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Short communication

First investigations of structural changes of the contact mass in the RESC process for hydrogen production

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Abstract

The reformer sponge iron cycle (RESC) process was introduced for the stationary, decentralised production of hydrogen from hydrocarbon-containing fuels. The RESC process consists of two steps: the reformation of higher hydrocarbon to synthesis gas and the fine purification of this gas to pure hydrogen with the sponge iron reaction (SIR) process. The SIR process uses iron ore as contact mass. The contact mass (iron oxide) is reduced to iron in the first cycle by a synthesis gas, and is re-oxidised into iron oxide in the second cycle, utilizing steam. Pure hydrogen is produced in the second cycle as reaction product of the process. Iron ore is a very inexpensive base material for the contact mass, but the contact mass still has to be stable over several thousand redox cycles. Test series with varying contact mass compositions have been performed in order to investigate the influence of the composition on the durability of the contact mass. Carbon monoxide and hydrogen were used for the reduction process. Thermogravimetry (TG), X-ray diffractometry (XRD), scanning electron microscope (SEM) and mercury porosimetry were applied for the evaluation of structural changes after cycling the contact mass. The results confirm the importance of the skeletal structure of the pellets.

Keywords: Hydrogen production; RESC; Sponge iron; Hydrocarbon reforming; Mercury porosimetry

1. Introduction

Hydrogen has attracted the attention of policy makers and industrialists as a possible future energy vector, being able to address at the same time environmental concerns and dependence on foreign energy sources (European Commission, High Level Group on Hydrogen, 2004). This long-term perspective might lead the fossil based energy system to a renewable based energy system with hydrogen as energy carrier. A first step for the introduction of hydrogen is a high efficient production of hydrogen out of fossil fuels, since the change of the infrastructure of the energy supply has to be carefully prepared. Hydrogen is therefore produced on-site, and will be offered not as a substitute, but in addition to the current energy carriers.

The reformer sponge iron cycle (RESC) [1–3] offers an uncomplicated and efficient technique for the production of high purity hydrogen from synthesis gas, natural gas and liquid hydrocarbons [4–6].

The RESC process is a process for stationary, decentralised hydrogen production, that is based on a redox reaction of iron in combination with a hydrocarbon reformer. The process is based on the reduction of a contact mass (iron) by a synthesis gas and the oxidation of the contact mass by steam for the production of hydrogen. Several industrial contact masses were investigated [7,8]. This paper investigates the structural change of the contact mass.

2. Experimental investigations

The substantial components of the iron ore pellets, which have an influence on the lifetime, are Fe_2O_3, Al_2O_3, SiO_2 and CaO [9–13]. In nature, the fraction of iron in the pellets

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Table 1
Composition of laboratory iron ore pellets (mass%)

Fe_2O_3	85	85	85	85	85	88	88	88	88	88
Al_2O_3	5	5	5	5	5	2	2	2	2	2
SiO_2	0	2.5	5	7.5	10	0	2.5	5	7.5	10
CaO	10	7.5	5	2.5	0	10	7.5	5	2.5	0
Sum (mass%)	100	100	100	100	100	100	100	100	100	100

is between 62% and 66%, and the content of Al_2O_3 is about 0.17–2%. The fraction of quartz is between 2% and 7%, and lime is about 0–6%. The laboratory pellets which were prepared for this test series cover the average composition of commercial products. The compositions of the pellets are listed in Table 1.

The laboratory pellets were manufactured by the industrial partner voestalpine Stahl GmbH. The components for each contact mass were homogenized in a mixer. The raw material is rolled in a pelletizing plate to iron ore pellets. The bonding agent is bentonite. Subsequently, the iron ore pellets are calcinated at a temperature of 1100 °C. For the investigations, pellet diameters of 4.0 mm up to 6.3 mm were selected.

The iron ore pellets, which consist at the beginning of the test out of haematite and gangue, are heated up in an inert atmosphere to a temperature of 800 °C. Then the contact mass is repeatedly reduced with hydrogen (or carbon monoxide) and re-oxidized with steam. The switch from oxidation to reduction and back is undertaken when the reaction rates become very low (the reaction rate becomes then limited by diffusion). Mass of the pellets, pellet temperature, furnace temperature, gas temperature and the mass flows are continuously measured and recorded. The reactor is loaded with 100 g iron ore pellets. The flow-rate of hydrogen and carbon monoxide are 200 l h^{-1}, respectively, and the mass flow-rate of water is 200 ml h^{-1}. Samples of the pellets are taken after the first and after the fifth redox cycle.

In Fig. 1, the periodic change of temperatures, mass flows and the change in mass are shown. The change in mass follows a characteristic sawtooth profile during the redox cycles. The pellet temperature raises in the oxidation stage due to the exothermic reaction process. In the endothermic reduction, the temperature decreases. Analyses are done with thermogravimetry (TG), scanning electron microscopy (SEM), X-ray diffractometry (XRD) and mercury porosimetry.

2.1. TG

Thermograms show the mass change of a sample online as function of temperature and time. Precision scales are used for the measurement. The working range of the scales is up to 35 kg, and the accuracy is 0.1 g. The data are recorded online with DASYLab software.

2.2. SEM

The SEM is suitable for the illustration of the topography of solids, since the surface can be displayed directly with high depth sharpness. The surface has to be electroconductive in vacuum. Gold is used for coating (sputter coater SC502F). The photos are made with a JEOL 35 electron microscope.

2.3. XRD

The intensity of the reflected X-rays depends on the material composition. This allows a quantification of the

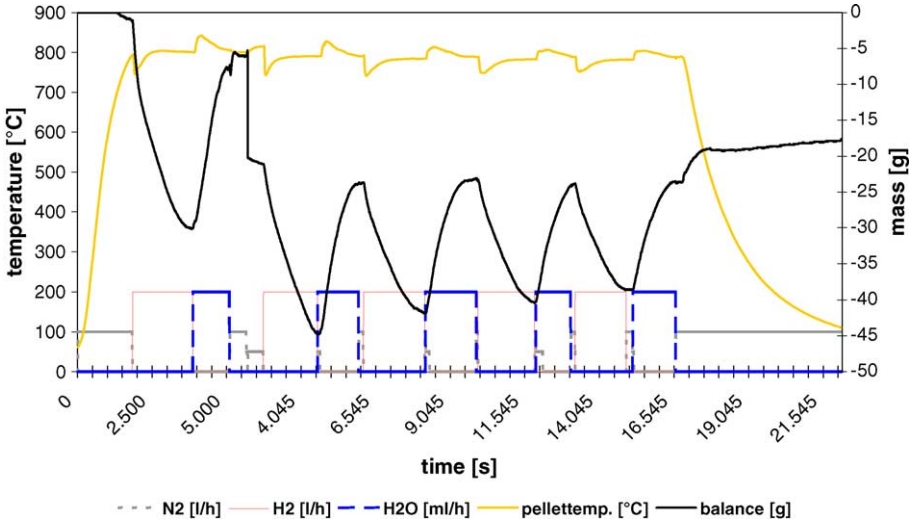

Fig. 1. Measurement of redox cycles with hydrogen: mass and temperature change of pellets, flow of reduction and oxidation gases.

contained components. The radiographic quantification of the redox products takes place with the Rietveld method. The used diffractometer is a Siemens D5005. The adjusted parameters are: generator 40 mA, 30 kV; step width/time: 0.02°/4 s; angle range: 10–90°.

2.4. Hg-porosimetry

The mercury porosimetry supplies information about structural changes of the pellet characteristics. With the Porosimeter PASCAL 140/440, the mercury volume penetrating into the pores of the sample is determined with a capacitive measuring system. The pressure is measured with pressure absorbers.

Although in almost all porous materials no perfectly cylindrical pores exist, the Washburn equation is generally used for the computation of the distribution of pore size. Considering a surface tension of 480 dyn cm^{-1} as well as a wetting angle of 141.3°, the following relationship is received (r = pore radius, p = mercury penetration pressure): $r = 7500/p$.

3. Results and discussion

TG-analyses show a continuous decrease for mass of oxygen removal from the iron oxides for the tests with hydrogen and also for the tests with carbon monoxide. The reduction of oxygen removal of the process decreases with the number of cycles. With only five cycles measured, it cannot be predicted if the oxygen removal will reach a constant value after a certain number of cycles. The tests with hydrogen do not differ substantially from the tests with carbon monoxide (Fig. 2).

3.1. XRD

The results of the measurements in the XRD show a variety of crystal components. After five oxidation cycles, the pellets primarily consists of magnetite, some iron and wuestite are also present due to the incomplete reduction and oxidation reactions. Depositions of iron, oxides, quartz, etc. can be explained by sintering processes. Areas that consist of pure iron, quartz, etc. are enclosed during the redox cycles as a consequence of the sintering processes. These components are detected with XRD after pulverisation. SiO_2 is found in samples containing more than 5% mass% quartz, Fe_2SiO_4 is found in samples containing more than 7.5% mass% quartz.

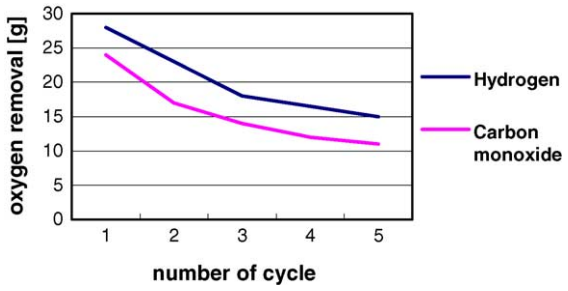

Fig. 2. Mass change due to oxygen removal during the first five cycles with hydrogen and carbon monoxide as reducing agent.

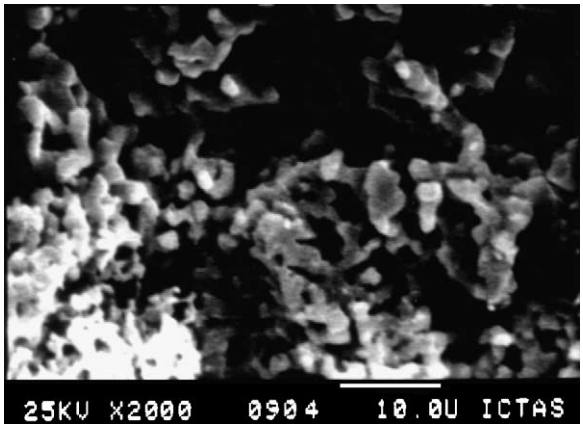

Fig. 3. Porous deposition of iron in the contact mass.

3.2. SEM

The deposition of iron takes place in three formations: porous, directed and compact (Figs. 3–5). The compact deposition leads to a decrease of oxygen removal within the reaction limiting range and lowers the porosity of the pellets. The directed, whisker-like deposition leads to intensified swelling and mechanical stress, which can cause the pellets to break. The porous deposition behaviour is the desired characteristic. With this structure, the porosity is consistent and the range of the reaction limitation decreases slightly.

The deposition behaviour of the different pellets can be attributed as shown in Table 2. The area with quartz content above 5% leads to the desired porous deposition after five cycles for the tests with hydrogen and carbon monoxide. In the lower quartz and higher lime area, the deposition is widely compact.

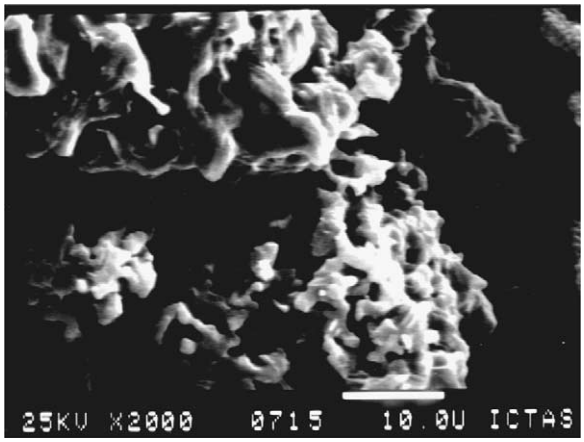

Fig. 4. Directed deposition of iron in the contact mass.

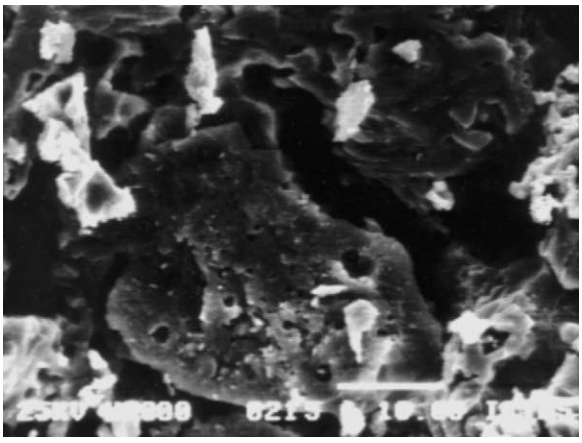

Fig. 5. Compact deposition of iron in the contact mass.

Table 2
Characteristic deposition behaviour of iron in the contact mass

Quartz content (%)	0	2.5	5	7.5	10
H_2 88	Compact	Directed	Porous	Porous	Porous
CO 88	Compact	Compact	Directed	Porous	Porous
H_2 85	Compact	Directed	Directed	Porous	Porous
CO 85	Compact	Directed	Directed	Porous	Directed

3.3. Hg-porosimetry

The pore volume has initial values of 200–300 $mm^3\,g^{-1}$. With increasing numbers of cycles, the volumes decrease down to 50 $mm^3\,g^{-1}$. This data can be explained by the change of the structure of the pellets as well as the sintering processes (Fig. 6).

3.4. Specific surface

At the beginning, the amount of the pore surface is about 0.6 $m^2\,g^{-1}$ with a low quartz content. This value raises up to 1.4 $m^2\,g^{-1}$ with high SiO_2 (quartz) fractions. A change in pore surface due to sintering effects was observed. Only tests with carbon monoxide and pellets with 88% haematite and 5% quartz, and with hydrogen and 85% Fe_2O_3, 5% and 10% SiO_2 resulted in constant pore surface areas (Fig. 6).

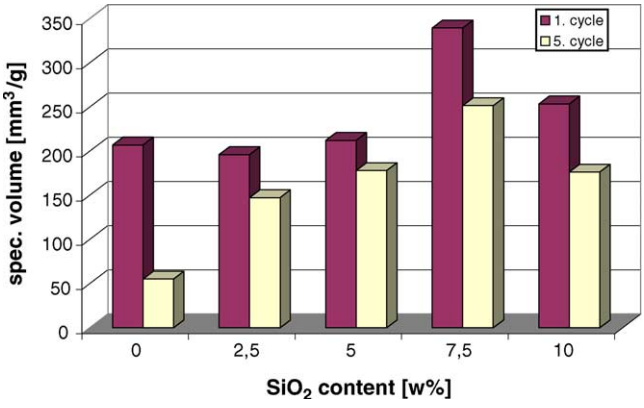

Fig. 6. Specific pore volume (Fe_2O_3-content 85%, reducing agent carbon monoxide) as a function of SiO_2-content and the number of redox cycles (first and fifth).

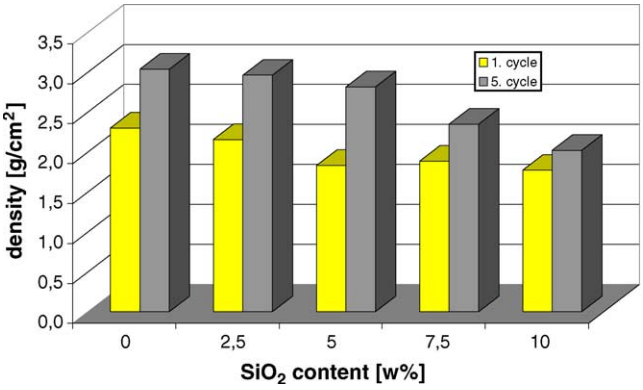

Fig. 7. Pellet density (Fe_2O_3-content 88%; reducing agent hydrogen) as function of SiO_2-content and of number of redox cycles (first and fifth).

3.5. Mean pore radius

The initial mean pore radius of all pellets investigated is in the order of 1 μm. In the tests with carbon monoxide, the pore radius generally tends to increase. Only in the tests with hydrogen, the pore radius of pellets with low quartz content decreases. No uniform trend could be indicated for the mean pore radius. The values rise up to 4 μm for pellets with 88% Fe_2O_3 and decrease down to 0.3 μm in the tests with 85% haematite. Smaller changes of the pore radius are detected for pellets with a high lime content compared to pellets with a high quartz content.

3.6. Change in porosity

The porosity decreases with increasing cycle numbers due to sintering effects. The initial porosity is about 50%. After five cycles, the porosity decreases considerably in the tests with pellets containing low SiO_2 fractions. For higher quartz contents, the porosity is quite constant after five redox cycles.

3.7. Pellet density

The pellet density increases with the cycle number. The increase in density yields to a decrease in porosity. The density at the beginning is in the range of 1.7–2.3 $g\,cm^{-3}$. The increase of density for pellets with Fe_2O_3 content of 88% (Fig. 7) declines with increasing quartz content.

4. Conclusions

The contact mass tests aim to find iron ore pellets, that do not break due to swelling and enable hydrogen production over a large number of cycles. The pellets were manufactured

with defined compositions of Fe_2O_3, SiO_2, CaO and Al_2O_3. First redox test series were made with carbon monoxide and hydrogen. Investigations with thermogravimetry, X-ray diffractometry, scanning electron microscope and mercury porosimetry were performed. The data gained confirms the importance of the matrix. Fayalite and quartz are the base materials for the skeleton and are essential to derive stable pellets that can be utilised in large numbers of redox cycles. For well-founded statements about influence of the composition and the structure of the pellets on lifetime behaviour, further extensive carefully designed fundamental investigations are necessary.

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References

[1] V. Hacker, A novel process for stationary hydrogen production: the reformer sponge iron cycle (RESC), J Power Sources 118 (1–2) (2003) 311–314.
[2] V. Hacker, G. Faleschini, H. Fuchs, R. Fankhauser, G. Simader, M. Ghaemi, B. Spreitz, K. Friedrich, Usage of biomass gas for fuel cells by SIR process, J. Power Sources 71 (1998) 226–230.
[3] V. Hacker, R. Fankhauser, H. Fuchs, G. Faleschini, K. Friedrich, M. Muhr, K. Kordesch, Hydrogen production by steam-iron process, J. Power Sources 86 (1–2) (2000) 531–535.
[4] F. Müller, Wasserstofferzeugung nach dem Messerschmittverfahren; Zeitschrift für komprimierte und flüssige Gase (1919) 4–8.
[5] L.v. Bogdandy, H.-J. Engell, Die Reduktion der Eisenerze, Verlag Stahleisen GmbH, Düsseldorf, 1967.
[6] J.O. Edström, The mechanism of reduction of iron oxides, J. Iron Steel Inst. 175 (1953) S289–S304.
[7] V. Hacker, Novel process for stationary hydrogen production from hydrocarbons based on REDOX reactions, in: Fuel Cells Science and Technology, 2002, Amsterdam, 25–26 September, 2002, P3B.11.
[8] V. Hacker, J. Hierzer, J. Besenhard, A novel process for stationary hydrogen production, in: Fuel Cell Seminar 2002, Palm Springs, USA, 18–21 November, 2002.
[9] R. Steffen, H.B. Lüngen, Stand der Direktreduktion, Stahl und Eisen 114 (1994) 6.
[10] U. J. Gebel, Einfluß von Fremdphasen auf das Ausscheidungsverhalten von Eisen während der Reduktion von Eisenoxid, Dissertation RWTH Aachen, Institut für Eisenhüttenkunde, 1989.
[11] H.P. Eisen, et al., Investigations in a reduction scanning electron microscope about the reduction behaviour if modern iron ore pellets and sinters with low SiO2 and CaO contents, in: Proceedings of the Third International Symposium Benefication and Agglomeratio, Bhubaneswar, India, 16–18 January, 1991, pp. S463–S475.
[12] U.F. Chinje, J.H.E. Jeffes, Effects of chemical composition of iron oxides on their rates of reduction, Ironmaking Steelmaking 16 (1989).
[13] H. Kortmann, K. Koch, B. Grover, O. Burghardt, G. Trömel, Bedeutung der Gangart für das Schwellverhalten von Eisenerzpellets, Stahl und Eisen 93 (11) (1973) 463–480 (und darin zitierte Referenzen).