

## Thermodynamic Feasibility of Pure Hydrogen Production and Storage in Iron and Germanium Based Double Chemical Looping Process

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Solid iron based low or medium temperature chemical loop is considered as a possible option of hydrogen storage and production. In the method, hydrogen is produced via iron oxidation with steam, and in the next phase iron oxide is reduced with hydrogen, synthesis gas or methane. In the reduction stage the reaction is terminated when the atmosphere still contains a large fraction of the reducing agent (often over 70 vol.%). In the paper the innovative idea of a double, iron and germanium based, chemical cycle was proposed. The thermodynamic calculations show that the reduction stage in the double iron-germanium cycle is more effective than the classical iron based loop.

Keywords: hydrogen storage, hydrogen production, steam-iron process, chemical loop, thermodynamics

## Introduction

The wide implementation of the hydrogen economy requires the development of reliable and cost-effective techniques of hydrogen storage and production.<sup>1,2</sup> Iron and iron oxides may be potentially applied in the process of hydrogen production and storage, respectively.<sup>3-6</sup> The main steps of the process may be presented as follows:

$Fe + H_2O = FeO + H_2$	(1)
FeO + C = Fe + CO	(2)

In the first step of the process discussed, molten iron reacts with steam and hydrogen is produced (see equation 1). Then wustite (FeO) is reduced with carbon (see equation 2). The recovered iron is recycled to the first stage of the process.

Although the hydrogen production in steam-iron process has been known since the 19<sup>th</sup> century, it is considered to be uneconomical nowadays in comparison with hydrogen production in the process of natural gas reforming. At the Ohio State University the innovative method of natural gas conversion with the application of a technology employing the chemical looping was proposed. In this option the iron based oxygen carrier and a novel gas-solid counter-current moving bed reactor for hydrogen production was proposed.<sup>7</sup> The idea of hydrogen production in steam-iron process has been previously proposed by Alchemix, as the Hydromax process, where the steam-iron stage is performed in a bath of 25% of iron and 75% of tin, which enables decrease in the operation temperature to about 1250 °C, resulting in a significantly improved process economics.<sup>8</sup>

Another technological option presented in the literature<sup>9</sup> comprises in performing the steam-iron process in a solid phase at the temperatures below 1000 °C. This low-temperature steam-iron process (LTSI) may be potentially applied in hydrogen production and/or storage. In the first stage of the process iron reacts with steam to form hydrogen and magnetite (the temperatures applied are more thermodynamically favorable for magnetite formation than for wustite):

$$0.75Fe + H_2O = 0.25Fe_3O_4 + H_2$$
(3)

In the next stage magnetite may be reduced with methane (see equation 4) or hydrogen (reversed equation 3):

$$Fe_3O_4 + CH_4 = 3Fe + CO_2 + 2H_2O$$
 (4)

The process of magnetite reduction with hydrogen may be applicable in hydrogen storage. The same process

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utilizing other reducing agents, like e.g. methane or syngas, could be employed in hydrogen production. The main operational issue of the LTSI process reported in the literature<sup>9-13</sup> is the deterioration of iron bed performance, resulting from sintering, carbon deposition and Fe<sub>3</sub>C formation, when carbon-containing fuels are utilized in the magnetite reduction stage. Another problem is low reaction rate at lower temperatures. The effects of sintering and the influence of iron doping on bed performance is widely discussed in the literature.<sup>11,14-17</sup> Doping agents, such as aluminum, molybdenum and cerium are reported to mitigate the sintering effect. Weak stabilizing effect was also observed for scandium, titanium, vanadium, chromium, yttrium and zirconium. Noble metals, like ruthenium, rhodium, palladium, silver and iridium expose a catalytic activity, and enhance the process kinetics. Platinum was also tested, but no reduction of the sintering effect was observed with its applications. Additions of manganese, cobalt, nickel, copper, zinc, gallium, niobium, tungsten, and rhenium have been reported to enhance the sintering. Also the thermodynamic constraints of the reduction stage have been reported among the main difficulties of the process discussed; magnetite reduction terminates when the atmosphere still contains considerable amounts of the reducing gas (H<sub>2</sub>, syngas).<sup>18</sup> This implies the need for a more advanced gas management system, which is disadvantageous in terms of the technological simplicity and process economics. The evaluation of the application of iron as a potential material for hydrogen storage or hydrogen production from carbonaceous materials reveals that the reduction stage of the iron cycle is quite problematic. The utilization of the reducing gases:  $H_2$ , CO and  $CH_4$  is weak. Furthermore, there is a possibility of disadvantageous phenomena, like carbon deposition, Fe<sub>3</sub>C formation, etc.<sup>18</sup> The poor thermodynamics of the reduction stage in the iron cycle was a stimulus for searching other materials with better potential performance, such as germanium.

In the paper the idea of a double chemical loop, comprising of Fe-Fe<sub>3</sub>O<sub>4</sub> and Ge-GeO<sub>2</sub> loops, potentially enabling avoidance of the above mentioned constraints is presented. The thermodynamic calculations, proving a modest improvement in the Fe-Ge loop in comparison with the iron cycle are given, since they constitute the first step of the feasibility assessment of any chemical process.<sup>18</sup> The kinetic limitations, inefficiency in the reduction stages, sintering and carbon deposition issues, gas management aspects, and considerations regarding the reactor design all remain significant concerns in terms of the practical implementation. The additional cost and complexity would also clearly be involved in the double chemical looping process. Taking into account all these limitations, the main objective of the study is therefore to supplement the currently available thermodynamic databases of chemical cycles for hydrogen production and storage, since the double Fe-Ge chemical looping process is considered to significantly improve hydrogen production in comparison with the classical iron cycle.

## Experimental

The combination of Fe-Fe<sub>3</sub>O<sub>4</sub> loop with Ge-GeO<sub>2</sub> loop may improve gas management in the reduction stage of the cycle. Germanium shows lower affinity to oxygen than iron, and thus may be reduced with the flue gas from magnetite reduction.

#### Germanium based loop

Germanium melting point temperature is 937 °C, while germanium dioxide melting point is 1115 °C, which implies that Ge-GeO<sub>2</sub> loop could be applied at temperatures of up to 800 °C.

#### Germanium oxidation with steam

Hydrogen is produced in the reaction of germanium oxidation with steam.

$$0.5Ge + H_2O = 0.5GeO_2 + H_2$$
(5)

Figure 1 shows the phase stability diagram for such a system. As it can be seen from Figure 1, temperatures below 600  $^{\circ}$ C may be used for generation of concentrated hydrogen stream. The maximum concentration of hydrogen achievable in Ge oxidation decreases from nearly 100 vol.% at low temperatures to 56 vol.% at 800  $^{\circ}$ C.

#### Germanium dioxide reduction with hydrogen

Germanium dioxide reduction with hydrogen proceeds by a reversed reaction given in equation 5. As it can be seen from Figure 1, the reduction should be performed at temperatures above 600 °C.

#### Germanium dioxide reduction with carbon monoxide

Germanium dioxide reduction with carbon monoxide may be described as follows:

$$0.5 \text{GeO}_2 + \text{CO} = 0.5 \text{Ge} + \text{CO}_2$$
 (6)



Figure 1. The phase stability diagram of Ge and  $\text{GeO}_2$  phases in the  $H_2\text{O-}H_2$  atmosphere.

The phase stability diagram for this system is given in Figure 2. It can be seen that the maximum concentration of carbon dioxide grows from 30 vol.% at 100 °C to nearly 58 vol.% at 800 °C. Thus, high temperatures (600-800 °C) are more favorable for  $\text{GeO}_2$  reduction with carbon monoxide.



Figure 2. The phase stability diagram of Ge and GeO<sub>2</sub> in the CO<sub>2</sub>-CO atmosphere.

#### Germanium dioxide reduction with methane

It is assumed that the reduction of germanium dioxide with methane proceeds as follows:

$$2\text{GeO}_2 + \text{CH}_4 = 2\text{Ge} + \text{CO}_2 + 2\text{H}_2\text{O}$$
(7)

The phase stability diagram of Ge and GeO<sub>2</sub> in CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O atmosphere is presented in Figure 3. In the temperature range of 400-800 °C, the equilibrium concentration of methane decreases strongly with the temperature increase; high temperature needs to be applied



Figure 3. The phase stability diagram of Ge and  $\text{GeO}_2$  in the  $\text{CH}_4$  atmosphere.

to achieve a satisfactory efficiency of methane consumption. The rise in pressure also increases the temperature of the phase stability border.

## **Results and Discussion**

The compound used in a cycle as a gas carrier may be in a liquid state, like in case of high temperature Fe-FeO cycle or nitrite-nitrate cycle, or in the solid state. Depending on the aggregation state, the cycle application is connected with different technical and material issues. Liquid state cycles are probably more convenient for larger industrial applications as they allow for potentially better reaction kinetics since the mass transport is easier in a liquid phase. Additionally, mass transport can be improved by stirring the bath of molten carrier. The liquid phase, however, is problematic mainly due to corrosive impact on container materials used. In case of solid state oxygen carriers the kinetics of the reactions is also dependent on the quality of the porous structure of the material, influencing the availability of the contact area. In the literature<sup>4,6,18</sup> numerous examples of iron application as a potential material for hydrogen storage or hydrogen production from carbonaceous materials are given, along with numerous problems reported, such as weak utilization of reducing gases ( $H_2$ , CO and  $CH_4$ ), carbon deposition and Fe<sub>3</sub>C formation. In the light of the above in the study presented, germanium was selected as potentially superior to iron.

The comparison of the potential performance of the Fe-Fe<sub>3</sub>O<sub>4</sub> loop and the double Fe-Fe<sub>3</sub>O<sub>4</sub> Ge-GeO<sub>2</sub> loop in hydrogen storage and production, assessed on the basis of compositions of thermodynamically feasible gas mixtures applied and produced during the studied cycles is discussed below.

Comparison of iron based loop and double iron and germanium based loop

The comparison was made for reactors of theoretical capacity of 100 mol of hydrogen during oxidation stage of the cycle. It is assumed that 100 vol.% hydrogen, carbon monoxide or methane is applied in the reduction stage and 100 vol.% steam in the oxidation stage. In case of using methane as a reducing agent, the pressure of 1 MPa is

Table 1. Fe reactor performance

considered. The hydrogen production process is assumed to be performed at 300  $^{\circ}$ C, and the reduction at 800  $^{\circ}$ C.

Hydrogen production in iron based loop - oxidation with steam

A reactor with the capacity of 100 mol of  $H_2$  contains 75 mol of Fe. The amount of steam consumed in hydrogen generation is 103.92 mol. The gas produced

Hydrogen production / oxidation stage; T = 300 °C       inlet gas     H,O     0.03.92 ml (100.00 ml) (96.23 vu.5))       H,O     3.92 ml (3.77 vu.5%)       reactor state     5.00 mol of Fe,O,O       Fe/Qu to Fe <sub>1547</sub> O stage     H,O     28.08 mol (100.00 vul.5%)       outlet gas     H,O     28.08 mol (100.00 vul.5%)       outlet gas     H,O     28.08 mol (100.00 vul.5%)       outlet gas     H,O     28.08 mol (100.00 vul.5%)       reactor state     H,O     28.08 mol (100.00 vul.5%)       reactor state     H,O     28.08 mol (100.00 vul.5%)       reactor state     H,O     28.08 mol (100.00 vul.5%)       outlet gas     H,I     28.08 mol (100.00 vul.5%)       outlet gas     H,I     28.09.11 mol (100.00 vul.5%)       outlet gas     H,I     28.09.11 mol (100.00 vul.5%)       outlet gas     H,I     28.09.11 mol (100.00 vul.5%)       outlet gas     CO     75.31 (100.00 vul.5%)       outlet gas     CO     24.50 mol (100.00 vul.5%)       outlet gas     CO     24.50 mol (100.00 vul.5%)       outlet gas     CO     24.50 mol (100.00 vul.5%)		Fe reactor; the capacity of 100 m	ol of H <sub>2</sub> , containing 75 mol of Fe		
inlet gas $H_cO$ 103.92 mol (100.00 vol.%)       outlet gas $H_cO$ 3.92 mol (3.77 vol.%)       H_cO     3.92 mol (3.77 vol.%)       reactor state     25.00 mol of Fe.O <sub>4</sub> State $H_cO$ 25.00 mol of Fe.O <sub>4</sub> Fe(o, to Fe.sar,O stage     inlet gas $H_c$ 28.08 mol (100.00 vol.%)       outlet gas $H_c$ 28.08 mol (100.00 vol.%)     0.00 mol (74.07 vol.%)       Fe(o, to Fe.sar,O stage     inlet gas $H_c$ 20.80 mol (74.07 vol.%)       eractor state     Fe.sar,O     7.22 mol (25.93 vol.%)     1.00.00 vol.%)       outlet gas $H_c$ 269.11 mol (100.00 vol.%)     1.00.00 vol.%)       outlet gas $H_c$ 269.11 mol (100.00 vol.%)     1.00.00 vol.%)       outlet gas $H_c$ 269.11 mol (100.00 vol.%)     1.00.00 vol.%)       outlet gas $H_c$ 79.20 mol     1.00.00 vol.%)       fold amount of pure $H_c$ consumed $CO$ 27.31 (100.00 vol.%)     1.00.00 vol.%)       outlet gas     CO     20.80 mol (76.16 vol.%)     1.00.00 vol.%)     1.00.00 vol.%)       outlet gas     <		Hydrogen production / ox	idation stage; T = $300 ^{\circ}$ C		
outlet gas $H_1$ 100.00 mol (96.23 vol.%)       I reactor state     25.00 mol of Fc,0,0       Reduction with $H_2$ , T = 800 °C       Fc,0,1 to Fc,sar,0 stage     inlet gas $H_2$ 28.08 mol (100.00 vol.%)       outlet gas $H_2$ 28.08 mol (100.00 vol.%)     0.00 mol (76.17 vol.%)       Fc,0,1 to Fc,sar,0 stage     inlet gas $H_2$ 28.08 mol (100.00 vol.%)       Fc,0,1 to Fc,sar,0 stage     inlet gas $H_2$ 26.911 mol (100.00 vol.%)       Fc,0,1 to Fc,sar,0 to Fe stage     inlet gas $H_2$ 26.911 mol (100.00 vol.%)       outlet gas $CO$ 79.20 mol       Total amount of pure $H_2$ consumed $CO_2$ 27.31 (100.00 vol.%)       consumed $CO_2$ 27.31 (100.00 vol.%)       consumed $CO_2$ 27.20 mol       Conol     27.20 mol     79		inlet gas	H <sub>2</sub> O	103.92 mol (100.00 vol.%)	
H <sub>2</sub> O     3.92 mol (3.77 vol.%)       reactor state     200 mol of Fe,O,C       Reduction with H <sub>2</sub> T = 800 °C     Reduction with H <sub>2</sub> T = 800 °C       Fe,O, to Fe <sub>0.94</sub> O stage     inlet gas     H <sub>1</sub> 28.08 mol (100.00 vol.%)       outlet gas     H <sub>2</sub> 2.08 mol (25.93 vol.%)     100.00 vol.%)       Fe,O, to Fe <sub>0.947</sub> O stage     inlet gas     H <sub>2</sub> 2.08 mol (74.07 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     H <sub>2</sub> 2.09.01 mol (10.00 vol.%)       outlet gas     H <sub>2</sub> 2.09.11 mol (10.00 vol.%)     0.00.00 vol.%)       outlet gas     H <sub>2</sub> 2.09.11 mol (10.00 vol.%)     0.00.00 vol.%)       outlet gas     H <sub>2</sub> 2.09.11 mol (10.00 vol.%)     0.00.00 vol.%)       outlet gas     H <sub>2</sub> 2.09.11 mol (10.00 vol.%)     0.00.00 vol.%)       Total amount of pure H <sub>2</sub> consumed     CO     2.03.00 mol (76.16 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     2.03.00 mol (76.16 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     2.09.00 mol (76.16 vol.%)       Teador state     Fe     7.50 mol     2.00.10 mol (68.18 vol.%)       ou		outlet gas	$H_2$	100.00 mol (96.23 vol.%)	
reactor state     Reduction with H <sub>2</sub> , T = 800 °C       Reduction with H <sub>2</sub> , T = 800 °C     28.08 mol (100.00 vol.%)       Peq.0 to PenserO stage     inlet gas     H <sub>2</sub> 28.08 mol (100.00 vol.%)       Outlet gas     H <sub>2</sub> 20.80 mol (74.07 vol.%)     20.80 mol (74.07 vol.%)       Peq.serO to Pe stage     inlet gas     H <sub>2</sub> 20.90 mol (70.57 vol.%)       Teactor state     Fe <sub>aser</sub> O     79.20 mol (70.57 vol.%)       reactor state     Fe     75.00 mol (75.7 vol.%)       reactor state     Fe     75.00 mol       Total amount of pure H <sub>2</sub> consumed     CO     27.31 (100.00 vol.%)       outlet gas     CO     24.80 mol (100.00 vol.%)       outlet gas     CO     24.80 mol (10.00 vol			$H_2O$	3.92 mol (3.77 vol.%)	
Reduction with H <sub>2</sub> T = 800°C       FeQ, to Fe <sub>base</sub> O stage     inlet gas     H <sub>2</sub> 28.08 mol (00.00 vol.%)       Peq.0 to Fe <sub>base</sub> O stage     H <sub>2</sub> 28.08 mol (00.00 vol.%)       reactor state     Fe <sub>base</sub> O     20.80 mol (74.07 vol.%)       Peq.or Stage     inlet gas     H <sub>2</sub> 20.80 mol (74.07 vol.%)       Peq.or State     Fe <sub>base</sub> O     79.20 mol     79.20 mol       Peq.or State     H <sub>2</sub> 26.91 1 mol (100.00 vol.%)     100.00 vol.%)       Peq.or State     H <sub>2</sub> 79.20 C9.43 4 mol.%)     79.20 C9.43 4 mol.%)       Teactor state     Fe     75.00 mol     79.20 C9.43 4 mol.%)       Teata amount of pure H <sub>2</sub> consumed     CO     27.31 (100.00 vol.%)     100.00 vol.%)       Outler gas     CO     20.80 mol (66.16 vol.%)     100.00 vol.%)     100.00 vol.%)       Peq.or Os faste     FebaserO     79.20 mol     10.00 vol.%)     100.00 vol.%)       Outler gas     CO     20.80 mol (66.16 vol.%)     100.00 vol.%)     10.00 vol.%)     10.00 vol.%)       Peg.ar O for Festage     inlet gas     Fe     75.00 mol     10.00 vol.%)     10.00 vol.%)     1		reactor state		25.00 mol of $Fe_3O_4$	
Fe,0, to Fe,sar,0 stage inlet gas H. 28.08 mol (00.00 vol.%)   outlet gas H, 7.28 mol (25.93 vol.%)   Fec,oar,0 to Fe stage inlet gas H, 7.28 mol (25.93 vol.%)   reactor state Fec,oar,0 79.20 mol   outlet gas H, 269.11 mol (100.00 vol.%)   outlet gas H, 189.91 mol (70.57 vol.%)   reactor state Fe 75.00 mol   reactor state Fe 75.00 mol   Total amount of pure H, consumed - 297.19 mol   Fe(o,1 to Fe,sar,0 Stage inlet gas CO 6.51 mol (23.84 vol.%)   outlet gas CO 27.31 (100.00 vol.%)   outlet gas CO 20.80 mol (76.16 vol.%)   Fector state Fector state Fector State 79.20 mol   reactor state Fector state 79.20 mol   reactor state CO 248.90 mol (100.00 vol.%)   outlet gas CO 248.90 mol (00.00 vol.%)   outlet gas CO 248.90 mol (00.00 vol.%)   outlet gas CO 20.80 mol (66.81 vol.%)   Fe Total amount of pure CO consumed - 75.01 mol   Fe Fe Total state CO 20.20 mol (0.01 vol.%)   outlet gas		Reduction with	$H_2, T = 800 ^{\circ}C$		
nullet gas     H2     7.28 mol (25.93 vol.%)       H2O     20.80 mol (74.07 vol.%)       reactor state     Fe <sub>0.87</sub> O       Fe <sub>0.87</sub> O to Fe stage     inlet gas     H2     269.11 mol (100.00 vol.%)       outlet gas     H2     189.91 mol (70.57 vol.%)       Total amount of pure H2 consumed     Fe     75.00 mol       Teactor state     Fe     75.00 mol       Fe <sub>0.40</sub> to Fe <sub>0.857</sub> O stage     inlet gas     CO     27.31 (100.00 vol.%)       outlet gas     CO     27.31 (100.00 vol.%)     0000 vol.%)     000 vol.%)       outlet gas     CO     27.31 (100.00 vol.%)     000 vol.%)     000 vol.%)       outlet gas     CO     20.80 mol (76.16 vol.%)     000 vol.%)     000 vol.%)       outlet gas     CO     20.80 mol (76.16 vol.%)     000 vol.%)     000 vol.%)       outlet gas     CO     20.80 mol (76.16 vol.%)     000 vol.%)     000 vol.%)       outlet gas     CO     20.80 mol (76.16 vol.%)     000 vol.%)     000 vol.%)       outlet gas     CO     20.80 mol (76.16 vol.%)     20.80 mol (76.16 vol.%)     20.80	Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage	inlet gas	$H_2$	28.08 mol (100.00 vol.%)	
Ho     20.80 mol (74.07 vol.%)       reactor state     Fe <sub>0.85</sub> ,0     79.20 mol       inlet gas     H <sub>2</sub> 269.11 mol (100.00 vol.%)       outlet gas     H <sub>2</sub> 189.91 mol (70.57 vol.%)       mount of pure H <sub>2</sub> consumed     Fe     75.00 mol       Teactor state     Fe     75.00 mol       Total amount of pure H <sub>2</sub> consumed     297.19 mol       Teactor state     Fe     75.10 (100.00 vol.%)       Total amount of pure H <sub>2</sub> consumed     CO     27.31 (100.00 vol.%)       Total amount of pure H <sub>2</sub> consumed     CO     25.1 mol (23.84 vol.%)       Total amount of pure H <sub>2</sub> consumed     CO     25.1 mol (23.84 vol.%)       Teactor state     Fe <sub>0.857</sub> O     79.20 mol       Teactor state     Fe <sub>0.857</sub> O     79.20 mol       Teactor state     Fe     75.00 mol       Total amount of pure CO consumed     CO     248.90 mol (100.00 vol.%)       Total amount of pure CO consumed     CO     25.20 mol (31.83 vol.%)       Teactor state     Fe     75 mol <td co<="" td=""><td></td><td>outlet gas</td><td><math>H_2</math></td><td>7.28 mol (25.93 vol.%)</td></td>	<td></td> <td>outlet gas</td> <td><math>H_2</math></td> <td>7.28 mol (25.93 vol.%)</td>		outlet gas	$H_2$	7.28 mol (25.93 vol.%)
reactor state     FeasysO to Fe stage     inlet gas     H_2     269.11 mol (100.00 vol.%) outlet gas       FeasysO to Fe stage     inlet gas     H_1     189.91 mol (70.57 vol.%)       H2O     79.20 (29.43 vol.%)     79.20 (29.43 vol.%)       reactor state     Fe     75.00 mol       Total amount of pure H2 consumed     297.19 mol     297.19 mol       Fe(ag.10 Fe_0sr,O stage     inlet gas     CO     6.51 mol (23.84 vol.%)       Fe(ag.10 Fe_0sr,O stage     inlet gas     CO     6.51 mol (23.84 vol.%)       Fe(ag.10 Fe_0sr,O stage     inlet gas     CO     6.51 mol (23.84 vol.%)       Fe(ag.10 Fe_0sr,O stage     inlet gas     CO     20.80 mol (100.00 vol.%)       outlet gas     CO     20.80 mol (100.00 vol.%)     0000 vol.%)       outlet gas     CO     20.80 mol (100.00 vol.%)     0000 vol.%)       outlet gas     CO     20.80 mol (100.00 vol.%)     0000 vol.%)       outlet gas     CO     20.80 mol (100.00 vol.%)     0000 vol.%)       outlet gas     CO     20.80 mol (0.00 vol.%)     0000 vol.%)       outlet gas     CH     60.00 zon ol (0.01 vol.%)<			$H_2O$	20.80 mol (74.07 vol.%)	
Feasist O to Fe stage     inlet gas     H_1     269.11 mol (100.00 vol.%)       outlet gas     H_2O     189.91 mol (70.57 vol.%)       H_2O     79.20 (29.43 vol.%)       reactor state     Fe     75.00 mol       Total amount of pure H_ consumed     297.19 mol     297.19 mol       Fe duction with CO, T = 800 °C     297.31 (100.00 vol.%)     000 vol.%)       Fe duction with CO, T = 800 °C     200.80 mol (76.16 vol.%)     000 vol.%)       Fe duction state     Fe dustro state     Fe dustro state     Fe dustro vol.%)       Fe dustro for Fe stage     inlet gas     CO     248.90 mol (100.00 vol.%)       outlet gas     CO     248.90 mol (100.00 vol.%)     000 vol.%)       outlet gas     CO     248.90 mol (100.00 vol.%)     000 vol.%)       outlet gas     CO     169.70 mol (68.18 vol.%)     169.70 mol (68.18 vol.%)       outlet gas     CO     79.20 mol (31.82 vol.%)     169.70 mol (68.18 vol.%)       outlet gas     CO     5202 mol (33.33 vol.%)     169.70 mol (68.18 vol.%)       Teator state     Fe     5202 mol (33.33 vol.%)     169.70 mol (66.66 vol.%)       fe dustro wit		reactor state	Fe <sub>0.947</sub> O	79.20 mol	
outlet gas $H_2$ 189.91 mol (70.57 vol.%) $H_2$ O     79.20 (29.43 vol.%) $H_2$ O     79.20 (29.43 vol.%)       reactor state     Fe     75.00 mol       Total amount of pure H, consumed     Reduction with CO, T = 800 °C     207.19 mol       Fe(o,4 to Fe <sub>0.947</sub> O stage     inlet gas     CO     6.51 mol (23.84 vol.%)       Outlet gas     CO     20.80 mol (76.16 vol.%)     20.80 mol (76.16 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     248.90 mol (100.00 vol.%)       Outlet gas     CO     248.90 mol (100.00 vol.%)     248.90 mol (100.00 vol.%)       Outlet gas     CO     248.90 mol (100.00 vol.%)     248.90 mol (100.00 vol.%)       Outlet gas     CO     248.90 mol (100.00 vol.%)     248.90 mol (100.00 vol.%)       Outlet gas     CO     79.20 mol     31.82 vol.%)       Total amount of pure CO consumed     Z7.51 mol     27.621 mol       Feo.94 to Fe_0.947 O stage     inlet gas     CH <sub>4</sub> 5.202 mol (0.01 vol.%)       Outlet gas     CH <sub>4</sub> 5.202 mol (0.01 vol.%)     20.901 mol (0.01 vol.%)       Feo.94 to Fe_0.947 O to Fe stage <tht< td=""><td>Fe<sub>0.947</sub>O to Fe stage</td><td>inlet gas</td><td><math>H_2</math></td><td>269.11 mol (100.00 vol.%)</td></tht<>	Fe <sub>0.947</sub> O to Fe stage	inlet gas	$H_2$	269.11 mol (100.00 vol.%)	
H <sub>0</sub> 79.20 (29.43 vol.%)       reactor state     Fe     75.00 mol       Total amount of pure H <sub>2</sub> consumed     297.19 mol       Reduction with CO, T = 800 °C     2       Fe <sub>0.94</sub> to Fe <sub>0.957</sub> O stage     inlet gas     CO     27.31 (100.00 vol.%)       Outlet gas     CO     27.31 (100.00 vol.%)     20.00       Fe <sub>0.957</sub> O to Stage     inlet gas     CO     27.31 (100.00 vol.%)       reactor state     Fe <sub>0.957</sub> O     20.80 mol (76.16 vol.%)       Fe <sub>0.957</sub> O to Fe stage     inlet gas     CO     248.90 mol (00.00 vol.%)       outlet gas     CO     248.90 mol (00.00 vol.%)     20.00       reactor state     Fe     75 mol     20.00       Total amount of pure CO consumed     Z76.21 mol     20.00     20.00     20.00       Feo_0.4 to Fe_0.947O stage     inlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)     20.00       CO     20.00 mol (36.33 vol.%)     20.00 mol (36.33 vol.%)     20.00     20.00     20.00       Feo_0.4 to Fe_0.947O stage     inlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)     20.00     20.00     20.00 </td <td></td> <td>outlet gas</td> <td><math>\mathrm{H}_2</math></td> <td>189.91 mol (70.57 vol.%)</td>		outlet gas	$\mathrm{H}_2$	189.91 mol (70.57 vol.%)	
reactor state     Fe     75.00 mol       Total amount of pure H <sub>1</sub> consumed     297.19 mol     297.19 mol       Fe <sub>0.947</sub> O stage     inlet gas     CO     27.31 (100.00 vol.%)       outlet gas     CO     6.51 mol (23.84 vol.%)     CO       CO2     20.80 mol (76.16 vol.%)     CO     6.51 mol (23.84 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     6.51 mol (23.84 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     248.90 mol (76.16 vol.%)       outlet gas     CO     169.70 mol (68.18 vol.%)     CO       reactor state     Fe     75 mol     79.20 mol       Total amount of pure CO consumed     206.2     79.20 mol (0.18.2 vol.%)       Fe <sub>0.947</sub> O stage     inlet gas     CH <sub>4</sub> 5.202 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 5.202 mol (0.001 vol.%)     001 vol.%)       outlet gas     CH <sub>4</sub> 5.202 mol (100.00 vol.%)     001 vol.%)       outlet gas     CH <sub>4</sub> 5.202 mol (0.00.10.01.%)     0.002 mol (0.01.01.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CH <sub>4</sub> 5.202 mol (0.00.10.01.%)			$H_2O$	79.20 (29.43 vol.%)	
Total amount of pure H <sub>2</sub> consumed     297.19 mol       Reduction with CO, T = 800 °C       Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage     inlet gas     CO     27.31 (100.00 vol.%)       outlet gas     CO     6.51 mol (23.84 vol.%)     CO       CO <sub>2</sub> 20.80 mol (76.16 vol.%)     CO     79.20 mol       reactor state     Fe <sub>0.947</sub> O     79.20 mol     79.20 mol       reactor state     Fe <sub>0.947</sub> O     79.20 mol     79.20 mol       outlet gas     CO     248.90 mol (100.00 vol.%)     79.20 mol       outlet gas     CO     169.70 mol (68.18 vol.%)     79.20 mol       outlet gas     CO     169.70 mol (68.18 vol.%)     79.20 mol       reactor state     Fe     75 mol     75 mol       Total amount of pure CO consumed     276.21 mol     276.21 mol       Colspan="2">Colspan= CH <sub>4</sub> 5.202 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)       outlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)       colspan="2">CO <sub>2</sub> 5.201 mol (0.00 vol.%)       outlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)		reactor state	Fe	75.00 mol	
Reduction with CO, T = 800 °C       Fe <sub>0.04</sub> to Fe <sub>0.047</sub> O stage     inlet gas     CO     27.31 (100.00 vol.%)       outlet gas     CO     6.51 mol (23.84 vol.%)     CO       CO     20.80 mol (76.16 vol.%)     CO     6.51 mol (23.84 vol.%)       Fe <sub>0.047</sub> O to Fe stage     reactor state     Fe <sub>0.047</sub> O     79.20 mol       reactor state     Fe <sub>0.047</sub> O     248.90 mol (100.00 vol.%)     0utlet gas     CO     169.70 mol (68.18 vol.%)       outlet gas     CO     169.70 mol (68.18 vol.%)     79.20 mol     18.92 vol.%)       reactor state     Fe     75 mol     75.00 mol     18.92 vol.%)       Total amount of pure CO consumed     CH <sub>4</sub> 5.202 mol (100.00 vol.%)     01.00 vol.%)     01.00 vol.%)     01.00 vol.%)     10.00 vol.%)	Total amount of pure H <sub>2</sub> consumed			297.19 mol	
Fe <sub>0.947</sub> O stage     inlet gas     CO     27.31 (100.00 vol.%)       outlet gas     CO     6.51 mol (23.84 vol.%)     CO2     20.80 mol (76.16 vol.%)       CO2     20.80 mol (76.16 vol.%)     CO2     20.80 mol (76.16 vol.%)       reactor state     Fe <sub>0.947</sub> O     79.20 mol     79.20 mol       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     248.90 mol (100.00 vol.%)       outlet gas     CO     169.70 mol (68.18 vol.%)       reactor state     Fe     75 mol       Total amount of pure CO consumed     276.21 mol     276.21 mol       Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage     inlet gas     CH <sub>4</sub> 5.202 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 5.202 mol (100.00 vol.%)     200 mol (66.66 vol.%)       Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O to Fe stage     inlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)       CO <sub>2</sub> 5.200 mol (33.33 vol.%)     10.40 mol (66.66 vol.%)     10.40 mol (66.66 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CH <sub>4</sub> 67.66 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 67.66 mol (100.00 vol.%)     10.40 mol (66.66 vol.%)       Fe <sub>0.947</sub> O t		Reduction with	CO, T = 800 °C		
outlet gas     CO     6.51 mol (23.84 vol.%)       CO2     20.80 mol (76.16 vol.%)       Pea.947O to Fe stage     inlet gas     CO     248.90 mol (100.00 vol.%)       outlet gas     CO     248.90 mol (100.00 vol.%)     0       outlet gas     CO     169.70 mol (68.18 vol.%)     0       coulet gas     CO     169.70 mol (68.18 vol.%)     0       reactor state     Fe     75 mol     0       Total amount of pure CO consumed     276.21 mol     276.21 mol       Fe3.04 to Fe9.947 O stage     inlet gas     CH4     5.002 mol (00.00 vol.%)       outlet gas     CH4     0.002 mol (00.01 vol.%)     0       co2     5.20 mol (33.33 vol.%)     10.40 mol (66.66 vol.%)     10.40 mol (66.66 vol.%)       Fe9.947 O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       co1     reactor state     Fe9.947 O     79.20 mol       Fe9.947 O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       co1     inlet gas     CH4     67.66 mol (100.00 vol.%)       co2     19.80 mol (18.46 vol.%)     20.40 mol (	Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage	inlet gas	СО	27.31 (100.00 vol.%)	
CO2     20.80 mol (76.16 vol.%)       reactor state     Fe <sub>0.947</sub> O     79.20 mol       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     248.90 mol (100.00 vol.%)       outlet gas     CO     169.70 mol (68.18 vol.%)     CO       CO2     79.20 mol (31.82 vol.%)     CO     169.70 mol (68.18 vol.%)       reactor state     Fe     75 mol     75 mol       Total amount of pure CO consumed     276.21 mol     276.21 mol       Feo_047 O stage     inlet gas     CH <sub>4</sub> 5.202 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)     0010 mol (66.66 vol.%)       Feo_047 O to Fe stage     inlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)       Feo_047 O to Fe stage     inlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)       Feo_047 O to Fe stage     inlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)       Feo_047 O to Fe stage     inlet gas     CH <sub>4</sub> 79.20 mol       Feo_047 O to Fe stage     inlet gas     CH <sub>4</sub> 79.20 mol       O tot fe gas     CH <sub>4</sub> 47.86 mol (44.62 vol.%)     CO <sub>2</sub> 19.80 mol (18.46 vol.%)		outlet gas	СО	6.51 mol (23.84 vol.%)	
reactor state     Fe <sub>0.947</sub> O     79.20 mol       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     248.90 mol (100.00 vol.%)       outlet gas     CO     169.70 mol (68.18 vol.%)       CO2     79.20 mol (31.82 vol.%)       reactor state     Fe     75 mol       Total amount of pure CO consumed     Fe     75 mol       Feq.04 to Fe <sub>0.947</sub> O stage     inlet gas     CH4     5.202 mol (100.00 vol.%)       outlet gas     CH4     0.002 mol (0.01 vol.%)     0001 mol (66.66 vol.%)       Feo_047O to Fe stage     inlet gas     CH4     0.002 mol (0.01 vol.%)       Feo_047O to Fe stage     inlet gas     CH4     0.002 mol (0.01 vol.%)       Feo_047O to Fe stage     inlet gas     CH4     0.002 mol (0.01 vol.%)       Feo_047O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       outlet gas     CH4     67.66 mol (100.00 vol.%)     CO2     19.80 mol (18.46 vol.%)       Feo_047O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)     CH4     67.66 mol (100.00 vol.%)     CO2     19.80 mol (18.46 vol.%)     19.00     19.60 mol (36.92 vol.%)			$CO_2$	20.80 mol (76.16 vol.%)	
Fe <sub>0.947</sub> O to Fe stage     inlet gas     CO     248.90 mol (100.00 vol.%)       outlet gas     CO     169.70 mol (68.18 vol.%)       CO2     79.20 mol (31.82 vol.%)       reactor state     Fe     75 mol       Total amount of pure CO consumed     276.21 mol       Reduction with CH4, T = 800 °C       Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage     inlet gas     CH4     5.202 mol (100.00 vol.%)       outlet gas     CH4     0.002 mol (0.01 vol.%)     0002 mol (0.01 vol.%)       outlet gas     CH4     0.002 mol (0.01 vol.%)     0002 mol (0.01 vol.%)       reactor state     Fe <sub>0.947</sub> O     5.202 mol (0.00 vol.%)     0002 mol (0.01 vol.%)       feo_0sar,O to Fe stage     inlet gas     CH4     0.002 mol (0.01 vol.%)       feo_0sar,O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       outlet gas     CH4     47.86 mol (44.62 vol.%)     0002 mol (18.46 vol.%)       outlet gas     CH4     47.86 mol (44.62 vol.%)     10.40 mol (66.69 vol.%)       feo_0sar,O to Fe stage     inlet gas     CH4     47.86 mol (44.62 vol.%)       fo0     19.80 mol (18.46 vo		reactor state	Fe <sub>0.947</sub> O	79.20 mol	
outlet gas     CO     169.70 mol (68.18 vol.%)       CO2     79.20 mol (31.82 vol.%)       CO2     79.20 mol (31.82 vol.%)       reactor state     Fe     75 mol       Total amount of pure CO consumed     276.21 mol       Reduction with CH4, T = 800 °C     276.21 mol       Fe30, to Fe0.347O stage     inlet gas     CH4     5.202 mol (100.00 vol.%)       outlet gas     CH4     0.002 mol (0.01 vol.%)     0002 mol (0.01 vol.%)       reactor state     Fe0.347O     5.202 mol (33.33 vol.%)     10.400 mol (66.66 vol.%)       Fe0.347O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       coullet gas     CH4     47.86 mol (44.62 vol.%)     10.400 mol (66.66 vol.%)       Fe0.347O to Fe stage     inlet gas     CH4     47.86 mol (44.62 vol.%)     10.400 mol (66.66 vol.%)       coullet gas     CH4     47.86 mol (44.62 vol.%)     10.400 mol (66.900 mol)     10.400 mol (66.900 mol)       fe0     19.800 mol (18.46 vol.%)     19.800 mol (18.46 vol.%)     19.800 mol (18.46 vol.%)     19.800 mol (18.46 vol.%)       fe1     Fe2     75.00 mol     19.800 mol (36.92 vol.%)     19.800 mol	Fe <sub>0.947</sub> O to Fe stage	inlet gas	CO	248.90 mol (100.00 vol.%)	
CO2     79.20 mol (31.82 vol.%)       reactor state     Fe     75 mol       Total amount of pure CO consumed     276.21 mol       Reduction with CH4, T = 800 °C     276.21 mol       Fe3.04 to Fe0.947 O stage     inlet gas     CH4     5.202 mol (100.00 vol.%)       Outlet gas     CH4     0.002 mol (0.01 vol.%)     000 mol (66.66 vol.%)       Fe0.947 O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       Fe0.947 O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       O tot Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       O tot Fe stage     inlet gas     CH4     47.86 mol (44.62 vol.%)       O tot fe stage     inlet gas     CH4     47.86 mol (44.62 vol.%)       O tot fe stage     inlet gas     CH4     47.86 mol (44.62 vol.%)       O tot fe stage     inlet gas     CH4     93.00 mol (36.92 vol.%)       Fea.04     Fea.04     Fea.04     93.00 mol (36.92 vol.%)       Fea.04     Fea.04     Fea.04     Fea.04		outlet gas	СО	169.70 mol (68.18 vol.%)	
reactor state     Fe     75 mol       Total amount of pure CO consumed     276.21 mol       Reduction with CH4, T = 800 °C       Fe3O4 to Fe0.947O stage     inlet gas     CH4     5.202 mol (100.00 vol.%)       outlet gas     CH4     0.002 mol (0.01 vol.%)     CO2     5.20 mol (33.33 vol.%)       Fe0.947 O to Fe stage     inlet gas     CH4     0.400 mol (66.66 vol.%)       Fe0.947 O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       outlet gas     CH4     67.66 mol (100.00 vol.%)     CO2       Fe0.947 O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       outlet gas     CH4     47.86 mol (44.62 vol.%)     CO2     19.80 mol (18.46 vol.%)       e0.947 O to Fe stage     inlet gas     CH4     47.86 mol (44.62 vol.%)     CO2     19.80 mol (18.46 vol.%)     CO2     19.80 mol (18.46 vol.%)     CO2     19.80 mol (36.92 vol.%)     CO3     19.80 mol (36.92 vol.%)			$CO_2$	79.20 mol (31.82 vol.%)	
Total amount of pure CO consumed     276.21 mol       Reduction with CH4, T = 800 °C       Fe3O4 to Fe0.947O stage     inlet gas     CH4     5.202 mol (100.00 vol.%)       outlet gas     CH4     0.002 mol (0.01 vol.%)     CO2     5.200 mol (33.33 vol.%)       H2O     10.40 mol (66.66 vol.%)     H2O     10.40 mol (66.66 vol.%)       Fe0.947O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       Outlet gas     CH4     67.66 mol (100.00 vol.%)     CO2       Fe0.947O to Fe stage     inlet gas     CH4     67.66 mol (100.00 vol.%)       Outlet gas     CH4     47.86 mol (44.62 vol.%)     CO2     19.80 mol (18.46 vol.%)       Pre.20     H2O     19.80 mol (18.46 vol.%)     H2O     19.80 mol (36.92 vol.%)		reactor state	Fe	75 mol	
Reduction with $CH_4$ , T = 800 °C       Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage     inlet gas     CH <sub>4</sub> 5.202 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 0.002 mol (0.01 vol.%)     CO <sub>2</sub> 5.20 mol (33.33 vol.%)       H <sub>2</sub> O     10.40 mol (66.66 vol.%)     H <sub>2</sub> O     10.40 mol (66.66 vol.%)       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CH <sub>4</sub> 67.66 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 47.86 mol (44.62 vol.%)     CO <sub>2</sub> 19.80 mol (18.46 vol.%)       H <sub>2</sub> O     39.60 mol (36.92 vol.%)     H <sub>2</sub> O     39.60 mol (36.92 vol.%)     CO <sub>2</sub>	Total amount of pure CO consumed			276.21 mol	
Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage   inlet gas   CH <sub>4</sub> 5.202 mol (100.00 vol.%)     outlet gas   CH <sub>4</sub> 0.002 mol (0.01 vol.%)     CO <sub>2</sub> 5.20 mol (33.33 vol.%)     H <sub>2</sub> O   10.40 mol (66.66 vol.%)     reactor state   Fe <sub>0.947</sub> O     Fe <sub>0.947</sub> O to Fe stage   inlet gas     Outlet gas   CH <sub>4</sub> Outlet gas   CO <sub>2</sub> Pa0   19.80 mol (18.46 vol.%)     H <sub>2</sub> O   39.60 mol (36.92 vol.%)     H <sub>2</sub> O   75.00 mol		Reduction with C	$CH_4, T = 800 \ ^{\circ}C$		
outlet gas     CH4     0.002 mol (0.01 vol.%)       CO2     5.20 mol (33.33 vol.%)       H2O     10.40 mol (66.66 vol.%)       reactor state     Fe0.947       Fe0.947     CH4       Oto Fe stage     inlet gas       Otutlet gas     CH4       Oto Fe stage     inlet gas       Otutlet gas     CH4       Otutlet gas     CO2       H2O     39.60 mol (36.92 vol.%)       H2O     39.60 mol (36.92 vol.%)       Feactor state     Fe     75.00 mol	Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage	inlet gas	$CH_4$	5.202 mol (100.00 vol.%)	
CO2     5.20 mol (33.33 vol.%)       H2O     10.40 mol (66.66 vol.%)       reactor state     Fe0.947O       Fe0.947O to Fe stage     inlet gas       Ottlet gas     CH4       CO2     19.80 mol (18.46 vol.%)       CO2     19.80 mol (18.46 vol.%)       H2O     39.60 mol (36.92 vol.%)       Fe0.947O to Fe stage     Fe		outlet gas	$\mathrm{CH}_4$	0.002 mol (0.01 vol.%)	
H2O   10.40 mol (66.66 vol.%)     reactor state   Fe0.947O     Fe0.947O to Fe stage   inlet gas     Outlet gas   CH4     Outlet gas   CH4     CO2   19.80 mol (44.62 vol.%)     H2O   19.80 mol (36.92 vol.%)     Fe0.947O to Fe stage   Fe     75.00 mol   75.00 mol			$CO_2$	5.20 mol (33.33 vol.%)	
reactor state     Fe <sub>0.947</sub> O     79.20 mol       Fe <sub>0.947</sub> O to Fe stage     inlet gas     CH <sub>4</sub> 67.66 mol (100.00 vol.%)       outlet gas     CH <sub>4</sub> 47.86 mol (44.62 vol.%)       CO <sub>2</sub> 19.80 mol (18.46 vol.%)       H <sub>2</sub> O     39.60 mol (36.92 vol.%)       reactor state     Fe     75.00 mol			$H_2O$	10.40 mol (66.66 vol.%)	
Fe <sub>0.947</sub> O to Fe stage   inlet gas   CH <sub>4</sub> 67.66 mol (100.00 vol.%)     outlet gas   CH <sub>4</sub> 47.86 mol (44.62 vol.%)     CO <sub>2</sub> 19.80 mol (18.46 vol.%)     H <sub>2</sub> O   39.60 mol (36.92 vol.%)     reactor state   Fe   75.00 mol		reactor state	Fe <sub>0.947</sub> O	79.20 mol	
outlet gas CH <sub>4</sub> 47.86 mol (44.62 vol.%)   CO <sub>2</sub> 19.80 mol (18.46 vol.%)   H <sub>2</sub> O 39.60 mol (36.92 vol.%)   reactor state Fe 75.00 mol	$Fe_{0.947}O$ to Fe stage	inlet gas	$CH_4$	67.66 mol (100.00 vol.%)	
CO2     19.80 mol (18.46 vol.%)       H2O     39.60 mol (36.92 vol.%)       reactor state     Fe     75.00 mol		outlet gas	$CH_4$	47.86 mol (44.62 vol.%)	
H2O     39.60 mol (36.92 vol.%)       reactor state     Fe     75.00 mol			$CO_2$	19.80 mol (18.46 vol.%)	
reactor state Fe 75.00 mol			$H_2O$	39.60 mol (36.92 vol.%)	
		reactor state	Fe	75.00 mol	
Total amount of pure $CH_4$ consumed 72.87 mol	Total amount of pure CH4 consumed			72.87 mol	

consists of 100 mol of  $H_2$  (96.23 vol.%) and 3.92 mol of  $H_2O$  (3.77 vol.%). During the oxidation stage 25 mol of  $Fe_3O_4$  is created. Table 1 summarizes the Fe reactor performance.

#### Reduction with hydrogen in iron based loop

In the first stage, 25 mol of  $Fe_3O_4$  is reduced to wustite. The amount of  $Fe_{0.947}O$  produced is 79.20 mol. The amount of hydrogen consumed is 28.08 mol. The composition of product gaseous mixture is:  $H_2O$ : 20.80 mol (74.07 vol.%) and  $H_2$ : 7.28 mol (25.93 vol.%). In the following step wustite is reduced to iron. The amount of iron produced is 75.00 mol, the amount of hydrogen consumed is 269.11 mol, and the composition of gas produced is:  $H_2O$ : 79.20 (29.43 vol.%) and  $H_2$ : 189.91 mol (70.57 vol.%).

#### Reduction with carbon monoxide in iron based loop

25 mol of Fe<sub>3</sub>O<sub>4</sub> is reduced to 79.20 mol of wustite with 27.31 mol of CO. The composition of the product gas is 20.80 mol (76.16 vol.%) of CO<sub>2</sub> and 6.51 mol (23.84 vol.%) of CO. Next, 79.20 mol of wustite is reduced to 75.00 mol of Fe with 248.90 mol of CO, and the resulting composition of the product gas is 79.20 mol (31.82 vol.%) of CO<sub>2</sub> and 169.70 mol (68.18 vol.%) of CO.

#### Reduction with methane in iron based loop

The reaction of 1 mol of methane with iron oxide creates 2 mol of  $H_2O$  and 1 mol of  $CO_2$ . Thus, the fraction of  $CH_4$  consumed during the reaction is correlated to the fraction of  $CH_4$  in an equilibrium gas according to the following equation:

$$X_{CH_{4}consumed} = \frac{(X_{H_{2}O} + X_{CO_{2}})/3}{X_{CH_{4}} + (X_{H_{2}O} + X_{CO_{2}})/3} = (8)$$
$$= \frac{(1 - X_{CH_{4}})/3}{X_{CH_{4}} + (1 - X_{CH_{4}})/3} = \frac{1 - X_{CH_{4}}}{1 + 2X_{CH_{4}}}$$

The calculation presented below is made for the pressure of 1 MPa. 25 mol of Fe<sub>3</sub>O<sub>4</sub> is reduced to 79.20 mol of wustite. The amount of CH<sub>4</sub> consumed is:  $\frac{25}{4.807} / \frac{1 - 0.0001}{1 + 2 \times 0.0001} = 5.202 \text{ mol. The gas produced is}$ composed of 0.01 mol of CH<sub>4</sub> (0.01 vol.%), 5.20 mol of CO<sub>2</sub> (33.33 vol.%) and 10.40 mol of H<sub>2</sub>O (66.66 vol.%). 79.20 mol of wustite is reduced to 75 mol of iron and the amount of CH<sub>4</sub> consumed is 68.40 mol. The resulting gas is composed of 47.86 mol of CH<sub>4</sub> (44.62 vol.%), 19.80 mol of CO<sub>2</sub> (18.46 vol.%) and 39.60 mol of H<sub>2</sub>O (36.92 vol.%).

Iron and germanium based double loop

Iron and germanium reactor with the capacity of 100 mol of  $H_2$  contains 37.5 mol of Fe and 25 mol of Ge. Hydrogen is generated by blowing Fe bed with steam, and subsequently by blowing Ge bed with produced  $H_2/H_2O$  stream. Hydrogen is generated at the temperature of 300 °C and the reduction reaction is performed at 800 °C. In case of methane, the pressure of 1 MPa is considered. The schematic diagram of Fe-Ge reactor performance is presented in Figure 4. Tables 2 and 3 summarize the Fe-Ge reactor performance.

#### Hydrogen production in iron and germanium double loop

37.5 mol of Fe is blown with 100.28 mol of  $H_2O$  to generate 12.5 mol of Fe<sub>3</sub>O<sub>4</sub>. The product gas is composed of 50 mol of  $H_2$  and 50.28 mol of  $H_2O$  (the reaction is limited by the availability of Fe). This gaseous mixture reacts with 25 mol of Ge which results in 25 mol of GeO<sub>2</sub> produced. The outlet gas is composed of 100 mol of  $H_2$  and 0.28 mol of  $H_2O$ .

#### Reduction with hydrogen in iron and germanium double loop

Magnetite is reduced with pure hydrogen to wustite and then to pure iron. The process is performed as described in Reduction with hydrogen in iron based loop sub-section. The compositions of the gas mixtures applied are similar, but the quantities are halved. The outlet gas from the  $Fe_3O_4/Fe_{0.947}O$  stage is vented. GeO<sub>2</sub> is reduced with the outlet gas from the Fe<sub>0.947</sub>O stage and some additional amount of hydrogen. The Fe<sub>0.947</sub>O/Fe process gas contains  $39.60 \text{ mol} (29.43 \text{ vol.}\%) \text{ of } H_2O \text{ and } 94.96 \text{ mol} (70.57 \text{ vol.}\%)$ of  $H_2$ , which is not sufficient to reduce 25 mol of  $GeO_2$ . The outlet gas from Ge reactor should contain 89.60 mol of H<sub>2</sub>O (50 mol produced in GeO<sub>2</sub> reduction). The outlet gas will also contain 71.00 mol of H<sub>2</sub> (44.21 vol.%). The inlet gas composition would be 121.00 mol (75.34 vol.%) of H<sub>2</sub> and 39.60 mol (24.66 vol.%) of H<sub>2</sub>O and the extra amount of  $H_2$  is 26.04 mol.

# Reduction with carbon monoxide in iron and germanium double loop

Magnetite is reduced with pure CO to wustite and then to pure iron in the process described in Reduction with carbon monoxide in iron based loop sub-section.

## Hydrogen production, T=300 °C



Reduction, 1<sup>st</sup> stage, T=800 °C



Figure 4. Schematic diagram of Fe-Ge reactor performance.

Table 2. The Fe-Ge reactor	performance, hydro	ogen production
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Fe-Ge	reactor; capacity of 100.00 mol of H <sub>2</sub> , contain	ning 37.50 mol of Fe and 25	.00 mol of Ge
	Hydrogen production / oxidation	on stage; T = 300 °C	
Fe reactor	inlet gas	$H_2O$	100.28 mol (100.00 vol.%)
	outlet gas/Ge reactor inlet gas	$H_2$	50.00 mol (49.86 vol.%)
		$H_2O$	50.28 mol (50.14 vol.%)
	reactor state		12.50 mol of $Fe_3O_4$
Ge reactor	outlet gas	$H_2$	100.00 mol (99.72 vol.%)
		$H_2O$	0.28 mol (0.28 vol.%)
	reactor state	$GeO_2$	25.00 mol
	Reduction with H <sub>2</sub> , 7	Γ = 800 °C	
$Fe_3O_4$ to $Fe_{0.947}O$ stage	inlet gas	$H_2$	14.04 mol (100.00 vol.%)
	outlet gas	$H_2$	3.64 mol (25.93 vol.%)
		$H_2O$	10.40 mol (74.07 vol.%)
	reactor state	Fe <sub>0.947</sub> O	39.60 mol
$Fe_{0.947}O$ to Fe stage	inlet gas	$H_2$	134.56 mol (100.00 vol.%)
	outlet gas	$H_2$	94.96 mol (70.57 vol.%)
		$H_2O$	39.60 (29.43 vol.%)
	reactor state	Fe	37.50 mol
Ge reactor	inlet gas	$H_2$	121.00 mol (75.34 vol.%)
GeO <sub>2</sub> to Ge		$H_2O$	39.60 mol (24.66 vol.%)
	outlet gas	$H_2$	71.00 mol (44.21 vol.%)
		$H_2O$	89.60 mol (55.79 vol.%)
	reactor state	Ge	25.00 mol
Total amount of pure H <sub>2</sub> consumed			174.64 mol

Table 3. The Fe-Ge rector	performance,	reduction	with methane
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Fe-Ge re	eactor; capacity of 100.00 mol of H <sub>2</sub> , contain	ning 37.50 mol of Fe and 25	.00 mol of Ge
	Reduction with CO,	T = 800 °C	
$Fe_3O_4$ to $Fe_{0.947}O$ stage	inlet gas	СО	13.64 mol (100.00 vol.%)
	outlet gas	СО	3.25 mol (23.83 vol.%)
		$CO_2$	10.39 mol (76.17 vol.%)
	reactor state	Fe <sub>0.947</sub> O	39.10 mol
$Fe_{0.947}O$ to Fe stage	inlet gas	СО	123.95 mol (100.00 vol.%)
	outlet gas	СО	84.85 mol (68.46 vol.%)
		$CO_2$	39.10 mol (31.54 vol.%)
	reactor state	Fe	37.50 mol
Ge reactor	inlet gas	СО	115.12 mol (74.41 vol.%)
GeO <sub>2</sub> to Ge		$CO_2$	39.52 mol (25.59 vol.%)
	outlet gas	СО	65.12 mol (42.09 vol.%)
		$CO_2$	89.60 mol (57.91 vol.%)
	reactor state	Ge	25.00 mol
Total amount of pure CO consumed			168.37 mol
	Reduction with CH <sub>4</sub> ,	T = 800 °C	
Fe reactor	inlet gas	$CH_4$	2.61 mol (100 vol.%)
Fe <sub>3</sub> O <sub>4</sub> to Fe <sub>0.947</sub> O stage	outlet gas	$CH_4$	0.01 mol (0.13 vol.%)
		$CO_2$	2.60 mol (33.29 vol.%)
		$H_2O$	5.20 mol (66.58 vol.%)
	reactor state	Fe <sub>0.947</sub> O	39.60 mol
Fe reactor	inlet gas	$CH_4$	33.53 mol (100 vol.%)
Fe <sub>0.947</sub> O to Fe stage	outlet gas/Ge reactor inlet gas	$CH_4$	23.93 mol (44.62 vol.%)
		$CO_2$	9.90 mol (18.46 vol.%)
		$H_2O$	19.80 mol (36.92 vol.%)
	reactor state	Fe	37.50 mol
Ge reactor	outlet gas	$CH_4$	11.40 mol (14.50 vol.%)
GeO <sub>2</sub> to Ge stage		$CO_2$	22.40 mol (28.50 vol.%)
		$H_2O$	44.80 mol (57.00 vol.%)
	reactor state	Ge	25.00 mol
Total amount of pure CH <sub>4</sub> consumed			36.43 mol

The composition of gaseous reactants applied are similar, while their quantities are halved. The Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>0.947</sub>O stage outlet gas is vented. GeO<sub>2</sub> is reduced with the outlet gas from the Fe<sub>0.947</sub>O stage and some additional amount of CO. The Fe<sub>0.947</sub>O/Fe process outlet gas contains 84.85 mol (68.46 vol.%) of CO and 39.10 mol (31.54 vol.%) of CO<sub>2</sub>. The amount of CO is too low for the reduction of 25 mol of GeO<sub>2</sub>. The outlet gas from Ge reactor would contain 89.60 mol of CO<sub>2</sub> (50 mol produced in GeO<sub>2</sub> reduction) and 65.12 mol (42.09 vol.%) of CO. The inlet gas composition should be as follows: 115.12 mol (74.41 vol.%) of CO and 39.60 mol (25.59 vol.%) of CO<sub>2</sub> and the amount of extra CO is 30.27 mol.

#### Reduction with methane in iron and germanium double loop

Magnetite is reduced with pure  $CH_4$  to wustite and then to pure iron in the process described in Reduction with methane in iron based loop sub-section. The composition of gases employed are similar and their amounts are halved. The Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>0.947</sub>O stage outlet gas is vented. GeO<sub>2</sub> is reduced with the outlet gas from the Fe<sub>0.947</sub>O stage. The Fe<sub>0.947</sub>O/Fe process outlet gas contains 23.93 mol of CH<sub>4</sub> (44.62 vol.%), 9.90 mol of CO<sub>2</sub> (18.46 vol.%) and 19.80 mol of H<sub>2</sub>O (36.92 vol.%). The amount of CH<sub>4</sub> is sufficient to reduce 25 mol of GeO<sub>2</sub>. The Ge reactor outlet gas would contain 22.40 mol of CO<sub>2</sub>, 44.80 mol of H<sub>2</sub>O (12.5 mol of CO<sub>2</sub> and 25 mol of H<sub>2</sub>O are produced in GeO<sub>2</sub> reduction) and 11.4 mol of CH<sub>4</sub> (12.5 mol of CH<sub>4</sub> is consumed). The methane content in gas is still higher than in the equilibrium atmosphere. The percentage composition of the outlet gas is: 14.50 vol.% of CH<sub>4</sub>, 28.50 vol.% of CO<sub>2</sub> and 57.00 vol.% of H<sub>2</sub>O.

## Conclusions

The LTSI process may be applied in hydrogen production and storage. The thermodynamic calculations

show that the reducing stage of the process may be problematic, since the reaction achieves equilibrium state when there is still a large fraction of the reducing gas (hydrogen, carbon monoxide or methane) present in the reaction atmosphere. The computations presented also indicate that the combination of iron and germanium loops may be an interesting option for the steam-iron process in a solid phase at temperatures below 1000 °C. In such a double cycle, the outlet gas contains a significantly smaller fraction of the reducing gas, since smaller quantity of the reducing gas needs to be used. For the double Fe-Ge loop a decrease of approximately 58.76, 60.96 and 49.99% for the reducing gases like  $H_2$ , CO and  $CH_4$  is reported, respectively.

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