Plasma Reduction of Iron Oxide by Methane Gas and its Process Up-scaling

Karim Badr, Eduard Bäck, Wilfried Krieger

Department of Metallurgy, University of Mining, Metallurgy and Materials, Leoben, Austria

This paper investigates the characteristics of the methane plasma reduction of iron ore in comparison to that of the hydrogen plasma reduction process. Although hydrogen plasma smelting reduction (HPSR) has potential advantages as a steel making alternative in terms of simplicity (less operation units) and less harmful detrimental environmental implications, its high cost has a negative influence on its usage. In this regard, natural gas (> 96 % methane) could be adopted in the field of plasma smelting reduction. A brief comparison between hydrogen and methane options has been carried out experimentally. Heat and mass balance models were conducted to explore the features of up-scaled processes with respect to consumption figures and CO_2 emissions. It was found that the methane plasma is a good alternative for iron oxide smelting processes.

Keywords: methane plasma smelting reduction, hydrogen plasma smelting reduction, reduction of iron ores, process up-scaling, CO_2 emissions.

Introduction

Many of the current research, technological and development (RTD) programs are dedicated to finding innovative solutions to decrease CO_2 emissions produced by the steel industry. After the Kyoto agreement, it became more sensible to find new technologies with no or less carbon input such as smelting reduction processes, steel production by electrolysis and the use of biomass.

As a futuristic technology, hydrogen plasma smelting reduction was developed at the University of Mining, Metallurgy and Materials in Leoben [1-4]. The defining characteristic of the process is no direct CO_2 emissions due to the replacement of carbon as a heat source and reducing agent by hydrogen plasma.

The present study was aimed at using methane argon mixture instead of hydrogen argon mixture as a plasma gas to utilise the existing carbon from the methane in the reduction process. From an equilibrium point of view, the carbon available could be converted primarily to carbon monoxide whilst only around 40 % of hydrogen could be used for the reduction of iron oxide to iron. Therefore, in an up-scaled process, it is believed that the methane plasma process has a greater potential when compared to the hydrogen plasma process due to the reduction in volume of recycled gas and the cheaper investment / operation cost as a result of the usage of natural gas without the need for the steam reforming step. However, taking environmental implications into consideration, it was clear that the hydrogen plasma CO_2 emissions are much lower.

Experimental Procedures

Figure 1 is a schematic illustration of the cross-section of the natural gas plasma reactor. A detailed description of the experimental apparatus has been described in previous works [5-7]. Argon is used as a plasma gas for arc stabilisation and fines melting. Methane gas is fed with argon via the hollow electrode a few minutes after the argon injection.
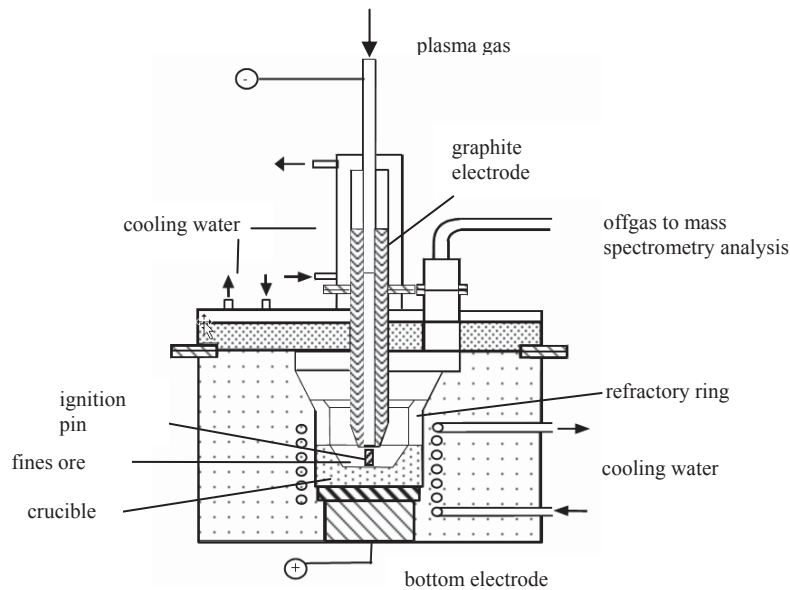
Figure 1. Plasma reactor

In all experiments, Carajas ore with few impurities was used. Its average composition in weight % was: Fe_{tot}: 66.16, CaO: 0.1, SiO_2: 0.92, Al_2O_3: 1.17, MgO: 0.07, Mn: 0.31, P: 0.02, S: 0.011. A 100 g charge of ore was placed in the furnace under a constant total Ar-CH_4 flow of 5 Nl/min. A series of experiments was carried out at Ar-CH_4 concentrations of 10 %, 15 %, 20 % and 25 % CH_4. A trial to increase the CH_4 concentration in Ar to 30 % was attempted but the experiment failed due to the plasma power supply limitations. Metal analyses of the reduced ore from experimentation were carried out by radio spectrometer.

Fundamentals of the Methane Plasma Process

CH_4 gas is fed to the transferred arc plasma to dissociate and ionise according to the applied electrical energy. At the arc-melt interface, the dissociated and ionised gases cool down and partially combine again. The existence of dissociated hydrogen and/or other gases is greatly dependant on the increasing temperature at the interface. However, CH_4 decomposes mainly to solid carbon and hydrogen molecules at the arc-melt interface (at temperatures of ~ 2000 ^{o}C-2600 ^{o}C) according to the following reaction:

$$\{CH_4\} \Leftrightarrow C_{(s)} + 2\ \{H_2\} \qquad\qquad (1)$$

From a stoichiometric point of view, it is clear that the products of 1 mole of CH_4 can reduce 4 atoms of oxygen (CO_2, $2H_2O$) while 1 mole of H_2 can only reduce 1 mole of oxygen (H_2O). Therefore, the usage of CH_4 in comparison to H_2 will result in higher reduction rate (i.e. 4 times higher reduction rate).

Figure 2 shows the thermodynamic equilibrium between 4 moles of FeO and 1 mole of CH_4 over a temperature range of 1500 ^{o}C to 3000 ^{o}C as calculated with FACTSAGE software [8]. The graph starts with total reduced oxygen of 2 moles at 1500 ^{o}C (summation of H_2O, CO and CO_2) which decreased to 1.74 moles at 2600 ^{o}C. Whereas, the reduced oxygen of 1 mole FeO (by 1 mole of H_2) at 1500°C and 2600°C is 0.43 and 0.36 moles respectively [7]. In other words, the CH_4 reduction rate is about 4.8 times the H_2 over the stated temperature range.

2

The assessment of CH_4 performance was carried out via calculating the oxide products (H_2O, CO and CO_2 from 1 mole of CH_4 according to the following formulas for the hydrogen and carbon utilisation degrees.

$$\eta_{H_2} = \frac{V_{H_2O}}{2*V_{CH_4}} \tag{2}$$

Where,

V_{H_2O} : Steam volume, mole

V_{CH_4} : Methane volume, mole, and

H_2 contained within methane is fully utilised when 1 mole of CH_4 is converted to 2 moles of H_2O. (i.e. $\eta_{H_2} = \frac{2}{2*1}*100 = 100$ %)

$$\eta_C = \frac{0.5*V_{CO} + V_{CO_2}}{V_{CH_4}} \tag{3}$$

Where,

V_{CO} : CO volume, mole

V_{CO_2} : CO_2 volume, mole, and

C contained within methane is fully utilised when 1 mole of CH_4 is converted to 1 moles of CO_2 or 50 % utilised if it is converted to 1 mole CO.

(i.e. $\eta_C = \frac{0.5*0+1}{1}*100 = 100$ % or $\eta_C = \frac{0.5*1+0}{1}*100 = 50$ %).

It is clear from figure 2 that the hydrogen utilisation degree varies from ~ 40 % to 33 % whilst the carbon utilisation degree varies from ~ 58 % to 54 % in a temperature range of 1500 °C to 2600 °C. In that sense, it should be noted that the carbon utilisation degree is higher than that of the hydrogen utilisation and its decrease over the shown temperature range is less than that of the hydrogen. Therefore, it is clear that the carbon in methane has a more significant role in comparison to the hydrogen with respect to the reduction process.
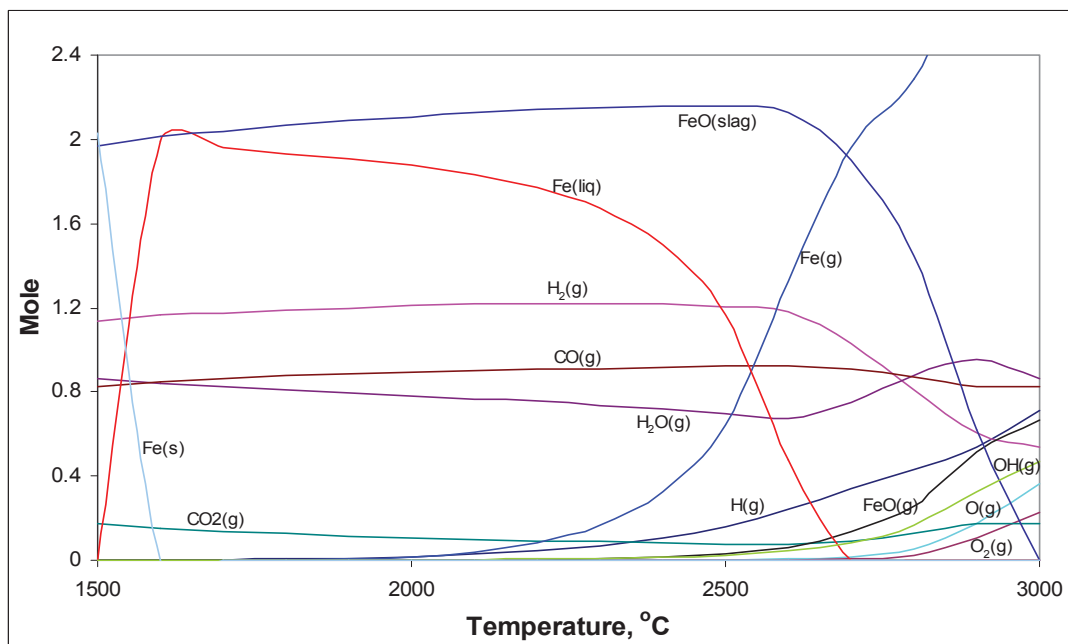

**Figure 2.** Equilibrium of 4 moles FeO-1 mole CH_4

Finally, it should be stressed that the operating temperature of the process is characterised by a high temperature gradient over the oxide bath. Its peak value can reach $2600^{o}C$ at the plasma bath interface while a significant drop in temperature to $1500^{o}C$ is found at the bath sidewall.
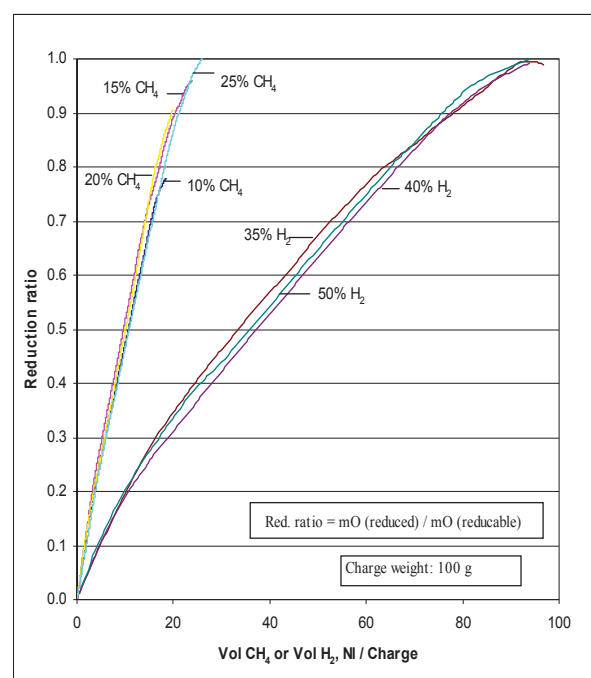
Experimental Results

1. Reduction reactions
A minor quantity of carbon, in the form of soot, was found in some experiments but it did not exceed 5 % of the total inlet carbon obtained from the methane. This soot was clearly visible at the colder zones of the furnace roof and the crucible refractory side wall. Moreover, some carbon deposits inside the electrode tip were found, which led to a reduction of the hollow electrode diameter during the experimentation.

Figure 3 shows the reduction ratio versus time. The reduction ratio was defined as the oxygen reduced by the reducing gas from iron oxide during the experiment, divided by the oxygen content of iron oxide in the ore. From the results it was clear that the reduction ratio developed over three phases as shown in figure 3. The first phase was mainly during the reduction of trivalent iron which was characterised by the highest reduction kinetics over the duration of the experiment. The second phase, the main linear phase, was the result of the divalent iron reduction which existed in a substantial amount in the oxide melt. In this phase, the Fe^{2+} was reduced to metallic iron by a constant rate. Finally the third phase started when the curve levelled off. This is due to the diminishing of the oxide melt-plasma interface reactions resulting in a rate limitation caused by oxygen transport. It should be noted that the slope of the reduction curves represents the various reduction rates. In other words, the greater the CH_4 content within the Ar-CH_4 mixture, the greater the slope/reduction rate. Nevertheless, the experimentation showed that with low CH_4 concentrations, high reduction degrees were not attainable.
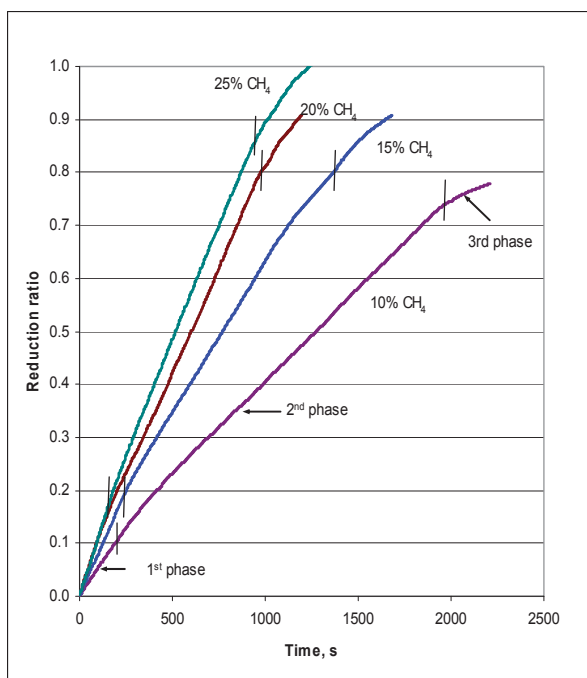
Figure 3. The effect of % CH_4 on the reduction rate

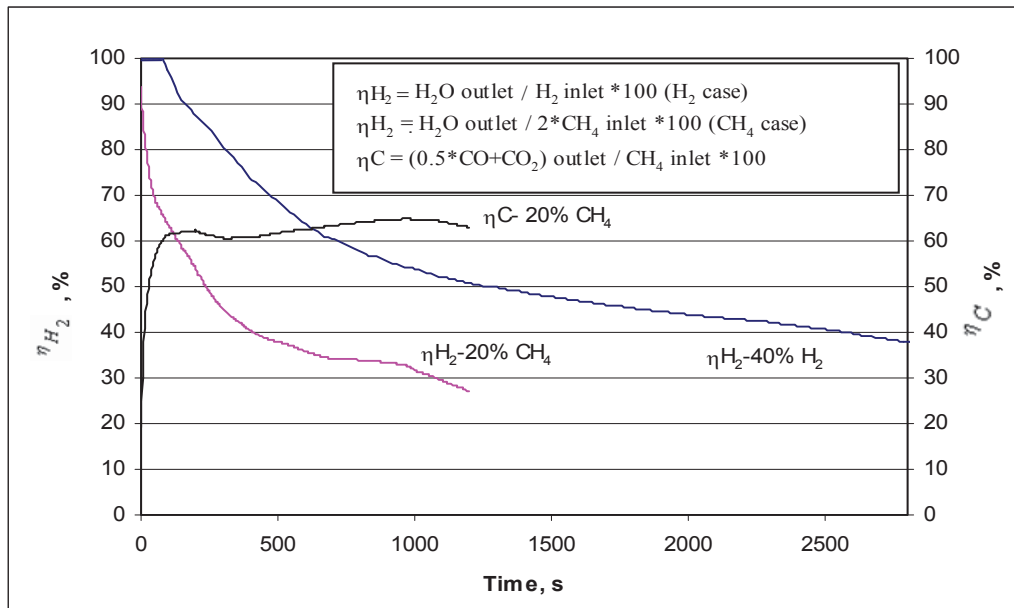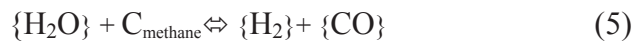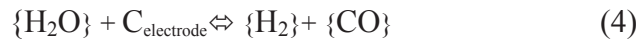**Figure 4.** Reduction ratio versus total supplied CH_4/H_2 volume

4

Figure 4 shows a graph of the reduction behaviour of CH_4 against the total amount of CH_4 fed per 100 g charge of ore (Nl/charge). H_2 experimentation results were plotted to compare both processes. It is clear from the figure that the average slope of the methane reduction curves was ~ 4 times the hydrogen reduction slope whereas with respect to stoichiometry and thermodynamics, the methane reduction rate was 4 and 4.8 times the hydrogen reduction rate respectively.

2. Reduction Kinetics

Figure 5 shows the H_2 and C utilisation degrees of the Ar-CH_4 experiment at 20 % CH_4 concentration. Moreover, it shows the H_2 utilisation degree of the Ar-H_2 experiment at 40% H_2 concentration, i.e. with the same flow of H_2 in both experiments .It is clear that the H_2 utilisation degree at the end of CH_4 experiment was almost 10 % lower than that of the hydrogen experiment. The lower hydrogen utilisation degree in this case, with respect to the hydrogen plasma experiment and thermodynamic values was attributed to the contribution of electrode – steam, cracked carbon from methane, and water gas shift reactions. This brought the H_2O content to lower and CO or CO_2 to higher values, according to the following reactions:

$$\{H_2O\} + C_{electrode} \Leftrightarrow \{H_2\} + \{CO\} \qquad (4)$$

$$\{H_2O\} + C_{methane} \Leftrightarrow \{H_2\} + \{CO\} \qquad (5)$$

$$\{H_2O\} + \{CO\} \Leftrightarrow \{H_2\} + \{CO_2\} \qquad (6)$$


Figure 5. Hydrogen / Carbon utilisation degree

The reduction kinetics was better assessed through the overall reduction ratio which is defined as: the total reduced oxygen, *during the second phase of the reaction*, per mole of the corresponding inlet reducing methane. Defining the exact operating temperature of the experimentation was difficult due to the high temperature gradient over the bath. It was found that the peak temperature at the anode spot was 2600 ^{o}C and decreased to about 1500 ^{o}C at the bath side parts. However, the experimental results obtained, using the ratio defined above, were consistent with those of the thermodynamics, at the plasma bath interface average temperature of 2000 ^{o}C (**figure 6**).
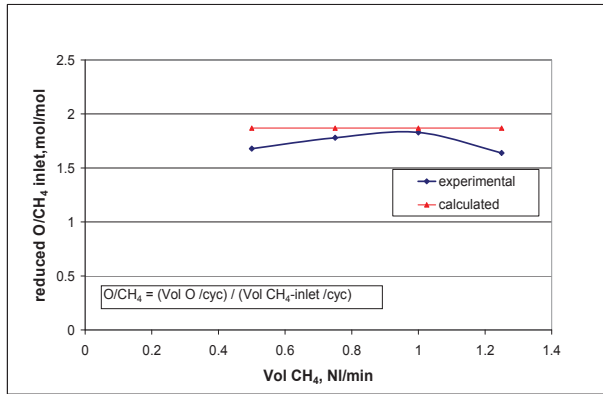
Figure 6. Comparison between thermodynamic calculations and experimental results
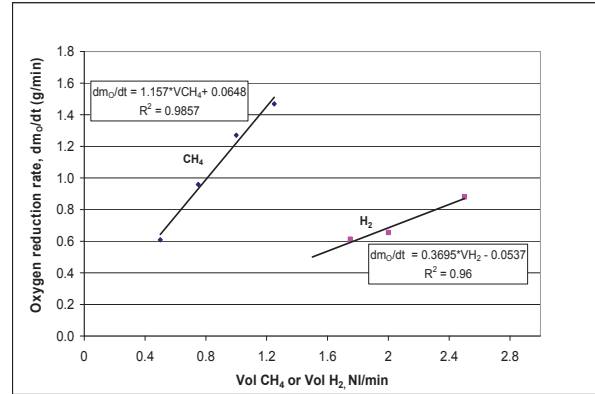
Figure 7. Oxygen reduction rate versus reducing gas flow

Finally, **figure 7** was plotted to compare the impact of methane with respect to hydrogen on the oxygen reduction rate in the second phase of reduction. A linear regression analysis was determined for CH_4/H_2 flow and the oxygen reduction rate. Both trend lines passed almost through the origin thereby indicating the direct proportionality of the reduction rate with the reducing gas flow.

3. Metal Analyses

Although the conducted experiments were carried out under methane plasma reduction, the metal analyses showed slightly more carbon content than that of the hydrogen plasma experiments as can be seen in **table 1.**

	% C	% Si	% Mn	% P	% S
10 % CH$_4$	0.075	0.035	0.182	0.012	0.013
15 % CH$_4$	0.169	0.024	0.312	0.018	0.016
20 % CH$_4$	0.049	0.021	0.250	0.016	0.017
25 % CH$_4$	0.069	0.040	0.293	0.018	0.014
40 % H$_2$	*0.011	0.026	0.144	0.012	0.007
Crucible	0.049	0.026	0.356	0.014	0.019

*: stems mainly from crucible melt out

Table 1. Metal analysis

Process Up-scaling

The potential for the up-scaling of CH_4/H_2 plasma processes has been explored within an RTD program known as the ULCOS project* [9]. This project aims at finding breakthrough solutions to decrease the CO_2 emissions of the steel industry. A conceptual design for an up-scaled production process of 1mt/y which could be adapted to both methane and hydrogen plasma gases, but with only minor changes, has been carried out via the following flow sheet (**figure 8)**.
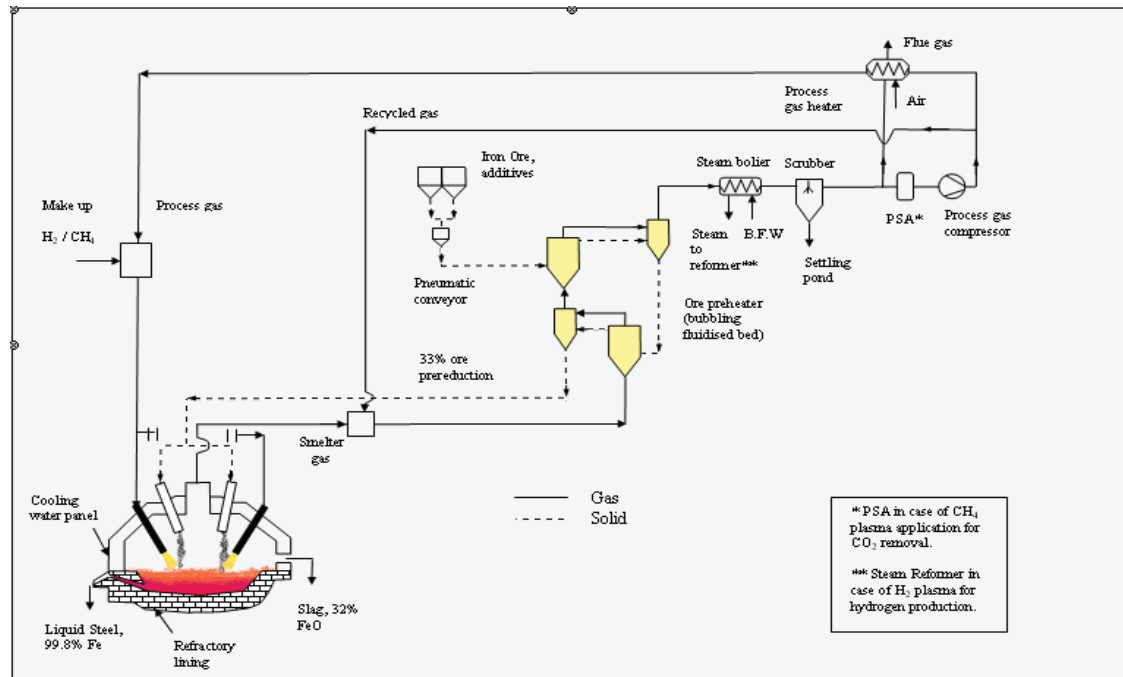

Figure 8. Hydrogen Plasma Smelting Reduction Process, HPSR

Examining the flow sheet, a fluidized bed pre-heater was adopted for pre-reduction purposes. The fed material (iron ore fines and fluxes) and high containing hydrogen gas were supplied to the gas pre-heater to obtain a maximum pre-reduction degree of ~ 33 % wustite. The remaining non-reacted hydrogen was recycled starting with a boiler to make use of the pre-heater top gas sensible heat, which was followed by a scrubber to scrub off the formed steam and a CO_2 adsorption unit (in the case of natural gas plasma).

After the scrubber, the recycled gas was divided into two branches. The first branch went to the smelter offgas to reduce the temperature of the inlet gas to the pre-heater. The second branch was mixed with a supplied gas of H_2/CH_4 (make-up gas).

It should be noted that a small amount of the recycled gas was exported before the gas was split. This enables the increase in gas volume, which arises from the inert gas supplied by natural gas and the calcination products from the used additives, to be handled. The high combustibles in the exported gas are burnt and the heat evolved is utilised via a heat exchanger to heat up the recycled gas going to the smelter.

Make-up H_2 was supplied through the steam reformer facility in the case of the H_2 Plasma process. This method was chosen due to its advanced technology leading to benefits in cost effectiveness and production capacity.

The recycled gas mixed with the make-up CH_4/H_2 was fed to the smelter via electrodes. The electrodes were non-cooled hollow graphite electrodes which have a characteristic high power capacity in comparison to water cooled plasma torches. The electrodes were fitted through the furnace roof whereas the pre-reduced ore was fed through feeding pipes that are distributed evenly across the roof.

The diameter of the reactor was calculated to be 6.4 m, allowing for the minimum permissible distance between the used electrodes, to avoid irregular interference between electromagnetic forces from the arcs. It should be noted that the minimum permissible distance varies with the plasma arc current and electrode diameter which have been chosen relevant to the electrical power per electrode required. The correlation between the permissible distance, plasma arc and the electrode diameter has been adopted with respect to AC-arc figures.

A stirring facility in the reactor bath was not necessary in the flow sheet due to the satisfactory effect of the plasma gas impulse. However, the gas impulse did not have enough potential to splash the slag which is a disadvantage in terms of extending the lifetime of the reactor cooling system as this makes use of the slag as a self liner.

Finally, a heat and mass balance model was developed at Corus RD&T and was named IRMA, Iron Making model [10]. This model has used the previously shown flow sheet to build the total process from simple building blocks. Calculations were based on a mix of thermodynamic equilibrium and empirical relationships. Thermodynamic calculations were carried out by the *ChemApp* library. ChemApp is a product of *GTT Technologies* and was based on a subset of the Factsage 5.0 database [8]. The model was validated using results of other models and literature.

The model was then optimised for hydrogen and natural gas processes to work out the consumption figures in terms of make-up gas, electricity and processing parameters, corresponding to 1 ton of steel produced and ~30 % FeO in the slag **(table 2).**

	Hydrogen plasma	Natural gas plasma
Make-up gas, Nm^3	690	157
Electrical Energy, MJ	3702	5191
Gas volume (smelter outlet), Nm^3	1522	924
*CO_2 emissions, kg	29	345

*CO_2 emissions resulting from the production of electricity is not considered

Table 2. Hydrogen/Natural gas process parameters

It is clear from table 2 that the consumed electrical energy in the natural gas plasma is higher than that of the hydrogen plasma process. This was due to the required additional energy for the natural gas cracking. The CO_2 emissions were also high due to the usage of carbon containing natural gas as a reducing agent. However, the CO_2 results did show significant low results in comparison to the CO_2 emissions of 1850 kg-CO_2/t-steel in the BF-BOF route.

Finally, analysing the shown figures entails precise cost analyses in terms of the reducing gas costs, CO_2 emissions and the additional cost for a CO_2 removal unit in the case of methane plasma process. Moreover, the competitive advantage of gas volume reduction and capital/running cost savings from the removal of the steam reformer for the hydrogen supply should be considered during the assessment of the natural gas plasma option.

Discussion

The reduction process has been developed with changing behaviours over the course of the reaction according to the Fe^{3+} / Fe^{2+} and oxygen concentrations in the oxide melt. However, it was evident through the overlap of the shown curves (H_2/CH_4) in **Figure 4,** and the linear relationship between the inlet reducing gases and the oxygen reduction rate in **Figure 7** that the *reducing gas supply* to the oxide melt was the *rate limiting determinant* during the main reduction phase.

However, it was noticed from the CH_4 reduction curves that an almost complete reduction was not attainable in most experiments. Such a phenomenon was attributed mainly to the encountered carbon deposition inside the hollow electrode and thus accordingly to the non uniform distribution of the plasma gas over the melt. This consequently led to a partial solidification of the melt and an inconsistency in reduction, with some zones fully reduced whilst other zones were not. However, it is believed that the hollow electrode susceptibility to the carbon deposition was significantly high due to the hollow diameter limitations (8 mm), whereas such a phenomenon is not expected to occur in wider diameters in the up-scaled process.

The methane plasma smelting of iron ore was found to produce carbon containing steel or very low carbon steel. In a batch wise reduction some carburisation can occur due to carbon pick-up by excessive methane. However, for an up-scaled process with continuous operation, no carburisation is expected. This is because of the existence of the protecting slag layer with high oxygen potential and the role of Vacher-Hamilton equilibrium on the metal in contact with the iron oxide containing slag.

The assessment of the utilisation degrees and the overall reduction ratio were compared with the corresponding thermodynamic equilibrium results. It was found that the values were in good agreement with the equilibrium calculations. Moreover, the experimental results showed a methane reduction rate 4 times that of the hydrogen reduction rate which was generally consistent with the thermodynamical calculated ratio of 4.8. The deviation between these ratios was attributed partially to the carbon soot formation.

During the assessment of the process up-scaling potential, the H_2/CH_4 plasma processes showed greater benefits in terms of flow sheet simplicity, carbon free/low steel, low CO_2 emissions, absence of sulphur arising from reducing agents and low slag generation (80 kg/t). However, there are some problems that need further investigation and investment for the up-scaling of the existing facility.

One of the main concerns identified in the up-scaling assessment was the high FeO content in the slag (~ 30 %) which rules out the usage of refractory lining applications due to erosion problems. In which case, the water cooling copper staves should be adopted.

However, an assessment of the heat losses encountered needs to be highlighted in further research work. Another point of concern is the feasibility of plasma stability when using 100 % reducing gases.

Conclusion

The methane argon plasma smelting of iron oxide has been examined in this study. The interest in this technique lies in its competitive advantage in terms of the carbon reduction potential as long as the CO_2 emissions are within the targeted limits of CO_2 reduction in comparison to the BF-BOF route.

Methane plasma smelting reduction experiments carried out in the laboratory have shown acceptable results in terms of kinetics and metal analysis. The up-scaled conceptual studies showed satisfactory results in terms of lower gas volume, relatively low CO_2 emissions and less capital/running costs in comparison to the hydrogen plasma alternative due to the elimination of the steam reformer unit from the process.

It should be stressed that the conducted work has been based on conceptual studies and experimentation but has not yet been proven on a pilot scale. Accordingly, there are still challenging points that have to be investigated to enhance the up-scaling potential of the hydrogen/natural gas plasma process. These points are mainly summarised as follows:

- Investigation of the plasma stability and the corresponding maximum methane/hydrogen percentage in the plasma gas.
- The implications of the high content of FeO in the slag.
- Heat loss assessment under the plasma arc radiation and the water cooled jacket application.

Acknowledgement

References

[1]   E. Bäck, H. Hiebler: BHM, 143 (1998), No. 5, 153-158.
[2]   A. Sormann, E.Bäck: BHM, 145 (2000), No. 1, 14-21.
[3]   H. Hiebler, J.F. Plaul: Metalurgija, 43 (2004), No. 3, 155-162.
[4]   W. Krieger, C. Bernhard, G. Gigacher, J. Korp, J.F. Plaul: BHM, 149 (2004), No. 5, 161-167.
[5]   J.F. Plaul, W. Krieger: BHM, 149 (2004), No. 7, 235-239.
[6]   J.F. Plaul, W. Krieger: Proc. 1st Chinese-German Seminar on Fundamentals of Iron and Steelmaking, Beijing, 18. - 19. October 2004.
[7]   J.F. Plaul, W. Krieger, E. Bäck: steel research int., 76 (2005), No. 8, 548-554.
[8]   C.Bale, W.Pelton, K. Hack et al.: Version 5.3, www.factsage.com, © Thermfact 1976-2004, GTT-Technologies.
[9]   Sixth Framework Programme Home Page: http://cordis.europa.eu/fp6/projects.htm, ULCOS Project.
[10]   R. Speets: Iron Making Model User Manual – IRMA version 1.1, Corus Research, Development & Technology, Confidential within ULCOS Project.