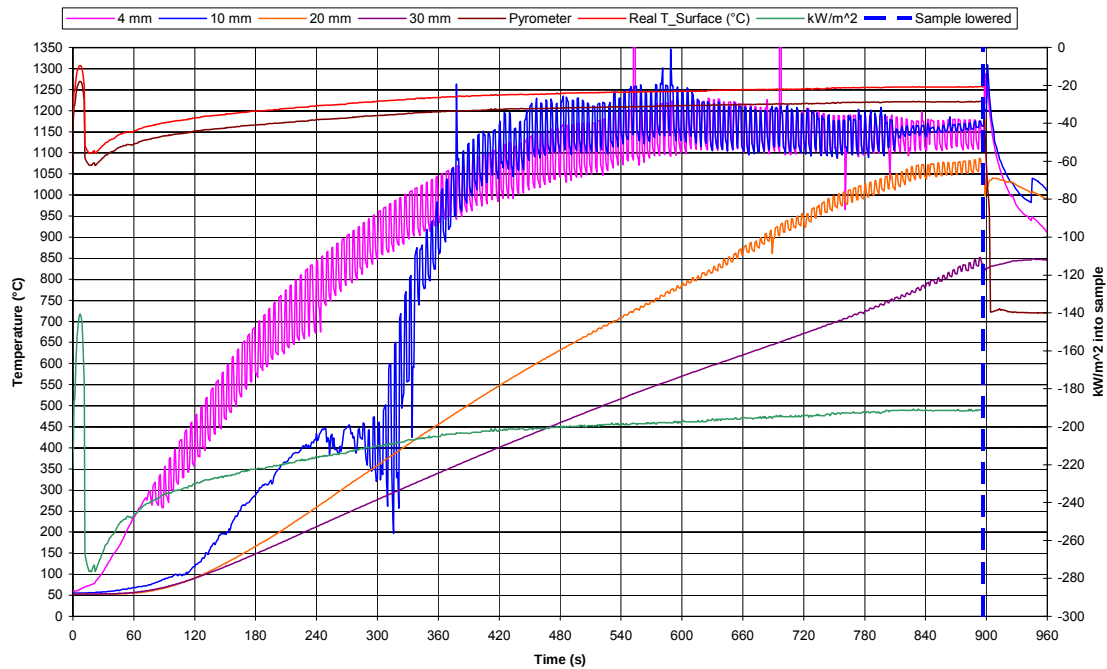
Coal-Ore; 40mm layer, 1500°C, 12minutes

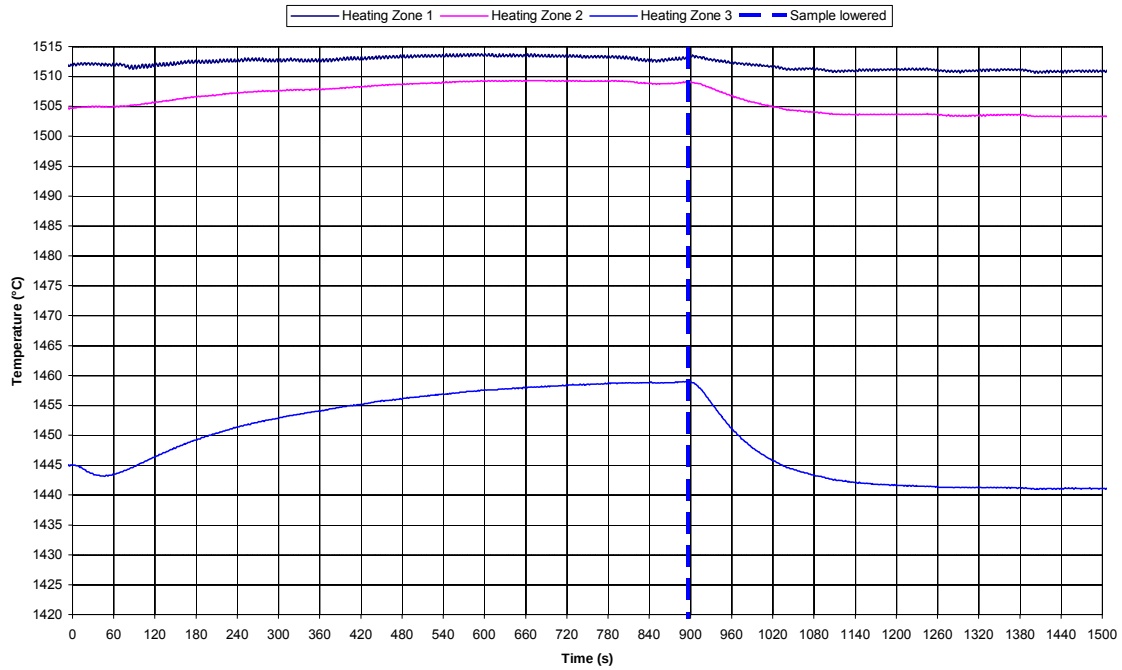




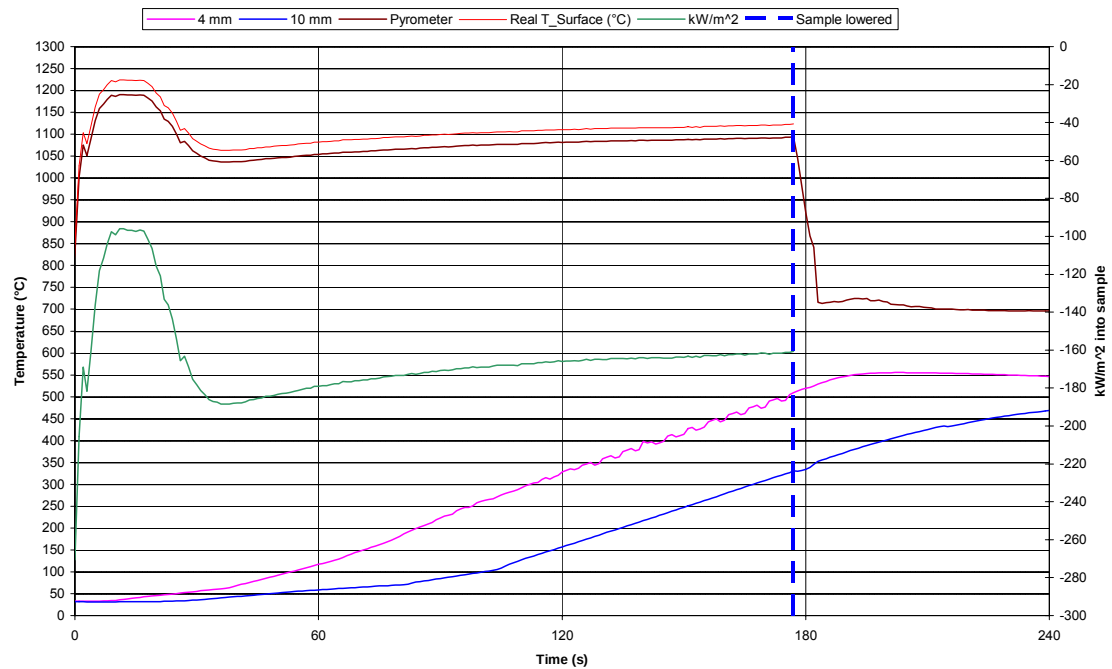


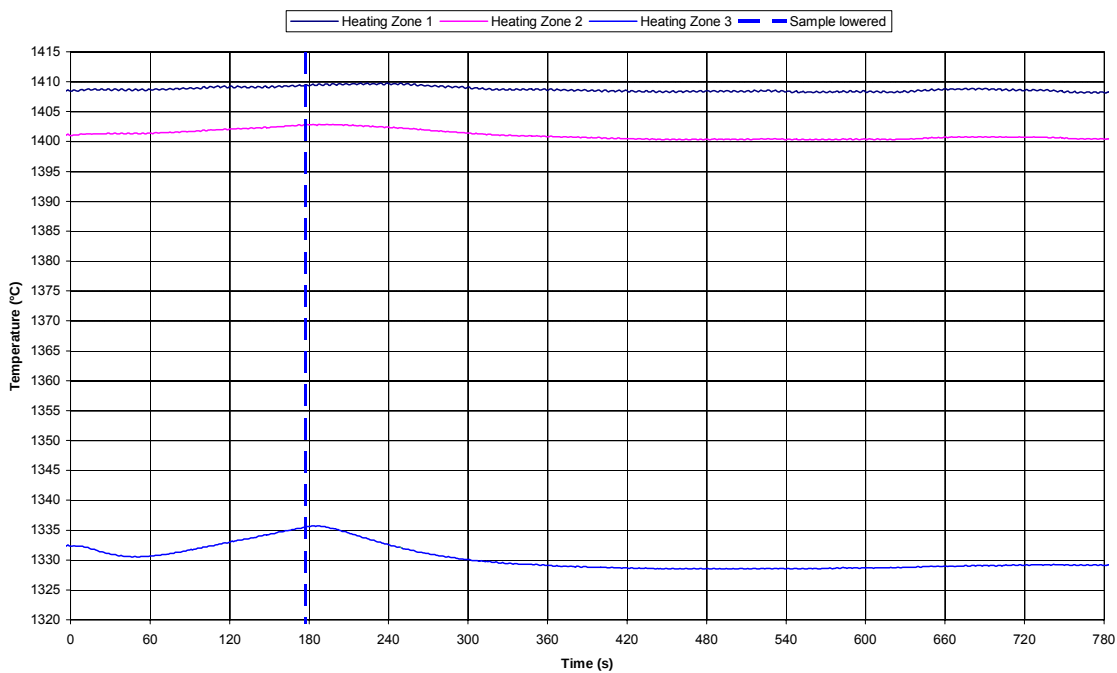
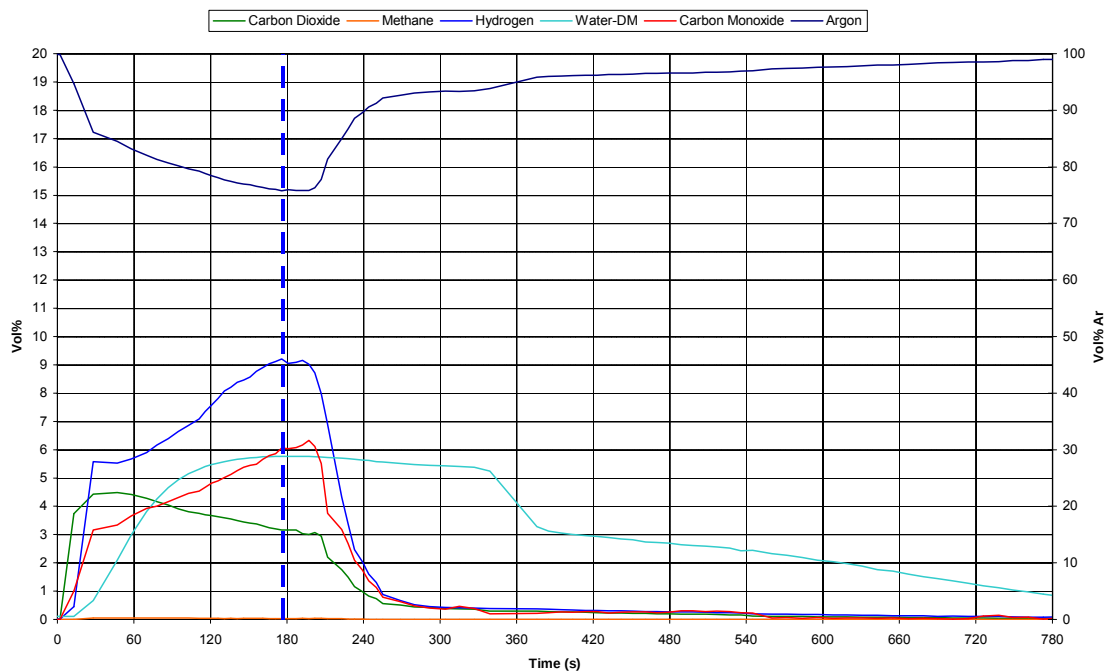
Coal-Ore; 40mm layer, 1500°C, 15minutes





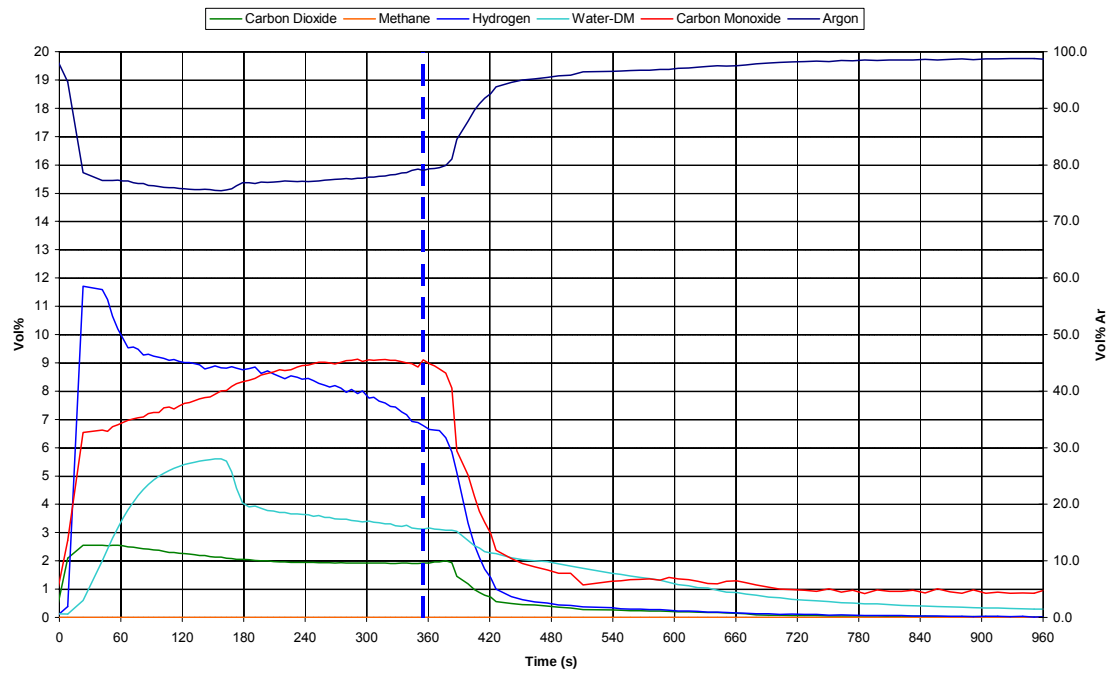
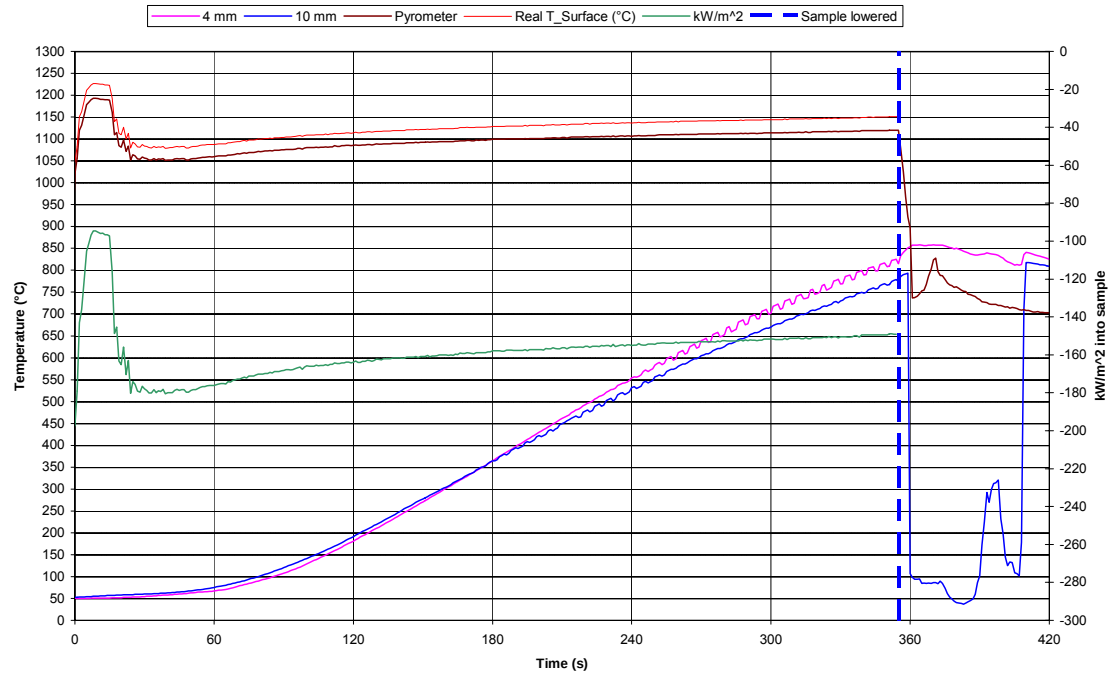
Coal-Ore; 16 mm layer, 1400°C, 3minutes

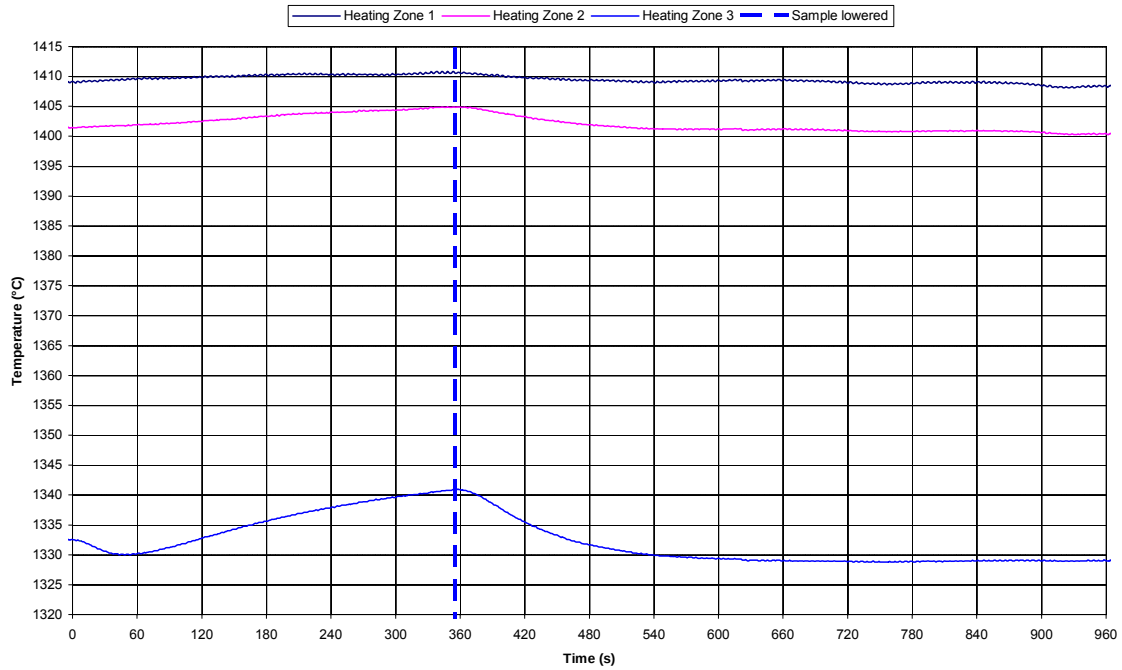




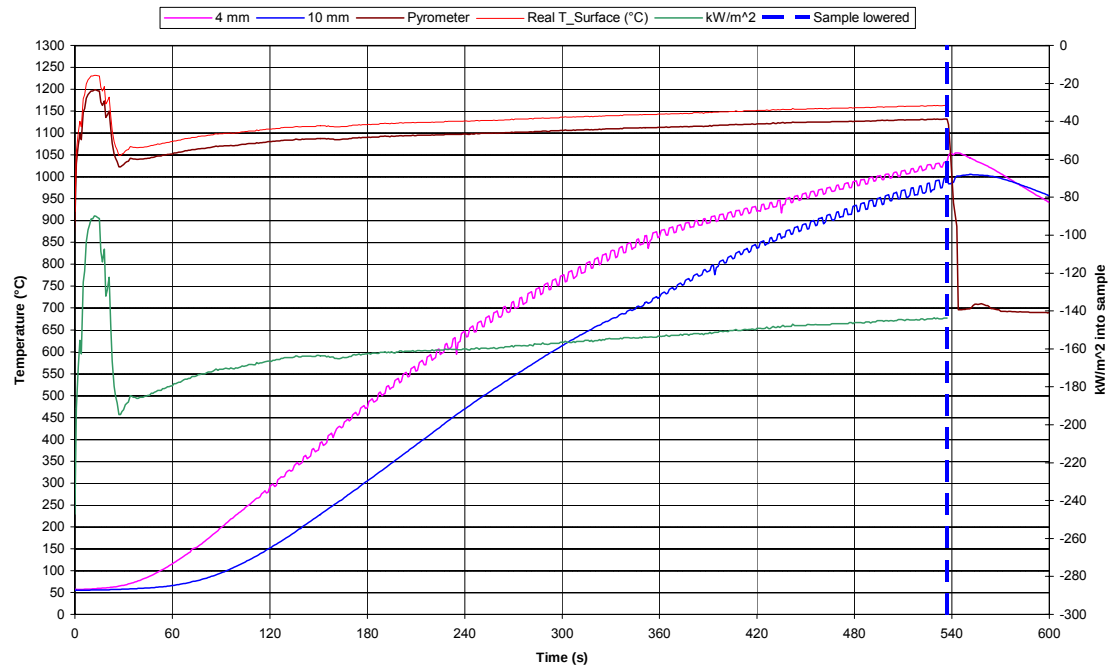


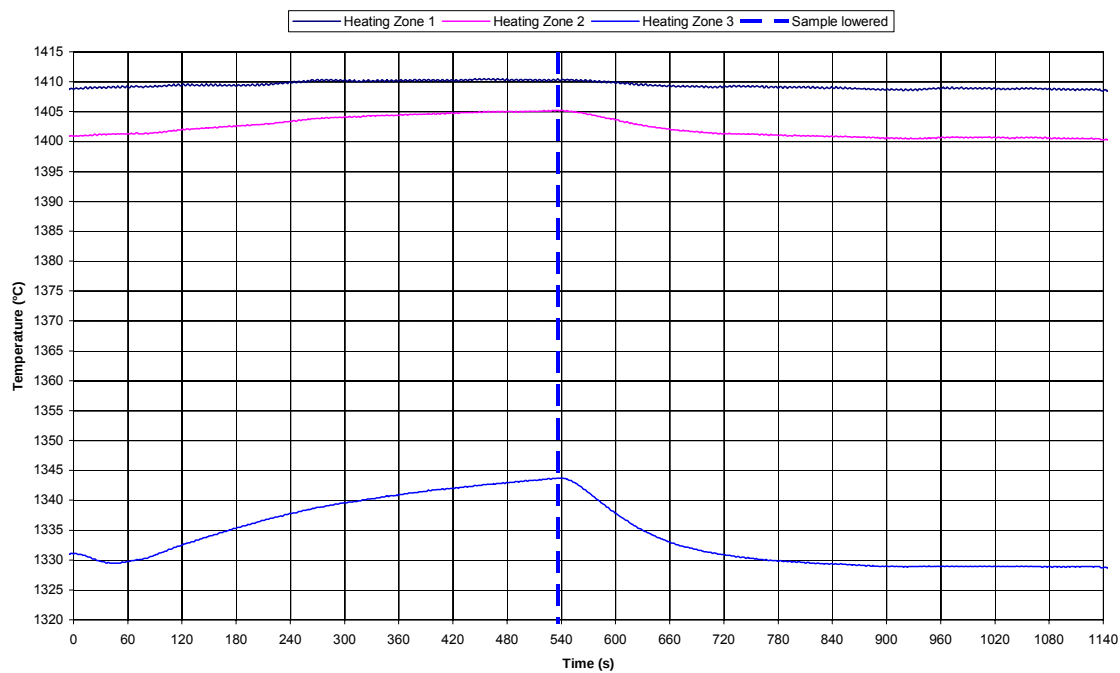
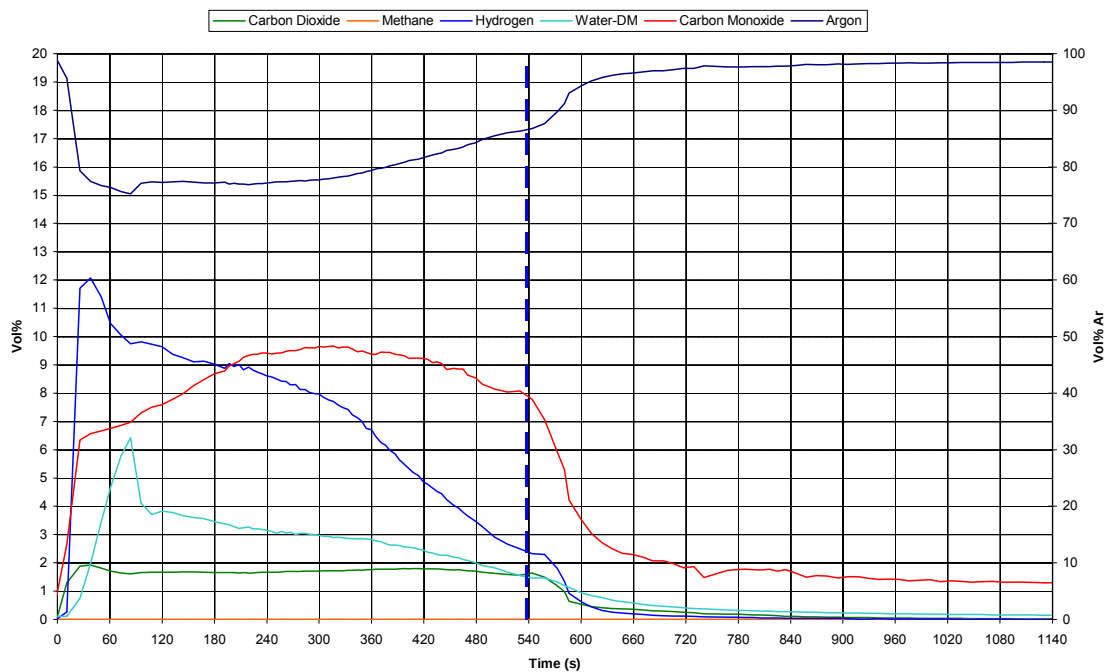
Coal-Ore; 16 mm layer, 1400°C, 6minutes





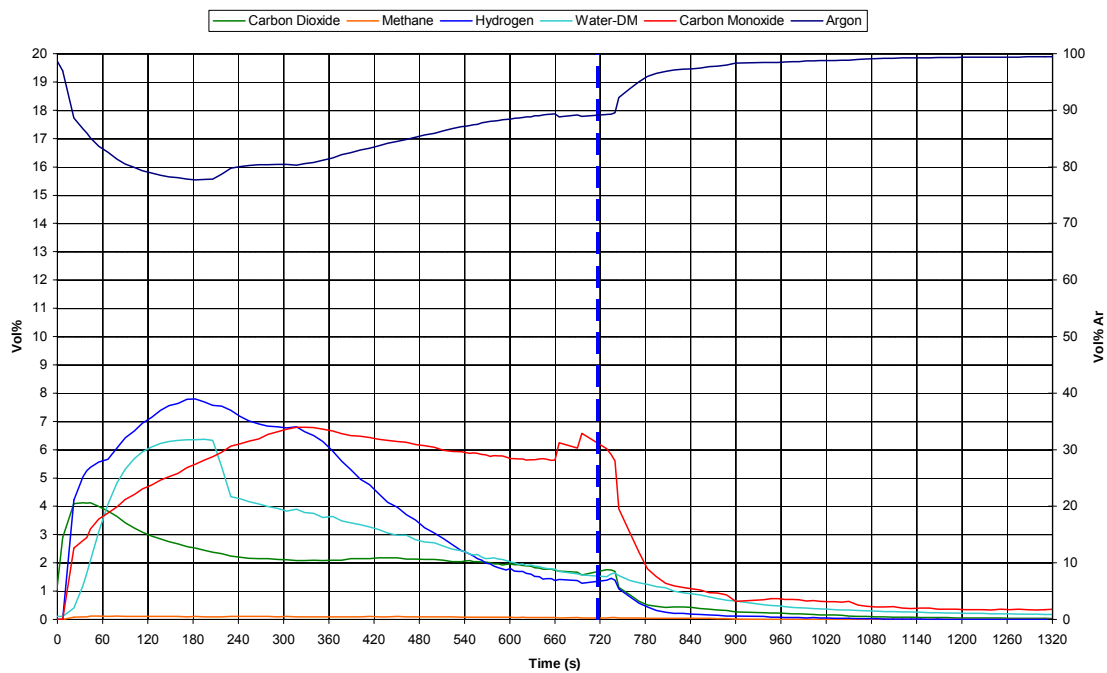
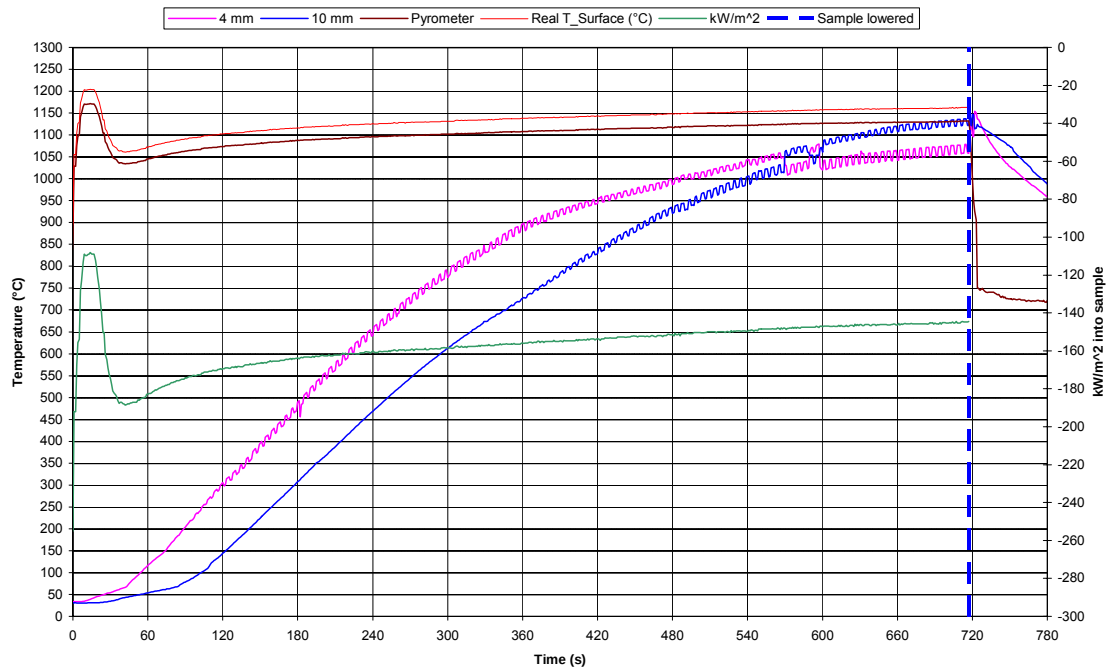
Coal-Ore; 16 mm layer, 1400°C, 9minutes

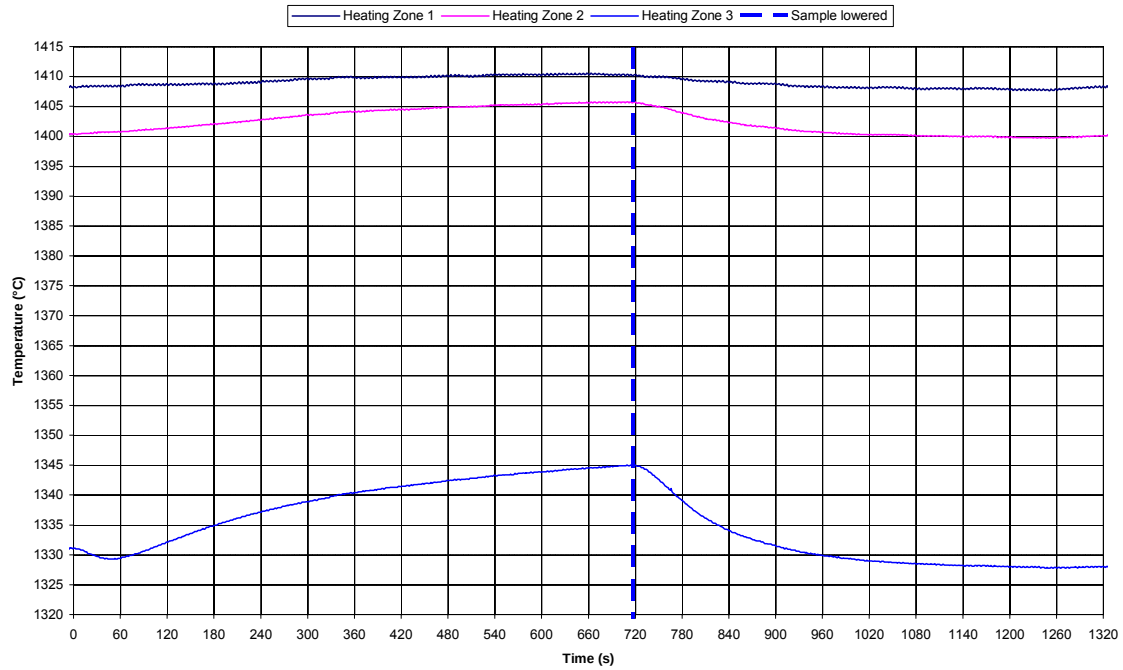




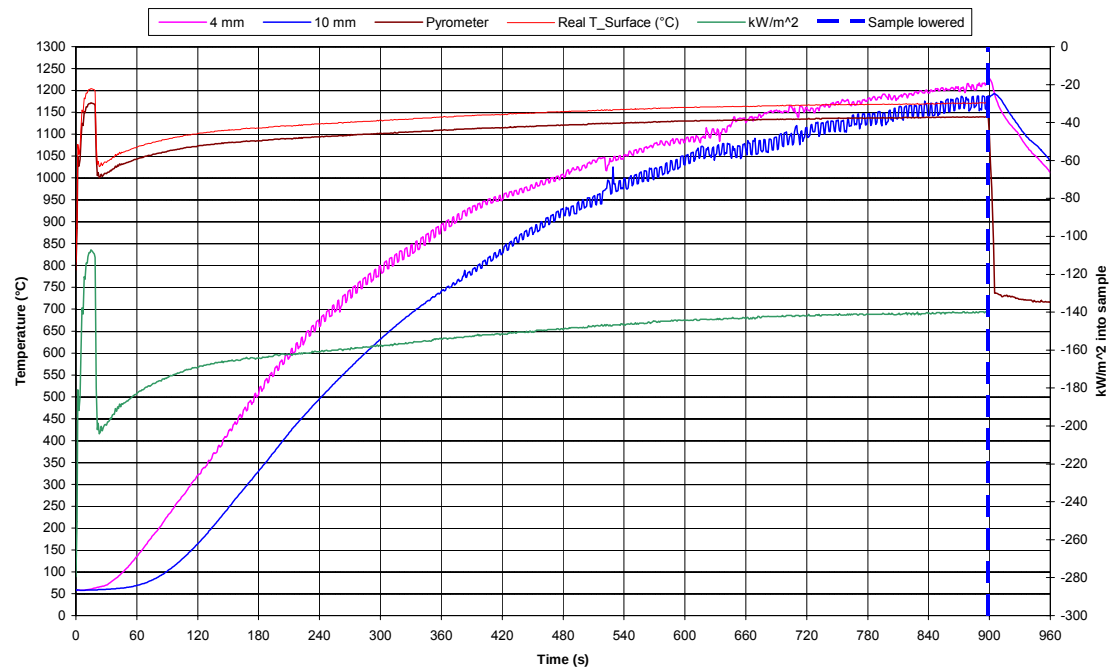


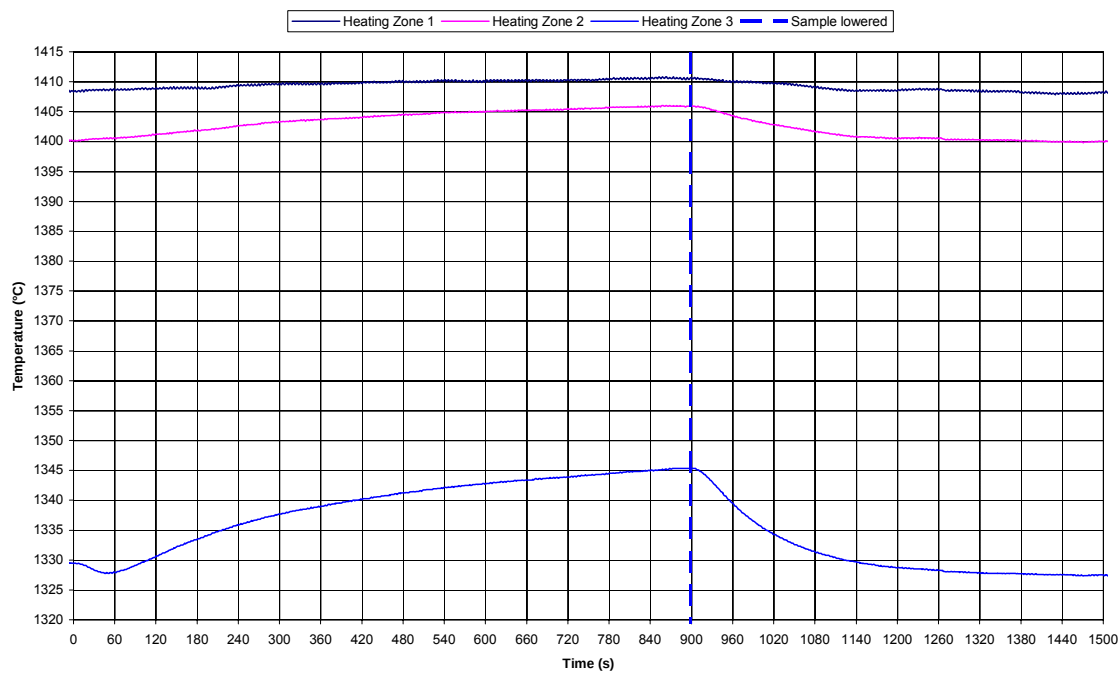
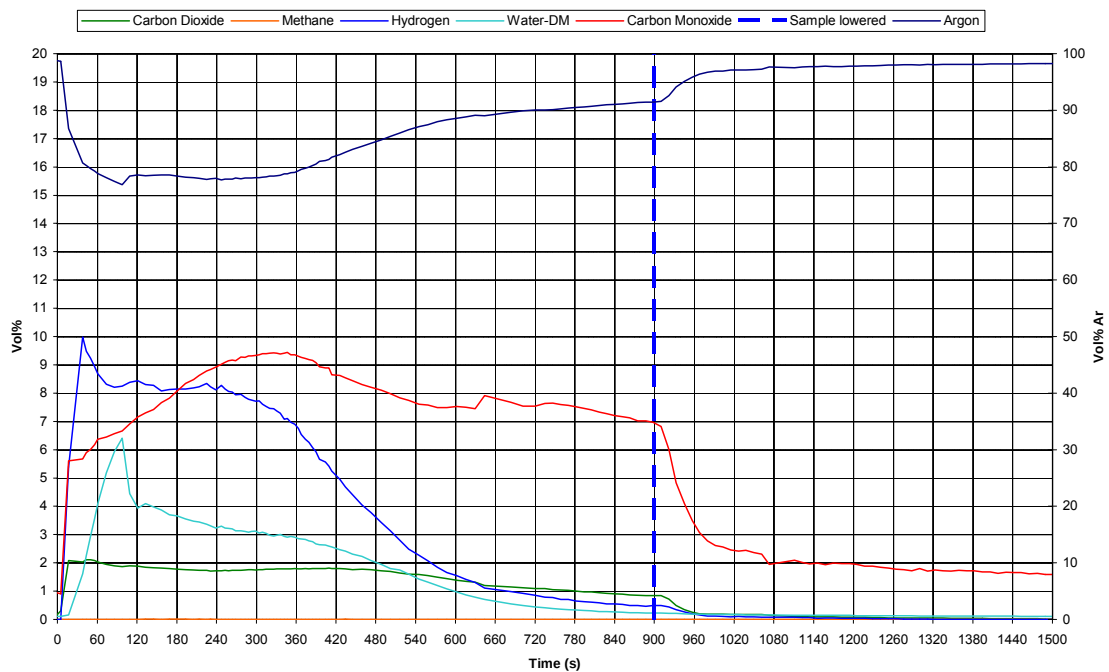
Coal-Ore; 16 mm layer, 1400°C, 12minutes





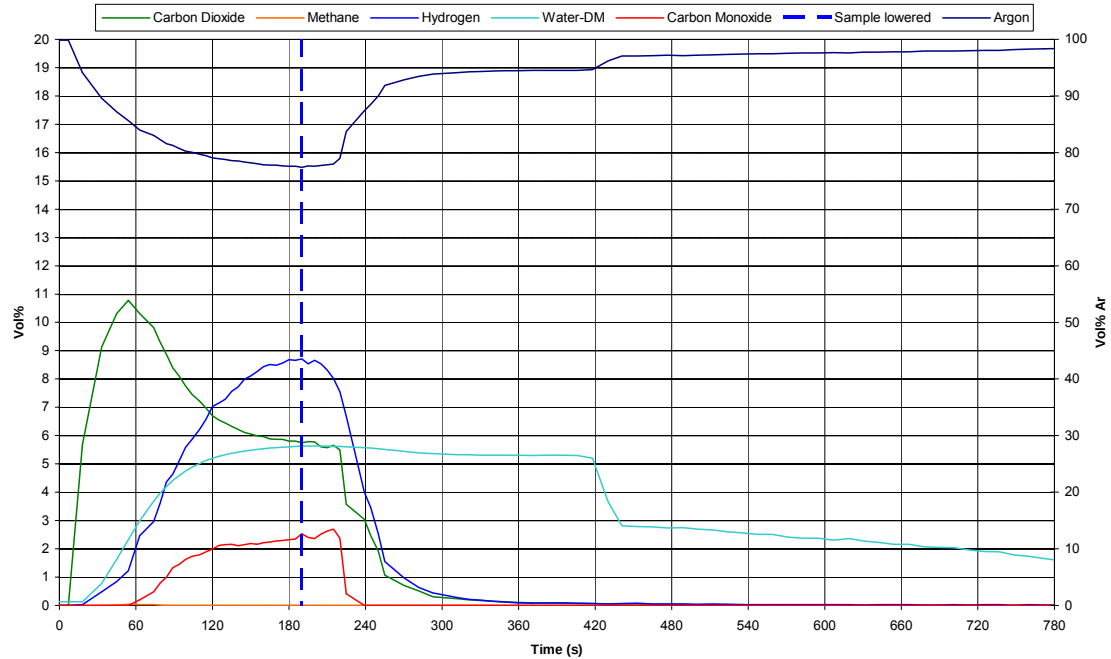
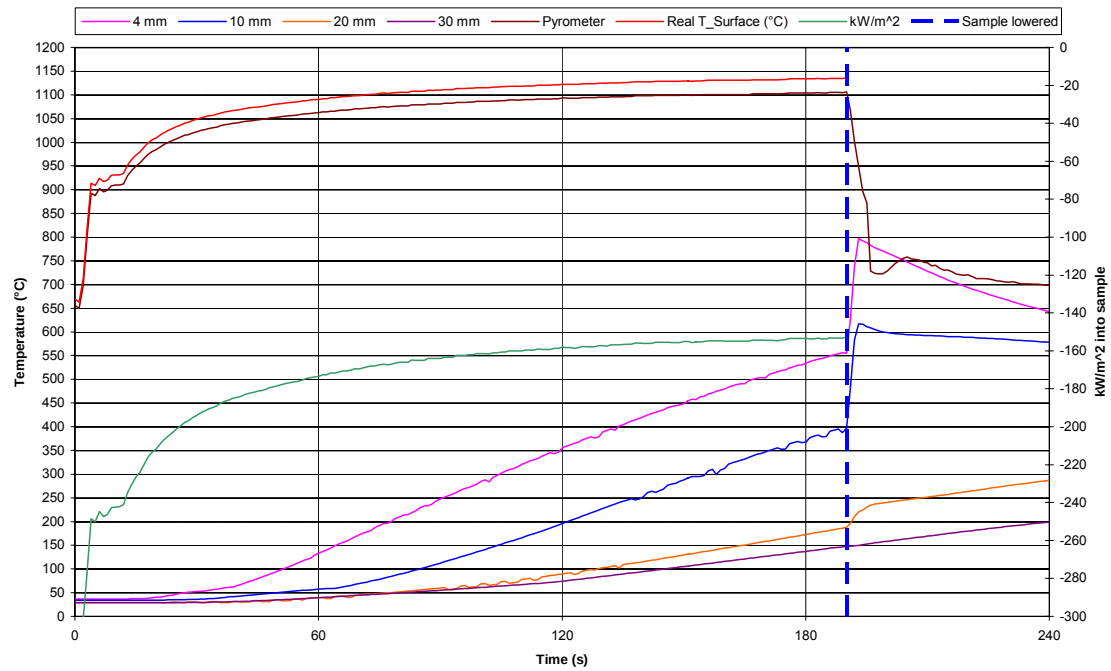
Coal-Ore; 16 mm layer, 1400°C, 15minutes

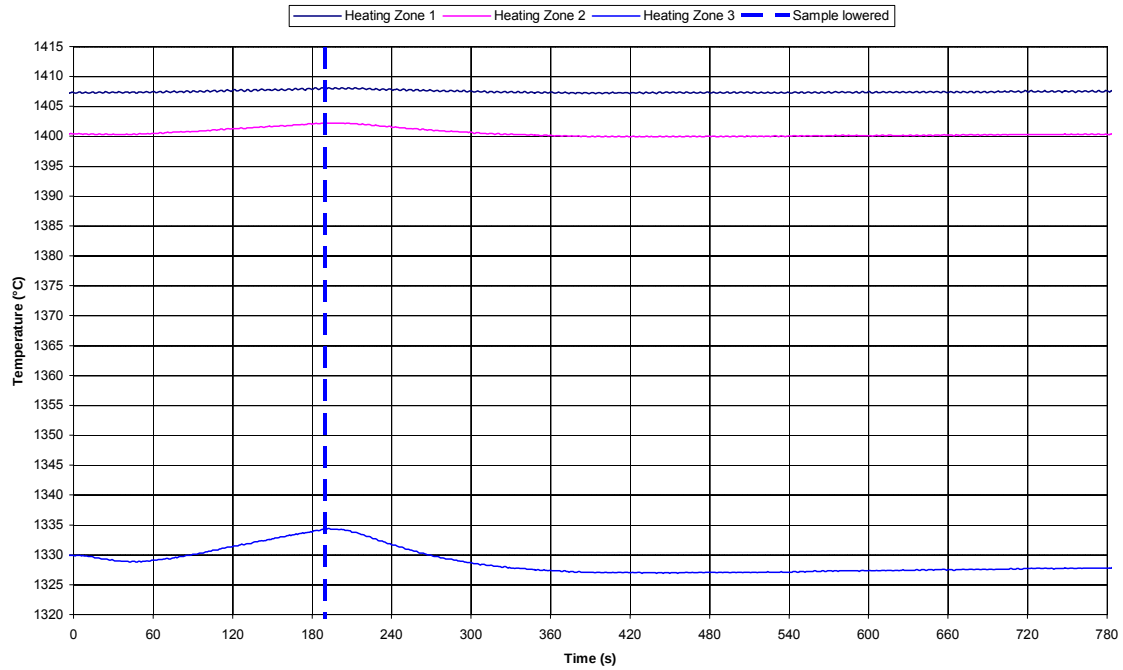




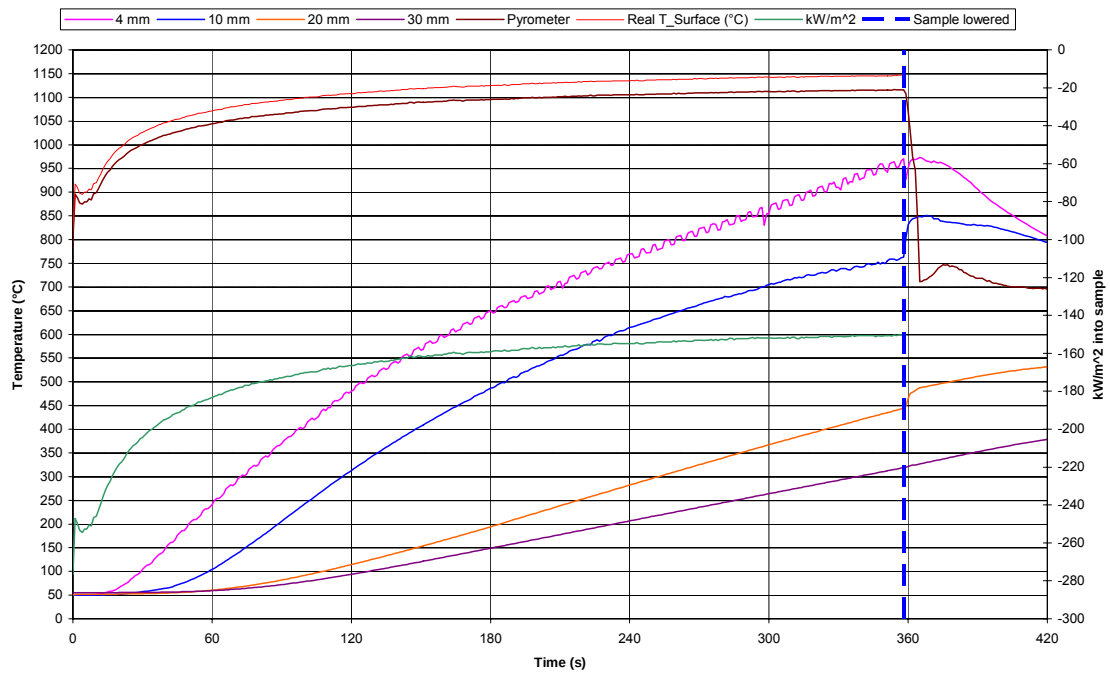


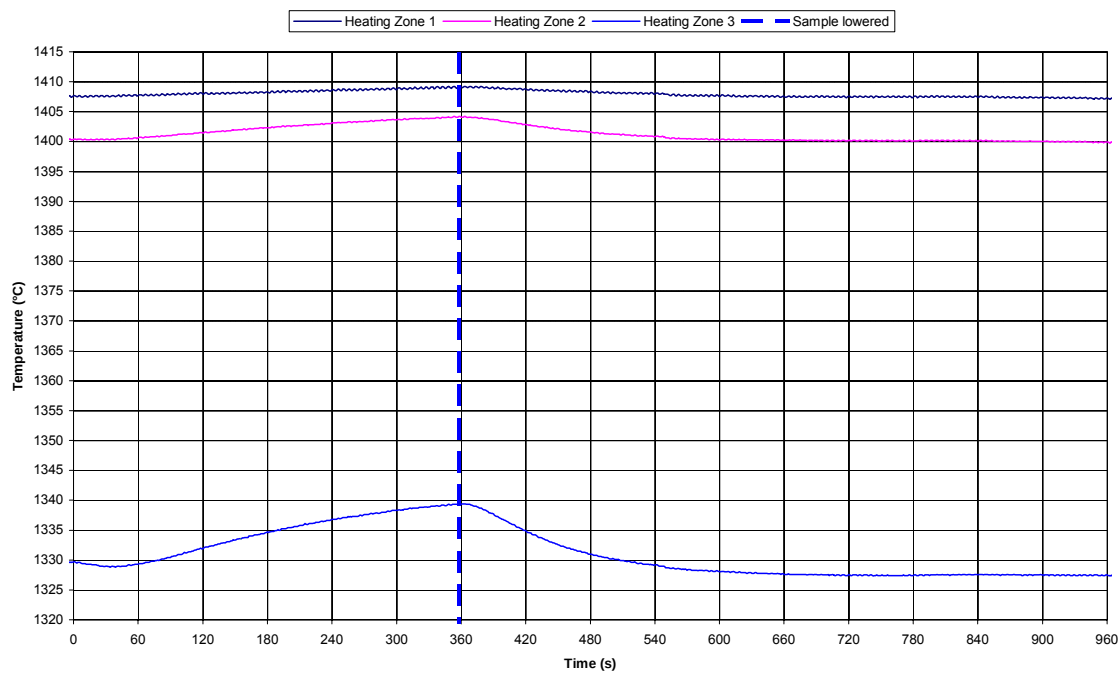
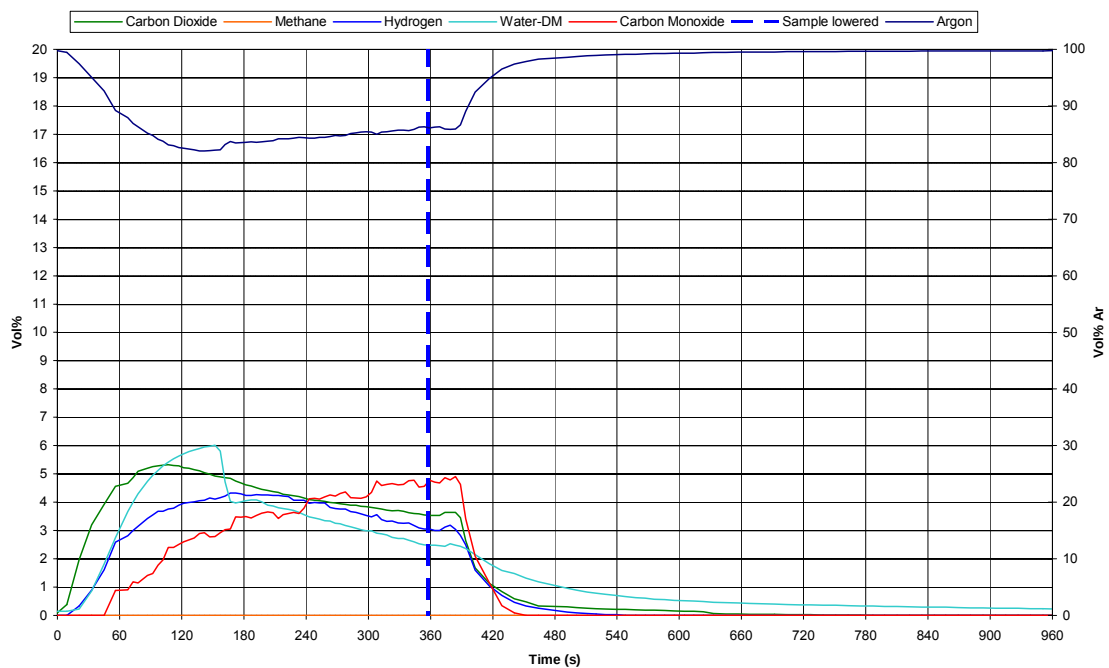
Char-Ore; 40 mm layer, 1400°C, 3minutes





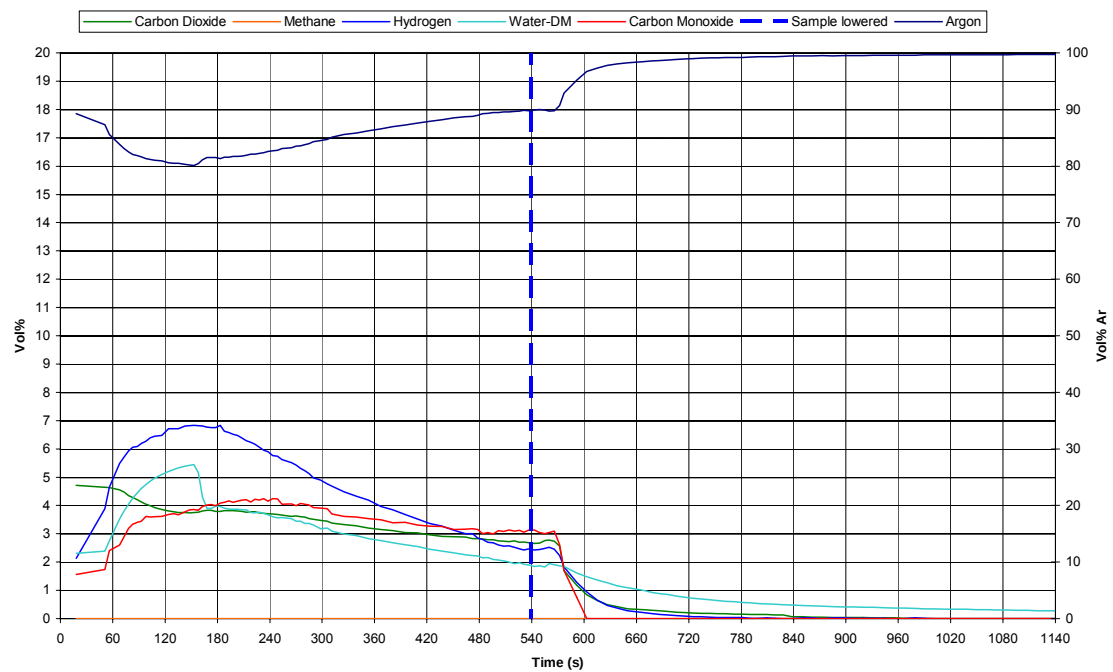
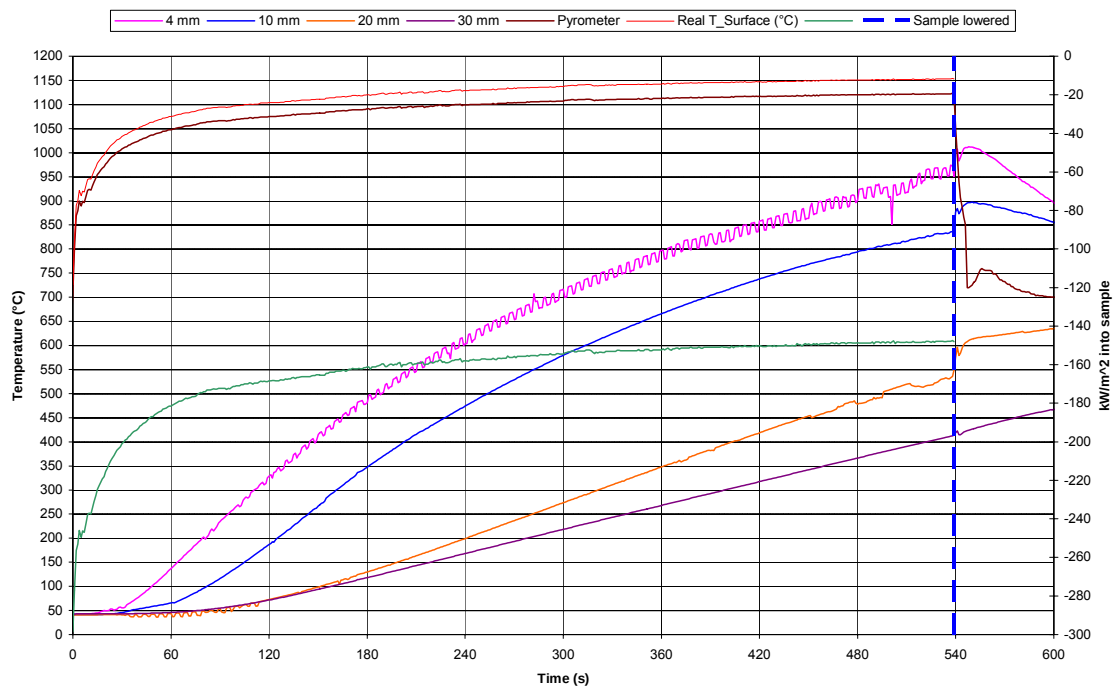
Char-Ore; 40 mm layer, 1400°C, 6minutes

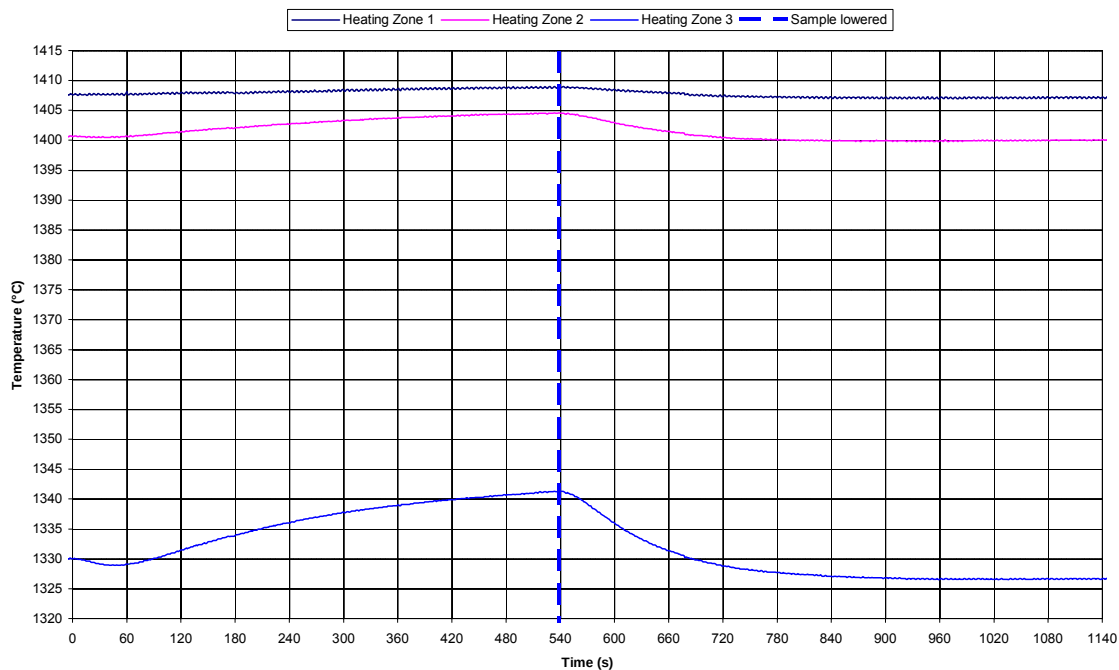




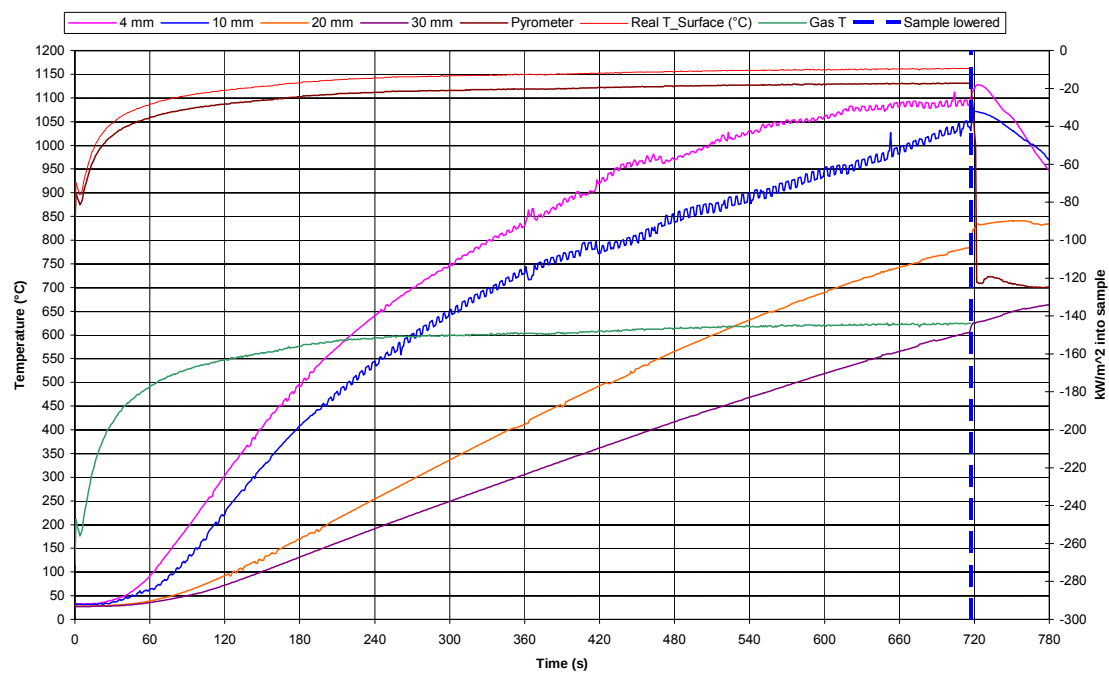


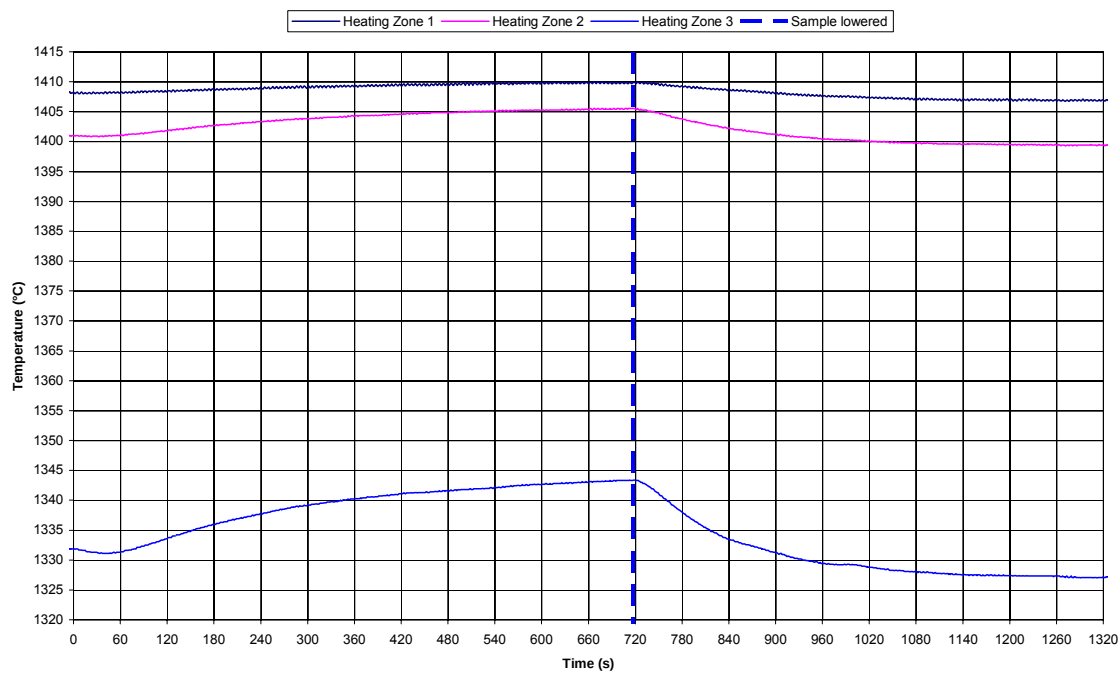
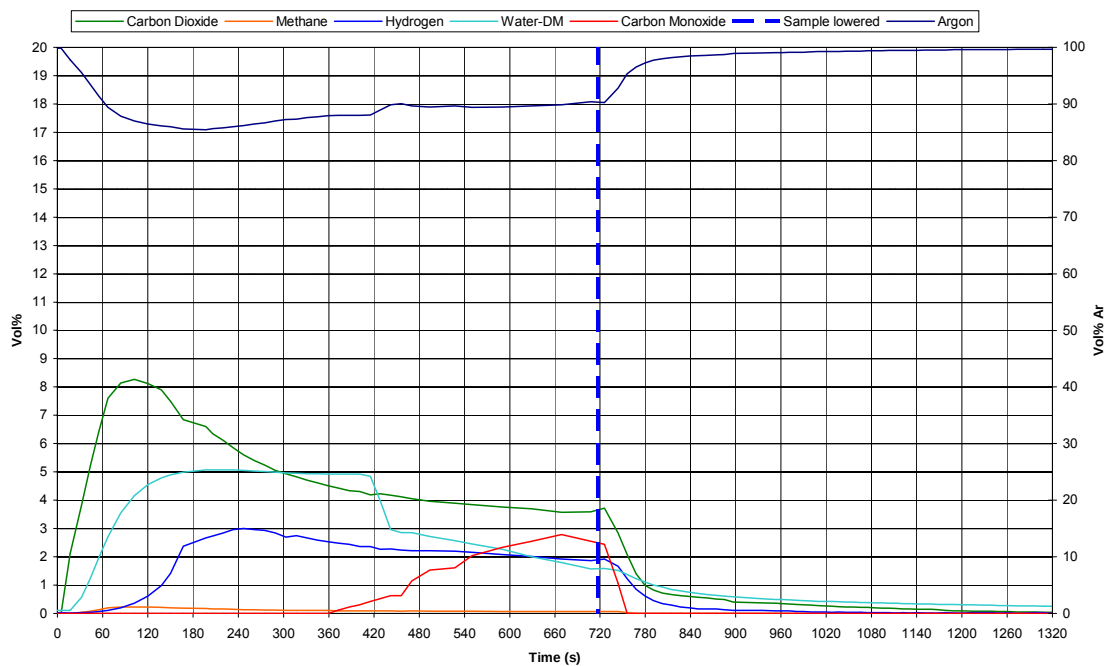
Char-Ore; 40 mm layer, 1400°C, 9minutes





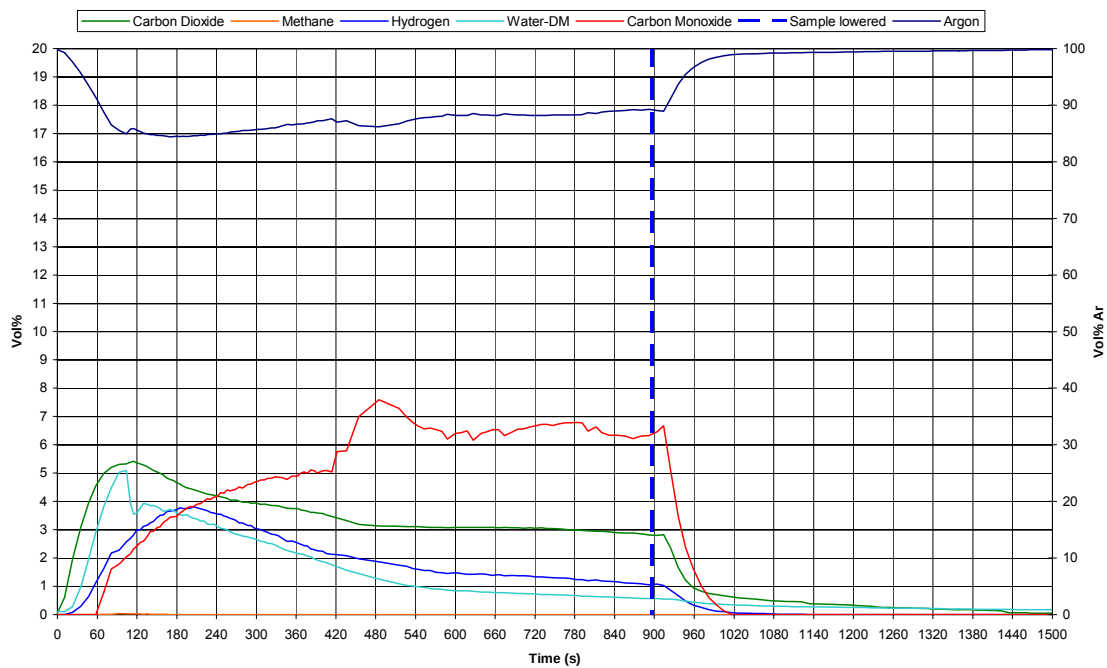
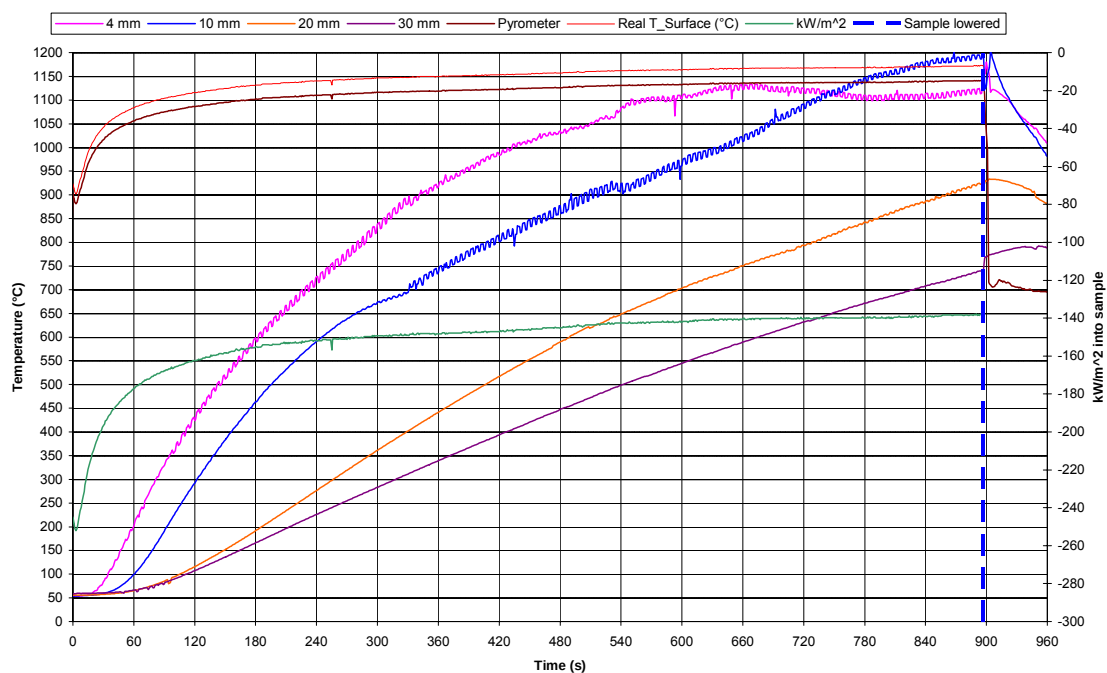
Char-Ore; 40 mm layer, 1400°C, 12minutes

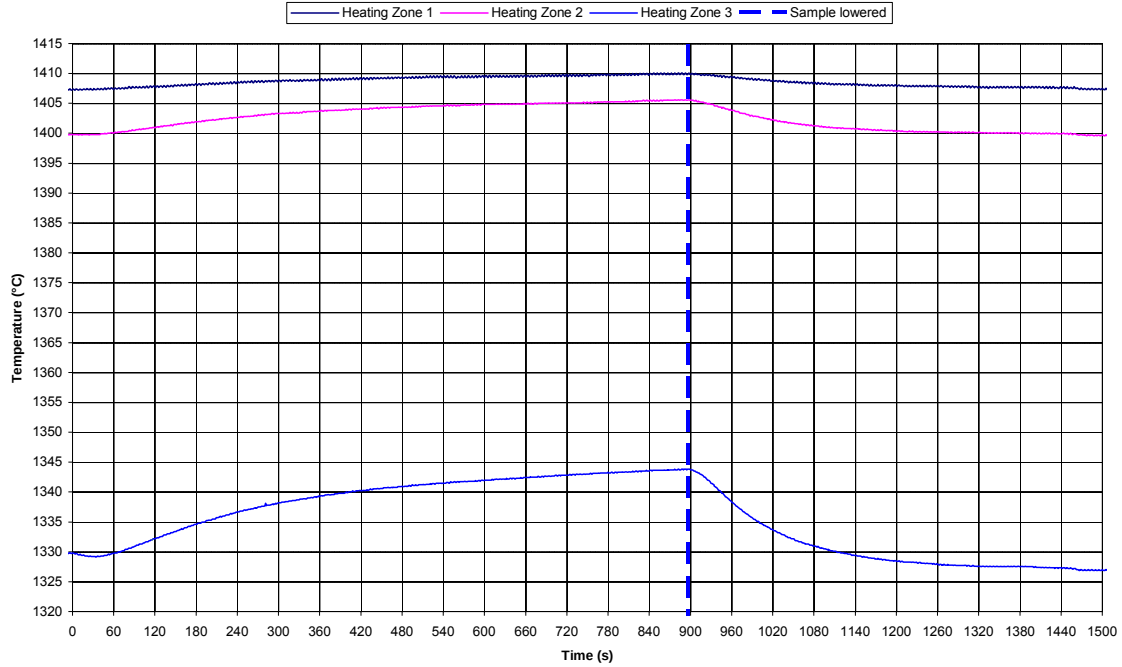




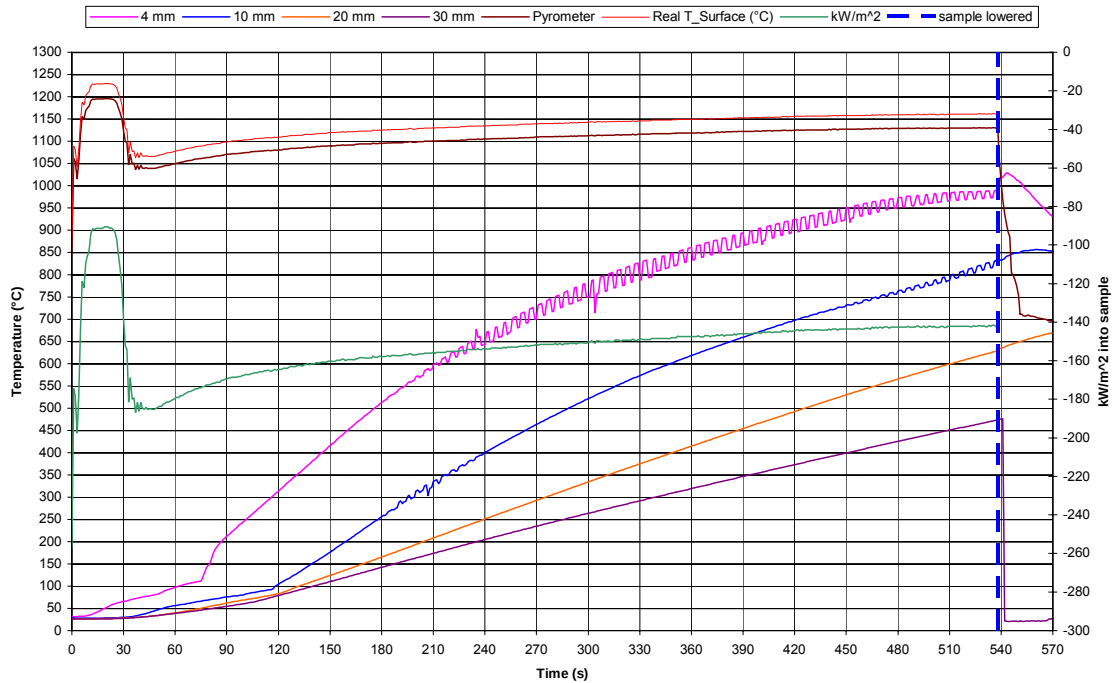


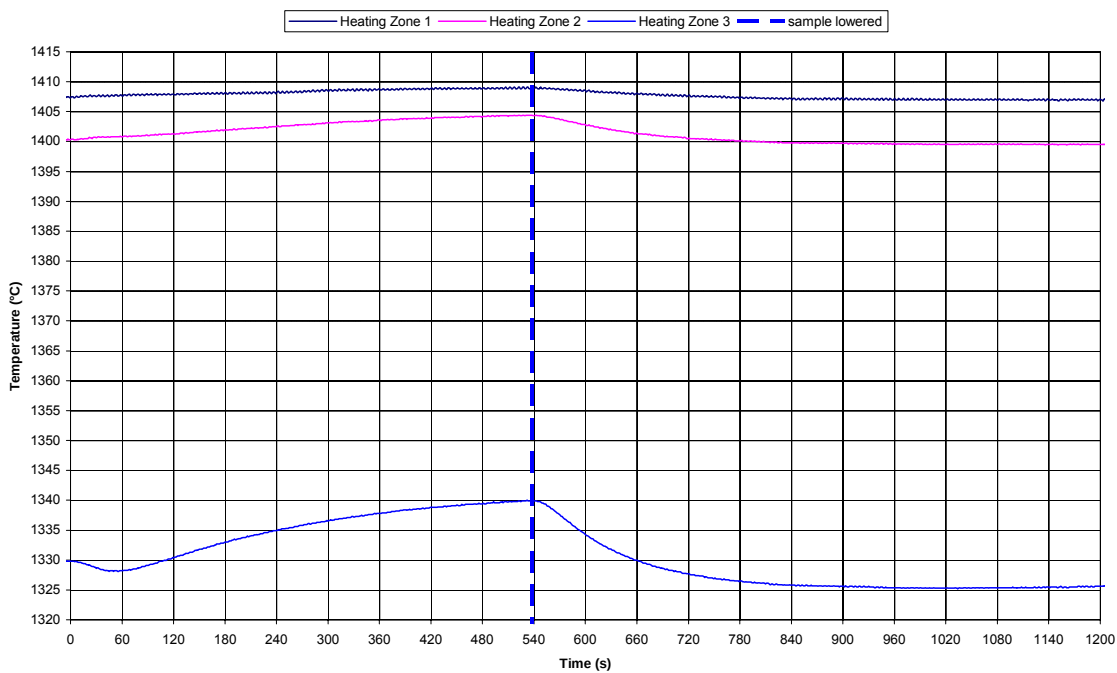
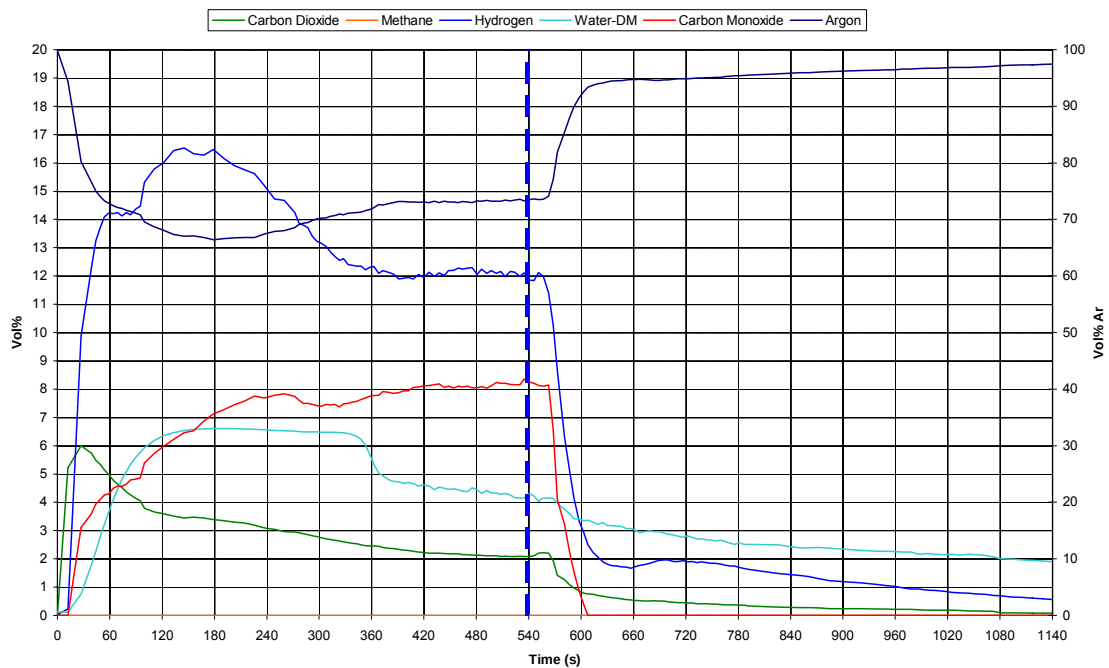
Char-Ore; 40 mm layer, 1400°C, 15minutes





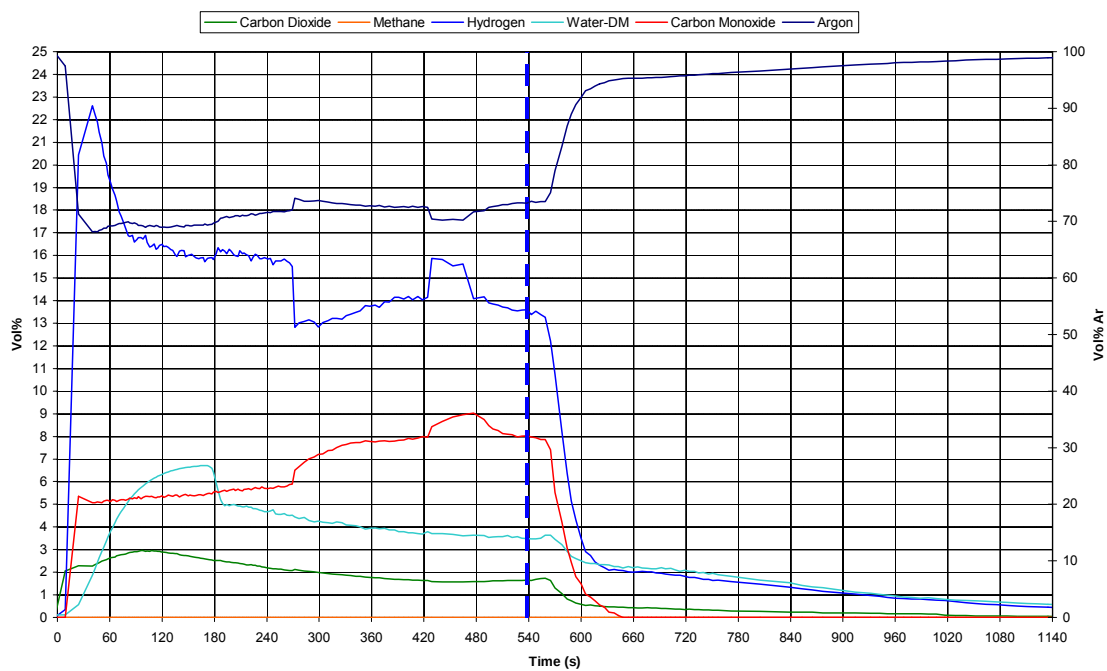
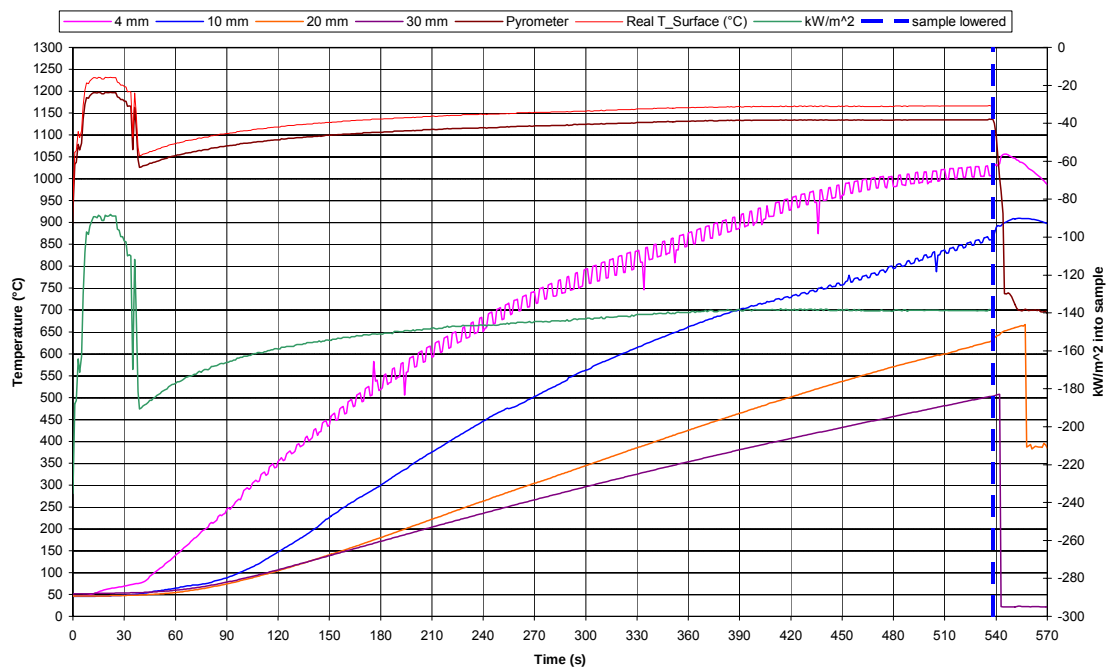
-850 +425 μ m Coal & -2000 +1400 μ m Ore; 40 mm layer, 1400°C, 9minutes

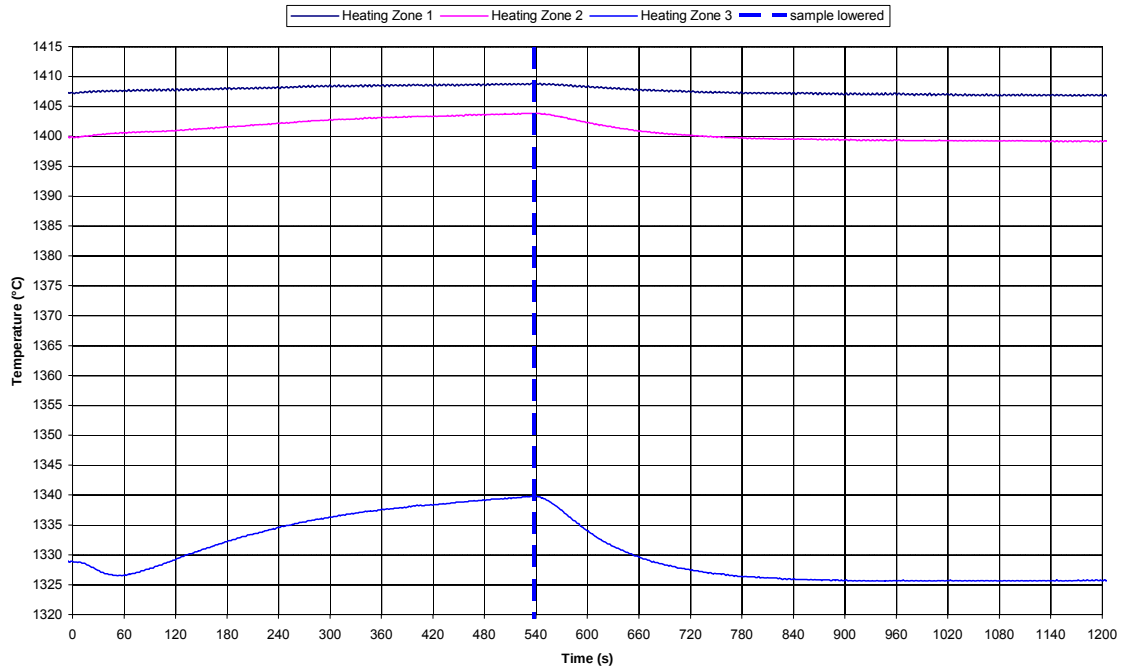




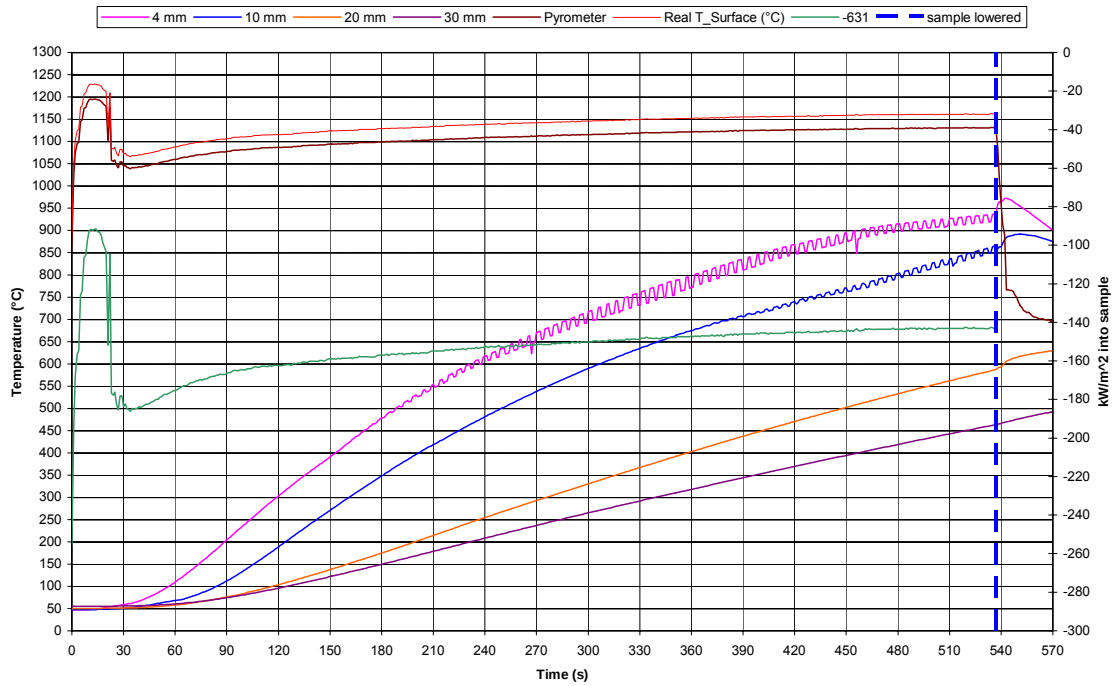


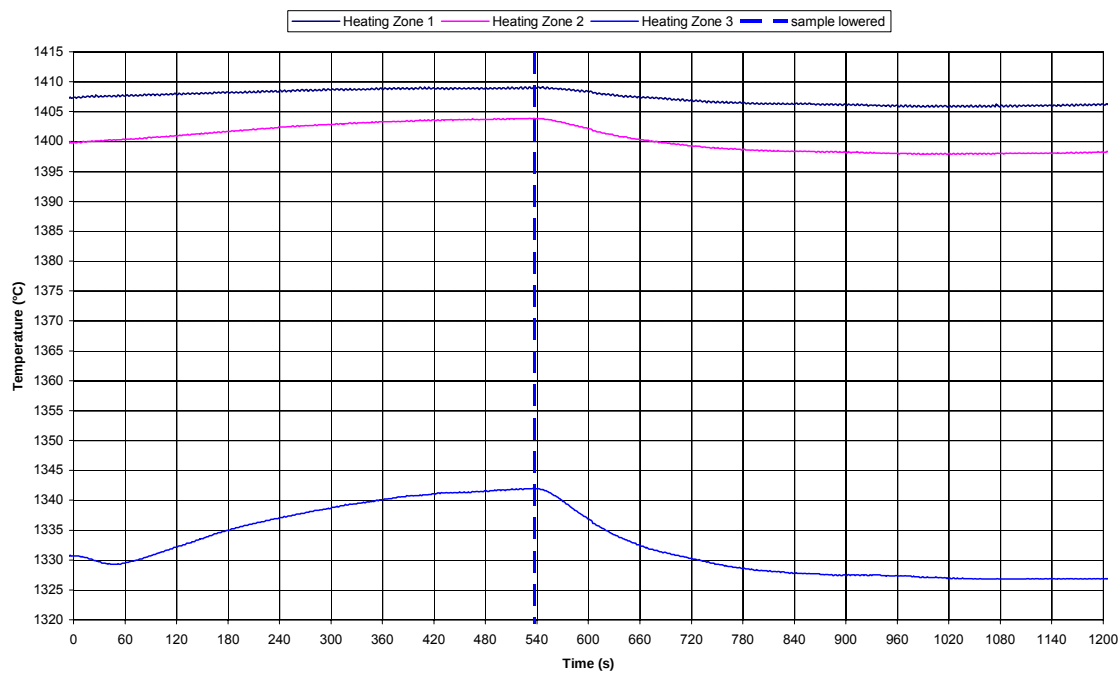
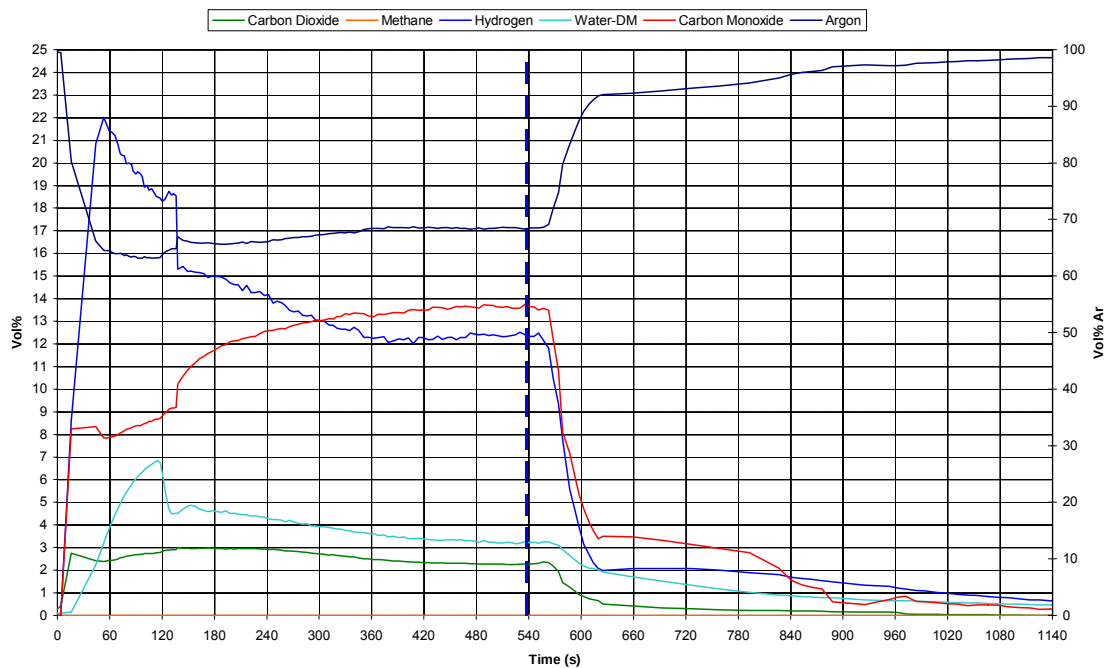
-2000 +1400 μm Coal & -850 +425 μm Ore; 40 mm layer, 1400°C, 9minutes





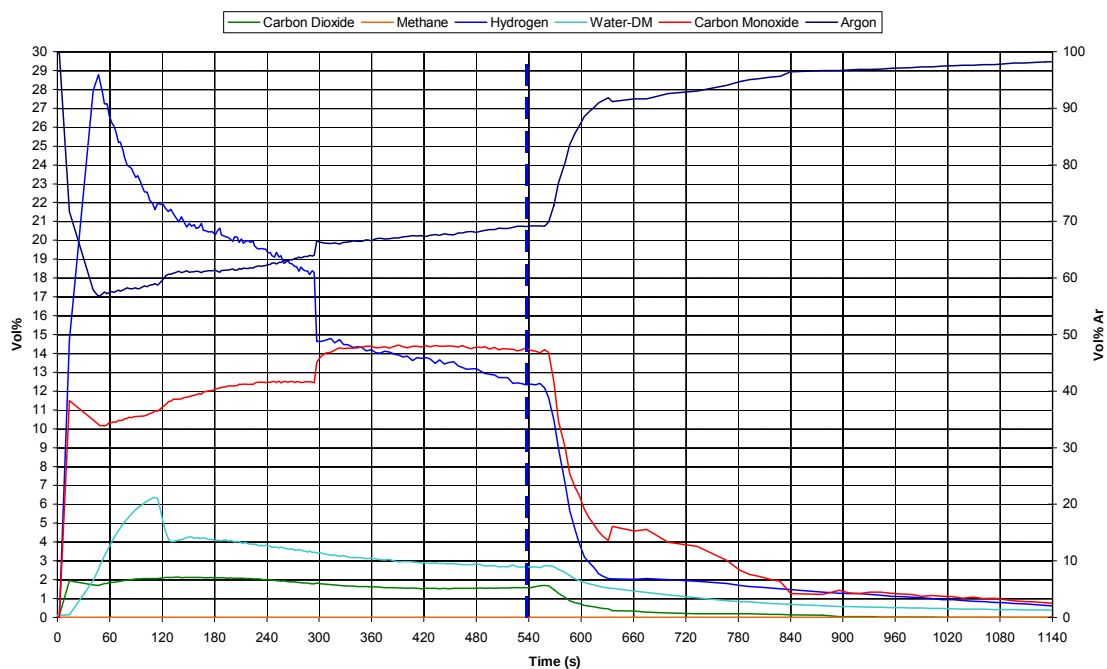
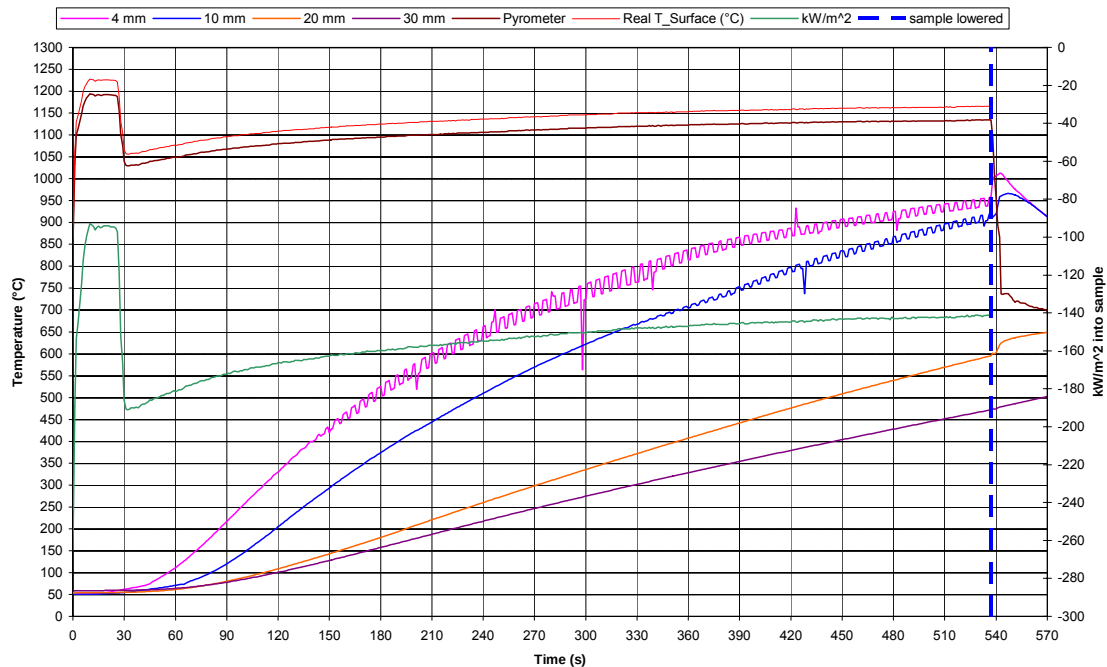
-425 +300 μ m Coal & -850 +425 μ m Ore; 40 mm layer, 1400°C, 9minutes

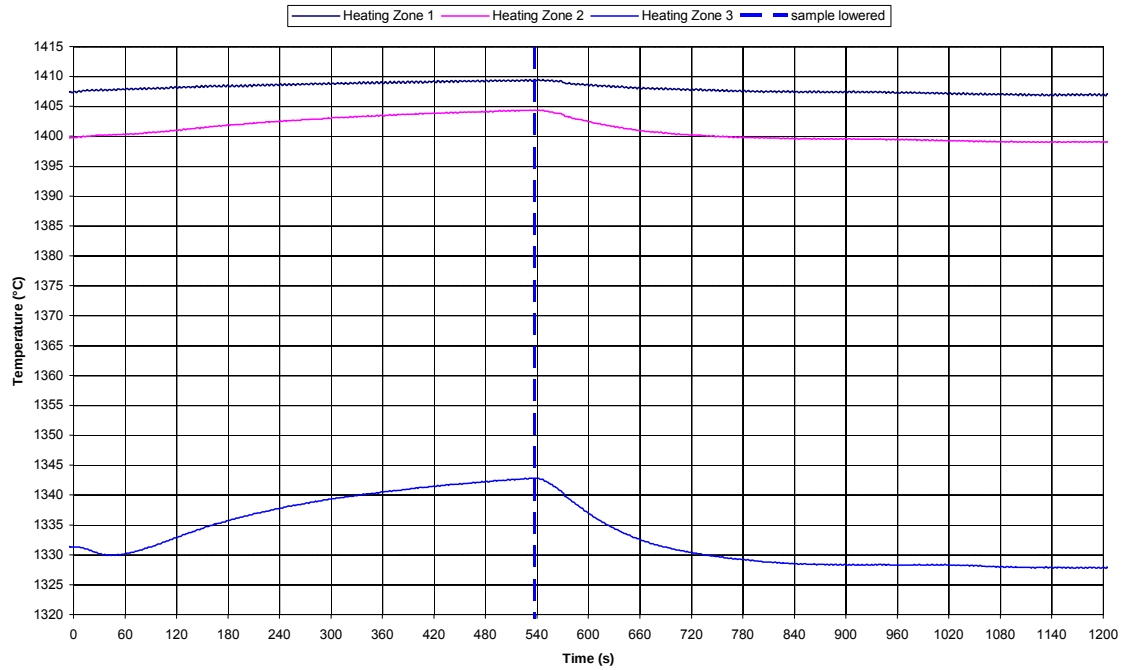




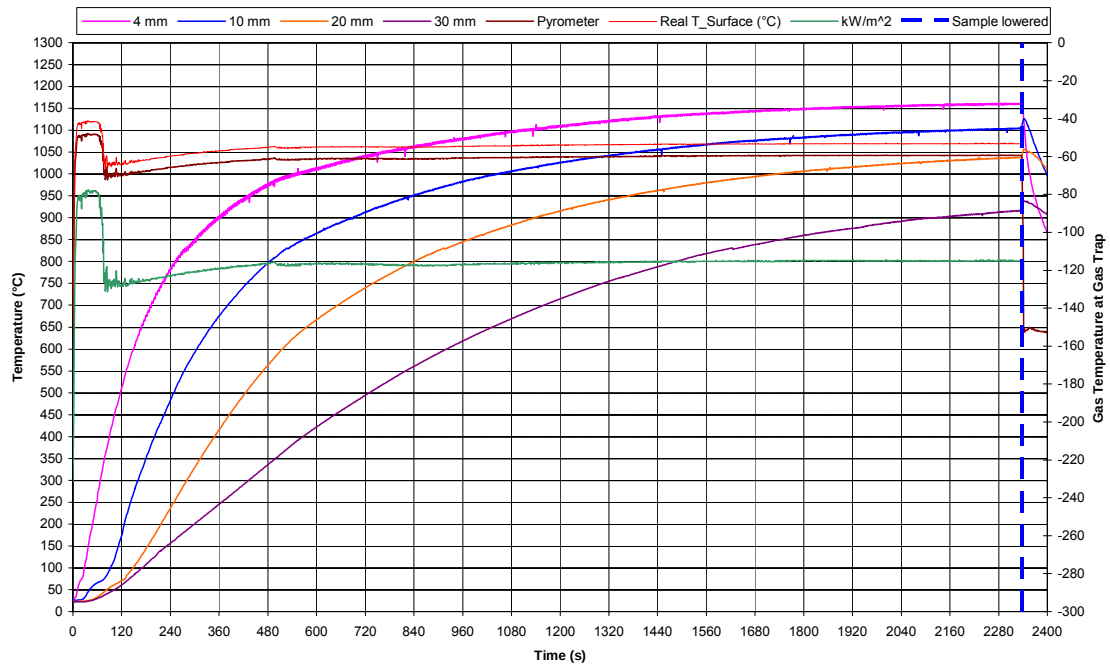


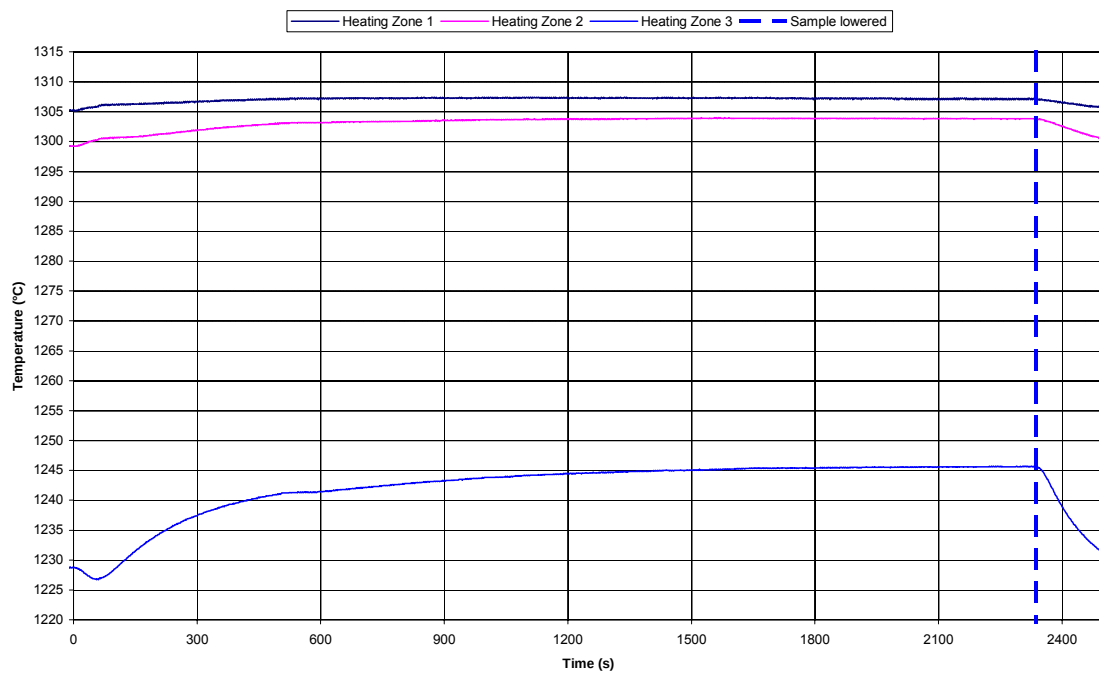
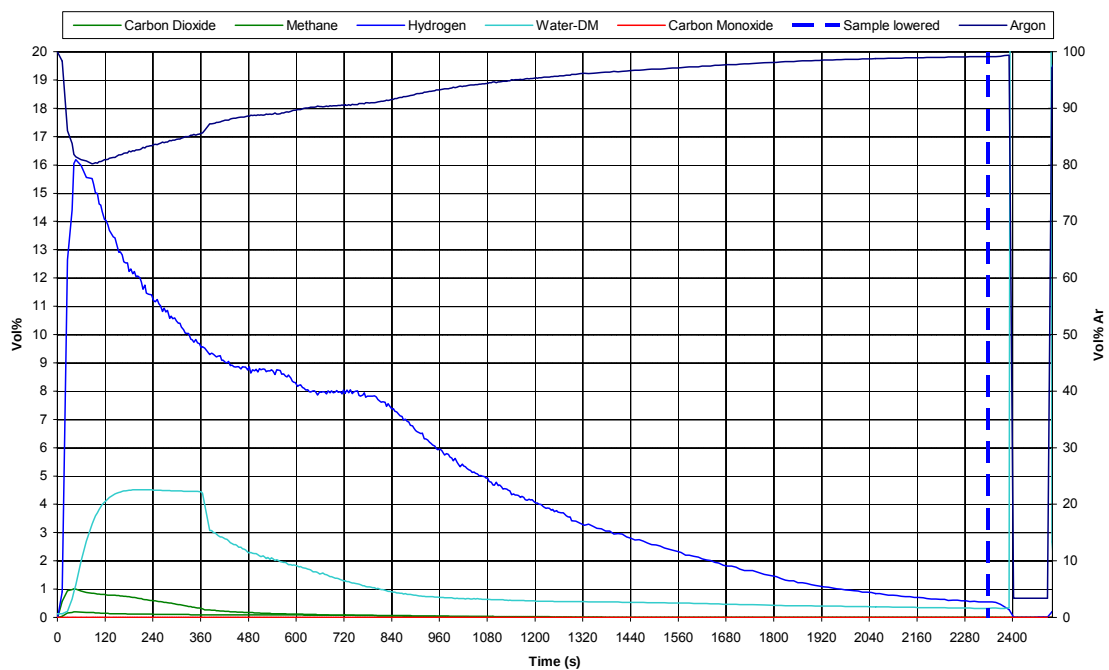
-850 +425 μ m Coal & -425 +300 μ m Ore; 40 mm layer, 1400°C, 9minutes





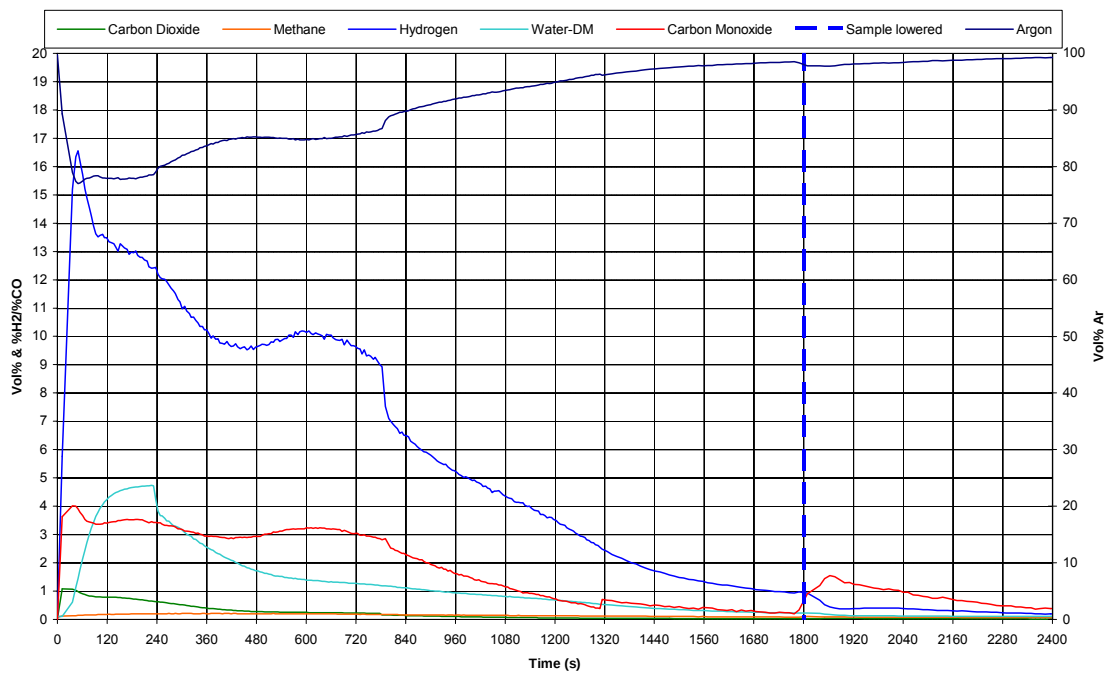
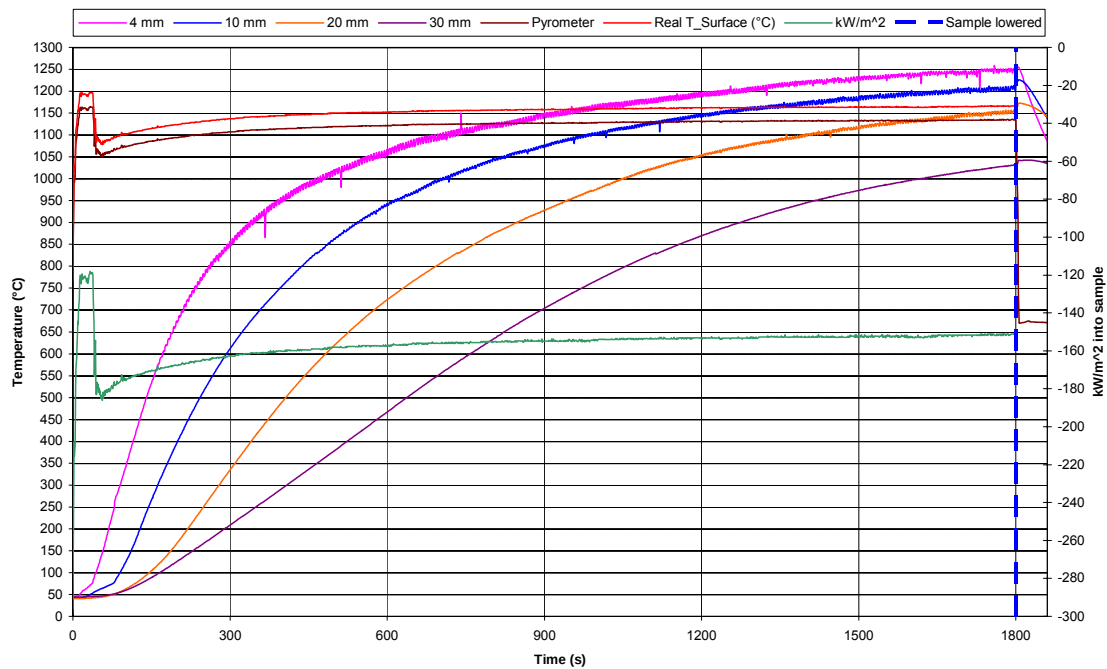
Alumina-Coal; 40 mm layer, 1300°C

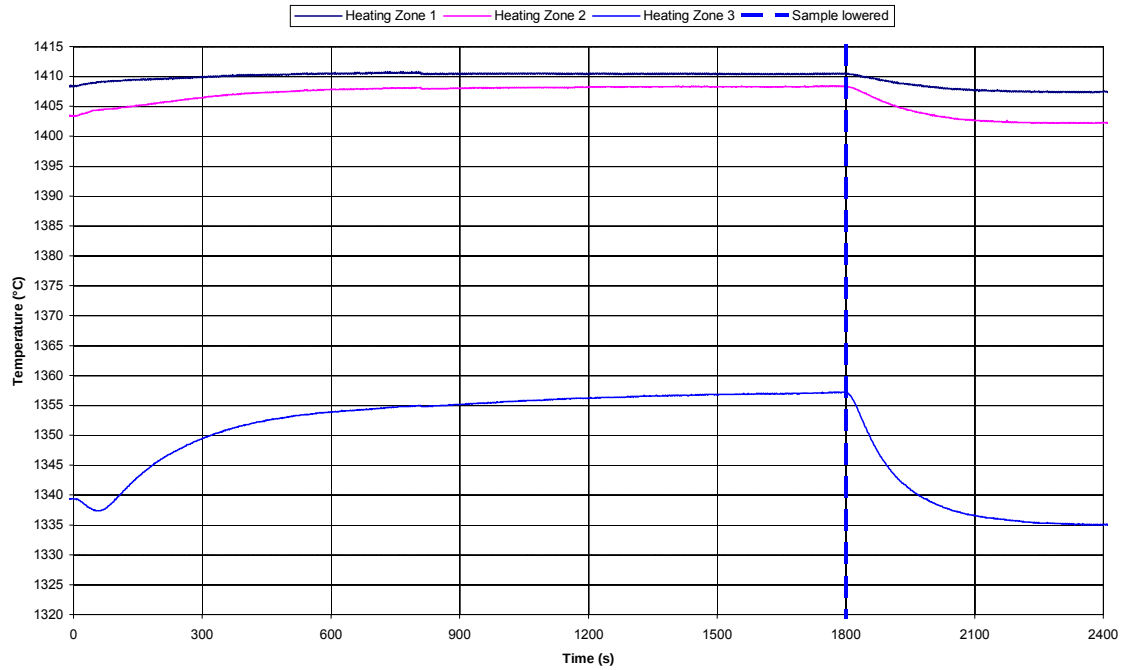




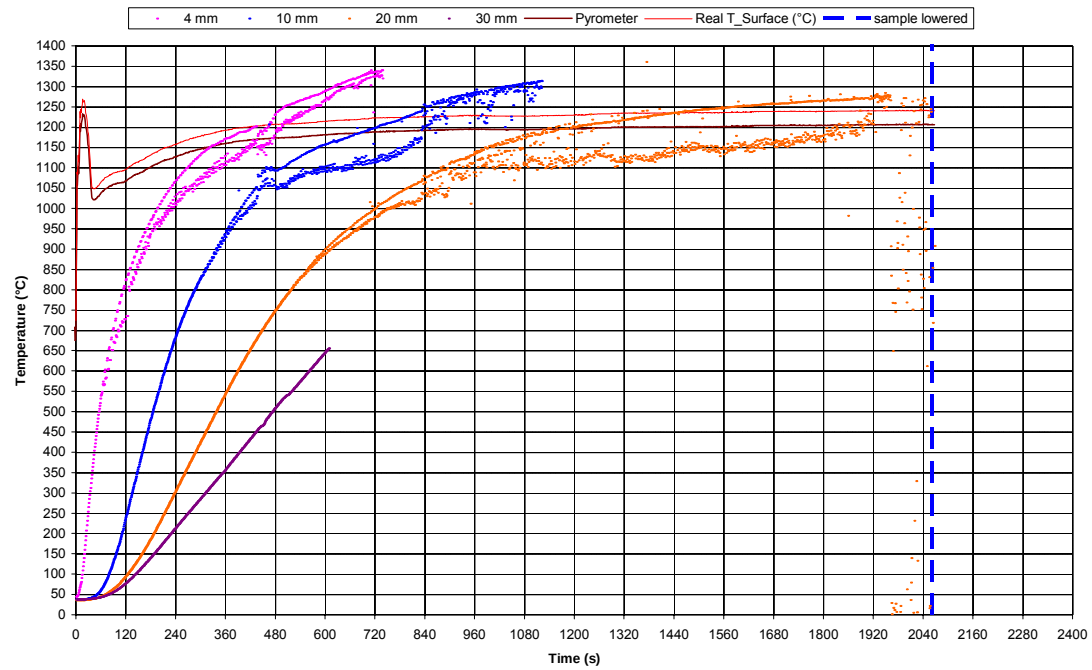


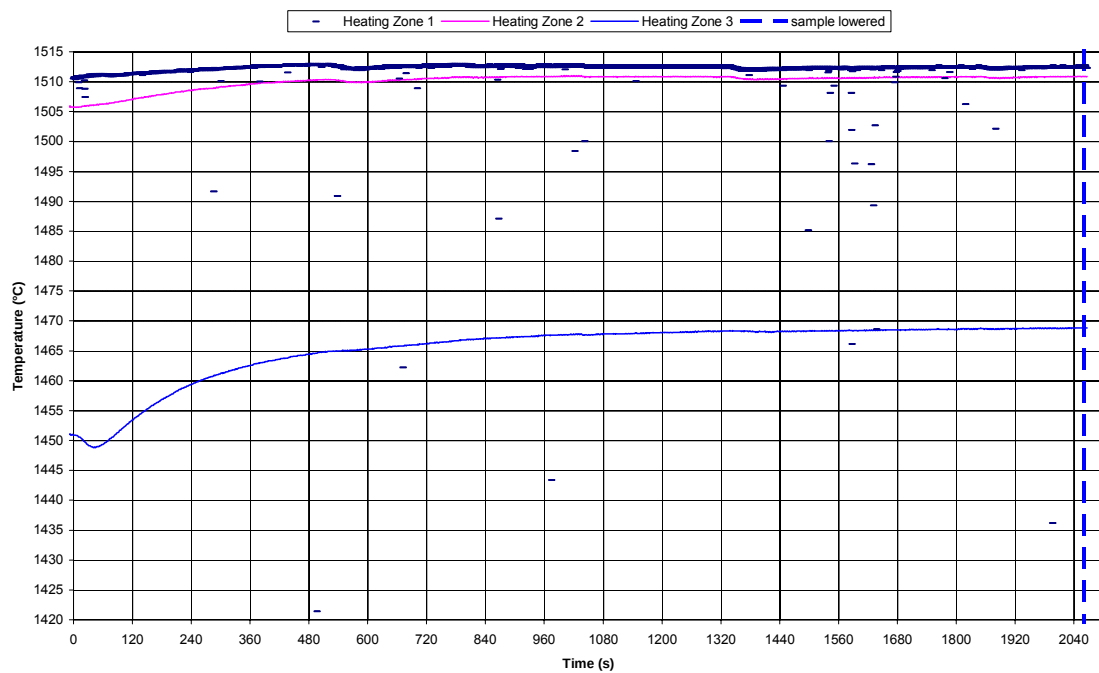
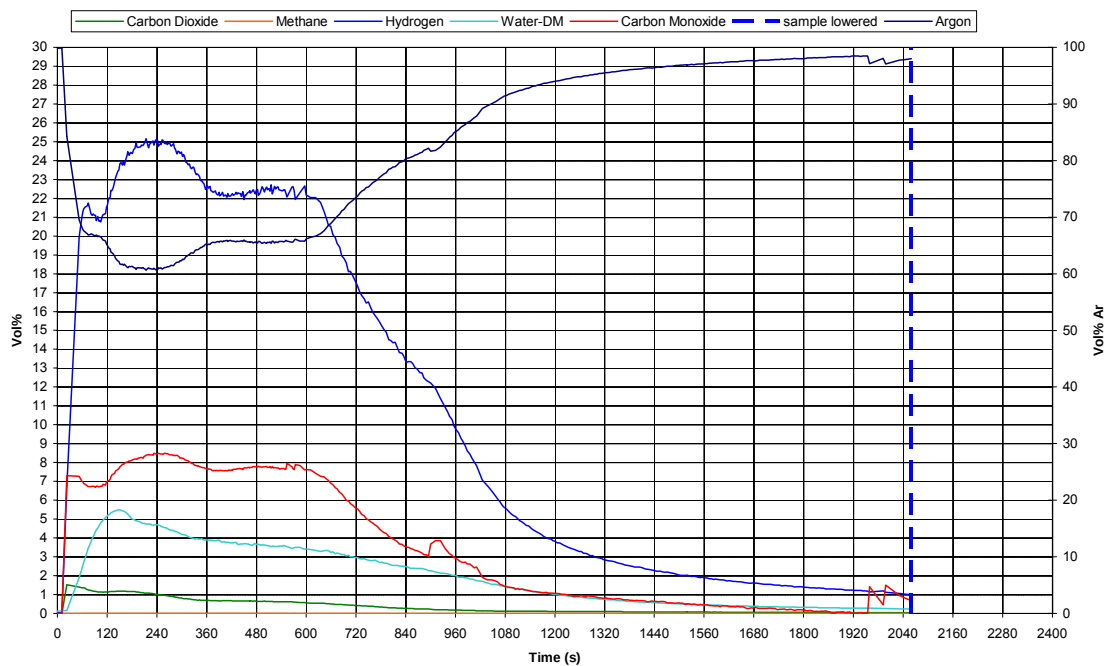
Alumina-Coal; 40 mm layer, 1400°C





Alumina-Coal; 40 mm layer, 1500°C





Appendix IX

Calculation of %Carbon consumption, %Reduction and Total mass loss

%Carbon consumption

$$m_{total}^{in} = m_{Fe}^{out} \cdot \frac{100}{\%Fe_{ore}^{in}} \cdot \frac{100}{\%Ore}$$

$$m_{C_total}^{in} = m_{total}^{in} \cdot \frac{\%Coal}{100} \cdot \frac{\%TotalC}{100}$$

$$m_{C_top_in}^{top} = X_{top} \cdot m_{C_total}^{in}$$

$$m_{C_top_out}^{top} = m_{total_corr}^{top_out} \cdot \frac{\%C_{corr}^{top_out}}{100}$$

$$\%C_{consumption}^{top} = \frac{(m_{C_top_in}^{top} - m_{C_top_out}^{top})}{m_{C_top_in}^{top}} \cdot 100$$

The %Carbon consumption is calculated similarly for the middle and bottom nodes

%Reduction

$$m_O^{top_in} = m_{total_corr}^{top_out} \cdot \frac{\%Fe(total)_{corr}^{top_out}}{100 \cdot mm_{Fe} \cdot 2} \cdot 3 \cdot mm_O$$

$$m_O^{top_out} = m_{total_corr}^{top_out} \cdot \left(\frac{\%Fe(+2)_{corr}^{top_out}}{100 \cdot mm_{Fe}} \cdot mm_O + \frac{\%Fe(+3)_{corr}^{top_out}}{100 \cdot mm_{Fe} \cdot 2} \cdot 3 \cdot mm_O \right)$$

$$\%R^{top} = \frac{(m_O^{top_in} - m_O^{top_out})}{m_O^{top_in}} \cdot 100$$

The %Reduction is calculated similarly for the middle and bottom nodes

Mass loss calculated from weighed masses and fibre board carry over correction

$$\Delta m_{total}^{weighed} = m_{total}^{in} - m_{total_corr}^{top_out} - m_{SiO_2}^{carry-over} - m_{Al_2O_3}^{carry-over}$$

Total mass oxygen in unreacted sample

$$m_{O_total}^{in} = m_O^{top_in} + m_O^{mid_in} + m_O^{bot_in} + m_{C_total}^{in} \cdot \left(\frac{\%H_2O_Coal}{100 \cdot mm_{H_2O}} \cdot mm_O + \frac{\%O_Coal}{100} \right)$$

$\%H_2O_Coal$ = %Moisture in Proximate analysis of coal



$\%O_{Coal} = \%O$ in Ultimate analysis of coal

$m_{Al_2O_3}^{carry-over} = \text{g. } Al_2O_3 \text{ carry-over from fibreboard to reacted sample mix in top node}$

$m_{SiO_2}^{carry-over} = \text{g. } SiO_2 \text{ carry-over from fibreboard to reacted sample mix in top node}$

$m_{total}^{in} = \text{total g. unreacted sample mix in crucible}$

$\Delta m_{total}^{weighed} = \text{sample mass loss calculated from weighed masses and fibre board carry over correction}$

$m_j^{i-in} = \text{mass of component } j \text{ in node } i \text{ of unreacted sample}$

$m_j^{i-out} = \text{mass of component } j \text{ in node } i \text{ of reacted sample}$

$m_{j-corr}^{i-out} = \text{corrected mass of component } j \text{ in node } i \text{ of reacted sample}$

$m_{total}^{in} = \text{total g. unreacted sample mix in crucible}$

$\%Y^{i-in} = \text{mass\% of component } Y \text{ in node } i \text{ of unreacted sample}$

$\%Y^{i-out} = \text{mass\% of component } Y \text{ in node } i \text{ of reacted sample}$

$\%Y_{corr}^{i-out} = \text{corrected mass\% of component } Y \text{ in node } i \text{ of reacted sample}$

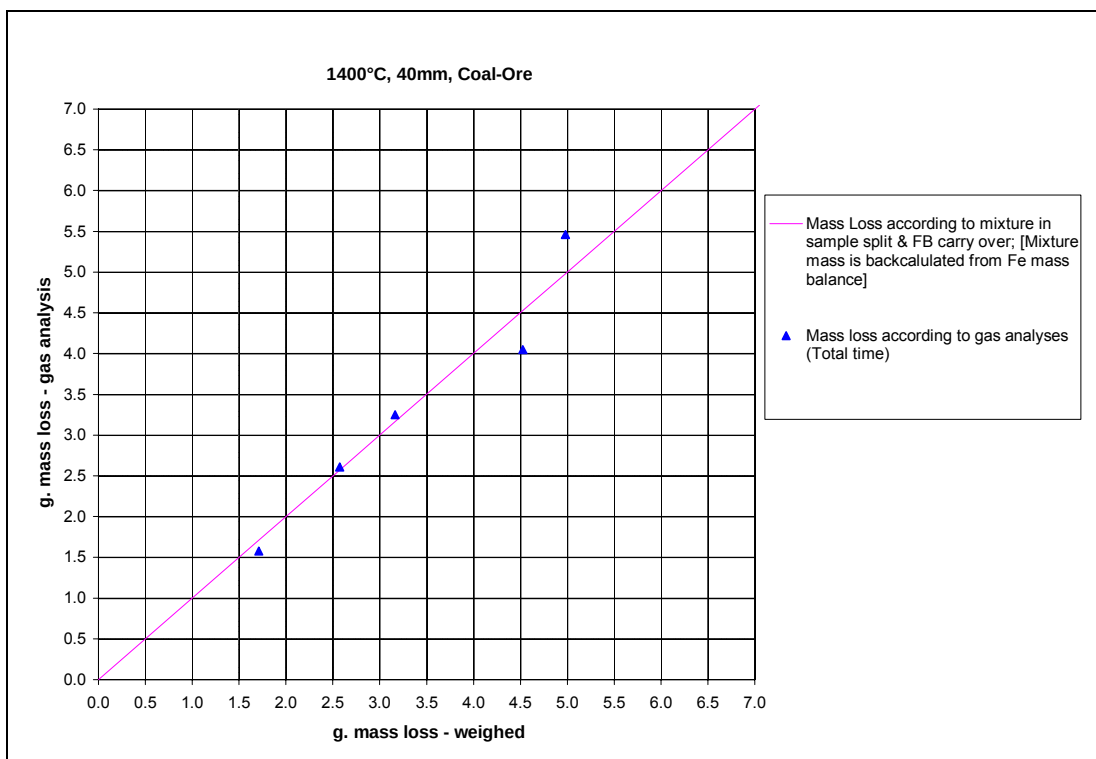
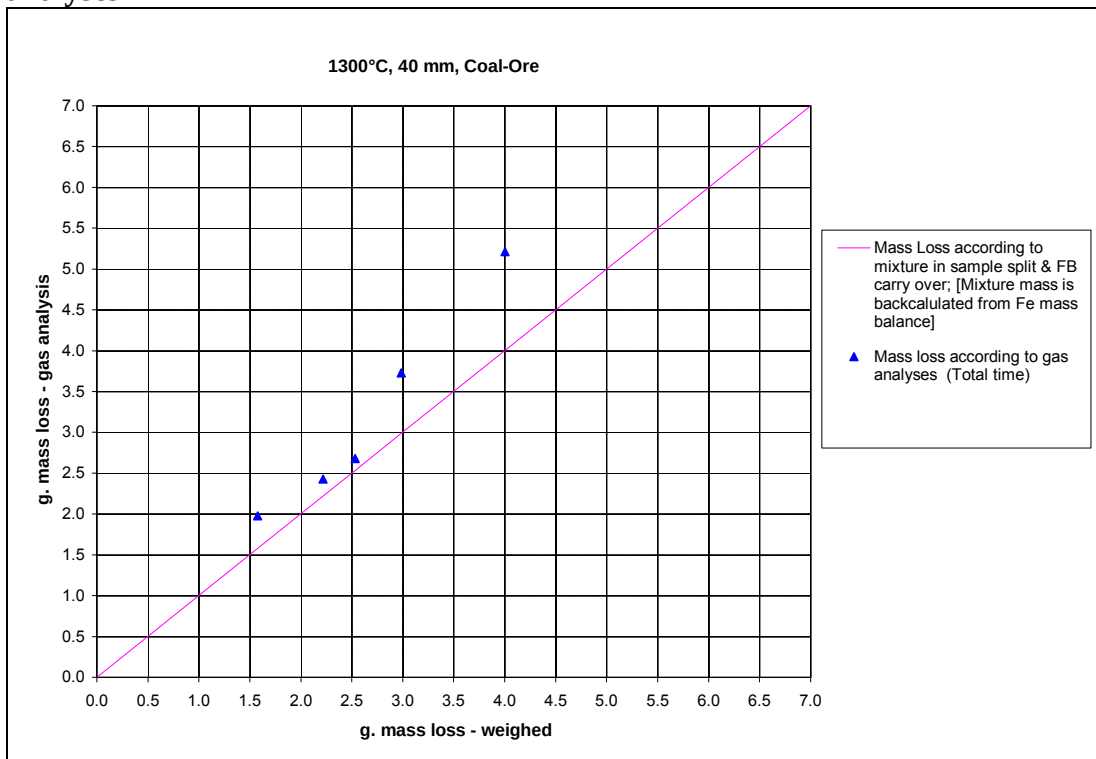
$mm_k = \text{molar mass of component } k$

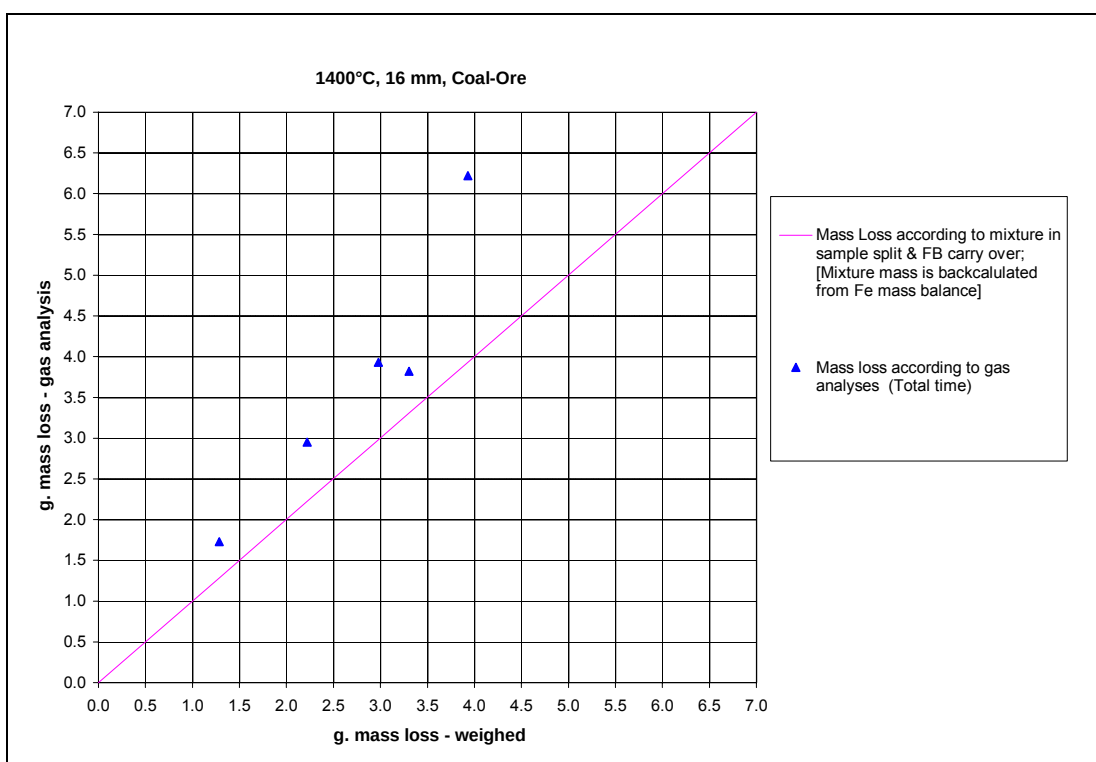
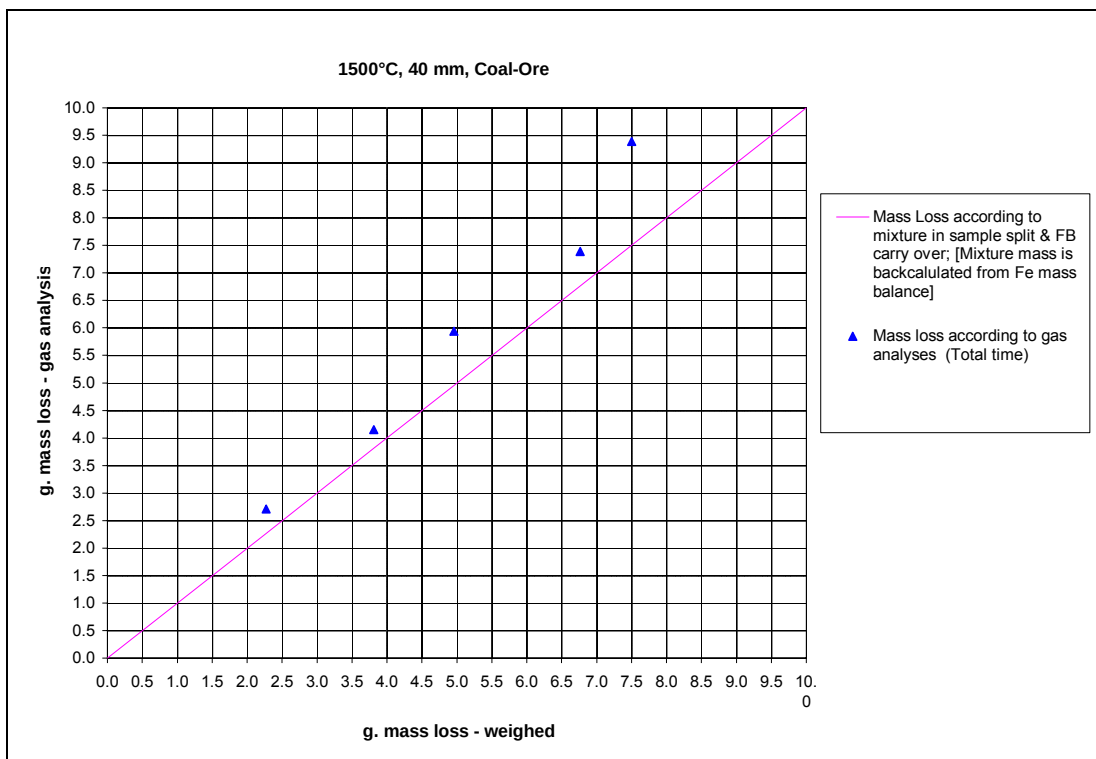
$X_i = \text{mass fraction of sample material mix in node } i, i = \text{top, mid, bot for top, middle or bottom node}$

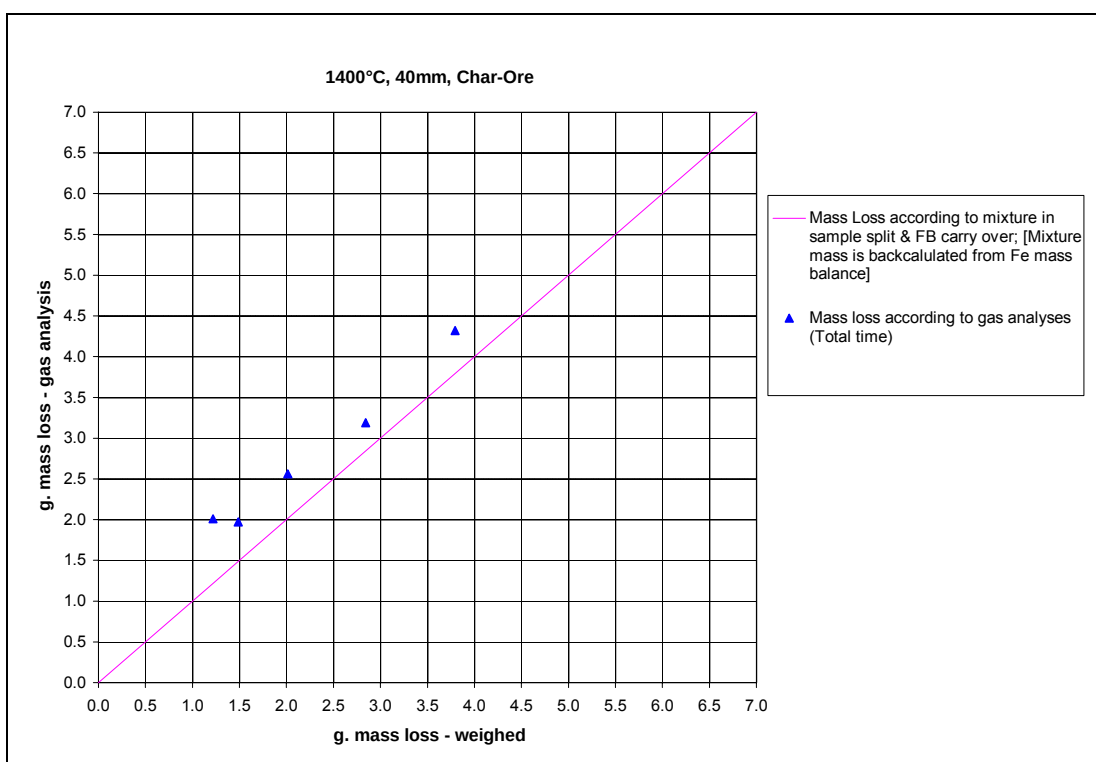
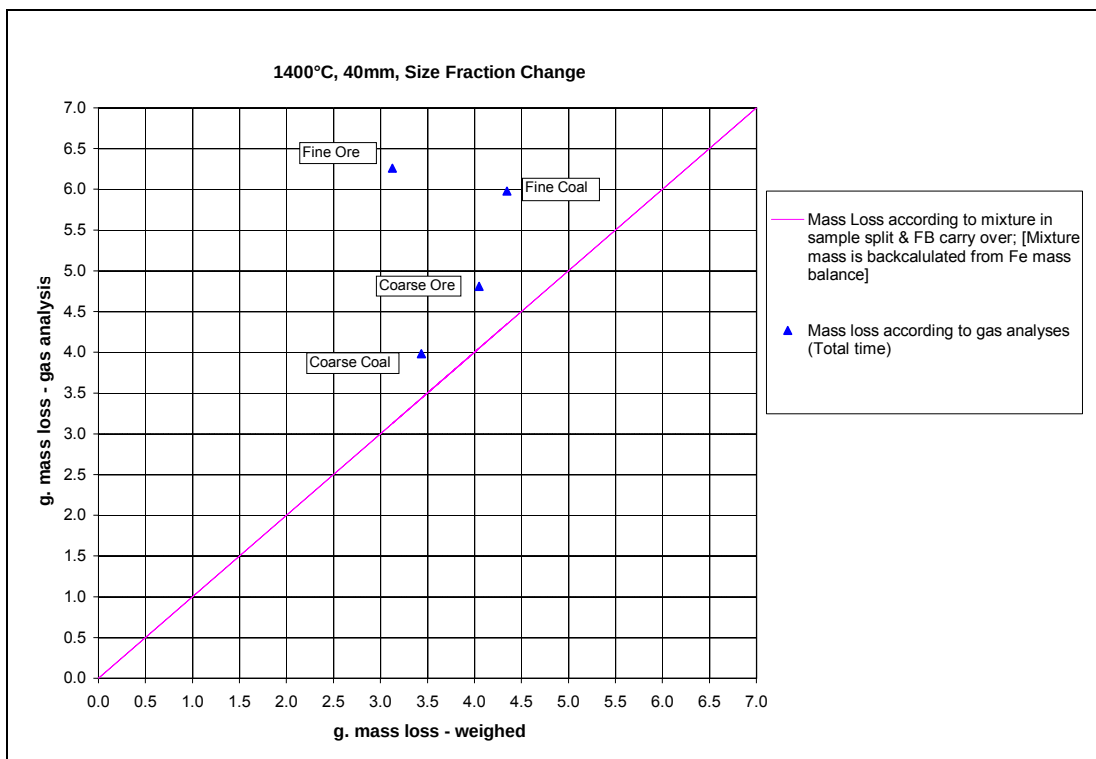
$i = \text{top, mid, bot for top, middle or bottom node}$

Appendix X

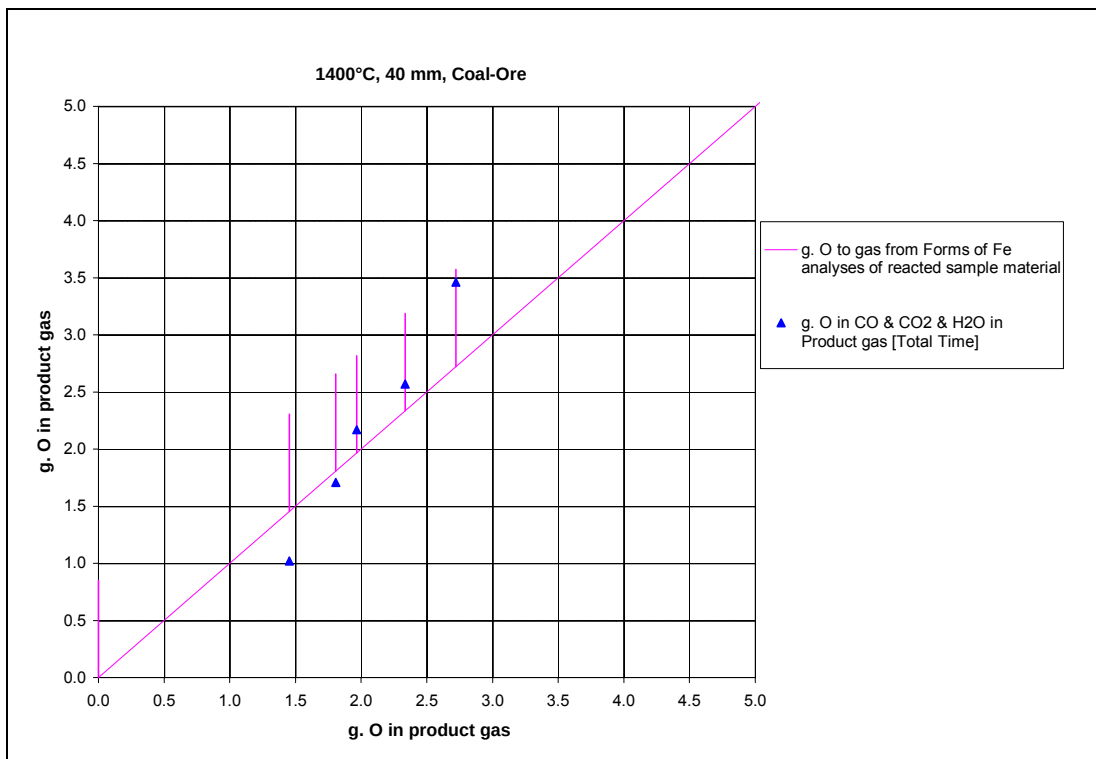
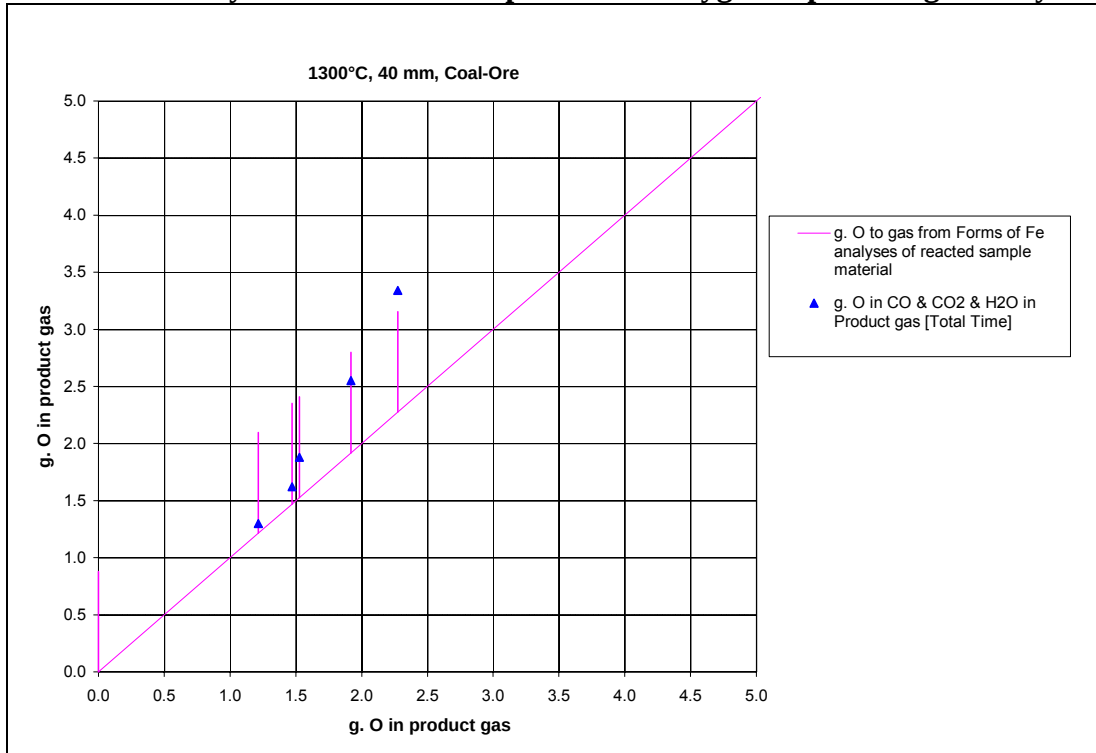
Appendix X (a): Graphs of total sample mass loss calculated from weighed masses and fibreboard (FB) carry over ($\Delta m_{total}^{weighed}$) vs. mass loss according to product gas analyses

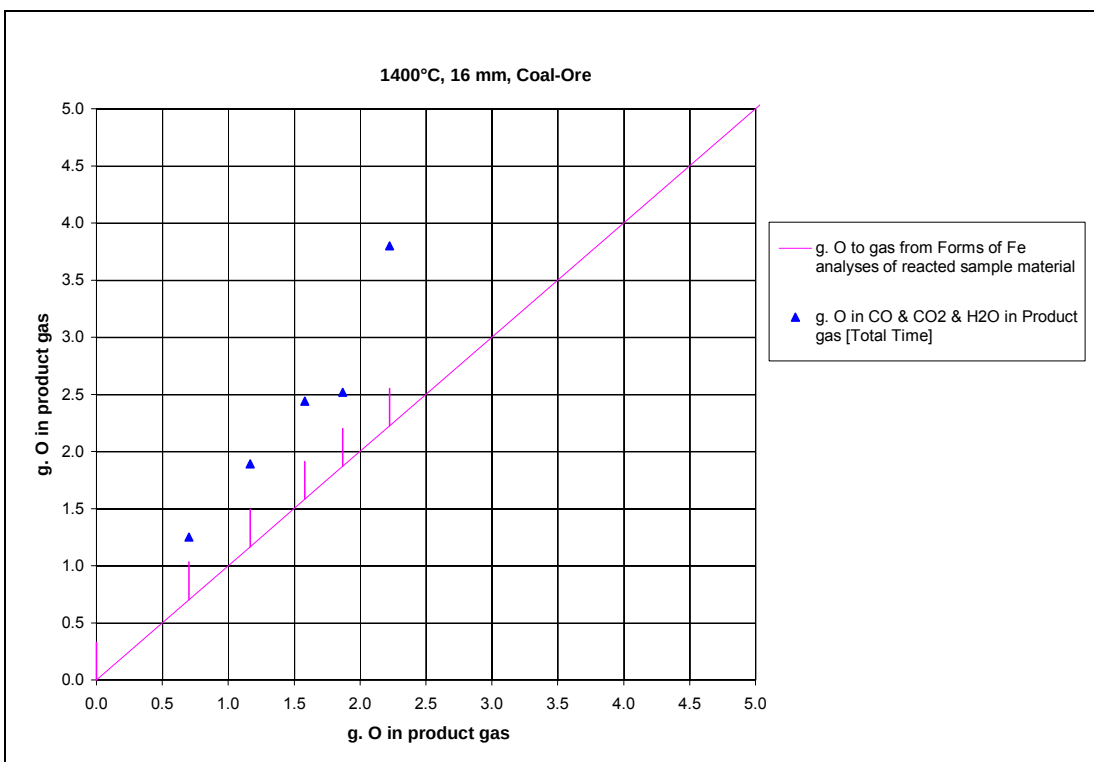
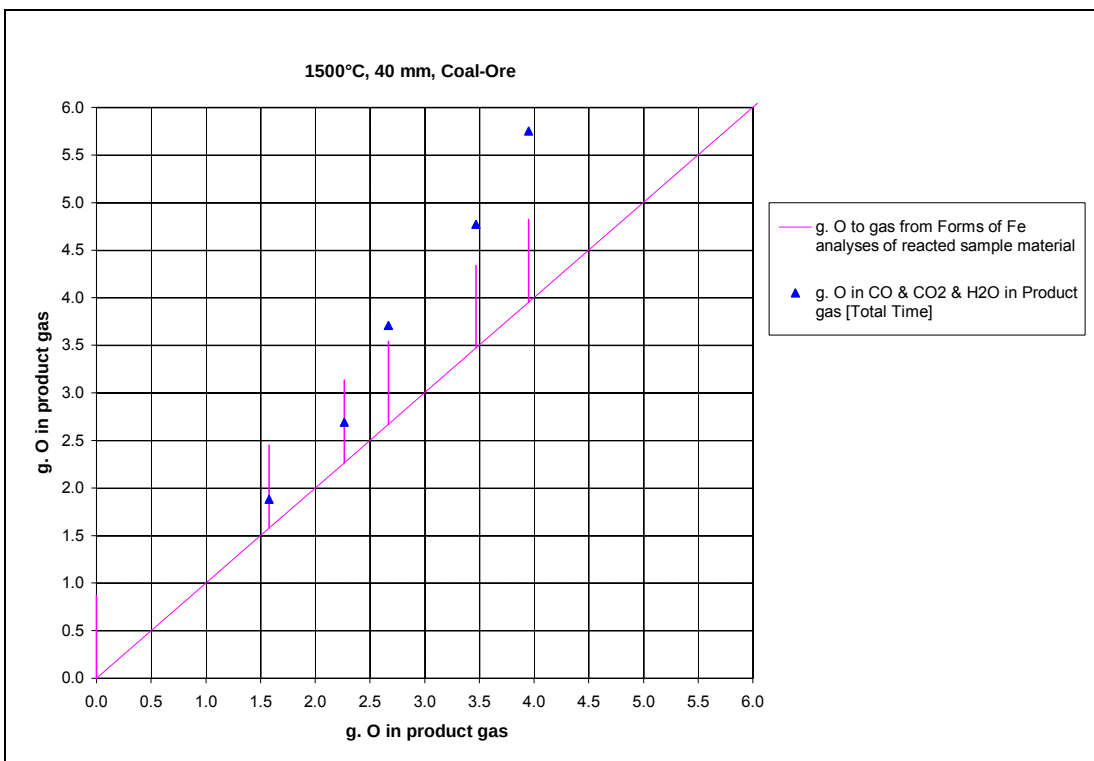


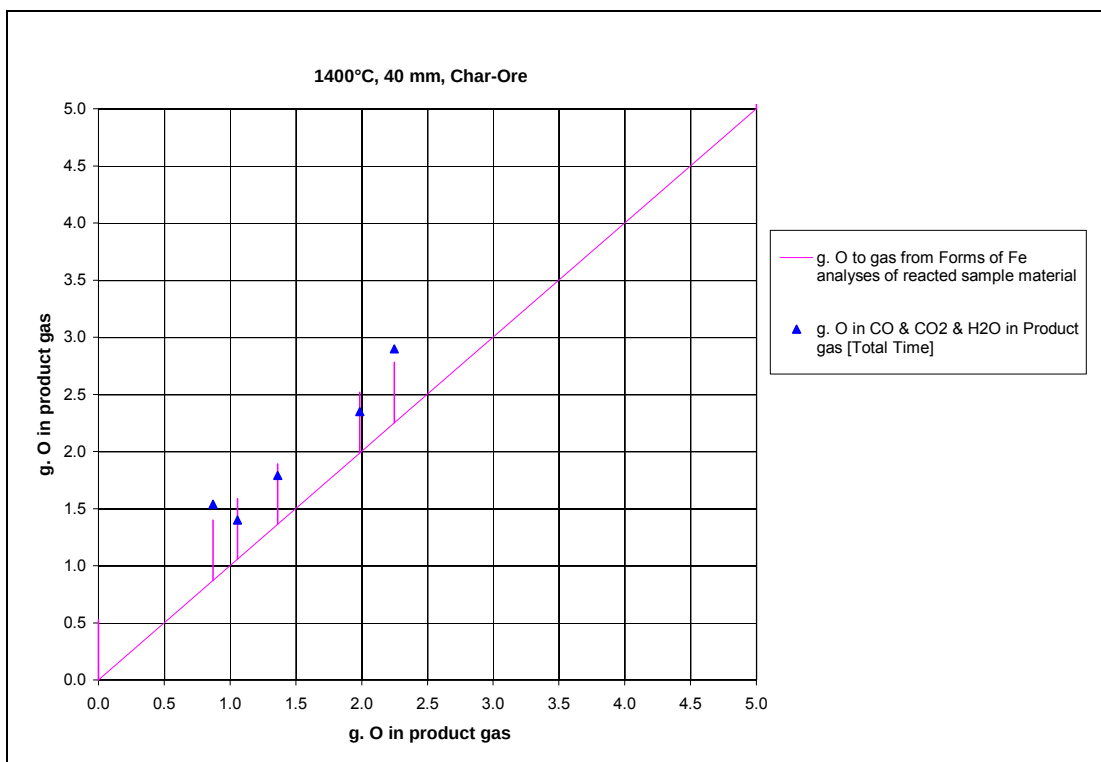
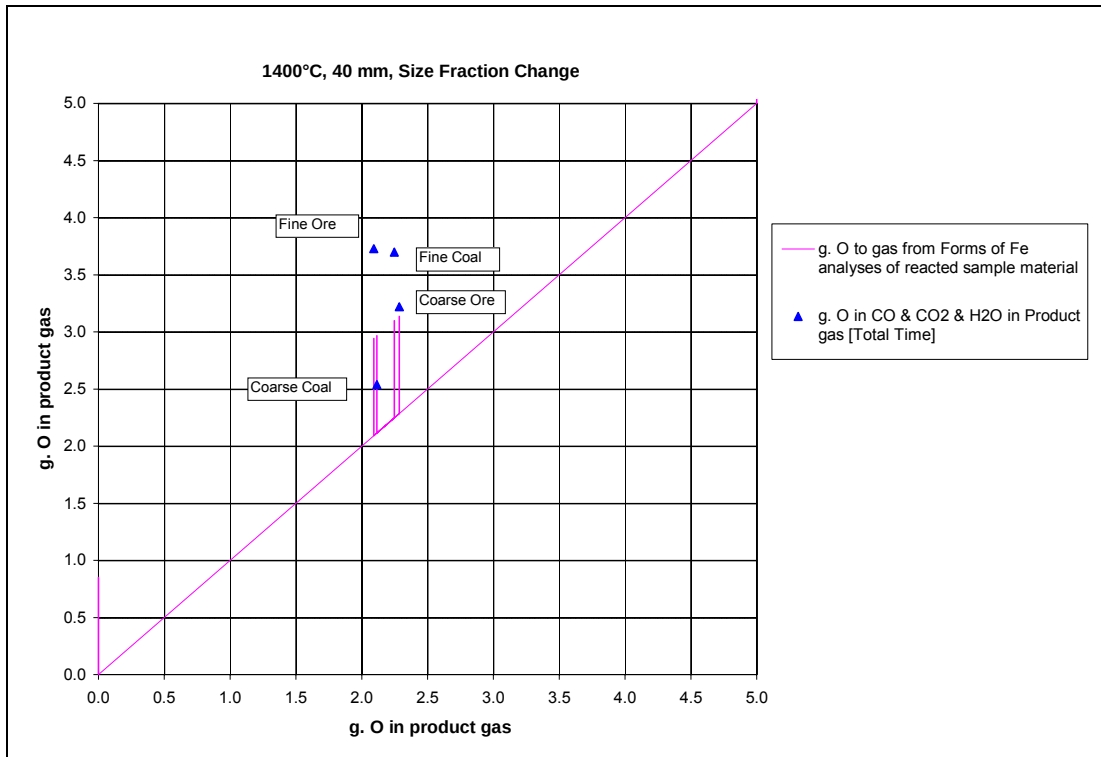




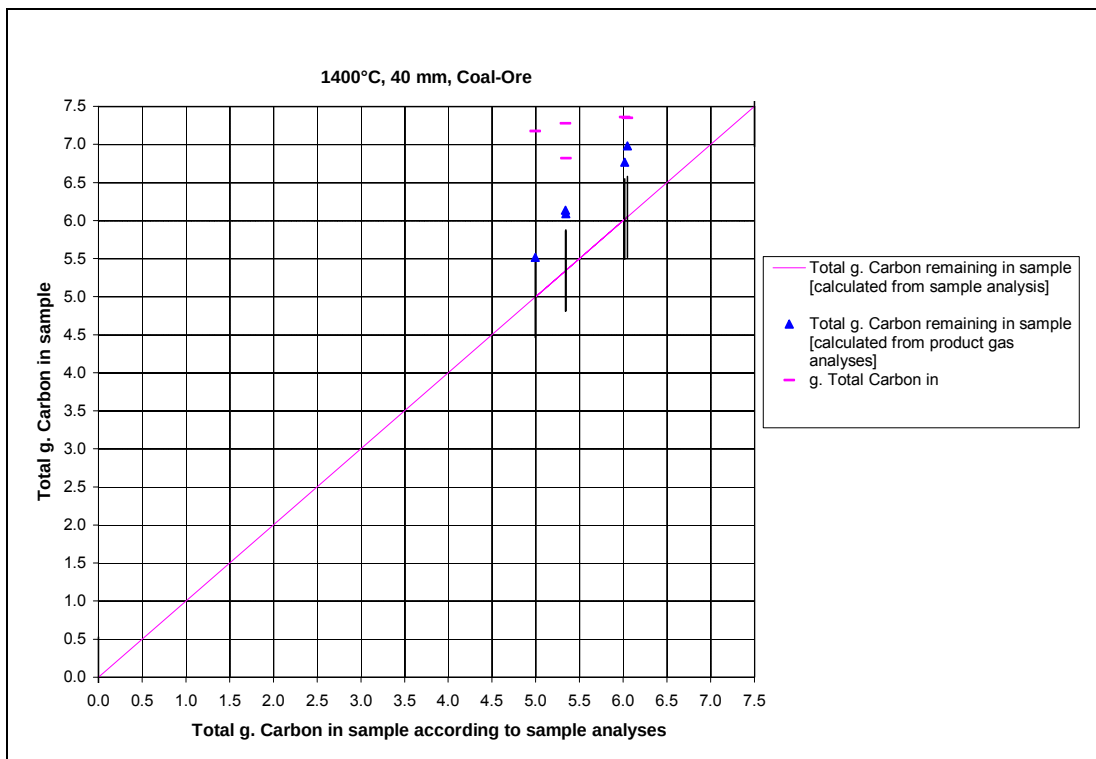
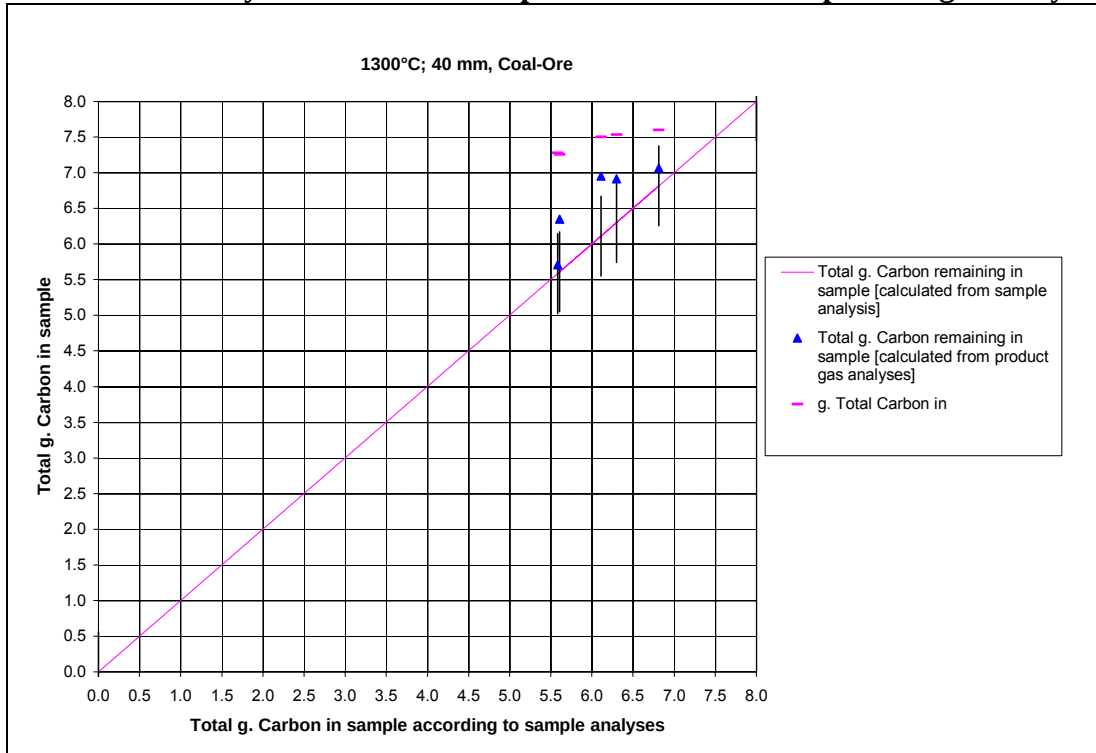
Appendix X (b): Graphs of total oxygen removed from sample as calculated from forms of Fe analyses for reacted sample vs. total oxygen in product gas analyses

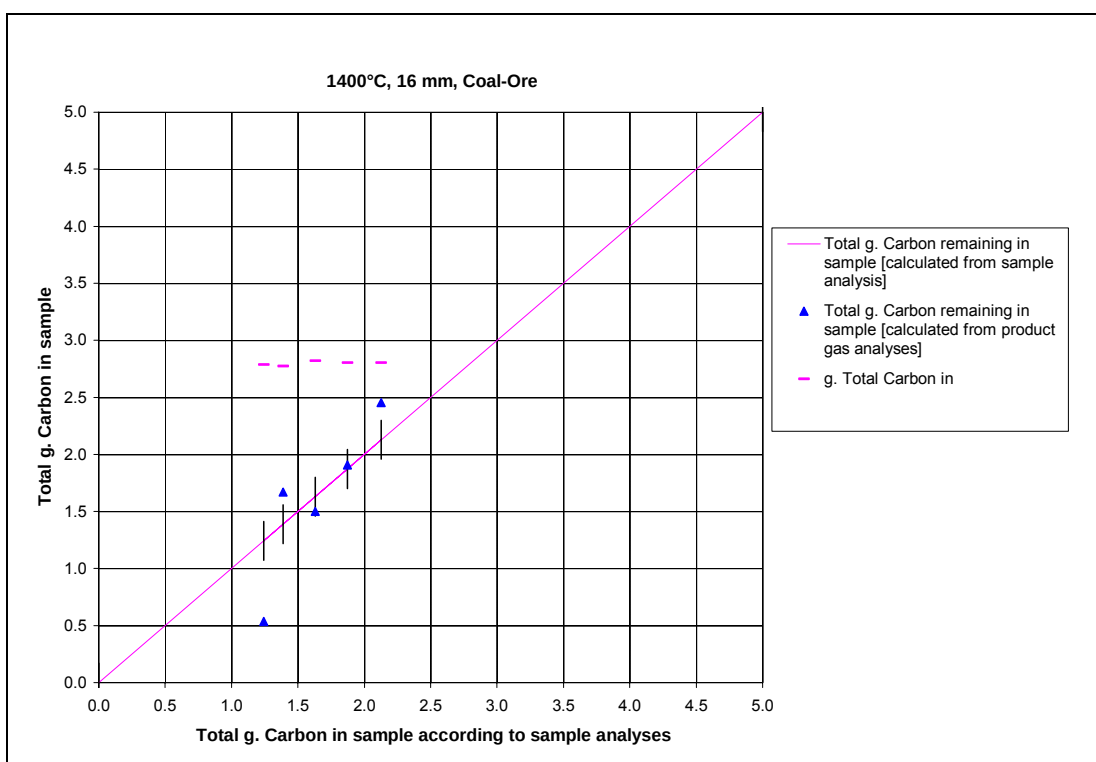
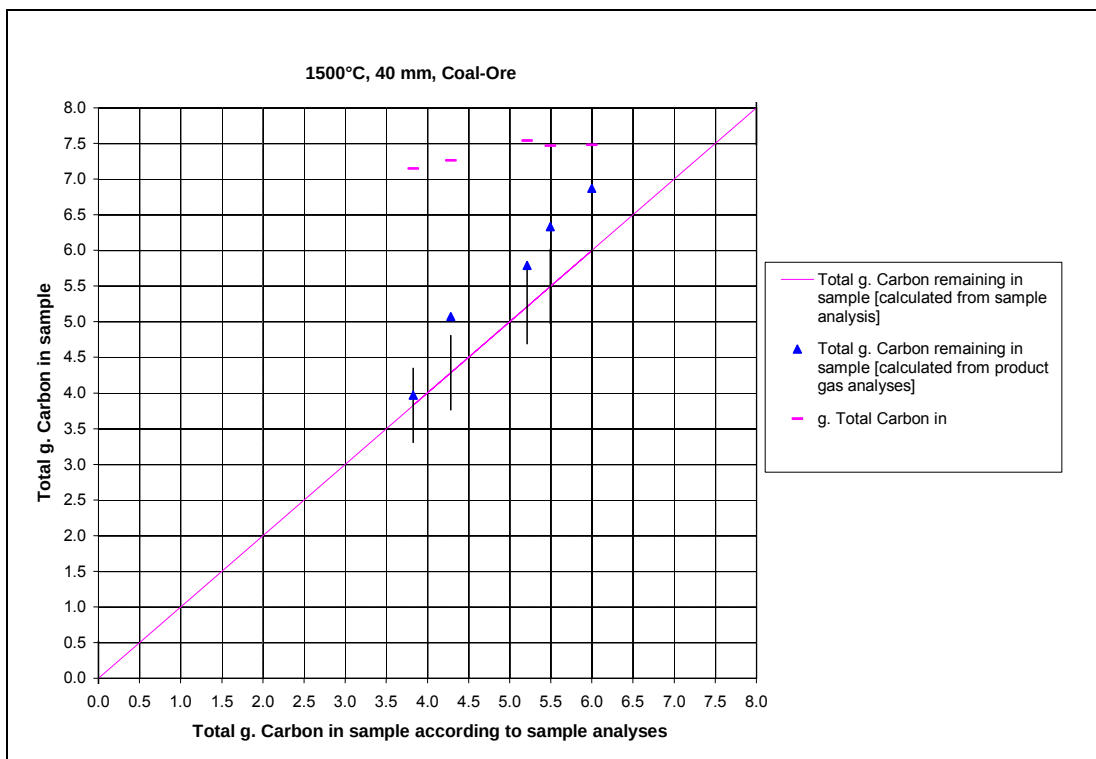


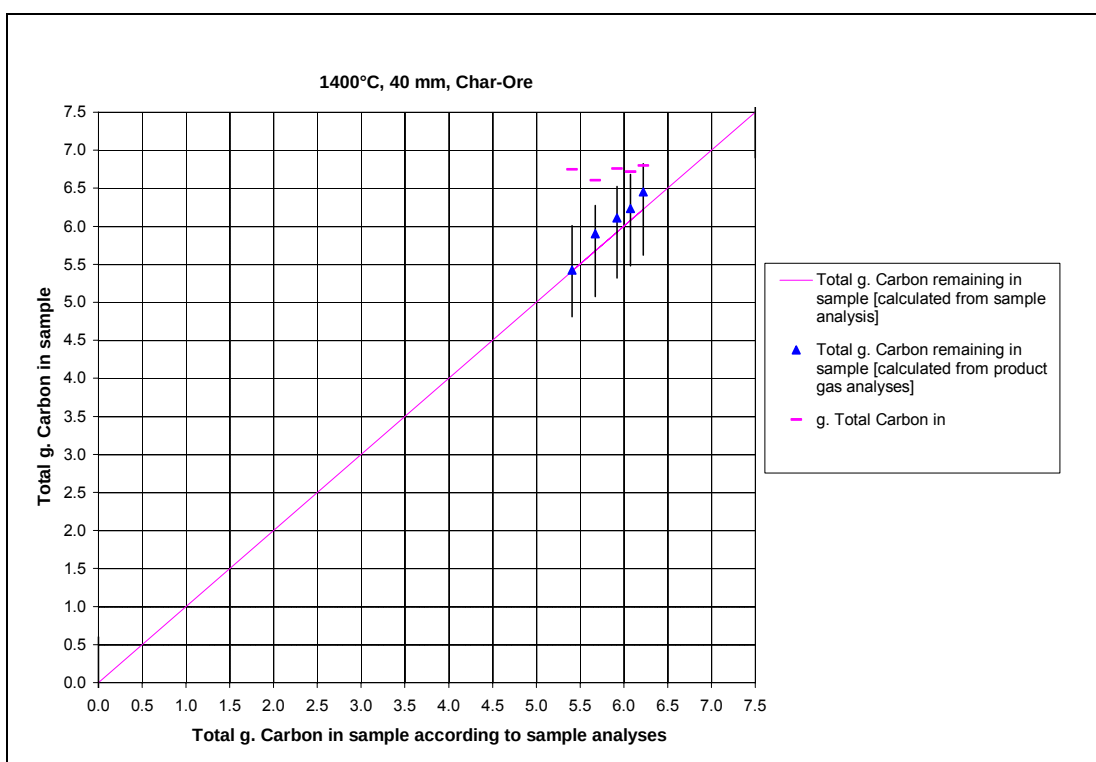
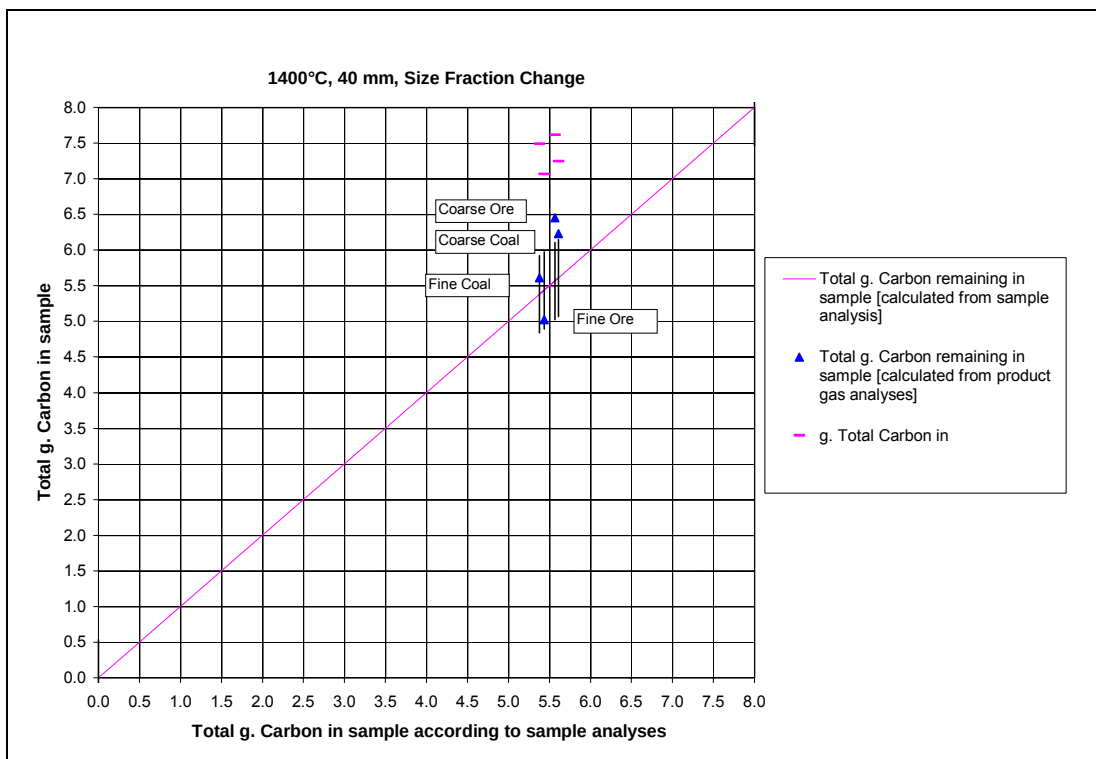




Appendix X (c): Graphs of total carbon remaining in reacted sample as calculated from carbon analyses for reacted sample vs. total carbon in product gas analyses







Appendix XI: Sample masses and analyses for coal-ore; coal-char and coal-alumina experiments

(*For Coal/Char Size and Ore Size: 1=-2000 +1400 µm; 2 = -850 +425 µm; 3 = -425 +300 µm; * Corrected for Fibreboard carry over)

Sample Number	Furnace Temperature (°C)	Coal/Char	Coal/Char Size*	Ore Size*	Reaction Time [min.]	Sample Layer Thickness [mm]	Mass% In		Sample Mix Out			Fibreboard			Thermocouples			Totals Out			Mass In			g. Mix in crucible before experiment according to analyses on reacted sample
							mass% Ore in	mass% Coal In	g. sample mix - top	g. sample mix - middle	g. sample mix - bottom				g. Fibreboard - top	g. Fibreboard -middle	g. Fibreboard -bottom				g. thermocouple - top	g. thermocouple - middle	g. thermocouple -bottom	
1300_3_40	1300	Coal	2	2	3	40	75.3	24.7	13.490	16.210	10.918	5.302	3.888	8.348	0	0	0	40.618	17.538	0	19.591	40.209	40.555	
1300_6_40	1300	Coal	2	2	6	40	75.3	24.7	12.843	15.862	10.792	5.480	3.880	8.668	0	0	0	39.497	18.028	0	19.849	40.167	40.197	
1300_9_40	1300	Coal	2	2	9	40	75.3	24.7	12.679	16.414	10.049	5.119	3.931	8.719	0	0	0	39.142	17.769	0	19.793	40.236	40.026	
1300_12_40	1300	Coal	2	2	12	40	75.3	24.7	15.389	13.901	8.118	10.975	6.266	13.045	0	0	0	37.408	30.286	0	32.529	38.875	38.721	
1300_15_40	1300	Coal	2	2	15	40	75.3	24.7	14.145	14.595	7.600	9.733	6.335	12.962	0	0	0	36.340	29.030	0	31.103	38.842	38.825	
1400_3_40	1400	Coal	2	2	3	40	75.3	24.7	15.831	15.024	7.378	11.234	6.314	13.137	0	0	0	38.233	30.685	0	31.865	39.092	39.199	
1400_6_40	1400	Coal	2	2	6	40	75.3	24.7	14.425	14.775	8.347	10.076	6.491	14.509	0	0	0	37.547	31.076	0	32.460	39.164	39.249	
1400_9_40	1400	Coal	2	2	9	40	75.3	24.7	13.755	15.042	5.246	10.804	6.814	12.634	0	0	0	34.043	30.252	0	31.637	39.383	36.382	
1400_12_40	1400	Coal	2	2	12	40	75.3	24.7	12.849	14.429	7.717	11.660	6.550	13.540	0	0	0	34.995	31.750	0	32.889	38.473	38.820	
1400_15_40	1400	Coal	2	2	15	40	75.3	24.7	11.930	14.693	7.968	9.972	6.138	13.187	0	0	0	34.591	29.297	0	30.991	38.503	38.267	
1500_3_40	1500	Coal	2	2	3	40	75.3	24.7	15.622	14.472	8.416	10.112	6.540	13.396	0	0	0	38.510	30.048	0	31.756	39.638	39.909	
1500_6_40	1500	Coal	2	2	6	40	75.3	24.7	12.993	14.785	9.013	10.692	6.396	12.863	0	0	0	36.791	29.951	0	31.451	39.523	39.852	
1500_9_40	1500	Coal	2	2	9	40	75.3	24.7	13.138	14.922	8.281	10.778	6.751	13.189	0	0	0	36.341	30.718	0	32.562	39.700	40.243	
1500_12_40	1500	Coal	2	2	12	40	75.3	24.7	11.468	14.448	7.901	9.697	5.810	12.630	0	0	0	33.817	28.137	0	30.528	38.342	38.734	
1500_15_40	1500	Coal	2	2	15	40	75.3	24.7	10.868	13.241	8.373	10.395	5.924	12.276	0	0	0	32.482	28.595	0	31.001	38.432	38.125	
1400_3_16	1400	Coal	2	2	3	16	75.3	24.7	13.723	0	0	36.794	0	0	0	0	0	13.723	36.794	0	37.172	14.999	14.946	
1400_6_16	1400	Coal	2	2	6	16	75.3	24.7	12.821	0	0	40.621	0	0	0	0	0	12.821	40.621	0	40.887	15.007	14.953	
1400_9_16	1400	Coal	2	2	9	16	75.3	24.7	12.159	0	0	37.403	0	0	0	0	0	12.159	37.403	0	37.730	14.997	15.063	
1400_12_16	1400	Coal	2	2	12	16	75.3	24.7	11.668	0	0	39.304	0	0	0	0	0	11.668	39.304	0	39.668	14.976	14.799	
1400_15_16	1400	Coal	2	2	15	16	75.3	24.7	11.188	0	0	39.941	0	0	0	0	0	11.188	39.941	0	40.357	14.980	14.855	
Coarse ore_I	1400	Coal	2	1	9	40	75.3	24.7	14.777	16.677	6.439	5.333	3.941	9.672	0	0	0	37.893	18.946	0	21.139	40.222	40.646	
Coarse coal_II	1400	Coal	1	2	9	40	75.3	24.7	16.635	14.001	5.650	6.559	3.798	8.538	0	0	0	36.286	18.895	0	20.495	39.340	38.605	
Fine coal_A	1400	Coal	3	2	9	40	75.3	24.7	11.779	15.669	9.383	5.652	3.875	9.075	0	0	0	36.831	18.602	0	20.440	40.241	39.901	
Fine ore_B	1400	Coal	2	3	9	40	75.3	24.7	9.598	16.092	10.185	5.231	3.917	9.316	0	0	0	35.875	18.464	0	20.514	39.089	37.698	
1400_3_40_char	1400	Char	2	2	3	40	79.7	20.3	14.929	17.208	10.078	5.445	4.132	9.093	0	0	0	42.215	18.67	0	20.606	42.074	42.522	
1400_6_40_char	1400	Char	2	2	6	40	79.8	20.2	15.509	16.130	9.916	5.408	3.908	9.115	0	0	0	41.555	18.431	0	20.082	42.003	42.041	
1400_9_40_char	1400	Char	2	2	9	40	79.8	20.2	15.333	16.019	9.813	10.124	5.815	14.334	0	0	0	41.165	30.273	0	32.236	41.992	42.288	
1400_12_40_char	1400	Char	2	2	12	40	79.8	20.2	15.974	15.371	8.380	6.053	3.896	9.277	0	0	0	39.725	19.226	0	21.024	41.427	41.368	
1400_15_40_char	1400	Char	2	2	15	40.0	79.7	20.3	15.118	14.743	9.377	5.751	3.881	8.984	0	0	0	39.238	18.616	0	21.278	41.792	42.038	

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Sample Number	g. Al2O3 In	g. Al2O3 out	g. SiO2 In	g. SiO2 out	Total g. Al2O3 pick-up	g. Al2O3 pick-up				g. SiO2 pick-up			%Al2O3 - Out			%SiO2 - Out				Corrected masses out			Correced Fibreboard masses		
						Total g. SiO2 pick-up	g. Al2O3 pick-up - top	g. Al2O3 pick-up - middle	g. Al2O3 pick-up - bottom	g. SiO2 pick-up - top	g. SiO2 pick-up - middle	g. SiO2 pick-up - bottom	%Al2O3 Analysed -Top	%Al2O3 Analysed -Middle	%Al2O3 Analysed -Bottom	%SiO2 Analysed -Top	%SiO2 Analysed -Middle	%SiO2 Analysed -Bottom		g. sample mix out - Top (Corrected)*	g. sample mix out - Middle (Corrected)*	g. sample mix out - Bottom (Corrected)*	g. Fibreboard out - Top (Corrected)*	g. Fibreboard out - Middle (Corrected)*	g. Fibreboard out - Bottom (Corrected)*
1300_3_40	0.97	2.05	1.84	2.40	1.07	0.57	0.17	0.56	0.35	-0.04	0.36	0.03	4.56	5.42	5.07	5.94	5.94	5.85	13.37	15.30	10.54	5.43	4.80	8.73	
1300_6_40	0.97	1.98	1.83	2.35	1.01	0.51	0.08	0.65	0.27	-0.08	0.40	-0.02	4.12	6.12	4.44	5.95	6.31	5.39	12.84	14.82	10.54	5.48	4.93	8.92	
1300_9_40	0.97	2.08	1.84	2.38	1.10	0.55	0.15	0.69	0.26	-0.05	0.43	-0.05	4.72	6.16	4.65	6.29	6.30	5.50	12.58	15.30	9.84	5.22	5.05	8.93	
1300_12_40	0.94	1.97	1.78	2.42	1.03	0.64	0.27	0.54	0.21	0.17	0.34	-0.08	4.59	6.14	5.04	6.42	6.67	6.22	14.94	13.02	7.99	11.42	7.15	13.18	
1300_15_40	0.94	1.87	1.77	2.36	0.93	0.59	0.22	0.55	0.16	0.11	0.37	-0.11	4.63	5.87	4.70	6.56	6.55	6.31	13.81	13.68	7.55	10.07	7.25	13.02	
1400_3_40	0.95	1.41	1.79	2.06	0.47	0.28	0.16	0.23	0.07	0.07	0.18	-0.19	3.78	3.64	3.62	5.65	5.12	5.42	15.59	14.61	7.50	11.47	6.73	13.02	
1400_6_40	0.95	1.52	1.79	2.09	0.57	0.30	0.15	0.32	0.10	0.03	0.20	-0.15	4.06	4.29	3.58	5.91	5.36	5.31	14.25	14.25	8.39	10.26	7.01	14.46	
1400_9_40	0.95	1.52	1.80	2.06	0.57	0.26	0.12	0.44	0.01	0.04	0.30	-0.30	4.08	5.00	3.95	6.30	5.94	5.63	13.59	14.30	5.54	10.97	7.55	12.34	
1400_12_40	0.93	1.41	1.76	1.98	0.48	0.22	0.08	0.31	0.09	-0.03	0.20	-0.16	3.94	4.25	3.74	6.09	5.40	5.44	12.80	13.92	7.78	11.71	7.06	13.47	
1400_15_40	0.93	1.77	1.76	2.23	0.83	0.47	0.19	0.51	0.13	0.04	0.35	-0.13	5.19	5.57	4.12	7.14	6.30	5.67	11.70	13.84	7.96	10.21	6.99	13.19	
1500_3_40	0.96	1.53	1.81	2.09	0.57	0.28	0.10	0.32	0.14	0.00	0.19	-0.12	3.49	4.39	4.11	5.30	5.43	5.70	15.52	13.96	8.39	10.21	7.05	13.42	
1500_6_40	0.96	1.45	1.80	2.05	0.49	0.24	0.02	0.38	0.09	-0.08	0.25	-0.15	3.53	4.73	3.22	5.81	5.70	4.97	13.05	14.15	9.07	10.64	7.03	12.80	
1500_9_40	0.96	1.62	1.81	2.19	0.65	0.38	0.10	0.46	0.09	0.03	0.29	-0.15	4.12	5.23	3.55	6.54	5.97	5.36	13.01	14.17	8.34	10.90	7.51	13.13	
1500_12_40	0.93	2.04	1.75	2.47	1.11	0.71	0.30	0.63	0.19	0.13	0.44	-0.07	6.32	6.46	4.86	8.20	7.05	6.41	11.04	13.38	7.78	10.13	6.88	12.75	
1500_15_40	0.93	2.07	1.75	2.45	1.14	0.70	0.30	0.61	0.23	0.11	0.40	-0.03	6.67	6.93	5.11	8.45	7.42	6.60	10.46	12.23	8.17	10.80	6.94	12.48	
1400_3_16	0.36	0.39	0.68	0.72	0.03	0.03	0.23	0.00	0.00	0.40	0.00	0.00	2.87	0.00	0.00	5.22	0.00	0.00	13.09	0.00	0.00	37.42	0.00	0.00	
1400_6_16	0.36	0.42	0.69	0.72	0.06	0.03	0.26	0.00	0.00	0.40	0.00	0.00	3.30	0.00	0.00	5.58	0.00	0.00	12.16	0.00	0.00	41.28	0.00	0.00	
1400_9_16	0.36	0.41	0.68	0.71	0.05	0.02	0.25	0.00	0.00	0.39	0.00	0.00	3.41	0.00	0.00	5.81	0.00	0.00	11.52	0.00	0.00	38.04	0.00	0.00	
1400_12_16	0.36	0.49	0.68	0.73	0.13	0.05	0.32	0.00	0.00	0.42	0.00	0.00	4.21	0.00	0.00	6.26	0.00	0.00	10.93	0.00	0.00	40.04	0.00	0.00	
1400_15_16	0.36	0.52	0.68	0.79	0.16	0.10	0.36	0.00	0.00	0.47	0.00	0.00	4.68	0.00	0.00	7.04	0.00	0.00	10.36	0.00	0.00	40.77	0.00	0.00	
Coarse ore_I	0.97	2.05	1.84	2.06	1.07	0.22	0.17	0.64	0.27	-0.07	0.28	-0.21	4.15	5.76	7.33	5.25	5.30	6.22	14.68	15.76	6.38	5.43	4.86	9.73	
Coarse coal_II	0.96	1.80	1.78	2.06	0.84	0.28	0.13	0.51	0.19	0.02	0.26	-0.22	3.46	5.93	6.95	5.04	6.07	6.50	16.48	13.22	5.68	6.71	4.57	8.51	
Fine coal_A	0.98	1.92	1.82	2.15	0.94	0.33	0.11	0.58	0.26	-0.11	0.32	-0.09	4.73	5.77	4.93	6.15	5.89	5.40	11.79	14.77	9.22	5.65	4.78	9.24	
Fine ore_B	0.95	2.00	1.78	2.04	1.06	0.25	0.06	0.73	0.27	-0.24	0.37	-0.09	5.12	6.45	4.64	6.03	5.97	4.87	9.78	14.99	10.00	5.04	5.01	9.50	
1400_3_40_char	1.03	1.92	2.16	2.18	0.89	0.02	0.09	0.59	0.21	-0.25	0.24	-0.22	3.77	5.39	4.25	4.98	5.52	4.84	15.09	16.38	10.09	5.28	4.96	9.08	
1400_6_40_char	1.03	1.84	2.15	2.35	0.81	0.19	0.09	0.48	0.24	-0.14	0.24	-0.17	3.61	5.08	4.60	5.49	5.91	5.47	15.56	15.41	9.84	5.36	4.63	9.19	
1400_9_40_char	1.03	1.87	2.15	2.20	0.84	0.05	0.14	0.49	0.22	-0.14	0.14	-0.20	3.99	5.16	4.43	5.52	5.28	5.15	15.34	15.40	9.80	10.12	6.44	14.35	
1400_12_40_char	1.01	1.93	2.12	2.40	0.92	0.28	0.17	0.52	0.23	-0.04	0.25	-0.19	3.97	5.57	5.28	5.89	6.20	6.09	15.84	14.60	8.34	6.18	4.67	9.32	
1400_15_40_char	1.02	1.83	2.14	2.33	0.81	0.19	0.15	0.44	0.21	-0.07	0.18	-0.18	4.14	5.27	4.58	6.04	6.02	5.64	15.04	14.12	9.34	5.83	4.50	9.02	

*Corrected for Fibreboard carry over

Sample Number	%Reduction			%Carbon out									Mass Carbon In							%Carbon consumption			
	%Reduction - Top	%Reduction - Middle		%Reduction - Bottom	%C analysed - Top								%C analysed - Middle	%C analysed - Bottom						%C out analysed - top (Corrected)*	%C out analysed - middle (Corrected)*	%C out analysed - bottom (Corrected)*	Composite %Carbon
1300_3_40	6.7	2.2	2.3	18.7	15.3	16.6	18.9	16.2	17.2	17.6	15.4	18.7	7.60	3.50	2.51	1.60	2.87	2.06	1.31	27.8	1.1	-13.5	10.3
1300_6_40	16.2	2.4	1.9	17.7	15.1	15.1	17.7	16.2	15.5	16.7	15.4	18.7	7.53	3.47	2.49	1.58	2.84	2.04	1.30	34.4	3.7	-3.0	16.4
1300_9_40	19.4	2.1	1.5	19.2	12.6	16.0	19.4	13.5	16.3	16.8	15.4	18.7	7.50	3.45	2.48	1.58	2.83	2.03	1.29	29.5	16.5	-2.1	18.6
1300_12_40	24.8	4.8	1.1	14.1	15.8	15.3	14.5	16.9	15.6	15.5	15.4	18.7	7.26	3.34	2.39	1.52	2.74	1.96	1.25	35.0	8.3	18.5	22.7
1300_15_40	35.1	5.1	3.7	13.3	17.4	15.3	13.6	18.6	15.4	15.6	15.4	18.7	7.28	3.35	2.40	1.53	2.74	1.97	1.25	43.8	-5.7	23.9	23.3
1400_3_40	15.0	1.7	2.1	18.7	12.3	16.8	19.0	12.6	16.5	16.4	15.4	18.7	7.35	3.38	2.42	1.54	2.77	1.99	1.26	12.4	23.8	19.7	17.7
1400_6_40	23.9	4.1	1.9	18.2	13.3	17.1	18.4	13.8	17.0	16.6	15.4	18.7	7.36	3.38	2.43	1.54	2.77	1.99	1.27	22.4	19.0	7.6	18.2
1400_9_40	31.2	3.0	2.8	15.9	14.4	18.9	16.1	15.1	17.9	16.2	15.4	18.7	6.82	3.14	2.25	1.43	2.57	1.84	1.17	30.3	3.7	30.8	21.6
1400_12_40	40.6	4.1	2.4	16.7	14.1	15.0	16.8	14.6	14.9	15.7	15.4	18.7	7.28	3.35	2.40	1.53	2.74	1.97	1.25	35.9	15.3	24.2	26.6
1400_15_40	52.6	6.5	4.1	15.5	13.1	15.3	15.8	13.9	15.3	15.1	15.4	18.7	7.17	3.30	2.37	1.51	2.70	1.94	1.23	44.0	18.7	19.1	30.4
1500_3_40	16.6	1.9	2.5	16.0	14.0	17.5	16.1	14.5	17.6	15.9	15.4	18.7	7.48	3.44	2.47	1.57	2.82	2.02	1.29	27.4	17.9	6.2	19.8
1500_6_40	38.6	3.0	2.2	16.0	13.9	15.1	15.9	14.5	15.0	15.3	15.4	18.7	7.47	3.44	2.47	1.57	2.82	2.02	1.29	39.5	16.6	13.2	26.4
1500_9_40	47.1	5.2	3.0	16.3	12.3	14.9	16.5	13.0	14.8	15.0	15.4	18.7	7.54	3.47	2.49	1.58	2.84	2.04	1.30	38.3	26.2	22.1	30.9
1500_12_40	69.9	9.6	4.6	10.4	13.7	14.1	10.8	14.8	14.3	12.9	15.4	18.7	7.26	3.34	2.40	1.52	2.74	1.96	1.25	64.3	17.4	26.9	41.0
1500_15_40	76.1	17.9	7.3	6.1	14.7	14.6	6.3	15.9	15.0	11.3	15.4	18.7	7.15	3.29	2.36	1.50	2.69	1.93	1.23	80.0	17.5	18.5	46.4
1400_3_16	11.8	0.0	0.0	15.5	0.0	0.0	16.2	0.0	0.0	7.5	15.4	18.8	2.80	2.80	0.00	0.00	1.06	0.76	0.48	24.1	0.0	0.0	24.1
1400_6_16	26.5	0.0	0.0	14.6	0.0	0.0	15.4	0.0	0.0	7.1	15.4	18.7	2.80	2.80	0.00	0.00	1.06	0.76	0.48	33.2	0.0	0.0	33.2
1400_9_16	39.4	0.0	0.0	13.4	0.0	0.0	14.1	0.0	0.0	6.5	15.4	18.7	2.82	2.82	0.00	0.00	1.06	0.76	0.49	42.3	0.0	0.0	42.3
1400_12_16	49.6	0.0	0.0	11.9	0.0	0.0	12.7	0.0	0.0	5.8	15.4	18.7	2.77	2.77	0.00	0.00	1.05	0.75	0.48	49.9	0.0	0.0	49.9
1400_15_16	60.7	0.0	0.0	11.1	0.0	0.0	12.0	0.0	0.0	5.5	15.4	18.8	2.79	2.79	0.00	0.00	1.05	0.75	0.48	55.4	0.0	0.0	55.4
Coarse ore_I	32.9	4.0	2.4	15.1	14.9	13.2	15.2	15.8	13.3	15.0	15.4	18.7	7.62	3.50	2.51	1.60	2.87	2.06	1.31	36.3	1.1	46.9	26.9
Coarse coal_II	25.1	6.8	4.5	11.8	18.7	18.2	11.9	19.8	18.1	15.8	15.3	18.8	7.25	3.33	2.39	1.52	2.72	1.95	1.24	41.1	-9.5	32.4	22.6
Fine coal_A	39.8	5.0	2.7	13.8	14.8	15.3	13.8	15.7	15.6	14.8	15.3	18.8	7.49	3.44	2.47	1.57	2.81	2.02	1.28	52.8	6.1	8.7	28.1
Fine ore_B	44.0	6.2	3.0	20.6	13.0	13.4	20.2	14.0	13.6	16.8	15.4	18.7	7.06	3.25	2.33	1.48	2.66	1.91	1.22	39.2	10.3	8.0	23.1
1400_3_40_char	8.5	1.0	0.5	15.8	14.2	14.1	15.6	14.9	14.1	15.1	15.7	16.0	6.80	3.13	2.24	1.43	3.07	2.20	1.40	24.6	-8.9	0.5	8.4
1400_6_40_char	13.2	0.8	0.9	13.2	15.4	15.6	13.2	16.1	15.7	14.7	15.7	16.0	6.72	3.09	2.22	1.41	3.03	2.18	1.39	33.7	-12.1	-9.7	9.5
1400_9_40_char	21.9	1.0	0.6	16.6	12.8	13.5	16.6	13.3	13.5	14.9	15.7	16.0	6.75	3.11	2.23	1.42	3.05	2.19	1.39	18.1	8.0	6.6	12.3
1400_12_40_char	33.3	2.9	1.1	12.5	15.7	15.1	12.6	16.5	15.2	14.4	15.7	16.0	6.60	3.04	2.18	1.39	2.98	2.14	1.36	34.3	-10.7	8.8	14.1
1400_15_40_char	38.0	5.1	1.5	11.1	15.9	14.8	11.2	16.6	14.9	13.7	15.8	16.0	6.74	3.10	2.23	1.42	3.05	2.19	1.39	45.9	-5.3	2.0	19.8

*Corrected for Fibreboard carry over

Sample Number	Mass Carbon remaining				Mass loss				Mass oxygen					Energy Input	
	Total g. Carbon remaining in sample [calculated from product gas analyses]	Total g. Carbon remaining in sample [calculated from sample analysis]	g. C Difference: (Total g. Carbon remaining in sample [calculated from product gas analyses]) - (Total g. Carbon remaining in sample [calculated from sample analysis])	g. Difference as % of analysed C remaining in reacted sample	Mass loss according to gas analyses (Total time)	Mass Loss according to mixture in sample split & FB carry over; [Mixture mass is backcalculated from Fe mass balance]	g. Mass loss difference: (Mass loss according to gas analyses (Total time)) - (Mass Loss according to mixture in sample split & FB carry over; [Mixture mass is backcalculated from Fe mass balance])	g. Difference as % of weighed mass loss	g. O in	g. O remaining in sample	g. O to gas from Forms of Fe analyses	g. O Difference: (g. O in CO & CO ₂ & H ₂ O in Product gas [Total Time]) - (g. O to gas from Forms of Fe analyses of reacted sample material)	g. Difference as % of g. O to gas from forms of Fe analysis	Average kW/m ² into sample - Radiation Network	Total radiation heat input to sample (MJ/m ²)
1300_3_40	7.07	6.82	0.25	4	1.98	1.6	0.4	26	9.42	8.21	1.21	0.09	7	-120	21
1300_6_40	6.92	6.30	0.62	10	2.43	2.2	0.2	10	9.34	7.87	1.47	0.15	10	-127	46
1300_9_40	6.95	6.11	0.84	14	2.68	2.5	0.1	6	9.30	7.77	1.53	0.35	23	-125	67
1300_12_40	6.35	5.61	0.74	13	3.73	3.0	0.7	25	8.99	7.08	1.92	0.63	33	-109	79
1300_15_40	5.71	5.58	0.12	2	5.21	4.0	1.2	30	9.02	6.74	2.28	1.06	47	-108	97
1400_3_40	6.98	6.05	0.93	15	1.58	1.7	-0.1	-8	9.11	7.65	1.45	-0.43	-30	-181	33
1400_6_40	6.77	6.02	0.75	12	2.61	2.6	0.0	1	9.12	7.31	1.81	-0.10	-5	-180	65
1400_9_40	6.09	5.34	0.75	14	3.25	3.2	0.1	3	8.45	6.48	1.97	0.20	10	-178	96
1400_12_40	6.14	5.34	0.80	15	4.05	4.5	-0.5	-11	9.02	6.68	2.34	0.23	10	-175	126
1400_15_40	5.52	4.99	0.52	10	5.46	5.0	0.5	10	8.89	6.17	2.72	0.74	27	-169	152
1500_3_40	6.87	6.00	0.87	15	2.71	2.2	0.5	20	9.27	7.69	1.58	0.30	19	-259	47
1500_6_40	6.33	5.49	0.84	15	4.15	3.8	0.4	9	9.26	6.99	2.26	0.43	19	-250	89
1500_9_40	5.79	5.21	0.58	11	5.94	4.9	1.0	20	9.35	6.68	2.67	1.04	39	-254	137
1500_12_40	5.07	4.29	0.78	18	7.39	6.7	0.6	10	9.00	5.53	3.47	1.30	37	-211	151
1500_15_40	3.97	3.83	0.14	4	9.39	7.5	1.9	26	8.86	4.90	3.95	1.80	45	-208	186
1400_3_16	2.45	2.13	0.33	15	1.73	1.3	0.4	35	3.47	2.77	0.70	0.55	78	-165	29
1400_6_16	1.91	1.87	0.03	2	2.95	2.2	0.7	33	3.47	2.31	1.17	0.72	62	-158	56
1400_9_16	1.50	1.63	-0.13	-8	3.93	3.0	1.0	32	3.50	1.92	1.58	0.86	54	-157	85
1400_12_16	1.67	1.39	0.28	20	3.82	3.3	0.5	16	3.44	1.57	1.87	0.65	35	-157	113
1400_15_16	0.54	1.24	-0.70	-57	6.22	3.9	2.3	58	3.45	1.23	2.22	1.58	71	-153	138
Coarse ore_I	6.45	5.57	0.88	16	4.81	4.0	0.8	19	9.57	7.29	2.29	0.93	41	-152	82
Coarse coal_II	6.23	5.61	0.62	11	3.98	3.4	0.5	16	8.93	6.81	2.11	0.43	20	-146	79
Fine coal_A	5.61	5.38	0.23	4	5.98	4.3	1.6	38	9.23	6.98	2.25	1.45	65	-153	82
Fine ore_B	5.02	5.43	-0.41	-8	6.26	3.1	3.1	100	8.88	6.79	2.09	1.64	78	-153	82
1400_3_40_char	6.45	6.22	0.23	4	2.01	1.2	0.8	65	10.00	9.12	0.87	0.67	77	-175	33
1400_6_40_char	6.23	6.08	0.16	3	1.97	1.5	0.5	33	9.88	8.83	1.06	0.34	33	-168	60
1400_9_40_char	6.11	5.92	0.19	3	2.56	2.0	0.5	27	9.94	8.58	1.36	0.43	31	-163	88
1400_12_40_char	5.90	5.68	0.23	4	3.19	2.8	0.3	12	9.73	7.74	1.99	0.36	18	-155	112
1400_15_40_char	5.42	5.41	0.01	0	4.32	3.8	0.5	14	9.88	7.63	2.25	0.65	29	-151	136

Sample masses and analyses for coal-alumina experiments

Sample Number	Furnace Temperature (°C)	Coal/Char	Coal/Char Size*	Ore Size*	Reaction Time [min.]	Sample Layer Thickness [mm]	Mass% In		Sample Mix Out			Fibreboard			Thermocouples			Totals Out			Mass In	
							mass% Alumina in	mass% Coal in	g. sample mix - top	g. sample mix - middle	g. sample mix - bottom	g. Fibreboard - top	g. Fibreboard -middle	g. Fibreboard -bottom	g. thermocouple - top	g. thermocouple - middle	g. thermocouple -bottom	Total g. sample mix out	Total g. Fibreboard out	Total g. Thermocouples out	g. Fibreboard in	g. Mix in
1300_Devol	1300	Coal	2	2	2337	40.0	75.3	24.7	9.716	15.024	9.417	5.102	3.954	8.716	0	0	0	34.157	17.772	0	19.738	35.172
1400_Devol	1400	Coal	2	2	1800	40.0	75.3	24.7	10.528	14.895	8.511	10.559	6.083	12.530	0	0	0	33.934	29.172	0	31.127	34.859
1500_Devol	1500	Coal	2	2	2060	40.0	75.3	24.7	11.509	14.390	8.666	11.215	6.172	12.742	0	0	0	34.565	30.129	0	32.707	35.166

	Product Gas					Product gas analysed						H2O - out				H In vs. H in Product Gas			O In vs. O in Product Gas		
Sample Number	Mass loss according to Product gas analysis [Total Time]	Mass loss according to Product gas analysis [Experimental Time only]	g. O in CO & CO2 in Product gas [Total Time]	g. O in CO & CO2 in Product gas [Experimental time only]	g. O in CO & CO2 & H2O in Product gas [Total Time]	Total g. CO2 in Product Gas	Total g. CH4 in Product Gas	Total g. CO in Product Gas	Total g. H2 in Product Gas	Total g. H2O in Product Gas	g. H2O in - Proximate analysis	g. H2O in - (Proximate analysis) + (All %O from Ultimate Analysis as H2O)	%H2O - Proximate Analysis	%H2O in - (Proximate analysis) + (All %O from Ultimate Analysis as H2O)	%H2O in - Product Gas Analysis	Total g. H in	Total g. H out - (From Product Gas Analysis)	g. H in/g. H out	g. O in	Total g. O out - (From Product Gas Analysis)	g. O in/g. O out
1300_Devol	1.28	1.28	0.14	0.14	0.79	0.19	0.02	0.00	0.33	0.73	0.29	0.90	3.3	10.1	8.2	0.35	0.8	0.5	0.8	0.79	1.0
1400_Devol	2.91	2.6	1.08	0.95	1.68	0.29	0.08	1.52	0.34	0.68	0.30	0.91	3.3	10.1	7.5	0.35	0.8	0.5	0.8	1.68	0.5
1500_Devol	5.79	5.79	2.29	2.29	3.35	0.55	0.00	3.32	0.73	1.19	0.30	0.92	3.3	10.1	13.1	0.36	1.6	0.2	0.8	3.35	0.2

Sample Number	Total C Balance											%Fixed carbon back-calculated			%Volatile Matter Content - back-calculated						Mass loss		
	g. Total Carbon In	Total g. Carbon to gas [calculated from product gas analyses]	Total g. Carbon remaining in sample [calculated from product gas analyses]	Total g. Carbon remaining in sample [calculated from sample analysis]	g. C deposited if all H2 off as CH4	g. C Difference: (Total g. Carbon remaining in sample [calculated from product gas analyses]) - (Total g. Carbon remaining in sample [calculated from sample analysis])	g. Difference as % of analysed C remaining in reacted sample	g. Total C out according to Product Gas analysis & %C analysed in reacted sample	g. C in/g. C out	%Total Carbon in Coal	% Total C in Coal calculated from Product Gas Analysis & %C analysed in reacted sample	%Fixed Carbon in coal - Proximate analysis	%Fixed Carbon in coal from Carbon remaining in reacted sample [calculated from product gas analyses]	%Fixed Carbon in coal from Carbon remaining in reacted sample [calculated from sample analysis]	%Volatile Matter Content - Proximate Analysis	g. Volatile Matter Content - Proximate Analysis	%Volatile Matter Content - Calculated from Product Gas Analysis	g. Volatile Matter Content - Calculated from Product Gas Analysis	%Volatile Matter Content - Calculated from Sample mass loss weighed	g. Volatile Matter Content - Calculated from Sample mass loss weighed	Mass loss according to gas analyses (Total time)	Mass Loss according to mixture in sample split & FB carry over [Mixture mass is backcalculated from Fe mass balance]	g. Mass loss difference: (Mass loss according to gas analyses (Total time)) - (Mass Loss according to mixture in sample split & FB carry over; [Mixture mass is backcalculated from Fe mass balance])
1300_Devo	6.75	0.07	6.69	5.34	0.98	1.4	25	5.40	1.2	75.9	61	62.2	75	60	22.5	2.00	14	1.28	24	2.10	1.28	2.10	-39
1400_Devo	6.85	0.79	6.06	5.01	1.01	1.0	21	5.80	1.2	75.9	64	62.2	67	56	22.5	2.03	32	2.91	31	2.75	2.91	2.75	6
1500_Devo	6.92	1.57	5.34	5.07	2.17	0.3	5	6.64	1.0	75.9	73	62.2	59	56	22.5	2.05	64	5.79	28	2.54	5.79	2.54	3.3

Sample Number	g. Al2O3 In			g. Al2O3 out			g. SiO2 In			g. SiO2 out			Total g. Al2O3 pick-up			Total g. SiO2 pick-up			g. Al2O3 pick-up - top			g. Al2O3 pick-up - middle			g. Al2O3 pick-up - bottom			g. SiO2 pick-up - top			g. SiO2 pick-up - middle			g. SiO2 pick-up - bottom			%Al2O3 Analysed - Top			%Al2O3 Analysed - Middle			%Al2O3 Analysed - Bottom			%SiO2 Analysed - Top			%SiO2 Analysed - Middle			%SiO2 Analysed - Bottom			Corrected masses out			Corrected Fibreboard masses			g. Al2O3 in/ g. Al2O3e out																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	

*Corrected for Fibreboard carry over

Sample Number	g. Coal in	g. Coal In back-calculated from Alumina mass balance	%Carbon out							Mass Carbon In						%Carbon consumption			
			%C analysed - Top	%C analysed - Middle	%C analysed - Bottom	%C out analysed - top (Corrected)*	%C out analysed - middle (Corrected)*	%C out analysed - bottom (Corrected)*	Composite %Carbon	g. Total C in - top	g. Total C in - middle	g. Total C in - bottom	g. Total FC in - top	g. Total FC in - middle	g. Total FC in - bottom	%C consumption - top	%C consumption - middle	%C consumption - bottom	Composite %C consumption
1300_Devol	8.7	8.9	18.9	14.9	13.4	18.9	15.1	13.4	16.5	3.11	2.23	1.42	2.55	1.83	1.16	40.9	-0.4	11.0	21.0
1400_Devol	8.6	9.0	17.0	13.0	15.1	17.0	13.1	15.1	15.3	3.15	2.26	1.44	2.58	1.85	1.18	43.2	14.3	10.6	26.8
1500_Devol	8.7	9.1	16.2	12.7	15.9	16.41	12.7	15.9	15.1	3.18	2.28	1.45	2.61	1.87	1.19	41.4	19.9	5.1	26.7

*Corrected for Fibreboard carry over

Appendix XII: Calculation of equilibrium %CO in CO-CO₂ gas

The heat capacity values and standard enthalpy and entropy values used are those from Kubashewski *et al.* (1993). The values used are summarised in the table below.

Enthalpy equation:

$$C_p(T) = A + BT + C/T^2 + DT^2 \text{ [J/mol K]}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT + \Delta H_{T_1} = A \cdot (T_2 - T_1) + B/2 \cdot (T_2^2 - T_1^2) - C/(T_2 - T_1) + D/3 \cdot (T_2^3 - T_1^3)$$

The $C_p(T)$ equations were obtained from Kubashewski *et al.* (1993).

Entropy equation:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT + \Delta S_{T_1} = A \cdot \ln\left(\frac{T_2}{T_1}\right) + B \cdot (T_2 - T_1) - \frac{C}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right) + D/2 \cdot (T_2^2 - T_1^2)$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln K$$

T = temperature (K)

$C_p(T)$ = heat capacity of component at constant pressure (J/mol K)

ΔH = change in enthalpy of component material when heated from T_1 to T_2 (J)

ΔS = change in entropy of component material when heated from T_1 to T_2 (J)

ΔG = Gibbs free energy change for reaction between T_1 to T_2 (J)

K = equilibrium constant

The enthalpy and entropy equation parameters used are shown below:

Component	$\Delta H_{T_1} [J/mol]$	$\Delta S_{T_1} [J/deg\ mol]$	$H_i [kJ/mol]$	$T_1 [K]$	$T_2 [K]$	[J/deg mol]			
						A	$B \cdot 10^3$	$C \cdot 10^{-5}$	$D \cdot 10^6$
Fe _{0.945} O	-263000	60.10	---	>=298		48.79	8.37	-2.8	---
Fe	0	27.3	---	298	800	28.18	-7.32	-2.9	---
	15571	56.95	---	800	1000	-263.45	255.81	619.23	---
	24408	66.74	---	1000	1042	-641.91	696.34	---	---
	27308	69.58	---	1042	1060	1946.25	-1787.5	---	---
	28525	70.73	---	1060	1184	-561.95	334.13	2912.11	---
	35002	76.54	0.9	1184	1665	23.99	8.36	---	---
	53069	89.22	0.8	1665	1809	24.64	9.9	---	---
	72893	100.32	13.8	1809	2000	46.02	---	---	---
CO	-110500	197.50	---	>=298		28.41	4.1	-0.46	---
CO ₂	-393500	213.7	---	>=298		44.14	9.04	-8.54	---
C(graphite)	0	5.7	---	298	1100	0.11	38.94	-1.48	---
	13998	26.56	---	>=1100		24.43	0.44	-31.63	---
H ₂	0	130.6	---	298		27.37	3.33	---	---
H ₂ O (liquid)	-285800	69.9	---	>=298		75.44	---	---	---
H ₂ O (gas)	-241800	188.7	---	>=298		30	10.71	0.33	---
CH ₄	-74800	186.3	---	>=298		12.45	76.69	1.45	-17.99
O ₂	0	205.1	---	>=298		29.96	4.18	-1.67	---

The linear plots for ΔG° :

