

Deposition of carbon from methane on manganese sources

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Abstract

Carbon has been deposited on HCFeMn slag from methane-containing gas with and without CO₂, creating C-MnO composites and giving a hydrogen-rich off-gas as a by-product. The maximum deposited amount corresponds to 37±4% of the carbon required for reduction of all manganese in the slag to metallic Mn. This was achieved at 1100 °C with a H₂-concentration in the off gas of 76%.

Temperature was an important parameter. At 790 °C, no deposited carbon was detected, at temperatures ≥1000 °C, deposition increased with temperature. A lower gas-flow leads to more methane decomposition.

Experiments with CO₂ in the process gas gave less deposited carbon than other experiments. This could be caused by dilution of methane or chemical reactions involving CO₂, or a combination.

Investigations of fines formation indicate that the deposited carbon sticks well to the HCFeMn-slag, and would not fall off easily during transport and handling.

This demonstrates that biogas can potentially be a non-fossil source of carbon in manganese production.

Introduction

As in any other industry, to reach the climate goals of the Paris Agreement, the manganese industry must reduce its fossil CO₂ emissions. Mn-alloys are mainly produced in submerged arc furnaces (SAF) by carbothermic reduction of oxidic raw materials. Since carbon in Mn-alloy production is used as a reductant to remove oxygen and not as an energy source it is not easily replaced. One option is to replace fossil carbon with biologically sourced carbon, which will reduce fossil (but not total) CO₂ emissions.

Several studies have looked at using solid biocarbon in the form of charcoal in manganese production [1, 2, 3]. There are challenges related to the mechanical strength and low density [1, 4], and charcoal also has a greater CO₂ reactivity than metallurgical coke [5].

Biogas, produced from the digestion of organic matter, is also a potential source of non-fossil carbon, in the form of methane gas, CH₄. While some studies show interesting results of using methane directly as the reducing agent in producing manganese [6], this has so far not been industrialised. A different option is to convert the methane in biogas into solid carbon through thermal cracking.

The main idea behind the current work is to treat Mn-ore with methane from biogas at high temperatures where the methane decomposes to carbon and hydrogen. If the carbon can be made to deposit onto the Mn-ore, to stick there during transport, and to act as a reductant in Mn-furnaces, the carbon in this composite material can be used as a non-fossil reducing agent by introducing a two-step process as shown in Fig. 1. The first step will be the deposition of carbon from methane onto manganese ore in a separate unit; the second step will be to use the produced composite material to produce manganese in a process very similar to that being used today. The hydrogen resulting from the decomposition step could be a valuable by-product.

The primary goal of the current work is to use thermal cracking of methane to demonstrate that it is possible to deposit solid carbon from biogas on manganese ore and that the carbon sticks to the manganese ore, in other words to demonstrate the feasibility of step 1 of Fig. 1.

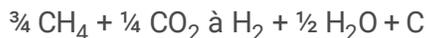
Without cleaning/upgrading, biogas contains large quantities of CO₂ [7, 8]. If the biogas could be utilised without CO₂ removal, this would obviously be a benefit. Therefore, both CH₄ and CH₄-CO₂ mixtures are examined as carbon sources in the current work. At the outset, it is expected that CO₂ could interact with the carbon deposition experiments in several ways, the first is to consume deposited carbon by the Boudouard reaction:



Another is to consume produced hydrogen by the water-gas-shift reaction:



Both of these reactions would be detrimental, but it is also possible that CO₂ could have positive effects. Normally, high temperatures are needed for thermal decomposition of methane, despite the reaction being thermodynamically favourable above 550°C. However, CO₂ can also shift the equilibrium towards more deposited carbon. As an example, the following reaction is thermodynamically favourable above 503.9°C, according to calculations in FactSage [9]:



It is thus not clear from the outset what overall effect CO₂ will have. A secondary objective of the current work is thus to investigate the effect of CO₂ on the decomposition of methane.

Experimental Setup And Method

The manganese source used was high-carbon ferromanganese (HCFeMn) slag. It was chosen because in this raw material the only manganese oxide present is MnO, as opposed to various ores that also contain higher order oxides like MnO₂. The higher order oxides could provide oxygen for reaction with the deposited carbon, making interpretation of the results harder.

The gases used were 99.999% Argon 5.0, scientific 99.9992% CO₂, and 99.5% CH₄ 2.5. As process gas, two different gas mixtures were used: 90%CH₄-10%Ar, and 63%CH₄-27%CO₂-10%Ar.

In each experiment, 2000g of HCFeMn slag, screened to sizes of 5-10mm, was charged in a steel crucible which in turn was placed inside a graphite crucible on top of an inlet gas dispersing plug. Experiments were run in a resistance heated furnace with the temperature controlled by an S-type thermocouple placed close to the heating elements. The furnace and crucible are illustrated in Fig. 2. The temperature was also measured inside of the charge, indicated by thermocouple 1 and thermocouple 2 in Fig. 2b. Process gases were mixed with mass flow controllers (5 SLPM and 100 SLPM) and purged through the bottom of the furnace into the bottom of the crucible. The gas-inlet was water-cooled to prevent carbon deposition and clogging of the inlet. From there, it travelled through the gas dispersing plug and into the material as shown in Fig. 2b. The off-gas exited at the top of the furnace where it was analysed by a micro gas chromatograph (Micro GC) for CH₄, CO, CO₂, H₂, N₂ and O₂. The sample was heated to 200°C at 13°C/min, and then to the designated temperature at 3° C/min while flushing with Ar at 5l/min. Once the temperature had stabilised at the target temperature, argon was switched off, the process gas was switched on, and the sample held in stable conditions for 2 hours. After the 2-hour holding period, the process gas and furnace power were switched off, and the sample was purged with Ar at 5l/min until cool.

The samples were weighed before and after the experiment, and carbon content in the material measured by combustion IR spectroscopy. Additionally, the samples were imaged by conventional camera and by back-scatter imaging in an Electron Probe Micro Analyser (EPMA). The samples also underwent an abrasion test. An abrasion test is an indication of how well the deposited carbon will stick to the Mn-material during handling after it has been deposited. This test involved sieving the material at 5mm and 500µm before and after 30 min in a Hanover drum at 40rpm and comparing the different size fractions.

Three different temperatures, two different gas compositions and two different total gas flows were investigated across 15 total experiments, shown in Table 1.

Table 1
Overview of all experiments.

Atmosphere	Exp. series #	Exp. #	Temp. [°C]	Total flow rate [L/min]	Flow CO ₂ [L/min]	Flow CH ₄ [L/min]	Flow Ar [L/min]
27% CO ₂ + 63% CH ₄ + 10%Ar	1	1	790	2.35	0.63	1.48	0.24
90% CH ₄ + 10% Ar	1	2	790	2.35		2.12	0.24
90% CH ₄ + 10% Ar	1	3	790	4.7		4.23	0.47
27% CO ₂ + 63% CH ₄ + 10%Ar	1	4	1000	2.35	0.63	1.48	0.24
27% CO ₂ + 63% CH ₄ + 10%Ar	1	5	1000	2.35	0.63	1.48	0.24
90% CH ₄ + 10% Ar	1	6	1000	2.35		2.12	0.24
90% CH ₄ + 10% Ar	1	7	1000	2.35		2.12	0.47
27% CO ₂ + 63% CH ₄ + 10%Ar	1	8	1000	4.7	1.27	2.96	0.47
27% CO ₂ + 63% CH ₄ + 10%Ar	1	9	1000	4.7	1.27	2.96	0.47
90% CH ₄ + 10% Ar	1	10	1000	4.7		4.23	0.47
27% CO ₂ + 63% CH ₄ + 10%Ar	1	11	1100	2.35	0.63	1.48	0.24
27% CO ₂ + 63% CH ₄ + 10%Ar	1	12	1100	2.35	0.63	1.48	0.24
90% CH ₄ + 10% Ar	2	13	1100	2.35		2.12	0.24
90% CH ₄ + 10% Ar	2	14	1100	2.35		2.12	0.24
90% CH ₄ + 10% Ar	2	15	1100	2.35		2.12	0.24

Results And Discussion

If carbon from methane is to be used in Mn-production as intended by the current scheme, three conditions need to be fulfilled:

1. The methane needs to decompose into carbon and hydrogen
2. The carbon formed needs to deposit onto the HCFeMn slag in appreciable amounts
3. The carbon needs to stick to the surface of the HCFeMn and not easily fall off, to be able to withstand transport etc.

For optimisation and scale-up of the process, it is also useful to know the effect of different parameters on the deposition rate. The following subsections presents the results with these issues in mind.

Methane decomposition

The off-gas measurements are presented in Table 2, averaged across the 2-hour holding period during which the samples were exposed to process gas. Since the total gas-flow and -composition into the furnace was known, and disregarding higher order hydrocarbons like C_2H_2 (which according to thermodynamic equilibrium should be present at levels orders of magnitude below 1%), the hydrogen- carbon- and oxygen mass balances give three equations with three unknowns:

$$\phi_0 \cdot \left(\frac{1}{4} [CH_4]_0 + \frac{1}{2} [H_2]_0 \right) = \phi_1 \cdot \left(\frac{1}{4} [CH_4]_1 + \frac{1}{2} [H_2]_1 + \frac{1}{2} [H_2O]_1 \right)$$

$$\phi_0 \cdot \left[\frac{1}{2} CO_2 \right]_0 = \phi_1 \cdot \left([CO]_1 + [H_2O]_1 + \frac{1}{2} [CO_2]_1 \right)$$

$$\phi_0 \cdot ([CH_4]_0 + [CO_2]_0) = \phi_1 \cdot ([CH_4]_1 + [CO_2]_1 + [CO]_1) + \{C_{(s)}\}_1$$

Here a subscript "0" denotes incoming, a subscript "1" denotes outgoing, [X] denotes the concentration (moles/l) of species X, ϕ denotes total gas-flow (L/min), and $\{C_{(s)}\}$ denotes the net rate of solid carbon formation (mol/min).

Solving these equations gives the unknowns ϕ_1 , $[H_2O]_1$ and $\{C_{(s)}\}_1$, and since argon is inert, the outgoing argon-concentration is simply the known incoming concentration scaled by the change in total gas flow.

Multiplying $\{C_{(s)}\}_1$ by the holding time gives the net solid carbon formed during each experiment. It should be stressed that the net solid carbon *formed* does not equate to the amount of carbon *deposited* on the HCFeMn slag. Some of the formed carbon can for example deposit on the crucible wall or be carried off as fine dust. These calculated values are also included in Table 2.

The (dried) slag contains 36.6% MnO. That means that for conversion of all MnO in a 2000g slag sample to Mn after the reaction $MnO + C = Mn + CO$, 123.8g of carbon is required. In the following discussion, " C_{stoich} " is introduced to mean: the amount of carbon deposited relative to the amount required for stoichiometric conversion of all MnO (in other words, relative to 123.8g in the current work). C_{stocih} is used not only when referring to carbon specifically deposited on HCFeMn slag, but also for example when describing the total amount of carbon formed in the system.

Table 2

Measured (μ -GC) and calculated (from mass balance) composition of off-gas and amount of solid carbon formed for all experiments. C_{stoich} means percentage of carbon necessary for self-reduction of all MnO in slag. Note that carbon *formed* does not equate to carbon *deposited*.

Exp.	Incoming gas			T	Flow-rate	Outgoing Gas Composition						Net Solid C Formed	
						Measured averages				Calculated		Calculated	
	CO ₂	CH ₄	Ar	[°C]	[L/min]	CO	CO ₂	H ₂	CH ₄	H ₂ O	Ar	[g]	C_{stoich}
1	27%	63%	10%	790	2.35	3%	28%	0%	66%	-2%	6%	-3.8	-3%
2	0%	90%	10%	790	2.35	0%	0%	1%	100%	0%	7%	0.3	0%
3*	0%	90%	10%	790	4.7	0%	0%	0%	0%	0	10%	0	0%
4	27%	63%	10%	1000	2.35	27%	5%	22%	36%	5%	9%	4.5	4%
5	27%	63%	10%	1000	2.35	30%	3%	24%	36%	7%	8%	7.1	6%
6	0%	90%	10%	1000	2.35	0%	0%	38%	58%	0%	9%	30.5	25%
7	0%	90%	10%	1000	2.35	1%	1%	34%	52%	0%	9%	31	25%
8	27%	63%	10%	1000	4.7	18%	8%	12%	37%	3%	8%	-0.8	-1%
9	27%	63%	10%	1000	4.7	25%	7%	18%	41%	8%	8%	15.6	13%
10	0%	90%	10%	1000	4.7	1%	0%	27%	68%	0%	9%	40.9	33%
11	27%	63%	10%	1100	2.35	31%	0%	43%	18%	3%	11%	18.3	15%
12	27%	63%	10%	1100	2.35	28%	0%	40%	14%	1%	3%	16.9	14%
13	0%	90%	10%	1100	2.35	1%	0%	82%	29%	0%	8%	73.6	59%
14	0%	90%	10%	1100	2.35	1%	0%	80%	29%	0%	8%	71.8	58%
15	0%	90%	10%	1100	2.35	1%	0%	67%	42%	0%	8%	55.8	45%

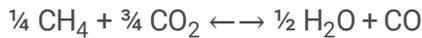
*) In Experiment 3, an error occurred which gave no signal to the off-gas measurements.

In the experiments at 790°C, no hydrogen was detected in the off-gas, so no carbon decomposition took place. This means that the presence of CO₂ was not sufficient to drive deposition of carbon at lower temperatures. In all other experiments hydrogen was detected in the off-gas, indicating that cracking did in fact take place. Figure 3 below shows the hydrogen levels averaged across experiments with identical experimental parameters. For data points with the same colour, the only different experimental parameter was temperature. For two sets of parameters (90% CH₄, 2.35l/min; 63%CH₄-27%CO₂, 2.35l/min) there is significant hydrogen evolution at two different temperatures (1000°C and 1100°C) with all other parameters the same. In both cases the amount of hydrogen is much higher at 1100°C than at 1000°C. The amount of data is too limited to quantify the effect, but this indicates that temperature is a very important parameter, and that methane decomposition increases with temperature.

For two sets of parameters (63%CH₄-27%CO₂, 1000°C; 90%CH₄, 1000°C) all parameters are the same except the total gas flow. In both cases the amount of hydrogen, and thus the degree of methane decomposition, is higher in

the case of a lower total gas flow.

In experiments with CO₂ in the process gas, this was converted into CO to a larger or smaller extent. At 790°C, only 3% of CO was found in the off gas. Since no hydrogen was detected and no solid carbon produced, the Boudouard reaction cannot be the source of this CO. A direct reaction between CO₂ and methane that does not produce hydrogen is a possible explanation, like for example the following reaction, which is thermodynamically favourable at 790°C:



At 1000°C, there was between 18–30% of CO, and the CO₂ level had dropped below 10%. At 1100°C, basically all CO₂ had been converted.

The experiments with CO₂ also had less hydrogen in the off-gas than when no CO₂ was present. It is not possible, within the uncertainties, to determine to what extent this is because of methane dilution or if reactions with CO₂ plays a role. On the one hand, the presence of CO in the off-gas indicates that CO₂ reacts with something, which could be the produced H₂. On the other hand, it is theoretically possible that all CO is produced from reactions between CO₂ and deposited C, which should not influence the H₂-levels.

While CO₂ in the process gas giving less hydrogen in the off-gas is a drawback in isolation, there could also be an upside to having CO in the off-gas. Syngas (H₂-CO-mixture) production from biogas without CO₂-emissions requires the upgrading (CO₂-removal) of biogas to biomethane, followed by storage/utilisation of the CO₂ and steam reforming of the methane into syngas. It is possible that a competitive option would be to use non-upgraded biogas as a solid carbon source as described here, avoiding the need for CO₂-removal and steam reforming.

The observations that temperature is a very important parameter, and that methane decomposition increases with temperature is in line with experiences from similar work [11, 12], as is the result that the degree of methane decomposition is higher in the case of a lower total gas flow [13].

Carbon deposition

The decomposition of methane is only the first step; the formed carbon needs to deposit onto the HCFeMn slag. Several techniques were used to verify the deposition of carbon and determine the amount deposited. The chemical analyses turned out not to be very useful for quantification since the slag contained inhomogeneously distributed carbon (likely in metallic droplets). Visual inspection of samples by eye was sufficient to identify that some samples turned completely black, suggesting carbon deposition. EPMA images showed carbon layers (verified by X-ray diffraction) on several of the samples. Example images are shown in Fig. 4.

The weight change measurements are seen as the most trustworthy estimates of amounts of deposited carbon. Figure 5 shows the results with uncertainties for all experiments, where repeat experiments have been grouped and averaged. The best results are with 90% CH₄ and 2.35 l/min total gas flow at 1100°C, where an average of 46g of carbon has been deposited, corresponding to $37 \pm 4\%$ of C_{stoich}. In Fig. 5, the results are plotted versus temperature. The first observation that can be made is that there is no significant carbon deposition at 790°C, an observation that matches the visual appearance of the material, as well as the absence of hydrogen in the off-gas for these experiments (Fig. 3).

For experiments with low gas flow (2.35l/min), there was significant weight change at both 1000°C and 1100°C, and the weight change at 1100°C was significantly higher than at 1000°C. This was true for experiments with and without CO₂ in the process gas. Increased temperature thus leads to increased carbon deposition rate.

At 1000°C, the average results with high gas flow (4.7 l/min) lie below the average results of experiments with low gas flow (2.35 l/min) for otherwise identical parameters. Since the uncertainty intervals of the low- and high gas flow experiments overlap for each set of parameters, it can not be concluded that this is a statistically significant trend. While the gas measurements showed less methane decomposition at higher gas flow, this alone should not give an expectation of less carbon deposited, since it is possible that a reduction in decomposition rate is outweighed by an increase in total amount of methane passing through the furnace. The picture remains unclear.

The final process parameter that can be discussed in terms of its influence on the carbon deposition is the process gas composition. At low gas flows (2.35 l/min) there was deposition at 1000°C and 1100°C both with and without CO₂ in the process gas. This demonstrates that carbon deposition from CO₂-containing gas is possible. At 1000°C and 2.35 l/min, the average deposited values are higher when there is no CO₂ in the process gas, but since the uncertainty intervals overlap the result is not significant. At 1100°C however, the result is much more pronounced and clearly significant. CO₂ is expected to have two potentially negative impacts on carbon deposition in this temperature range: The first is the simple dilution of methane, meaning that less carbon is available to deposit. The second is the potential consumption of already deposited carbon through the Boudouard reaction. The indicated negative impact of CO₂ also at 1000°C is thus expected to be valid. However, at present it is not possible to say whether this difference is due simply to the dilution of methane, or whether chemical reactions involving CO₂ also plays a role.

Abrasion strength of carbon layer

Figure 6 below shows the fraction (Wt.%) of material below 500 µm before and after the abrasion test for all experiments in the first series of experiments. In all cases, treatment in the drum increases the amount of fines. It can be noted that the fines-generation in the experiments at 790°C is comparable to that of the other samples. If the carbon layer had disintegrated easily and created a lot of fines, it would be expected that there was a big difference between samples from 790°C and the other experiments, since the samples at 790°C had no methane decomposition and no carbon deposited.

The generated fines-fraction was analysed for its carbon content. Where pre-drum analyses were available, an average of 99% of C remained in the > 500µm fraction and 96% in the > 5mm fraction. As it was mentioned earlier in the section, the Leco analysis is not the best method of comparing carbon levels in this work. As worst-case scenarios, it can be assumed that the generated fines are 100% carbon. In this scenario, for samples with significant carbon deposition, 81% of the deposited carbon material would remain in the > 500µm fraction. When also considering the 500µm-5mm fraction, the weight of material < 5mm is greater than the weight of the deposited carbon. However, this worst-case scenario is not realistic. As the comparison of fines-generation in carbon-free materials shows, the fines fractions are far from 100% carbon.

These results point towards good adhesion between the carbon and the slag. There is nothing in these results that indicate that the material would not survive normal transport to/around an industrial plant.

Estimation of accuracy

As was mentioned, the chemical analyses were not judged to be trustworthy estimates of the deposited carbon, and weight change data was used. However, loss of material during transfer, and dust/flakes of crucible material falling into the charge could also lead to weight change, giving rise to uncertainties in these estimates. The uncertainties can be estimated from the experiments at 790°C, where the expected weight change is 0 but the recorded values are - 7.9g, + 4.9g and + 0.2g. This means that uncertainties are at least $\pm 7.9\text{g}$, and in this work, a value of $\pm 8\text{g}$ has been used.

Conclusions And Outlook

This work has shown the potential for use of biogas/biomethane as a non-fossil source of carbon in manganese production, with hydrogen and/or syngas as a potential by-product.

It has been shown that carbon can be deposited on HCFeMn slag from CH_4 and $\text{CH}_4\text{-CO}_2$ gas mixtures. While the process has not been optimised, the best achieved results gave an amount of deposited carbon equal to $37 \pm 4\%$ of the amount necessary for reduction of all MnO in the slag. This result was obtained with 90% CH_4 -10%Ar at 1100°C and with 2.35 l/min total gas flow.

Temperature was the most important parameter. No CH_4 -decomposition or carbon deposition was detected below 1000°C, and increasing the temperature from 1000°C to 1100°C gave increased CH_4 -decomposition and carbon deposition. For other parameters, a lower gas flow gave more CH_4 -decomposition, but it could not be determined whether this translated into a greater deposition of carbon. The presence of CO_2 reduced the carbon deposition, but it is not clear at present whether it is because of dilution of methane or other effects like Boudouard reaction.

The process produces hydrogen-rich off-gas as a by-product, more than 70% in the best cases. CO_2 in the process gas was converted into CO, and while its presence decreased the carbon deposition it did not fully suppress it. It is thus possible to use non-enriched biogas as the carbon source, in which case the gaseous by-product is a mixture of H_2 and CO. Which of these options will be the optimal solution is far too early to tell, and will not at least depend on the performance of the composite material in manganese production.

Declarations

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Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

Author Information and contribution

All authors are affiliated with the Department of Metal Production and Processing, SINTEF Industry, Trondheim, Norway.

H. Dalaker helped plan the experiments and wrote and prepared the manuscript. J.E. Gjøvik planned and performed the experiments and revised the manuscript. E. Ringdalen helped plan the experiments and revised the manuscript.

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Figures

Step 1
New additional process

Step 2
Existing Mn-alloy furnaces

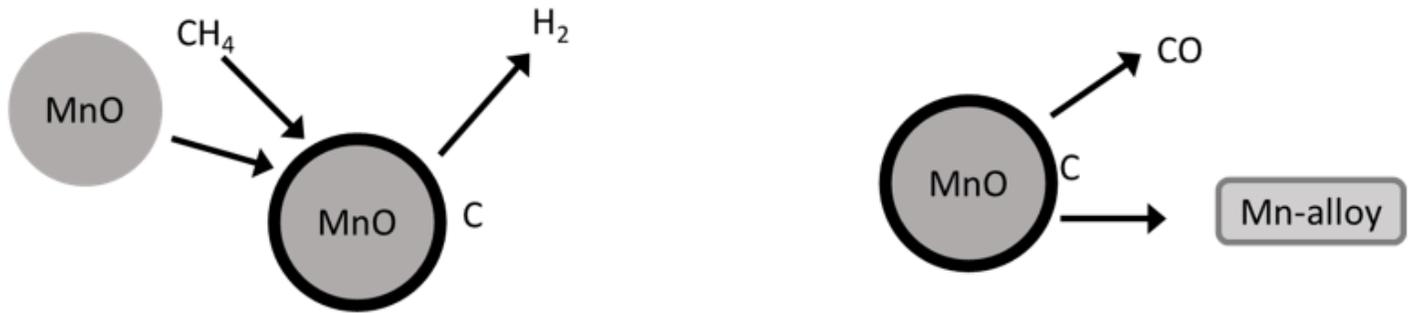


Figure 1

Principle sketch of the idea behind the current work. A two-step process is imagined. Step 1 is a new process: the deposition of carbon on MnO from methane, with hydrogen as a by-product. Step two is to use the produced composites in existing furnaces, in a process very similar to today's.

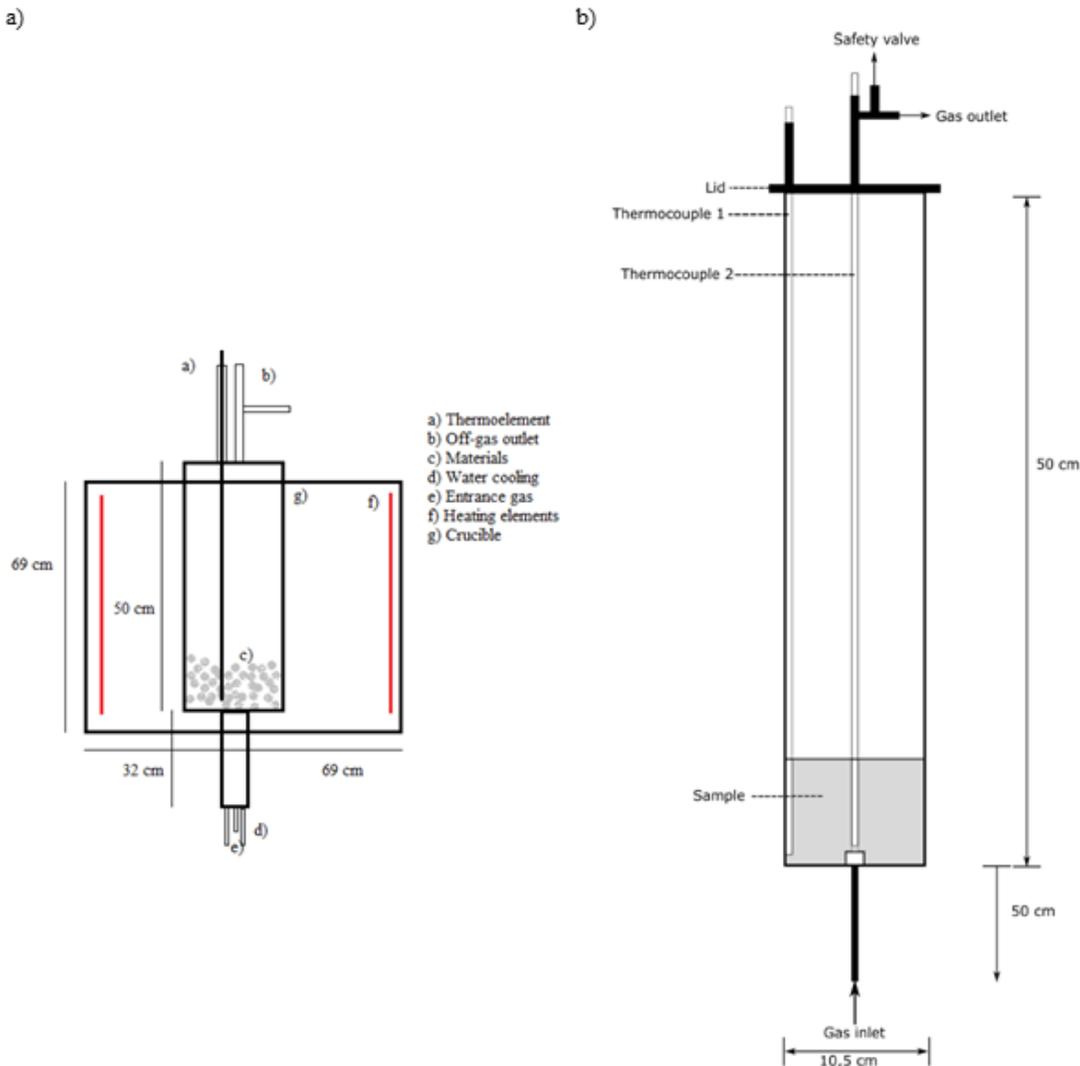


Figure 2

Sketch of the experimental setup. Figure 2a shows a sketch of the whole furnace chamber[10], while 2b shows the crucible in more detail.

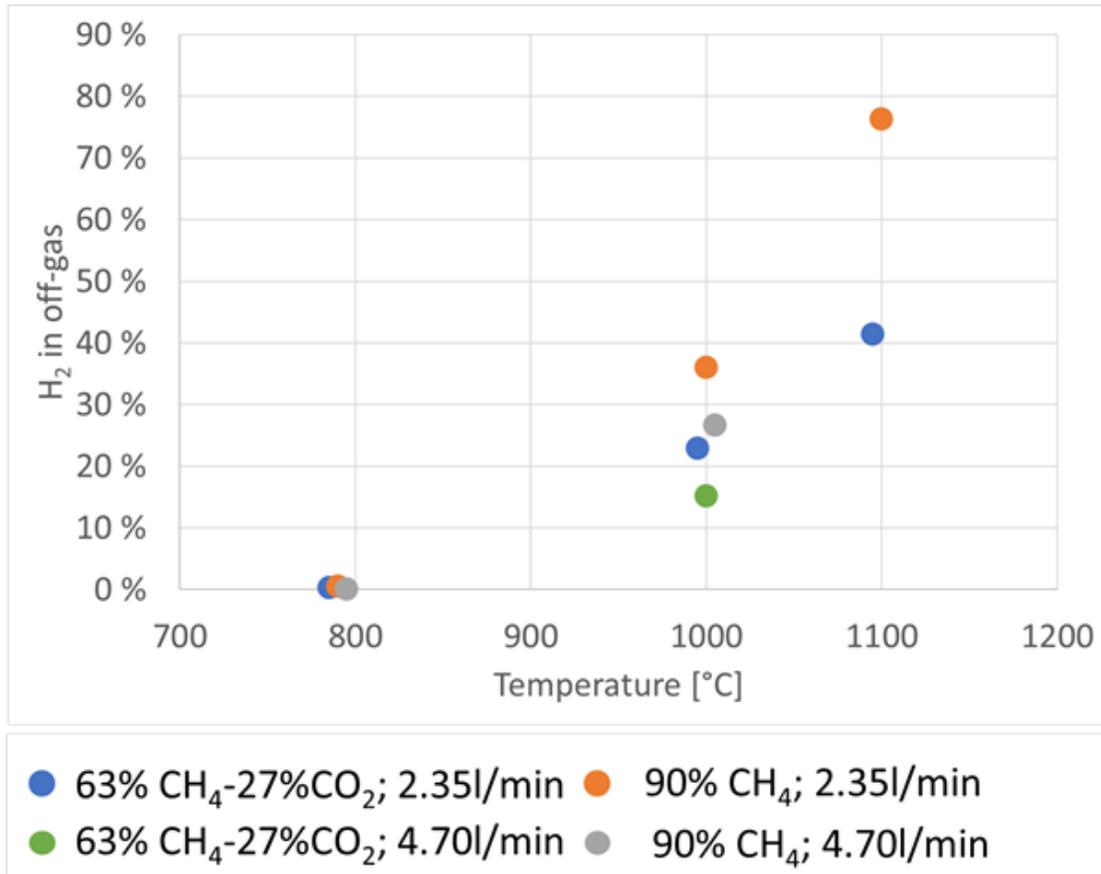


Figure 3

Hydrogen content in the off gas of all experiments, plotted versus temperature. For repeat experiments, each data point represents an average of all experiments with identical experimental parameters. The data points at common temperatures have been spaced out along the x-axis to improve readability. All data points have been recorded at T= 790 °C, 1000 °C or 1100 °C, respectively.

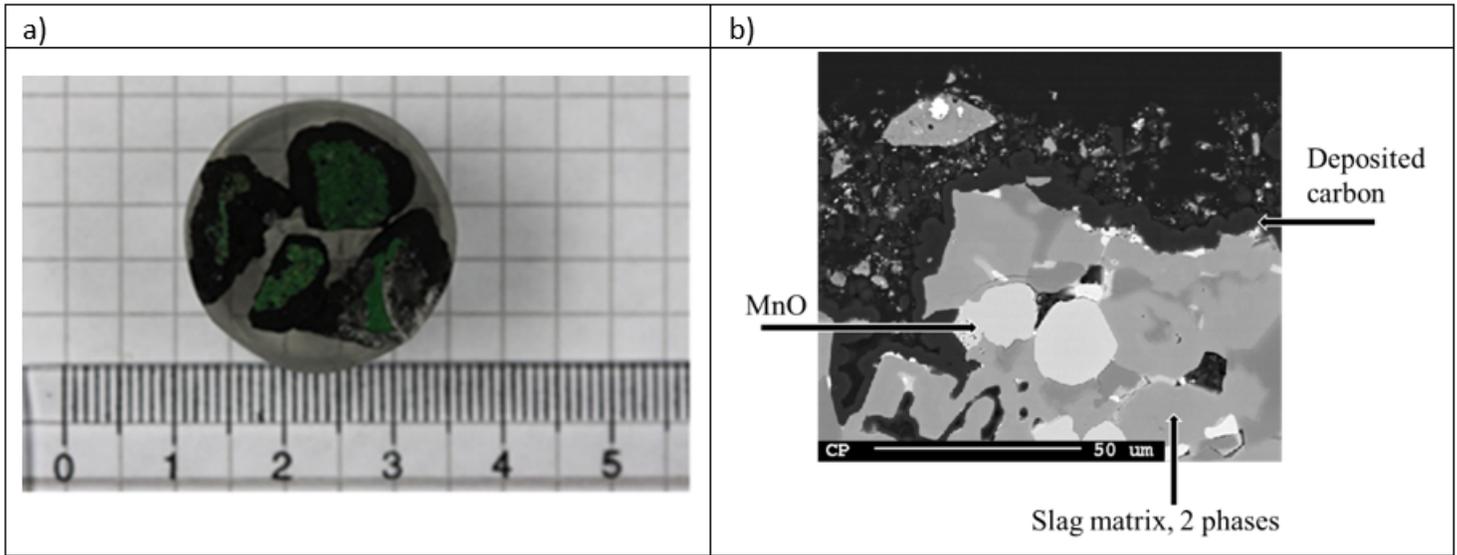


Figure 4

Example images of samples showing deposited carbon, both from experiment 6 (1000 °C, 90%CH₄-10% Ar, 2.35l/min) a) Macroscopic image showing black layers on the greenish slag. b) 500x magnification back scatter EPMA image showing the different slag-phases and the deposited carbon layer.

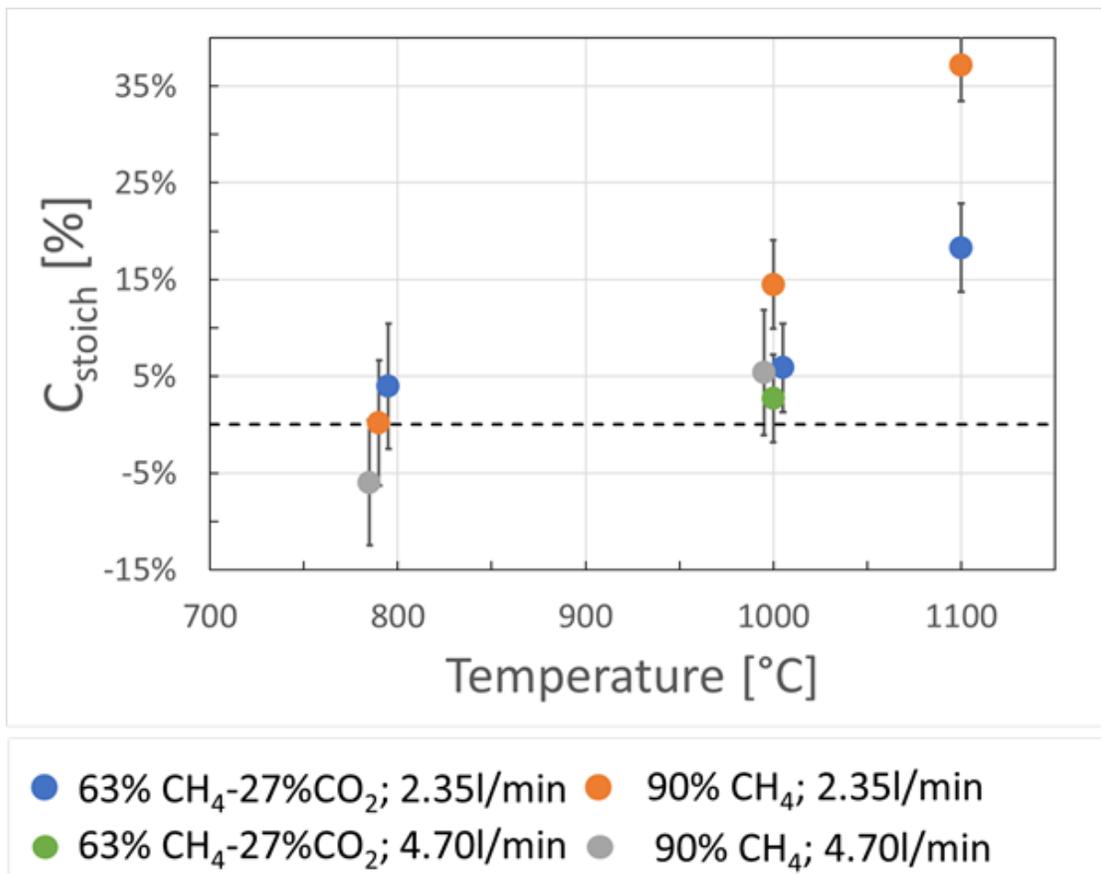


Figure 5

Amount of carbon deposited for all experiments, based on weight measurements, expressed as C_{stoich} (see text). For repeat experiments, each data point represents an average of all experiments with identical experimental parameters. The data points at common temperatures have been spaced out along the x-axis to improve readability. All data points have been recorded at T= 790 °C, 1000 °C or 1100 °C, respectively.

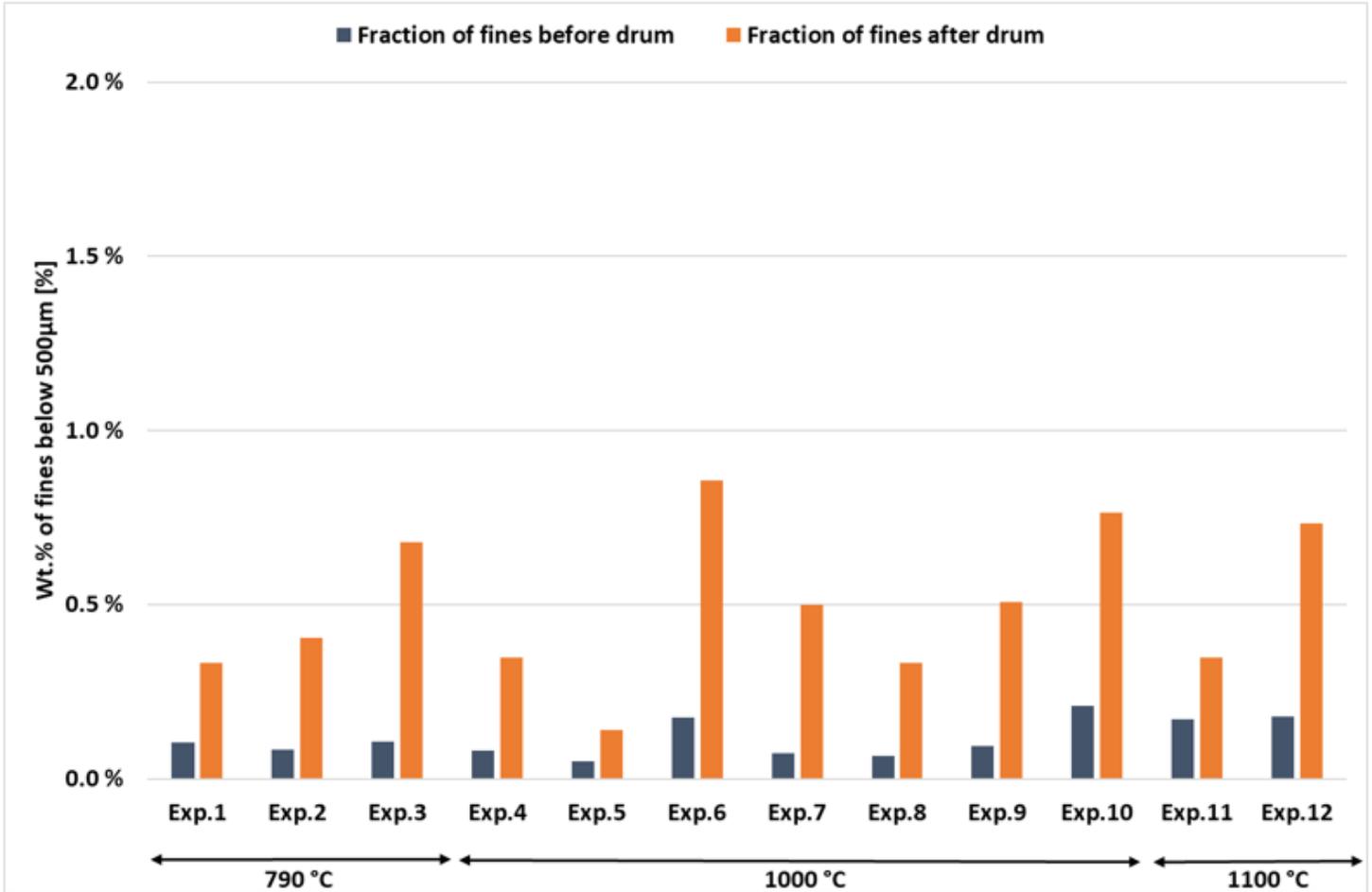


Figure 6

Fraction of fines (<500µm) before and after abrasion treatment in Hannover drum for alle experiments in experimental series 1.