Reducing Ultra-Clean Transportation Fuel Costs with HyMelt$^{\circledR}$ Hydrogen

Quarterly Report

April 1 – June 30, 2003

July 31, 2003

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

For
U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 10940
626 Cochrans Mill Road
M/S 922-273C
Pittsburgh, PA 15236-0940

By
Donald P. Malone and William R. Renner
EnviRes LLC
1509 Bull Lea Drive
Suite 500
Lexington, KY 40511

DISCLAIMER

ABSTRACT

This report describes activities for the third quarter of work performed under this agreement. Atmospheric testing was conducted as scheduled on June 5 through June 13, 2003. The test results were encouraging, however, the rate of carbon dissolution was below expectations. Additional atmospheric testing is scheduled for the first week of September 2003.

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1.0 PROJECT OBJECTIVES, SCOPE AND DESCRIPTION OF TASKS

1.1 Introduction

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

1.2 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 stream. 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.

1.3 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 completed most of this task.

Task 2.0 Project Testing

Task 2.1 HyMelt Atmospheric Pressure Testing in a Molten Iron Bath

MEFOS will fabricate the petroleum liquid feed system. All injection systems will be tested in a cold flow environment. The injection systems will be hot commissioned. Any equipment revisions indicated by cold flow testing and hot commissioning will be made. Process performance testing will be performed for each feed. This task is being executed.

2.0 EXECUTIVE SUMMARY OF WORK DONE DURING THIS REPORTING PERIOD

On May 23, we formally requested a follow-up audit of the financial reporting and accounting system of EnviRes by letter to Andrew Ferlic. The audit was subsequently scheduled for early July. (Note: The audit was conducted by Brad Quinlan, auditor for the Defense Contract Audit Agency [DCCA] under contract by U. S. Department of Energy, on July 9 and 10 and an exit conference was held on July 10 with the auditor and Dan French, Controller. On July 25 we received an electronic copy of the audit report concluding, “EnviRes’ accounting system is adequate for accumulating costs under Government contracts”).

We received Amendment No. M005 dated June 25 revising Clause 2.26 “Monetary Exchange of Foreign Currency,” allowing EnviRes to bill for the MEFOS subcontract at the exchange rate in effect at the time of payment. We subsequently have submitted a bill to DOE reflecting the new exchange rates at the time of the MEFOS payments.

EnviRes and Siemens Westinghouse executed a subcontract for the combustion testing tasks described in the DOE-EnviRes agreement under which this work is being performed. Donald P. Malone and Dennis Horazak co-authored a paper for the Pittsburgh Coal Conference to be held September 15 to 19, 2003. This paper has been submitted to DOE for review. It deals with data generated before the contract for this work was executed.

Kvaerner developed a flowsheet and some preliminary simulations using Aspen Plus to evaluate the alternate CO disposition by shifting it to hydrogen instead of using CO for Fuel. Kvaerner has incorporated catalyst vendor data into this model. Figure AII-1 is a process flow diagram (PFD) for this alternate and table AII-1 gives the stream flows, compositions, and conditions for this proposal. Kvaerner is also developing a detailed amine system using data from UOP.

3.0 Experimental

EnviRes finalized the design for the Oil injection system, purchased the equipment, and fabricated the system. We successfully hot tested the system (oil was injected into the converter with no metal in the converter, oxygen injection combusted the oil in the converter) on June 4. Figure 1 is a photograph of the oil feed system. The large rectangular shape is the tank for holding the heated oil. Other items (some not visible) include the high-pressure pump; temperature, pressure and flow metering sensors; electrical heaters; control valves; and recycle piping.

MEFOS performed additional thermodynamic calculations using the FactSage system. MEFOS made comparisons, where possible, with the HSC Chemistry for Windows system. MEFOS issued an interim report on this work that appears in Appendix I. EnviRes directed MEFOS to make additional changes before the final report issues to incorporate complete reactor heat balances and other minor input changes. We believe that the work to date shows that sulfur removal for high sulfur feeds (more than 1 to 2 w% S) will require that sulfur not removed as H_2S produced by hydrogen indigenous in the feed must be removed with CaO injections as CaS in the slag. The CaO requirement for this approach is still less than half that required by processes that rely exclusively on CaO as the means of sulfur removal.

MEFOS began feed injection on June 5. Each day of experimental operation began by melting 5,000 to 5,500 kg of metal in the electric arc furnace (eaf), adjusting the metal composition if necessary, and transferring the metal to the Universal Converter by ladle. Figure 2 shows the metal being transferred to the Universal Converter. After completing the metal transfer, the operator typically decarburized the melt with oxygen to get the metal temperature and carbon content to the desired level. Figure 3 shows the Universal Converter during decarburization. The intense flame shown in the photograph occurs at the gap between the hood and the converter where ambient air flows into the hood and reacts with CO and other decarburization gases. After decarburization and feed injection the operator typically tilted the converter for slag and metal sampling. Metal samples were also taken during decarburization and feed injection, but MEFOS considers tilted samples to be more representative of the melt composition. Figure 4 shows an operator taking a slag sample from the tilted converter. At the end of each day of operation, MEFOS poured metal and slag separately from the converter. Figure 5 shows the operator pouring the metal from the converter. The converter was left over night with a burner inside of it to keep the refractory hot for the next day of testing.

MEFOS continuously sampled converter gas during both feed injection and decarburization. The sample probe had a ceramic filter on the end inside the converter and a finer filter after the gas cooled and before it went to analyzers. Figure 6 shows the ceramic probes use inside the converter. These ceramic filters or the finer filters often became obstructed resulting in a greater vacuum in the sample train than intended. This caused significant air infiltration into the samples. MEFOS must make corrections for air in the gas samples. Figure 7 shows the Mass Spectrometer that MEFOS temporarily set up to measure converter gas composition.

MEFOS generated a vast amount of raw data from these tests. MEFOS traditionally takes the month of July as holiday so little data analysis has been done. Some of the raw data generated and some of the limited data analysis appear in Appendix I. The data acquisition system samples most variables at a rate of once per second. Approximately 150 variables are sampled at this rate. A notable exception is the metal temperature; it is measured every 3 to 5 minutes during operation. This creates an enormous amount of data. To make the data more useable the raw data presented in this document are averaged to one-minute values unless otherwise noted. Table AI-1 contains data generated on June 10, 2003 during the fifth coal injection. The data are averaged from 30 seconds before to 30 seconds after the time indicated in the first column. A large number of columns containing less significant information were left out to allow a reasonable width table. These data are given to represent a small sample of the data generated. Figures AI-1 to AI-11 show various gas compositions vs. time during coal injection on June12 and during petroleum coke injection on June 13. Please note that these data have not been corrected for air leakage into the samples. The COS channel did not work on either day and the H_2S channel did not work on June 13. A complete data set will be presented later.

Figure 1. Liquid Feed System for MEFOS Testing

Figure 2 Metal Transfer to the Universal Converter

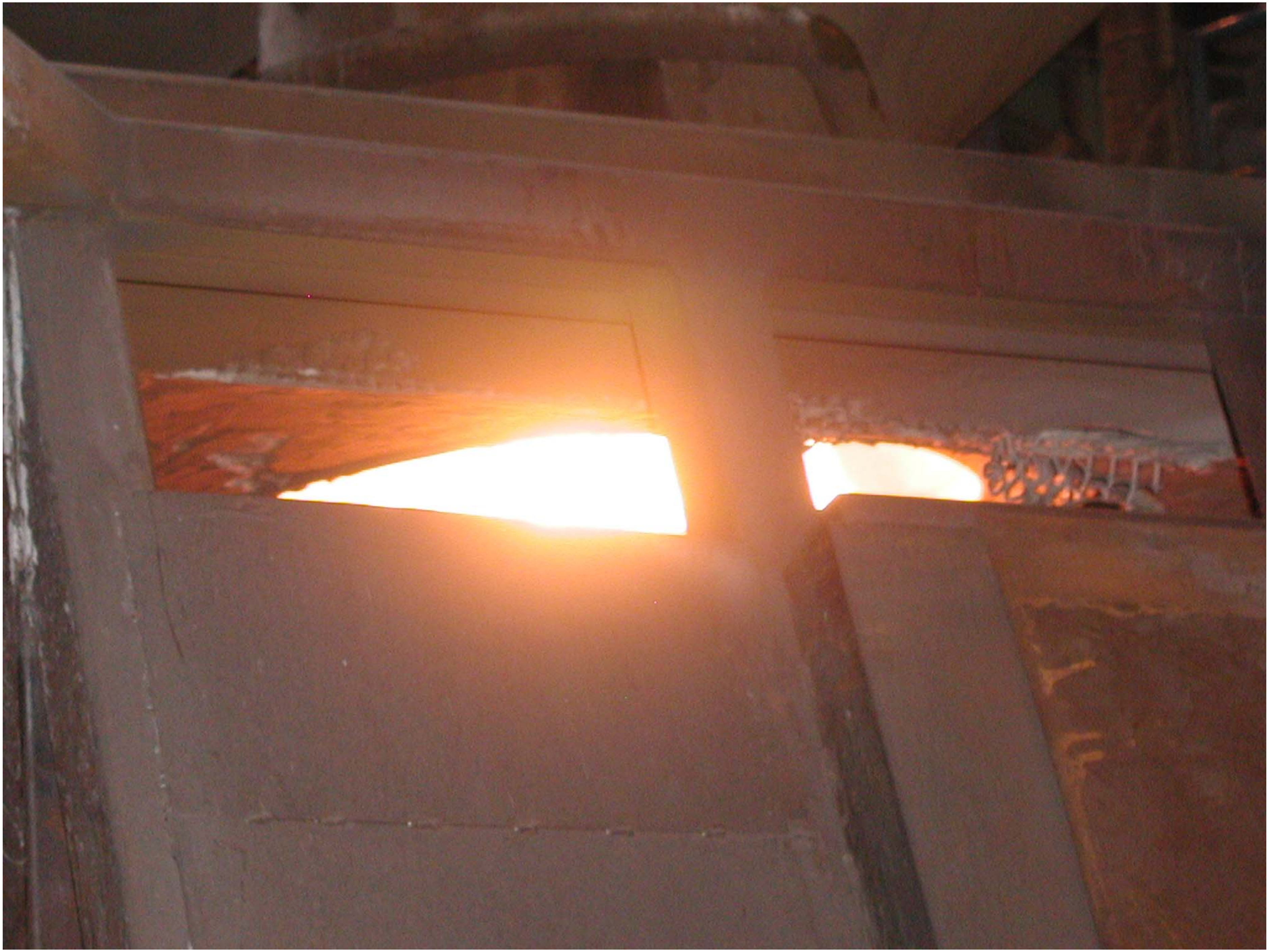

Figure 3. The Universal Converter During Decarburization

Figure 4 Slag Sampling from Tilted Converter

Figure 5 Metal Pour from Converter at Day’s End

Figure 6 Used Ceramic Filters from Gas Sample Probe

Figure 7. On-Line Mass Spectrometer for Gas Analysis

4.0 Results and Discussion

Although the data developed so far are preliminary, it is clear that the top entry lance injection system did not adequately penetrate the slag and metal to give acceptable carbon dissolution in the metal phase. During feed injection significant amounts of carbonaceous material were observed on top of the slag layer. The high levels of methane in the product gas are another indictor of poor feed injection. Methane levels should not exceed 0.5 %v in the product gas. During the tests methane levels often exceeded 6 %v.

Oil injection appeared to produce an unacceptable level of soot. We observed this problem visually and from the rate at which the gas sample ceramic filters became obstructed. We plan to give oil injection a low priority in future testing.

No problems with accretions or other solid metal formations were observed. Nitrogen stirring gas and transport injection gas made detection of air leakage into the sample system more difficult to detect and quantify.

The data generated to date will be analyzed to a much greater detail in the next few months. By MEFOS, Kvaerner and EnviRes.

5.0 Conclusion

EnviRes and MEFOS have discussed the injection problems and agree that further atmospheric testing should be performed using submerged lances. Submerged lances are not commercially feasible because of the relatively short operating life. Submerged lances do offer a quick and cost effective approach to simulating tuyere injection. The pressure vessel to be built for super-atmospheric testing can be fitted with tuyeres.

We will endeavor to use argon instead of nitrogen for stirring and transport injection gas. This will make air leakage and infiltration much easier to detect.

6.0 References

No references were cited in this document.

7.0 PLAN FOR THE NEXT QUARTER

Additional atmospheric testing is scheduled for the first week of September 2003. The testing will last 3 days. Illinois #6 coal and petroleum coke will be the feeds to be tested using submerged lances. The vessel for super-atmospheric testing will be finalized and ordered in the upcoming quarter.

Kvaerner will continue evaluating amine systems and complete the carbon monoxide shift study. Kvaerner will begin atmospheric test data evaluation for commercial design studies.

EnviRes and Siemens Westinghouse will finalize all input parameters for a combustion turbine and Siemens Westinghouse will begin combustion simulations in the upcoming quarter.

APPENDIX I

MEFOS DATA

Box 812, 971 25 LULEÅ

Dokument:	MEFOS-rapport	*Reg nummer:*	MEF03039SK
Fo-uppgift:		*Datum:*	2003-05-23
Konto:	386420	*Rev datum:*	
Ämnesomr:		*Avdelning:*	MM

SUMMARY OF THE THERMODYNAMIC CALCULATIONS ON THE HYMELT PROCESS USING FACTSAGE 5.1

by

Guozhu Ye

Godkänd av forskningschef: ....
Slutlig: Y
Projektledare: Nils-Olov Lindfors
Sekr: ta
Distribution: EB, NOL, GY, SÅ, Don Malone (EnviRes)

Summary of the Thermodynamic calculations on the HYMELT process
using FACTSAGE 5.1
Guozhu Ye
MEFOS

SUMMARY

This report summarized the calculations carried out under the subproject "Desk study" as part of the EnviRes pilot project at MEFOS. The major conclusions are drawn in the followings.

The H_2-cycle

	Injection time per H_2-cycle, min (10 kg/min and 5 ton iron melt)	Injected material/ton iron melt-ratio for one H_2-cycle, kg/ton
P-coke	22	44
Aromatic extract	21	42
Coal ILL#116	30	60
Spent tyres	22.5	45

The H_2-cycle is thus only related to the C-content in the injected carbon-materials.

The de-C cycle

This is the same as a LD-process where C-content is removed by oxidation except the pressure provided. One interesting point here is that if the cycle time for de-C step will be in the same range as that for the H_2-cycle time the gas system for the CO- and H_2 could be quite different. Since the flow rate of CO will be 2-3 times that of the H_2-gas.

The simulations are based on a variation of carbon content in the metal between 0.5-4 %.

The S-cycle

The S-cycle is mostly determined by the S/C-ratio in the used materials and the H/C-ratio as shown in the following table. Sulphur is assumed to vary between 0.5-1.25 %.

	S/C-ratio	H/C	C-/S-cycle ratio
P-coke	0.075	0.058	3
Aromatic extract	0.045	0.077	6
Coal ILL #6	0.049	0.069	0*
Spent tyres	0.021	0.088	20

*10 % ash in the coal and about 10 % CaO is added. S is thus removed in the slag already. There will not be S-accumulation.

S-removal by H_2- purging

Due to the unfavourably thermodynamical conditions provided for H_2S-formation, the method for S-removal by H_2-purging is highly inefficient. To remove the S dissolved in the iron melt it will consume much more H_2-gas than it has been produced during the H_2-cycles.

S-removal by slag treatment

Slag treatment is efficient. Using a slag with a CaO/SiO_2-ratio of 2 and a minimum amount of 60 kg/ton iron melt, the dissolved S will be removed. The slag used in the calculation consists of 60 % CaO, 30 % SiO_2 and 10 % MgO. This slag could be reused after S-removal of the slag by hot treatment.

The V-cycle

The V iron melt can contain up to 13 % V before V will be oxidised to VOx. This means:

1 V-cycle = 1 360 C-cycles

The Ni-cycle (only P-coke)

Theoretically Ni-solubility in the iron melt is not limited. Practically an iron melt with 20 % Ni is reasonable with regards to the reactor volume. This means:

1 Ni-cycle = 11 V-cycles

Heat balance

The temperature drop for a H_2-cycle is shown in the following table.

	ΔT (FACT), °C	ΔT (HSC), °C
P-coke	285 °C	230 °C
Aromatic	300 °C	260 °C
Coal ILL#6	240 °C	Nd

A temperature increase of about 450 °C is expected during the de-C cycle according to the FACTSage calculations.

A net temperature increase of 150-200 °C is thus expected (H_2-cycle + de-C cycle).

This net energy will cover heat losses of reactor and energy needed for smelting of the added slag for metal protection and S-removal.

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1 INTRODUCTION

The HyMelt process consists mainly of two cycles:

- a H_2-cycle during injection of coal/coke/oil in a hot metal bath where high purity H_2 is produced and carbon is dissolved in the metal phase.

- a de-C cycle where the dissolved carbon is oxidized to CO, as a separate product.

The HyMelt process thus produces two separate gas products directly.

As part of the pilot project at MEFOS, thermodynamic calculations on the HyMelt process have been carried out using the thermodynamic computation program FACTSage 5.1 available at MEFOS.

The aim of the calculations is to thermodynamically determinate the following cycles:

- the H_2-cycles
- the CO-cycle
- the S-cycle
- the V-cycle (only for P-coke)
- the Ni-cycle (only for P-coke)

The cycle range of C and S has been set by EnviRes: 0.5-4 % C and 0.5-1.25 % S respectively.

The calculations include simulations on S-removal by:

- H_2-purging
- slag treatment

The effect of temperature on the S-removal, V-cycle etc has also been considered. Both adiabatic and isothermal equilibrium calculations have been performed. In order to ensure the quality of the calculations results, heat balance calculations were also performed by HSC 5.1(A thermochemical computational program developed by Outokompu, Finland)

The calculations have mainly been performed at conditions of 20 bars but also atmospheric pressure calculations have been made.

Effect of pressure on the equilibria has also been calculated.

According to the project plan three basic materials have been simulated. In addition to these, some calculations on spent tyres were also made.

This report will summarize the most interesting calculation results and some special cases will be highlighted such as V-calculations, S-removal by H_2-purging and by slag treatment.

Some calculations for spent tyres have also been calculated.

2 RESULTS OF THERMODYNAMIC CALCULATIONS BY FACTSAGE 5.1

Following phases are included for all calculations:

- gas phase, ideal gas mixture.
- metal phase, diluted solution model for Fe-liquid.
- slag model, the quasi-chemical slag model developed by the CRCT group (Center for Research in Computational Thermochemistry) at the Ecole Polytechnique de Montreal.
- condensed phases, all condensed phases involved in the considered system are included in the calculations.

The detail of the FACTSage program have been described in a 40-page paper published in Vol 26 of the CALPHAD journal [1]which provide an excellent overview on the program and its various modules.

The calculations have been made according to the MEFOS scale of 5 tons metal and an assumed industrial scale of 10 tons. In case of the MEFOS 5 ton converter, an injection rate of 10 kg coal/coke/oil per minute has been used for the calculation. The 10 ton scale converter, the injection rate of 100 kg/min has been used.

From equilibrium point of view the rate is however not important. It is more interesting to use the ratio of “amount of the injected material/ton of the iron melt” for comparison of the different cycles.

The rate of O_2 during the de-C cycle has been related to the H_2-production rate using the H_2-cycle so that the CO-production rate will be the same as that of H_2. It will be slightly different for the three considered materials.

2.1 P-coke

Table 1 shows the chemical composition of P-coke used for the calculations.

Table 1 - Chemical composition of P-coke.

C	H	N	S	O
86.3	5	1	6.5	1

Table 2 shows the most interesting elements dissolved in the metal during the H_2- and CO-cycles.

Table 2 - Concentration of the major elements in the iron melt during the different cycles.

Cycles	C	S	V	Ni	O
initial	0.5%C	0.5%S	0	0	0
1st H_2-cycle 22 min	4.03%C	0.7636%S	0.0092%V	0.00167%Ni	0.0263%O
1st de-C cycle 65 min	0.52%C	0.751%S	0.00921%V	0.00174%Ni	0.157%O
2nd H_2-cycle 22 min	3.95%C	0.994%S	0.0184%V	0.00334%Ni	0.011%O
2nd de-C cycle 64 min	0.51%C	1.027%S	0.0184%V	0.00346%Ni	0.18%O
3rd H_2-cycle 23 min	4.08%C)	1.255%S	0.0275%V	0.0050%Ni	0.012%O
3rd de-C cycle 64 min	0.50%C	1.286%S	0.0275%V	0.0052%Ni	0.18%O

Table 3 shows the mass balance and distribution of the most interesting elements during injection.

Table 3 - Mass distribution of the major elements in the 5 ton iron melt during the H_2- and de-C cycles.

Cycles	C	S	V	Ni	O
initial	25 kg C	25 kg S	0	0	0
1st H_2-cycle 22 min	211 kg C 97.89% to metal	38.8 kg S 96.50% to metal	0.484 kg V 100% to metal	0.088 kg Ni 100% to metal	0.138 kg O
1st de-C cycle 65 min	26.12	38.74	0.467	0.088	7.96
2nd H_2-cycle 22 min	208 96% to metal	52.35 95.17% to metal	0.967 100% to metal	0.176 100% to metal	0.58
2nd de-C cycle 64 min	25.934	52.271	0.938	0.176	8.495
3rd H_2-cycle 23 min	207 95% to metal	65.73 93.91% to metal	1.45 100% to metal	0.264 100% to metal	0.64
3rd de-C cycle 64 min	25.454	65.63	1.4476	0.2640	9.14

2.1.1 The H_2-cycle

With an injection rate of 10 kg/min, in a reactor with 5 tons iron melt it will take 22 minutes to increase the C-content from 0.5 % to 4 %. Related to the total amount of the iron melt, it is 44 kg P-coke/ton iron, see also Figure 6.

As shown in the tables, theoretically a high carburization rate is expected. Over 95 % of carbon in the P-coke is reported to the metal phase.

For the other elements, 94-96 % of sulphur, 100 % of both V and Ni are reported to the metal phase during the injection (the H_2-cycle).

The adiabatic temperature

Figure 1 shows the temperature decrease during the H_2-cycle. A temperature drop of 285 °C will be expected after injection of 220 kg P-coke into the 5 ton iron melt.

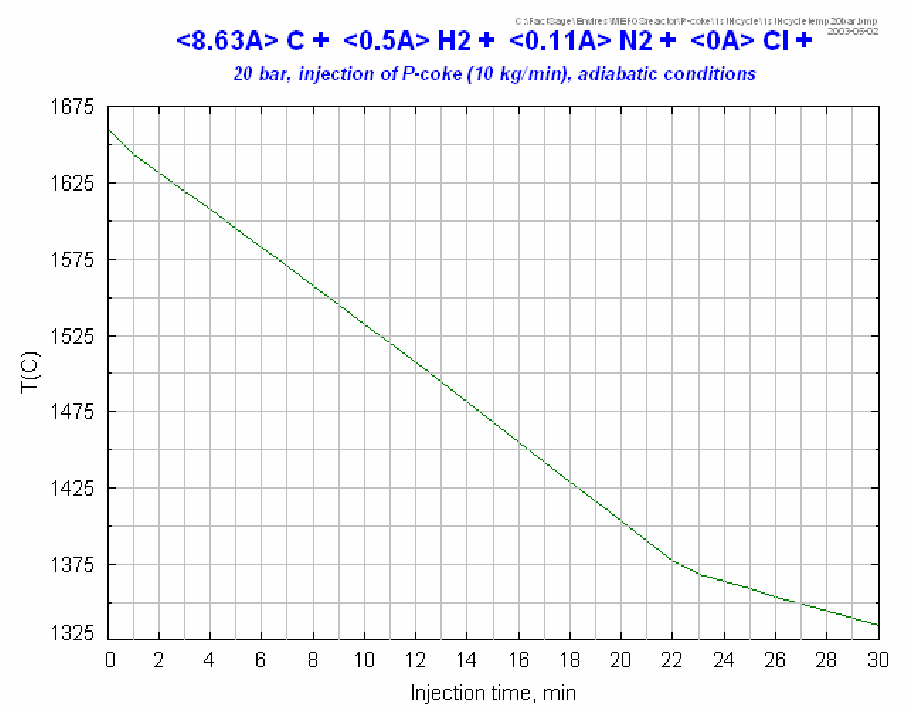


Figure 1 - Temperature drop during the 1st H2-cycle.

The quality of H_2-gas

The purity of the produced H_2 is dependent on the dissolved elements such as O and N in the iron melt and also these elements in the injected P-coke. Figure 2 shows that H_2-content in the gas product from first H_2-cycle is almost 96 %, the minor amount of CO and N_2 is mainly due to the O- and N-content in the P-coke.

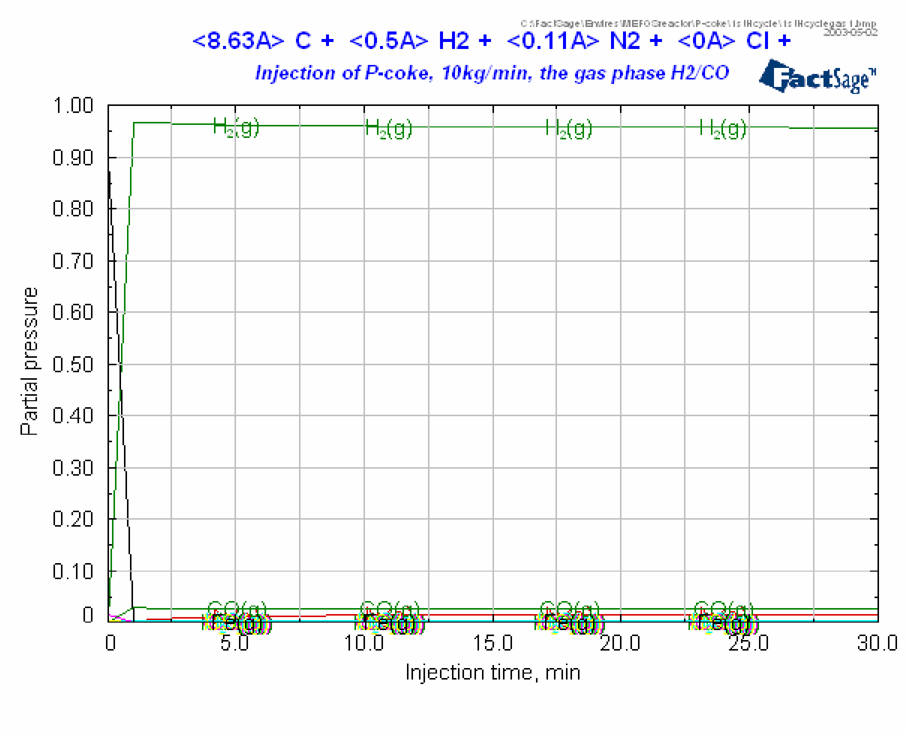


Figure 2 - The purity of H_2-gas produced during the 1st H_2-cycle.

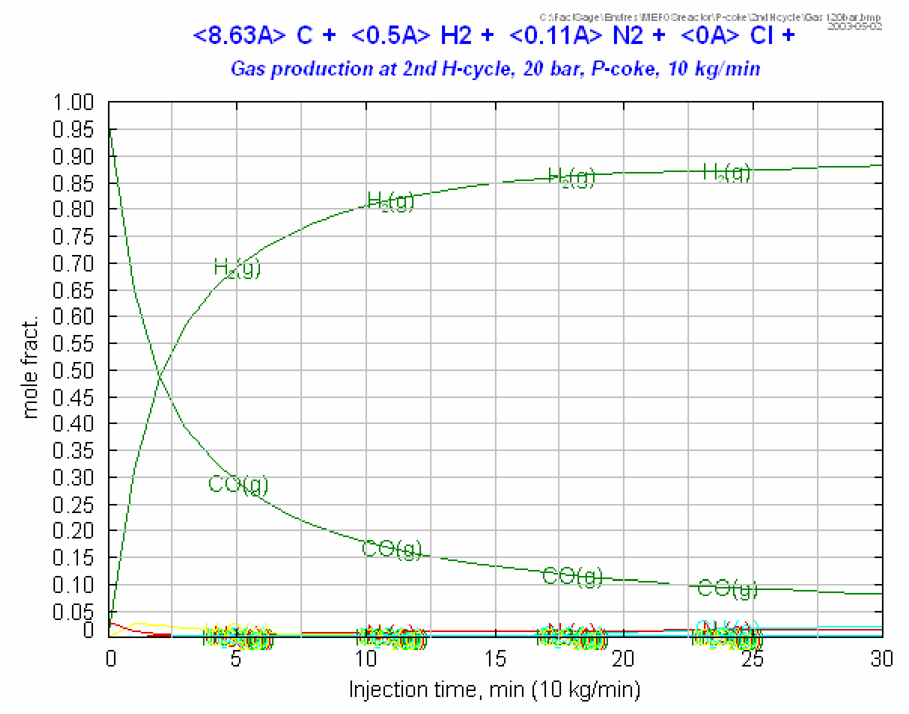


Figure 3 - Purity of H_2-gas produced during the 2nd H_2-cycle.

In the second and third H_2-cycle the H_2-gas quality becomes much poorer. Due of the high pressure of 20 bars applied during the CO-cycles, the O-solubility after de-C process is as high as 0.18 % is the iron melt. The high O-concentration makes a large amount of dissolved oxygen available prior to the C-cycles. As shown in Figures 3-4, the H_2-cycle starts with a gas with up to 95 % CO and gradually the CO-concentration decreases to 28 % after 5 minutes of injection, to 17 % after 10 minutes and 10 % after 20 minutes. The H_2-concentration increases accordingly to about 87 %.

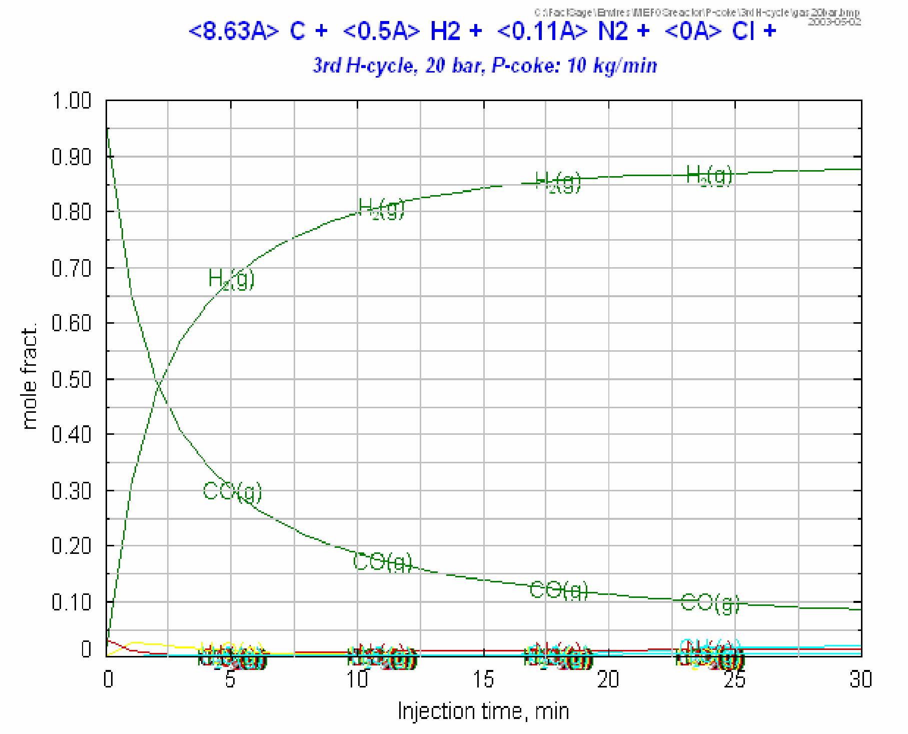


Figure 4 - Purity of H_2-gas produced during the 3rd H_2-cycle.

In reality, the CO-gas produced in the first few minutes will leave the system directly and they should not be available for the coming equilibrium steps. A more precise diagram will be similar to Figure 2, probably a few intensive minutes for CO-generation and then a rather pure H_2-production.

Concentration of the gases of minor amount is shown in Figure 5 (from the second H_2-cycle).

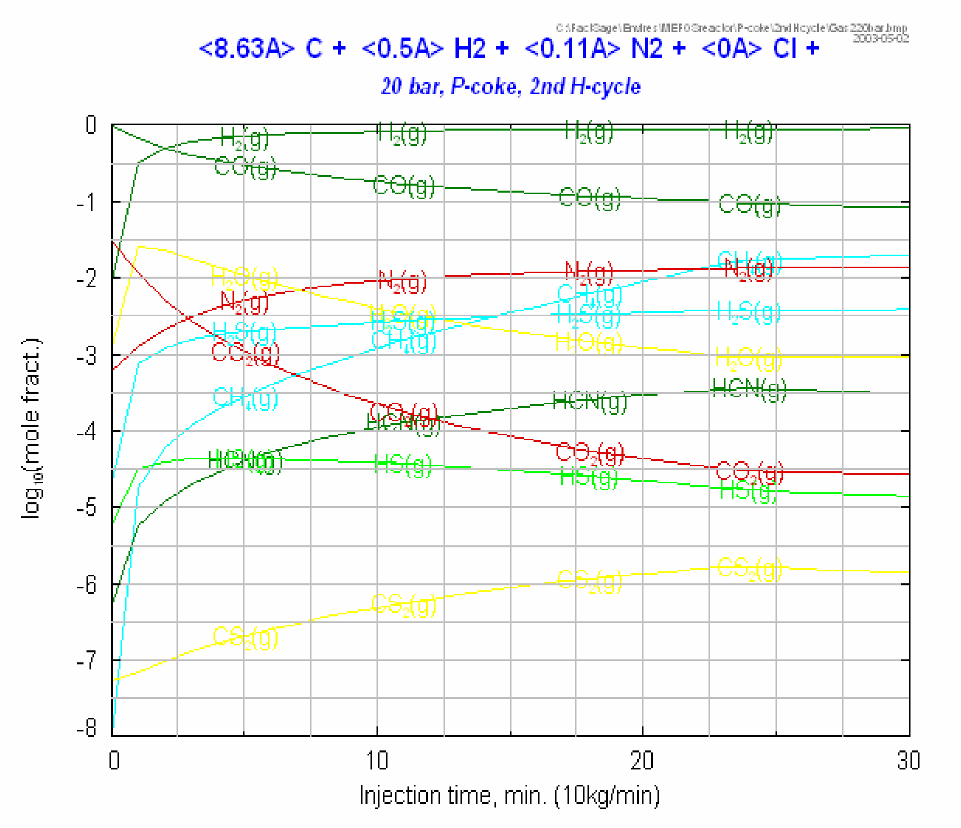


Figure 5 - Gaseous species of minor amount, from 2nd H_2-cycle.

Chemistry of the iron melt

Concentration of the dissolved elements of interest during the first H_2-cycle is shown in Figure 6. As shown, C-content increases to from 0.5 % to 4 % C in 22 minutes of injection, S-, V- and Ni-content increases proportionally with the amount of the injected P-coke. The same trends are observed for the second and third H_2-cycle.

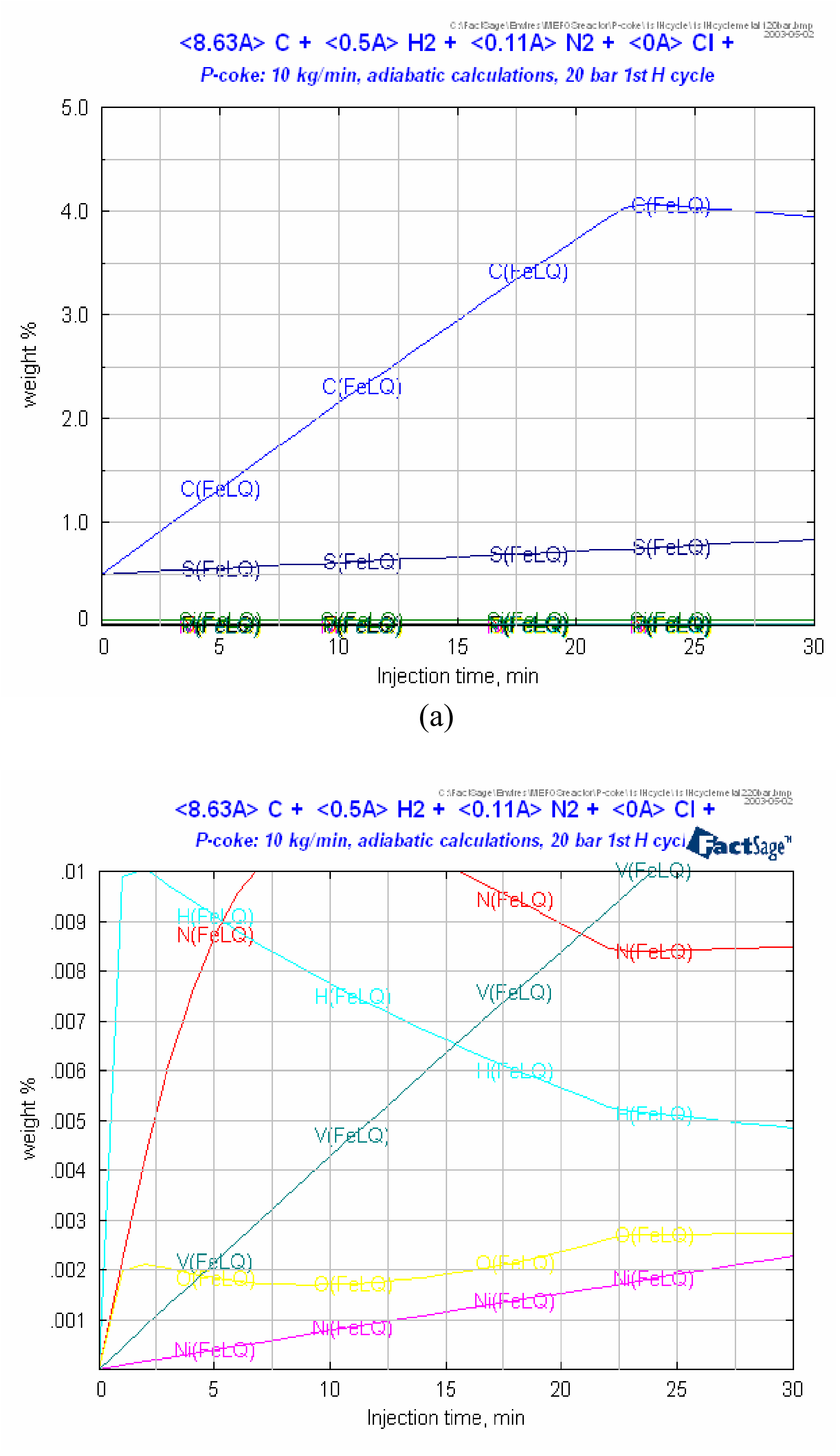


Figure 6 - Chemistry of the iron melt, (a) major element, (b) elements of minor amount.

2.1.2 The CO-production cycle

As shown in Table 2 and 3, it he O_2-blowing rate is defined so that the production rate of CO will be in the same range as that for the H_2-production, it will take 65 minutes to remove C-content in the iron melt from 4 % to 0.5 %. See also Figure 8 (from the second cycle).

The adiabatic temperature

According to the adiabatic calculations the iron melt could be heated up to 1 800 °C from 1 350 °C during the oxidation cycle, as shown in Figure 7.

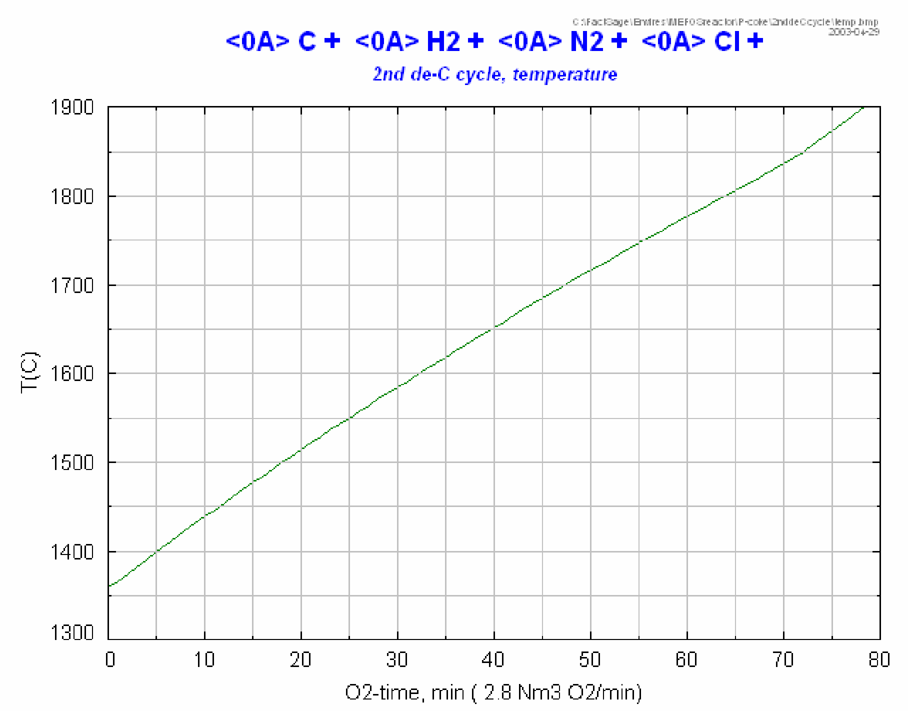


Figure 7 - Temperature increasing during the de-C cycle.

Purity of the CO-gas

During the H_2-cycle, some H is dissolved in the iron melt. The H_2-concentration is about 0.3 % under the pressure of 20 bars. During the first few minutes of the de-C cycle, the dissolved hydrogen will be released and a pure CO-gas will be expected. See Figure 8.

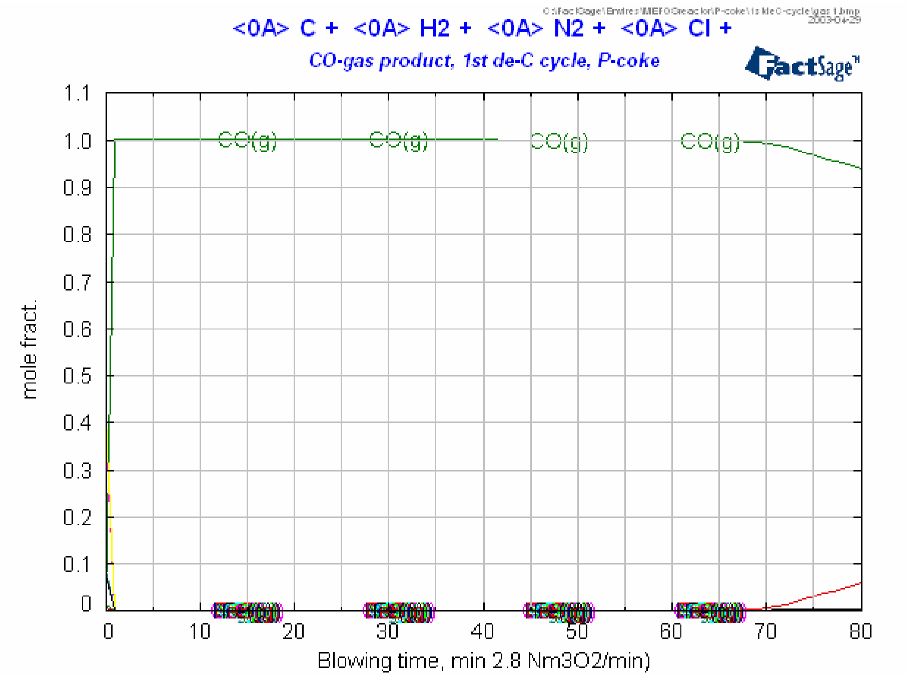


Figure 8 - CO-gas purity during a de-C cycle.

Chemistry of the iron melt

Figure 9 shows the C-content decrease from 0.4 to 0.5 % during O_2-blowing with a rate of 2.8 Nm^3/min.

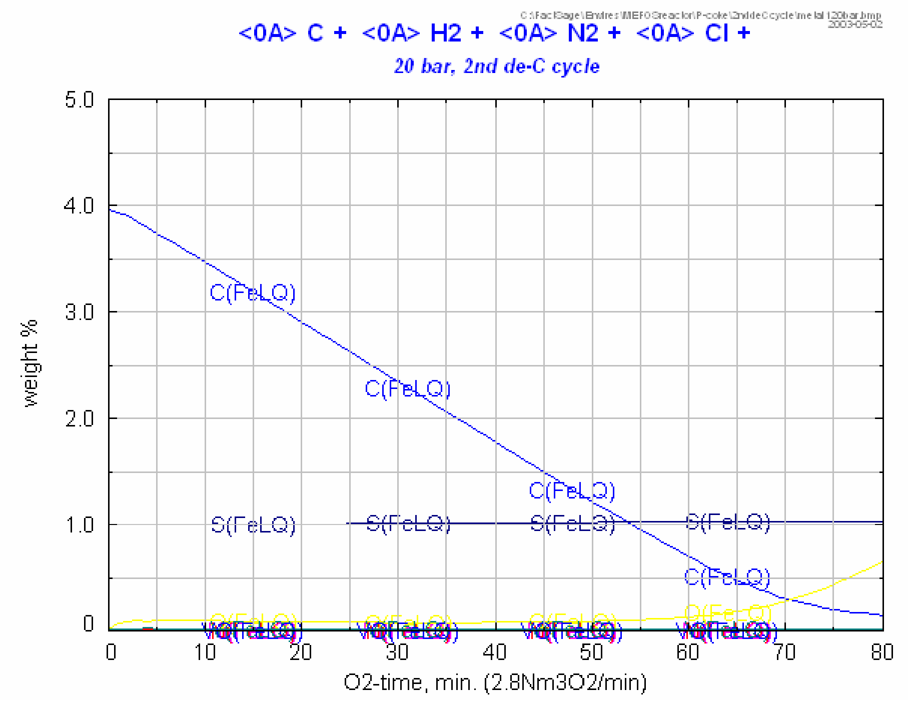


Figure 9 - Change of the concentration of the major elements in a typical de-C process.

As shown in the Figure and Tables 2-3 the S-, V- and Ni-content remain in the iron melt during the de-C cycles.

2.1.3 The S-cycle

As shown in Table 2 and Figure 10, the S-content increases proportionally with the injected material during the H_2-cycle, over 95 % of S is the iron melt. During the de-C cycle, the S-content in the melt remains unchanged. This indicates that H_2-purging is not an efficient way for S-removal.

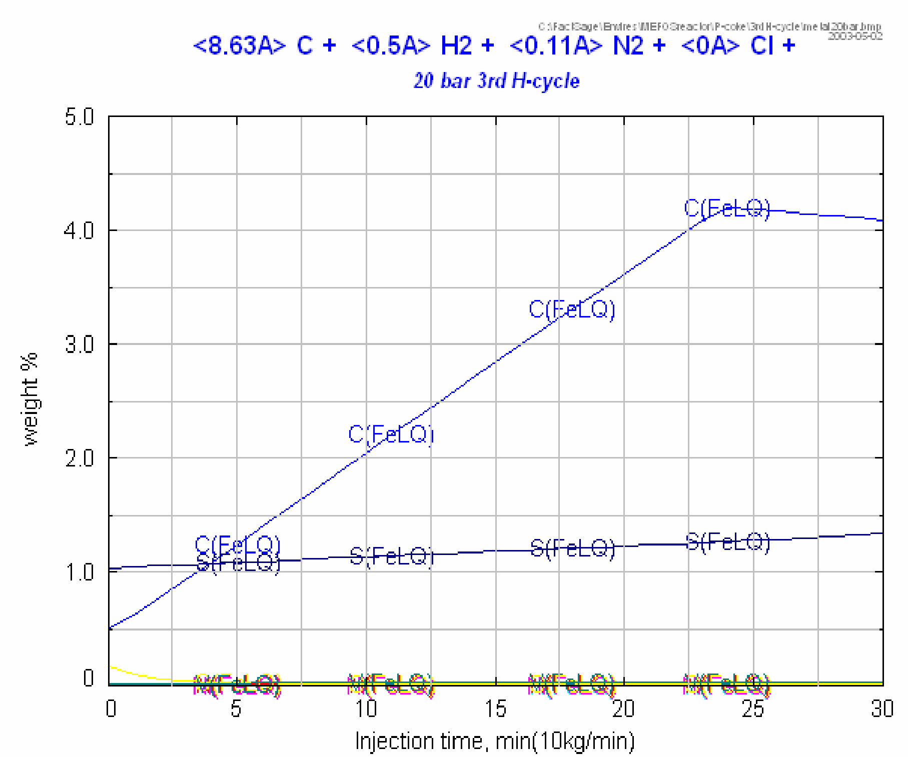


Figure 10 - Major elements in the iron melt during the 3rd H2-cycle.

The S-cycle has been set to 0.5- 1.25 %. After three H_2-cycles (and three de-C cycles), the S-content reaches the upper S-limit.

1 S-cycle = 3 C-cycles

Thus after we have injected totally 660 kg P-coke in 5 ton iron melt, or 132 kg P-coke/ton iron melt, an S-removal step has to be taken.

2.1.4 S-removal by H_2-purging

Using the equilibrium composition of iron melt obtained from the calculations in the third H_2-cycle and various H_2-amount as input. S-removal by H_2-purging has been simulated.

H_2S formation

As shown in Figure 11, the H_2S formation is rather limited. The partial pressure of H_2S is as low as 0.004.

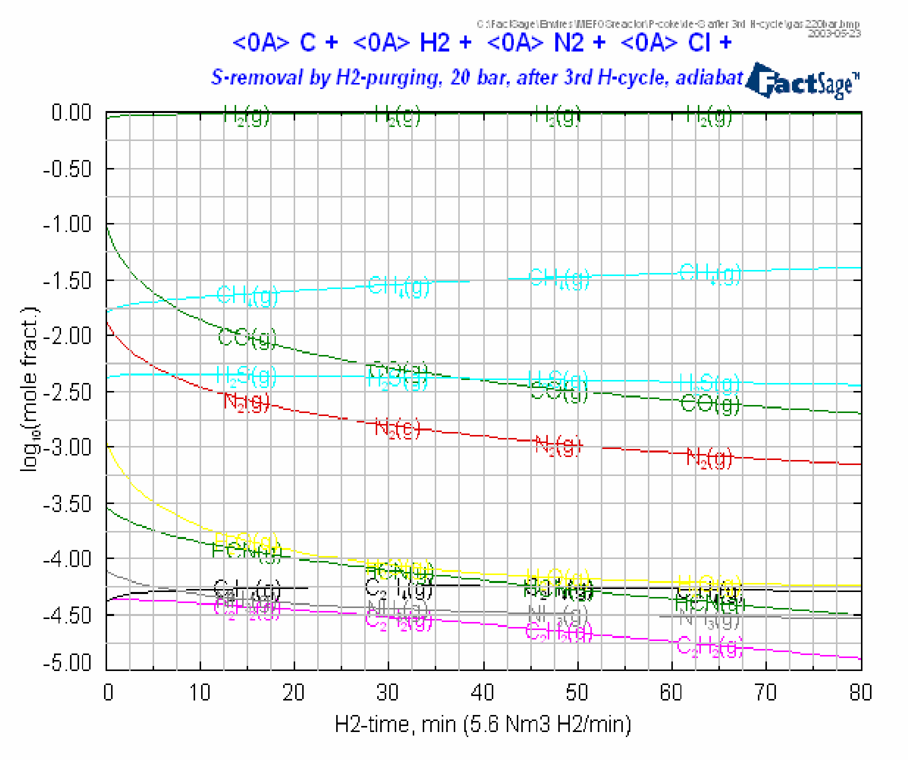


Figure 11 - Formation of H_2S and other gaseous species of minor amount.

S-removal efficiency

With a H_2-purging rate of 5.6 Nm^3/min (which is the same as the H_2-cycle), it will take 80 minutes to reduce S-content in the iron melt from 1.24 % to 1.20 % and it will take over 38 hours to reduce 1 % S in the iron melt. The total amount of H_2 needed will be 12 800 Nm^3 which is about 34-35 times the H_2-gas produced during three H_2-cycles (370 Nm^3/S-cycle), see Figure 12 and Table 4.

Table 4 shows summary calculations of S-removal under various conditions over a treating period of 80 minutes. The best case is having a start S-content of 5 % and treatment at 1 700 °C. For this 2 448 Nm^3 H_2 is required which is 7 times of the H_2 produced. H_2-purging time will be 7.3 hours (with a H_2-feed rate of 5.6 Nm^3/h for a 5 ton reactor).

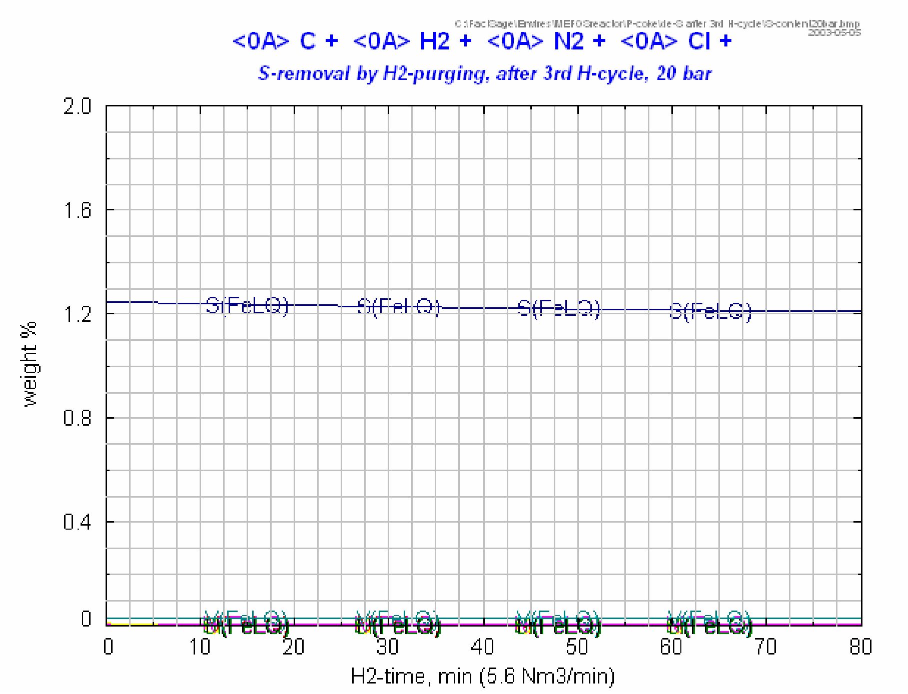


Figure 12 - S-removal by H_2-purging.

Table 4 - S-removal calculations for 4 cases.

De-S by H_2, 5.6 Nm^3 H_2 /min %S=1.255, adiabatic	Temp. drop 1393 to 1248°C 80 min	From 1.246%S to 1.21%S	**<u>12800 Nm^3</u>** H_2 required for removal of 1%S in metal	If 5.6Nm^3 H_2/min it will take **<u>2286 min. (38.10h)</u>**
De-S by H_2, 5.6 Nm^3 H_2 /min %S=4.75, adiabatic	Temp drop 1475 to 1320°C 80 min	From 4.75%S to 4.7%S	**<u>8960 Nm^3</u>** H_2 required for removal of 1%S in metal	If 5.6Nm^3 H_2/min it will take **<u>1600 min. (26.67h)</u>**
De-S by H_2, 5.6 Nm^3 H_2 /min %S=5, 1700°C	1700°C 80 min	From 4.805%S to 4.622%S	**<u>2448 Nm^3</u>** H_2 required for removal of 1%S in metal	If 5.6Nm^3 H_2/min it will take **<u>437 min. (7.29h)</u>**
De-S by H_2, 5.6 Nm^3 H_2 /min %S=1.24, 1700°C,	1700°C 80 min	From 1.25%S to 1.17%S	**<u>5600 Nm^3</u>** H_2 required for removal of 1%S in metal	If 5.6Nm^3 H_2/min it will take **<u>1000 min. (16.67h)</u>**

Temperature

The temperature drop will be about 2 °C/min, meaning we need to put extra energy to keep the reactor hot. The temperature drop will be over 850 °C.

It is concluded from the FACT-calculations that S-removal by H_2-purging is not efficient.

2.1.5 S-removal by slag treatment

The S-removal by slag treatment has been calculated at 20 bars and atmospheric pressure. No differences has been observed (S-bearing gaseous species has been involved).

Figure 13 show that temperature has no effect at all in the S-removal efficiency. The calculation uses a slag of 500 kg (for 5 ton iron melt) consisting of 60 % CaO, 30 % SiO_2 and 10 % MgO.

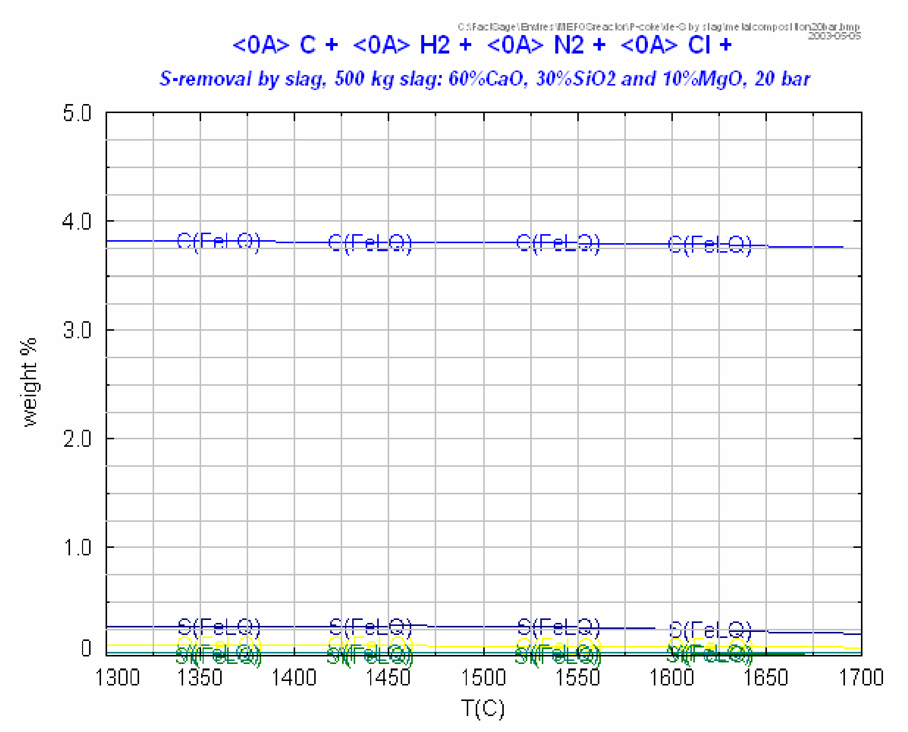
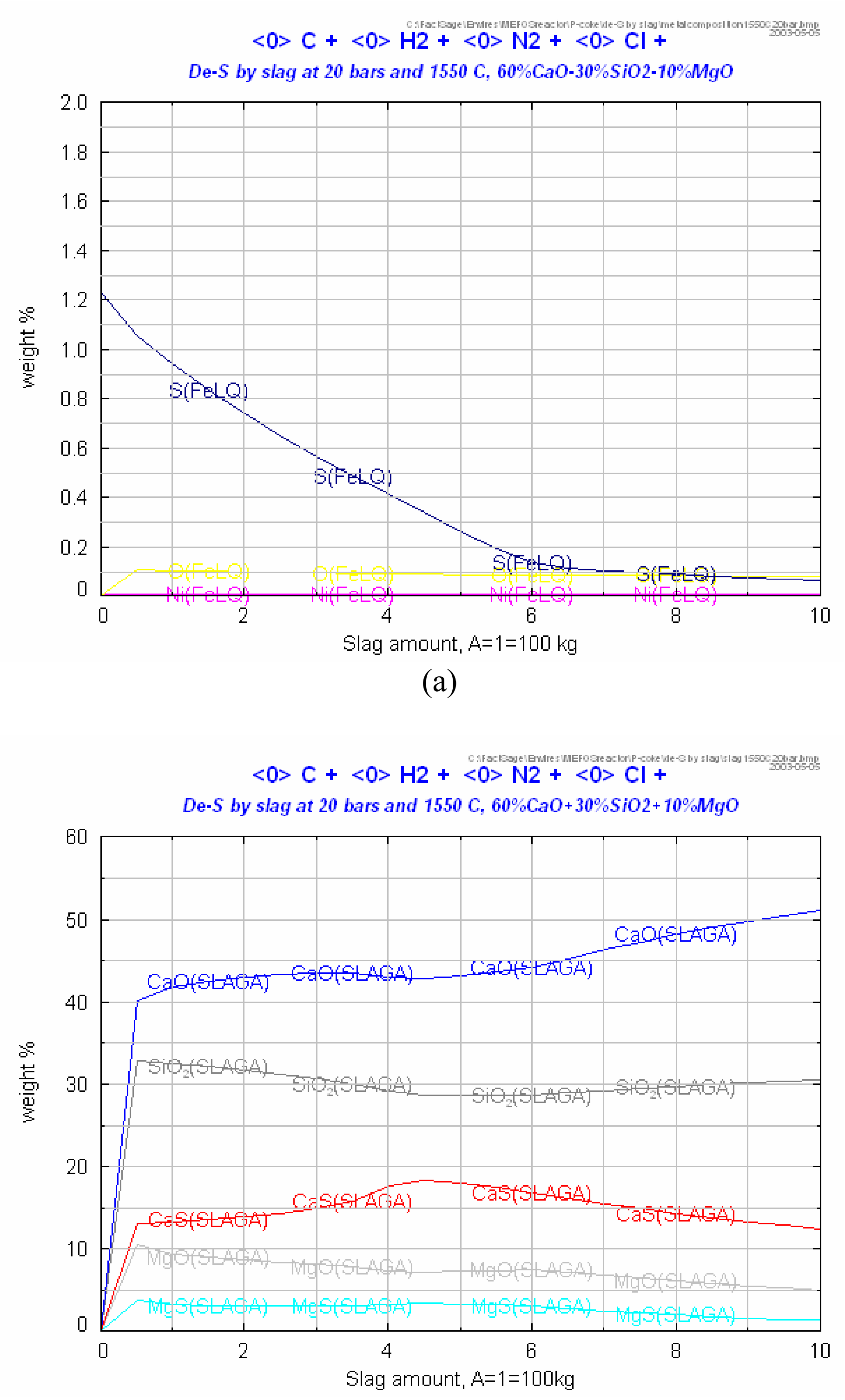


Figure 13 -S-removal by slag at temperature 1300-1700°C; 100 kg slag/ton iron melt.

The minimum slag amount required for S-removal (from 1.25 % to 0.5 % S) at 1 550°C and 20 bars is about 300 kg for the 5 tons iron melt or 60 kg /ton iron melt, or 450 kg slag/ton injected P-coke, see Figure 14.



(a)

(b)

Figure 14 -Minimum slag amount for S-removal at 1 550 °C.
(a) S-content in the iron melt. (b) Slag composition.

This slag could however be recycled after a hot treatment where S in the slag (CaS) is oxidised to SO_2.

2.1.6 The V-cycle

Since the V-content in P-coke is only 0.22 % and almost all V reports to the iron melt in the first cycles. It is decided to calculate at which V-level, vanadium will firstly be oxidised.

Figure 15 shows that when V-content is increased to 13 % the V-oxidation (to VOx) will start. The system used for the equilibration calculations is Fe-V-4 % C - 1.5 % S-VO_x.

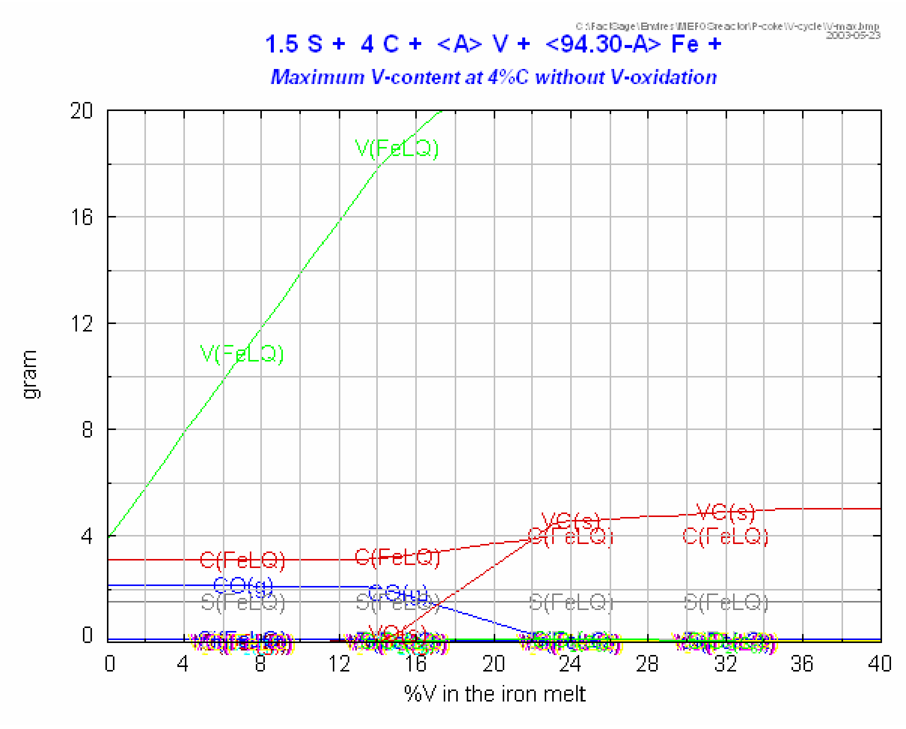


Figure 15 - Maximum V-level in the iron melt before the initial V-oxidation.

For a reactor start with 5 000 kg iron melt the composition at maximum V-content (13 %) will be:

- 5 000 kg Fe
- 240 kg C
- 650 kg V
- 90 kg S

The amount of V (650 kg) in the iron melt corresponding to 300 ton P-coke.

This means:

1 V-cycle = 1 360 C-cycle

The Ni-cycle

It is realistic to assume that Ni-level could increase to 20 % (due to the limitation of the reactor volume, not due to the chemistry). The amount of Ni will be 1 316 kg corresponding to 3 290 ton injected P-coke.

1 Ni-cycle = 11 V-cycles = 15 000 C-cycles

2.2 Aromatic extract

The chemical composition of aromatic extract is shown in the following table.

Table 5 - Chemical composition of aromatic extract.

Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
90.31	6.99	0.24	4.09	0

2.2.1 The H_2-cycle

The H_2-cycle for aromatic extract is almost the same as that for P-coke. About 21 minutes are needed for the H_2-cycle from 0.5 to 4 % C with a feeding rate of 10 kg/min and 5 ton iron melt. This corresponds to 42 kg Aromatic extract per ton iron melt, see Figure 16 and Table 6.

Table 6 - Concentration of major elements in the iron melt during the different cycles, injection of aromatic extract.

Cycles	Cycle time, min	% C	% S	% O
initial		0.5	0.5	0
1st H_2-cycle	21	4.02	0.63	0.02
1st de-C cycle	47	0.50	0.65	0.154
2nd H_2-cycle	21	3.96	0.78	0.066
2nd de-C cycle	46	0.52	0.81	0.171
3rd H_2-cycle	21	3.97	0.93	0.07
3rd de-C cycle	47	0.48	0.96	0.172
4th H_2-cycle	23	4.07	1.07	0.08
4th de-C cycle	48	0.50	1.11	0.172
5th H_2-cycle	22	4.09	1.22	0.08
5th de-C cycle	48	0.51	1.26	0.172
6th H_2-cycle	21	3.94	1.36	0.08

Table 6 shows the most interesting elements dissolved in the metal during the H_2- and CO-cycles.

Table 7 shows the mass balance and distribution of the most interesting elements during injection.

Table 7 - Mass distribution of C and S in the 5 ton iron melt during the H_2- and de-C cycles, injection of aromatic extract (190 kg input C /cycle).

Cycles	Cycle time, min	C in iron melt, kg	S in iron melt, kg
Initial		25	25
1st H_2-cycle	21	212	33
1st de-C cycle	47	25.5	33
2nd H_2-cycle	21	208	41
2nd de-C cycle	46	26.3	41
3rd H_2-cycle	21	209	49
3rd de-C cycle	47	24.1	49
4th H_2-cycle	23	215	57
4th de-C cycle	48	25.4	57
5th H_2-cycle	22	216	65
5th de-C cycle	48	26.13	64
6th H_2-cycle	21	216	72

Table 7 shows that over 95 % of C and over 90 % of S in the aromatic extract will be reported to iron melt during the injection period.

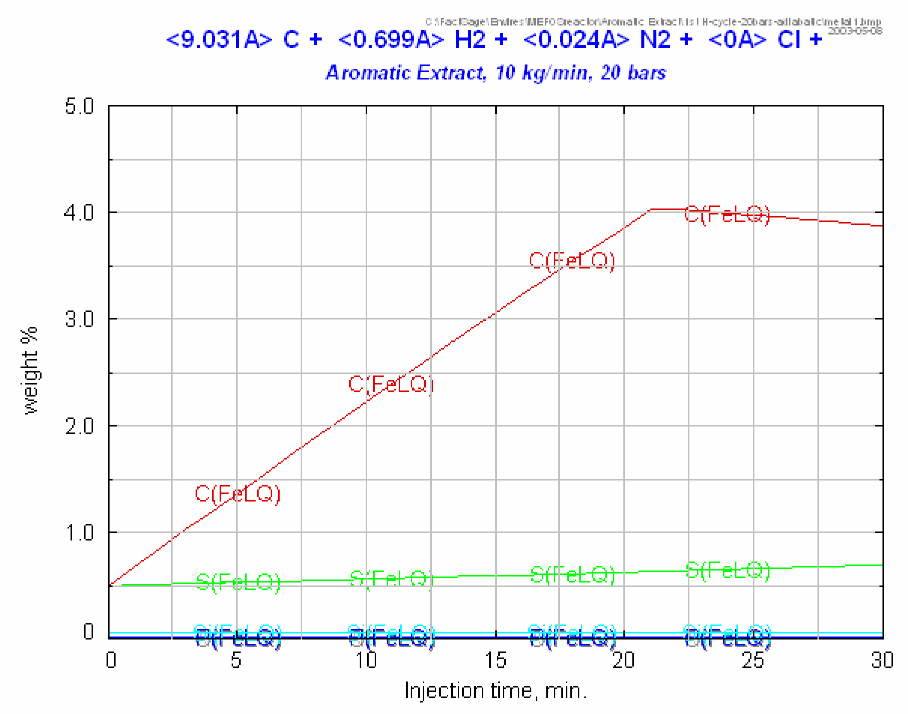


Figure 16 - C- and S-content in the iron melt during injection of aromatic extract.

The adiabatic temperature

Figure 17 shows the adiabatic temperature during a injection period. The temperature drop over a H_2-cycle is 300 °C.

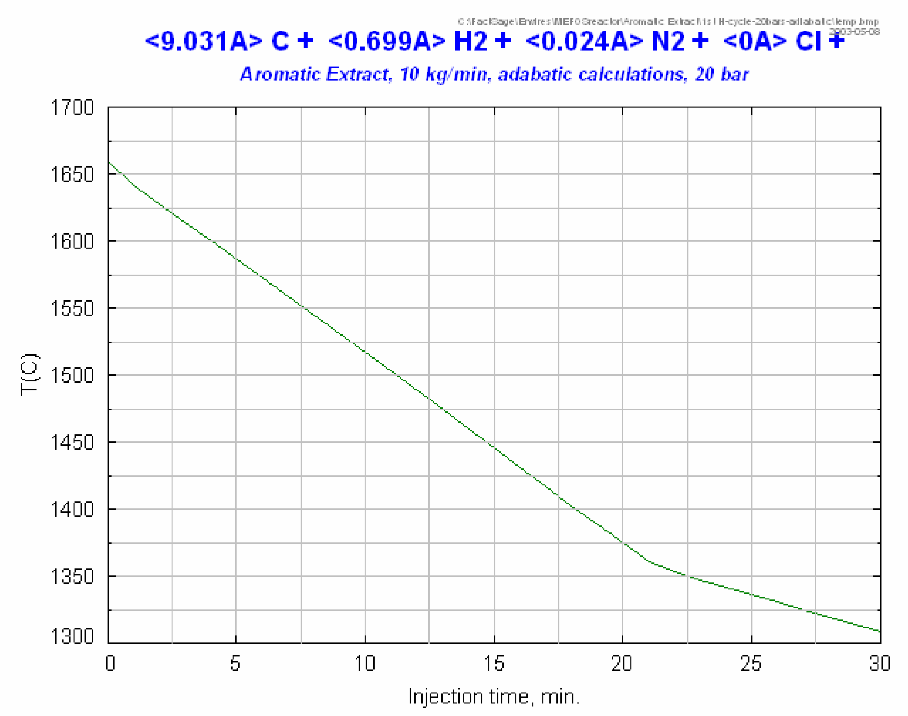


Figure 17 - Temperature drop during injection of aromatic extract.

The quality of H_2

As for P-coke, during the de-C cycle some oxygen will dissolve in the iron melt due to the oxidation step and the high pressure of 20 bars. This will affect the quality of H_2-gas in the beginning of each H_2-cycle. See Figure 18.

Chemistry of the iron melt

As shown in Tables 6-7 about 90 % of the input S is reported in the iron melt, about 10 % of S leaves the reactor as H_2S. The S-content increases proportionally with the injection, see Figure 16.

2.2.2 The de-C cycle

The de-C cycle is the same as for P-coke and will not be repeated here.

2.2.3 The S-cycle

Due to the lower S/C ratio, the S-cycle for aromatic extract is much longer compared to that of P-coke. As shown in Table 6 after fifth H_2-cycle, the S-content reaches 1.22 % S and after fifth de-C cycle 1.28 % S after sixth H-cycle 1.38 % S.

This means for aromatic extract:

1 S-cycle = 6 C-cycles

After we have injected totally 1 260 kg aromatic extract to the 5 ton reactor, a S-removal step is needed.

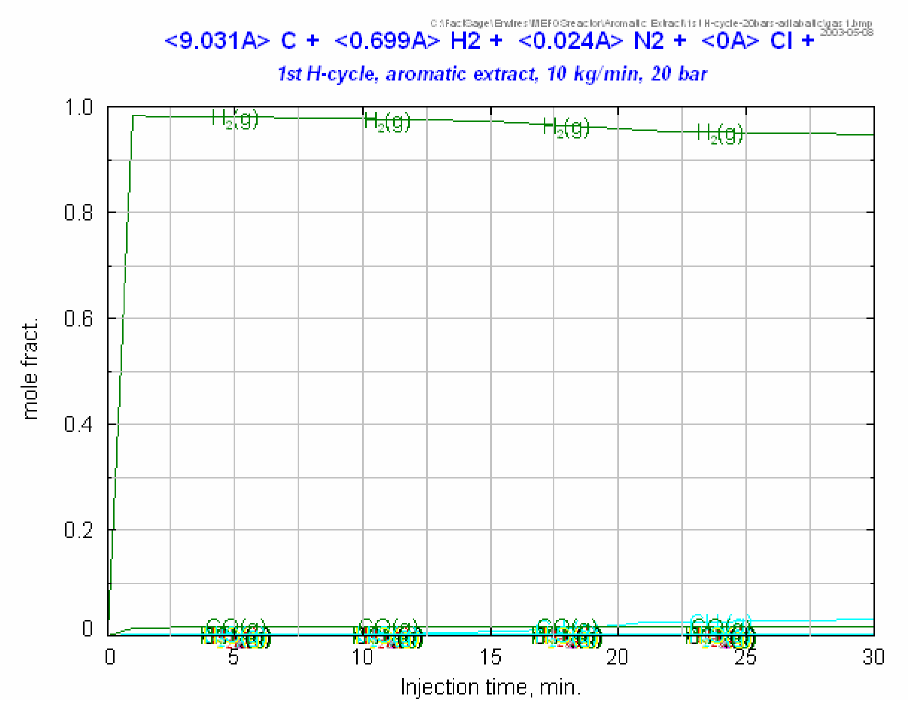


Figure 18 - H_2-production by injection of aromatic extract, the 1st H_2-cycle.

2.3 Coal ILL #6

The chemical composition of coal is shown in Table 8 and Table 9.

Table 8 - Chemical composition of coal ILL #6.

C	H	N	Cl	S	O	Ash
71.14	4.91	1.48	0.13	3.48	8.26	10.81

Table 9 - Mineral analysis of ash.

SiO_2	Al_2O_3	TiO_2	CaO	K_2O	MgO	Na_2O	Fe_2O_3	RO_5	SO_3
50.65	20.15	0.96	4.01	2.16	1	1.25	16.25	0.28	2.95

Coal ILL #6 is a special material since it has high contents of oxygen and ash compared to the other two materials.

The H_2-cycle

As shown in Figure 19 the H_2-cycle (C from 0.5 to 4 %) is about 30 minutes with an injection rate of 10 kg/min.

The temperature drop will be 240 °C, see Figure 20.

Due to the high content of ash, about 1 kg CaO/min is added together with the coal to balance the SiO_2 in the ash. The purpose of CaO addition is to have a CaO/SiO_2-ratio equal to 2.

As shown in Figure 19, the generated slag amount (CaO + ash) seems to be able to pick up all sulphur in the injected coal. S-removal is thus not necessary.

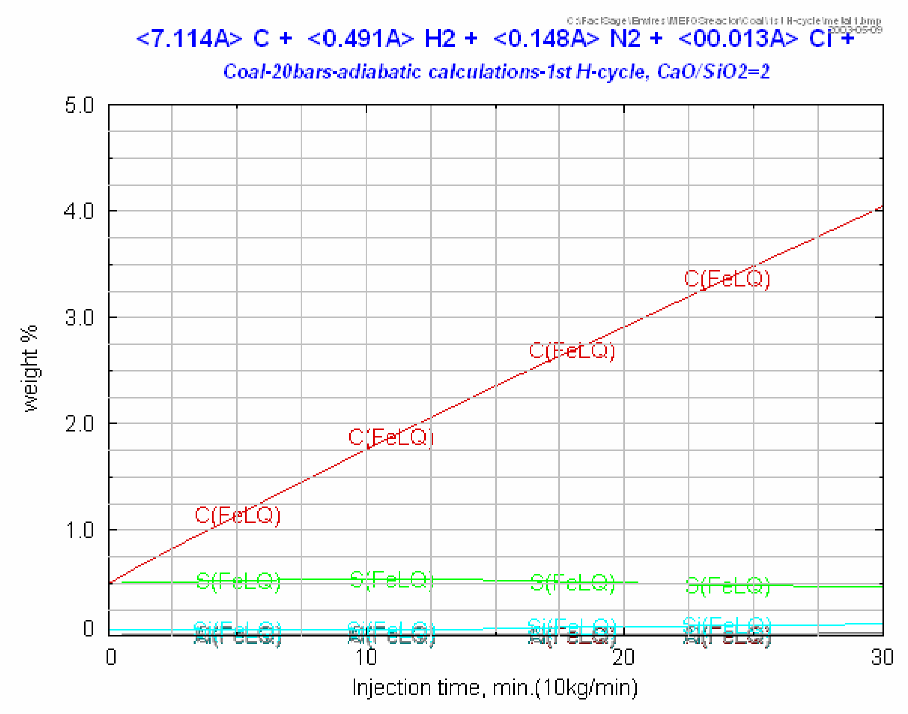


Figure 19 - Major elements in the iron melt during injection of coal.

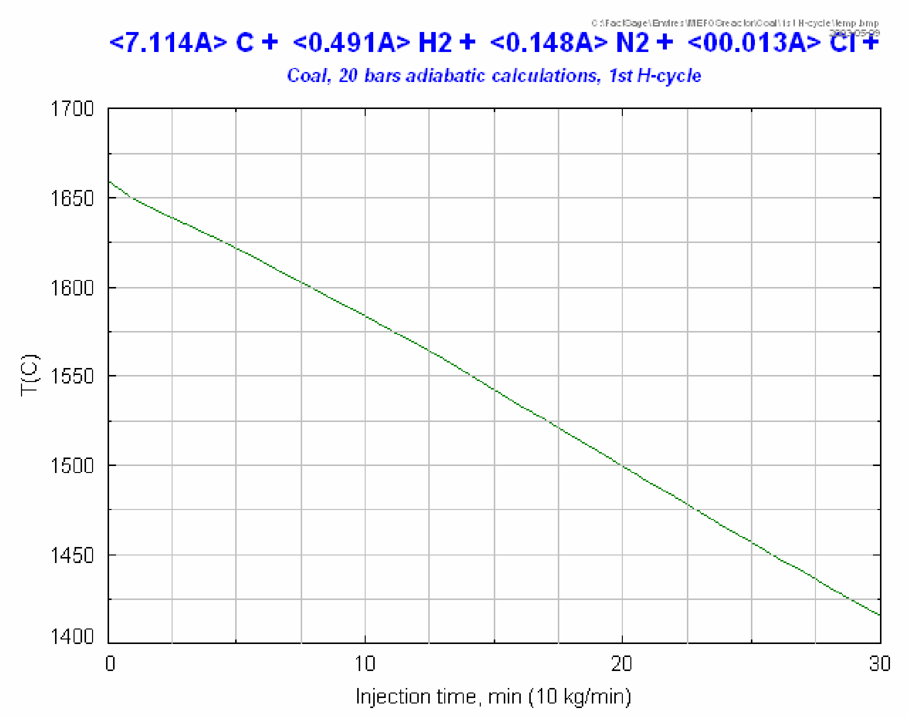
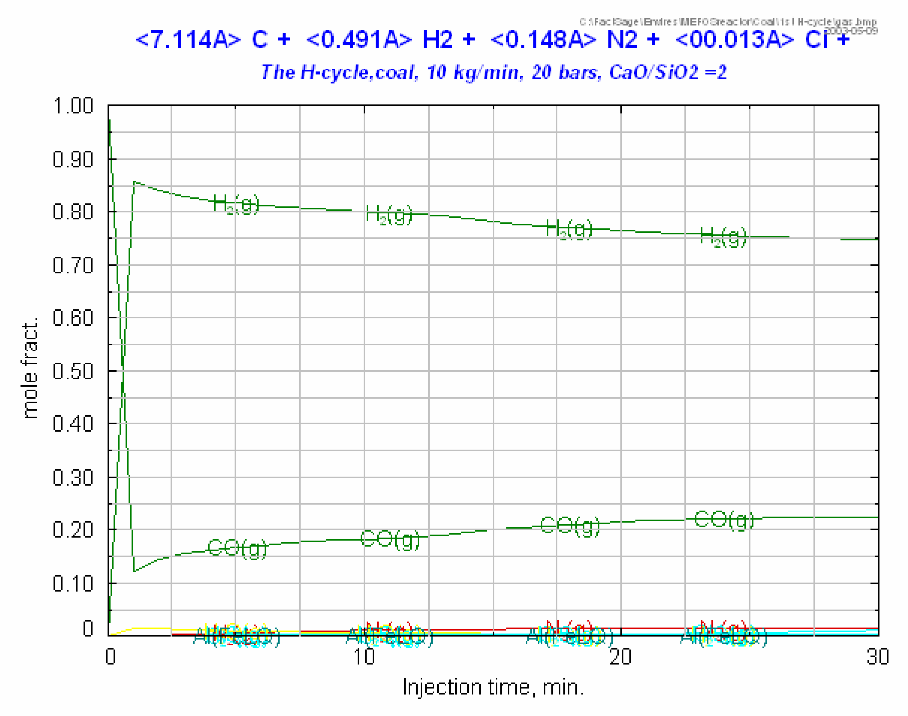
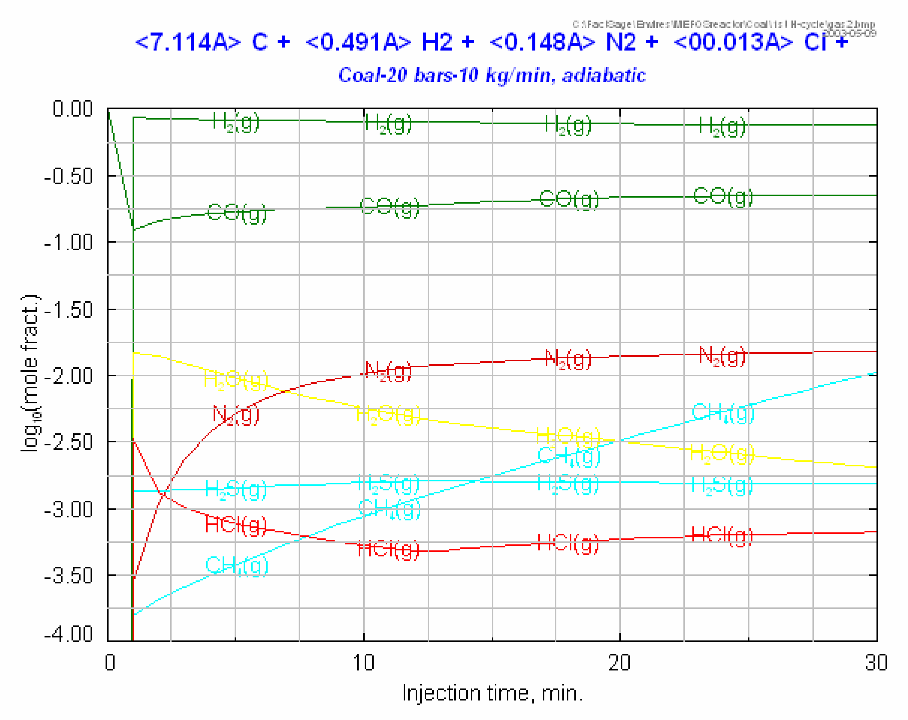


Figure 20 - Temperature drop during injection of coal.

Due to the high oxygen in the coal, the gas produced contains about 20 % CO as shown in Figure 21. The high Cl-content results in the formation of HCl.



(a)



(b)

Figure 21 -The gas composition during injection of coal.
(a) Purity of the H_2-production.
(b) Concentration of gaseous components of minor amount.

2.4 Calculation on spent tyres

In addition to the three materials from EnviRes some calculations on spent tyres have also been calculated .

The C-cycle: 45 kg tyres/ton iron melt

The S-cycle: 1 S-cycle = 20 H_2-cycles

The calculations are quite similar as those for the EnviRes materials except the S/C-ratio and the high content of Zn. Zn is recovered in the H_2-gas system.

The complete analysis of spent tyres is shown in Appendix I.

3 SUMMARY OF THE CALCULATIONS

The H_2-cycle

Based on 10 kg/min injection rate and a 5 ton iron melt the H_2-cycle for the three EnviRes materials and spent tyres have been calculated and the shown results are summarized in the following table.

	Injection time per H_2-cycle, min	Injected material/ton iron melt-ratio for one H_2-cycle, kg/ton
P-coke	22	44
Aromatic extract	21	42
Coal ILL#116	30	60
Spent tyres	22.5	45

The H_2-cycle is thus only related to the C-content in the injected carbon-materials.

The de-C cycle

This is the same as a LD-process where C-content is removed by oxidation except the pressure provided. One interesting point here is that if the cycle time for de-C step will be in the same range as that for the H_2-cycle time the gas system for the CO- and H_2 could be quite different. Since the flow rate of CO will be 2-3 times that of the H_2-gas.

The S-cycle

The S-cycle is mostly determined by the S/C-ratio in the used materials and the H/C-ratio as shown in the following table.

	S/C-ratio	H/C	C-/S-cycle ratio
P-coke	0.075	0.058	3
Aromatic extract	0.045	0.077	6
Coal ILL #6	0.049	0.069	0*
Spent tyres	0.021	0.088	20

* 10 % ash in the coal and about 10 % CaO is added. S is thus removed in the slag already. There will not be S-accumulation.

During the injection time, over 90 % of input S will dissolve in the iron melt, the rest will leave the reactor as H_2S together with the produced H_2. The higher the S/C-ratio the shorter the S-cycle will be, the higher the H/C-ratio, the longer the S-cycle will be. Higher H/C means more specific H_2-production and more removal of S from the iron melt (to H_2S).

S-removal by H_2- purging

Due to the unfavourably thermodynamical conditions provided for H_2S-formation, the method for S-removal by H_2-purging is highly inefficient. To remove the S dissolved in the iron melt it will consume much more H_2-gas than it has been produced during the H_2-cycles.

S-removal by slag treatment

Slag treatment is efficient. Using a slag with a CaO/SiO_2-ratio of 2 and a minimum amount of 60 kg/ton iron melt, the dissolved S will be removed. The slag used in the calculation consists of 60 % CaO, 30 % SiO_2 and 10 % MgO. This slag could be reused after S-removal of the slag by hot treatment.

The V-cycle

The V iron melt can contain up to 13 % V before V will be oxidised to VOx. This means:

1 V-cycle = 1 360 C-cycles

The Ni-cycle (only P-coke)

Theoretically Ni-solubility in the iron melt is not limited. Practically an iron melt with 20 % Ni is reasonable with regards to the reactor volume. This means:

One Ni-cycle = 11 V-cycles

Heat balance

Most of the calculations presented here are under adiabatic condition. The temperature drop for a H_2-cycle is shown in the following table.

	ΔT (FACT), °C	ΔT (HSC), °C
P-coke	285 °C	230 °C
Aromatic	300 °C	260 °C
Coal ILL#6	240 °C	Nd

The lower temperature drop of coal injection is due to the high oxygen content in the material which reacts with carbon in the H_2-cycle and produces extra energy to the system. The control calculation with HSC-program shows about 30-40 °C lower temperature drop than the FACTSage results. HSC-calculations are based on pure compounds and FACTSage calculations include the heat of mixing (dissolution of elements to the iron melt.

FACTSage shows a temperature increase of about 450 °C during the de-C cycle whereas HSC-heat balance shows a much lower temperature rise, about 330 °C.

The heat balance shows that it will be a net temperature increase of 150-200 °C based on the calculations (H_2-cycle + de-C cycle).

This net energy will cover heat losses of reactor and energy needed for smelting of the added slag for metal protection and S-removal.

4 REFERENCES

[1] FACTSAGE Thermochemical Software and Databases, C.W. Bales, and co-workers, CALPHAD 26 (2), 2002, pp 189-228.

Analysis of Swedish spent tyres

Parameter	Content (cut)	Powder
Moisture	2.2	< 0.01
Ash, %	8.2	7.7
Heat value, MJ/kg	32.48	35.41
Volatile, %	61.7	68.9
C, %	82.1	0.5
H (total), %	7.2	
IV, %	0.2	0.3
S, %	1.69	2.07
Cl, %	0.09	0.5
Pb, µg/g	31	68
Zn, %	1.6	18
Cd, µg/g	2.5	4.5
Cr, µg/g	2.2	3.7
Ni, µg/g	1.7	4.9
Fe, µg/g	240	4.0
Hg, µg/g	0.09	0.07

Table AI-1 Raw Data from June 10 Coal Injection

Time	A! 4.0	A! 4.1	A! 4.2	A! 4.3	A! 4.4	A! 4.5	A! 4.6	A! 4.7	A! 5.5	A! 5.6	A! 5.7	RO2I	YINC	KOLTOT	TEMPSOND	
	Waste gas CO %	Waste gas CO2 %	Waste gas O2 %	Waste gas SO2 %	Process gas CO %	Process gas CO2 %	Process gas O2 %	Process gas H2 %	MS process H2S %	MS process gas COS ppm v	MS process gas CH4 %	Tot oxygen yield %	C in (oil/coal) kg/min	Tot coal kg	Temp metal last measured C	MS Process gas H2 %
13:35	0.020	1.123	19.101	0.032	6.552	0.336	8.466	21.676	0.001	-50.833	0.015	84.782	4.832	5.071	1,701	28.595
13:36	0.030	1.895	17.495	0.061	7.348	0.689	4.006	20.667	0.056	-50.000	3.044	84.936	13.163	20.144	1,674	33.564
13:37	0.041	2.198	17.148	0.068	10.424	0.804	1.010	21.388	0.119	-50.000	4.997	86.882	16.281	38.082	1,674	55.079
13:38	0.048	2.379	16.977	0.072	11.584	0.692	1.041	21.386	0.142	-50.000	4.997	89.117	14.471	55.060	1,674	56.879
13:39	0.080	2.460	16.918	0.073	12.050	0.678	1.174	21.388	0.138	-50.000	4.997	91.436	15.346	73.154	1,674	55.466
13:40	0.085	3.111	16.227	0.082	13.456	0.727	1.250	21.402	0.125	-50.000	4.997	94.139	14.627	90.258	1,628	53.658
13:41	0.066	2.899	16.463	0.079	13.918	0.799	1.459	21.411	0.110	-50.000	4.997	97.170	14.428	106.662	1,446	51.663
13:42	0.056	2.536	16.831	0.074	12.899	0.734	1.774	21.398	0.099	-50.000	4.997	99.852	15.925	124.819	1,446	50.404
13:43	0.057	2.438	16.861	0.074	11.938	0.691	1.949	21.388	0.097	-50.000	4.997	102.268	15.539	142.734	1,446	49.952
13:44	0.050	2.409	16.898	0.074	10.922	0.637	2.036	21.377	0.097	-50.000	4.997	104.608	15.432	160.422	1,446	49.508
13:45	0.050	2.254	17.036	0.074	10.218	0.605	2.120	21.369	0.084	-50.000	4.997	106.911	15.457	177.548	1,446	48.460
13:46	0.046	2.179	17.104	0.074	9.859	0.593	2.340	21.366	0.085	-49.999	4.997	109.032	15.436	194.475	1,446	48.437
13:47	0.046	2.156	17.077	0.075	9.323	0.542	2.414	21.358	0.083	-50.000	4.497	111.164	15.883	213.759	1,446	47.610
13:48	0.043	2.099	17.142	0.076	9.157	0.549	2.466	21.358	0.080	-50.000	4.997	113.229	16.147	232.829	1,446	47.074
13:49	0.051	2.131	17.097	0.077	9.361	0.576	2.521	21.361	0.066	-50.000	4.997	115.270	15.906	251.751	1,446	45.611
13:50	0.063	2.319	16.958	0.080	9.225	0.560	2.531	21.359	0.021	-50.000	4.997	117.493	14.881	268.811	1,446	40.910

Figure AI-1 HyMelt 5:6

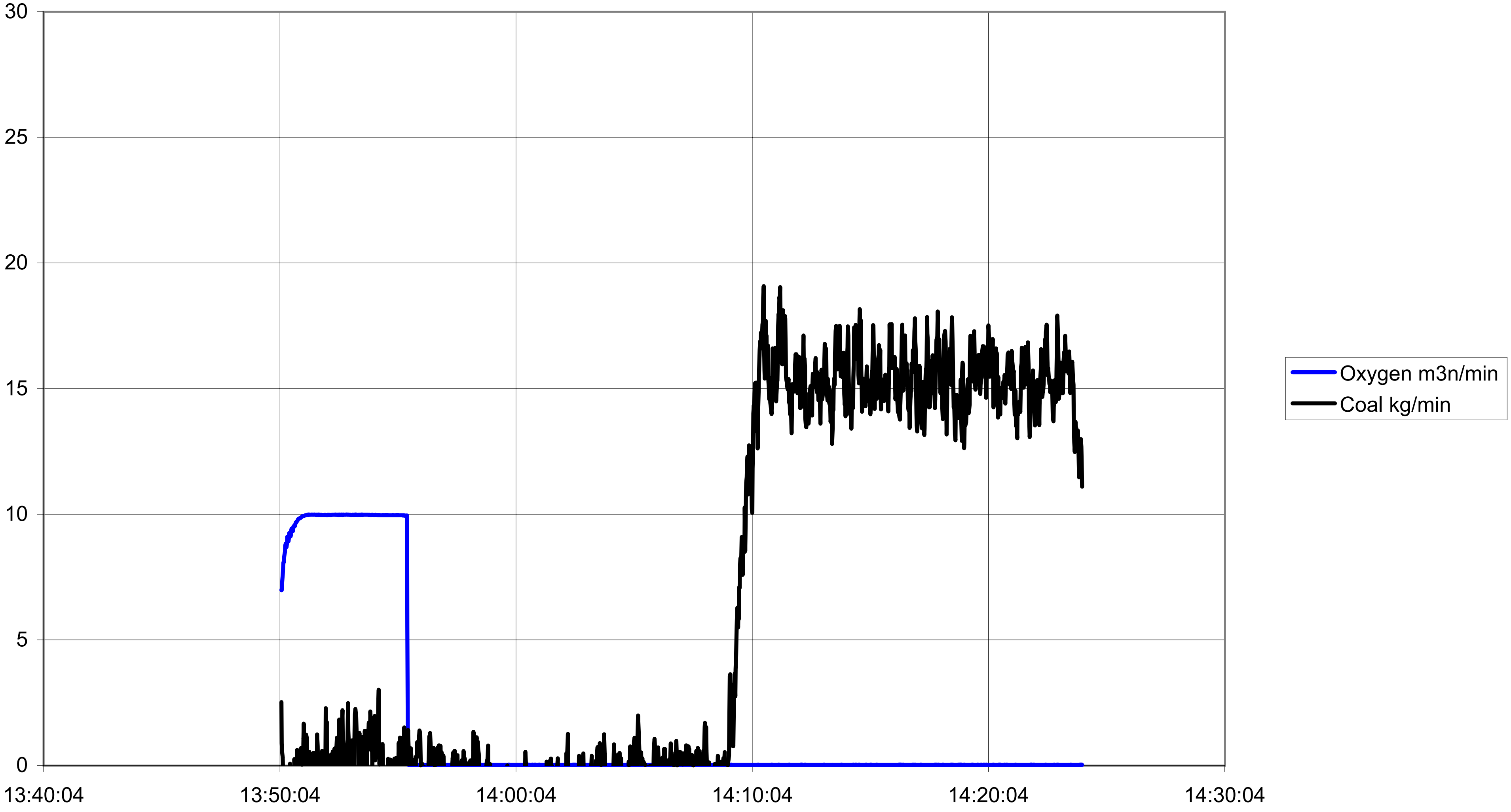


Figure AI-2 %CO HyMelt 5:6

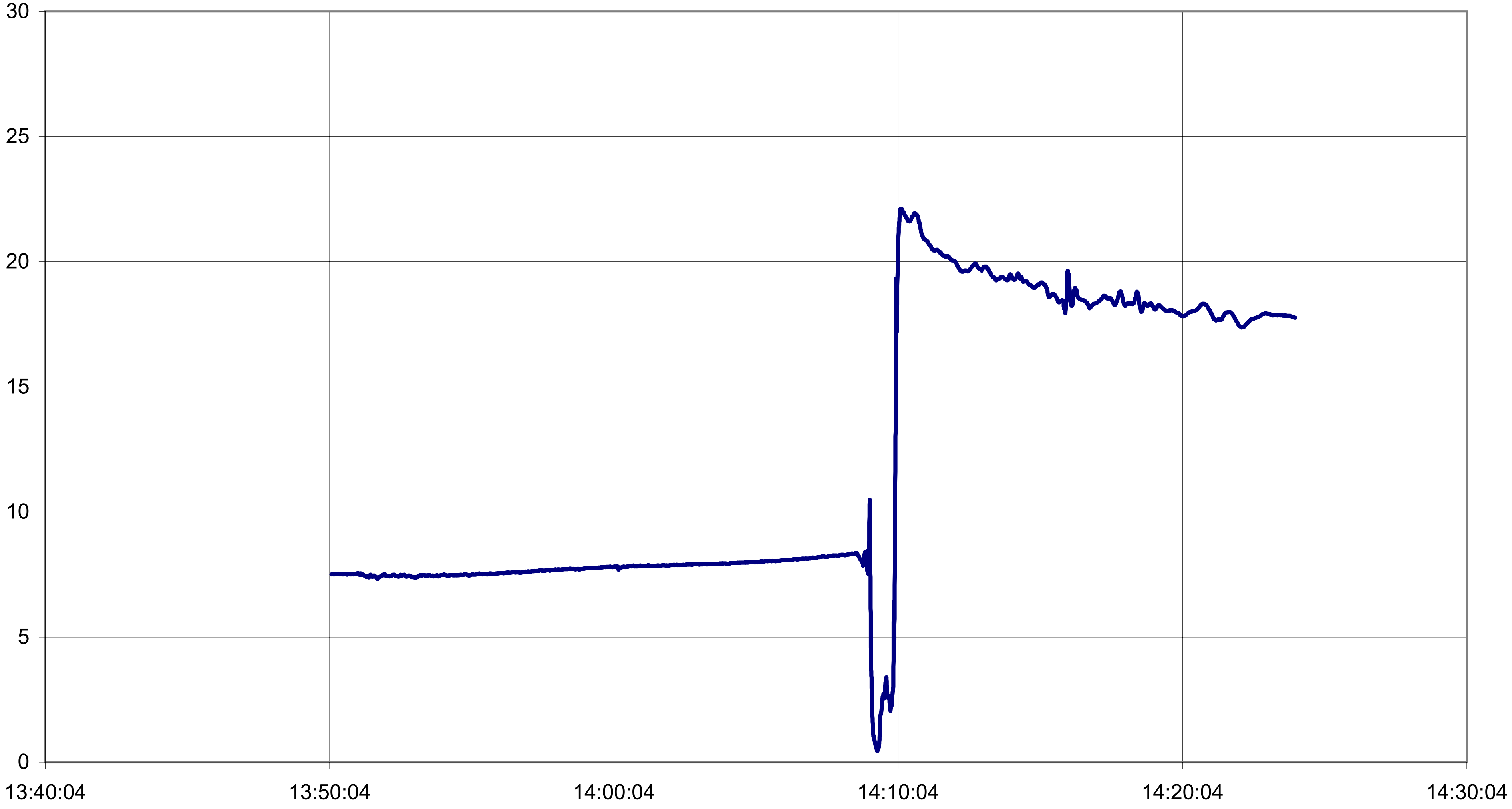


Figure AI-3 %CO2 HyMelt 5:6

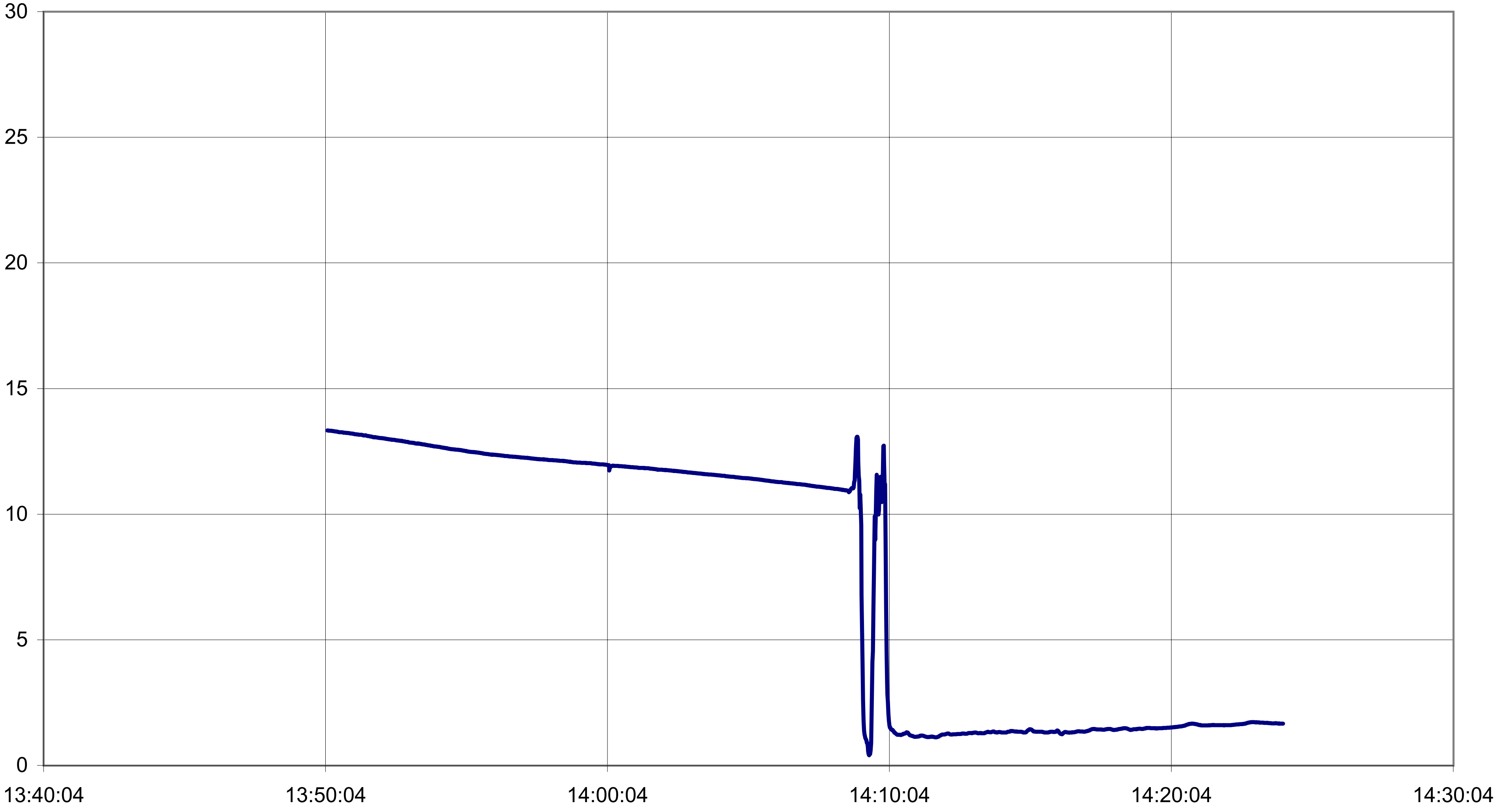


Figure AI-4 %H2 HyMelt 5:6

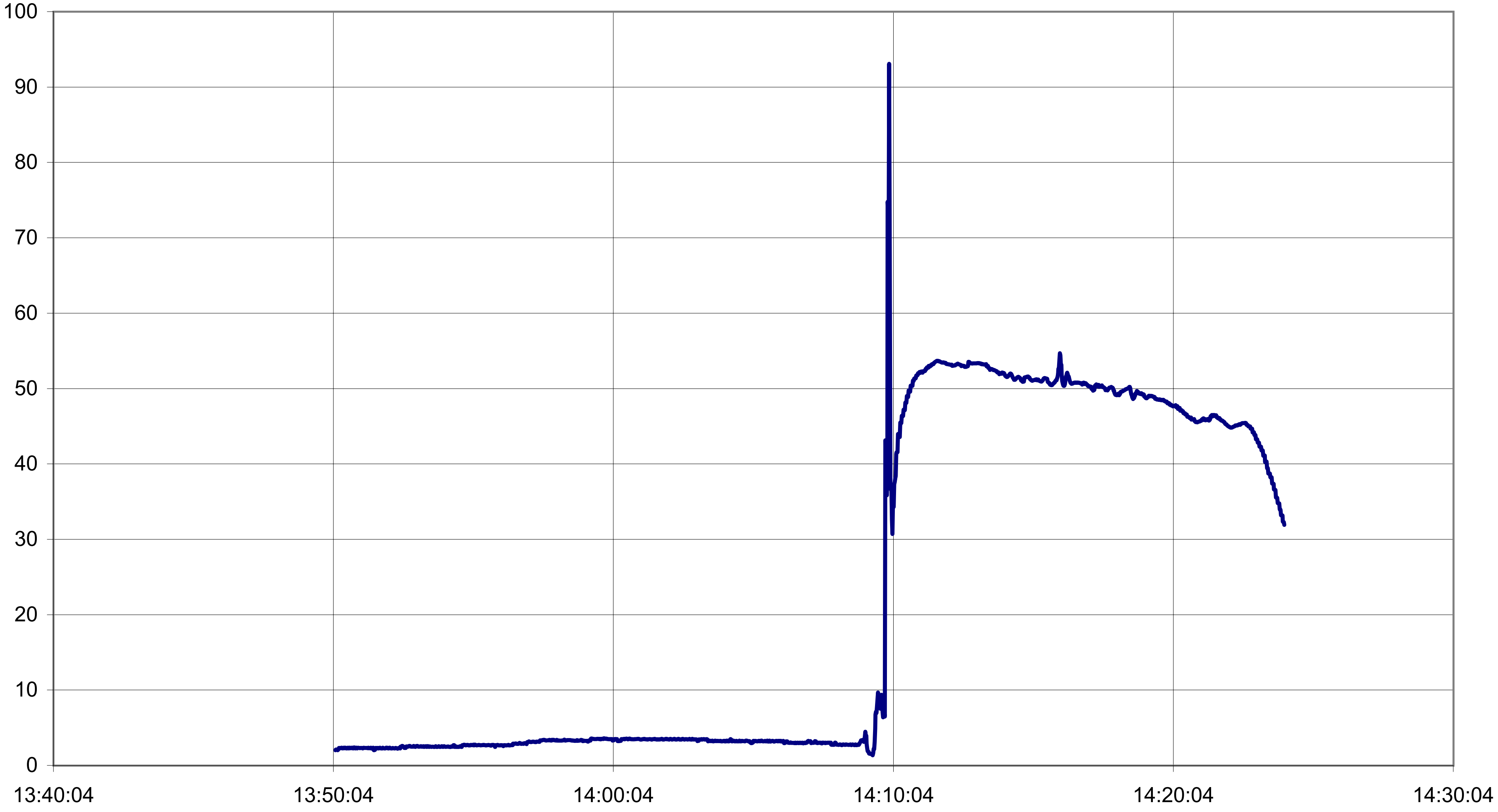


Figure AI-5 %H2S HyMelt 5:6

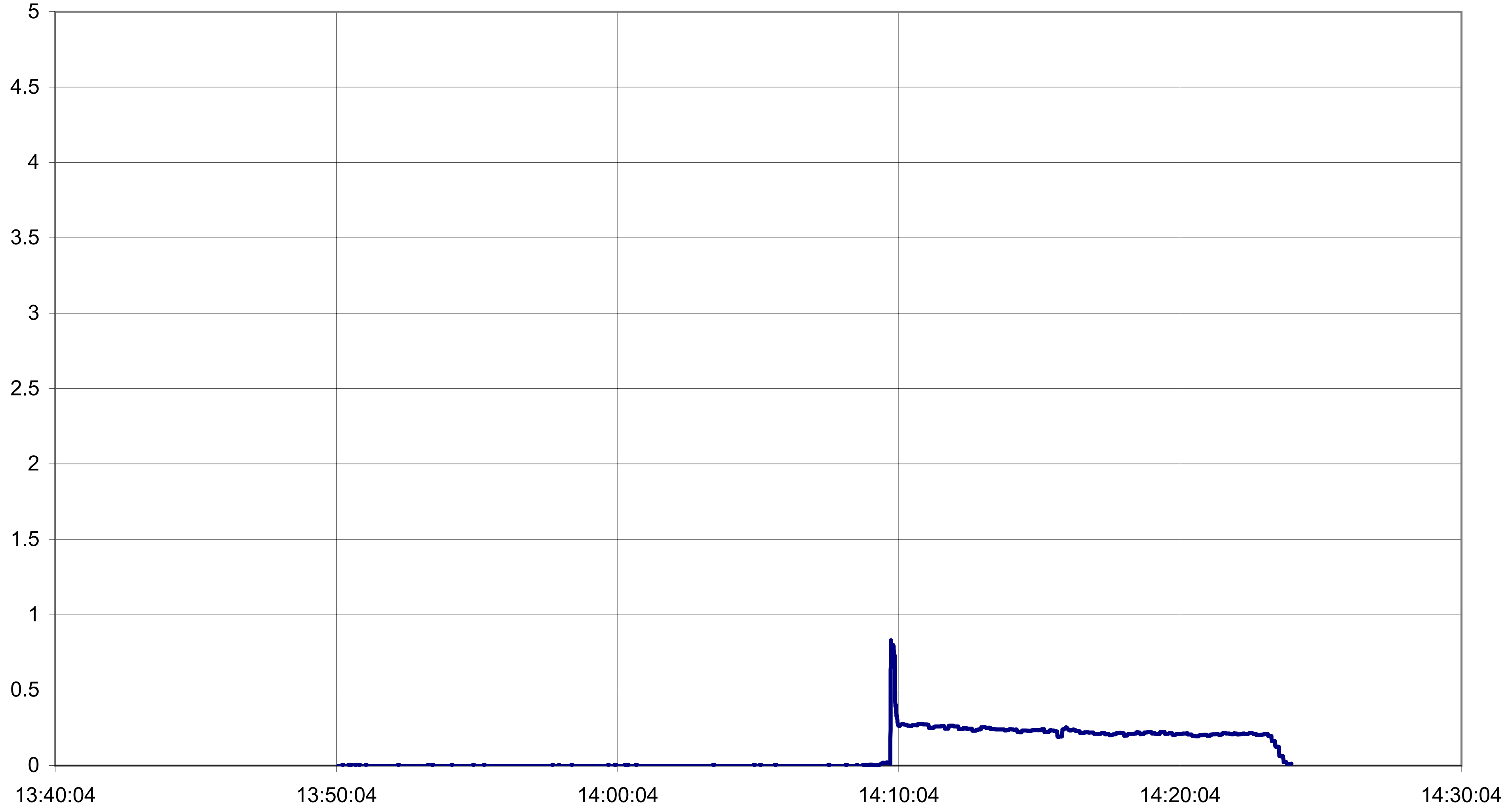


Figure AI-6 %CH4 HyMelt 5:6

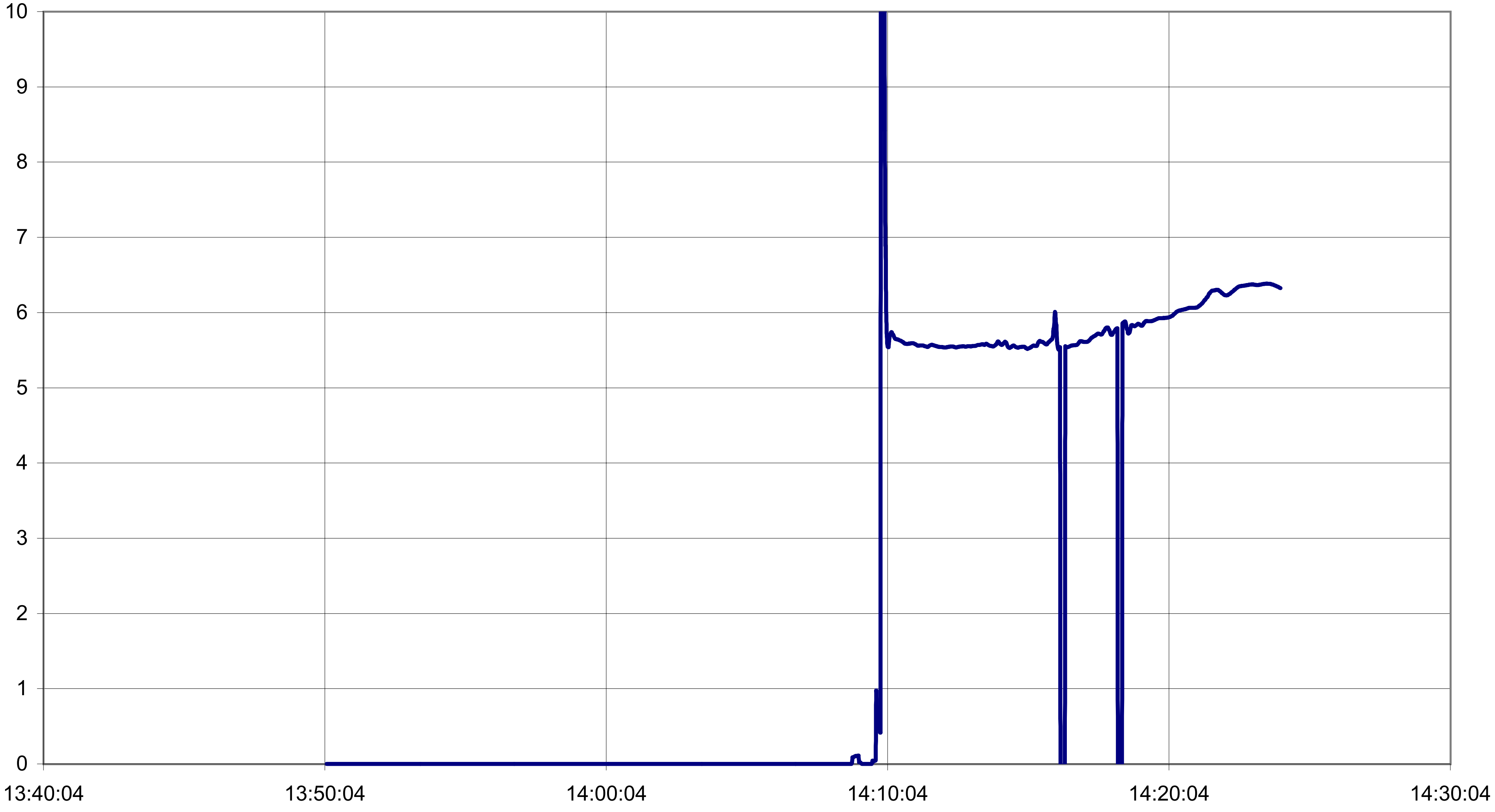


Figure AI-7 HyMelt6:1

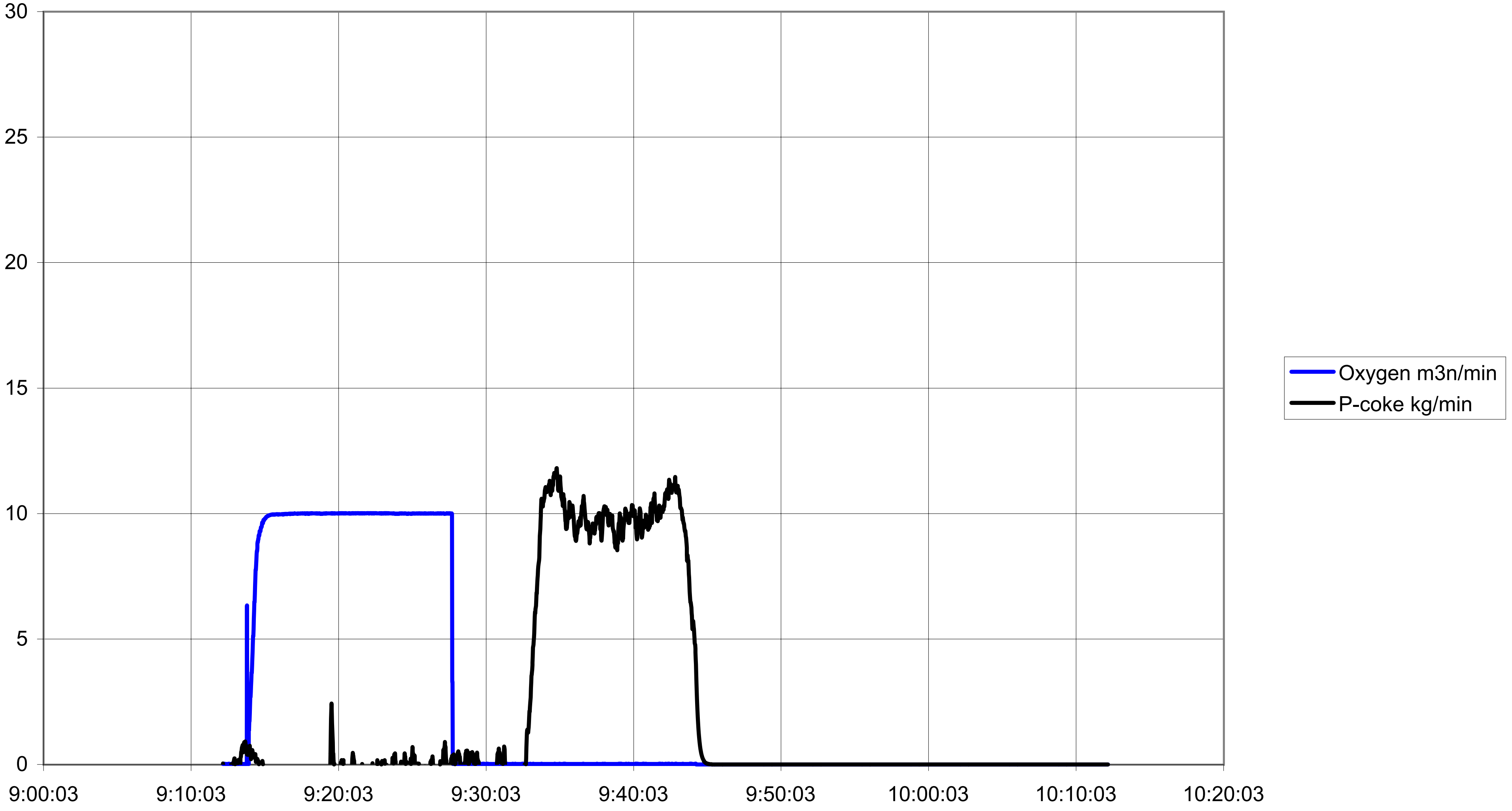


Figure AI-8 %CO HyMelt 6:1

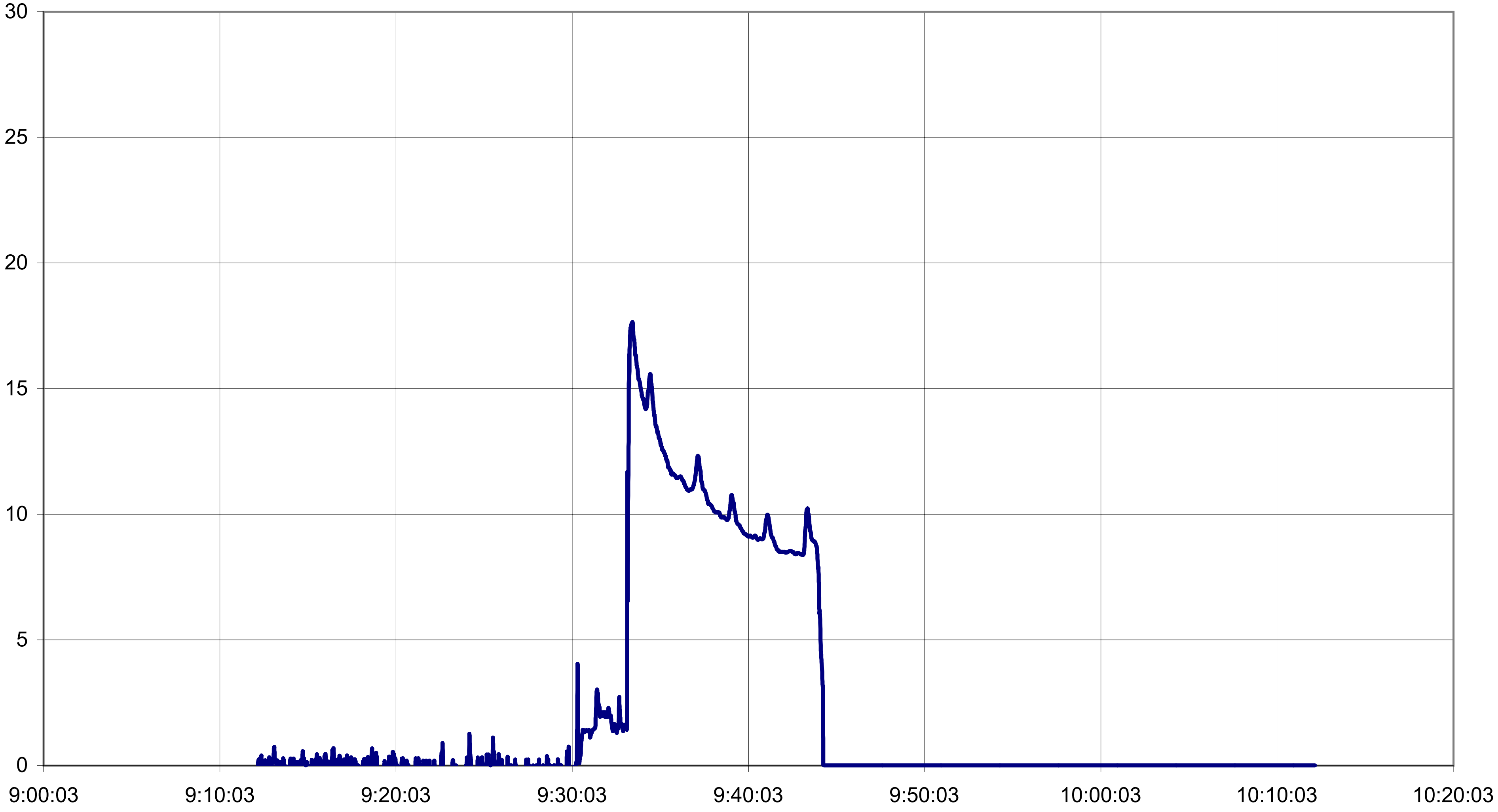


Figure AI-9 %CO2 HyMelt 6:1

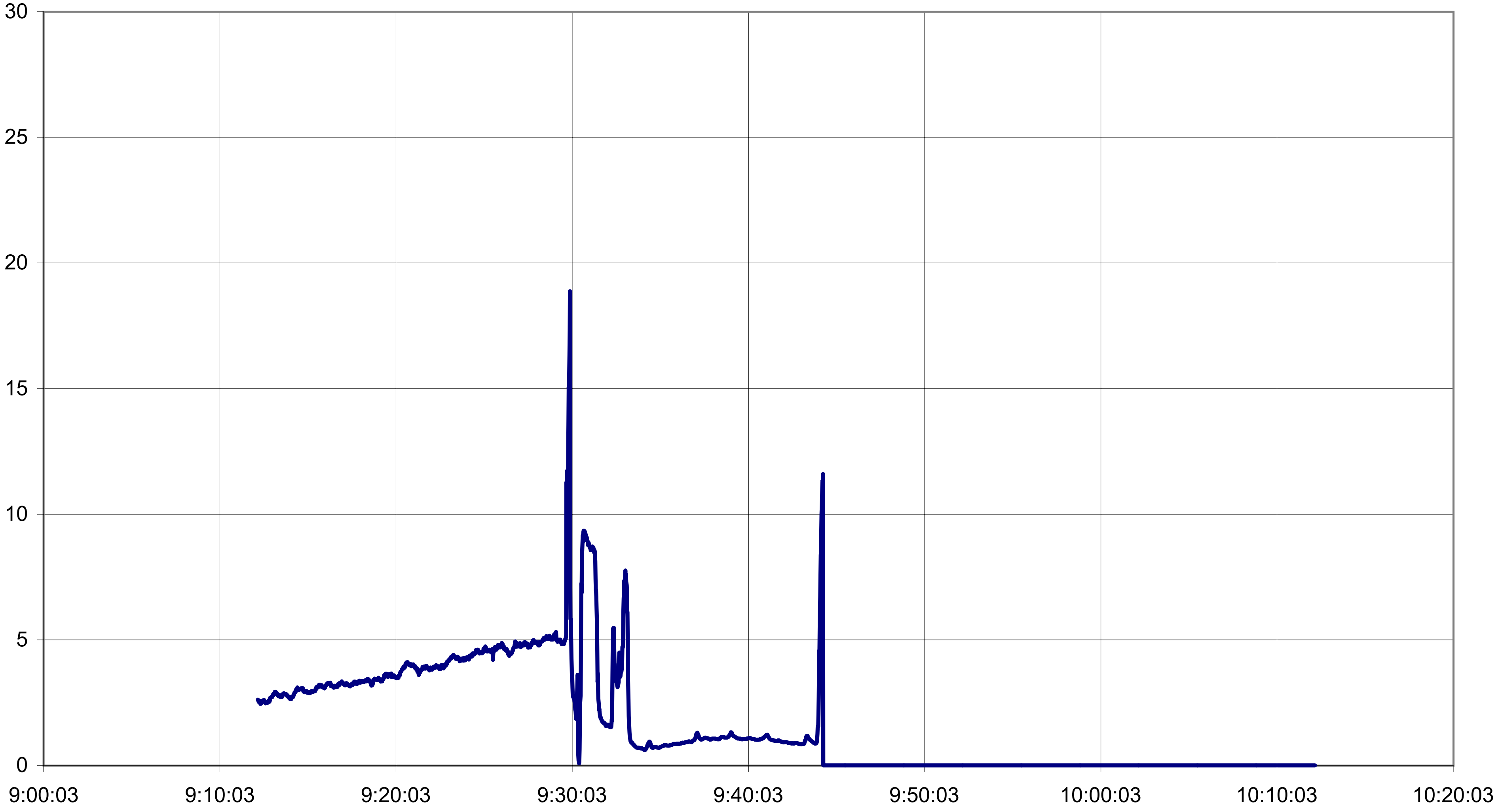


Figure AI-10 %H2 HyMelt 6:1

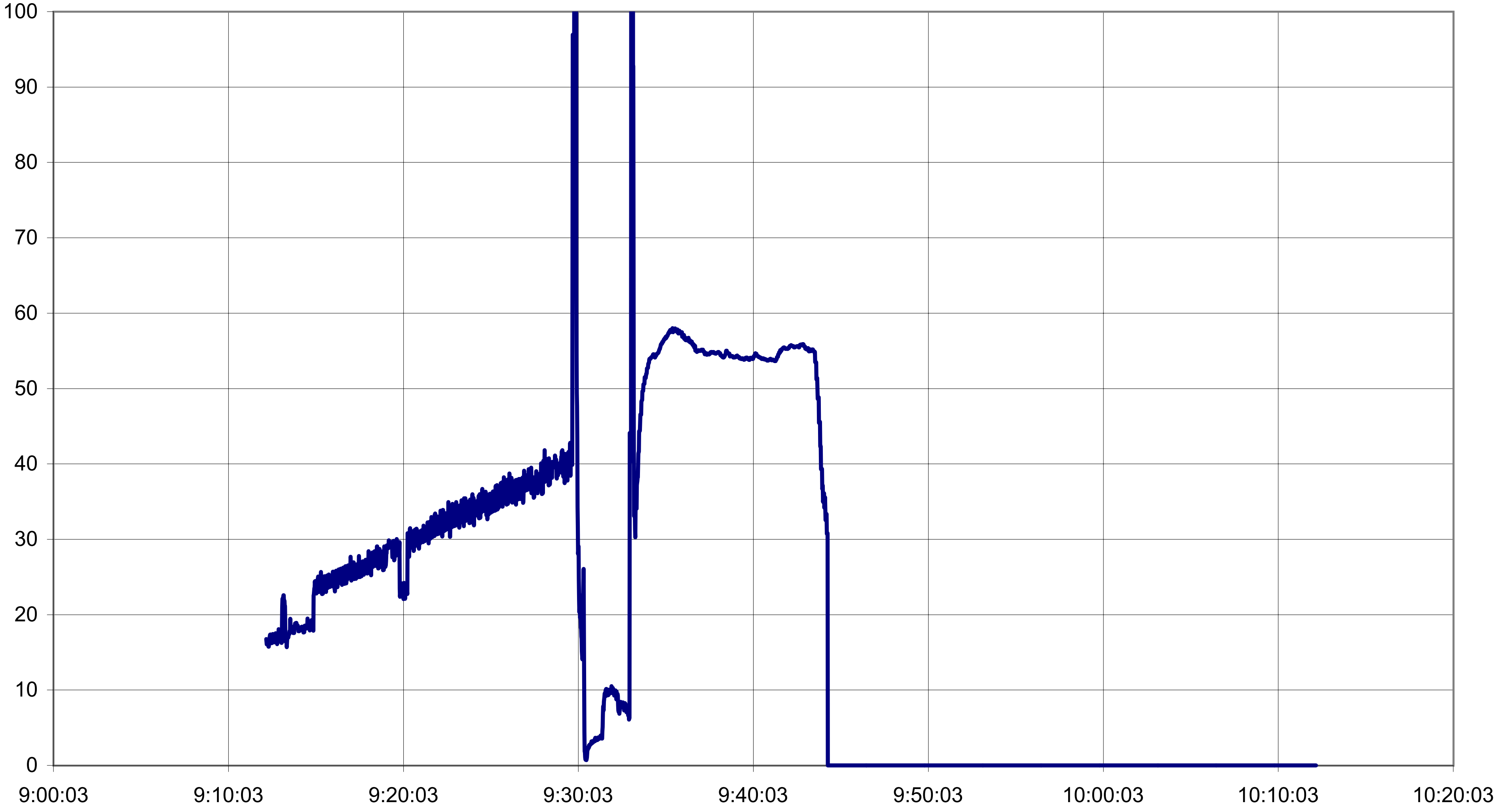
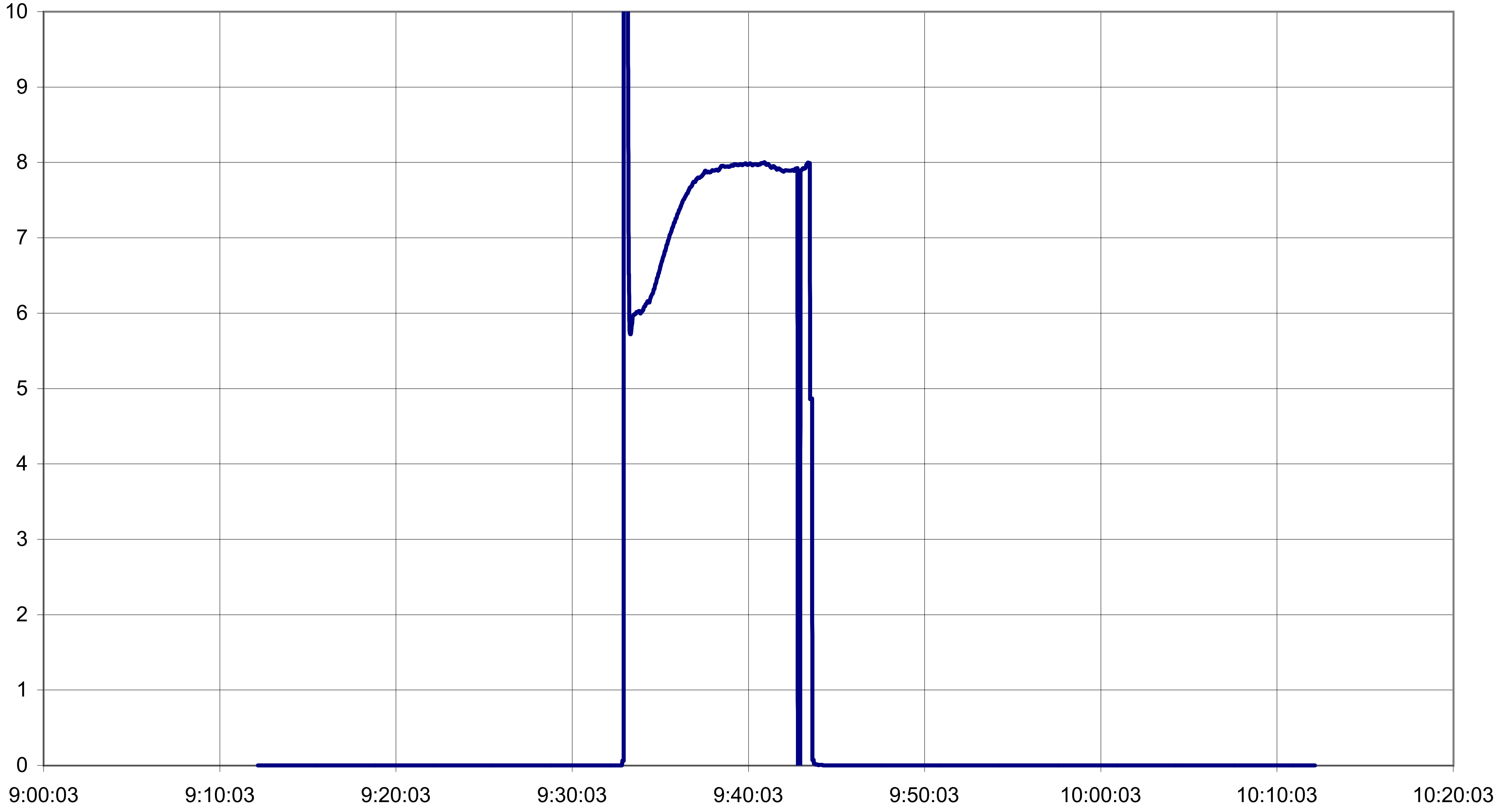
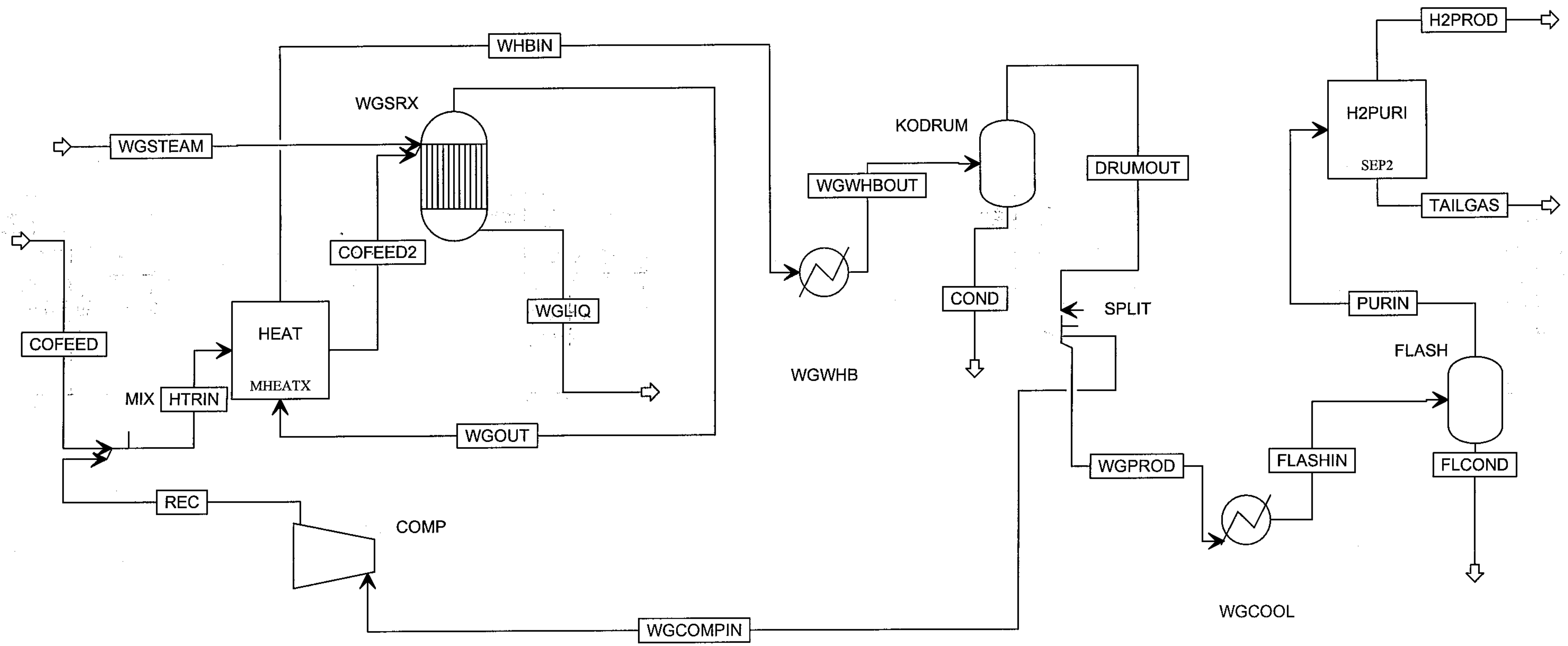


Figure AI11 %CH4 HyMelt 6:1



Appendix II

Kvaerner CO-Water Gas Shift Studies



EnviRes HyMelt
Water Gas Shift PFD
Run 9 3JUN03
AKEC c99268

Water Gas Shift Run 9 3-Jun-03
EnviRes HyMelt
AKEC C99268

	COFEED	COFEED2	COND	DRUMOUT	FLASHIN	FLCOND	H2PROD	HTRIN	PURIN	REC	TAILGAS	WGCOMPIN	WGLIQ	WGOUT	WGPROD	WGSTEAM	WGWHBOUT	WHBIN
Temperature F	350	600	351.9	351.9	100	99.9	99.9	351.9	99.9	354	100	351.9		834.3	351.9	475	350	720.2
Pressure psi	500	499	496	496	495	494	494	500	494	500	50	496	498	498	496	520	496	497
Vapor Frac	1	1	0	1	0.646	0	1	1	1	1	1	1		1	1	1	0.799	1
Mole Flow lbmol/hr	1816.315	4644.061	1974.584	7069.364	4241.619	1502.921	1409.4	4644.061	2738.697	2827.746	1329.297	2827.746	0	9044.061	4241.619	4400	9043.948	9044.061
Mass Flow lb/hr	51524.224	110899.288	41725.332	148437.661	89062.597	36935.258	2842.052	110899.288	52127.338	59375.06	49285.29	59375.06	0	190166.52	89062.597	79267.232	190162.993	190166.521
Volume Flow cuft/hr	31717.019	105791.921	813.399	121022.738	33400.187	567.567	17477.789	79924.007	32899.648	48151.05	158116.5	48409.1	0	250509.01	72613.643	75280.065	123944.23	227988.464
Enthalpy MMBtu/hr	-91.895	-315.953	-244.814	-584.214	-380.613	-201.965	0.242	-325.531	-178.648	-233.636	-178.674	-233.686		-761.552	-350.529	-445.619	-829.028	-771.129
Mole Flow lbmol/hr																		
CO	1702.668	1810.201	0.753	268.832	161.299	5.6	0.016	1810.201	155.699	107.533	155.684	107.533	0	269.587	161.299	0	269.585	269.587
H2	25.356	1069.335	0.002	2609.949	1565.969	0	1409.372	1069.335	1565.969	1043.98	156.597	1043.98	0	2609.95	1565.969	0	2609.951	2609.95
H2O	3.051	753.038	1737.402	1874.965	1124.979	1120.099	0	753.038	4.881	749.986	4.88	749.986	0	3612.423	1124.979	4400	3612.368	3612.423
CH4	0.163	0.27	0.004	0.266	0.16	0.032	0	0.27	0.128	0.106	0.127	0.106	0	0.27	0.16	0	0.27	0.27
C2H2	0.272	0.425	0.044	0.381	0.229	0.07	0	0.425	0.158	0.152	0.158	0.152	0	0.425	0.229	0	0.425	0.425
N2	1.108	1.844	0.005	1.839	1.103	0.03	0.001	1.844	1.074	0.736	1.073	0.736	0	1.844	1.103	0	1.844	1.844
CO2	83.55	1008.725	236.347	2312.935	1387.761	377.032	0.01	1008.725	1010.729	925.174	1010.719	925.174	0	2549.339	1387.761	0	2549.283	2549.339
H2S	0.031	0.048	0.005	0.043	0.026	0.011	0	0.048	0.015	0.017	0.015	0.017	0	0.048	0.026	0	0.048	0.048
COS	0.114	0.176	0.023	0.153	0.092	0.047	0	0.176	0.044	0.061	0.044	0.061	0	0.176	0.092	0	0.176	0.176

Notes: H2O/CO Ratio		2.8
CO in product	PPM	11.4
WasteHeat Boiler Duty	MM BTU/HR	57.9
CO conversion	%	85.1
Cooler Duty	MM BTU/HR	-30.1
Tail Gas Energy	MM BTU/HR	38.2
Heat Exchanger Duty	MM BTU/HR	9.6