

A technology to simultaneously produce clean hydrogen and iron powder

Stefanoiu Horatiu George, Stanasila Virgil Corneliu, Stanasila Octavian, and Stefanoiu Dan

Abstract — The redox steam–iron process, which has been discovered in the early 1900’s, was finally abandoned because the degradation of the iron oxide ores within a few cycles. Recently, this process has been reconsidered, due to the necessity to yield cheap and pure hydrogen. In this article, we introduce a related but improved technology. At the first stage, the inlet iron oxide for the steam–iron process is the hematite, which has to be reduced to metallic iron in a gasifier called *HG*, by using syngas from coke (or cellulose). The hydrogen is then produced in a cyclic process, based upon the reduction of metallic iron by means of steam. At the second stage, another hematite, at any granulation, is reduced to iron powder in a reactor called *IPR*, at about 570°C by using the hydrogen of *HG*.

Keywords — alternant heat transfer, hydrogen, iron powder, steam–iron process by gaseous agents recycling.

I. PRELIMINARY INTRODUCTION

AFTER 1990, the energy consumption continued to increase, as result of the galloping industrialization and the social economic growth. The earth’s nonrenewable fossil fuel resources will be exhausted and the environment cannot assimilate the products of fossil fuel without suffering large levels of pollution.

The hydrogen is a non pollutant fuel. When burnt with air, it produces heat and steam. (When condensed, the water is obtained.) There are many methods to yield hydrogen, all expensive and, moreover, there are many difficulties to store it safely [4], [10]. It is well known that some metals (such as Mg, Zn, Fe, etc.) do not displace hydrogen from water at ambient temperature, but they shall do so if heated and the water replaced by steam. For instance, when the steam is passed over heated magnesium, this burns brightly producing solid magnesium oxide and clean hydrogen gas (like in: $\text{Mg}_{(s)} + \text{H}_2\text{O}_{(v)} \rightarrow \text{H}_{2(g)} + \text{MgO}_{(s)}$). The same holds for iron [2], [11], [12]. Some non-metals, such as carbon, can also displace hydrogen from water at high temperature (like e.g. $\text{C}_{(s)} + \text{H}_2\text{O}_{(v)} \rightarrow \text{H}_{2(g)} + \text{CO}_{(g)}$). Since such reactions are endothermic, it is necessary to supply heat to keep them alive.

The essential problem of the hydrogen production (and profitable use in metallurgy, fertilizers or artificial fuels) is to limit its cost and preserve the environment [5], [10].

Moreover, the iron is obtained from iron ores (hematite mainly) by removing oxygen through reduction (i.e.

deoxidizing) reactions. The term *redox* is an abbreviation of the syntagm *reduction–oxidation*, met also in several scientific domains.

In this paper, we first refer to the *reduction* with carbon or cellulose based waste of an iron ore broken in small pieces (e.g. under 2 mm), followed next by *reoxidation* with steam of the resulted iron, mainly by the reaction iron–steam $\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2$. One thus releases *clean hydrogen*, which is comparable with that from electrolysis, This hydrogen can be employed as such or as *reducing agent* of a mass of another powder hematite at any desired granulation, without pelletization. The obtained iron powder contains no carbon, which is useful, for instance, in steelworks.

A special role devolves to the thermo-dynamical aspects. For instance, the heat capacity depending on the absolute temperature T is:

$$c_p(T) \cong a + 10^{-3}bT + 10^{-6}cT^2, \quad (1)$$

where the constants a , b and c are specific to different aggregation states. Then the heat contents (i.e. the *enthalpy*) H is determined by integration over the range of temperature; taking 298°K as reference:

$$H_T - H_{298} = \int_{298}^T c_p(T) dT. \quad (2)$$

Hence,

$$H_T \cong aT + \frac{1}{2}10^{-3}bT^2 + \frac{1}{3}10^{-6}cT^3 + H_c, \quad (3)$$

where H_c is including all the constants. For each phase of the involved substances, one thus gets the enthalpy as a sum of terms representing the transition heat. Similarly, the *entropy* S is obtained by integration as well:

$$\begin{aligned} S_T - S_{298} &= \int_{298}^T \frac{c_p(T)}{T} dT \Rightarrow \\ \Rightarrow S_T &\cong a \ln T + 10^{-3}bT + \frac{1}{2}10^{-6}cT^2 + S_c. \end{aligned} \quad (4)$$

The free energy is then: $G_T = H_T - TS_T$. As already known, without any constraints, thermo-dynamical systems are spontaneously evolving to a state of minimum free energy. The change in free energy is given by $\Delta G_T = \Delta H_T - T\Delta S_T$. Negative values of ΔH_T or a positive values of ΔS_T are associated to exothermal reactions, which yields spontaneity. For $\Delta H_T > 0$, the reactions cannot be enabled or initiated, whereas for $\Delta G_T > 0$ there are no reactions.

From our experimental tests concerning direct reduction of pyritic ash with a ceramic granular mass, heated separately in a rotary oven [9], resulted that the unbinding between iron and oxygen, in order to extract the metal from oxide, requires the following enthalpies to form 1 kg of reduced iron:

- 1,758 kcal (= 7.36 MJ) for hematite Fe_2O_3 ;
- 1,583 kcal (= 6.63 MJ) for magnetite Fe_3O_4 ;
- 1,150 kcal (= 4.81 MJ) for wustite FeO .

The inferior burning heat (calorific value) of hydrogen is 57,810 kcal/kmol (= 242 MJ/kg Fe). In the following reaction of hematite reduction, $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$, the missing heat is $q = 1.758 - 3 \times 57.81 / 2 / 56$ kcal/kg Fe, which gives 209 kcal/kg Fe (= 0.87 MJ/kg Fe). Similarly, in case of magnetite, $q = 0.85$ MJ/kg Fe. For the wustite, $q = 0.48$ MJ/kg Fe.

The paper is structured as follows. Next section shortly describes the plant and the technology. Some calculations as well as a new type of heat transfer are presented in section III. A numerical example is given in section IV. The alternant heat transfer technique (which is essential for the reactions intensification, uniformity of the temperature field, thermodynamical equilibrium between the gaseous agents and iron particles and good conversion efficiency) is described in section V. Some ecological and economical considerations (section VI) followed by concluding remarks complete the article.

II. SHORT DESCRIPTION OF PLANT AND TECHNOLOGY

A. The Plant

Two interconnected thermo-chemical reactors are integrated within the experimental plant illustrated by the photo of Fig. 1. The first one is a gasifier that generates hydrogen. The second one is a reactor that generates iron powder and performs complete deoxidation of iron ore (hematite) having a similar granulation to final iron powder. Here and hereafter, the following acronyms will be used: **HG** for the *Hydrogen Generator* and **IPR** for the *Iron Powder Reactor*.

Fig. 2 illustrates the schemata of HG and IPR as a whole. The main body (1) of RH and IPR is mainly composed by vertical channels, which are fed on top by the raw material (a mixture of hematite, sand and coke or cellulose waste). As the gasifying process evolves, the raw material is partially consumed, while advancing towards the bottom of RH body, where only some diamagnetic iron oxide and sand are collected. The steam produced by the generator (9) enters the RH inferior zone (8) through the versatile distributor (3). This device is designed to allow not only the steam insertion into the RH but also the evacuation of generated hydrogen (10) from the RH+IPR. Thanks to its ferromagnetism, the iron powder is first collected from IPR by means of some (electro)magnets and then post processed, as described within the next subsection. The reducing gas is generated at the level of deoxidation zone (2). After evacuation through another versatile distributor (3), the gas is externally processed by means of the coolers system (4) acting as heat exchanger.

Some auxiliary (but necessary) devices complete the scheme: condensers and purging gates (6), the steamroller compressor (5) and the decarbonizer (7). In order to keep the schemata simple and easy to understand, no other auxiliary devices (such as: elevators, kneader-homogenizer, various sensors, gauges, monitoring manometers, automatic feedbacks, etc.) are shown.

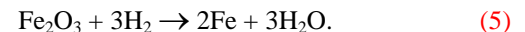
Both HG and IPR constitute a compact plant, on a relatively small surface (as exhibited by Figs. 1 and 2).

B. The Technology

The raw material (hematite with relatively large granulation, e.g. 1.5–2 mm) is mixed up with coke (or cellulose based waste), previously broken in small pieces (at the same granulation). The mixing is introduced in HG. The advanced deoxidation with carbon requires a temperature of about 950°C [3], [7]. In order to avoid the agglomerations and soldering of iron granules, in the mixture of ore and coke is introduced a relatively mono-granular mass of sand, up to 50% volumetric, with a mean diameter of 1.5–2 mm. All this mixture will be rummaged [1], [6].

The sterile is separated at the bottom end of HG and the mixture ore + sand is recycled, i.e. reintroduced in reactor after homogeneously mixed up with coke. The mixture is heated at 950°C and introduced inside the deoxidation zone, by some vertical channels having a special structure. By reduction with carbon, the iron ore determines theoretically a gaseous mixture of 15–71% CO and 85–29% CO₂. Some preheated steam is introduced in HG, in order to accomplish the evolution of carbon and its conversion into CO and H₂, both being reducing gaseous agents. From the gaseous mixture CO + CO₂ + H₂ + H₂O, one retains H₂O (by cooling) and CO₂ (inside the decarbonizer). The reducing gas CO + H₂ is reintroduced in HG. After the deoxidation zone, with a reduction of at least 90%, some steam from an external generator is introduced in the iron mass, by reforming the ore and *releasing hydrogen of high purity*, ready for employment.

For the iron powder production, the hydrogen will be consumed only in the IPR, where another hematite, with a prescribed granulation (eventually much finer) is introduced in some vertical special channels and heated at about 550°C. The channels are traversed by the hydrogen from HG. The main chemical reaction is then:



The gaseous mixture H₂ + H₂O leaves IPR and is cooled, thus condensing H₂O. The heat transferred in a cooler is partially recovered by heating the hydrogen, which is reintroduced in IPR, together with a hydrogen of completion brought from HG. Again, in order to avoid soldering and to improve the gaso-dynamical conditions, the hematite from IPR is mixed up with sand, having a granulation of 0.4–0.8 mm. The pyroforicity of the resulted iron powder has to be avoided as well. Therefore, it is necessary to perform post processing by first heating at about 800°C and then cooling at the ambient temperature. Now, the iron powder is ready to be employed.



Fig. 1 Photo of the experimental plant to produce hydrogen and iron powder.

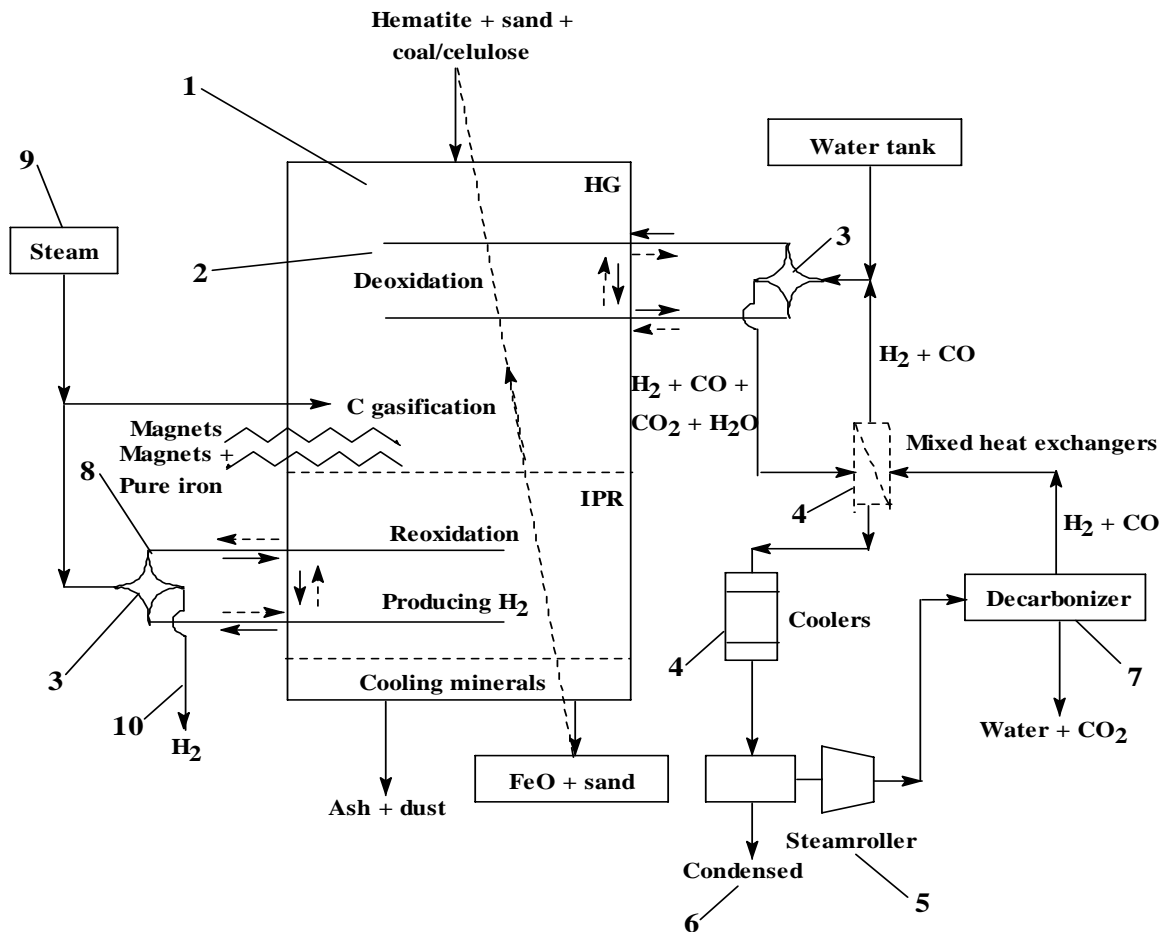
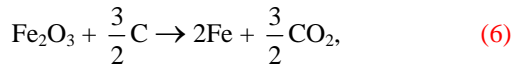


Fig. 2 Schemata of the experimental plant that integrates RH and IPR as a whole.

III. COMPUTATIONAL NOTES

The CO₂ has to be removed from the gaseous mixture in HG, since CO is recycled. The theoretical consumption of carbon is determined by the reaction below:



which requires:

$$M_c = \frac{1.5 \times 12}{2 \times 56} \cong 0.16 \text{ [kg C / kg Fe]} \quad (7)$$

and generates:

$$M_{\text{CO}_2} = 0.16 \times \frac{22.4}{12} \cong 0.3 \text{ [kg CO}_2\text{ / kg Fe]}. \quad (8)$$

During the reduction with carbon, one also produces:

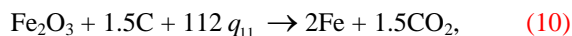
$$M_{\text{O}_2} = \frac{3 \times 16}{2 \times 56} \cong 0.43 \text{ [kg O}_2\text{ / kg Fe]}, \quad (9)$$

but the oxygen is captured within CO. The initial hematite ore has the density of about 3 kg/dm³, thus a content of 3×0.66≅2 kg Fe/dm³ (under the hypothesis that Fe₂O₃ ore is containing 66% Fe). After the deoxidation zone, one obtains a mixture of 90%+10% oxides, so that the redox reaction will lead to a smaller density of iron:

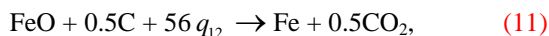
$$\rho_{\text{Fe}} = 2 \times (0.9 - 0.1) = 1.6 \text{ [kg Fe / dm}^3\text{]}. \quad (9)$$

This amount of iron is actually involved into the technological cycles. The granules of ore have the mean diameter of 1.5-2 mm and specific surface of heat and mass change between 1570 m²/m³ and 2094 m²/m³ (about 3 times bigger than in the case of pellets or lumps). The deoxidation process will implicitly have a great intensity and will take about 45 minutes (already verified experimentally).

We will now give an estimation of the energy consumption. The redox transform in HG shows that one consumes 90% from the heat q_1 necessary to process Fe₂O₃, minus 10% from the heat q_2 necessary to process FeO. In the case of coke as raw material, on one hand, from the thermo-chemical reaction:



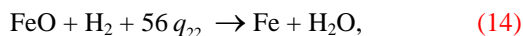
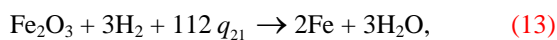
it follows that $q_{11} \cong 450.3$ kcal/kg Fe. On the other hand, the thermo-chemical reaction:



involves $q_{12} \cong 278.7$ kcal/kg Fe. Thus,

$$Q_1 = 0.9q_{11} - 0.1q_{12} \cong 377.4 \text{ kcal/kg Fe or} \\ Q_1 \cong 437.8 \text{ Wh/kg Fe}. \quad (12)$$

In case of cellulose as raw material, two other thermo-chemical reactions have to be considered, as follows:



with: $q_{21} \cong 209.6$ kcal/kg Fe and $q_{22} \cong 118.2$ kcal/kg Fe. Thus:

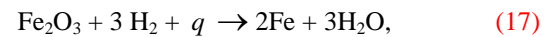
$$Q_2 = 0.9q_{21} - 0.1q_{22} \cong 176.8 \text{ kcal/kg Fe or} \\ Q_2 \cong 205.1 \text{ Wh/kg Fe}. \quad (15)$$

The ore deoxidation is made 60% by CO and 40% by H₂. The theoretical consumption is then:

$$Q = 0.6Q_1 + 0.4Q_2 \cong 344.7 \text{ Wh/kg Fe}, \quad (16)$$

which is smaller than in case of using coke. In the deoxidation zone, the walls of the above mentioned channels are traversed by a gaseous mixture (formed by CO, CO₂ in the case of coke and CO, CO₂, H₂, H₂O in that of cellulose), in an *alternant* sense at any 3 to 5 minutes. This technique is described in section V. The same procedure is applied for the flow of steam that circulates alternately and transversally through the zone located after the deoxidation zone, thus generating the hydrogen, which is forwardly employed within IPR as reducing agent.

At IPR level, the main theoretical reaction is the following (with a temperature of about 550°C):



from which $q \cong 23.48$ kcal/kmol Fe or $q \cong 209.6$ kcal/kg Fe, as we already have seen. Generally, the consumption of hydrogen, necessary for the iron ore deoxidation is:

$$V_{\text{H}_2} = \frac{3 \times 2.4}{2 \times 56} \cong 0.6 \text{ [m}^3\text{ H}_2\text{ / kg Fe]}. \quad (18)$$

IV. A NUMERICAL EXAMPLE

Our experiments were made on the plant of Fig. 1, with the described technology, yielding 20 kg/h of high purity iron powder and 12 m³/h of clean hydrogen. The hematite ore had the following composition: 66% Fe, 4% SiO₂, 1.5% Al₂O₃ and 28% O₂. According to (7), the hourly consumption of carbon was of about 3.2 kg/h. The volume of the used coke was about 9 dm³/h. According to (9), the volume of recycled hematite is approximately equal to 12.5 dm³/h, which corresponds to a mass of about 37.5 kg/h (since the hematite density is 3 kg/dm³, as previously mentioned). In order to avoid soldering of iron granules (at 950°C), the ore and coke were mixed up with sand. At HG level, an initial volume of 12.5+12.5+9=34 dm³/h was recycled. The duration of the process being about 45 minutes, in HG there were permanently 34×(45/60)=25.5 dm³/h ore+coke+sand, with the mass of 60.7 kg/h. For the production of 20 kg/h of iron powder, the CO₂ production was, by (8), of about 6 m³/h CO₂ per hour. Only 29% of CO₂ was exhausted. Hence, the debit of CO + CO₂, recycled in HG, was of 6/0.29 ≅ 20.7 m³/h. (In the case of cellulose, the debit increases by about 50%.)

The real velocity of the gaseous reducing agent at 950°C, confirmed experimentally, was of about 0.02 m/s. The surface area of passing through layer is (20.7×1.6)/(0.02×3,600) ≅ 0.5 m², with an increase of 60% for supplementary heaters. In order to reduce the pressure drop and the specific load of the heaters, the accepted surface is 0.9 m², whence the thickness of the ore layer is (25.5×10⁻³)/0.8 ≅ 32 mm. The power necessary to reduce 20 kg/h of iron is: 20 [kg/h] × 437.8 [Wh/kg Fe] = 8.8 kW.

The powder ore mass circulated through IPR, at a granulation of 30 μm , with 3% losses, is: $20/(0.66 \times 0.97) \cong 31.2$ kg/h. With a density of about 3 kg/dm³, the volume is 10.4 dm³/h. The volume of sand was twice, i.e. 20.8 dm³/h. Within the 45 minutes process (like in HG), at IPR level the material debit is of $(10.4+20.8) \times (45/60) \cong 23.4$ dm³/h.

The composition of the gaseous mixture hydrogen–steam is: 97% H₂ + 3% H₂O at the input and 79% H₂ + 21% H₂O at the output. The debit of gas traversing the reactor is: $20 \times 0.6 / (0.97 - 0.79) \cong 66.7$ m³/h, with an initial amount of 97% hydrogen, as resulted from HG. At 570°C, this debit was of $66.7 \times (273+570)/273 \cong 206$ m³/h. The gaseous mixture in IPR had an average composition like: 88% H₂ and 12% H₂O. Also, the mean dynamic viscosity is of 18.7×10^{-6} Pa.s (at 570°C [8]).

The velocity v of an ore granule was estimated by applying the classical Stokes formula, like below:

$$6\pi r\eta v = \frac{4}{3}\pi r^3 \rho g \Rightarrow \eta v = \frac{2}{9}r^2 \rho g, \quad (19)$$

where r is the granules radius (1.5–2 mm), ρ is the density (5500 kg/m³), g is the gravitational constant acceleration (9.81 m/s²) and η is the mean dynamic viscosity (18.7×10^{-6} Pa.s). It follows that $v \cong 0.14$ m/s, which means that the granules over 30 μm were not driven. The surface area of ore cooling layer results to be of about 0.8 m².

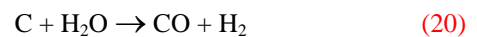
The heat necessary to perform endothermic deoxidation is: $20q_{21} = 20 \times 209.6 = 4192$ [kcal/h] $\cong 4.9$ kW.

The iron powder (with a granulation of about 30 μm) and the sand (with 200 μm granular diameter in average) were unloaded by a convenient sieve and separated. The sand was homogeneously mixed up with a new ore quantity and introduced in the IPR accumulator. The iron powder was collected in boxes. The working pressure was the atmospheric one and the average temperature in IPR was of 550°C, with an accepted variation between 540°C and 570°C.

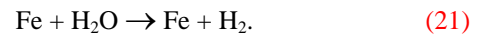
We now describe the coolers and the decarbonizer that are necessary, in order to make HG operational. In the zone of deoxidation, the gaseous mixture composed by CO, CO₂, H₂ and H₂O is evacuated at 950°C. About 31 m³_n/h of mixture is thus delivered at a pressure close to the atmospheric one. A part of it (which practically has the same calorific capacity as the mixture CO + H₂) is reinserted within the HG and passes through two coolers R₁, R₂, connected in parallel. Meantime, the whole gaseous mixture, at about 80°C, crosses a third cooler R₃, filled with water, and goes out at 30°C. All the mixture is taken over by a compressor and suppressed in a decarbonizer, which is endowed by a small gravel padding, immersed in water as well. A water flow will evacuate at sewerage the whole CO₂ production. Theoretically, from the decarbonizer will emerge a relatively dried mixture CO + H₂ + a little water (under 20°C), which, once being introduced in R₁, is heated at about 920°C. During the experimentations, the

supplementary preheating at 950°C (the temperature of operation in the deoxidation zone) was realized electrically.

In order to remove C from the reduced iron ore, in a second zone of HG, about 2 m³_n/h of steam is introduced. The steam is prepared in an external generator. In this way, C is gasified:



and Fe is oxidized:



A part of hydrogen partially reduces the iron ore. After the ore layer leaves the zone, the gaseous mixture CO + H₂ is introduced in the compressor upstream. The steam prepared in the above mentioned external generator is introduced in a last third zone of HG, in order to generate H₂ and reoxidate the existing Fe. The reducing gases are CO and H₂. The CO reacts three times slower than H₂ at 950°C, which involves, by recycling, the increase of the CO concentration from the reactor. From HG, it goes out a gas having 28% CO, 18% CO₂, 10% H₂ and 44% H₂O, at 950°C. The mean volumetric heats of the compounds at different temperatures are indicated in Table I below (according to [8]).

TABLE I
VOLUMETRIC HEATS OF HG COMPOUNDS [kcal/m³_nK]

T [°C]	CO	CO ₂	H ₂	H ₂ O
950	0.3358	0.5221	0.3167	0.4082
350	0.3165	0.4578	0.3107	0.3712
80	0.3108	0.4013	0.3076	0.3590
30	0.3104	0.3893	0.3064	0.3077

Consequently, at 950°C, the specific calorific capacity of gases can be evaluated as follows:

$$C_s = 0.28 \times 0.3358 + 0.18 \times 0.5221 + 0.10 \times 0.3167 + 0.44 \times 0.4082 \cong 0.3993 \text{ [kcal/m}^3\text{ }_n\text{K]}. \quad (22)$$

Similarly, one gets 0.348 kcal/m³_nK at 80°C and so on. The corresponding flow will be found again between the cooler R₃ and decarbonizer, being suppressed by the compressor. After the decarbonizer, which restrains 17 from the 18% CO₂, the gaseous mixture will contain 28% CO, 1% CO₂, 10% H₂ and 4% H₂O. Their flow will have is of 13.3 m³_n/h. The cooler R₁ receives then the flow:

$$\phi = 13.3 \times \frac{0.3414 \times 920 - 0.3157 \times 30}{0.3993 \times 950 - 0.348 \times 80} \cong 11.5 \text{ m}^3\text{ }_n\text{/h}. \quad (23)$$

So, the volumetric flow of gases varies from $11.5 \times 1223/273 \cong 51.5$ m³_n/h (at the entrance, when the temperature is 950°C) and $11.5 \times 353/273 \cong 14.9$ m³_n/h (at 950°C). In order to design the cooler R₁, the value of global coefficient for heat transfer is necessary. After some computations, its value results to be of 75 kcal/m².K.h. Consequently, the geometrical dimensions of R₁ are $0.2 \times 0.1 \times 1.5$ m³. Similar computations can be carried out for the cooler R₂. Finally, the cooler R₃ is practically like a small car radiator.

The HG can generate $31 \text{ m}^3_{\text{n}}/\text{h}$ of gaseous mixture, such that CO_2 takes 18% of it. The hourly flow of CO_2 is estimated at: $0.15 \times 31 \cong 4.65 \text{ m}^3_{\text{n}}/\text{h} \cong 11.2 \text{ kg/h}$. However, the decarbonizer will only receive $\text{CO} + \text{CO}_2 + \text{H}_2$, without 40% of water. Hence, the hourly volume of all generated gases is: $0.6 \times 31 = 18.6 \text{ m}^3_{\text{n}}/\text{h}$. Considering that the CO_2 absorption from these gases, at the atmospheric pressure, needs 30 s for the contact between gases and water, the mean volume of gases in decarbonizer will be: $18.6 - 2.8 = 15.8 \text{ m}^3_{\text{n}}/\text{h}$. When taking into account the volume of water, gravel and gases, the volume of the decarbonizer is: $15.8 \times 30 / 3600 / 0.3 \cong 1 \text{ m}^3$. The decarbonizer looks like a vertical cylinder of 1 m diameter and 1.5 m height.

In order to yield the estimated weight of 20 kg iron powder, 34.3 kg/h iron ore and $12 \text{ m}^3_{\text{n}}/\text{h}$ hydrogen are necessary. To avoid the piroforicity of the final iron powder, we have applied a well-known procedure, by heating it at 800°C , followed by its cooling. When operating with such a high temperature, the major risk is the birth of the inner glue, which can irreversibly damage the raw material and the HG. For this reason, the ore has previously been mixed with 35.4 kg/h coarse sand. The final separation of sand and ore enforced diameters of 0.4 mm to 1 mm for the sand granules and 0.2 mm for the iron ore granules. Consequently, this is also the diameter of iron powder granules. The $12 \text{ m}^3_{\text{n}}/\text{h}$ of hydrogen were produced in HG at about 550°C by means of the alternant sense technique described within the next section. A mixture of 21% $\text{H}_2\text{O} + 79\% \text{ H}_2$ at 550°C crosses another cooler, where its temperature decreases down to 70°C (avoiding water condensation). The mixture is thus exchanging heat with recycled hydrogen.

In order to compute the drop of pressure Δp in the granular layer from the cooler R_1 , one can apply the classical formula below:

$$\Delta p \cong m^{-4.2} \left(1.5 + \frac{23}{\text{Re}_l} + \frac{120}{\text{Re}_l} \right) \frac{\rho v^2 h}{2g d} \text{ [Pa]} \quad (24)$$

where m is the layer porosity (estimated at 45%), Re_l is the Reynolds criterion in the layer, ρ is the layer density, v is the speed of cooling flow, g is the gravitational acceleration, h is the layer height and d is the mean granular diameter. Normally, Re_l is defined as:

$$\text{Re}_l = \frac{0.45}{(1-m)\sqrt{m}} \text{Re} \cong 1.22 \cdot \text{Re}, \quad (25)$$

where Re is the Reynolds number for granules.

For the cooling zone between 950°C and 350°C , with $\text{Re} = 694$, it follows that $\text{Re}_l = 847$. If $\rho = 0.335 \text{ kg/m}^3$, $v = 3.2 \text{ m/s}$, $h = 0.62 \text{ m}$ and $d = 0.007 \text{ m}$ in eq. (24), then $(\Delta p)_1 \cong 10.566 \text{ Pa}$, which means about 1080 mm of water column. For the cooling zone between 350°C and 80°C , the parameters are as follows: $\text{Re} = 409$, $\text{Re}_l = 499$, $\rho = 0.618 \text{ kg/m}^3$, $v = 1.73 \text{ m/s}$, $h = 0.55 \text{ m}$ and $d = 0.007 \text{ m}$.

According to eq. (24), $(\Delta p)_2 \cong 5.5 \text{ Pa}$, which means about 570 mm of water column. Thus, the total drop of pressure in the cooler R_1 is:

$$(\Delta p)_1 + (\Delta p)_2 = 1080 + 570 = 1650 \text{ mm of water column.} \quad (26)$$

The same is obtained for R_2 , whereas in R_3 one gets about 70 mm of water column. The pressure drop in HG is small (about 20 mm of water column). Thus, the compressor will have to recover about 4900 mm of water column, that is 0.45 bar. The total drop of pressure in IHR is at most 0.1 bars.

V. ALTERNANT CONVECTIVE HEAT TRANSFER

There are situations – like the one described so far – when the thermal transfer between a granular layer and a fluid shall exhibit high efficiency. In order to reach for this goal, one solution (probably not unique) is to enforce the fluid circulation to be *alternant*. In one word, this means the gas has to periodically be sent from a side to another inside the plant. In case of plant HG+IPR, the thermal change is realized between the reducing gas and the mixture iron ore+coke+sand, as well as between steam and iron. Each time, the reducing gas and the steam have to enter the solid (but granular) bed from two sides, alternatively, one side at a time (for a specific period of time).

Consider that the granular layer is located between two vertical walls with simplified coordinates $x_0 = 0$ and $x_1 = \delta$, respectively. Denote by t the field of temperatures for the fluid (i.e. for the gaseous agent) and by t_g the one for granules. One assumes that the granular bed is homogenous. Then, according to the Fourier law, one can compute the spatial gradient of fluid temperature:

$$\frac{dt}{dx}(x) = -m\alpha(x)(t(x) - t_g(x)), \quad \forall x \in [0, \delta], \quad (27)$$

where $m > 0$ is a constant and α (as function of distance x) is the *thermal transmissivity* (or the *convection coefficient*). In both cases of laminar and turbulent running, the thermal transmissivity varies as follows:

$$\alpha(x) = A \cdot x^{-n}, \quad \forall x \in [0, \delta], \quad (28)$$

where $A > 0$ is a constant and $n \in [0, 1/2]$.

Assume that the marginal temperatures $t(0)$ and $t(\delta)$ are known and set the following natural conditions:

$$t_g(x) = t_g(\delta - x), \quad \forall x \in [0, \delta]; \quad (29)$$

$$\alpha(x)(t(x) - t_g(x)) + \alpha(\delta - x)(t(\delta - x) - t_g(\delta - x)) = r, \quad \forall x \in [0, \delta]. \quad (30)$$

In equation (30), $r > 0$ is a specific constant, depending on the plant.

The differential equation (27), together with variation law (28) and conditions (29)-(30), describes the convective heat transfer between the gaseous agent and the granular layer, when the sense of agent periodically alternates. Condition (29) shows that the law of temperature variation inside the granular

bed is independent on the side wall from which the gaseous agent is injected (thanks to homogeneity hypothesis). The alternant effect is actually described by condition (30).

The alternant circulation of agent is next compared to the (regular) one way circulation. In case of the latter, equations (27), (28) and (29) are unchanged, but equation (30) has to be replaced by:

$$\alpha(x)(t(x) - t_g(x)) = r, \quad \forall x \in [0, \delta], \quad (31)$$

where all constants m, A, n, r are the same.

Then, from (27) and (30), one derives that:

$$\frac{dt}{dx}(x) + \frac{dt}{dx}(\delta - x) = -mr, \quad \forall x \in [0, \delta]. \quad (32)$$

By integration of equation (32), one obtains:

$$t(x) - t(\delta - x) = -mrx + t(0) - t(\delta), \quad \forall x \in [0, \delta]. \quad (33)$$

If $x = \delta$, one gets an interesting expression of product mr :

$$mr = 2 \frac{t(0) - t(\delta)}{\delta}, \quad (34)$$

which involves:

$$t(x) - t(\delta - x) = \frac{t(0) - t(\delta)}{\delta}(\delta - 2x), \quad \forall x \in [0, \delta]. \quad (35)$$

Conditions (29) and (30) allow one to determine the variation of t_g field:

$$t_g(x) = \frac{\alpha(x)t(x) + \alpha(\delta - x)t(\delta - x) - r}{\alpha(x) + \alpha(\delta - x)}, \quad \forall x \in [0, \delta]. \quad (36)$$

When accounting the variation (28), equation (36) becomes:

$$t_g(x) = \frac{t(x)x^{-n} + t(\delta - x)(\delta - x)^{-n} - r}{x^{-n} + (\delta - x)^{-n}}, \quad \forall x \in [0, \delta]. \quad (37)$$

Return now to equation (27), where t_g is given by (37). It follows that the equation to solve is:

$$\frac{dt}{dx}(x) = -mAx^{-n} \frac{(t(x) - t(\delta - x))(\delta - x)^{-n} + r}{x^{-n} + (\delta - x)^{-n}}, \quad \forall x \in [0, \delta]. \quad (38)$$

After few manipulations based upon properties (34) and (35), equation (38) is equivalent to:

$$\frac{dt}{dx}(x) = \frac{Amr}{2} \cdot \frac{m(2x - \delta) - 2(\delta - x)^n}{x^n + (\delta - x)^n}, \quad \forall x \in [0, \delta]. \quad (39)$$

Equation (39) describes the evolution of the temperature for the gaseous agent in contact with the granular layer and can be solved by numerical means. However, in case of the above analyzed thermo-chemical process, α has a very weak variation, being almost constant. Therefore, one could take $n = 0$. By direct integration of (39) (with $n = 0$) one obtains:

$$t(x) = \frac{Am^2rx^2}{4} - \frac{Amrx}{4}(m\delta + 2) + t(0), \quad \forall x \in [0, \delta]. \quad (40)$$

In this particular case, the variation law of agent temperature is actually a convex parabola with a minimum point at least equal to $x = x_1 = \delta$. Consider now an orthonormal frame xOt (with t instead of y). Beside the parabola (40), one can take into account its symmetric with

respect to the vertical axis $x = \delta/2$ (i.e. for $\delta - x$ instead of x in equation (40)). Then the average of agent temperature is:

$$t_a(x) = \frac{t(x) + t(\delta - x)}{2}, \quad \forall x \in [0, \delta]. \quad (41)$$

One can be proven that the minimum of parabola (41) is now reached for $x = \delta/2$. Moreover, according to equations (37) and (41), the temperature of granular bed varies like below (recall that $n = 0$):

$$t_g(x) = t_a(x) - \frac{r}{2}, \quad \forall x \in [0, \delta], \quad (42)$$

which shows why the average temperature of agent is so important. Anyway, the phenomenon revealed by equation (42) is quite natural: the coolest point of granular bed that lies between the two walls is in the middle, since the heat comes from both sides.

Following the same rationale as above (but using condition (31) instead of (30)), in case of one way heating, one obtains:

$$t(x) = t(0) - mrx, \quad \forall x \in [0, \delta]. \quad (43)$$

Clearly, this time, the minimum point is touched for $x = \delta$ (on the opposite wall). Moreover,

$$t_g(x) = t(x) - \frac{r}{A}, \quad \forall x \in [0, \delta]. \quad (44)$$

Now, the comparison becomes possible. The differences between the extreme temperatures of the granular layer are:

$$\Delta t_g = t_g(0) - t_g\left(\frac{\delta}{2}\right), \quad \text{for alternant heating}; \quad (45)$$

$$\Delta t_g = t_g(0) - t_g(\delta), \quad \text{for one way heating}. \quad (46)$$

After some simple manipulations, one derives that:

$$\Delta t_g \Big|_{\text{one way}} = 4 \Delta t_g \Big|_{\text{alternant}}. \quad (47)$$

Thus, the difference between the extreme values of the granules temperatures is *four times* smaller in case of alternant heating comparing to one way heating. This proves the technique of alternant circulation leads to superior efficiency of heat exchange with the granular mass.

VI. ECOLOGICAL AND ECONOMICAL CONSIDERATIONS

There are no CO or NO_x emissions in atmosphere. We have seen that, by the proposed technology, one obtains 0.3 m³_n CO₂ / kg Fe, i.e. 594 kg CO₂ / t Fe. The energy consumption of iron production being about 8.1 GJ/t Fe, the amount of released CO₂ is 594/8.1 ≈ 73 kg/GJ. The gas is pure. Thus, it can contribute to the growing of a new biomass by photosynthesis, which furthermore releases oxygen.

The hydrogen is now obtained from different fossil media, according to the Table II. The second column of Table I shows the mass contents of released CO₂ upon the energy unit, after the substance oxidation (for example the combustion of C generates about 10⁶ × 22.4/97,650 ≈ 229 m³_n CO₂ / Gcal ≈ 109 kg CO₂ / GJ). The non fossil sources generate an expensive hydrogen, which is industrially prohibitive (over 350 € for 1000 m³_n) [5], [10].

TABLE II
EMISSIONS OF CO₂ AND COSTS OF HYDROGEN PRODUCTION FOR DIFFERENT FOSSIL MEDIA

Fossil media	Combustion [kg CO ₂ / GJ]	Hydrogen generation [kg CO ₂ / GJ]	Cost of 1000 m ³ H ₂ [€]
Coke C, current technology	109	73	120
Cellulose	70	90	135
Crude oil CH _{1.5} ... 2	75	118	120
Natural gas CH _{3.75}	62	70	110

For an installation which applies the proposed technology, the estimated energy consumption is of 13.4 GJ for 1000 m³_n clean hydrogen and of 8.1 GJ/t Fe. Let p_{GJ} be the price in € for each GJ spent to produce hydrogen and p_{io} the price in € for 1 t of iron ore. Then the cost of 1000 m³_n H₂ production is:

$$P_{H_2} = \frac{13.4}{0.8} p_{GJ} \cong 16.8 p_{GJ}, \quad (48)$$

whereas the cost to produce 1 t of iron powder is:

$$P_{Fe} = \frac{1.5 p_{io} + 8.1 p_{GJ}}{0.65} \cong 2.3 p_{io} + 12.5 p_{GJ}. \quad (49)$$

For instance, if $p_{io} = 100$ €/t and $p_{GJ} = 7$ €/GJ, one gets $P_{H_2} = 120$ € and $P_{Fe} = 320$ € (the scrap iron being now estimated at 400 €/t).

VII. CONCLUDING REMARKS

In this paper, an improved stem-iron process has been introduced. Here, the hydrogen is produced in a cyclic set of reactions, based upon the partial reduction of hematite by coke or cellulose based waste, followed by the reoxidation of reduced iron by means of steam. We underline some characteristics of our approach:

- there is a *direct contact* between the reducing gaseous agents (syngas or steam) and the particles of non pelletized iron ore;
- the technology *does not require* any technical oxygen (which would dramatically increase the cost);
- the heat transfer between the gas and the iron ore or metallic iron particles is efficiently performed by means of *alternant circulation of gas*;
- hydrogen and iron powder (eventually extra-fine), are *simultaneously produced* through a reducibility (reoxidation) over a number of cycles;
- the *hydrogen is clean* (i.e. it does not requires post-processing) and the *iron powder is almost pure* (more than 97% iron);
- the *cost of technology is smaller* than the currently employed ones for the same purposes;
- the technology is *ecologically clean*.

Refineries require clean hydrogen to reduce the cost of the artificial fuels. Moreover, the tars, heavy oils and other degraded hydrocarbons from huge deposits could be converted in semi-liquid matters and then in petrol, by using hydrogen. If the clean hydrogen would be cheap and practically unlimited, so will be the liquid fuels, composed by water and CO₂ extracted from atmosphere and oceans.

ACKNOWLEDGMENT

This work was supported by the Romanian National Center for Projects Management (CNMP) under Grant TECOGAHI-32100/2008 and the Research Center for Automatic Process Control (ACPC) from "Politehnica" University of Bucharest, Romania. The authors are very grateful to both of them.

REFERENCES

- [1] S. Arrelakis, H. Gehrman et al., "Agglomeration problems during gasification", *Fuel*, Vol. 82, pp. 1261-1270, 2003.
- [2] L.S. Fan, "A high efficiency chemical looping process to produce low-cost hydrogen", Research report, Ohio University, USA, 2008.
- [3] J. Corella, J.M. Toledo et al., "Biomass gasification with pure steam", *Intl. Journal of Oil Gas and Coal Technology*, Vol. 1, No. 1-2, pp. 194-207, 2008.
- [4] St. Horvath, "Hydrogen production", US Patent no. 4490349, 1984.
- [5] K. Knopp, "Reduction of CO₂ emissions as a result of using hydrogen", *Stahl und Eisen*, No. 11, 2002.
- [6] T. Murakami, G.W. Xu et al., "Some fundamental processes of biomass gasification", *Fuel*, Vol. 86, pp. 244-255, 2007.
- [7] C. Pfeifer, P. Rauch, "Hydrogen rich gas production with a biomass gasifier", *In Proceedings of the second World Conference on Biomass for Energy*, Rome, Italy, May 10-14, 2004.
- [8] K. Raznjević, "Thermodynamical tables and diagrams", Editura Tehnica, Bucharest, Romania, 1978 (in Russian).
- [9] V.C. Stănășilă, "Method and installation to produce iron powder, associated or not with the hydrogen production", RO Patent no. 121605, 2007.
- [10] K.H. Tache, R. Steffen, "Hydrogen for the reduction of iron ores", *Stahl und Eisen*, No. 4, 2004.
- [11] S. Velu, S.K. Gangwal et al., "Highly dispersed nickel hydrogenation catalysts", US Patent no. 849479, 2006.
- [12] S. Velu, S.K. Gangwal, "Pure hydrogen production from syngas by steam-iron process", Technical Report, Center for Energy Technology, 2007.



Horatiu G. Stefanoiu (M'93, PhD'02) graduated the "Politehnica" University of Bucharest (Romania) in 1993, at the Faculty of Industrial Chemistry. His Ph.D degree was obtained in 2002, at the same university, with an extended research study on polyanilines. During the period of 1993-1996, he was with National Romanian Research Institute for Chemistry, where he started his research on polyanilines. Afterwards, he joined the research departments of several industrial companies, where he approached a wide range of topics (including polyanilines) and designed new products such as: CETARIL (a water based adhesive), CHIMALCHYD (alkyd resins family), DISKOBOL (water based car varnish). The research on hydrogen and iron powder production started in 2008, in the framework of a National Romanian Research grant. Since 2010 he is an assistant professor at BIOTERRA University of Bucharest, Romania. He is author of 10 papers. His research interests are focused on polyanilines synthesis with new catalyst systems, emeraldine-pernigraniline doping, ecological resins and varnish, green energy (especially solar).