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“Steam-Iron” Process for Hydrogen Production: Recent Advances

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The “Steam-Iron” process is one of the oldest commercial methods for the production of hydrogen. The process was practised from the early 1900s well into 1930s for supplying small quantities of pure hydrogen to some industries (e.g., aerial navigation). Later, the technology was supplanted by the more efficient and economical natural gas reforming process [1]. However, the interest in the “Steam-Iron” process has grown in recent times, due to its simplicity, the high purity of hydrogen obtained, which is especially important for the use of hydrogen in fuel cells, the feedstock flexibility and the possibility to use renewable energy sources in this process.

The “Steam-Iron” process produces high-purity hydrogen by separating the hydrogen production and feedstock oxidation steps using iron oxides subjected to redox cycles. Simplistically, the chemistry of the “Steam-Iron” process involves two subsequent reactions, as shown schematically in Figure 1.

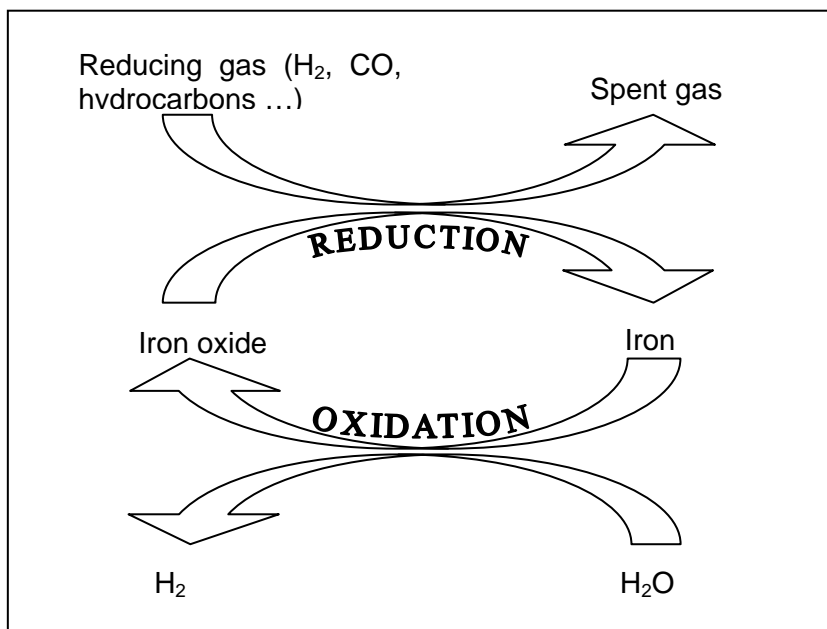


Figure 1: Principle of the “Steam-Iron” process.

In the reduction step, the iron oxide is treated with a reducing feedstock (such as hydrogen, mixtures of hydrogen and CO, and various other fuels), and as a result of the reaction, the metal (iron) or a partially reduced oxide is obtained. The second step consists in the oxidation of the reduced material by means of steam, which decomposes, resulting in a pure

hydrogen stream (without carbon oxides), while the metal oxide is partially regenerated and therefore it can be recycled to the reduction step.

In practice, the process is much more complex due to the presence of various reduced forms of iron oxides and the simultaneous occurrence of a number of feedstock decomposition/oxidation reactions. A few studies have been devoted to the solid-state kinetics of the process [2-4]. Models based on nucleation and growth mechanisms have been proven to describe both the reduction and oxidation reactions. Furthermore, the decrease in reactivity of the oxide caused by cyclic operation of the alternative reduction and oxidation stages, has been investigated and mathematically modelled [5].

On the other hand, in order to improve the long-term stability of the oxide as well as enhance the rate of reactions, the use of foreign metals (acting as promoters) has been proposed. Several research groups have been exploring the influence of different metal additives on the redox properties of iron oxides [6-8]. The use of additives such as Al, Cr or Ce has shown to prevent the deactivation of the oxide associated with the repetition of reduction and oxidation cycles. Other metals (such as Rh) improve the oxidation rates at low temperatures. It has been also considered the combination of two/three promoters with different properties, in the search for a synergistic effect.

Alternatively, the use of fumed-Fe-dust [9] and mill-scale waste [10] from the steel industry has been suggested as inexpensive base materials rather than synthesized iron oxides.

One of the advantages of the "Steam-Iron" process relates to high feedstock feasibility. Table 1 shows a relation of several reducing gas stream for the "Steam-Iron" process that have been proposed and studied by different authors. The use of gas obtained from gasification or reforming in the reduction step, offers an interesting opportunity for developing and optimizing the "Steam-Iron" process in combination with a gasifier or a reformer unit. The advantage of this integrated process concept is the possibility of enhancing the overall efficiency of the system, by means of energy recovery and recycling of product streams.

Table 1: Reducing agents used in the "Steam-Iron" process.

Reducing agent	Authors (reference No.)
Gas resulting from coal gasification	Gupta et al., 2007 [11]
Gas resulting from biomass gasification	Hacker et al., 1998;2000 [12,1] Sime et al., 2003 [13]
Gas resulting from pyrolysis oil gasification	Bleeker et al., 2007 [14]
Gas resulting from light hydrocarbons reforming	Hacker, 2003 [15] Galvita et al., 2008 [16]
Methane	Takenaka et al., 2003; 2004 [17,18] Galvita and Sundmacher, 2005 [19]
Mixtures CH ₄ /H ₂	Otsuka et al., 2001 [20] Peña et al., 2006 [2]

The "Steam-Iron" process can be performed in continuous as well as discontinuous manner. The main application of the continuous operation alternative is the selective separation of

hydrogen from other gases, such as hydrogen-containing natural gas, biomass or coal pyrolysis and/or gasification, or the stream resulting from thermal decomposition of natural gas. For this option, the simultaneity of the reduction and oxidation steps can be achieved by using either fixed bed reactors in parallel with alternate flows or fluidized bed reactors with circulation of solids between separated reaction zones. The application of a simulated moving bed-type reactor has been also proposed to achieve the advantages of the moving bed reactor by moving not the solid materials but the fluid stream [21].

When the "Steam-Iron" process is operated in the discontinuous manner, it can be considered as a method of hydrogen storage. The theoretical maximum amount of hydrogen capable to be stored and transported as the reduced oxide is 4.8 wt%, according to the mass ratio of H₂ to Fe in the hydrogen release reaction ($3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$). This corresponds to 537 L of hydrogen gas (STP) that can be stored per kg of iron, and it is comparable to the hydrogen storage density of conventional metal hydrides.

While reactor design and modelling are matters that have been analysed by several research groups [21-24], these topics still require more attention and investigation in order to increase the feasibility of hydrogen production by the "Steam-Iron" process in comparison with other technologies.

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