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<b>Deliverable number:</b>	D1.2.1
<b>Deliverable title:</b>	Report on 1000 hour catalyst stability
<b>Work package:</b>	WP 1 H <sub>2</sub> supply chain and H <sub>2</sub> -CO <sub>2</sub> separation
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Abstract
<p>The main objective of WP1 with respect to the water gas shift (WGS) was to test the capability of commercial WGS catalyst to operate outside their normal operation window by testing gas representative of metal processing systems with CO contents of 60%, and up to about 20% of both CO<sub>2</sub> and N<sub>2</sub> in the presence of the contaminants typically present in the gas of a basic oxygen furnace, BOFG, at H<sub>2</sub>O/CO ratio 2-2.3.</p> <p>The main findings with respect to the above-mentioned tasks are:</p> <ul style="list-style-type: none"> <li>-The results of catalytic testing of commercial FeCr-based high temperature water gas shift (HTWGS) catalysts (i.e., KATALCO™ 71-6) demonstrate the suitability of this commercial catalyst for the WGS unit of the SEWGS technology.</li> <li>-The conversion loss over 1000 hr testing with and without the BOFG contaminants (SO<sub>2</sub> and NO<sub>2</sub>) is 4 - 5%. The conversion of CO to CO<sub>2</sub> and H<sub>2</sub>O and the conversion of NO<sub>2</sub> was complete and no hydrocarbon and oxygenates have been found during the course of the testing. The conversion of SO<sub>2</sub> was not monitored (below detection limits). We speculate the conversion loss we observed in the present testing may be further delayed by adjusting the steam/carbon ratio to slightly higher value. However, no post-test characterization on the catalyst pellets was carried out, hence, no indication as to the cause of the slight deactivation was obtained in the present experimental campaign.</li> </ul>



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## 1 INTRODUCTION

### 1.1 SEWGS

High temperature separation through sorption enhanced water gas shift concept (SEWGS) is investigated by ECN part of TNO and Swerea MEFOS. The technology relies on the use of fixed bed filled with solid sorbents that retain CO<sub>2</sub> while producing H<sub>2</sub>. Within Elegancy, ECN part of TNO and Swerea MEFOS will mature the SEWGS technology, with specific application to steelworks gas: Preparation for the experimental validation and demonstration using the STEPWISE pilot will be made, including sensitivity analysis performed at TRL 5 facilities at ECN part of TNO.

In the SEWGS process water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ) is carried out in the multiple vessels filled with catalytically active high-temperature adsorbent, such as promoted hydrotalcite. The removal of CO<sub>2</sub> product, from the gas phase drives equilibrium to the right hand side, maximizing H<sub>2</sub> production, and minimizing CO and steam requirement. The sorbent is regenerated by steam. SEWGS is a cyclic process that comprises high pressure adsorption and rinse, pressure equalization, and low pressure purge. In SEWGS, steam is added in the rinse (**high-pressure** rinse steam, expressed on a molar basis as  $\text{Steam}/C_{\text{rinse}}$ , where C refers to C captured) and in the purge (**low-pressure** purge steam, expressed on a molar basis as  $\text{Steam}/C_{\text{purge}}$ , where C refers to C captured). An example of 7 steps SEWGS cycle is given in Figure 1.1.

A mixture of pre-shifted, CO<sub>2</sub> enriched, residual steel gases (BOFG, BFG and COG<sup>1</sup>) enters the adsorption column at the bottom. After the adsorption step, a co-current steam rinse is performed to improve the CO<sub>2</sub> product purity, by preventing the loss of efficiency due to H<sub>2</sub> slip into CO<sub>2</sub> product. Depressurization is followed by a counter-current steam purge to allow high CO<sub>2</sub> recovery and to enhance sorbent regeneration. The final re-pressurization of the column is done with the product gas. Thermal effects within the cycle are caused by the exothermicity of the WGS reaction and also due to the heats of adsorption of both CO<sub>2</sub> and steam.

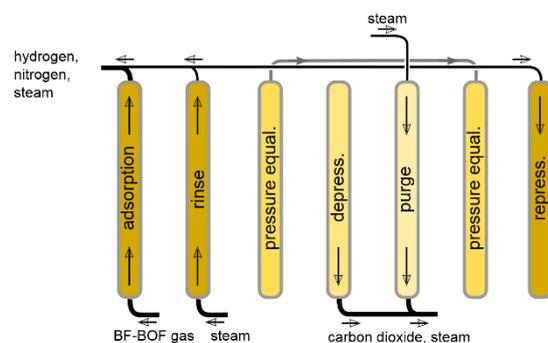


Figure 1.1: 7 steps SEWGS cycle with co-current rinse

<sup>1</sup> BOF = Basic Oxygen Furnace Gas ; BFG = Blas Furnace Gas ; COG = Cokes Oven Gas

The pressure equalization steps are used to increase CO<sub>2</sub> product purity and to balance/minimize steam used in rinse and purge steps. Example of 9 process steps carried in 6 vessels is described in Figure 1.2.

1. A: Adsorption
2. R: Co-current steam rinse
3. PE1: Pressure equalization 1 (providing step)
4. PE2: Pressure equalization 2 (providing step)
5. DP: Depressurization (DP)
6. P: Purge
7. PE1: Pressure equalization 2 (receiving step)
8. PE2: Pressure equalization 1 (receiving step)
9. RP: Repressurization

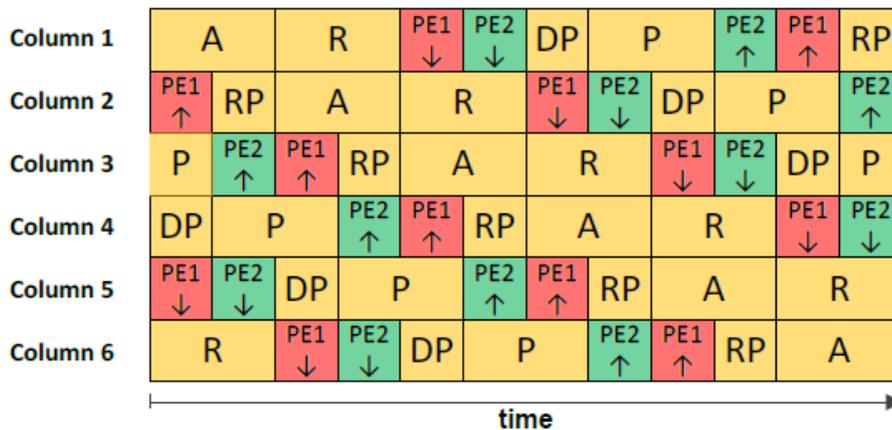


Figure 1.2: Cycle with 9 steps carried in 6 columns.

For a given column lay-out and size, the steam consumption, purge pressure and number of pressure equalizations steps are dependent variables and can be varied in order to achieve the desired carbon dioxide purity and capture ratio. The amount of rinse affects the CO<sub>2</sub> purity, while purge influence CO<sub>2</sub> capture rate (CCR). The final number of the pressure equalization steps, total steam consumption and purge pressure are result of the cycle optimization.

The pre-shift section of the SEWGS process is a very important one. Here, the CO content of the steel-gas will be lowered to a level suitable for adsorption and reaction in the hot temperature PSA part of SEWGS. Industry-standard steam to CO ratios for WGS systems is around 2.3 to 1 in order to prevent carbon deposition under sweet conditions. In the present report we aim to prove the ability of commercial high temperature water gas shift catalysts to operate in the presence of Basic oxygen furnace gas (BOFG) characterized by its very high carbon content (CO >60% and CO<sub>2</sub> ~20% dry gas composition), including contaminants at less than 5% conversion loss over 1000 hr testing.

## 1.2 High temperature shift catalyst

The high temperature water gas shift (HTWGS) catalyst used in the present study is a commercial catalyst (KATALCO™ 71-6) provided by Johnson Matthey (JM) formulated from iron oxide, chromia and copper oxide, and provide efficient operation due to enhanced activity. The catalyst is reported to be robust, also at low steam to gas ratios. The catalyst must be reduced before it can be used. The reduction of high temperature shift catalyst is invariably carried out with process gas under conditions that allow the haematite to be converted to magnetite without further reduction to metallic iron. Reduction also converts any of the small quantity of residual hexavalent chromium ( $\text{CrO}_3$ ) to trivalent chromium ( $\text{Cr}_2\text{O}_3$ )[1]. It is very important that steam should be present during the reduction procedure in order to prevent over-reduction of the catalyst. If the  $\text{H}_2\text{O}/\text{H}_2$  ratio exceeds 0.18 at  $400^\circ\text{C}$  or 1.0 at  $550^\circ\text{C}$  the desired magnetite is the stable phase.

## 1.3 Basic oxygen furnace gas

In the steel plant iron ore is reduced to hot metal and energy rich process gases are released. These gases are utilized in the steel production. Blast furnace gas (BFG) originates in the blast furnace. It is a gas mixture containing mostly carbon monoxide and carbon dioxide from the reduction process: The oxygen bound in the iron ore is converted to CO and  $\text{CO}_2$  through a reaction with the carbon in the coke and coal powder. Although the gas has a low heating value, given the large volume it still contains a considerable amount of energy that can be utilized through either combustion through own processes, where the energy content is used for coke or pig iron production, or in a combined heat and power plant, where the energy content is converted to electricity and heat. The electricity is used in production processes, while the majority of the heat is supplied to the local district heat network. In another process, the oxygen steelmaking process (LD convertor process, the name comes from the Austrian cities of Linz and Donawitz) employs a converter (vessel) and top blowing oxygen lance to refine the blast furnace hot metal into crude steel. The LD process also gives rise to energy rich gases that consist mainly of carbon monoxide. LD gases are named Basic Oxygen Furnace Gases (BOFG) and are mixed with the blast furnace gas before combustion in the power plant. For instance, the combined heat and power plants at SSAB's production sites in Sweden and Finland produce 40% of SSAB's electricity requirement in the Nordics, as well as supplying the district heat networks in Luleå, Oxelösund and Raahe with heat.[2]

The typical BOFG composition derived from the SSAB steel making process at the Lulea site in Sweden is shown in Table 1.1. The composition represents the highest CO+ $\text{CO}_2$  concentration encountered during operation. Periodically some decreased CO+ $\text{CO}_2$  (approximately 65%+16%) is noticed during operation. The principle dry gas BOFG composition is translated to a composition that is workable on the high pressure rig used in the water gas shift testing at the ECN part of TNO premises. Further information is given in the experimental section below.

*Table 1.1: BOFG composition (dry gas).*

	<b>BOFG SSAB Lulea</b>	<b>BOFG ECN.TNO Exp.</b>
CO	68%	62%
CO2	18%	17%
H2	2%	7%
N2	13%	14%

## 2 EXPERIMENTAL

A single JM catalyst pellet pellet (8.3x4.8 mm) with high dense purity  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> balls as spacers was used in the testing. The reactor diameter was tuned to the pellet size ( $d_{\text{reactor}}/d_{\text{pellet}} = 1.4$ ). The spacers consist of 2.5 mm diameter high purity  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres (Condea). The purpose of the spacers is i) to aid the exposure of the entire pellet surface area to the bulk gas phase and ii) to serve as a mixer for the gas contacting the pellet. The total number of pellets used in the testing is four. Due to the manufacturing details of the catalyst the pellet cannot be crushed into sieve fraction that would otherwise allow for better axial and radial distribution of the catalyst surface area in the reactor. The single pellet approach is efficient to monitor catalyst stability. Determination of the intrinsic activity of the material with the single pellet reactor should not be aimed for. Prior to testing at ECN>TNO the commercial catalyst batch of pellets was part of the general quality testing procedures of JM. The results obtained with the four pellets at ECN>TNO (Chapter 3) and particularly the JM quality testing of the batch of catalyst did not indicate significant variations in the product quality among the catalyst pellets.

Figure 2.1 shows a schematic representation of the Spider test-rig used for the testing at 8 bar total pressure. It contains 4 reactors in parallel, each capable of holding either sieve fractions or pellets. The temperature is measured at the outer wall of the reactor at the height of the catalyst bed. The reactors are placed by sets of 2 reactors in 2 separate heaters. A dry mixture gas consisting of N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> is created using Bronkhorst mass flow controllers. This mixture is distributed over the reactors by means of Bronkhorst mass flow controllers. Each reactor is equipped with a miniature evaporator, in which the dry mixture gas is used to evaporate a Bronkhorst Liquiflow controlled liquid water flow. Between the evaporator and the reactor, additional feed lines for contaminants are installed. Two of the reactors can be fed with a contaminant in Ar or N<sub>2</sub> mixture, the other two reactors are fed with the same amount of N<sub>2</sub>. The reactors are made of Inconel-600 and the catalyst bed is held in position by means of a clamped metal gauze. The bed is positioned such that the catalyst is in the isothermal zone of the reactor oven blocks. Within this isothermal zone of 3 cm height, the temperature is constant within 1°C. Accordingly, the measurements are at isothermal conditions. In order to adjust flow settings accurately (100 ml/min per reactor) the number of reactors used in the present testing was limited to 4. The BOF gas composition compiled in Table 1 also contains ppm levels of NO<sub>x</sub> (NO<sub>2</sub>) and SO<sub>2</sub>, respectively amounting to a maximum of approximately 11 ppm and 0.5 ppm and may vary marginally during the steel making process. These potential catalyst poisons were accordingly involved in the shift testing: To represent possible worst case scenarios for the shift catalyst the concentrations were increased to 55 ppm NO<sub>2</sub> and 5 ppm SO<sub>2</sub>. Reactor 1 (R1) and 5 (R5) were fed with the contaminants while reactors 3 (R3) and 7 (R7) were fed without contaminants. The conditions of the testing are listed in Table 2.1

Each reactor outlet is sequentially sampled by a micro-GC (Perkin Elmer) for N<sub>2</sub>, Ar/O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>S and COS. The sample is depressurized to 1.5 bar and dried by means of a Perma Pure prior to injection in the GC. The outlet of every reactor is connected to a common outlet in which the pressure is controlled. In parallel, a NO<sub>x</sub> analyzer (CL3020 CLD ABB) was used to monitor the fate of the NO<sub>2</sub> component during the reaction.

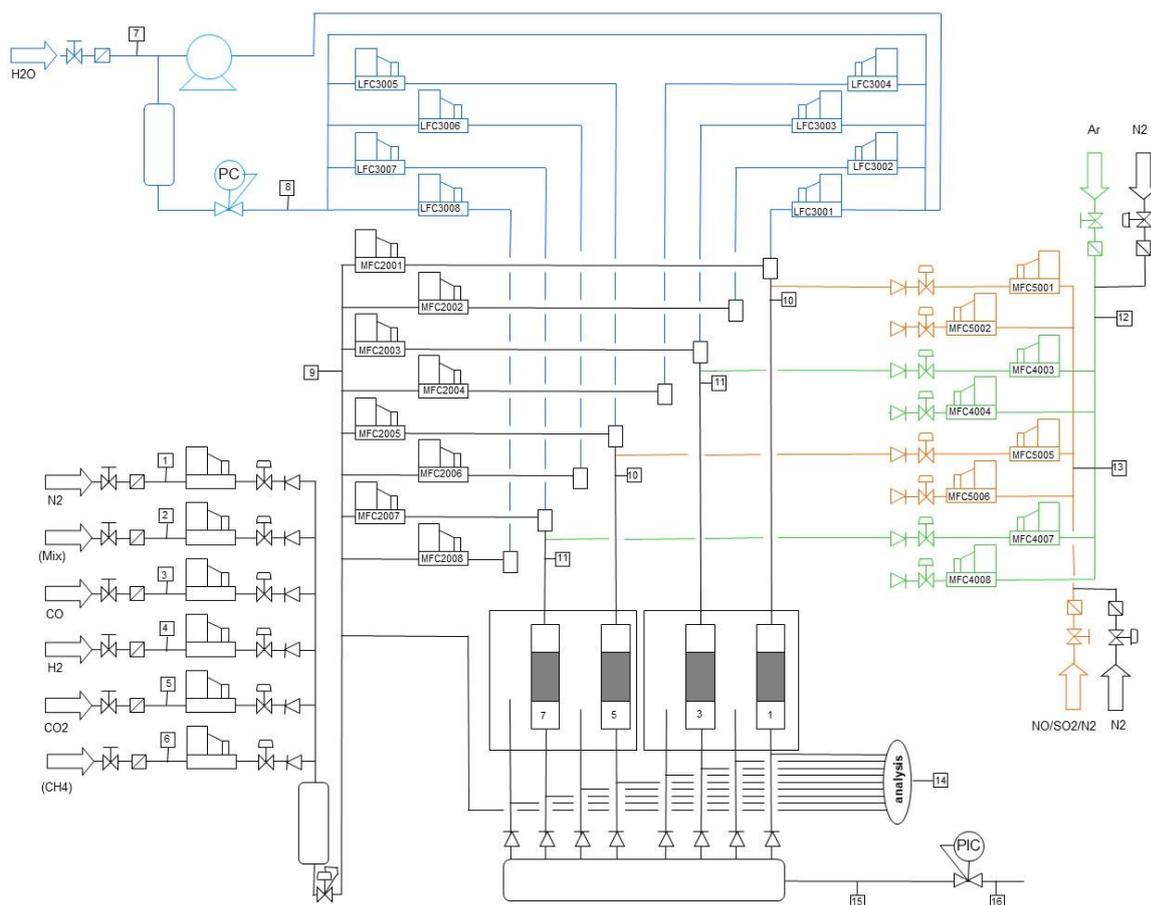


Figure 2.1: Schematic representation of the Spider test-rig configuration. Note the 3 feeding sections: i) in black the dry clean feed section produces a dry mixture of CO, CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub>, ii) in blue the steam feed adds water to the evaporator for the reactors producing a clean wet feed and iii) in orange the contaminants feed which is added to the clean wet feed producing a wet contaminated feed for reactors 1 and 5.

Table 2.1: BOFG composition (wet gas). R1, R3, R5 and R7 denote the reactor number.

	BOFG (dry vol%)	BOFG (wet vol%) R3&R7		BOFG (wet vol%) R1&R5
CO	62%	26	CO	26
CO <sub>2</sub>	17%	7	CO <sub>2</sub>	7
H <sub>2</sub>	7%	3	H <sub>2</sub>	3
N <sub>2</sub>	14%	6	N <sub>2</sub> +NO <sub>2</sub> +SO <sub>2</sub>	6
H <sub>2</sub> O		58	H <sub>2</sub> O	58

The measurement sequencing was carried out as following:

1. Catalyst activation:

- a. Increase to 5 bara at RT in N<sub>2</sub>, 5°C/min to 250°C. Add steam (1h dwell). Add H<sub>2</sub> (1 h dwell). Add CO and CO<sub>2</sub>, increase to 8 bara, 250-400°C(4h dwell), cool to 300°C.
2. Catalyst conversion activity testing:
  - a. Conversion activity plot as function of temperature
    - i. Temperature from 300°C to 480°C
3. Measure catalyst stability for 1000 hours (steady-state)
  - a. Influence trace components: 5 ppm SO<sub>2</sub> & 55 ppm NO<sub>2</sub>
  - b. Comparing reactor fed with BOFG w/o contaminant components with reactors fed with BOFG with contaminant components. Compare at two temperatures, i.e. 430 and 470 °C.

### 3 RESULTS AND DISCUSSION

To explore the suitability of the commercial iron-based (FeCr) catalyst for the WGS unit of the SEWGS technology, a catalyst testing programme was initiated and carried out following the measurement sequence listed in Chapter 2.

Figure 3.1 shows the CO conversion achieved with the 4 reactors. The information extracted from this experiment is limited to determination of the flow rates and temperatures used in the stability testing: Stability testing ideally is carried out at conversion levels far from equilibrium conversion. The CO conversion obtained with R7 seems slightly higher but this is likely caused by a small mismatch in the flow distribution over the reactors. Likewise, one may argue that the CO conversion obtained with R5 is slightly lower. It should be noted however that, due to a deviation in the liquiflow, the effective steam/CO ratio of R5 turned out to be 2.0 contrary to the steam/CO ratio of 2.2 for the other reactors. Moreover, gas channeling may not be fully prevented with the pellet configuration and may affect the reactors slightly different. Alternatively, the catalysts surface area may slightly differ for the pellets. In summary, all reactors show essentially similar conversion trends with temperature. A possible effect, i.e. inhibitive or otherwise, of the presence of contaminants is not indicated in the test results.

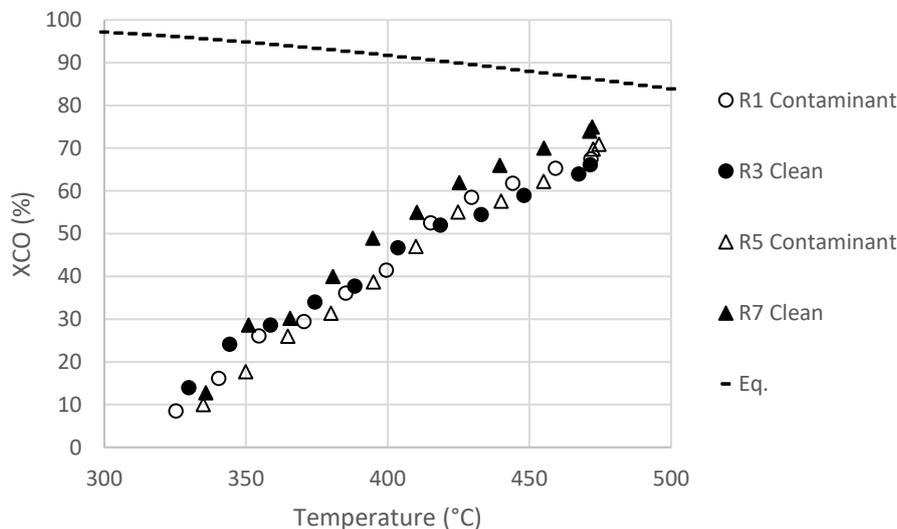


Figure 3.1: WGS CO conversion activity for FeCr pellet under BOFG ( $H_2O/CO = 2.2$ , 8 bar)

Time on stream temperature-dependent CO conversion is shown in Figure 3.2 and 3.3, respectively the results obtained at 470 and 430 °C. The ability of the water gas shift catalysts to operate in the presence of high carbon content ( $\text{CO} > 60\%$  and  $\text{CO}_2 \sim 20\%$  dry gas composition,  $\text{H}_2\text{O}/\text{CO} = 2.2$ ), including major contaminant components at less or equal to 5% conversion loss over 1000 hr testing is verified.

During the 1000+ hr period of testing several hardware problems were encountered. Since the four reactors were tested in parallel at the same time, the hardware problems affected all experiments in the same time interval. The problems affected the contaminant supply MFC's. In particular, results with the contaminant feed in the period between 630 hr and 1000 hr on stream was affected. During this period the contaminant feed supply was obscured by partial plugging of lines that in turn occurred after power blackout failure. The obstruction was resolved online by switching on and off to an extra, high pressure, inert flow. However, during this period the total flow varied causing the noisy conversion trends in this period. Overall the experiment was negatively affected by the problems over a period of two weeks: the significant length of this period relates to unattendance of the test rig and not to an intrinsic problem with the test rig. Note that during this difficult period the exposure of the catalyst to representative contaminant levels was retained. During the period of partial obstruction the contaminant flow was never close to zero as verified by the tracer gas fed with the contaminant gas: the minimum concentrations of  $\text{NO}_2 + \text{SO}_2$  was approximately 15 % of the original concentration used during the other periods on stream, e.g. 8 ppm  $\text{NO}_2 + 0.8$  ppm  $\text{SO}_2$ . In other words, the reactors with contaminant have been exposed to BOFG representative levels of contaminant during the entire course of the experimental campaign. As a result of the problems encountered the testing was extended beyond the anticipated 1000 hours and continued for an additional 100 hour. At approximately 950 hr on stream the contaminant flow was restored to the original settings and, due to the retained stability of the flow settings, CO conversion started to follow the expected trends again.

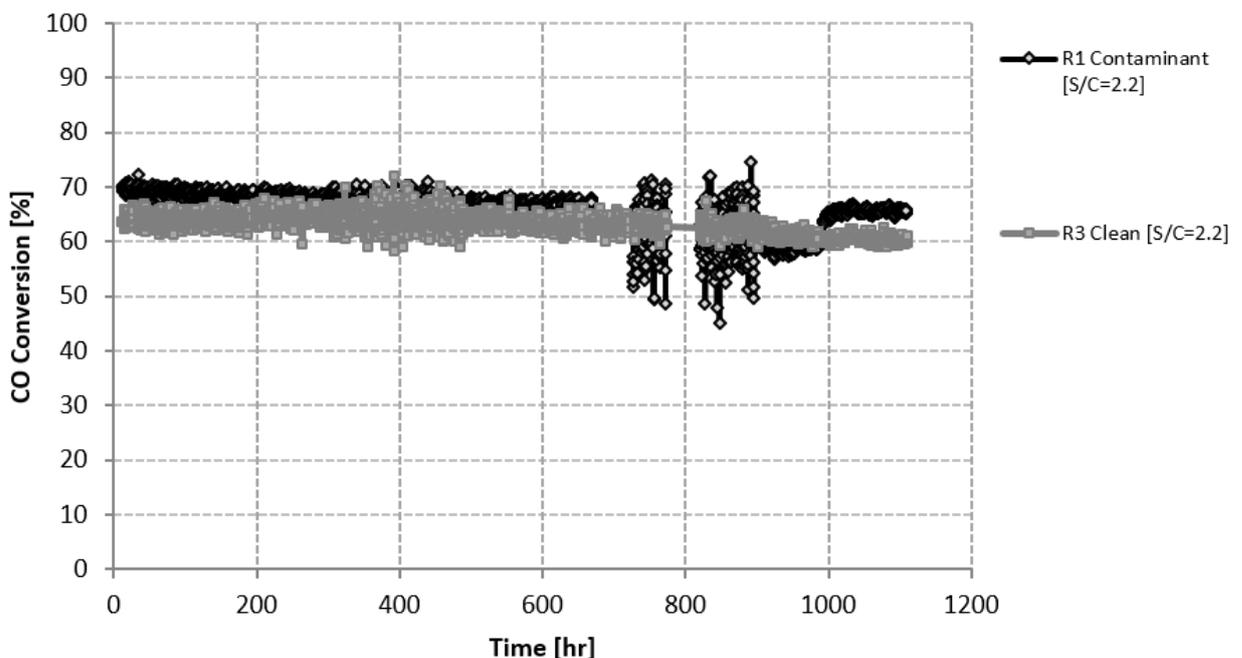


Figure 3.2: WGS CO conversion activity for FeCr pellet under BOFG ( $\text{H}_2\text{O}/\text{CO} = 2.2$ , 8 bar, 470°C)

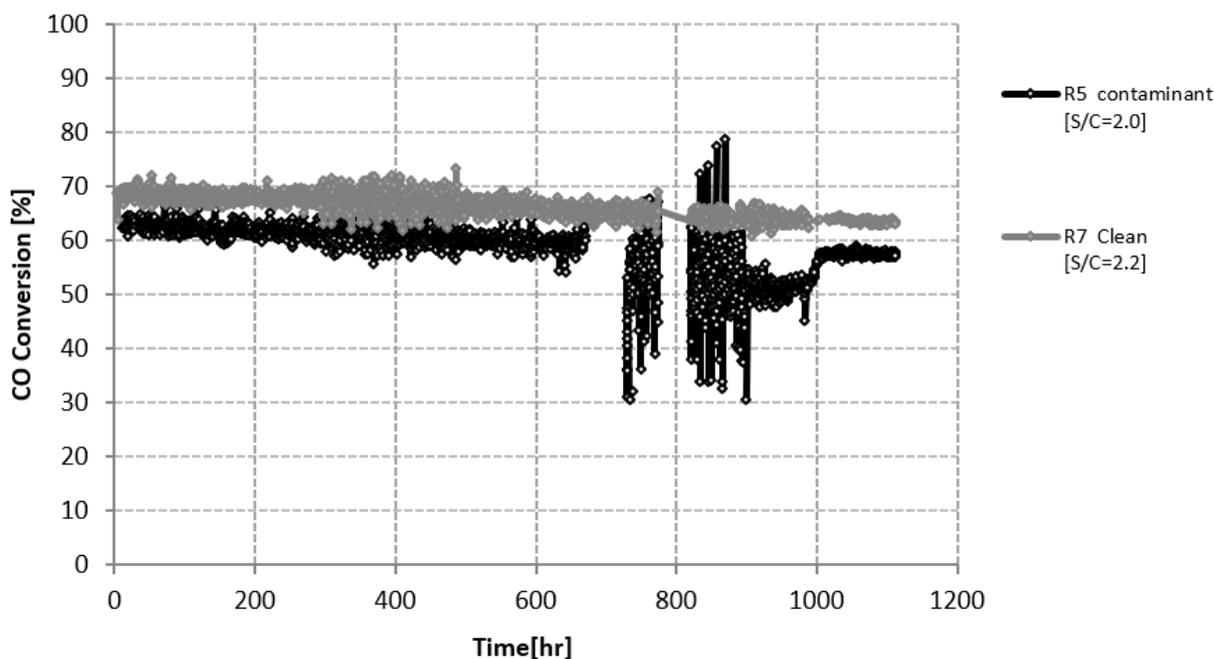


Figure 3.3: WGS CO conversion activity for FeCr pellet under BOFG ( $H_2O/CO = 2.2$ , 8 bar,  $430^\circ C$ )

The conversion of CO to  $CO_2$  and  $H_2O$  and the conversion of  $NO_2$  was complete and no hydrocarbon and oxygenates have been found during the course of the testing. The conversion of  $SO_2$  was not monitored (below detection limits). One may argue the conversion loss in the presence of contaminant may exceed the degradation of the clean situation at the  $430^\circ C$  testing (Figure 3.3). However, this is very difficult to judge considering the deviation levels in the CO concentration over the span of the full testing period. Also, exactly reverse thoughts may arise from the results at  $470^\circ C$ . Overall, we believe the effect of contaminants is not unambiguously observed and virtually absent. The  $470^\circ C$  could be a little higher than the highest operational temperature foreseen for HTWGS catalysts (i.e. inlet  $360^\circ C$  with maximum  $70^\circ C$  temperature rise). However, the extent of deactivation appears rather similar for the reaction at  $430^\circ C$  and  $470^\circ C$ . We speculate the conversion loss we observed in the present testing may be further delayed by adjusting the steam/carbon ratio to slightly higher value. However, no post-test characterization was carried out and therefore no indication as to the cause of the slight deactivation was obtained in the present experimental campaign.

## 4 CONCLUSION

The main objective of WP1 with respect to the water gas shift (WGS) was to test the capability of commercial WGS catalyst to operate outside their normal operation window by testing gas representative of metal processing systems with CO contents of 60%, and up to about 20% of both CO<sub>2</sub> and N<sub>2</sub> in the presence of the contaminants typically present in the gas of a basic oxygen furnace, BOFG at H<sub>2</sub>O/CO ratio 2-2.3. The results of catalytic testing of commercial FeCr-based high temperature water gas shift (HTWGS) catalysts (i.e., KATALCO 71-6) show that the 71-6 catalyst meets the requirements of both high water gas shift activity and stability under BOFG conditions with absence of methanation and is a suitable WGS catalyst for the proposed application. The conversion loss over 1000 hr testing with and without the BOFG contaminants (SO<sub>2</sub> and NO<sub>2</sub>) approaches 5%. The conversion of CO to CO<sub>2</sub> and H<sub>2</sub>O and the conversion of NO<sub>2</sub> was complete and no hydrocarbon and oxygenates have been found during the course of the testing. We speculate that the conversion loss we observed in the present testing may be further delayed by adjusting the steam/carbon ratio to slightly higher value. However, no indication as to the cause of the slight deactivation was obtained in the present experimental campaign.

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