

# Переробка сировини та енергозбереження

УДК 621.216:621.762.3:621.783.23

DOI: 10.33070/etars.4.2020.04

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## Obtaining of carbon-free iron powders by reduction method in conveyor furnaces with recirculation and regeneration of "green" hydrogen

The use of absolutely pure hydrogen to obtain carbon-free iron is justified. Such hydrogen can be obtained only by water electrolysis. According to modern trends it can be called "green" hydrogen". Some aspects of pure iron powders obtaining by the method of hydrogen reduction in a conveyor furnace are described. Thermodynamic analysis of the process has shown the expediency of reduction gas re-circulation for the full utilization of its chemical potential. The concept of hydrogen utilization factor is introduced and considered. The concept of hydrogen utilization factor is introduced and considered. It is ascertained that the realization of hydrogen recirculation is possible only in a gas-tight aggregate. Powder locks for sealing the end faces of conveyor furnaces for reduction and annealing of metal powders are developed. The basics of energy-efficient scheme for a reduction of iron with hydrogen recirculation and regeneration have been developed and realized on practice. This innovation allows to reduce gas consumption almost to the stoichiometric index. *Bibl. 15, Fig. 4, Tab. 2.*

**Key words:** reduction, hydrogen, iron powder, recirculation, regeneration.

### Introduction

The need to use pure electrolytic hydrogen existed before the term "green" hydrogen arised. For example: for refining or decarburizing metals and metal powders to obtain highly plastic and/or soft magnetic materials. The latter, by the way, have very low "watt" losses during reversal magnetization and are increasingly used in the creation of miniature devices and micromotors for cars, missiles, robots, and so on. Technically pure iron – iron that contains a limited amount of

impurities, primarily carbon. With high magnetic properties, technically pure iron has found application as the cheapest and most technologically soft magnetic material. The use of pure powdered iron in electrical engineering is due to the high saturation magnetization, satisfactory magnetic permeability and low coercive force. Pure powdered iron allows you to make magnetic circuits of complex shape, stators and rotors of micromotors with high accuracy at low energy and iron powder consumption. Soft magnetic powders solve the problem of product miniaturization.

Miniaturization or reduction of overall dimensions is constrained by heat release in electric machines. Thanks to the properties of soft magnetic powders, it is possible to create products of smaller size.

All processes of gas reduction of metal powders use expensive hydrogen-containing atmospheres as a reducing agent. In some cases, for example, in the production of soft magnetic iron powders [1] (carbon content  $C \leq 0.007\%$ ) or in the reduction of metals with high affinity for carbon (tungsten, molybdenum) it is necessary to use only electrolytic hydrogen. In the industry for metal powders reduction, their annealing and/or thermochemical processing pusher (-type) furnaces are used. In recent years, pusher (-type) furnaces of mainly conveyor type have become widespread [2-4]. The reduction furnace is a device which purpose is to ensure the maximum possible mass transfer between the reducing atmosphere and the renewable materials. Mass transfer conditions are determined by thermodynamic and actually mass transfer (hydrodynamics, diffusion) factors.

#### **Reducing-decarburizing annealing of iron powders**

Iron powders obtained by industrial methods contain a certain amount of impurities (oxygen, carbon, silicon, manganese, etc.). Most impurities, except oxygen and carbon, belong to the category that are difficult to remove. Reducing the amount of such impurities is provided at the stages of selection or preparation of raw materials for the production of reduced powders and at the stages of smelting liquid metal in the production of atomized powders. The increased content of oxygen and carbon in the powders, as well as various types of work hardening lead to a significant deterioration of the compression of powders, increased wear of molds and instability of the characteristics of the products. The reason of workhardening can be the grinding of sponge iron, wire, scrap in mills, thermal and structural stresses that occur during rapid cooling of the sprayed melts. It is also possible "pseudo- work hardening", which occurs in the case of intensive reduction of metals from oxides at low tempera-

tures. In this case, the lattice of the new phase is unbalanced, strained – so to speak, "cold working". To obtain powders with high and stable technological characteristics, additional thermochemical treatment is required – reducing-decarburizing annealing (RDA). From definition it follows that at RDA there is a removal from powders of oxygen and carbon and removal of internal stresses.

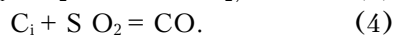
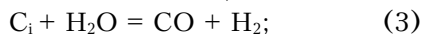
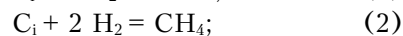
Carbon and oxygen are the main impurities that need to be removed during RDA process. Depending on the method of production (reduction, atomizing) an iron powder with a wide range of content of these impurities (from 0,4 to 12.0 % for oxygen and from 0.05 to 4.00 % for carbon) can be fed to the annealing. Accordingly, annealing is possible in various reducing atmospheres, which are modified by additives if necessary. The choice of atmosphere is determined by the requirements for the final content of impurities and economic considerations. The reduction of oxides in the presence of solid carbon is significantly influenced by the atmosphere in which the reduction is carried out. The use of a reducing atmosphere drops the degree of carbon participation. Increasing the amount of oxidants in the gas atmosphere to a certain limit accelerates the processes of combined reduction due to carbon gasification.

The peculiarities of the reducing-decarburizing processes of metal powders are: rather high temperatures, a large specific surface area which ensures a significant approximation of the gas-metal system to equilibrium. This opens up opportunities for wider use of thermodynamic methods of calculation and analysis of powder reduction for the choice of influence on the required course of the process. The gaseous medium in the reduction process is usually a system of C-H-O-(N) of a rather complex chemical composition, which causes the complexity of the interaction between its components, as well as in general in the gas-metal system. This allows us to call the gas phase a complex gas system (CGS). Thermodynamic study of the process involves the calculation and analysis of compositions, properties of CGS entering the reactor, as well as the equilibrium compositions of CGS, which are formed in the Fe-C-H-

O system. The calculation data make it possible to predict the thermodynamically expected concentrations of O<sub>2</sub> and C in the product taking into account its phase state.

### Process temperature

The kinetics of iron ore materials reduction indicates that the higher the temperature, the faster the reaction [5]. However, the upper temperature range of push furnaces is 1150 °C, with a walking hearth – 1300 °C, and for conveyor – 1050 °C. The latter limitation is due to the decrease in tensile strength of the conveyor belt at high temperatures. At determining of the decarburization temperature the features associated with the solid phase in which carbon may be are constrained. Carbon sources can be different. For example, the so-called humic inclusions, which are present in iron concentrates; equipment, namely: muffle, conveyor belt. The tape is covered with a thin layer of soot to prevent the sintered iron "cake" from sticking to it. To finally determine the required reduction temperature let's consider in more detail the process of carbon exchange. The main elementary reactions responsible for carbon exchange are:



Here, C<sub>i</sub> means solid phase carbon in any of the states: free, bound, or dissolved. Heterogeneous processes of metals carbon exchange with a gas phase, as well as processes of oxygen exchange, are multi-link and include external mass transfer, surface reactions and internal mass transfer. External mass transfer depends on the speed and nature of the gaseous medium movement. External mass transfer processes can limit mass transfer at relatively low gas flow rates and small values of transfer potentials. Surface reactions include adsorption-desorption acts and chemical transformations. Most often, internal mass transfer is the most important (limiting) stage, which is determined by different types of solid-phase diffusion.

The basis for the analysis of the phase state in the Fe-C-H-O system is a state diagram of the iron-carbon system. A large number of works are devoted to the study of the iron-carbon system. A significant bibliography and history of research on the state diagram of the Fe-C system is reflected in a large number of monographs, in particular, in the work [6-8].

From the iron-carbon state diagram it is known that there is a significant difference between the solubility of carbon in α- and γ-iron. The solubility of carbon in α-iron obeys the laws of infinitesimal solutions. Empirical equations of the dependence of thermodynamic activity of carbon on temperature and carbon concentration (standard state – graphite) are given in [9]. For α-solid solution, the formula is as follows:

$$\lg a_c = 20000 / 4,575 T - (7,23 - 366,6|C|) / 4,575 + \lg|C|, \quad (5)$$

where a<sub>c</sub> – the activity of carbon.

The activity of the element in solution quantitatively reflects the tendency of the component to leave this phase or to enter into a chemical reaction. Experimental data on the interaction parameter in ferrite are very few due to the difficulty of measuring low concentrations of carbon and due to the fact that the alloying elements either narrow the region of the ferrite, or lead to the release of carbides. At equilibrium of the gas and solid phases, the carbon content in the solid phase is equal to the carbon potential of the atmosphere C<sup>atm</sup>. In some cases, instead of carbon potential, it is more convenient to use the concept of carbon activity in the atmosphere. The activity of carbon in the atmosphere of a<sub>c</sub><sup>atm</sup> is determined by its composition and temperature and is numerically equal to the activity of carbon in the solid phase, i.e. a<sub>c</sub>=a<sub>c</sub><sup>atm</sup>. The solubility of carbon in ferrite does not exceed 0.02 % wt., so when the temperature decreases as a result of polymorphic transformation in the system γ-Fe→α-Fe, the solubility of carbon in iron decreases sharply [10].

In work [11], the issues of reducing and decarburizing processes of iron powders are considered in detail, and an array of calculated data of equilibrium compositions of gas phases in Fe-C-H-O systems in full is given. Lines of carbon

isoactivity at different its content and activities are calculated. The lines are plotted on an iron-carbon diagram. Fig. 1 shows a fragment of the state diagram of the Fe-C system, namely the region of ferrite, which is characterized by the minimum carbon content in iron. You can see that with activities such as 0.004–0.4 you can get soft-magnetic iron (content C  $\leq$  0.007 %). Analysis of the Fe-C diagram and the data of the equilibrium compositions of CGS allows us to conclude that to obtain iron with ultra-low carbon content you should carry out the reduction process in the ferrite region which temperature range is limited to 911 °C. Raising the temperature of the process, respectively, we get to the area of austenite. In turn, this inevitably leads to the possibility of carbon entering the final iron powder, even at negligible values of  $a_c$ . It should be considered also that the reduction of iron powder at high temperatures changes not only the chemical composition but also the physical properties. Thus, in the temperature range of 1000-1200 °C it is strongly sintered. Subsequent operation of long grinding causes work hardening, as well as deterioration of the technological characteristics of the powder (plasticity, compressibility, formability and etc.) At moderate temperatures (700-910 °C) technological characteristics are improved due to a pronounced defect in the crystal construction of the iron lattice. This leads to restrictions on the conditions for obtaining iron with ultra-low carbon content, namely: the reduction of iron must be carried out

in the ferritic area, i.e. at a temperature not exceeding 911 °C. Obviously, the reduction of iron at lower temperatures is much slower. Therefore, given the accuracy of the devices, we stopped at temperatures not exceeding 890-900 °C.

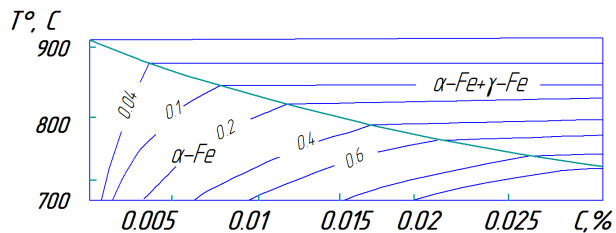


Fig. 1. Fragment of the state diagram of the Fe-C system (ferrite area) [11]. The activity of carbon  $a_c$  indicates on the lines.

### Stoichiometry and thermodynamics of the iron reduction process

The reducing gas can be chemically used to the maximum extent when the process is brought closer to the conditions of thermodynamic equilibrium [12]. Table 4 shows the compositions of equilibrium mixtures of  $H_2+H_2O$  at different stages of iron reduction, as well as the stoichiometric amount of hydrogen required for each stage. When counter-current, the gases of the  $FeO-Fe_{met}$  stage are able to reduce  $Fe_3O_4-FeO$  and  $Fe_2O_3-Fe_3O_4$ , because their number and equilibrium oxidation with a margin exceeds the required values for the reduction of higher oxides [5].

**Table 1.** Compositions of equilibrium mixtures  $H_2 + H_2O$  for the reduction reactions of iron oxides at temperatures of 600-1100 °C.

	Temperature, °C					
	600	700	800	900	1000	1100
$FeO + H_2 \leftrightarrow Fe + H_2O$ [ $Q_{st} = 0,4 \text{ m}^3 \text{ H}_2/\text{kg}_{Fe}$ ]						
H <sub>2</sub> O, %	23.9	29.9	34.0	38.1	41.1	42.6
H <sub>2</sub> , %	76.1	70.1	66.0	61.9	58.9	57.4
The minimum amount of gas for reduction of 1 kg of Fe, m <sup>3</sup>	1.77	1.34	1.18	1.05	0.95	0.93
$Fe_3O_4 + H_2 \leftrightarrow 3FeO + H_2O$ [ $Q_{st} = 0.133 \text{ m}^3 \text{ H}_2/\text{kg}_{Fe}$ ]						
H <sub>2</sub> O, %	30.1	54.2	71.3	82.3	89.0	92.7
H <sub>2</sub> , %	69.9	45.8	28.7	17.7	1.0	7.3
The minimum amount of gas for reduction of 1 kg of Fe, m <sup>3</sup>	0.441	0.245	0.186	0.161	0.149	0.143
$Fe_2O_3 + H_2 = 2Fe_2O_4 + H_2O$ [ $Q_{st} = 0.066 \text{ m}^3 \text{ H}_2/\text{kg}_{Fe}$ ]						
$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$ [ $Q_{st} = 0.6 \text{ m}^3 \text{ H}_2/\text{kg}_{Fe}$ ]						

where:  $Q_{st}$  – stoichiometric flow rate of hydrogen

Thus, at the stage of reduction of magnetite to wustite, the reducing capacity of the gas will be used in full. An even greater excess of hydrogen than it is necessary under equilibrium occurs at the stage of reduction of hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ).

According to the stoichiometry for the stage  $\text{Fe}_2\text{O}_3\text{-Fe}_{\text{met}}$  (900 °C) per 1 kg of Fe it is required  $0.4 + 0.133 + 0.066 = 0.6 \text{ m}^3$  of  $\text{H}_2$ , and the theoretical (thermodynamic) minimum of hydrogen for the  $\text{FeO-Fe}$  stage is  $1.05 \text{ m}^3$ ; that is theoretically remains  $1.05 - 0.6 = 0.45 \text{ m}^3$  of  $\text{H}_2$ . This amount will be unspent. As the reduction reaction temperature decreases, the amount of unused hydrogen increases. In normal practice, this gas is burned on a gas bleeder.

With regard to the industrial implementation of the process, in order to achieve an acceptable speed of the iron reduction process, the hydrogen consumption at the  $\text{FeO-Fe}$  stage instead of the theoretical  $1.05 \text{ m}^3/\text{kg}$  should be  $2\text{-}3 \text{ m}^3/\text{kg}$ . In

this case, the amount of "discharged" residual hydrogen reaches  $(2\text{-}3) - 0.6 = 1.4\text{-}2.4 \text{ m}^3/\text{kg}$ . The only possible solution to eliminate this shortcoming is to organize the recirculation and regeneration of hydrogen. Regeneration consists of the removal of dust and product of iron reduction –  $\text{H}_2\text{O}$ .

### Reduction gases

Let consider the main reduction atmospheres containing hydrogen. Analyzing the chemical composition of reducing agents (Table 2) in terms of the minimum content of impurities in the final metal powder (oxygen and carbon), we refuse to use the convertible natural gas (CG). This is due to the fact that a large number of C-containing components in the CG will inevitably get into the final product during the annealing of the raw powder. Dissociated ammonia, which contains 25 % of nitrogen, fully meets the requirements for high-quality carbon-free powder production.

**Table 2.** Compositions of some industrial reduction atmospheres

	CO	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
Converted Natural Gas (CG)	21.6	3.0	0.1	72.6	1.3	1.4
Dissociated ammonia (DA)	-	-	0.1	75	-	25
Technical hydrogen (TH)	0.5	0.1	1.5	96	1.4	2.0
Electrolysis hydrogen (EH)	0.1		0.1	99.8	-	-

However, it is impractical to recycle it, because as you "scroll" the gas in the system residual nitrogen will be accumulated. As a result, the reduction potential of the gas is reduced and the efficiency of the process decreases.

Obtaining of reduction, hydrogen-containing atmospheres is a rather energy-intensive process. For the production of  $1 \text{ m}^3$  of electrolytic hydrogen, energy consumption is approximately  $5,0 \text{ kW}\cdot\text{h}$ . At iron reduction, hydrogen, even when using its thermodynamic reducing potential of 100 % is still spent only 29–33 % of its stoichiometric amount. In normal practice, after leaving the reaction zone unreacted gas is irretrievably lost during combustion by flare device. At tungsten or molybdenum reducing, the degree of hydrogen utilization is even lower.

Gas recirculation is sometimes used in tungsten reduction furnaces. To do this, there used

pass-through tubular furnaces with loading material into the boats. Furnaces were provided with gas-tight tambours at the loading and unloading ends of the furnace. However, such furnace designs are not acceptable for such large-scale productions as production of iron powder. A necessary condition for the implementation of recirculation in conveyor furnaces is the maintenance of excess pressure in the muffle of the furnace (above 100 Pa). The Gas Institute of the National Academy of Sciences of Ukraine has developed «know-how» that has maintained a stable positive intra-furnace pressure. Improved powder locks on the ends of the conveyor furnace is the elaborated "know-how". The method completely eliminated gas leaks through the upper layer of the powder shutter, eliminated "break throw" of the atmosphere through the powder lock and sudden depressurization of the furnace [13].

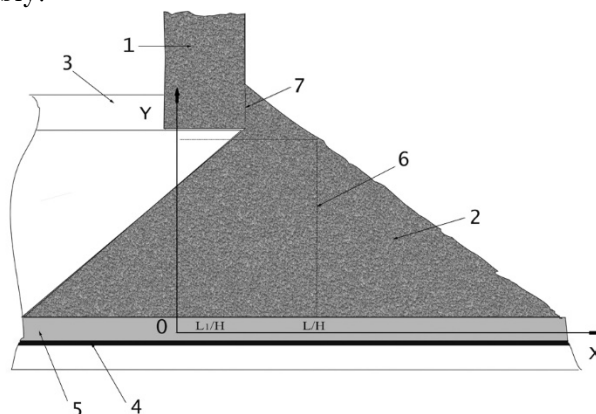


The essence of the method is that immediately before the sintered material removed from the hydrogen-containing atmosphere, a reduced powder of class 0.01–1.0 mm of the same chemical composition as sinter is added to it. After removal from the hydrogen-containing atmosphere, the powder is separated and sent back to the additive. Testing of the method was carried out at the Sulin Metallurgical Plant (Russia) on the basis of the pilot industrial furnace SKZ-2.5.

Let's describe the new method in more detail. The scheme of the powder lock is shown in Fig. 2. Metal powder is loaded through the loading hopper onto the conveyor belt 4. The powder on the belt enters the heating chamber. In which at a temperature of 600–900 °C is it annealed in a hydrogen-containing atmosphere. At annealing process, the powder is caked to the sinter 5 and on the belt 4 enters the cooler 3, which is connected to the heating chamber and the crusher. The crusher is located above the belt in the cooler. The sinter is grinded to a class of 20.0–0.001 mm. Next, the crushed sinter 5 in the form of powder on the belt 4 moves to the discharge slot. Annealed powder of the same composition with crushed powder of a class 1.0–0.01 mm is fed continuously in the hydrogen-containing atmosphere of the cooler 3. It is done immediately before the cut of the unloading slit of the hopper 1. The powder is poured evenly over the entire width of the slit. As a result of pouring the powder, a permanent sealing of the furnace atmosphere is formed. Level sensors signaling a decrease in powder level are installed in the hopper 1. The backfill powder coming from the outlet branch of the belt is collected and separated on a separator, from where it is again sent to the backfill hopper 1.

The gap in the slit 6 is set equal to 37 mm, which completely eliminates the jamming of the grit in the visible slit. Due to the sealing of the furnace with a powder gate, the pressure in the furnace 30 Pa was maintained at hydrogen consumption of 5-7.5 m<sup>3</sup>, which in terms of 130 m<sup>3</sup> per 1 ton of annealed powder. From the outlet of the conveyor belt 4, the crushed sinter and bulk powder is fed into the separator, where part of the powder class 1.0...+ 0.01 is separated and

sent back to the hopper 1. The required level of bulk powder in the hopper 1 is maintained according to level sensors. The furnace works stably.



**Fig. 2.** Powder lock scheme: 1 – hopper, 2 – additive powder, 3 – cooler, 4 – conveyor belt, 5 – sinter, 6 – calculation area, 7 – addition powder window. X axis – L/H. Y axis – current function, H – backfill height, L – backfill length.

Two main modifications of the furnace are developed: SKN-8 with a productivity of 350 kg/h and SKN-10 with a productivity of 700 kg/h (productivity is conditionally calculated on annealing of powders with the oxygen content of O<sub>2</sub> = 1.5-2 % and carbon C = 0.1 % to their final values of O<sub>2</sub> ≤ 0.25; C ≤ 0.02). The SKN-8 an electric furnace became the first in the world practice gas-tight conveyor furnace of reducing-decarburizing annealing. Its introduction at the Sulin Metallurgical Plant in the 80-es of previous century made it possible to establish the production of high-quality powders and to refuse from their import. The presence of gas-tight conveyor furnaces allowed to move closely to the implementation of energy-saving technology of hydrogen recirculation and regeneration.

### Hydrogen utilization factor (HUF)

Under HUF H<sub>2</sub> we will understand the ratio of the actually used amount of hydrogen to the total amount supplied to the reactor. Used hydrogen leaves the reactor in the form of H<sub>2</sub>O. By analogy with the efficiency of heat engines can be written:

$$\eta_{H_2} = [(H_2^{\text{initial}} - H_2^{\text{end}}) / H_2^{\text{initial}}] \cdot 100 \%. \quad (6)$$

Because, the numerator of the expression in the formula is actually the amount of moisture at the reactor outlet, therefore, it is easier to write (6) in another form:

$$\eta_{\text{H}_2} = (\text{H}_2\text{O}^{\text{initial}} - \text{H}_2\text{O}^{\text{end}}) / 100. \quad (7)$$

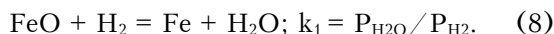
A distinction should be made between stoichiometric hydrogen HUF and thermodynamic hydrogen HUF. The stoichiometric view of the reduction reaction assumes only  $\text{H}_2$  in the left part and only  $\text{H}_2\text{O}$  in the right part. Hydrogen HUF in this case is:

$$\eta_{\text{H}_2}^{\text{st}} = [(100 - 0) / 100] \cdot 100 \% = 100 \%.$$

If, for example, a gas with a humidity of 45 % leaves the reactor and the initial humidity is 5 %, then the HUF of hydrogen will be equal to:

$$\eta_{\text{H}_2}^{\text{st}} = [(45 - 5) / 100] \cdot 100 \% = 40 \%.$$

At calculating of thermodynamic hydrogen HUF, the equilibrium constant of the reduction reaction of the strongest oxide must be taken into account. For our case, this is the wustite reduction:



The joint solution of the equations of the equilibrium constant  $k_1$  and Dalton allows us to find the equilibrium composition of the gas from the known values of the equilibrium constants.

The value of the equilibrium constant  $K_p$  at wustite and magnetite reduction of by the reaction  $\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$  at 900 K – 0.376; 1000 K – 0.465; 1200 K – 0.633; 1500 K – 0.822; by the reaction  $\text{Fe}_3\text{O}_4 + \text{H}_2 = 3 \text{FeO} + \text{H}_2\text{O}$  at 900 K – 0.471; 1000 K – 0.895; 1200 K – 2.423; 1500 K – 6.567.

The reduction reactions proceed without changing the volume of the gas phase. Therefore, in the field of moderate pressure, the equilibrium constant does not depend on the pressure, which allows to replace the partial pressures  $P_{\text{H}_2\text{O}}$  and  $P_{\text{H}_2}$  by percent. Then we get:

$$\text{H}_2^{\text{equilibrium}} = [1 / (k_1 + 1)] \cdot 100 \% ; \text{H}_2\text{O}^{\text{equilibrium}} = [k_1 / (k_1 + 1)] \cdot 100 \%. \quad (9)$$

It is clear that the thermodynamic HUF of hydrogen depends on temperature. Thus, for 1200 K we obtain:  $\text{H}_2\text{O} = (0.633 / 0.633 + 1) 100 \% = 38.76 \%$ . Thermodynamic HUF of hydrogen can be calculated by the formula:

$$\eta_{\text{H}_2}^{\text{td}} = \text{H}_2\text{O}^{\text{fact}} / \text{H}_2\text{O}^{\text{p}} = [\text{H}_2\text{O}^{\text{equilibrium}} (k_1 + 1) / k_1] \cdot 100 \%. \quad (10)$$

Expressions (6) and (9) would be useful further in assessing the effectiveness of various factors. Increasing the thermodynamic HUF of hydrogen is possible due to the optimization of mass and heat transfer factors. However, thermodynamic HUF limits the limit of stoichiometric HUF that can be obtained in one pass through the reactor. Thus, at 1200 K  $\eta^{\text{td}} = 100 \%$  at  $\eta^{\text{st}} = 38.1 \%$ . In the case of a recirculation process, the stoichiometric HUF can be calculated by the percentage of hydrogen discharged from the reactor minus the humidity of this hydrogen.

$$\eta_{\text{H}_2}^{\text{st}} = 100 - \text{H}_2^{\text{discharge}} - W,$$

Thus, when discharging 15 % of  $\text{H}_2$  with a humidity of 10 % we get:

Where  $\text{H}_2^{\text{discharge}}$  – the percentage of hydrogen discharge,  $W$  – hydrogen humidity

$$\eta_{\text{H}_2}^{\text{st}} = 100 - 15 - 1.5 = 86.5 \%.$$

Theoretically, the thermodynamic hydrogen HUF does not exceed 35 %. Due to the introduction of the recirculation-regenerative circuit in the reduction scheme, we were able to achieve the value of thermodynamic hydrogen HUF at the level of 70 %.

### Optimization of iron powder production in a muffle conveyor furnace

According to the results of the research, the optimal height of powder layer was selected, the design of the muffle "clamped" in height was created, hydrogen heating was organized and, most importantly, a system of hydrogen recirculation and regeneration was designed and implemented.

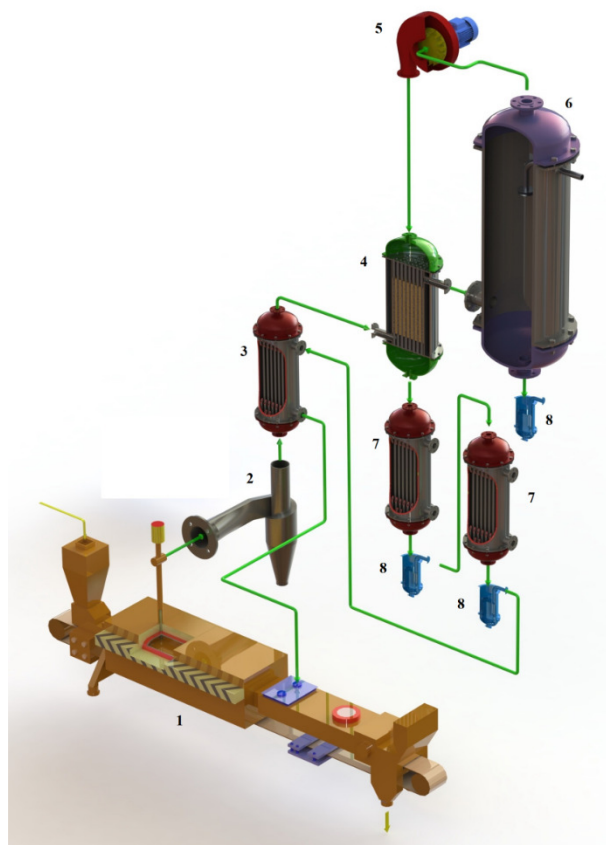
In the work [14] the thermophysical and technological bases of hydrogen recirculation and regeneration at iron powders reduction developed at the Gas Institute of NASU are stated. The main results of the work were the basis of the implemented tender documentation for the establishment of production of carbon-free iron powder in Hyderabad, India. A pilot project for the production of spongy iron with a capacity of 300 tons/year was launched. As the raw material it was used a unique Indian iron superconcentrate "Blue Dust" with a total iron content up to 70 %.

### Recirculation system

The scheme of one of the developed hydrogen recirculation and regeneration systems is shown in Fig. 3. The principle of operation of the recirculation scheme is as follows. The raw material in powder form, containing iron oxide, is loaded into the reduction furnace 1. Due to the electric heating of the muffle heat is supplied to the raw material. Reduction gas – electrolytic hydrogen, which enters into chemical interaction with raw material, is continuously supplied from the furnace cooler. Hydrogen from the recirculation system is fed to the hot zone of the furnace. The reduced material in the form of sinter is sent to the cooler of the furnace. Hydrogen that reacted with the metal oxide is removed from the reduction furnace with a temperature of  $T=870\text{ }^{\circ}\text{C}$  and sent to the cyclone to separate dust particles. Next, hydrogen is fed to the heat exchanger, where the gas gives off heat for heating purified, dried, recirculating hydrogen to  $T=500\text{--}550\text{ }^{\circ}\text{C}$ . Then hydrogen is sent to the catalytic hydrogenation apparatus, where the binding of oxygen to water is occurred on the palladium catalyst at  $T=80\text{--}200\text{ }^{\circ}\text{C}$ . Next, hydrogen enters the scrubber 6 for cooling. Drop moisture is removed in the drop trap 8, to which hydrogen cooled to  $+30\text{ }^{\circ}\text{C}$  is directed. After gas blower 5 hydrogen is directed for hydrogenation. Catalytic hydrogenation is designed to bind air oxygen by hydrogen when it enters the system. After the catalytic hydrogenation apparatus, the gas is cooled in tubular heat exchangers 7, first to a dew point temperature of  $+30\text{ }^{\circ}\text{C}$ , then to  $+15\text{ }^{\circ}\text{C}$ . The dried hydrogen is sent to the cooler of the reduction furnace, where

it cools the reduced material to a temperature of  $\leq 70\text{ }^{\circ}\text{C}$ .

Fig. 3 shows a photo of a new gas-tight furnace. As a result of measures for energy optimization of the unit, the productivity of the furnace is increased by 2.2 times. And the specific consumption of hydrogen is reduced by 2.5 times, i.e. came nearer to the theoretical (stoichiometry) indicators.



**Fig. 3.** Conveyor muffle furnace with hydrogen recirculation and regeneration system.

1 – conveyor furnace; 2 – cyclone; 3 – heat exchanger for heating of recirculating hydrogen; 4 – catalytic hydrogenation reactor; 5 – gas blowers; 6 – scrubber; 7 – heat exchanger-cooler; 8 – drop trap.

Proposed solution allows to return part of the heat to the reduction zone together with purified, recirculating hydrogen. Also, water consumption reduces for the scrubber for cooled, selected after the furnace hot hydrogen [15]. In addition, the heat of hot hydrogen outcoming after the reduc-



tion process is used to heat the catalyst in the heat exchanger of the catalytic hydrogenation reactor, and this also saves energy. Mixing of heated, purified recirculating hydrogen with fresh, deep-dried heated hydrogen and feeding the resulting mixture to the reduction of metals provides the most efficient use of heat in the process, and as a consequence, decreases energy consumption for the process.



**Fig. 4.** Gas-tight conveyor furnace. Design of Gas Institute of NAS of Ukraine. Pilot plant for production of iron powder (300 t/year). Hyderabad, India (photo – D.M. Fedorov).

The authors express their sincere gratitude to Ph.D. Fedorov D.M. for his great contribution to the practical implementation of hydrogen reduction technology, in particular during the launch of a pilot plant in Hyderabad, India.

### Conclusions

A complex of theoretical and experimental studies has led to a number of generalizing conclusions. The purest but energy-consuming gas reducing agent of metal powders is electrolytic hydrogen. According to modern trends it can be called "green" hydrogen. But only its use is the key for obtaining pure on impurities metal powders, in particular carbon-free iron. Ensuring the maximum efficiency of hydrogen use is one of the main factors of energy-technological optimization of the process of high-quality iron production. It was proposed to carry out the process in a conveyor, gas-tight electric furnace by design of Gas Institute of NASU. The gas supply system pro-

vides recirculation of the reducing gas, with its purification from moisture. This measure allows to make full use of gas reducing potential, as well as to intensify the mass transfer process. Technical solutions have been found to ensure the "gas density" of hydrogen conveyor furnaces. The technology and design of industrial, conveyor, hydrogen electric furnace with H<sub>2</sub> recirculation and regeneration have been developed and implemented on a pilot scale.

### References

1. Heck, C. (1974) *Magnetic Materials and Their Applications*. Crane, Russak, New York.
2. Pyron expands across the powder range. (1995). *Metal Powder Report*, 50 (2), pp. 22–26. doi:10.1016/s0026-0657(99)81136-9.
3. Information from the company SECO/WARWICK GROUP – leading global manufacturer of heat treatment furnaces and equipment – access mode <https://www.secowarwick.com/en/>
4. Information from the company Easy Fashion Metal Products Co., Ltd. – access mode <http://easyfashionindustry.supplier.ecer.com/c1562119-reduction-furnace/>
5. Hou, B., Zhang, H., Li, H., & Zhu, Q. (2012). Study on Kinetics of Iron Oxide Reduction by Hydrogen. *Chinese Journal of Chemical Engineering*, 20 (1), pp. 10–17. doi:10.1016/s1004-9541(12)60357-7.
6. Mogutnov B.M., Tomilin I.A., Schwartzman L.A. [Thermodynamics of iron-carbon alloys]. Moscow : Metallurgiya, 1972. 328 p. (Rus.)
7. Naraghi, R., Selleby, M., & Egren, J. (2014). Thermodynamics of Stable and Metastable Structures in Fe–C System. *Calphad*, Vol. 46, pp. 148–158. doi:10.1016/j.calphad.2014.03.004.
8. Chipman, J. (1972). Thermodynamics and Phase Diagram of the Fe–C System. *Metall Mater Trans.* B 3, pp. 55–64. – <https://doi.org/10.1007/BF02680585>.
9. Leonidova M.N., Schwartzman L.A., Schultz L.A. [Physico-chemical bases of interaction of metals with controlled atmospheres]. Moscow : Metallurgy, 1980. 264 p. (Rus.)
10. Rines F. [Diagrams of phase equilibrium in metallurgy]. Moscow : Metallurgiya, 1961. 180 p. (Rus.)
11. Bondarenko B.I., Kurgansky N.P., Pekach V.F. [Reduction-decarburizing annealing of metal powders]. Kiev : Naukova Dumka, 1991. 328 p. (Rus.)
12. J. Bilik , P. Pustejovska , S. Brozovac, S. Jursova (2013). Efficiency of hydrogen utilization in reduction processes in ferrous metallurgy. *Scientia Iranica, Transactions B: Mechanical Engineering*. Vol. 20. pp. 337–342.

13. Certificate of authorship 789248 USSR, MPK B 22F 1/00, [Method of iron powder processing] B.I.Bondarenko, V.F.Pekach, N.P.Kurgansky, A.M.Sviatenko and others. Publ. 23.12.80, Bull. 47. (Rus.)

14. Khovavko A.I. [Development of thermophysics and technological essentials of hydrogen recirculation and regeneration at iron powders reduction: Abstract of Thesis for a Candidate of Technical Sciences Degree].

Kiev: NAS of Ukraine, The Gas Institute, 2007. 20 p. (Ukr.)

15. Pat. Utility model UA 57380 UA, MPK B 22 F 9/22. [Method of Reduction of Metal Oxides in Continuous Units]. Glike A.P., Bondarenko B.I., Sviatenko A.M., Khovavko A.I., Nebesny A.A., Filonenko D.S. u201009438; zayavl. 28.07.2010; Publ. 25.02.2011, Bull. 4. (Ukr.)

Received August 30, 2020

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## Отримання безвуглецевих залізних порошків методом відновлення у конвеєрних печах із рециркуляцією та регенерацією «зеленого» водню

Обґрунтовано використання абсолютно чистого по домішкам водню для отримання безвуглецевого заліза. Такий водень можна отримати тільки електролізом води, відповідно до сучасних трендів його називають «зеленим». В роботі викладено деякі аспекти отримання якісного заліза за методом водневого відновлення у конвеєрній печі. Термодинамічний аналіз процесу показав доцільність застосування рециркуляції відновлювального газу для повного використання його хімічного потенціалу. Введено та розглянуто таке поняття, як коефіцієнт використання водню. Встановлено, що реалізація рециркуляції водню можлива лише на газощільному агрегаті. Розроблено порошкові затвори для ущільнення торців конвеєрних печей відновлення й відпалу металевих порошків. Запропоновано та реалізовано енергоефективну схему відновлення заліза з рециркуляцією та регенерацією водню. Даний спосіб дає можливість наблизити витрати газу до стехіометричних показників. *Бібл. 15, рис. 4, табл. 2.*

**Ключові слова:** відновлення, водень, залізний порошок, рециркуляція, регенерація.

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## Получение безуглеродистых железных порошков методом восстановления в конвейерных печах с рециркуляцией и регенерацией «зеленого» водорода

Обосновано использование абсолютно чистого по примесям водорода для получения безуглеродного железа. Такой водород можно получить только электролизом воды, согласно современным трендам его называют «зеленым». В работе изложены некоторые аспекты получения качественного железа методом водородного восстановления в конвейерной печи. Термодинамический анализ процесса показал целесообразность применения рециркуляции восстановитель-

ного газа для полного использования его химического потенциала. Введено и рассмотрено такое понятие, как коэффициент использования водорода. Установлено, что реализация рециркуляции водорода возможна только на газоплотном агрегате. Разработаны порошковые затворы для уплотнения торцов конвейерных печей восстановления и отжига металлических порошков. Предложено и реализовано энергоэффективную схему восстановления железа с рециркуляцией и регенерацией водорода. Данный способ дает возможность приблизить расходы газа до стехиометрических показателей. *Библ. 15, рис. 4, табл. 2.*

**Ключевые слова:** восстановление, водород, железный порошок, рециркуляция, регенерация.

## Охорона навколишнього середовища

UDC 66.074.52

DOI: 10.33070/etars.4.2020.05

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## Peculiarities of Absorption of Sulfur Dioxide and Nitrogen Oxide in Suspensions and Solutions of Manganese Compounds

It is proposed to use manganese compounds to reduce emissions of sulfur and nitrogen oxides, large deposits of which are in Ukraine. The results of experimental studies of the binding of sulfur dioxide and potassium permanganate of nitric oxide in water by manganese oxide are presented. In the experiments, the model gas in the form of small bubbles was passed through the reactor with liquid. Heat and mass transfer processes between the gas and liquid phases occurred on the bubble surface. The gas-liquid contact time is the bubble rise time. The absorption reactions take place in the liquid phase. Complete absorption of sulfur dioxide takes place in an acidic environment, provided that the molar ratio  $MnO_2/SO_2$  is not less than 2. The reaction product is manganese sulfate, which is a useful product. The maximum absorption of nitrogen oxide is achieved at a molar ratio of  $KMnO_4/NO$  not less than 5. The reaction forms a precipitate of manganese oxide, which can later be used in the desulfurization process. *Bibl. 12, Fig. 6, Tab. 3.*

**Key words:** flue gas, gas purification, sulfur dioxide, nitric oxide, manganese.

The problem of reducing emissions of pollutants generated by fuel combustion in boilers of thermal power plants, heating plants and boilers is becoming increasingly important. Ukraine's implementation of the Energy Community Treaty [1] provides for the incorporation of EU envi-

ronmental directives into Ukrainian environmental legislation, in particular Directive 2010/75/EU on industrial emissions [2] and Directive 2015/2193 / EU on the limitation of emissions of certain pollutants from medium incinerators [3]. To comply with their require-