Reducing Ultra-Clean Transportation Fuel Costs with HyMelt® Hydrogen

Quarterly Report

October 1 – December 31, 2003

January 2003

Work Performed Under Cooperative Agreement No. DE-FC26-02NT41102

For

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ABSTRACT

This report describes activities for the fifth quarter of work performed under this agreement. A third round of atmospheric testing was conducted as scheduled on December 9 through December 12, 2003. The test results demonstrated a much-improved rate of carbon dissolution with gas yields close to thermodynamic equilibrium at nearly doubled feed rates of September testing and a commercially viable feed and oxygen injection technique. Additional super-atmospheric testing to perform the last task in the MEFOS experimental program is scheduled for the week of August 2004.

TABLE OF CONTENTS

1.0 Project Objectives, Scope and Description of Tasks

1.1 Introduction

1.2 Scope of Work

1.3 Phase I Task Description

2.0 Executive Summary of Work Done During This Reporting Period

3.0 Experimental

4.0 Results and Discussion

5.0 Conclusion

6.0 References

7.0 Plans for the Next Quarter

Appendix I MEFOS DATA

1.0 PROJECT OBJECTIVES, SCOPE AND DESCRIPTION OF TASKS

1. Introduction

EnviRes and DOE executed the cooperative agreement for this work on September 19, 2002. This document is the fifth quarterly progress report under this agreement. Kvaerner, MEFOS and Siemens Westinghouse will conduct most of the significant tasks in this project through subcontracts with EnviRes.

1.1 Scope of Work

Phase I of the work to be done under this agreement consists of conducting atmospheric gasification of coal using the HyMelt technology to produce separate hydrogen rich and carbon monoxide rich product streams. In addition smaller quantities of petroleum coke and a low value refinery stream will be gasified. DOE and EnviRes will evaluate the results of this work to determine the feasibility and desirability of proceeding to Phase II of the work to be done under this agreement, which is gasification of the above-mentioned feeds at a gasifer pressure of approximately 5 bar. The results of this work will be used to evaluate the technical and economic aspects of producing ultra-clean transportation fuels using the HyMelt technology in existing and proposed refinery configurations.

1.1 Phase I Task Description

Task 1.1 Project Management and Planning

This task includes all project planning; experimental test plans; risk analysis; implementation of a bridge loan, purchasing, contracting and accounting systems with requisite auditing; and execution of contracts with MEFOS, Kvaerner and Siemens Westinghouse. This task is being executed.

Task 1.2 Preparation and Shipment of Feedstock Materials

This task consists of procuring 25 tons of coal, 15 tons of petroleum coke and 48 – 55 gal drums of aromatic extract oil; transporting the coke and coal to a pulverizing facility; pulverizing, drying and loading the coke and coal into bags; and shipping the feedstocks to MEFOS in Lulea, Sweden. EnviRes completed this task

Task 1.3 Predictive Modeling of the HyMelt Process

This task consists of generating detailed reactor energy and material balances for each feedstock using the Fact Sage pyrometallurgical thermodynamic modeling program. Kvaerner will perform detailed process simulation using the Aspen Plus process simulator. Kvaerner,

MEFOS and EnviRes will evaluate and analyze the results of predictive modeling. This task is being executed.

Task 1.4 Combustion Modeling and Analysis

Siemens Westinghouse will perform combustion turbine modeling using fuel gas conditions and compositions provided by task 1.3. This task is being executed.

Task 1.5 Design and Fabrication of Pilot Plant Specific Molten Iron Bath Apparatus

MEFOS will design and fabricate all solid feeding systems and oxygen injection systems required by the testing. EnviRes will assist MEFOS in designing the petroleum liquid feed system. MEFOS will design the shell of the high-pressure reactor. MEFOS and EnviRes completed the originally planned injection system for this task. MEFOS and EnviRes designed and fabricated a tuyere for submerged injection. MEFOS and EnviRes designed and fabricated a commercially feasible tuyere for testing in December. We performed the testing as planned.

Task 2.0 Project Testing

Task 2.1 HyMelt Atmospheric Pressure Testing in a Molten Iron Bath

MEFOS designed and fabricated the petroleum liquid feed system. This injection system was tested in a cold flow environment. The injection systems were hot commissioned. Any equipment revisions indicated by cold flow testing and hot commissioning were made. Process performance testing was performed for each feed. Execution of this task continues.

2.0 EXECUTIVE SUMMARY OF WORK DONE DURING THIS REPORTING PERIOD

MEFOS completed the technical report of testing performed September 2-4, 2003. This report contains a detailed analysis of the work performed for this test period. We present additional analyses and comments on this work with comparisons to previous testing and computer modeling. EnviRes and MEFOS performed additional testing December 9-12, 2003. We present preliminary reporting of the testing performed in December in this report.

The September activity tested feed introduction with a submerged tuyere to improve carbon dissolution in the metal bath. It demonstrated that submerged tuyeres give significantly superior performance in contacting feed with bath metal as compared to top entry lances. Decarburization was still performed with a top entry lance during September testing.

Once we realized the benefits of submerged tuyeres for feed introduction, we felt it necessary to test submerged tuyeres in a commercially practical configuration. Testing in December successfully demonstrated this. This configuration allows oxygen injection by submerged tuyere, which we feel is an added benefit of this design. We believe that submerged oxygen injection will result in less FeO in the slag and therefore less CO in the product hydrogen.

We incorporated design concepts demonstrated by the September and December testing into the vessel to be used for pressure testing. We believe that pressure testing will incorporate the best known configuration and design features of the HyMelt process.

3.0 Experimental

MEFOS Activities

Testing performed September 2 to 4, 2003 using a submerged injection tuyere demonstrated much better carbon dissolution in the metal bath. The mechanical arrangements and preliminary results of this testing were reported in the previous quarterly report for this project. The MEFOS technical report for this activity issued on October 27, 2003 and can be found in Appendix I of this report. A more detailed analysis of the September 2003 testing appears later in this document. Detailed mechanical drawings of the tuyere used in September testing appear on page 4 of Appendix I. Photographs of this tuyere and a description of the experimental activities conducted in September appear in the previous quarterly report.

The work done in September demonstrated that a submerged tuyere gave much better results for feed injection, but a top entry lance still performed the oxygen injection decarburization step. This is not a practical method for commercial operation because a submerged tuyere in a molten iron bath requires a substantial flow through it as long as it is submerged to prevent metal infiltrating the tuyere and occluding the follow path. During the September testing a large flow of nitrogen kept the tuyere open when oxygen blowing through the top entry lance occurred. This is not practical commercially because any gas other than the product gas used to keep the tuyere open would dilute the product gas. Even if the product gas is recycled to the tuyere during decarburization, a substantial heat penalty occurs because the recycle gas must be cooled to less than 250°C to facilitate compression and other handling. This gas then reheats in the melt to 1400° or 1500°C. Greater capital and operating costs ensue to facilitate the recycle stream.

Normally the universal converter could not be kept in heat balance because it was tipped after each decarburization and each feed injection for slag sampling, metal sampling and inspection. MEFOS kept the system in heat balance by adding aluminum bars to the melt before the oxygen blow. Aluminum reacts very exothermically with oxygen. The aluminum oxide reports to the slag. During 2 consecutive cycles on September 4 we were able to stay in heat balance without adding aluminum bars even though the heat loss from the UC is proportionately much larger than the heat loss would be for a larger size vessel.

Since larger molten iron containing reactor vessels must be used in commercial operation, a second issue of multiple injection tuyeres arises. Generally, multiple injection tuyeres allow higher injection rates for the same level of carbon dissolution because multiple injection tuyeres result in better mixing and spread out the carbon over the vessel. Mutiple injection tuyeres can be more problematic with respect to mechanical arrangement. If one tuyere starts to occlude, more flow goes to the other tuyere(s) and exacerbates the occlusion problem unless separate flow systems are used for each tuyere.

Once we demonstrated that a submerged tuyere gave acceptable performance for feed injection we felt obliged to demonstrate a commercially acceptable method that incorporated submerged tuyere feed injection with an acceptable method for decarburization using multiple tuyeres. Such a configuration was developed and successfully demonstrated in the December testing.

MEFOS observed some refractory erosion in the refractory wall after September testing. The erosion was primarily in the vicinity of where the submerged tuyere had been. This tuyere entered through the side of the vessel near the bottom rather than through the bottom. MEFOS added a course of refractory brick in the lower section of the UC. Figure 1 depicts the added refractory addition on the left side of the figure only. The refractory was, of course applied to the entire interior of the UC. This made the UC id somewhat smaller resulting in a bath height of 800 mm instead of 500 mm for the standard metal charge of 5500 kg.

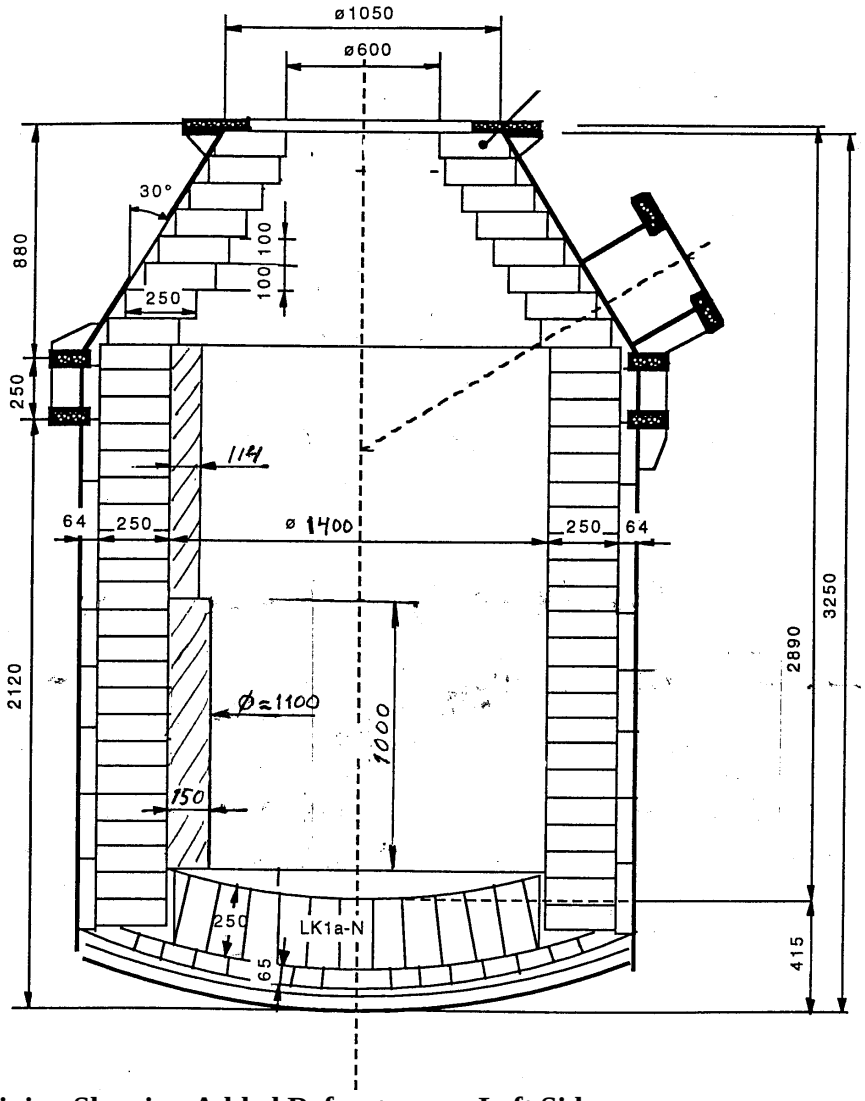

Figure 1. UC Lining Showing Added Refractory on Left Side

MEFOS performed as analysis in the September testing with two mass spectrometers in addition to the infared analyzers for CO, CO_2 and H_2 and a paramagnetic analyzer for O_2. Two mass spectrometers were used because one gave poor results for lower atomic weight species while the other gave poor results for higher atomic weight species. MEFOS used a single mass spectrometer of later design in December testing.

The first day of operation with the new tuyere system was December 9, 2003. The metal charge for the UC, as always, must be melted in a separate electric arc furnace (EAF), transported by ladle to the UC and poured into the tilted UC. On this day MEFOS experienced hydraulic problems with the EAF. The EAF had melted the charge, but couldn't be tilted to pour the charge into the ladle. The MEFOS maintenance group fixed the problem. The charge metal was poured into the UC at 1:30 pm, approximately 3 hours later than planned. As usual, we decarburized the melt with an oxygen injection. We observed that the maximum oxygen injection rate was 7 to 8 m^3n/min where we had been able to get 10 m^3n/min in September testing. After completing oxygen injection we injected coke. We used coke because we felt

that it was less likely to stick in the tuyere.. After feed injection, we made a second oxygen injection for decarburization. MEFOS does not normally sample the product gas during decarburization, but on this test we decided to sample the decarburization gas so the sample probe was inserted into the UC at the beginning of the oxygen injection. After the conclusion of oxygen injection when the operator tilted the vessel for melt sampling, he neglected to remove the sample probe from the UC first. The sample probe was badly bent. The sample probe is water-jacketed. Straightening the sample probe in this configuration had never been done before. Leaking a large volume of water into the UC during operation can be dangerous. MEFOS concluded that the sample probe could not be repaired in a reasonable time to allow further testing. We decided to pour the metal out of the UC. The MEFOS maintenance group worked into the night repairing the sample probe.

MEFOS had the sample probe repaired by the beginning of shift on December 10. After we charged the pig iron from the EAF to the UC we performed a normal oxygen injection for decarburization and metal heating. We injected coke at 27 kg/min to a target metal carbon of 4%. We performed a second decarburization. At the end of this decarburization, the flow meter for propane going into the annular slit of the tuyere exploded. No other damage or injuries occurred, but no further testing could be performed until we replaced the flow meter. This meant that no further testing could be done on this day. MEFOS found a replacement flow meter and completed installation of it by the beginning of the shift on December 11.

We determined that a leaking check valve in the air line caused the flow meter explosion. Air mixed with propane at 7 to 8 bar. The thermal conductivity cells in the flow meter were probably the ignition source. We replaced the check valve with a remotely actuated ball valve to preclude a second failure.

Metal charge was melted in the EAF and transferred uneventfully to the UC as scheduled on the morning of December 11. We decarburized the metal according to schedule. The initial injection feed for testing was ILL #6 coal. We injected coal for 4 cycles. We followed each coal injection with an oxygen decarburization. This nearly emptied the charge hopper. We emptied the remaining coal and filled the hopper with coke. We planned to inject coke for 2 cycles before the end of the workday. After the first coke injection, where we achieved a maximum injection rate of 27 kg/min, we observed some of the refractory brick, added after September testing, floating on the surface. This was not dangerous because the refractory thickness behind the bricks that came loose was sufficient for safe operation, but continuing to operate with refractory bricks in the slag would result in very viscous slag. We tapped the slag with the bricks still floating in the slag and then we tapped the metal. December 11 was the last scheduled day of testing. MEFOS decided to test on December 12 because we had experienced so much down time. The MEFOS maintenance group gunned castable refractory over the top layer of bricks that were coming loose. This prevented further loss of bricks in subsequent operation. In Figure 2 the refractory bricks float near the bottom of the throat of the UC as it is tilted for tapping slag.

On the morning of December 12, we charged and decarburized the metal in the UC as described earlier. We made 3 coal injections and 3 decarburizations after the initial decarburization. We achieved a maximum coal injection rate of 27 kg/min. A problem with the in-blow temperature probe and sampler precluded temperature measurement or sampling

during injection. We performed temperature measurement and sampling with the UC tilted at the end of each injection. We monitored the accretion formation on the bottom of the UC by visual inspection. While the size of the accretion on each tuyere increased and decreased from injection to injection, we did not observe any general increase in the accretion on either tuyere. The accretions on both tuyeres at the end of testing on December 11 appear in Figure 3.

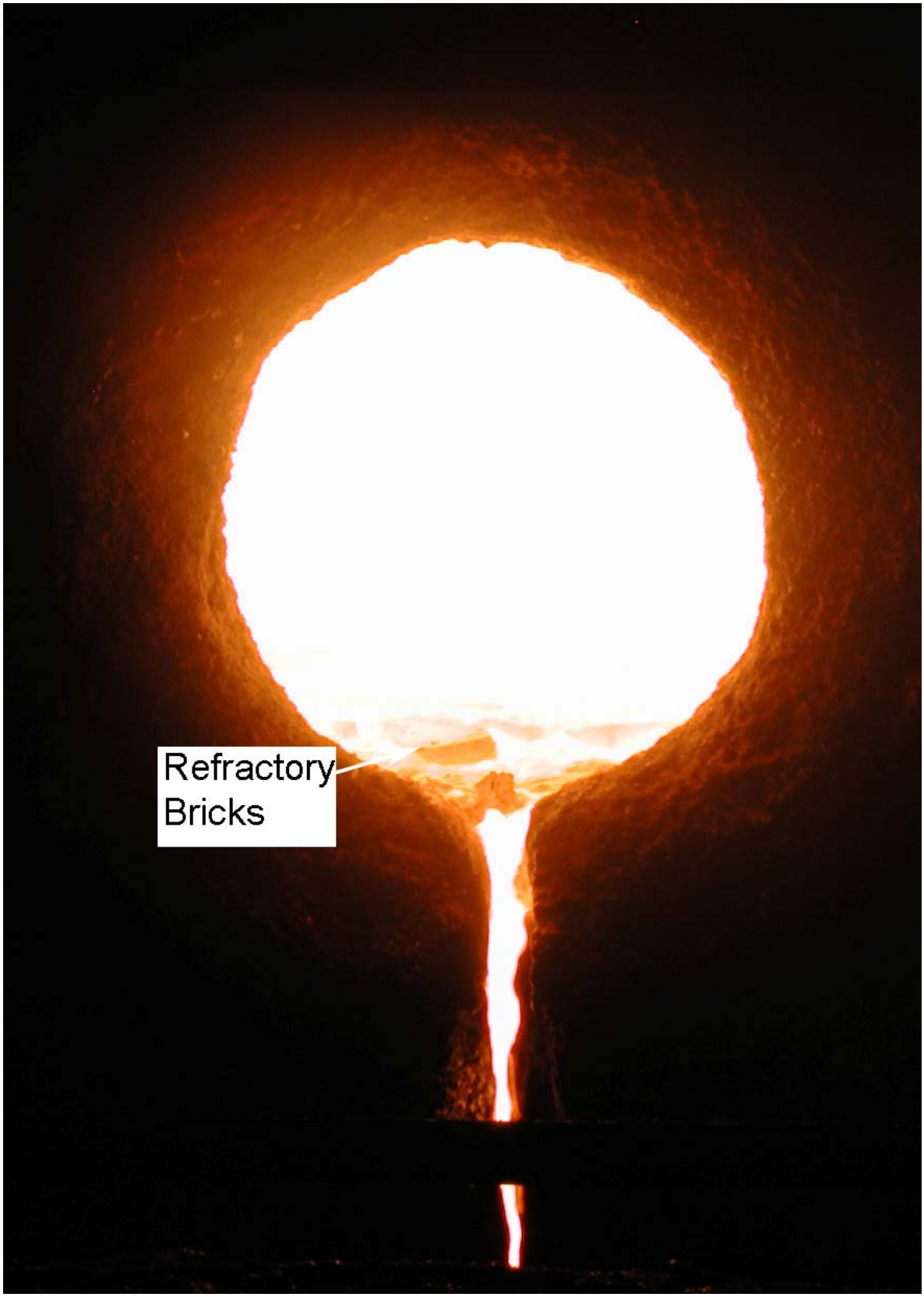

Figure 2. A View of Refractory Bricks after Becoming Disloged

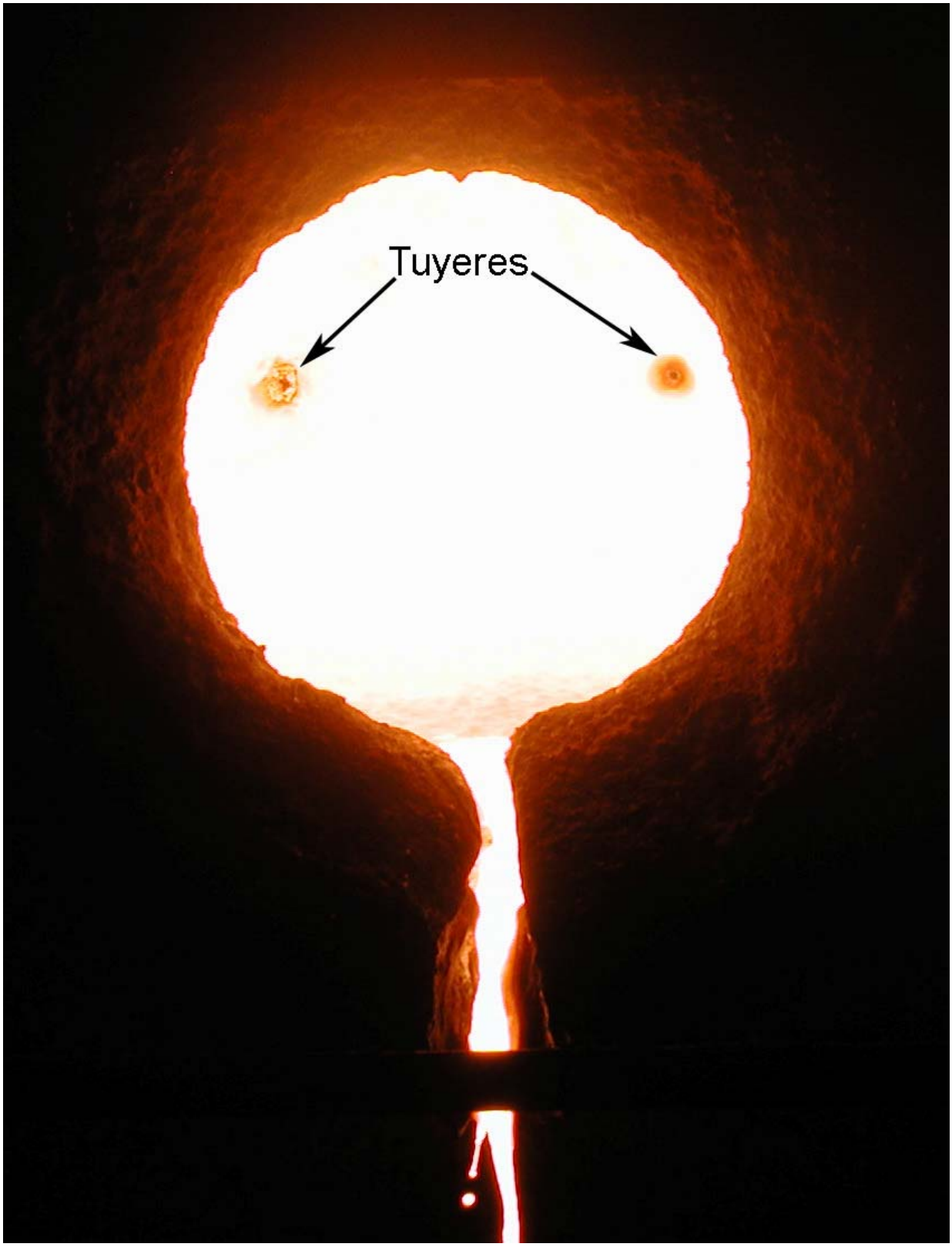

Figure 3. A View of Tuyeres and Accretions at the End of Testing, 11 Dec 03

Kvaerner Activities

No activities were performed pending completion of atmospheric testing.

Siemens Westinghouse Power Corporation Activities

No activities were performed pending completion of atmospheric testing.

4.0 Results and Discussion

MEFOS Activities

For all injections performed in June, the methane content of the product gas was in the range of 5 to 10%. In September testing the methane content typically remained below 0.5% as shown on pages 12 and 13 of Appendix I. High values of methane in the product gas indicate poor feed metal contact. The carbon yield to metal ranged from 58% to 88% for petroleum coke while it was fairly steady at 55% for coal. The carbon yield to metal was significantly worse in June testing especially as the feed rate increased. Carbon yield to metal is evaluated as the quotient of the change in the total mass of carbon dissolved in the metal divided by the total mass of carbon contained in the injectant for the period in question. Since the yield to metal is expressed as a percentage, the quotient above should be multiplied by 100. We gave a discussion of some of the mechanisms that cause the yield to metal to be less than 100% in the previous quarterly report.

MEFOS gives a detailed presentation of data generated in September testing in Appendix I. We will provide some analysis of these data in this section. We believe that the hydrogen purity of the product gas during feed injection is perhaps the most important gas component. A retractable, water jacketed sample probe with a coarse, castable high alumina plug at its end conveys the sample stream from the upper part of the interior of the UC, through a more efficient secondary filter and then to the various analyzers. The UC operated at near atmospheric pressure this necessitates the use of a suction pump to move the sample stream. MEFOS points out in Appendix I that they analyze for hydrogen with three different analyzers. As noted the infrared analyzer can read a maximum value of 21% hydrogen.

Figures 9 and 10 on page 10 of Appendix I show plots of the readings of these three analyzers versus time. It appears that the two mass spectrographic analyzers give good agreement when the difference in response time between the two analyzers is considered. Raw hydrogen values of 45% to 65% appear in these tables. MEFOS observed that oxygen appears in all of the product gas samples. Oxygen and hydrogen values in the product gas as a function of time appear in figures 7 and 8 on page 9 of Appendix I. The presence of oxygen in this stream can only be explained by air leaking into the sample stream after cooling since the temperature of the UC is well above the autoignition temperature for these mixtures. Normalized values for hydrogen ranging from 60 to 80% appear in figures 29 and 30 on page 21 of Appendix I. These normalized values still contain 7% to 12% argon, the transport gas for coal and coke. The slit air for the injection tuyere accounts for 2 to 4% of the CO in both figures. Oxygen in coal accounts for approximately 13% CO in the process gas stream. The rest of the CO comes from reaction of FeO in the slag with carbon in the metal. This accounts for the high initial

value of CO that decreases with injection time. Note that the CO value for coal injection is 10 to 15% higher that for coke injection in figure 30. This is consistent with the expectation that oxygen in coal converts entirely to CO. Coke contains little oxygen. The first three injections were coal the last three were coke in figure 30.

As noted in Appendix I, COS values range from 50 to 200 ppm compared to 100 to 300 ppm observed in June testing. Figures 21 and 22 in Appendix I show that the benzene value in the product gas stays below 100 ppm. Figures 23 and 24 show that acetylene values range around 1500 ppm. Figures 27 and 28 show that HCH values generally stayed below 20 ppm. The H_2S value stays below 0.020%. It does increase with metal sulfur content, but is well below the expected thermodynamic value. We suspect that the highly basic slag captured some of the H_2S from the product gas. Since the sample stream appears to contain up to 50% air, the above values should be multiplied by 2 to be consistent with the treatment of H+ and CO. Thermodynamic simulation reported earlier[1] gave values for trace constituents similar to these.

Figures 44 and 45 indicate that the slag captured most of the sulfur in the feed. Figures 41 and 42 show that FeO in the slag after decarburization normally ranged from 2 to 5%, but on occasion exceeded 12 %. Figures 47 and 48 show that dust loses range from 5% to 8% of feed. In commercial operation the reactor should operate at up to 30 bar. This will substantially reduce the gas superficial velocity and presumably the dust loss. The commercial design anticipates capturing dust and recycling it. Refractory wear may not be significant since the refractory in the UC was not optimized for this operation.

We see little difference in trace impurities between coal and coke injection. For the most part this is not surprising since the elemental compositions of the two feeds are similar except for significantly higher values of ash and oxygen for coal and correspondingly higher values for the other major constituents for coke. The one trace constituent value that is surprising is benzene. Coal has more benzene like structures than petroleum coke. One would think that the values for benzene would therefore be higher for coal than for coke if one accounts for the formation of benzene by the incomplete destruction of the feed.

5.0 Conclusions

We significantly improved carbon dissolution rates by injecting feed with a submerged tuyere rather than a top entry lance. It appears that the 5% to 8% dust loss is the only carbon that is not otherwise reacted as thermodynamically predicted or fails to dissolve in the metal. We believe that much less dust loss will occur in pressurized operation. We would capture and recycle most of this material in commercial operation. We attained a maximum feed rate of 10 kg/min for coal and 18 kg/min using petroleum coke with a single tuyere in September testing. In December testing we attained a maximum feed rate of 27 kg/min for coal and 27 kg/min for coke using two submerged injection tuyeres. This leads us to believe that higher carbon dissolution rates could be attained with an additional tuyere or tuyeres.

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[1] Malone, D.P. and Renner, W R, “Reducing Ultra-Clean Transportation Fuel Costs with HyMelt Hydrogen”, Quarterly Report, April 1 – June 30, 2003, Agreement Number DE-FC26-02NT41102, July 31, 2003, Appendix I, p 11.

We were able to measure and quantify trace constituents. We observed gas yields for major and trace constituents to be near thermodynamic equilibrium. Other than increased CO in the product hydrogen stream when coal is fed resulting from oxygen contained in the coal, there is little difference in the product stream compositions for coal compared to that for coke.

We were able to demonstrate a commercially viable tuyere configuration in December testing. We await the technical report from MEFOS on this testing. Getting slag samples analyzed accounts for most of the delay in completing the MEFOS technical report.

The pressurized reactor being designed now will incorporate submerged tuyere(s) for feed injection.

6.0 References

Malone, D.P. and Renner, W R, "Reducing Ultra-Clean Transportation Fuel Costs with HyMelt Hydrogen", Quarterly Report, April 1 – June 30, 2003, Agreement Number DE-FC26-02NT41102, July 31, 2003

7.0 PLAN FOR THE NEXT QUARTER

The newly demonstrated tuyere system will be incorporated into the design of the pressurized reactor. The design should be finalized by the end of February. We anticipate pressurized testing to begin in August 2004.

When the technical report for December testing which includes gas composition from decarburization as well as gas composition from feeding coal and coke, issues from MEFOS, Kvaerner will resume process simulation for a commercial design. Siemens Westinghouse will also initiate computational studies of turbine performance.

APPENDIX I

MEFOS DATA

CONFIDENTIAL

MEFOS

Box 812, 971 25 LULEÅ

Dokument:	Tekniskt meddelande	*Reg nummer:*	TM03054K
Fo-uppgift:		*Datum:*	2003-10-27
Konto:	387460	*Rev datum:*	
Ämnesomr:		*Avdelning:*	MM

HYMELT CAMPAIGN II,

2-4 SEPTEMBER 2003

by

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SUMMARY

A second camping has been made in the development of the HyMelt process. The equipment set up was, compared to the first campaign, rearranged. The most important modification was that the top lance injection was replaced by a side wall tuyere injection.

Two test days with stable operation and measurements were made. The first tuyere tested had to be replaced to a tuyere with an annular slit for air injection. The new design showed good performance for the rest of the camping.

Important results achieved compared to top lance injection:

- Improved carbon yield to metal, especially for petroleum coke
- Higher concentrations of hydrogen in the process gas and reduced amounts of hydrocarbons
- More stable operation and generally better routines for sampling and measurements

Remaining process difficulties:

- Metal sculling on the lance
- Not sufficient yield for coal
- Reducible oxides in the slag after oxygen blowing

1 Introduction

This document describes tests and results from the HyMelt II campaign at MEFOS, 2-4 September 2003. Campaign I is reported in MEFOS document TM03037K, and conditions equal to Campaign I are not be repeated.

Remaining issues from the HyMelt campaign I concerned:

- Carbon yield to metal during carburisation
- Evaluation of melt temperature in the process computer
- System and code for calculation of coal/coke flow rate
- Leakage air in sampled process gas for measurement
- Improved in blow metal sampling system

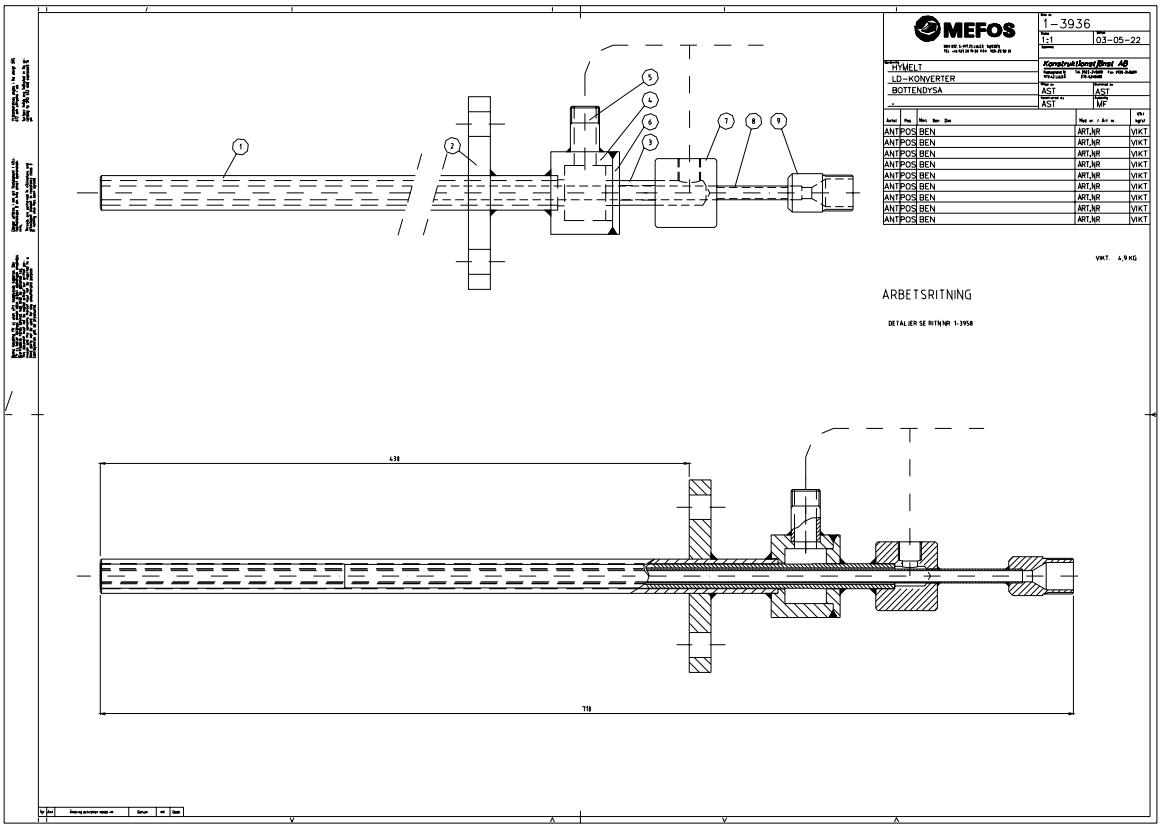
2 Equipment

Rearrangements made:

- Material injection through a wall tuyere replaced the top lance
- The bottom tuyere was plugged and not used.
- Argon was used as material carrier gas replacing nitrogen.
- A new set up of gas analysers were arranged

2.1 Tuyere design

The first tuyere tested was a single pipe tuyere with 8 mm inner diameter. Severe problem with blocking occurred early and made a replacement to a tuyere with an annular slit, Figure 1. In the slit, actually two slits, dried air was blown to prevent metal freezing and mushroom formation in the tuyere outlet. The tuyere design is optimised for other applications and it can for this process most likely be simplified to only one slit.



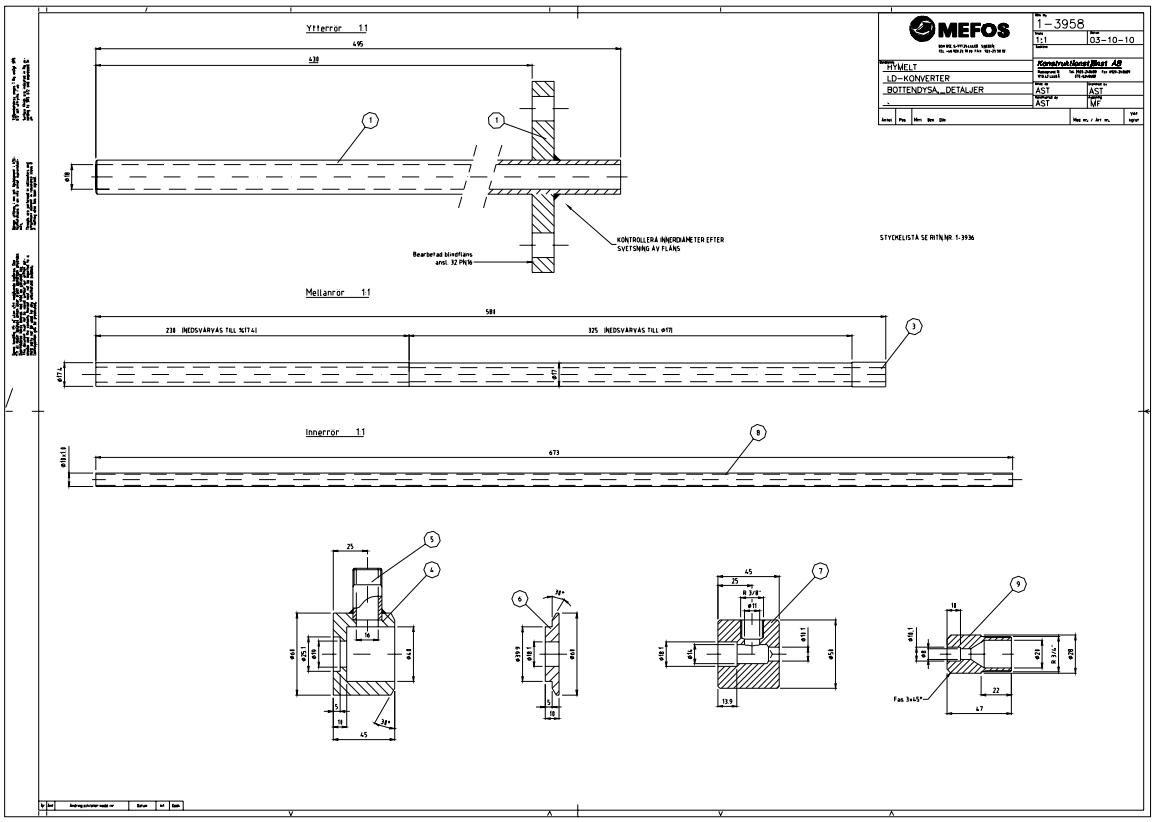


Figure 1 – Annular slit tuyere

2.2 Set up of gas analysing system

The modified set up for process gas analysers is schematically shown in Figure 2. For detail information of H-Sence and AS200 (AirSence) see Appendix 1 and 2,

The option for Hg sampling was not used in this campaign.

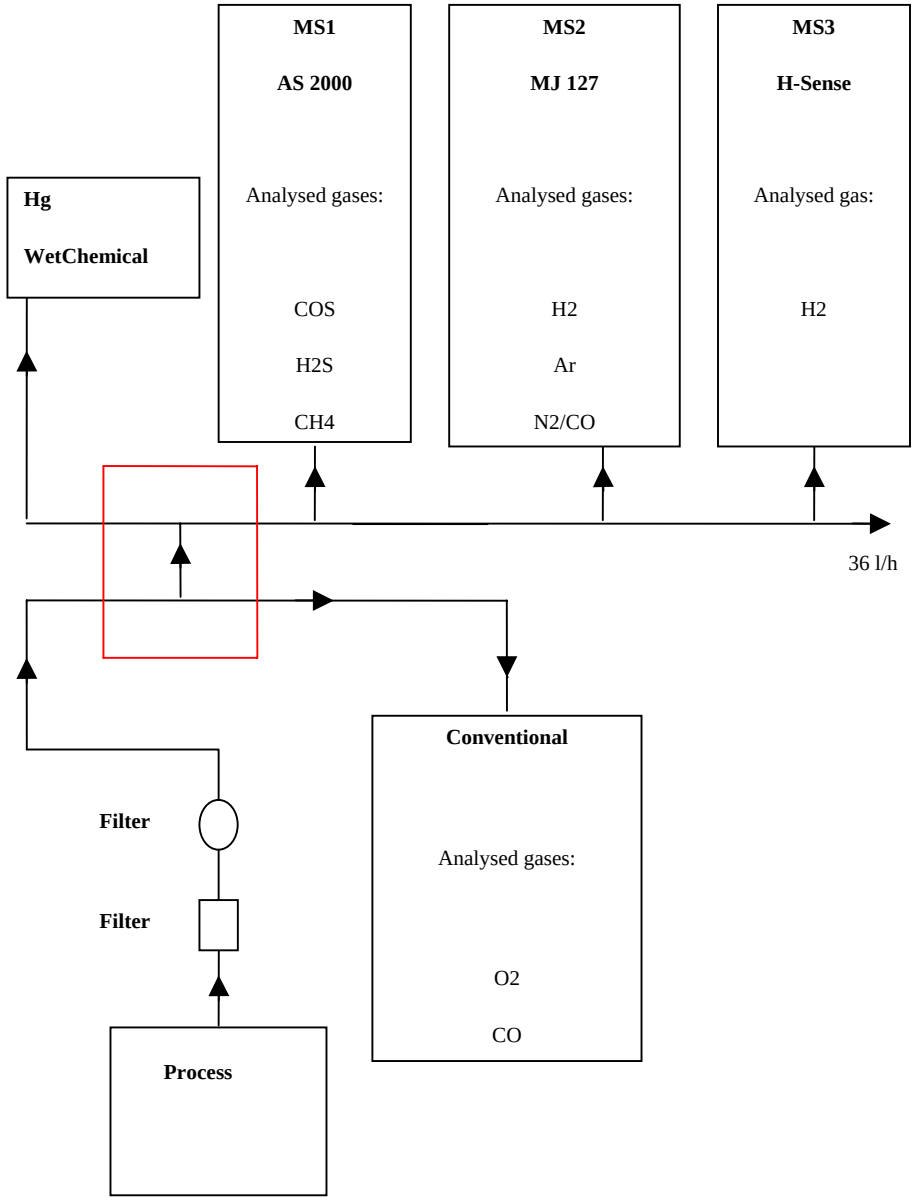


Figure 2 – Schematic set up of gas analysers

From the figure it can be seen that hydrogen was analysed by three methods. This arrangement was a result from the previous campaign in which both response time, linearity and accuracy was discussed.

Figure 3 and 4 demonstrate the problem where known mixtures of argon and hydrogen have been measured by two of the instruments.

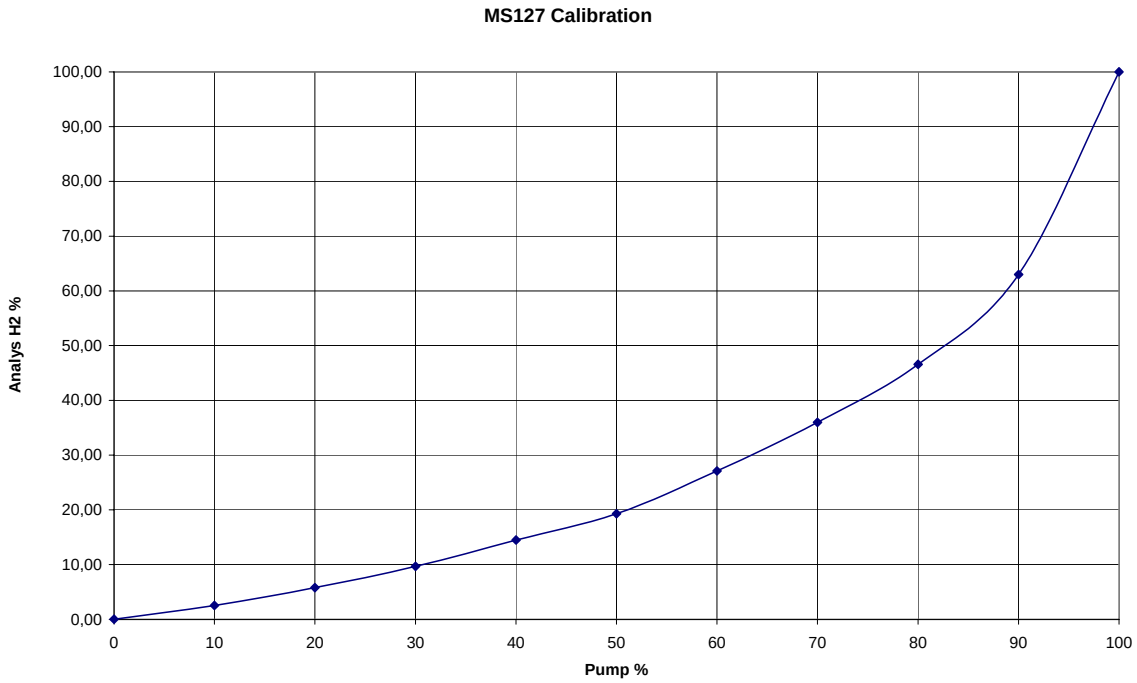


Figure 3 – MS127 results from known gas mixes

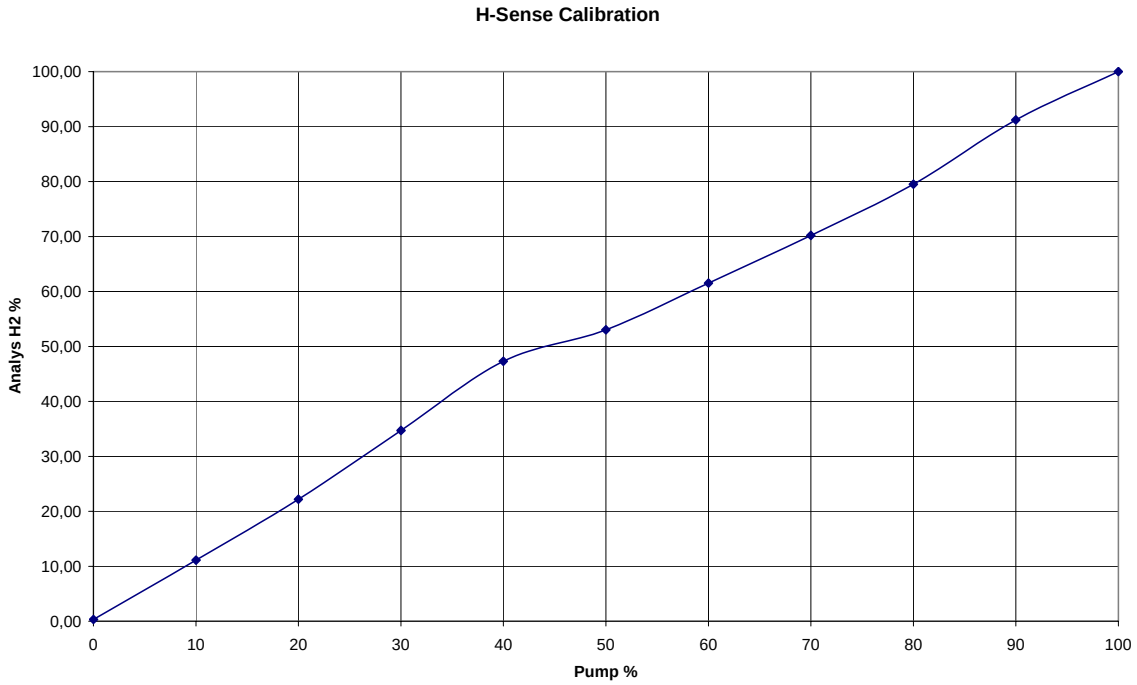


Figure 4 – H-Sense, results from known gas mixes

The H-Sense instrument is gives more reliable data and has a faster response which is of great importance due to short measuring periods.

3 Material

The same materials as for previous test were used, for information see TM03037K.

4 Test procedure

The tests were carried out according to the same routines as for the previous test, for information see TM03037K.

5 Heat notes

5.1 HyMelt 7, 2 September 2003

The test was interrupted after a water leakage from the oxygen lance during initial decarburisation. The steel was tapped and transferred to the EAF.

5.2 HyMelt 8, 2 September 2003

The wall tuyere was immediately blocked during the first coal injection period. After tapping it was removed and replaced by a concentric tuyere. In the outer slits dried air was blown. The idea was to avoid freezing of metal, mushroom formation, in front of the tuyere by a balanced oxygen feed. The air flow supply was arranged in a separate system, manually controlled and logged.

5.3 HyMelt 9, 3 September 2003

Five coke injection tests were made during the day. Sampling of metal, slag, gases and dust could be made for all periods.

5.4 HyMelt 10, 4 September 2003

Three coal and tree coke injection periods where made. Sampling of metal, slag, gases and dust could be made for all periods.

An obvious higher part of injected carbon is transferred to metal from coke compared to coal.

6 Results

6.1 Test periods

Evaluation has been made for HyMelt 9 and HyMelt 10. HyMelt 7 and 8 are not evaluated because of short tests and unstable conditions.

6.1.1 HyMelt 9

For all injection periods coke were used. The injection rate varied between 6 to 14 kg/minute.

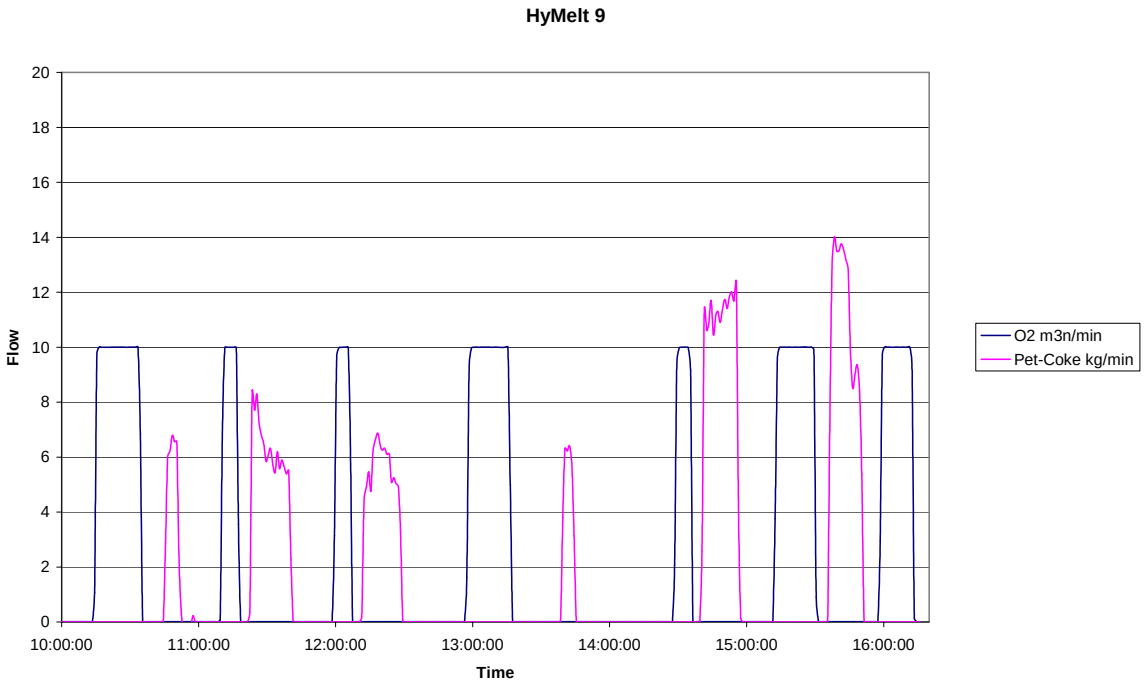


Figure 5 - Injection periods and oxygen blowing periods for HyMelt 9

6.1.2 HyMelt 10

For the first three periods coal were injected and for the remaining three coke were used. The injection rate varied between 6 to 18 kg/minute.

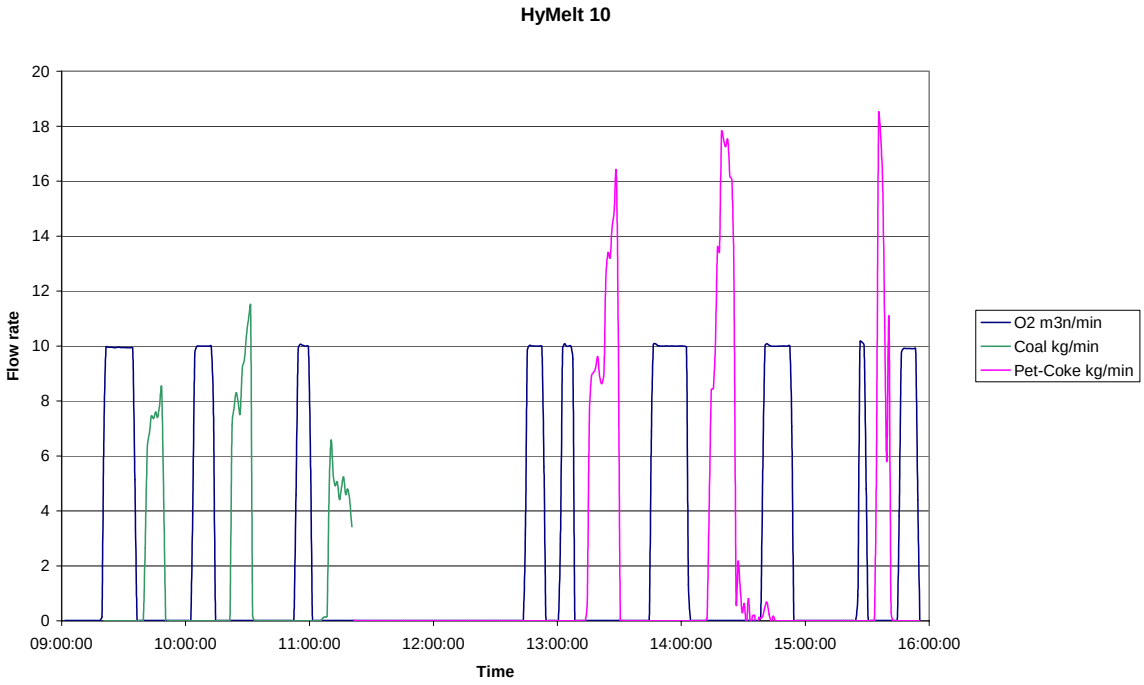


Figure 6 - Injection periods and oxygen blowing periods for HyMelt 10

6.2 Generated gas

The recorded gas analysis shows a common tendency for all the periods.

A peak value for H_2 and CO occurs immediately when gas sampling starts followed by a slow decrease of CO and finally a shift of CO to CO_2.

The presence of O_2 and CO_2 are not thermodynamically motivated and must be explained by leakage of air into the converter atmosphere or into the sampling system. Leakage air will also dilute other components than N_2 and O_2.

6.2.1 H_2 and O_2

The dilution of process gas by air is indicated in the graphs where H_2 and O_2 can be compared. The leakage increases during the period probably because of clogging of the sampling lance. A concentration of 10% O_2 shows that the analysed gas is composed of about 50% air and 50% process gas. Consequently if 10% of O_2 is found the measured H_2 concentration corresponds to approximately the double concentration in the process gas.

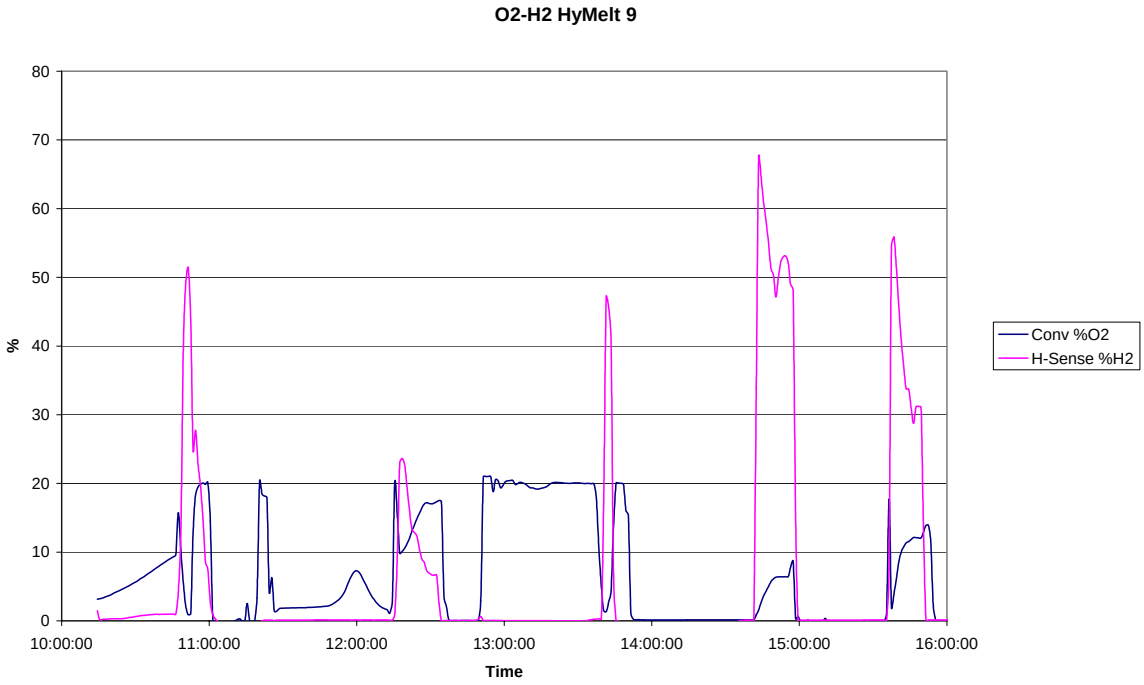


Figure 7 – H_2 and O_2 analysis of process gas HyMelt 9

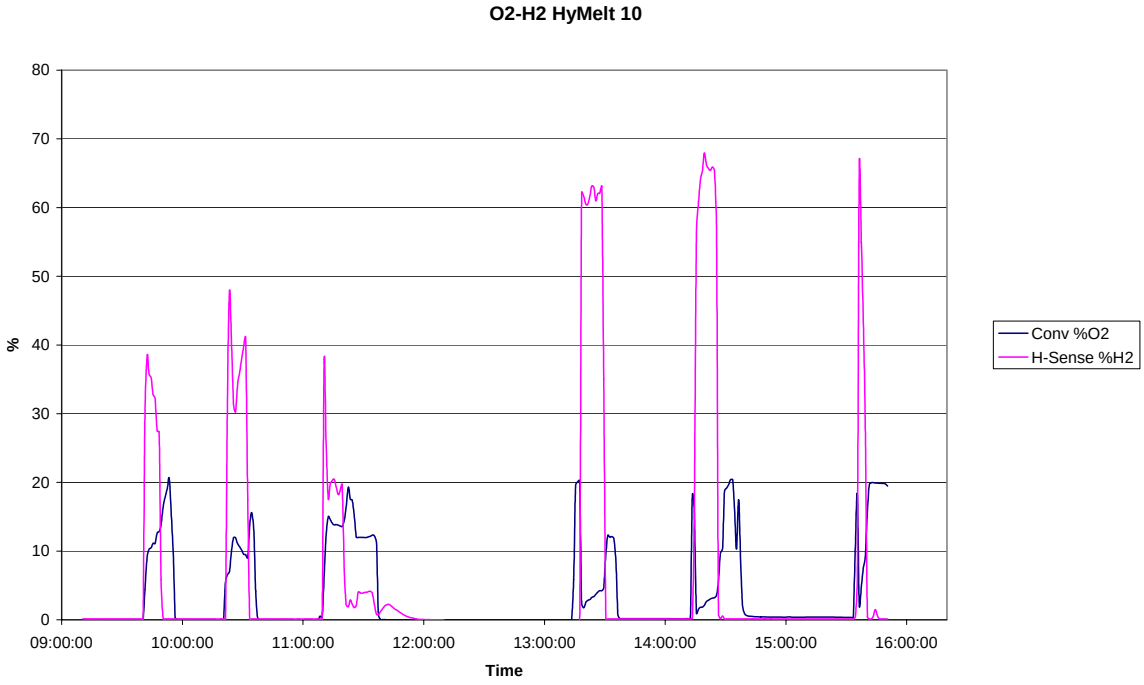


Figure 8 – H_2 and O_2 analysis of process gas HyMelt 10

6.2.2 H_2

Three principals for H_2 analysis were used. The conventional method can only measure up to 20% H_2 and MS127 shows, as expected, lower concentration than the H-sense device. The H-sense system has also a shorter response time and a better linearization and can be considered as most correct.

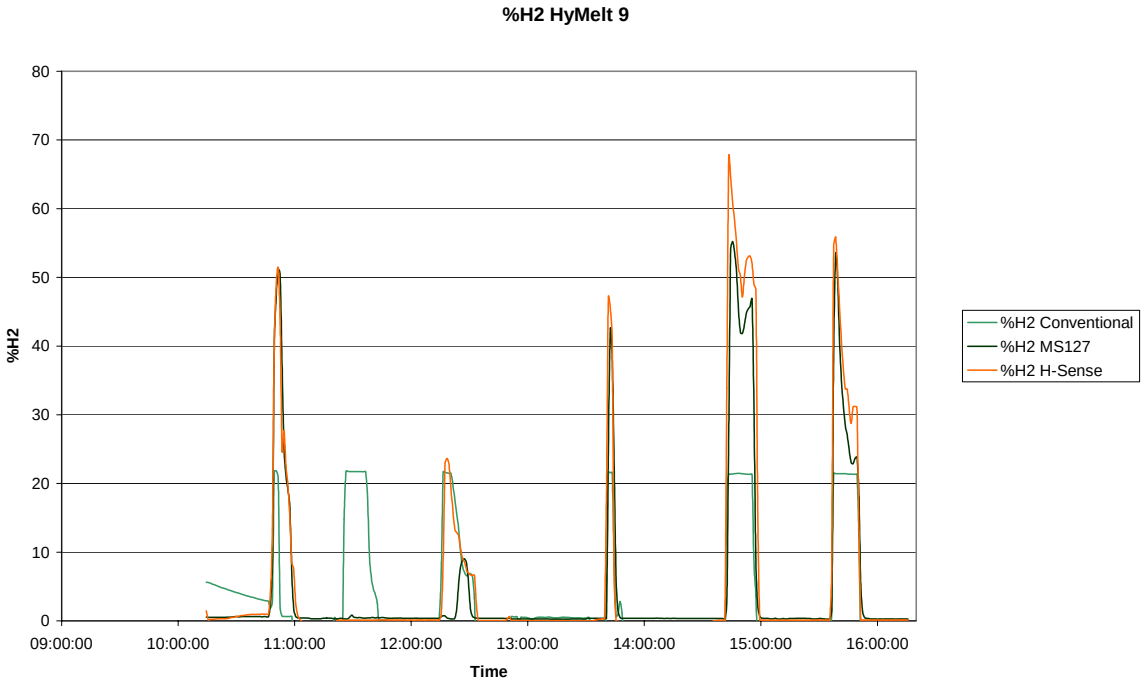


Figure 9 – Alternative methods for H_2 analysis of process gas HyMelt 9

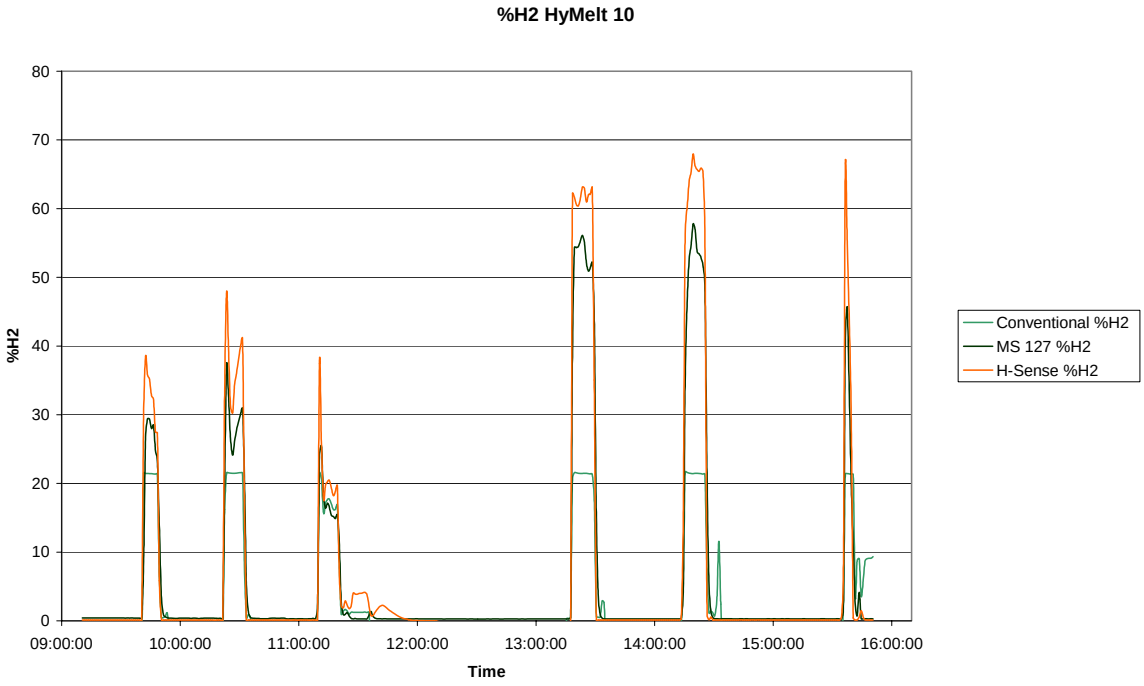


Figure 10 – Alternative methods for H_2 analysis of process gas HyMelt 10

6.2.3 CO and CO_2

The major part of injected carbon solutes into metal, however a fraction is reacting with oxygen to CO. Possible oxygen sources are reduction of metal oxides of the slag and ash or from air injection in the tuyere slits. The air flow rate was in the range of 600 ln/minute or 125 ln O_2 /minute forming 250 ln CO /minute. This flow rate contributes with about 2 – 4 % CO.

The presence of CO_2 is unexpected and can only be explained by air leakage. The highest values are also found, with some exceptions, in the end of the measuring period. Leakage air can effect the CO_2 concentration in two ways, reaction with CO and by dilution.

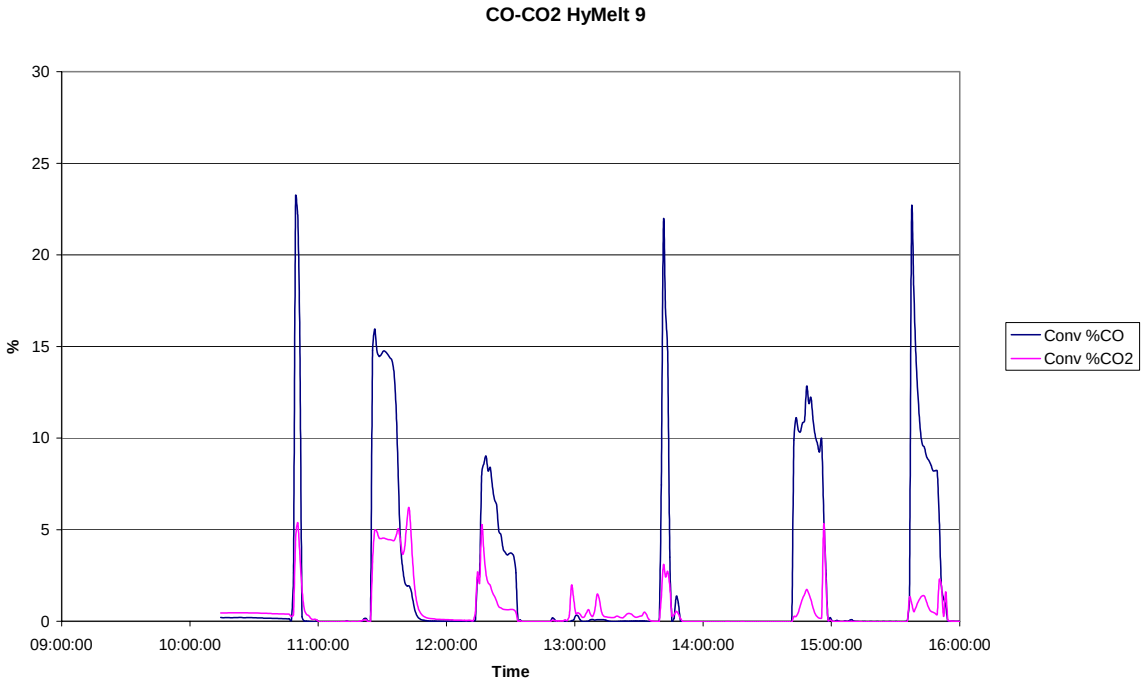


Figure 11 – CO and CO_2 analysis of process gas HyMelt 9

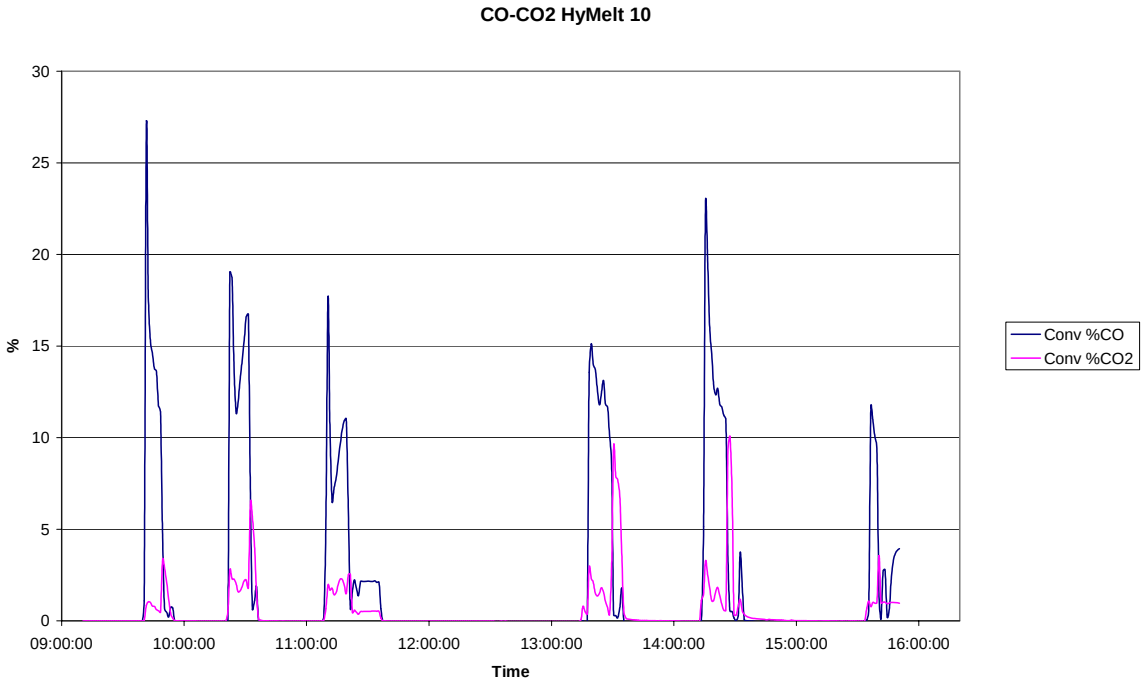


Figure 12 – CO and CO_2 analysis of process gas HyMelt 10

6.2.4 CH_4

The methane concentration is below 0.5 %, considerably lower than the previous trials by top injection, 5– 12% CH_4.

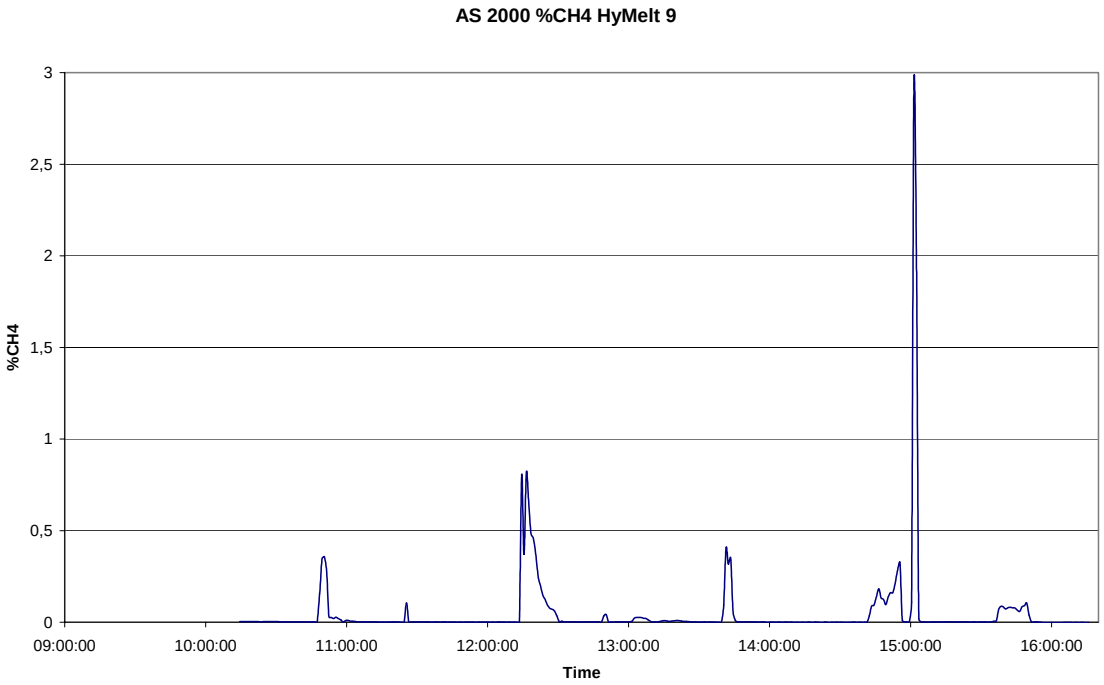


Figure 13 – CH_4 analysis of process gas HyMelt 9

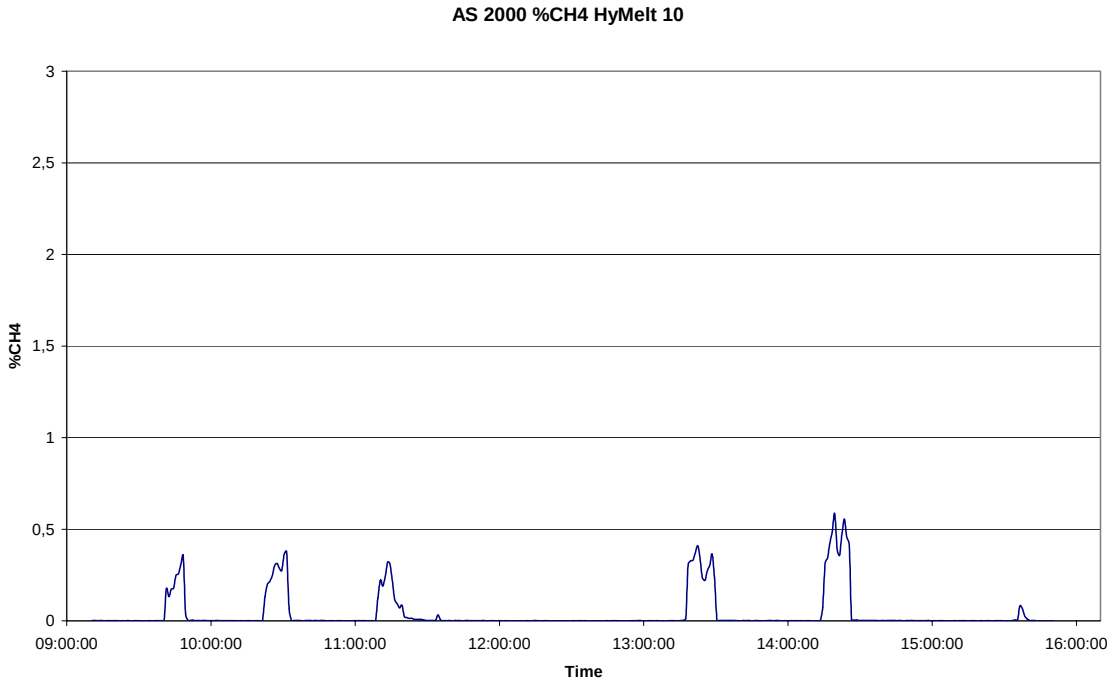


Figure 14 – CH_4 analysis of process gas HyMelt 10

6.2.5 COS

The measured COS is also lower than in previous campaign, typical 50 to 200 ppm compared to 100 to 300 ppm.

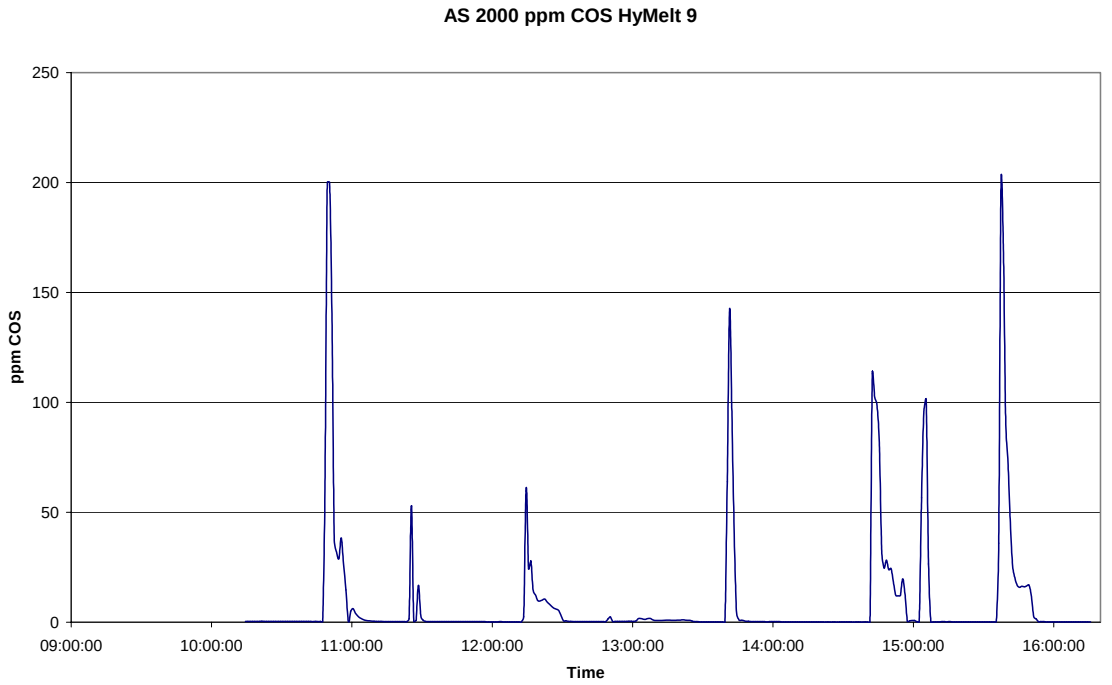


Figure 15 – COS analysis of process gas HyMelt 9

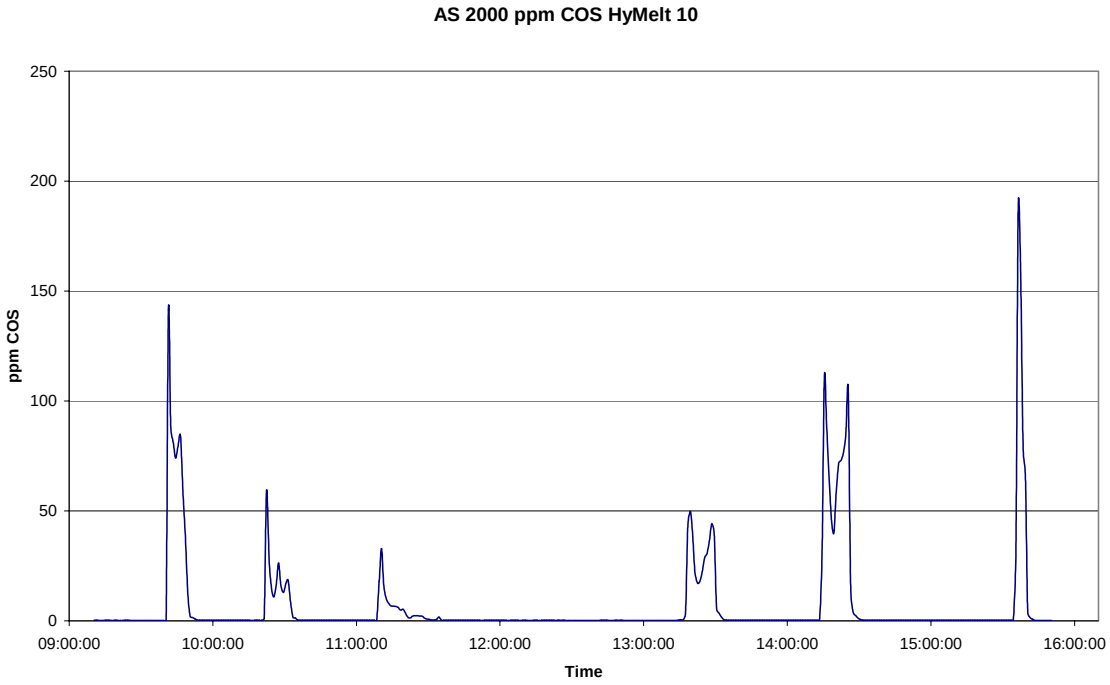


Figure 16 – COS analysis of process gas HyMelt 10

6.2.6 Ar

Argon was used as cleaning gas in the probe between the measurements. The source for readings during operation is originated from carrier gas.

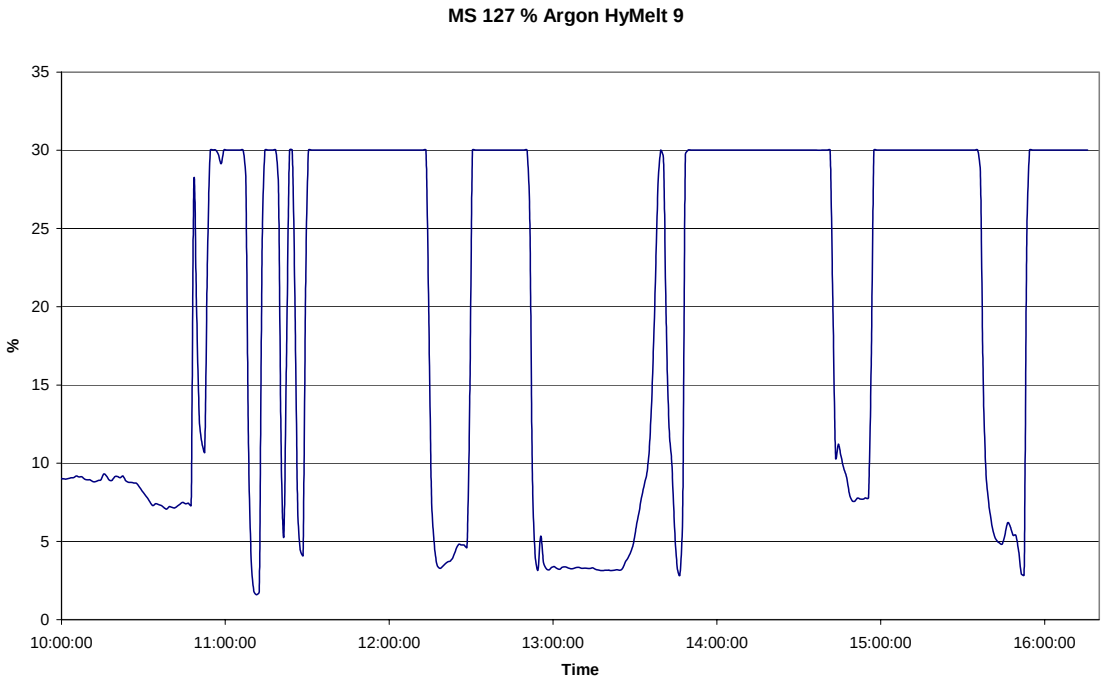


Figure 17 – Ar analysis of process gas HyMelt 9

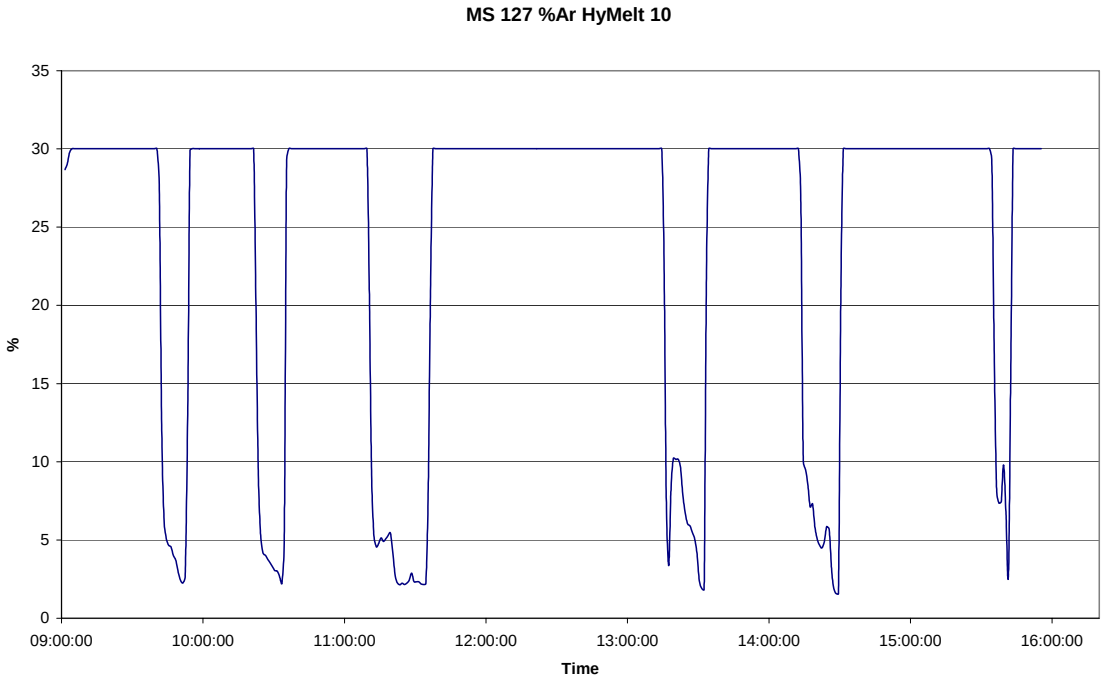


Figure 18 – Ar analysis of process gas HyMelt 10

6.2.7 Mass 28

By detecting mass weight 28 it was tested whether N_2 could be calculated by compensation for separately analysed CO concentration. Both compounds have the same mass but the analyser senility is different. However, a simple linear algorithm does not give any realistic results for N_2 determination.

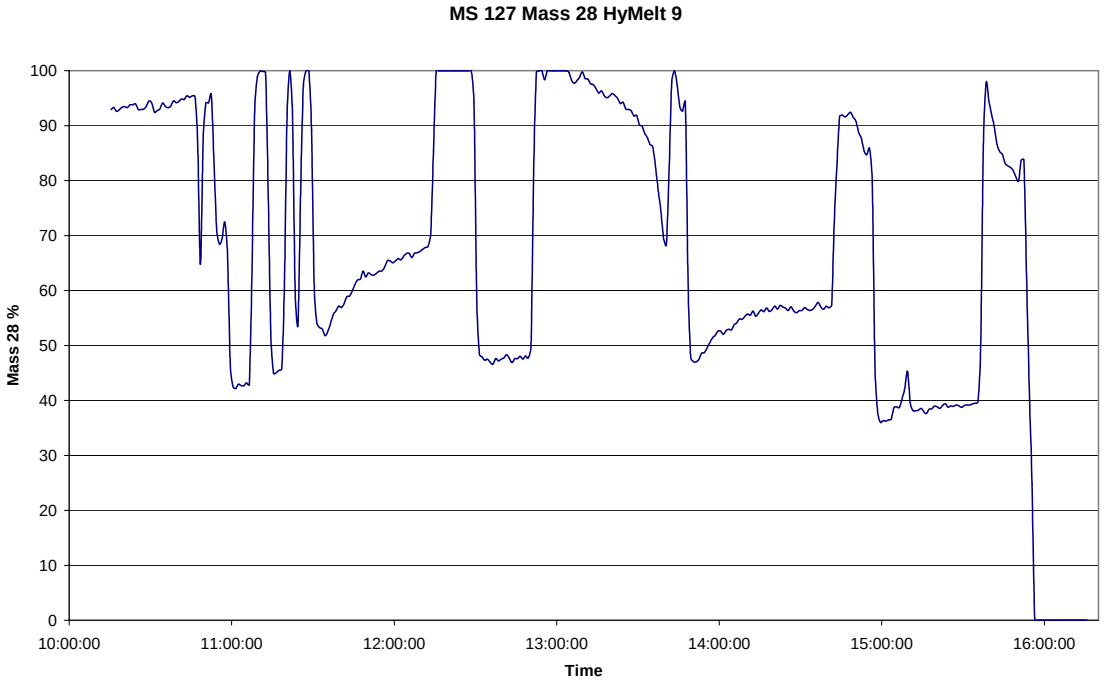


Figure 19 – Mass 28 analysis of process gas HyMelt 9

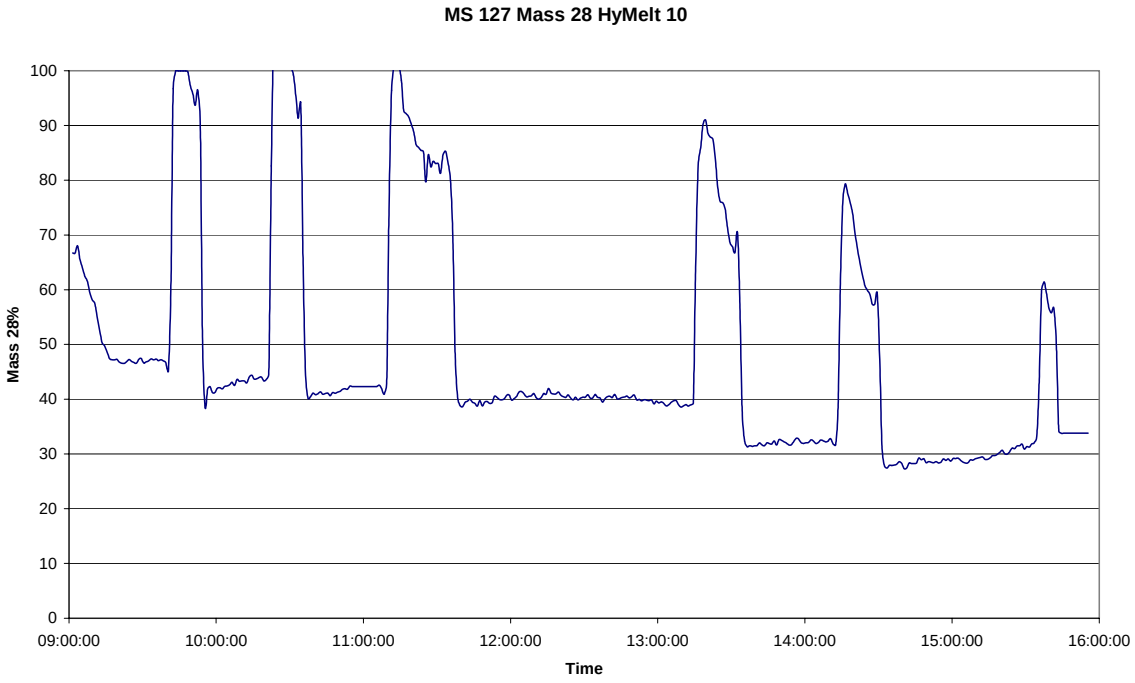


Figure 20 – Mass 28 analysis of process gas HyMelt 9

6.2.8 Benzene

Benzene was not analysed for top injection, results from submerged injection shows typical concentrations below 100 ppm.

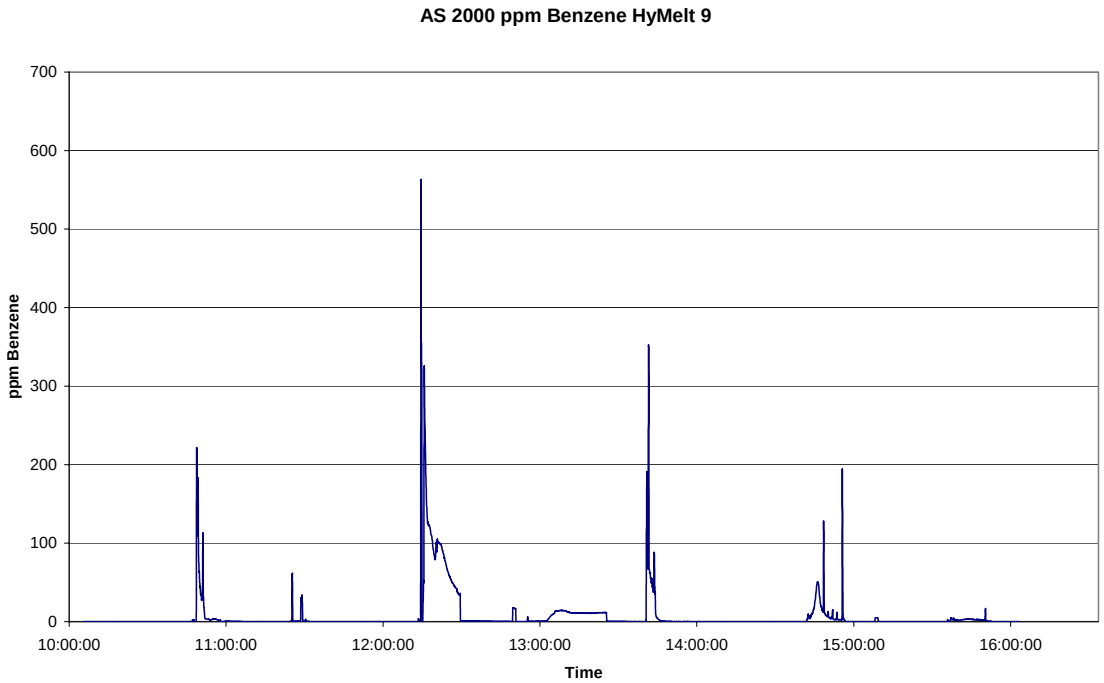


Figure 21 – C_6H_6 analysis of process gas HyMelt 9

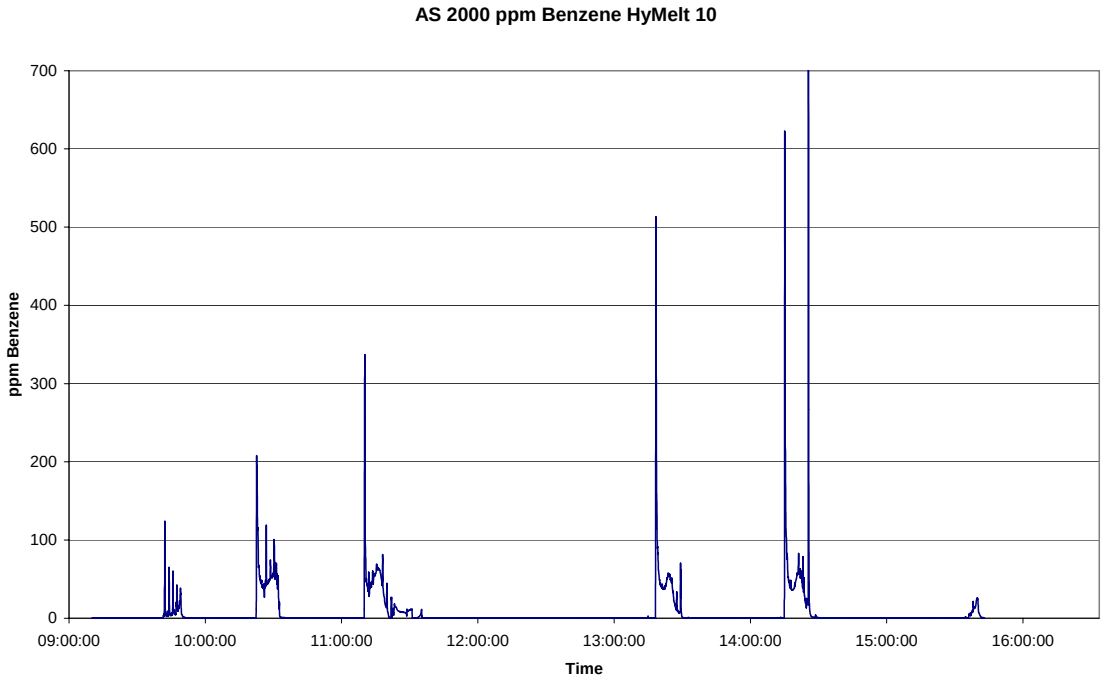


Figure 22 – C_6H_6 analysis of process gas HyMelt 10

6.2.9 C_2H_2

The compound was not analysed for top injection. Result from this campaign shows peak values of more than 1500 ppm. More typical values are below 1000 ppm.

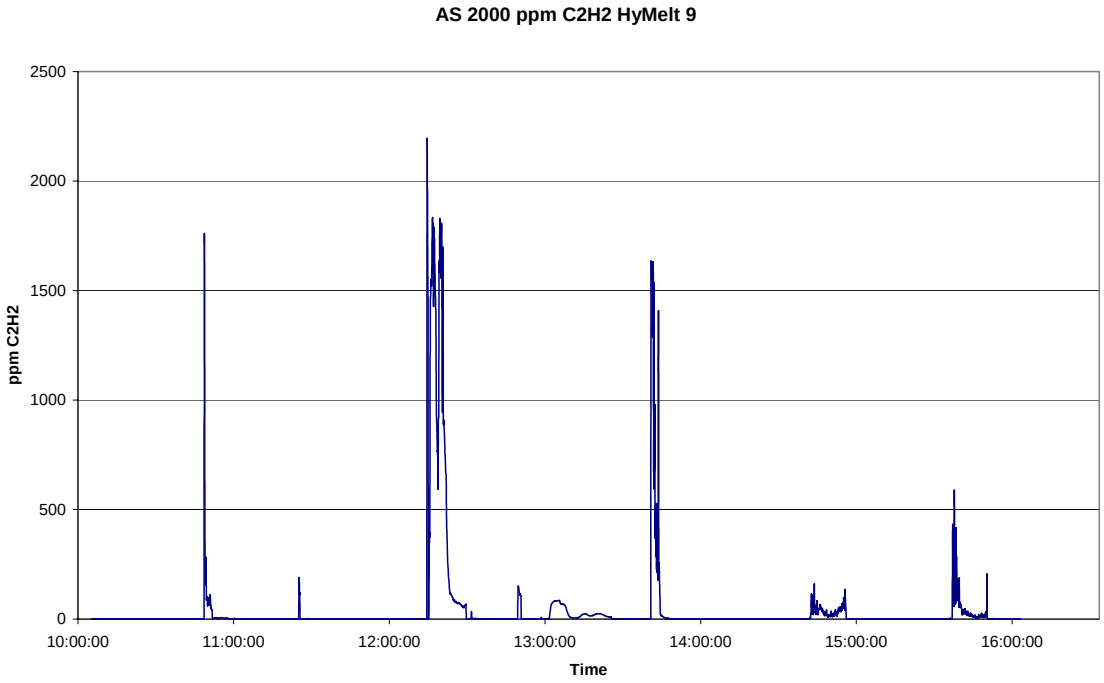


Figure 23 – C_2H_2 analysis of process gas HyMelt 9

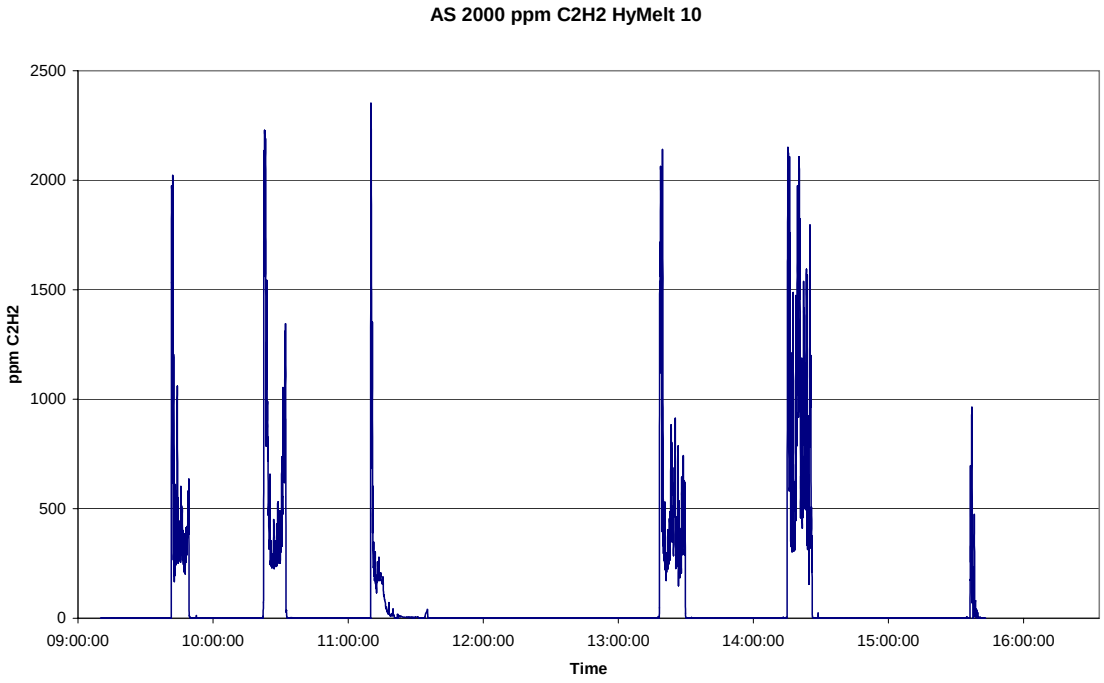


Figure 24 – C_2H_2 analysis of process gas HyMelt 10

6.2.10 H_2S

The level is lower than for top injection, 0,2 – 0,4 %. The reading increases during the day and correlate to the sulphur content of the metal.

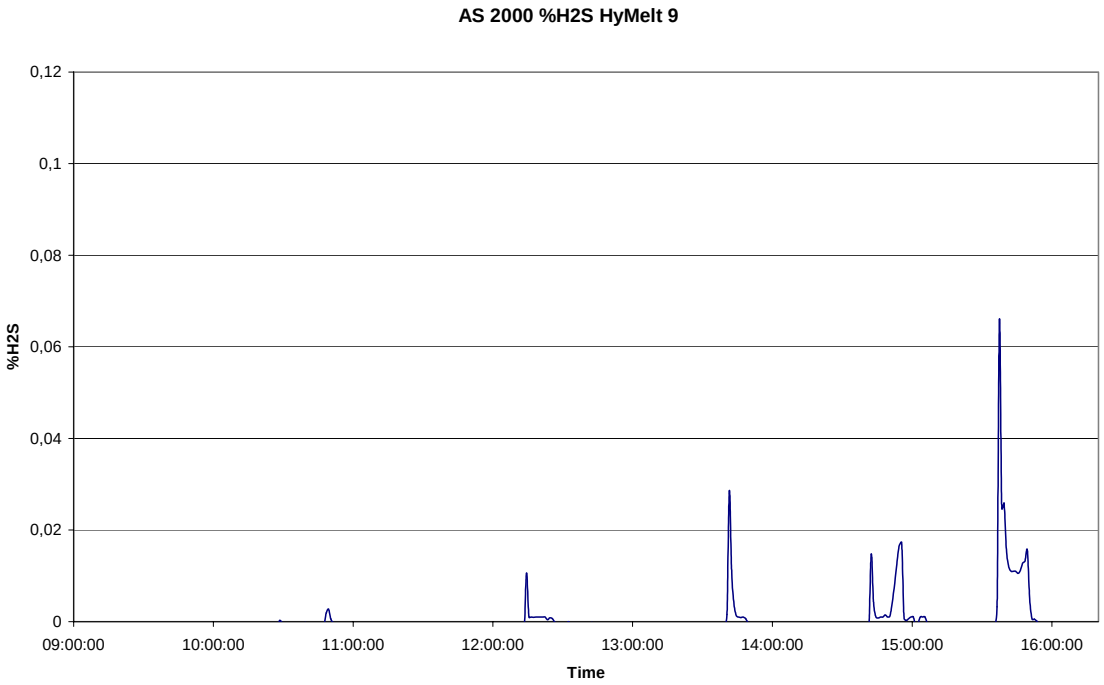


Figure 25 – H_2S analysis of process gas HyMelt 9

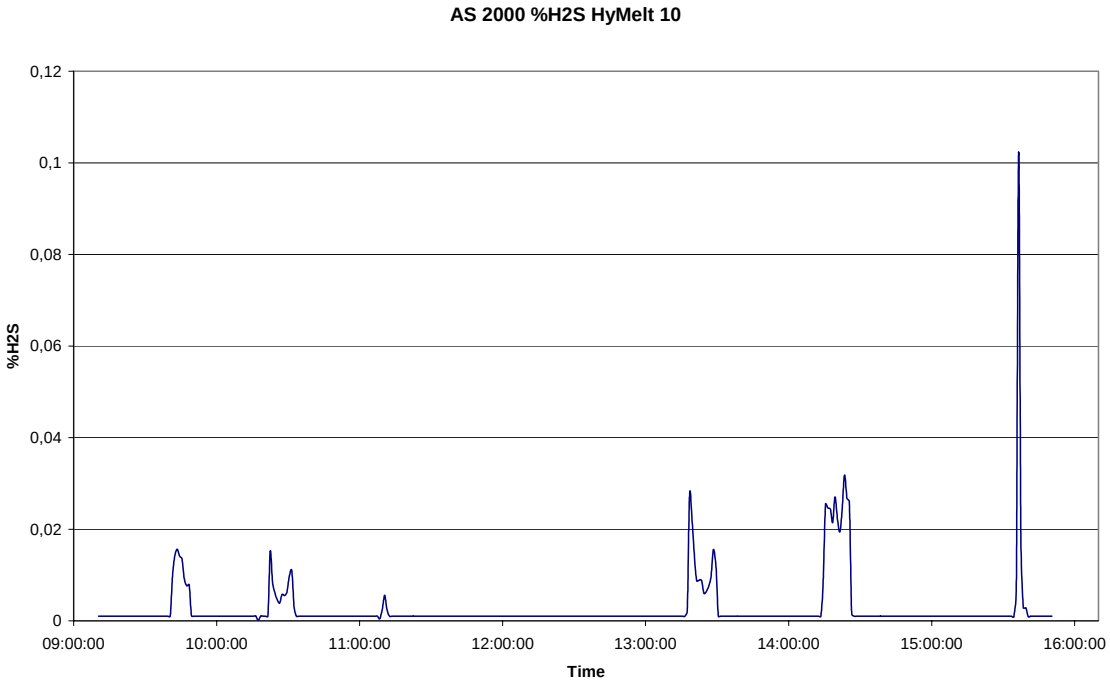


Figure 26 – H_2S analysis of process gas HyMelt 10

6.2.11 HCN

Cyanide concentrations are analysed in concentrations typically below 20 ppm. The compound was not analysed in previous campaign.

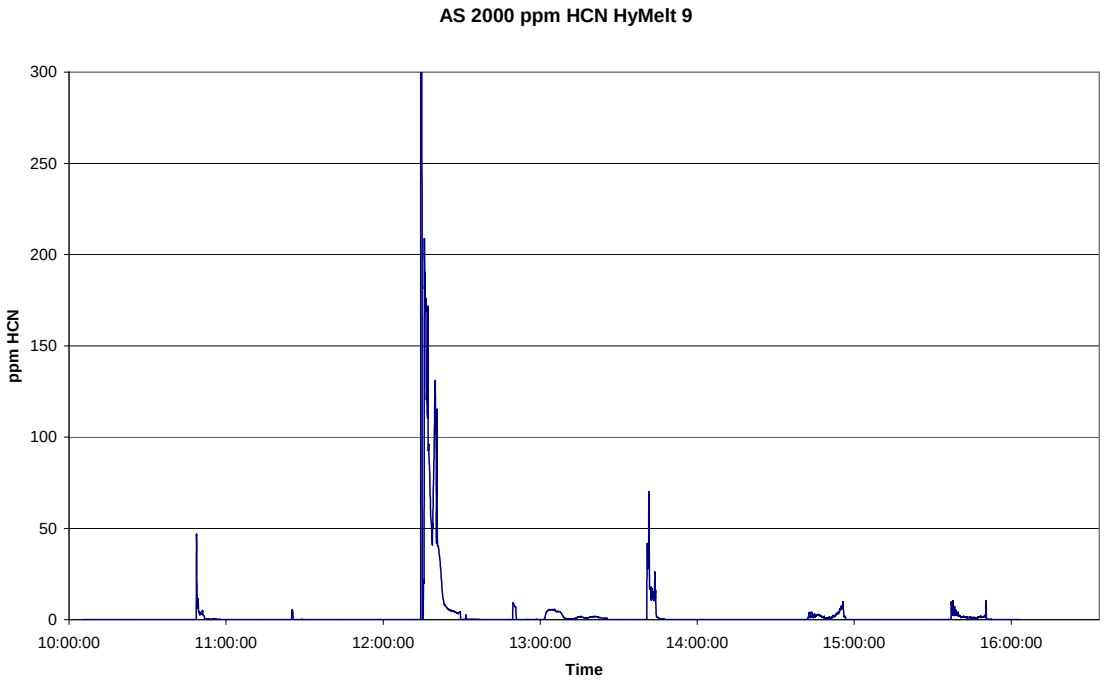


Figure 27 – HCN analysis of process gas HyMelt 9

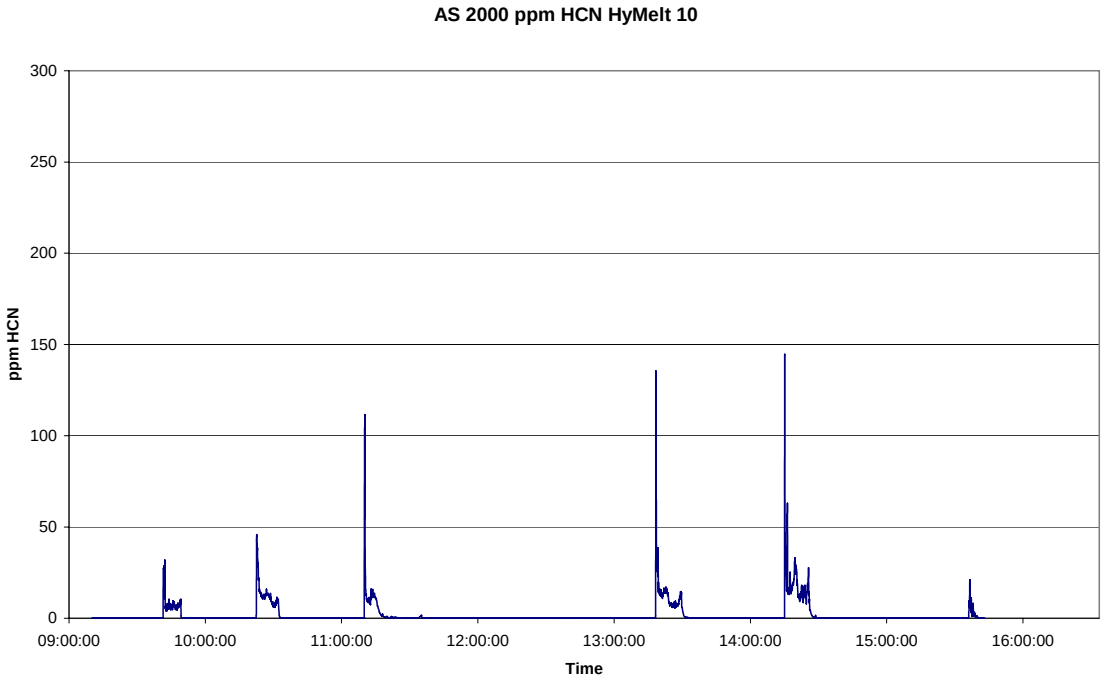


Figure 28 – HCN analysis of process gas HyMelt 10

6.2.12 Normalized gas composition

The partly confusing gas analysis can be presented in an alternative way based on a few assumptions:

- CO_2 can not be present together with an iron melt and the fraction of CO_2 can be consider as CO by ignoring post combustion
- The major part of N_2 originates from leakage air either directly into the converter gas atmosphere or into the gas sampling system.
- O_2 can not be present in an environment of liquid iron

If the gas components of low concentration, <1%, are neglected normalized process gas mixtures of H_2, ($CO+CO_2$) and Ar can be calculated as in Figure 29 and 30.

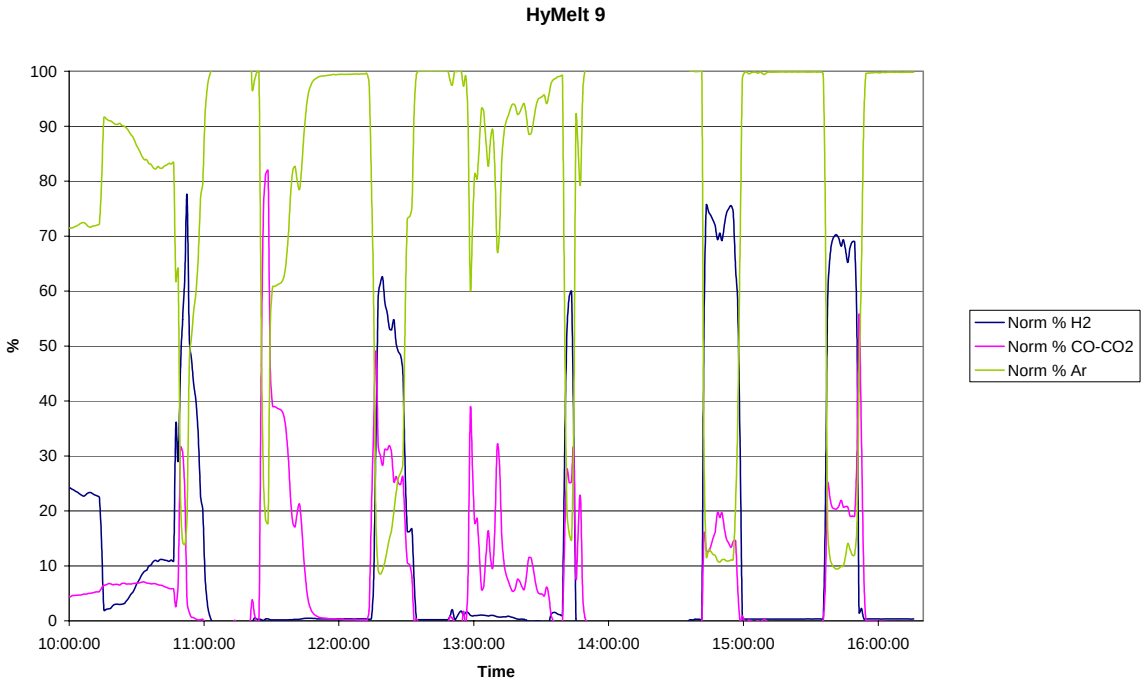


Figure 29 – Normalized gas composition, HyMelt 9

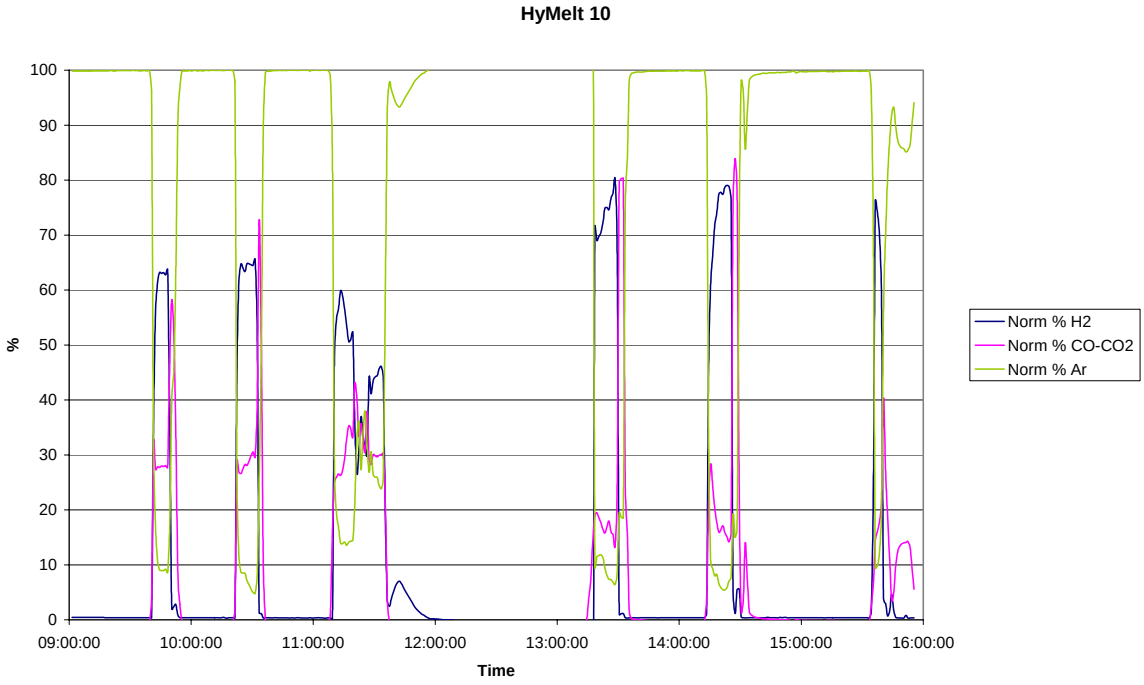


Figure 30 - Normalized gas composition, HyMelt 10

The variations of gas composition can be explained:

- CO has the highest value in the start of injection period when slag reduction takes place. The peaks in the end of periods are not likely to have process signification.
- The H_2 increases until clogging of the probe, a consequence of reduced amount of CO.
- Injection of coal gives higher CO analysis than coke injection because of oxides in the ash.

By comparing Ar concentration with Ar feed rate a normalized process gas flow rate can be estimated and an in-out mass balances of C and H can be made.

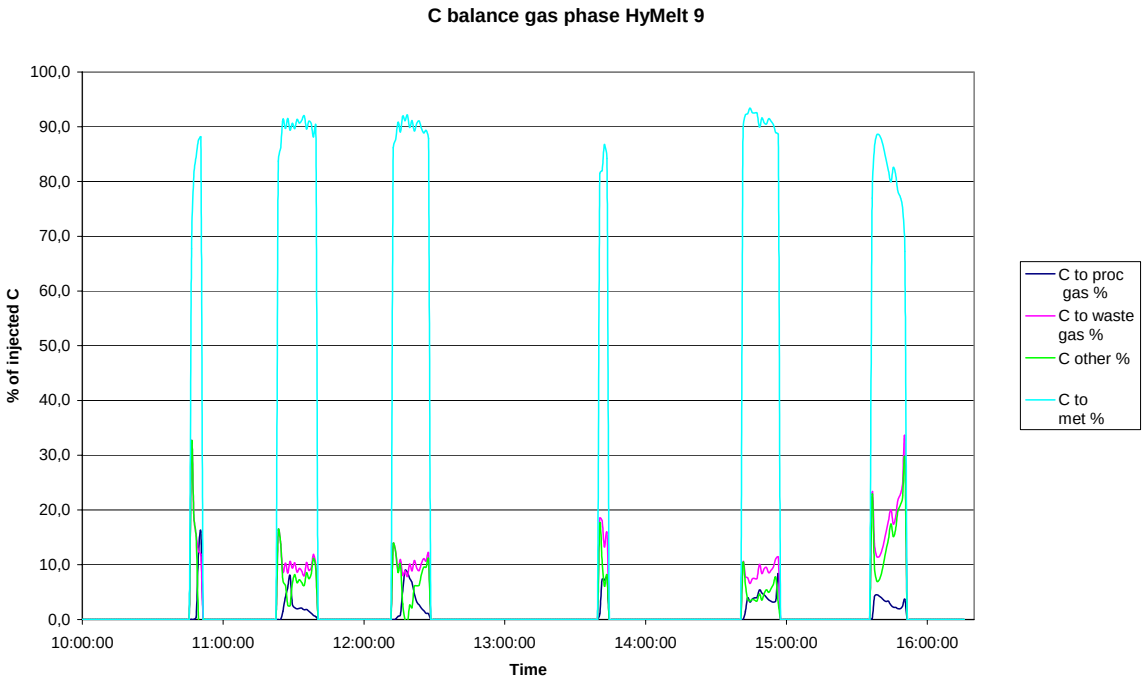


Figure 31 – Gas phase carbon balance HyMelt 9

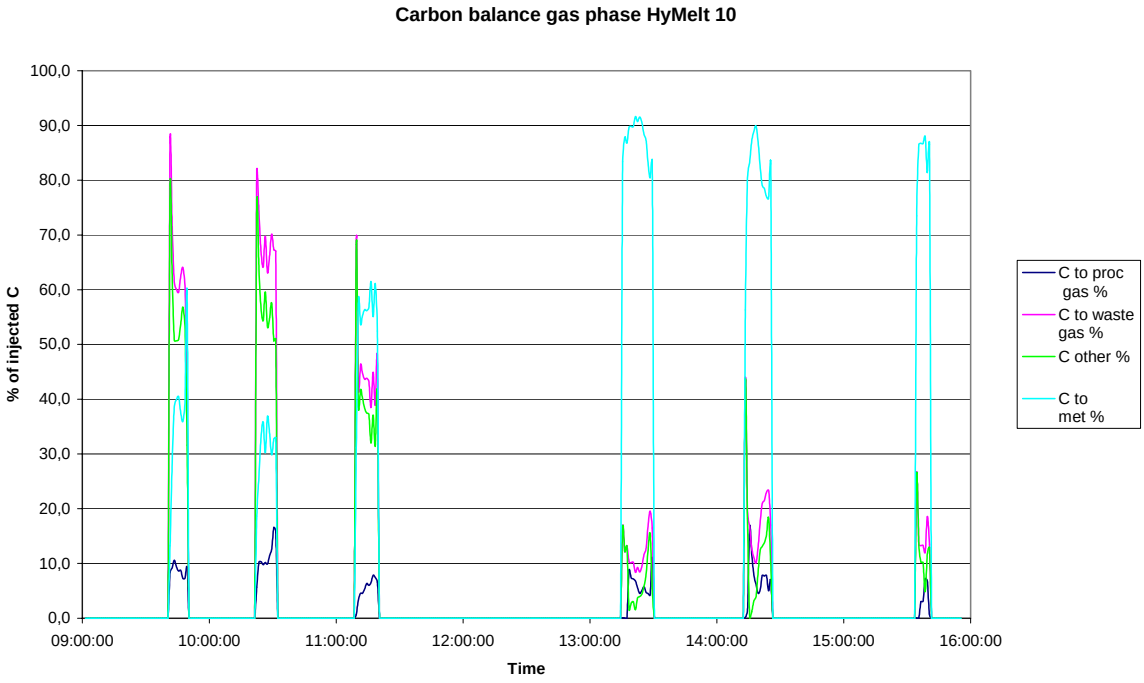


Figure 32 – Gas phase carbon balance HyMelt 10

There are some obvious differences between coal and coke injection:

- The C amount for balance, in this case assumed to be found in metal, are lower in case of coal, 35 – 65% compared to 80 – 90% for coke.
- By assuming that the amount of CO_2 detected in the combusted gas is equal to the total amount of coal compounds including dust in the process gas, it can be concluded that coal generates more dust or soot.

6.3 Hydrogen balances

There are significant difference between the hydrogen yield between HyMelt 9 and 10, the difference is greater than between coal and coke. Until now, no explanation has been found, most likely it indicates the accuracy of measuring and the method for evaluation

It shall also be observed that the calculated H yield can reach values above 100%, one possible explanation is different delay time times for measurements.

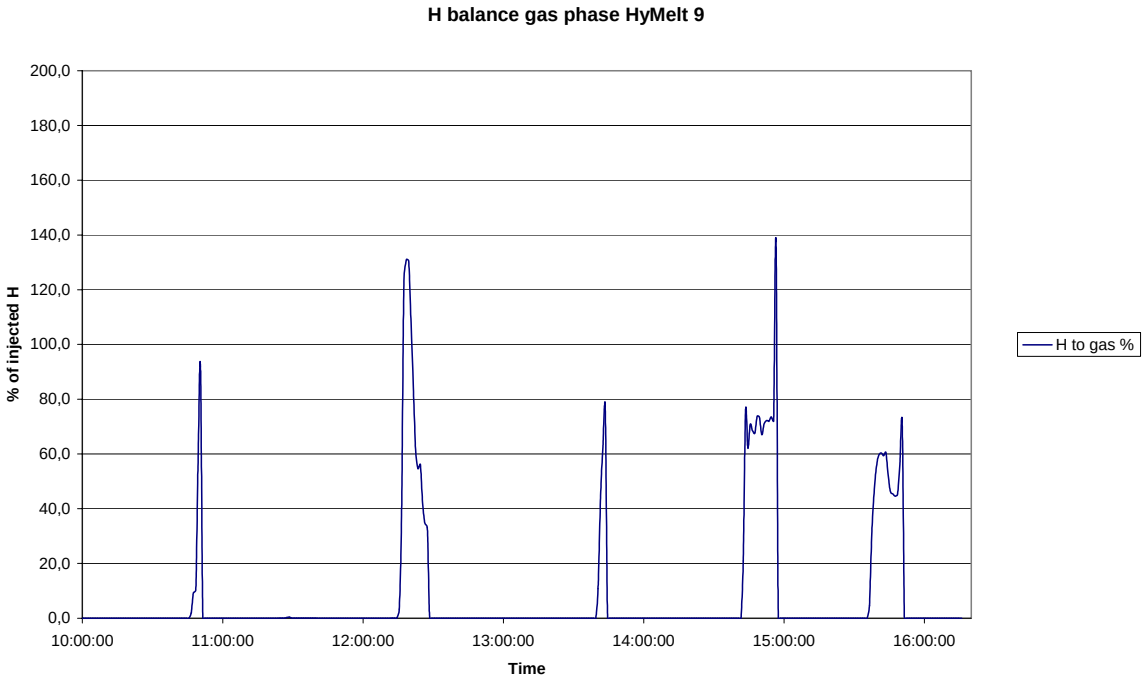


Figure 33 – Gas phase hydrogen balance HyMelt 9

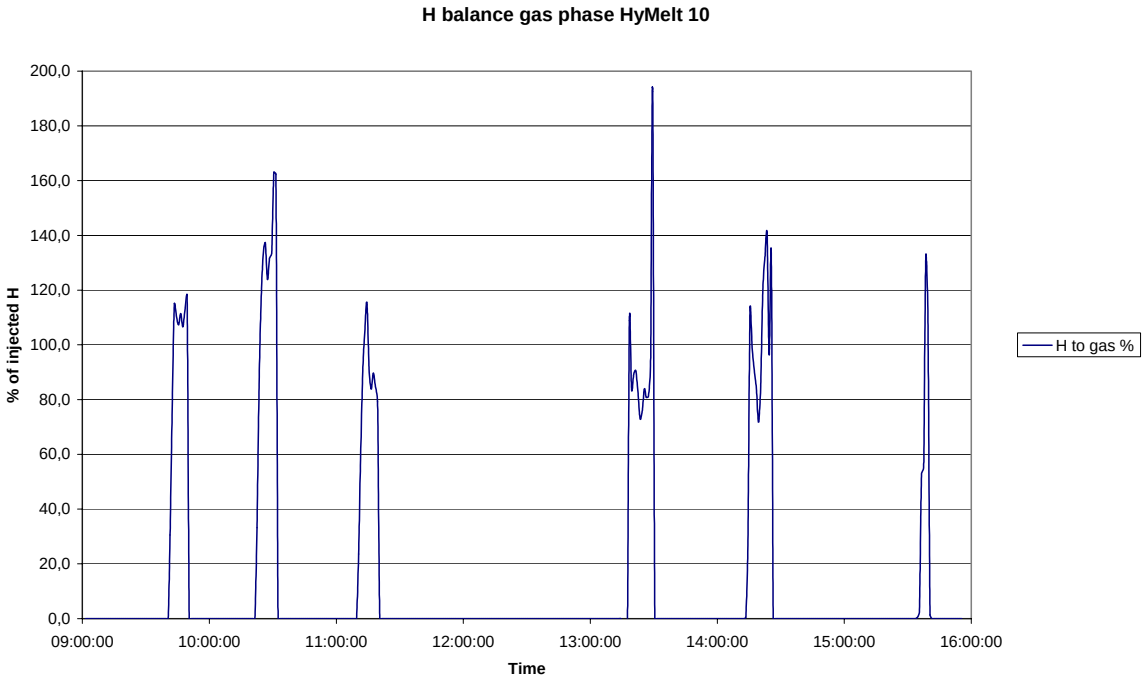


Figure 34 – Gas phase hydrogen balance HyMelt 10

6.4 Temperature and melt analysis

6.4.1 Temperature

The temperature variation is a consequence of the heat balance between the cooling gasification period and heating during decarburisation. The target was set to be in the range of 1400 ^{o}C to 1650 ^{o}C.

Heat losses during replacement of the gas probe, sampling of slag etc gave non operational times resulting in a need for excess fuel of FeSi and Al for the oxidation period. In an industrial process this will not be necessary. The trials when coke were injected indicated almost a balanced process already for 5 ton scale.

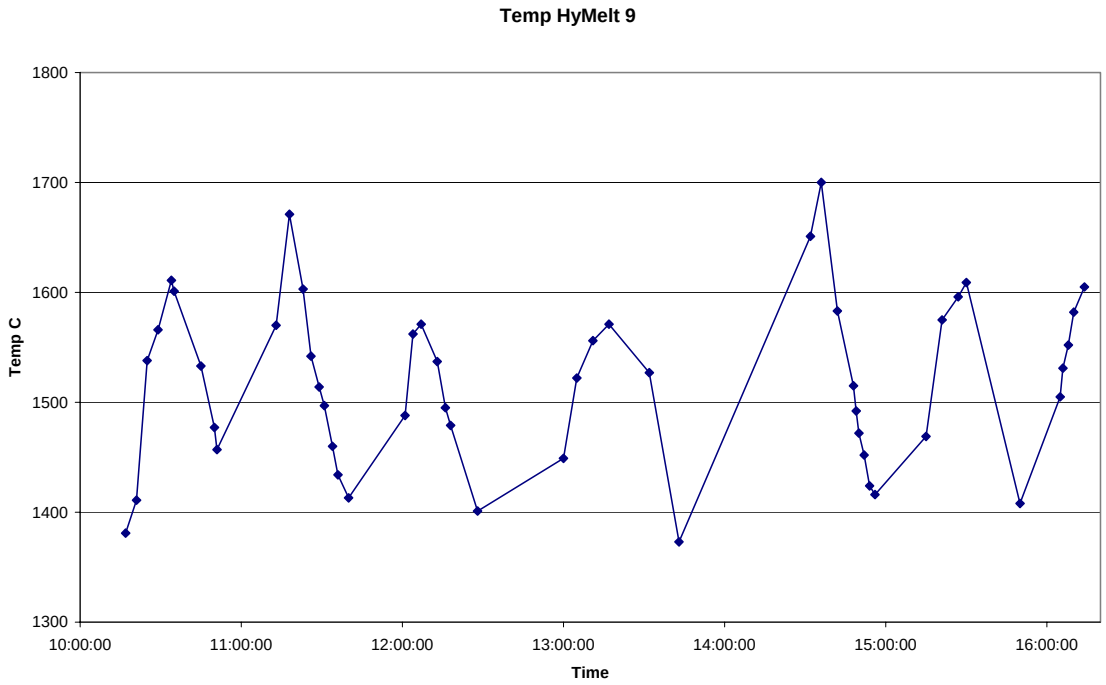


Figure 35 – Metal temperature HyMelt 9

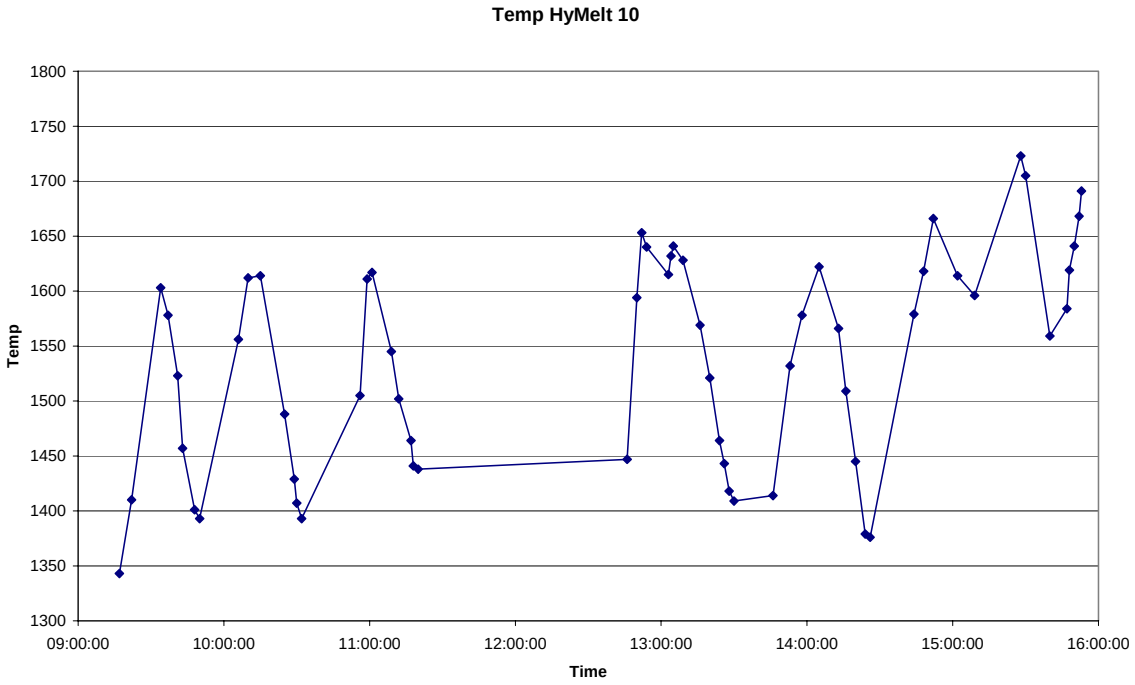


Figure 36 – Metal temperature HyMelt 10

6.4.2 C-metal

The operational carbon content in the metal was set to 0,5 to 4,0 %C. To simplify the tests the temperature was selected for primary control and the carbon content came out as variable.

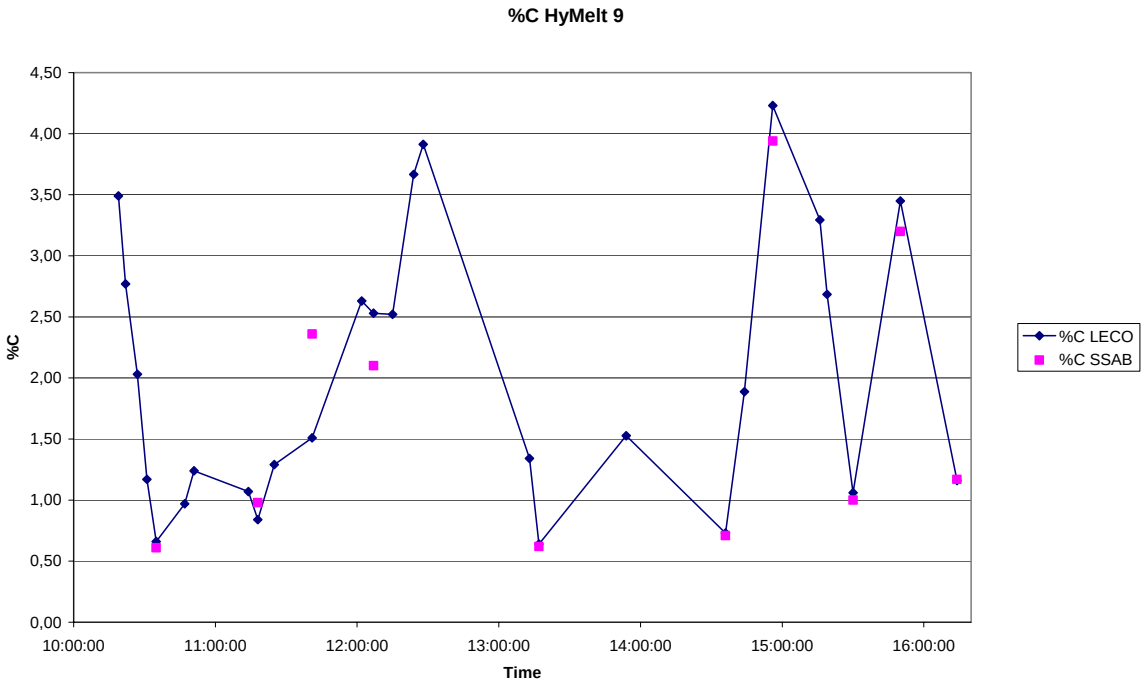


Figure 37 – Carbon content in metal HyMelt 9

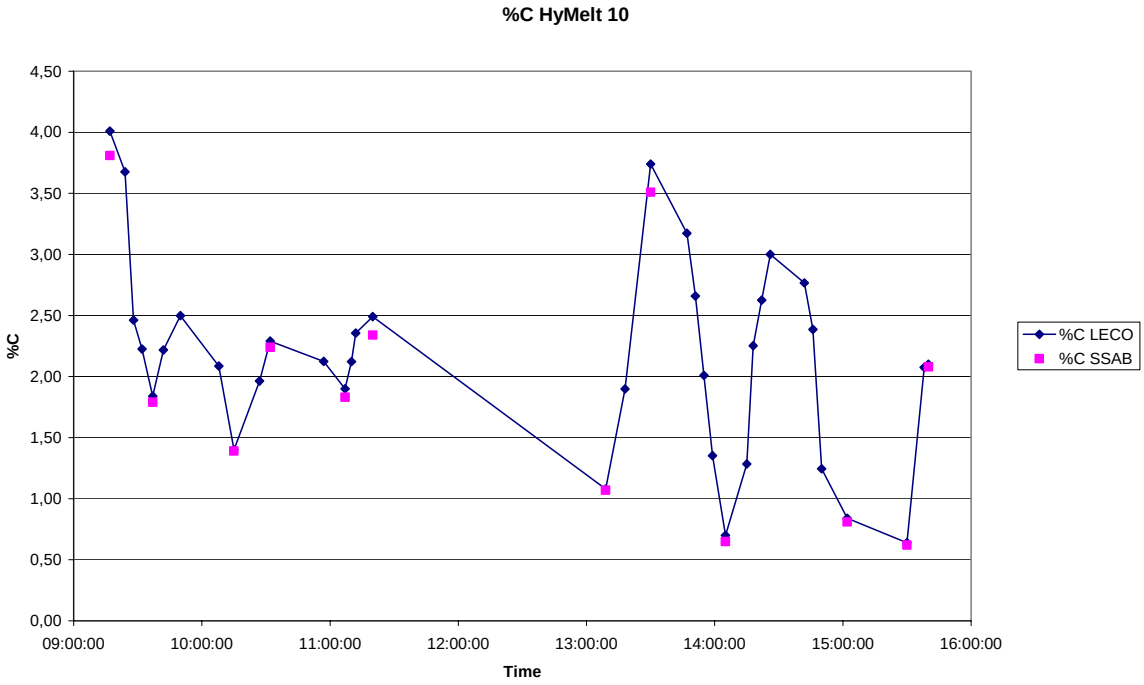


Figure 38 – Carbon content in metal HyMelt 10

6.4.3 S-metal

The sulphur in the metal confirm the relation of total load of sulphur by additions, oxygen potential of the slag (% FeO) and the CaO/SiO_2-ratio of the slag.

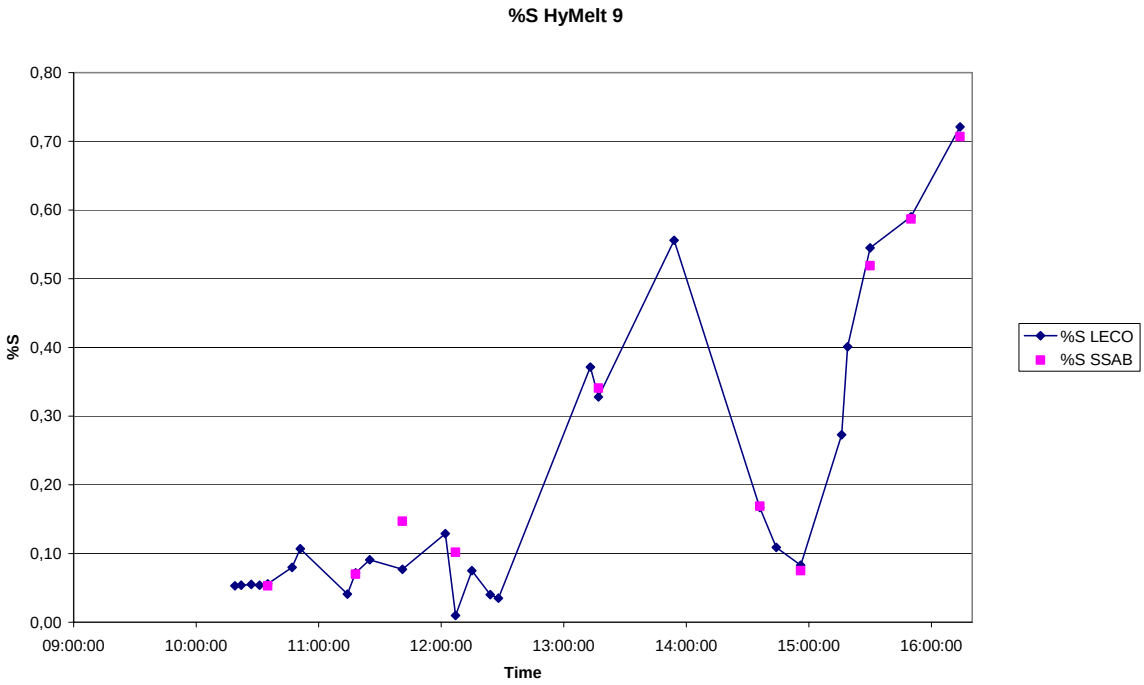


Figure 39 – Sulphur content in metal HyMelt 9

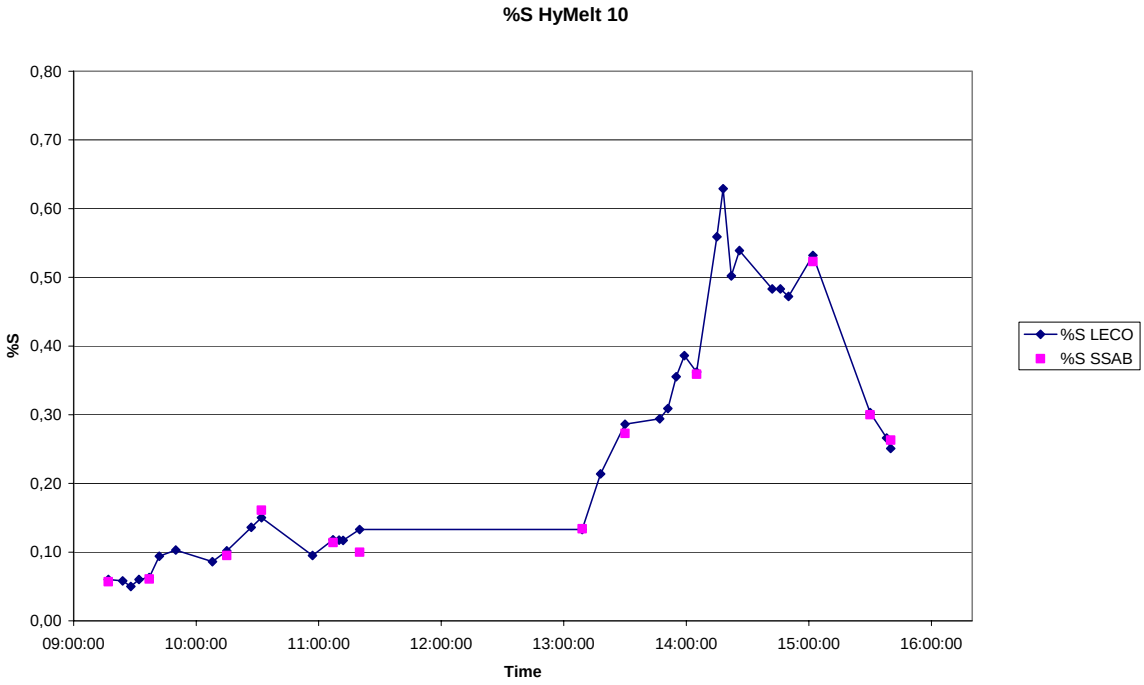


Figure 40 – Sulphur content in metal HyMelt 10

6.4.4 FeO-slag

To achieve a rich H_2 gas it is of interest to keep FeO content in the slag low. The FeO content is a consequence of oxidation which is pronounced by low carbon content of the metal, soft bottom stirring in combination with top blowing. The Fe_{tot} given in the figure can be calculated to FeO by multiplication with 1.28.

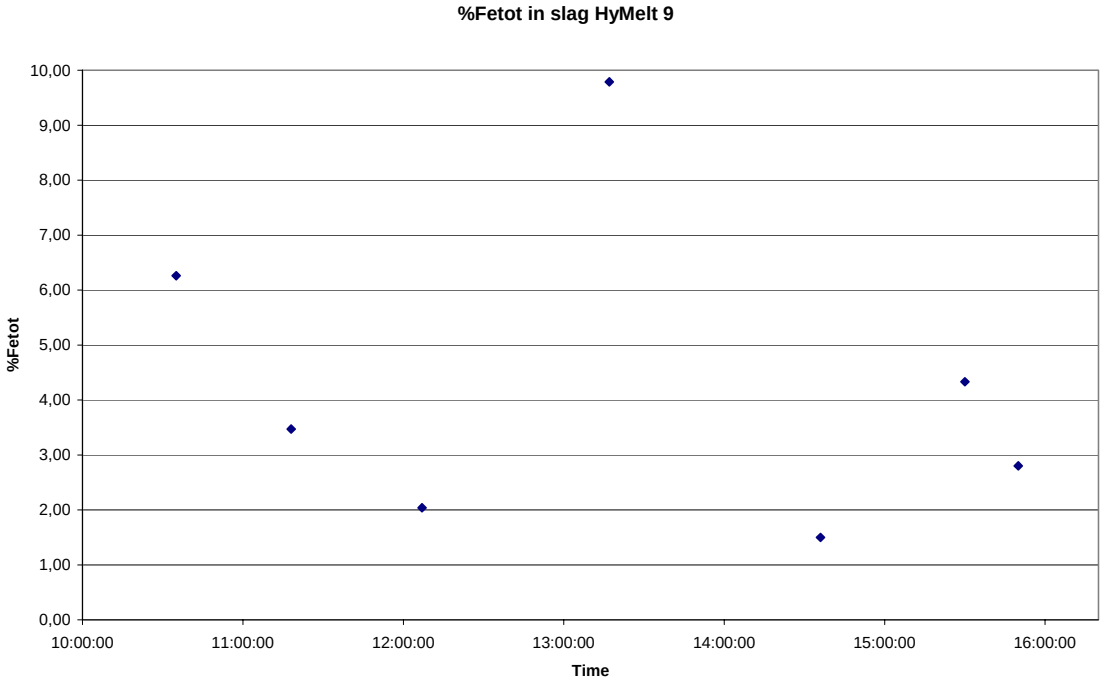


Figure 41 – Fe_{tot} of slag HyMelt 9

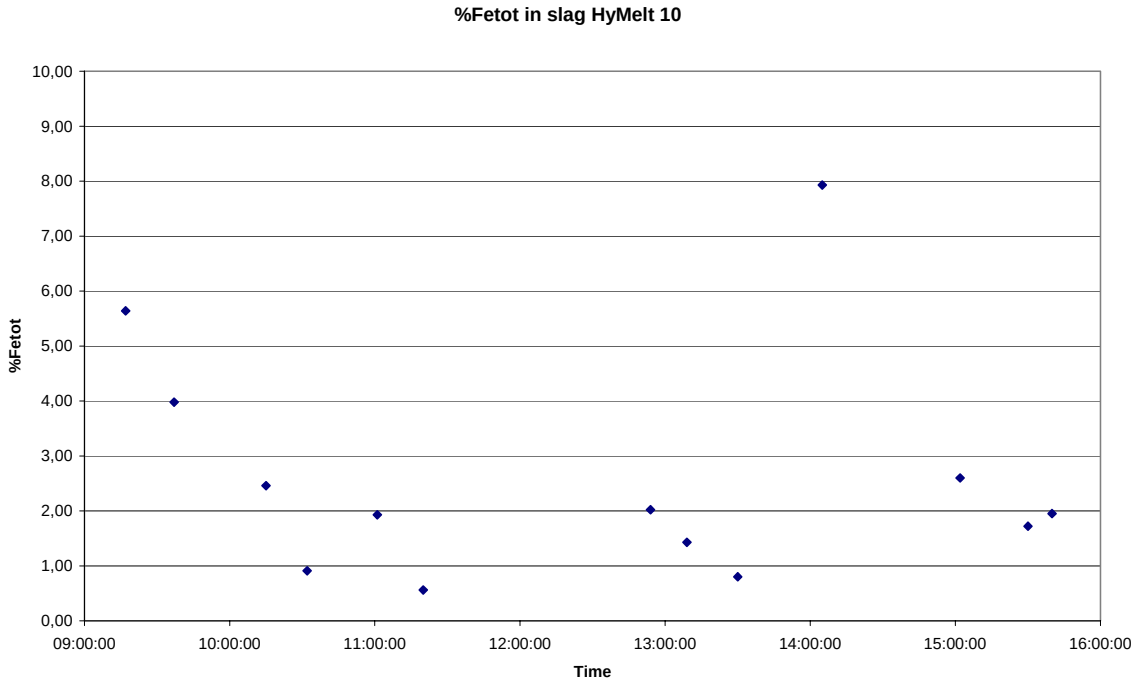


Figure 42 – Fe_{tot} of slag HyMelt 10

6.4.5 CaO/SiO_2-slag

The CaO/SiO_2-ratio was mainly controlled by fuel and lime addition. The process itself generates only small amount of slag depending of ash content and desired slag composition. Stable ratios were achieved for both HyMelt 9 and 10, however the refractory wear is reduced for ratios above 2 which is preferred.

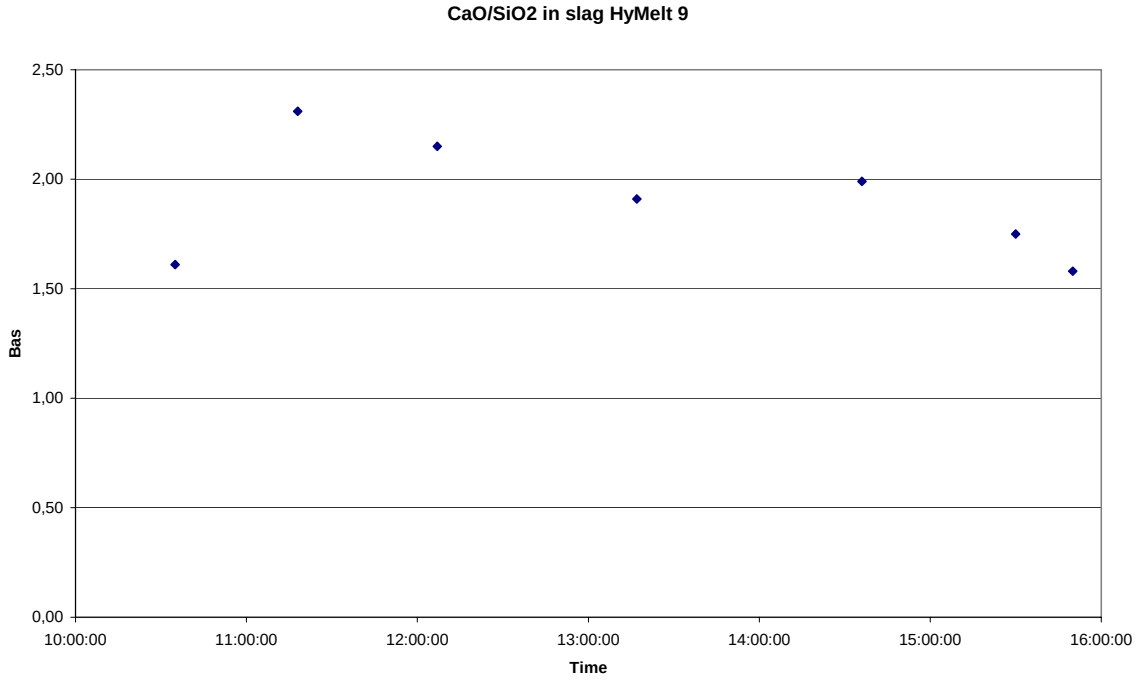


Figure 43 – CaO/SiO_2 of slag HyMelt 9

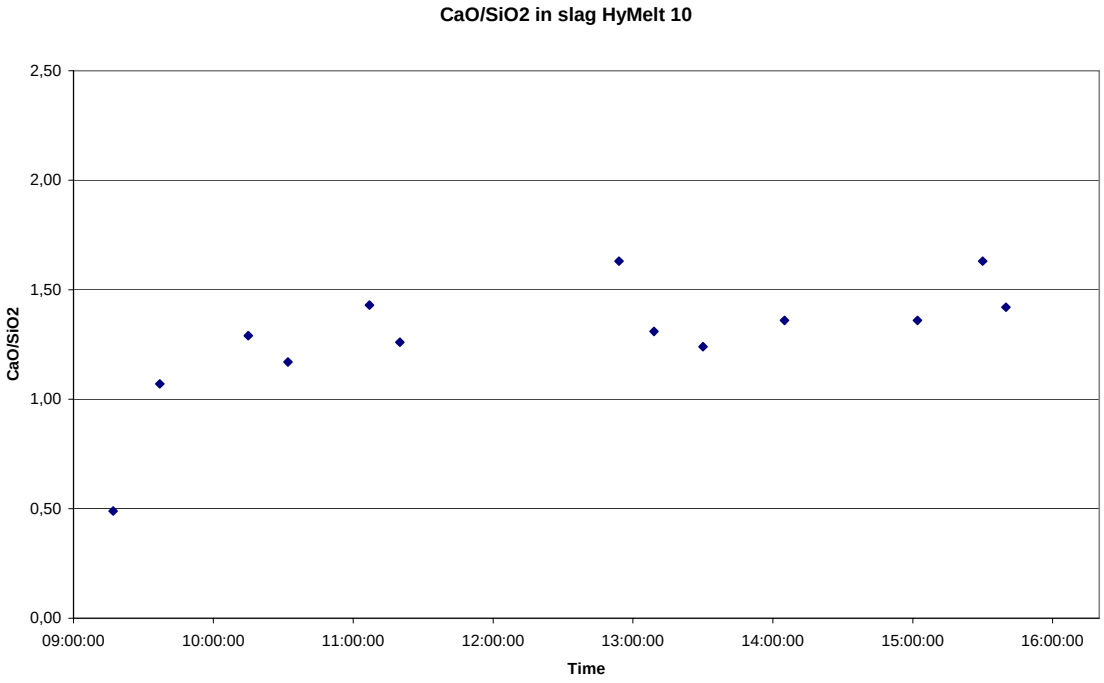


Figure 44 – CaO/SiO_2 of slag HyMelt 10

6.4.6 S-slag

The sulphur in slag is to a large existent the inverse of sulphur of metal and it is obvious that the element can easily be transferred between the liquid phases.

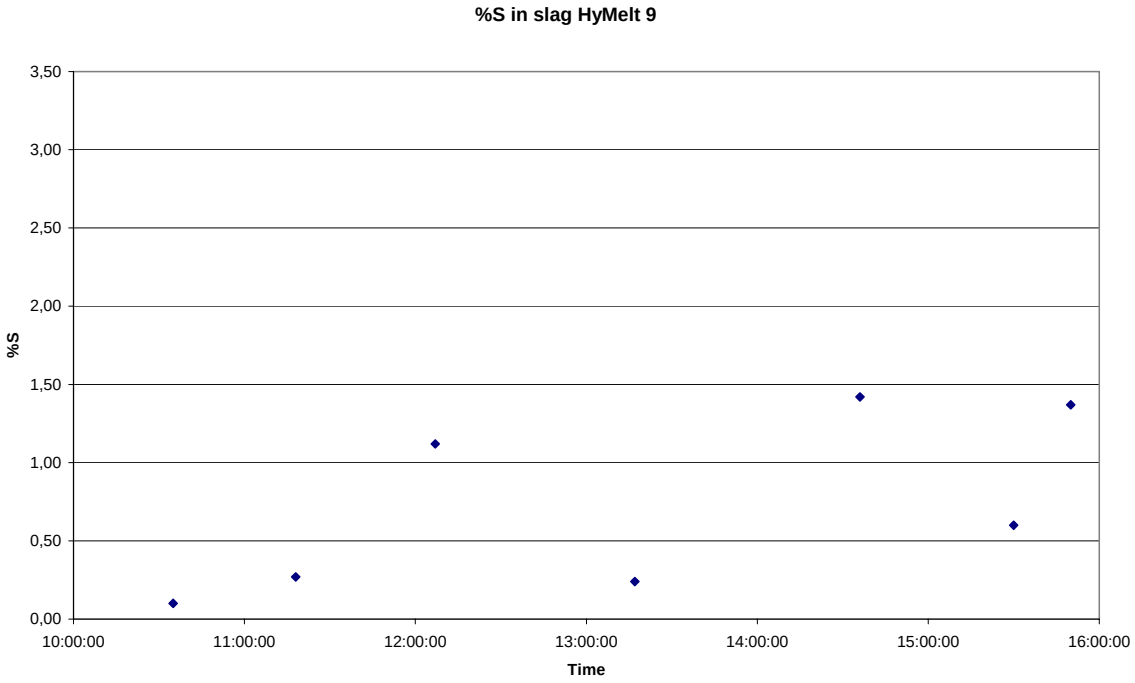


Figure 45 – Sulphur analysis of slag HyMelt 9

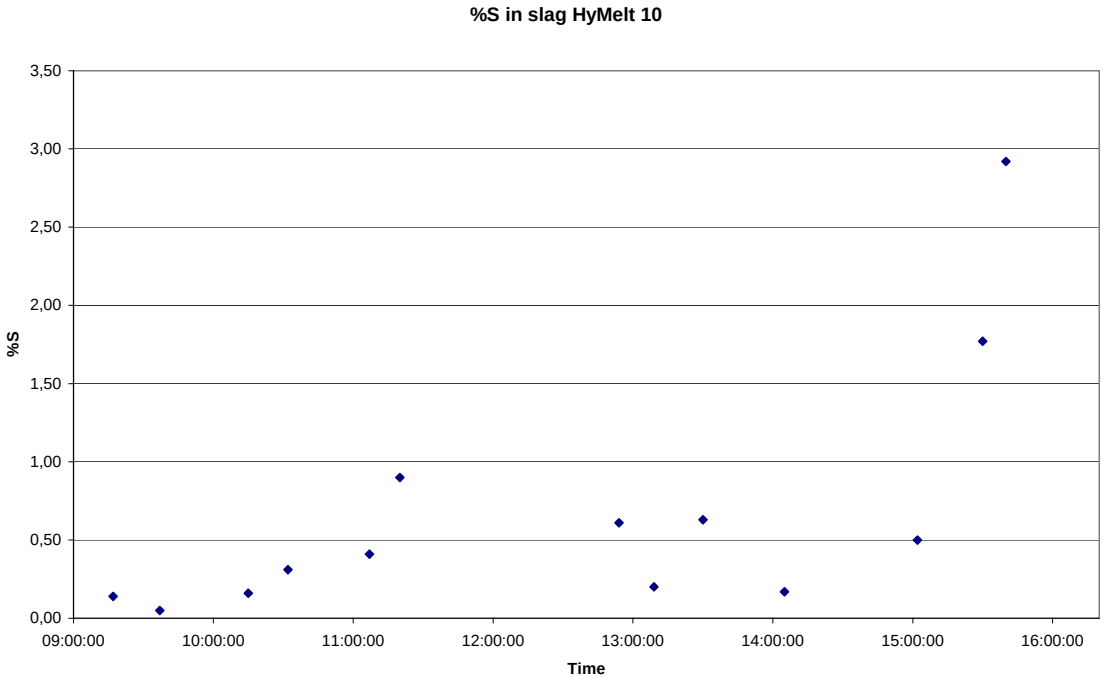


Figure 46 – Sulphur analysis of slag HyMelt 10

6.5 Generated dust

Dust samples were collected from the filter in the gas probe for process gas analysis and from the combusted gas. In the later also the amount of dust could be estimated.

Both types of dust were analysed for total carbon according to DIN ISO 10694 by the laboratory Analytica in Täby.

6.5.1 Dust in process gas

Results from process dust indicate high concentrations of carbon 80 to 90 % C independent of injected material.

Table 1 – Carbon in dust coke injection

Charge	%C
S1790-1	83
S1790-2	85
S1790-3	89
S1790-4	83
S1790-5	83
S1790-6	100
S1791-4	87
S1791-5	81
S1791-6	not avail

Table 2 – Carbon in dust coal injection

Charge	%C
S1791-1	90
S1791-2	94
S1791-3	84

6.5.2 Dust in combusted gas

It is a strong relation between amount of dust in the combusted gas and material feed rate. The correlation is expected and seems to be valid for both coal and coke.

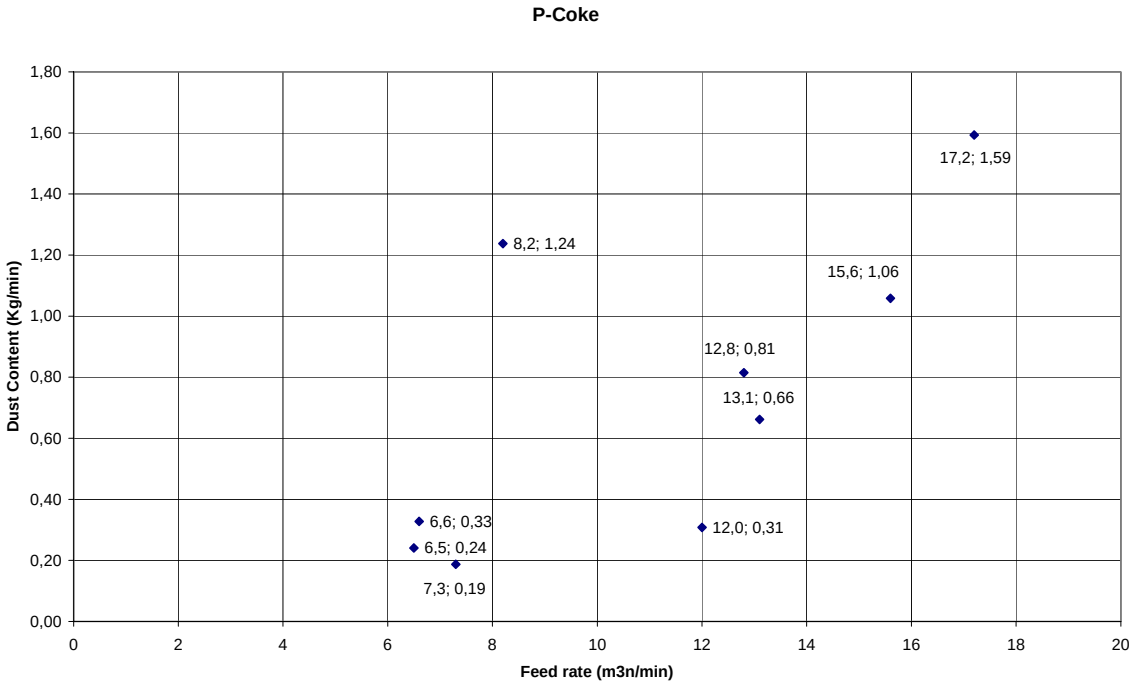


Figure 47 – Dust content of combusted gas at coke injection

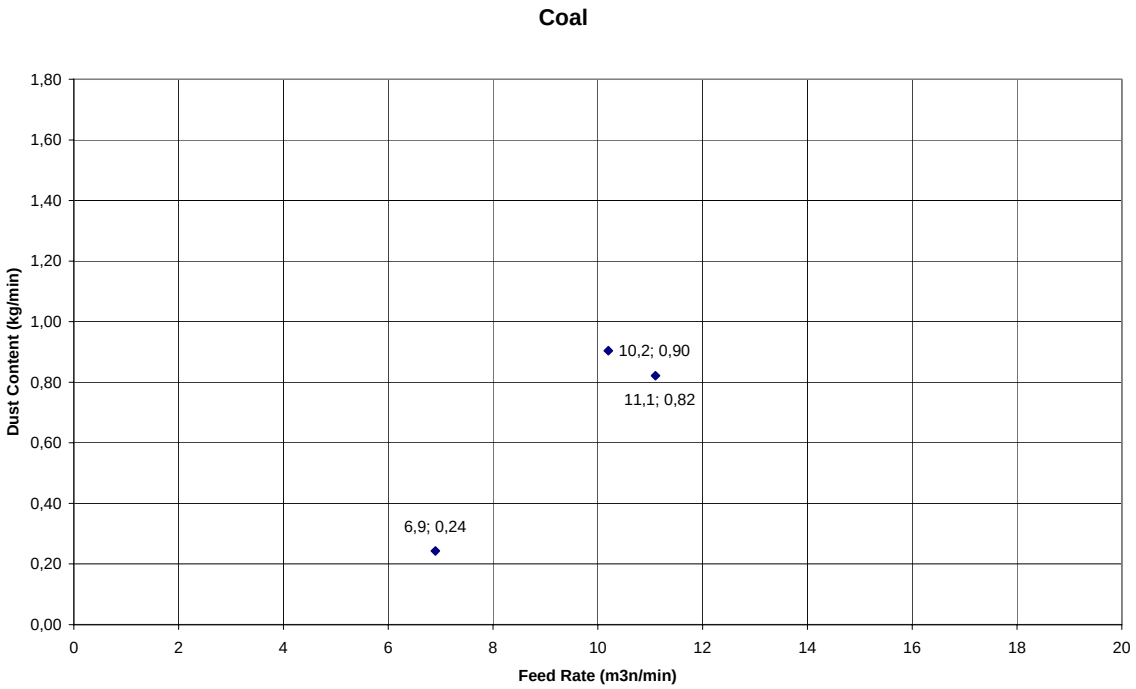


Figure 48 – Dust content of combusted gas at coal injection

Process gas and dust in the process gas are combusted above the converter mouth before reaching the waste gas cleaning system. While the gas components are completely combusted some carbon remains un oxidised in the dust. The amount is low compared to the total throughput low as can be seen in the table 3 and 4.

Table 3 – Carbon amount in combusted dust for coke feed

Charge	Dust Content (g/m3n)	Waste gas (m3n)	Dust Content (gr)	Dust comp %C	Carbon in dust (kg)
S1790-1	5,30	1404	7,4	2,4	0,2
S1790-2	0,80	4206	3,4	not avail	
S1790-3	1,03	3972	4,1	13	0,5
S1790-4	1,40	1398	2,0	22	0,4
S1790-5	1,32	4200	5,5	43	2,4
S1790-6	3,49	3498	12,2	79	9,6
S1791-4	2,98	3330	9,9	18	1,8
S1791-5	7,17	2664	19,1	68	13,0
S1791-6	4,76	1554	7,4	26	1,9

Table 4 – Carbon amount in combusted dust for coal feed

Charge	Dust Content (g/m3n)	Waste gas (m3n)	Dust (kg)	Dust comp %C	Carbon in dust (kg)
S1791-1	3,14	2886	9,1	2,8	0,3
S1791-2	2,67	3684	9,8	1,6	0,2
S1791-3	1,11	2820	3,1	61	1,9

6.6 Carbon balances

The carbon yield calculated by gas balance can be compared with calculation based on carbon content in the metal and the methods have rather good agreement.

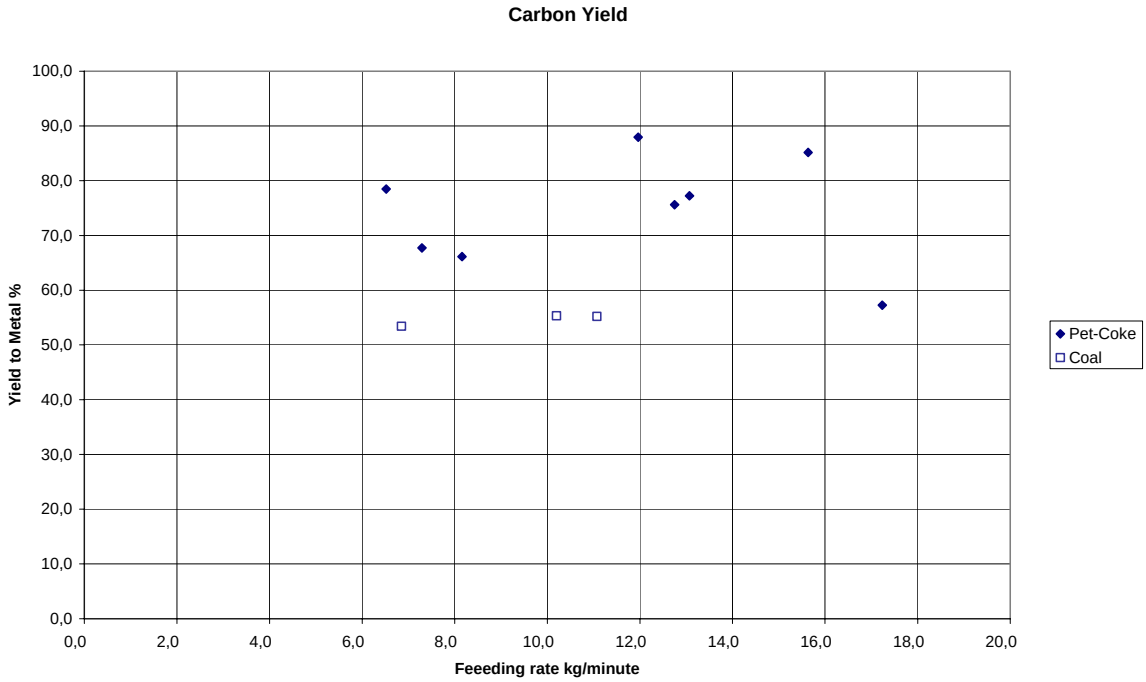


Figure 49 – Carbon to metal yield

6.7 Refractory wear

Severe wear was found in the area for injection which must be repaired. The overall lining can be used for further trials.

Table 5 – Refractory wear

	New lining		After HyMelt 10		Wear
Level	N/S	E/W	N/S	E/W	
Cone	1410	1410	1430	1375	-4
1500	1410	1410	1485	1430	24
1250	1410	1410	1490	1490	40
1000	1410	1410	1520	1510	53
750	1410	1410	1510	1520	53
500	1410	1410	1540	1525	61
250	1410	1410	1510	1525	54
0	1410	1410	1380	1400	-10
Hight	2893		2970		77

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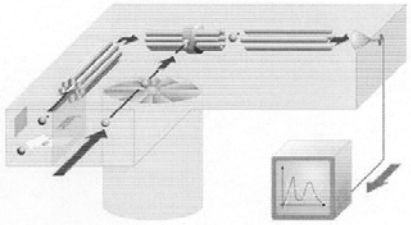
Airsense

Trace Mass Spectrometer



Higher demands for cost reduction, enhanced process control efficiency, coupled with increased environmental awareness is pushing the development of faster and more sensitive next generation analyzers. With years of advanced technical development and process monitoring experience these demands have been met with the Airsense series.

Instrument operation is based on quadrupole mass spectrometry with soft ionization. This combination allows for unrivalled performance in sensitivity, speed, selectivity and robust and reliable operation in industrial use.

Application and system control run under Windows and can be completely automated with pre-programmed methods. Extension to other applications with additional compounds is easily performed.

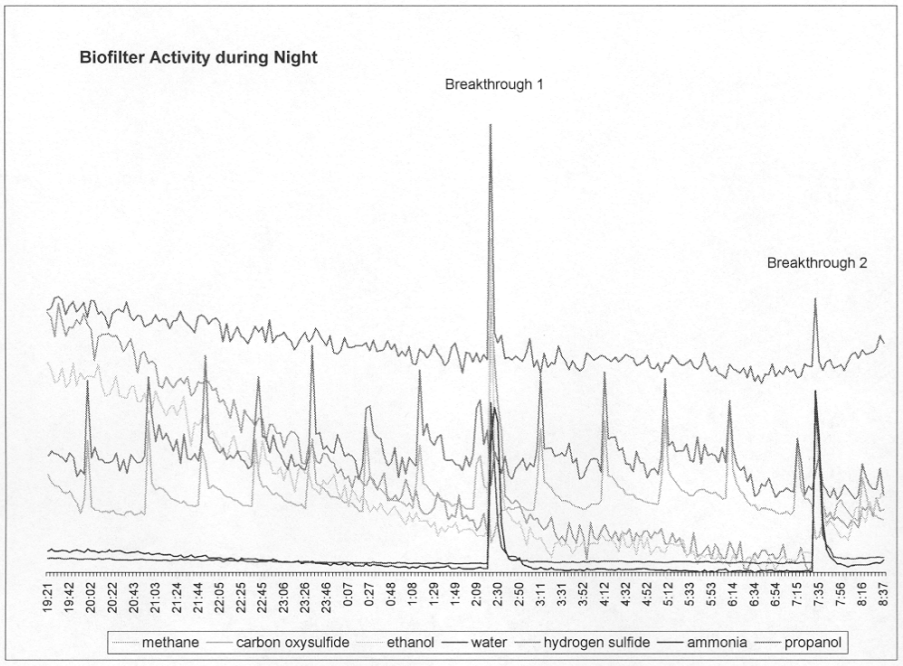
Technical Specification and Rating Data

Mass Range	0 – 500 amu
Analysis Time	10 – 6500 msec/amu
Measuring Range	10^6 with automatic compensation of inlet pressure
Response Time	T 90 < 50 msec
Detection Limit	< 10 ppb benzene in exhaust gas < 1 ppb benzene in air
Zero Drift	≥ 2 ppb over 24 h for benzene
Linearity	10^4
Reproducibility	< +/- 3 % over 24 h for benzene
Accuracy	< +/- 2 % over 24 h for benzene
Temperature	20°C – 40°C
Inlet Temperature	80 – 190°C, adjustable
Humidity	80 % max., non condensing
Gas Consumption	30 – 250 ml/min
Power Supply	220 V / 50 Hz or 115 V / 60 Hz, 800 W
Dimension	590 x 650 x 730 mm
Weight	87 kg
Service Interval	Preventative maintenance once / year
Software	SCP for Windows or ACP for Windows

The Airsense is used in the following applications:

- Incineration Stack Gas
- Fuel Cell
- Fast Pre/Post Catalyst Converter
- $DeNO_x$ Converter
- Sulphur Components in Engine Exhaust
- Catalyst Efficiency
- CO_2 Quality Control
- Online PET Bottle Control
- Environmental Monitoring
- Aircraft Emission in Ambient Air
- Gas Phase Analysis of Human Breath
- Workplace Control
- Fast Measurement of non regulated Hydrocarbons
- Desulphuration
- Steel Converter Control
- Cement Industry

- Multi Component Analysis in %, ppm and ppb area
- Soft ionization provides a high level of confidence for component identification in complex gas streams
- Excellent response and reproducibility
- Simple extension of the molecule database
- Typical detection limit in the ppb area
- 3 to 4 decades dynamic range
- Fast sampling rate
- Compact design for mobile operation
- Low annual operating costs



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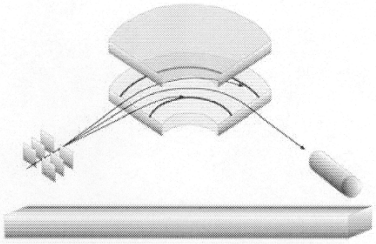
HSense

High Resolution Hydrogen Mass Spectrometer

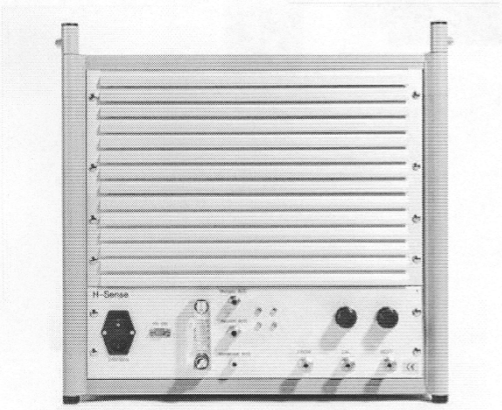
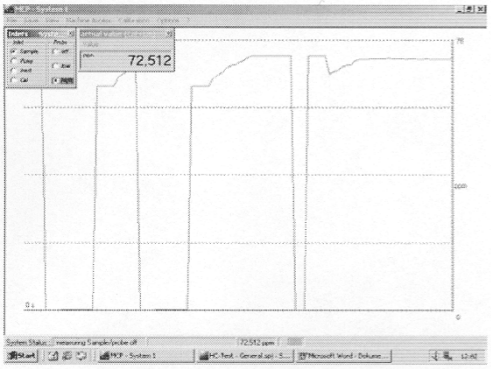


The instrument comprises of a magnetic sector mass spectrometer for the analysis of hydrogen concentrations in the vehicle exhaust. Gas samples are ionized by electron impact ionization. Ions generated are separated by magnetic sector according to their molecular mass. Only hydrogen or helium is analyzed for their concentrations. The well proven gas inlet system automatically compensates for pressure fluctuations. Oil free vacuum pump supply ensures minimal service requirements with only one single routine maintenance per year.

The system is ideal for on-line analysis of hydrogen and helium in vehicle exhaust gas, process control and environmental monitoring.

Technical Specification and Rating Data

Mass Range	2 – 4 amu
Mass Separation	min. 1 amu over the mass range
Cycle Time	100 msec min.
Dynamic Range	1 – 10000 ppm / 0,1 – 100 %
Response Time	< 300 msec
Dynamic	10^6
Linearity	± 3%
Drift	< 2% over one hour – measured with 100 ppm H_2
Inlet Pressure Compensation	200 mbar – 2 bar
Gas Consumption	20 ml/min
Calibration Cycle	Automatically controlled, adjustable by the software
Calibration Time	Typical 120 sec.
Analog Output	2-channel on-line outputs
Supply Voltage	220 V / 50 Hz or 115 V / 60 Hz, max. 500 W
Temperature	10°C – 40°C
Humidity	90 % max., non condensing
Weight	67 kg
Dimensions	590 x 650 x 640 mm
Service Interval	Preventative maintenance once / year
Software	MCP for Windows



- Single Component Analysis in ppm and % area
- Excellent response and reproducibility
- Typical detection limit in the ppm area
- 3 to 4 decades dynamic range
- Fast sampling rate
- Easy to use software
- Datastorage in ASCII format
- Low annual operating costs