



ELSEVIER

Journal of Power Sources 61 (1996) 247-253

JOURNAL OF
**POWER
SOURCES**

Sponge iron: economic, ecological, technical and process-specific aspects

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Abstract

The process cycle sponge iron/hydrogen/iron oxide offers a simple possibility to store the energy of synthesis gases in the form of sponge iron, and at the same time to reform and to condition these synthesis gases. As 'product' of this energy storage one receives pure hydrogen which is intended for the running of fuel cells. The process cycle is investigated on two levels: (i) on a general level, economic, ecological and technical conditions are investigated and established, and (ii) on the process-specific level industrially produced iron ore pellets are tested for their suitability for employment in cyclic operation with synthesis gases. Mechanical strength, porosity, speed of reaction, additives and attendant materials (gangue) determine the properties of the pellets. The reaction degree of the iron contained in the pellets should be large and will remain constant. Negative influences such as sintering and carbonization should be avoided as far as possible in order to achieve a high number of cycles.

Zusammenfassung

Eine einfache Möglichkeit die Energie von Synthesegasen in Form von Eisenschwamm zu speichern und diese Synthesegase gleichzeitig zu reformieren und konditionieren, bietet der Prozesszyklus Eisenschwamm/Wasserstoff/Eisenoxid. Als 'Produkt' dieses Energiespeichers erhält man reinen Wasserstoff, der für den Betrieb von Brennstoffzellen vorgesehen ist. Der Prozesszyklus wird auf zwei Ebenen untersucht: (i) auf der einen, allgemeinen Ebene werden ökonomische, ökologische und technische Rahmenbedingungen untersucht und festgelegt, und (ii) auf der anderen, prozessspezifischen Ebene werden industriell gefertigte Eisenerzpellets auf ihre Eignung für den Einsatz in einem Zyklusbetrieb mit verschiedenen Synthesegasen getestet. Festigkeit, Porosität, Reaktionsgeschwindigkeit, Additive und Begleitstoffe (Gangart) bestimmen die Eigenschaften der Pellets. Der Reaktionsgrad des in den Pellets enthaltenen Eisens soll groß sein und konstant bleiben. Negative Einflüsse dagegen, wie Sinterung und Aufkohlung sollen weitgehend vermieden werden um eine hohe Zyklenzahl zu erreichen.

Keywords: Iron; Sponge iron; Gas conditioning; Energy storage; Hydrogen; Fuel cells

1. Introduction

Since the beginning of the industrial use of electricity about one hundred years ago, a search has been made for a direct means of storage for electrical energy. Until today there is, however, there is no important process on industrial scale that permits the storage of electricity economically in large quantity. The storage of electricity by means of super-conductors is a well-known method, but its application in energy management is not yet available. The storage of electrical energy must be carried out through its conversion into another form of energy. Great amounts of energy can be stored in the form of potential energy. The conversion is affected by means of pumped storage power stations. For isolated situations (refuge huts in alpine regions) or small applications (peak

load cover in the supply to buildings) secondary cells are on offer. Electricity is then converted into chemical energy and stored.

The sponge iron reactor offers a new possibility to store the energy content of synthesis gases in the form of chemical energy, to release hydrogen at any time, and by means of a fuel cell convert it into electricity and heat. The project envisages a combination of the sponge iron reactor and a fuel cell.

The process cycle sponge iron/hydrogen/iron oxide offers the possibility to employ synthesis gas for the reduction of iron oxide. The iron oxide exists in pelleted form, see Section 3.1. The reduction product, sponge iron, is of 'higher energetic value' and thus serves as a method of storing energy. If one needs energy one passes water vapour over the sponge iron and receives pure hydrogen. Energy storage, reforming

General Aspects:

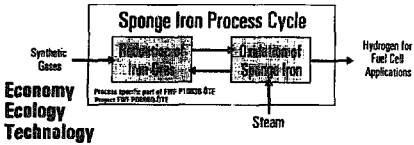


Fig. 1. The sponge iron process cycle.

Economy Ecology Technology

and gas conditioning take place in one step in this process cycle. The simple process and the cheap raw material — iron ore pellets are used in great numbers in steel production — anticipate an inexpensive sponge iron reactor that is simple to run. In contrast, conventional reformers and gas conditioning plants lead to high investment and running costs. In addition, the storage of hydrogen as a fuel is only possible with great expenditure, both technically and of energy, as for example the liquifying of hydrogen and its storage in refrigerated tanks.

The project FWF P10636-ÖTE ‘Sponge iron: cycle behaviour with synthesis gases’ is divided into two sections (see Fig. 1): (i) general project, and (ii) process specific investigations.

In the general section of the project, the environment of the ‘sponge iron reactor with fuel cell’ system is investigated and the prevailing economic, ecological, and technical conditions determined. In the other, process-specific level industrially produced iron ore pellets are tested for their suitability for employment in a cyclic operation with synthesis gases.

In this paper, an outline of the state of the situation analysis is given in the general section: the basic considerations are given and the rough directions of further investigations indicated. In the process specific section, initial measurement data are presented based upon the completed project FWF P09960-ÖTE ‘Sponge iron-energy storage’.

2. General section

2.1. Economic aspects

If the costs of ‘new energy technologies’ are calculated (these are technologies that have as yet not been introduced onto the market — such as fuel cells or the sponge iron reactor) then very often only the capital costs for the power station itself are taken into account. However, the cost of the product of the power station — electricity and/or heat — is not only the cost of building the plant which is charged to the product ‘energy’ (in US \$/kWh) but also the cost of operating and maintenance) and the cost of demolition of the plant and disposal of its parts. The total sum of these costs are known as ‘life-cycle costs’.

These are the prime standards of comparison to quote for various types of energy conversion plant or to be determined

as cost of energy supply from the power station on the basis of the life-cycle costs.

Especially in the case of the so-called ‘new energy technologies’ often the pure capital investment cost of the plant are only taken into account. The new energy technologies that are reliable in operation and cause hardly any disposal expenditure, but because of their small production numbers necessitate a high initial investment, are at a disadvantage compared with technologies that are already established in the market. Plants for these technologies are produced in large numbers and therefore cheap to make.

The ‘Boston effect’ leads to a reduction in the cost per unit of about 25–30% when doubling the cumulative production volume. Ignoring the higher operating cost or expensive disposal in making a cost comparison leads to a cost advantage for the established technologies which is generally successful in preventing new products being introduced into the market. If one extends the horizon of consideration, not only in the short term by including the demolition of the plant and disposal of its parts in the energy price calculation, but considers also in the long term the external effects of energy supply such as the emission of pollutants or the use of land, then one obtains the so-called ‘true total costs’ of the system. These can also be designated holistic costs.

Energy cost ex power station related to the quantity of energy produced during the lifetime of the plant (in US \$/kWh) includes: (i) investment or production cost; (ii) use cost, e.g. O&M cost and the price of fuel; (iii) disposal cost, and (iv) external or social cost.

In particular, the external cost which is based on atmospheric pollution gives an advantage for fuel cell technology since its direct emission is at least one degree of magnitude lower than that of the conventional energy conversion technologies [1]. At this point the problems in determining external costs are indicated. The difficulties range from the field of operation — the complexity of the system in making a factual balance is difficult to manage — to the basic difficulty of evaluation.

2.2. Ecological aspects

Analytical considerations of energy should result in the determination of the cumulative energy expenditure:

‘The cumulative energy expenditure (CEE) expresses the total of the estimated primary energy expenditure arising in connection with the production, use and disposal of an economic property (product or service) or which can be attributed as source. This energy expenditure is composed of the sum of the cumulative energy expenditures for production (CEE_p), use (CEE_u), and disposal (CEE_d) of the economic property, where the preliminary and subsidiary stages included are to be given for these subtotals’ [2].

$$CEE = CEE_p + CEE_u + CEE_d \tag{1}$$

This definition is based on a holistic viewpoint. All phases of the life of a property, a technical plant or a service are

considered. The distinctive feature of the aggregated value 'cumulative energy expenditure' is that it sub-divides the energy expenditure with reference to the life cycle as do the life-cycle costs with respect to the monetary expenditure.

Estimates of possible environmental effects of the sponge iron reactor should result in a preliminary, rough factual statement of the system 'sponge iron reactor with fuel cell' — classified according to type of fuel cell — together with available life-cycle inventories of various fuel cells. Ecological investigations are at present the most difficult part of the project since as yet no comprehensive international studies are published in English concerning the environmental effects of fuel cells. An energy study by Central Research Institute of Electric Power (CRIEPI) is available only in Japanese and a general study by the Netherlands Energy Research Foundation (ECN) is only in Dutch. It is intended to investigate in detail various energy supply networks which include a sponge iron reactor and fuel cell with software support.

2.3. Technological aspects

Fuel cell technology is a typical example of a 'back-stop technology'. Fuel cells in general and the 'sponge iron reactor with fuel cell' system in particular are both an alternative technology of a transition strategy and also a pilot or advance-guard technology of a renewable energy system of the future.

After conversion, for example reforming of natural gas, nearly all forms of fossil fuel can be used to run fuel cells. The employment of prepared fossil energy resources, and especially natural gas, as fuel for cells is an option for the immediate future because of the low emission and the high degree of efficiency, making this energy conversion technology an important element in a transitional strategy from a fossil to a renewable energy system of the future. In this case, fuel cell technology is an alternative technology to the existing energy supply plant.

In a future 'renewable energy economy', in the opinion of many experts hydrogen will hold a key position and again fuel cells will be an important component of the energy-supplying system. In this case, they are described as a pilot or advance-guard technology, fuel cells being part of a system in which 'renewable resources can be exploited to such an extent that the exhaustion of non-renewable resources can be overcome' [3].

Determination of the technical conditions are based on two levels: (i) technical guidelines can be determined from the economic and ecological conditions in a kind of top-down approach, and (ii) measurement results of the process-specific section lead to selection of certain technical solutions. This way is based on the bottom-up method.

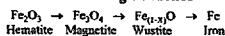
3. Process-specific section

3.1. Chemistry and process description

The great importance of iron and steel production in this century means that the physical and chemical processes in

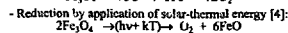
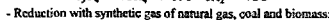
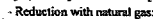
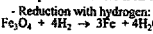
Process description, Chemistry

Phases During Reduction



Reduction Processes

Reduction possibilities for iron oxide:



Oxidation Process

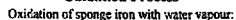


Fig. 2. Phase reactions occurring during the reduction of hematite. Various possibilities for the reduction of iron oxide with synthesis gases and the oxidation of sponge iron with water vapour are shown.

the iron ore reduction are among the best-studied industrial processes and have been published in numerous journals and textbooks. Because of the variable composition of the ores and their gangues, in practice many reactions proceed side by side; the main reactions are depicted in Fig. 2 [4].

Most of the investigations published describe the reduction of iron oxides at high temperatures as they take place in current processes in the iron and steel industry (liquid- or solid-phase reduction). They do not, however, deal with cyclic processes at low temperatures. In project FWF P09960-ÖTE basic preparatory work in this field was carried out [5]. In the following project FWF P10636-ÖTE the investigations continued further with synthesis gases. Iron ore pellets, see Fig. 3, are produced on an industrial scale and serve as basic material in steel production.

Meyer [6] characterizes the pellets as follows: pellets are balls produced from concentrates and natural iron ores of different mineralogical and chemical composition with some remarkable properties such as: (i) uniform size distribution within a main range of 9–15 mm diameter; (ii) high and even porosity of 25–30%; (iii) high iron content of more than 63% iron; (iv) practically no loss on ignition or volatiles; (v)

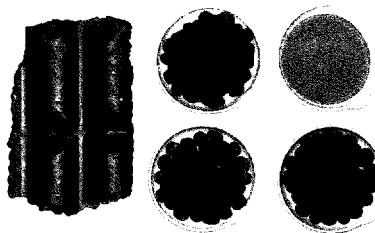


Fig. 3. Various types of iron ore and sponge iron: (left) sponge iron briquettes; (top centre) Sek pellets; (bottom centre) Malmberget pellets; (top right) sponge iron powder, and (bottom right) sponge iron pellets.

uniform mineralogical composition in the form of easy reducible hematite or hematite-bearing compounds; (vi) high and uniform mechanical strength; (vii) low tendency to abrasion and good behaviour during transportation, and (viii) sufficient mechanical strength even at thermal stress under reducing atmosphere.

Iron resources have varying percentages of hematite and magnetite depending on their origin. After preparation of the ore there are residues of gangue in the concentrate. Additives such as lime, bentonite and cement change the character of the pellets which may be acid or alkaline. After formation into pellets they are fired at temperatures between 1250 and 1340 °C. They are available mostly as hematitic iron oxide.

3.2. Experimental

The experiments for the reduction and oxidation were carried out in a tube reactor heated from outside. Here the pellets were heated to the prescribed temperature. The reaction gases were mixed with the aid of an armature mixer and fed into the reactor. A gas chromatograph at the output of the test plant analysed the gases flowing out and permitted one to draw conclusions about the course of the reaction, see Fig. 4. A gravimetric analysis of the pellets and the weight of the reaction condensation water that was formed by the reduction with hydrogen completed the data. The gases used were employed in excess (25 l/h total gas stream) in order to keep the reaction equilibrium more or less stationary. The speed of reaction depends on the diameter of the pellets since the duration of the gas diffusion within the pores is the determinant factor [7].

The reaction conditions of the measurements are as follows:

(i) Cycle with H_2 as reaction gas:

(a) reduction with H_2 : reaction time 1 h, temperature 800 °C, composition of the reduction gas 80% H_2 and 20% N_2 , and

(b) oxidation with H_2O_2 : reaction time 1 h, temperature 800 °C, composition of the reaction gas 90% H_2O_2 and 10% N_2 .

(ii) Cycle with CO as reduction gas:

(a) reduction with CO: reaction time 1 h, temperature 900 °C, composition of the reduction gas 60% CO and 40% N_2 , and

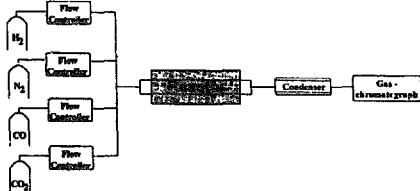


Fig. 4. Diagram of the apparatus used for the reaction experiments.

(b) oxidation with H_2O_2 : reaction time 1 h, temperature 800 °C, composition of the reaction gas 90% H_2O_2 and 10% N_2 .

The pellets examined have different compositions depending on their deposits of origin and preparation, both in respect of the iron oxide (hematite, magnetite) and the gangue. The experimental conditions were extreme, leading to almost complete conversion of the iron present and making high mechanical and thermal demands on the pellets. The elements contained in the gangue (see Table 1) greatly influence the behaviour of the pellets in the process cycle.

For use in a process cycle, the following properties of the pellets employed are determinant to obtain a high number of cycles: (i) sufficient porosity and volume of pores; (ii) sufficient reaction speed [7]; (iii) high resistance to thermal stress; (iv) low tendency to sintering; (v) naturally occurring catalysts; (vi) low swelling behaviour [8]; (vii) high resistance to pressure, and (viii) high resistance to abrasion.

The number of crystal nuclei in the pellets is important, in the presence of calcium it is large. Through the firing of green pellets — pellets as yet unfired — calcium ferrite is formed which promotes the formation of crystal nuclei. The calcium ferrite also leads to an instability of wustite in reduction and a porous iron morphology [9]. These properties have positive effects on the reaction course.

3.3. Results

Twenty cycles each were carried out in order to investigate the cycle behaviour of the individual sorts of pellets, one cycle consisting of one reduction and one oxidation phase. The pellet types Sek and Malmberget were chosen, see Table 1. The pellet type Sek has a magnesium oxide content of 1.04% and a calcium oxide content of 3.91%, giving an alkaline character. After the twentieth cycle no reduction in capacity of the converted iron, compared to that during the first cycle, can be established, see Fig. 5 below. (For reasons of

Table 1
Composition of Sek and Malmberget Pellets (wt. %)

Chemical analysis	Sek	Malmberget
Fe	57.83	66.70
SiO ₂	7.95	1.16
Mn	0.03	0.06
CaO	3.91	1.21
O	1.04	0.81
Al ₂ O ₃	0.39	0.33
P	0.01	0.033
S	0.024	0.001
Na	0.075	0.045
Ti	0.025	0.10
K	0.094	0.03
Zn	0.025	0.0038
Pb	0.001	0.0002

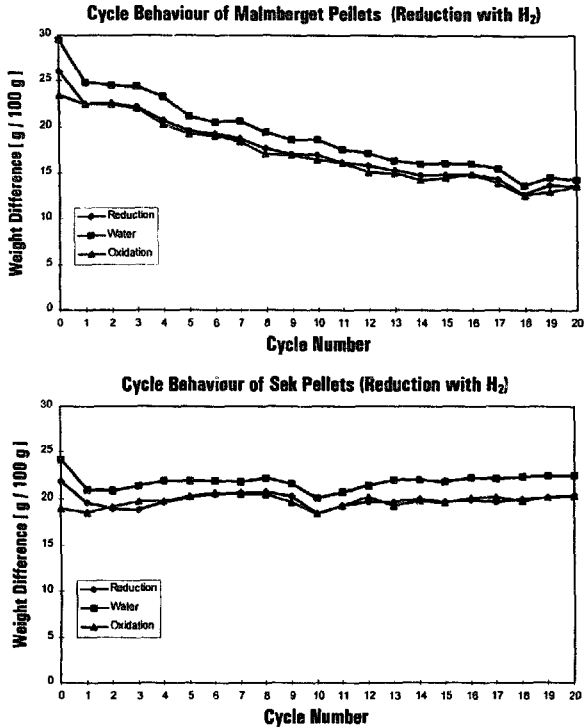


Fig. 5. Comparison of the cycle behaviour of Malmberget and Sek pellets in reduction with hydrogen.

comparison, the weight of the pellets was standardized at 100 g.) The converted reduction or oxidation weight corresponds to the weight of the reacting oxygen. In reduction with hydrogen the reaction condensation water was weighed. There were small weight losses caused by thermal and mechanical stressing of the pellets during measurement. The pellet type Malmberget, see Fig. 5 above, has an acidic character and after the twentieth cycle it shows a clear reduction in capacity of the converted iron compared to that during the first cycle. The reason for this is a change in pore structure (sintering and the emigration of ferric ions that take place especially in an acidic environment [10]). These ferric ions consequently form a compact shell around the individual nuclei. This shell is formed during progress through the various phase reactions (see Fig. 2) with the removal of oxygen atoms from the crystal cage. In reduction with carbon monoxide both pellet types behave similarly, see Fig. 6. The Boudouard equilib-

rium is not reached. There is a precipitation of carbon and a formation of iron carbide in the pellets.

The speed of reduction of the iron oxides with carbon monoxide is in general lower than with hydrogen. If the reaction temperature is raised the reaction speed does increase as well as the energy expenditure with an increase in thermal and mechanical stress to the pellets.

3.4. Discussion

The experiments carried out confirm the possibility of employing iron ore pellets for storing energy and gas conditioning, whereby both hydrogen and carbon monoxide are suitable for reduction in the sponge iron/hydrogen/iron oxide process cycle. The most important results of the investigations are as follows: if the sponge iron pellets are reduced with carbon monoxide, the resulting oxidation yields almost

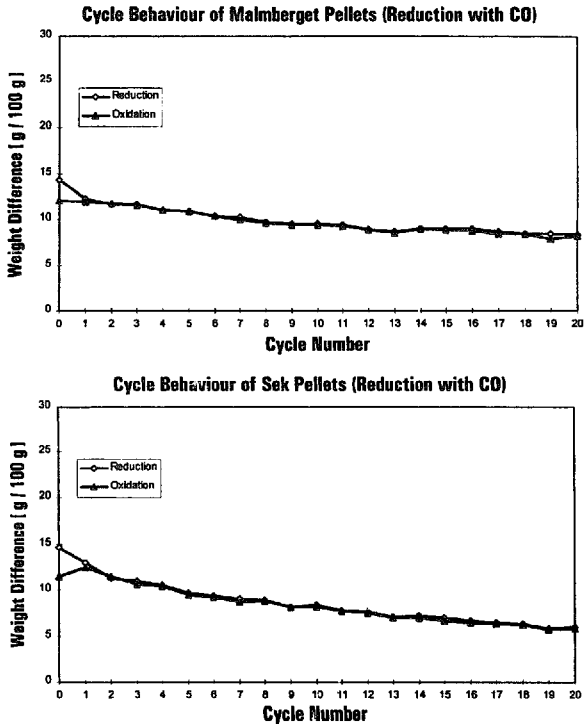


Fig. 6. Comparison of the cycle behaviour of Malmberget[†] and Sek pellets in reduction with carbon monoxide.

pure hydrogen which is suitable for the running of all types of fuel cells. Only traces of carbon monoxide and carbon dioxide were found. The carbonization that occurs reduces the number of cycles. The amount of calcium, magnesium, silicon, aluminium, etc., in the pellets determines the cycle behaviour, see Figs. 5 and 6. Thus, the effectiveness of reduction with hydrogen decreases more with the chemically pure Malmberget pellets than with the Sek pellets which have higher gangue and additive content, see Table 1. The tendency is not so marked in the reduction with carbon monoxide, whereby the carbonization compensates for the weight reduction following the loss of activity, see Fig. 7. After several cycles, the carbon monoxide curve therefore lies above the hydrogen curve, although the activity of the pellets is reduced. This behaviour needs to be elucidated.

The cycle behaviour of the reference pellets of corrosive oxide — iron oxide Fe_2O_3 after precipitation from a mordant

— compared with pellet types which contain catalysts and additives are the subject of further investigation.

Interesting results may also be expected concerning the reduction behaviour of pellet types with synthesis gases and with natural gas [11,12].

Acknowledgements

The authors thank the Austrian National Bank for financing the research work and the Austrian Science Fund for the accompanying project organization. Dipl.-Ing. W. Trimmel and Dipl.-Ing. B. Fritz of VA Stahl AG gave expert and material support, Dipl.-Ing. E. Bäck, Mining University Leoben kindly made literature available and Professor O. Fruhwirth gave specialist contributions.

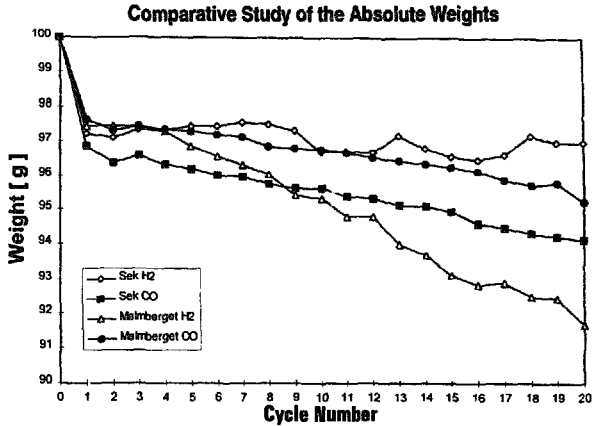


Fig. 7. Comparison of changes in the total weight of pellets in cycles and in reduction with hydrogen and carbon monoxide.

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