http://dx.doi.org/10.21577/0103-5053.20160267

J. Braz. Chem. Soc., Vol. 28, No. 6, 1098-1105, 2017.
Printed in Brazil - ©2017 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

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.[1,2] Iron and iron oxides may be potentially applied in the process of hydrogen production and storage, respectively.[3-6] The main steps of the process may be presented as follows:

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

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 19th 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.[7] 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.[8]

Another technological option presented in the literature[9] 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):

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

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

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

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[9-13] is the deterioration of iron bed performance, resulting from sintering, carbon deposition and Fe_3C 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.[11,14-17] 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_2, syngas).[18] 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_3C formation, etc.[18] 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_3O_4 and Ge-GeO_2 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.[18] 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_3O_4 loop with Ge-GeO_2 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_2 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.

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

Figure 1 shows the phase stability diagram for such a system. As it can be seen from Figure 1, temperatures below 600 °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 °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:

$$0.5GeO_2 + CO = 0.5Ge + CO_2 \quad (6)$$

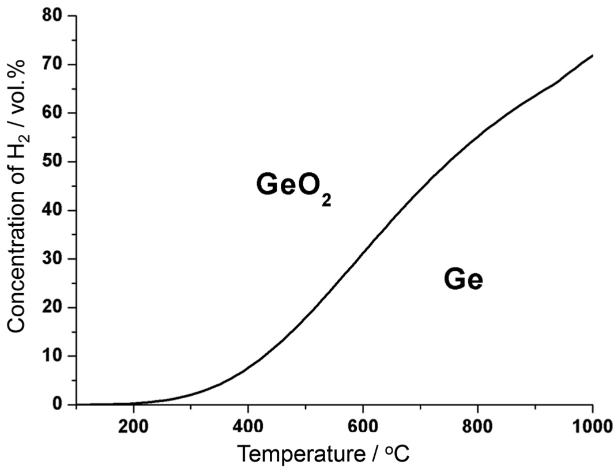

Figure 1. The phase stability diagram of Ge and GeO_2 phases in the H_2O-H_2 atmosphere.

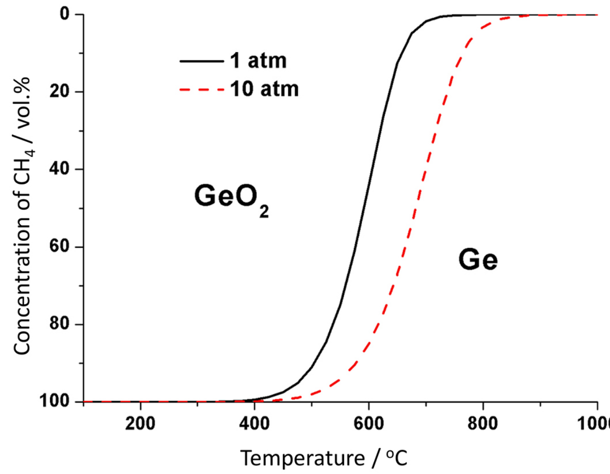

Figure 3. The phase stability diagram of Ge and GeO_2 in the CH_4 atmosphere.

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 GeO_2 reduction with carbon monoxide.

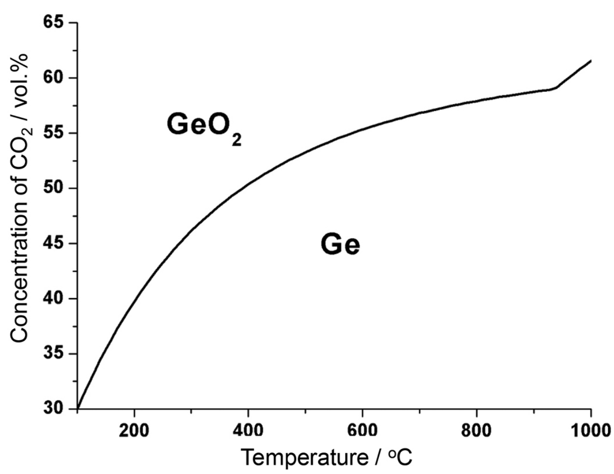

Figure 2. The phase stability diagram of Ge and GeO_2 in the CO_2-CO atmosphere.

Germanium dioxide reduction with methane

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

$$2GeO_2 + CH_4 = 2Ge + CO_2 + 2H_2O \quad (7)$$

The phase stability diagram of Ge and GeO_2 in CH_4, CO_2 and H_2O 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 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[4,6,18] 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_3C 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_3O_4 loop and the double Fe-Fe_3O_4 Ge-GeO_2 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 considered. The hydrogen production process is assumed to be performed at 300 °C, and the reduction at 800 °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

Table 1. Fe reactor performance

Fe reactor; the capacity of 100 mol of H_2, containing 75 mol of Fe			
Hydrogen production / oxidation stage; T = 300 °C			
	inlet gas	H_2O	103.92 mol (100.00 vol.%)
	outlet gas	H_2	100.00 mol (96.23 vol.%)
		H_2O	3.92 mol (3.77 vol.%)
	reactor state		25.00 mol of Fe_3O_4
Reduction with H_2, T = 800 °C			
Fe_3O_4 to $Fe_{0.947}O$ stage	inlet gas	H_2	28.08 mol (100.00 vol.%)
	outlet gas	H_2	7.28 mol (25.93 vol.%)
		H_2O	20.80 mol (74.07 vol.%)
	reactor state	$Fe_{0.947}O$	79.20 mol
$Fe_{0.947}O$ to Fe stage	inlet gas	H_2	269.11 mol (100.00 vol.%)
	outlet gas	H_2	189.91 mol (70.57 vol.%)
		H_2O	79.20 (29.43 vol.%)
	reactor state	Fe	75.00 mol
Total amount of pure H_2 consumed			297.19 mol
Reduction with CO, T = 800 °C			
Fe_3O_4 to $Fe_{0.947}O$ stage	inlet gas	CO	27.31 (100.00 vol.%)
	outlet gas	CO	6.51 mol (23.84 vol.%)
		CO_2	20.80 mol (76.16 vol.%)
	reactor state	$Fe_{0.947}O$	79.20 mol
$Fe_{0.947}O$ to Fe stage	inlet gas	CO	248.90 mol (100.00 vol.%)
	outlet gas	CO	169.70 mol (68.18 vol.%)
		CO_2	79.20 mol (31.82 vol.%)
	reactor state	Fe	75 mol
Total amount of pure CO consumed			276.21 mol
Reduction with CH_4, T = 800 °C			
Fe_3O_4 to $Fe_{0.947}O$ stage	inlet gas	CH_4	5.202 mol (100.00 vol.%)
	outlet gas	CH_4	0.002 mol (0.01 vol.%)
		CO_2	5.20 mol (33.33 vol.%)
		H_2O	10.40 mol (66.66 vol.%)
	reactor state	$Fe_{0.947}O$	79.20 mol
$Fe_{0.947}O$ to Fe stage	inlet gas	CH_4	67.66 mol (100.00 vol.%)
	outlet gas	CH_4	47.86 mol (44.62 vol.%)
		CO_2	19.80 mol (18.46 vol.%)
		H_2O	39.60 mol (36.92 vol.%)
	reactor state	Fe	75.00 mol
Total amount of pure CH_4 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_3O_4 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_2 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_2 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:

$$X_{CH_4 consumed} = \frac{(X_{H_2O} + X_{CO_2})/3}{X_{CH_4} + (X_{H_2O} + X_{CO_2})/3} = \frac{(1 - X_{CH_4})/3}{X_{CH_4} + (1 - X_{CH_4})/3} = \frac{1 - X_{CH_4}}{1 + 2X_{CH_4}} \quad (8)$$

The calculation presented below is made for the pressure of 1 MPa. 25 mol of Fe_3O_4 is reduced to 79.20 mol of wustite. The amount of CH_4 consumed is: $\frac{25}{4.807} / \frac{1 - 0.0001}{1 + 2 \times 0.0001} = 5.202$ mol. The gas produced is composed of 0.01 mol of CH_4 (0.01 vol.%), 5.20 mol of CO_2 (33.33 vol.%) and 10.40 mol of H_2O (66.66 vol.%). 79.20 mol of wustite is reduced to 75 mol of iron and the amount of CH_4 consumed is 68.40 mol. The resulting gas is composed of 47.86 mol of CH_4 (44.62 vol.%), 19.80 mol of CO_2 (18.46 vol.%) and 39.60 mol of H_2O (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_3O_4. 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_2 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_2 is reduced with the outlet gas from the $Fe_{0.947}O$ stage and some additional amount of hydrogen. The $Fe_{0.947}O$/Fe process gas contains 39.60 mol (29.43 vol.%) of H_2O and 94.96 mol (70.57 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_2O (50 mol produced in GeO_2 reduction). The outlet gas will also contain 71.00 mol of H_2 (44.21 vol.%). The inlet gas composition would be 121.00 mol (75.34 vol.%) of H_2 and 39.60 mol (24.66 vol.%) of H_2O 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.

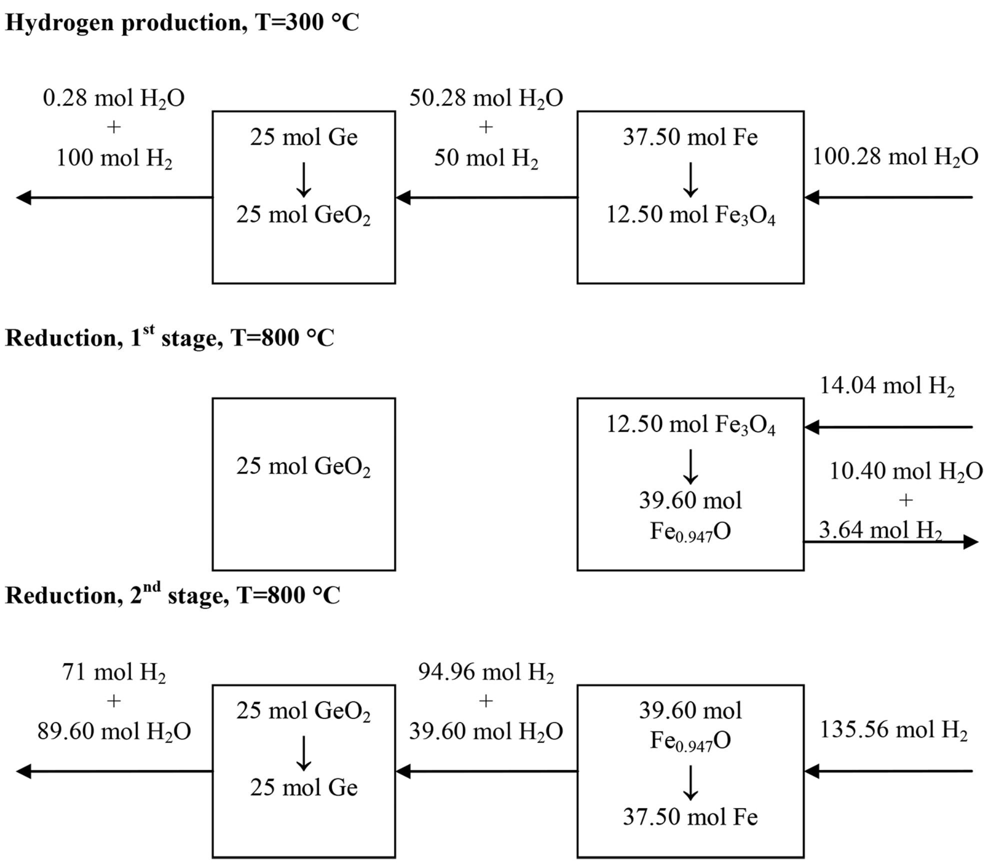

Figure 4. Schematic diagram of Fe-Ge reactor performance.

Table 2. The Fe-Ge reactor performance, hydrogen production

Fe-Ge reactor; capacity of 100.00 mol of H_2, containing 37.50 mol of Fe and 25.00 mol of Ge			
Hydrogen production / oxidation 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_2, T = 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	$Fe_{0.947}O$	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 GeO_2 to Ge	inlet gas	H_2	121.00 mol (75.34 vol.%)
		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_2 consumed			174.64 mol

Table 3. The Fe-Ge rector performance, reduction with methane

Fe-Ge reactor; capacity of 100.00 mol of H_2, containing 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	CO	13.64 mol (100.00 vol.%)
	outlet gas	CO	3.25 mol (23.83 vol.%)
		CO_2	10.39 mol (76.17 vol.%)
	reactor state	$Fe_{0.947}O$	39.10 mol
$Fe_{0.947}O$ to Fe stage	inlet gas	CO	123.95 mol (100.00 vol.%)
	outlet gas	CO	84.85 mol (68.46 vol.%)
		CO_2	39.10 mol (31.54 vol.%)
	reactor state	Fe	37.50 mol
Ge reactor GeO_2 to Ge	inlet gas	CO	115.12 mol (74.41 vol.%)
		CO_2	39.52 mol (25.59 vol.%)
	outlet gas	CO	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_4, T = 800 °C			
Fe reactor Fe_3O_4 to $Fe_{0.947}O$ stage	inlet gas	CH_4	2.61 mol (100 vol.%)
	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	$Fe_{0.947}O$	39.60 mol
Fe reactor $Fe_{0.947}O$ to Fe stage	inlet gas	CH_4	33.53 mol (100 vol.%)
	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 GeO_2 to Ge stage	outlet gas	CH_4	11.40 mol (14.50 vol.%)
		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_4 consumed			36.43 mol

The composition of gaseous reactants applied are similar, while their quantities are halved. The Fe_3O_4/$Fe_{0.947}O$ stage outlet gas is vented. GeO_2 is reduced with the outlet gas from the $Fe_{0.947}O$ stage and some additional amount of CO. The $Fe_{0.947}O$/Fe process outlet gas contains 84.85 mol (68.46 vol.%) of CO and 39.10 mol (31.54 vol.%) of CO_2. The amount of CO is too low for the reduction of 25 mol of GeO_2. The outlet gas from Ge reactor would contain 89.60 mol of CO_2 (50 mol produced in GeO_2 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_2 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_3O_4/$Fe_{0.947}O$ stage outlet gas is vented. GeO_2 is reduced with the outlet gas from the $Fe_{0.947}O$ stage. The $Fe_{0.947}O$/Fe process outlet gas contains 23.93 mol of CH_4 (44.62 vol.%), 9.90 mol of CO_2 (18.46 vol.%) and 19.80 mol of H_2O (36.92 vol.%). The amount of CH_4 is sufficient to reduce 25 mol of GeO_2. The Ge reactor outlet gas would contain 22.40 mol of CO_2, 44.80 mol of H_2O (12.5 mol of CO_2 and 25 mol of H_2O are produced in GeO_2 reduction) and 11.4 mol of CH_4 (12.5 mol of CH_4 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_4, 28.50 vol.% of CO_2 and 57.00 vol.% of H_2O.

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.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education, Poland, under Grant No. 11310046.

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Submitted: July 26, 2016
Published online: September 29, 2016