

HYDROGEN PLASMA SMELTING REDUCTION - AN OPTION FOR STEELMAKING IN THE FUTURE

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The steel industry is a mayor source of global CO₂-emission. Lager reductions of greenhouse gases are the challenge to develop new processes, like Hydrogen Plasma Smelting Reduction (HPSR). The scientific basis and results of HPSR laboratory experiments led to the development of a concept for an HPSR-plant on industrial scale. A technology assessment shows the potential for a cheaper and most environmental friendly steelmaking in the future, when extensive development work has been done.

Key words: *Hydrogen Plasma Smelting Reduction, CO₂-emission, direct steel making, iron ore*

Plazma vodikovo redukcijsko pretaljivanje - opcija za izradu čelika u budućnosti. Industrija čelika je glavni izvor globalne emisije CO₂. Veće smanjivanje stakleničkih plinova predstavlja izazov za razvoj novih procesa poput plazma vodikovog redukcijskog pretaljivanja (HPSR). Znanstvena dostignuća i rezultati HPSR laboratorijskih pokusa doveli su do razvoja koncepta za HPSR postrojenja na industrijskoj razini. Tehnološki trošak pokazuje mogućnost jeftinije i ekološki povoljnijeg načina izrade čelika u budućnosti kada prestane intenzivni razvoj.

Ključne riječi: *plazma vodikovo redukcijsko pretaljivanje, emisija CO₂, direktna izrada čelika, železna ruda*

INTRODUCTION

Because carbon is the main energy carrier and the reducing agent used in iron making, the steel industry is considered to be one of those responsible for global warming. 95 % of all steel made from iron ore is currently made via the blast furnace / basic oxide furnace route (BF-BOF) and 5 % via direct reduction and electric arc furnace (DR-EAF) [1].

A reduction in CO₂-emissions for these processes as required by the Kyoto agreement is only possible to a certain extent since they have already been extensively optimised for energy efficiency over the years [2]. As the demand for steel increases, CO₂-emissions will therefore continue to rise.

The "cap and trade" system, which will set limits on permissible emissions for industry from 2005 and will allow the trading of "emission allowances" in the form of certificates, will increase the pressure on the industry to reduce CO₂-emissions, but will lead to cost disadvantages compared to competitors who must not adhere to this system [3]. In the long term, the only solution is to use hydrogen and electricity obtained without using fossil fuels in-

stead of carbon. A promising solution is hydrogen-smelting reduction - a process that has been under research at the Department of Ferrous Metallurgy at the University of Leoben, Austria, for 15 years [4 - 9].

BASICS

All iron-based materials are originally produced from iron ore. The manufacturing of steel from scrap, a recycling process, will therefore not be considered and compared here. The Fe-O and Fe-Fe₃C phase diagrams are the basis of iron and steel making. In Figure 1., the areas corresponding to the raw materials, semi-finished products and finished products are indicated on these equilibrium diagrams, along with schematic manufacturing routes.

The longest and most time-consuming route is the production of liquid steel via blast furnace and BOF. This is a four-step route in total, since the production of coke from coal and processing of ore fines (sintering or pelleting) are indispensable stages in the route. Although this is the route with the highest CO₂ and other emissions, it is also the route most optimised for energy efficiency. Around 95 % of all steel made from ore is produced in this way. The COREX process can also be deemed to be a variant of this route. Currently, it is estimated that CO₂-emissions can be cut by up to 10 to 15 %, based on current technology. [2].

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5 % of all steel is made from sponge iron (DRI) via various direct reduction processes and the electric arc furnace. This is a 3-step route, including pelleting, or a 2-step route when ore fines are used directly (FINMET). The main reducing agent and energy carrier are reformed methane and electrical energy respectively. The CO₂-emissions per tonne of steel are therefore only 1/2 or 1/3 of those from route 1 [2]. A significant reduction in energy consumption would be possible if DRI could successfully be charged hot and continuously into the EAF.

LI: Liquid Iron HPSR: Hydrogen Plasma Smelting Reduction

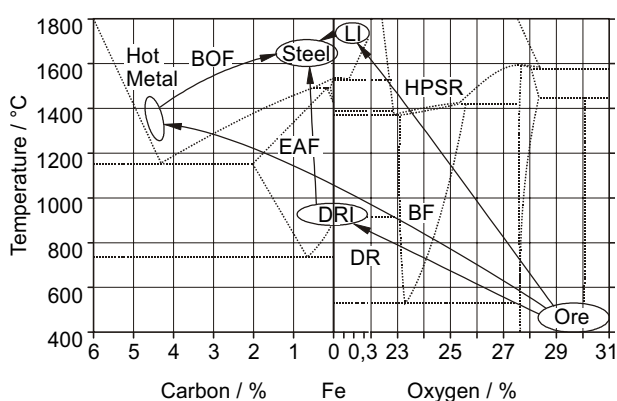


Figure 1. Manufacturing routes for steel
Slika 1. Načini proizvodnje čelika

A third route in future should be the production of liquid iron (LI) in one step, continuously, from ore fines (sinter feed). The LI could then undergo secondary metallurgy, as in the other routes, to produce the required grade. In our opinion, hydrogen plasma smelting reduction (HPSR) is the most suitable process. When hydrogen and electrical energy are generated without using fossil fuels, then CO₂-emissions are very low.

The reducing potential of hydrogen is given in comparison to other redox equilibrium reactions in the Ellingham-Richardson diagram (Figure 2.) [10, 11].

The enthalpies, ΔG°, of the reactions 2H₂ + O₂ → 2H₂O and 2Fe + O₂ → 2FeO are approximately equal over the temperature range shown, meaning that when only thermodynamics are considered, molecular hydrogen does not have sufficient potential to reduce liquid iron oxide.

The situation is completely different for atomic and ionised hydrogen, whose ΔG°-lines are theoretically three resp. fifteen times lower. Both of these states can only be achieved at very high temperatures, such as those present immediately in the vicinity of an electric or plasma arc. Hydrogen then reduces all other oxide systems.

The temperature ranges at which iron oxides (activity = 1) are stable in equilibrium with H₂/H₂O and CO/CO₂ mixtures can be taken from the Baur - Glaessner diagram (Figure 3.) [12]. The curves in the literature are given only up to 1300°C. For this reason the relevant equilibrium curve

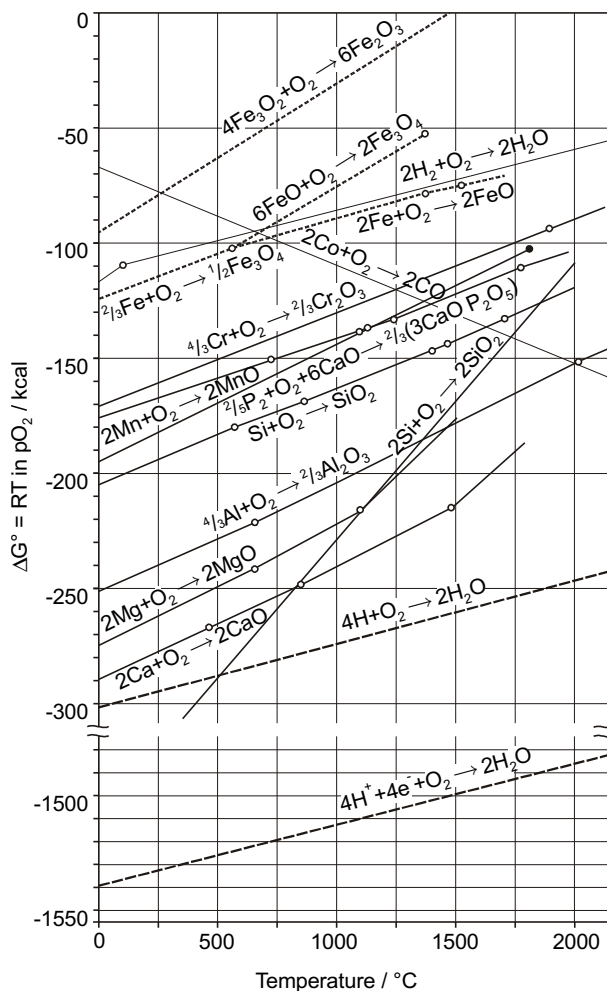


Figure 2. Ellingham-Richardson-Diagram [10,11]
Slika 2. Ellingham-Richardsonov dijagram [10,11]

FeO + H₂/2H ↔ Fe + H₂O was calculated for higher temperatures (3 and 3a).

Hydrogen compared with CO is the better reducing agent with regards to degree of utilisation at temperatures over 800 °C. At 1300 °C an H₂ content of 50 to 55 % in the gas mixture is sufficient to reduce FeO to Fe, whereas at least 80 % CO is required. Above 1500 °C in the liquid oxide-iron phases, the equilibrium ratio of 60 % H₂ / 40 % H₂O remains constant up to 2400 °C, and then falls continuously due to the increasing fraction of reactions of type 3a to below 20 % H₂ / 80 % H₂O-vapour. This means that the degree of gas utilisation at theoretical equilibrium in hydrogen smelt reduction remains constant for a wide temperature range and increases enormously in the arc.

EXPERIMENTS AND RESULTS

The reduction kinetics - the speed at which a reaction moves towards equilibrium and the rate of reaction - cannot be gleaned by considering the equilibrium. The kinet-

ics was measured in comprehensive laboratory tests. Initial blow-through- and top-blow-tests with pure hydrogen in iron oxide melts did not lead to success. No significant reduction occurred within realistic, practical timeframes and the degree of utilisation of hydrogen lay well under the expected 40 % and scattered greatly depending on the test conditions [4 - 6]. The cause was recognised to be the

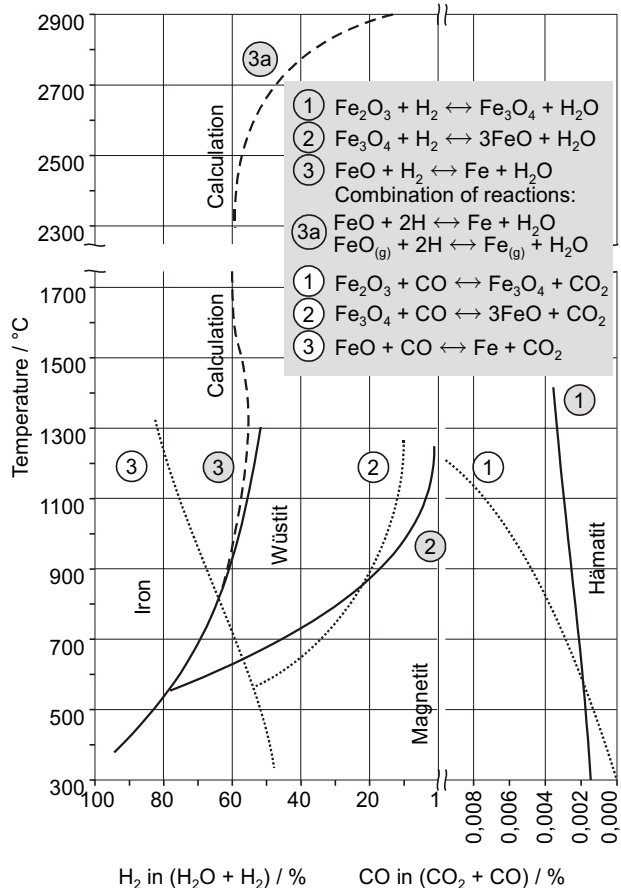


Figure 3. **Baur-Glaessner-Diagramm at higher temperatures [12]**
Slika 3. **Baur-Glaessnerov dijagram kod viših temperatura [12]**

short stay time of hydrogen in the oxide melt and the fact that the reducing potential of the hydrogen lies too low for liquid iron oxide. This led to the construction of a plasma smelting reduction furnace on a laboratory scale [7]. Figure 4. shows the current configuration of the furnace.

Approx. 100 g ore fines or iron oxide (pure or with various additives) are melted in an extra - low carbon steel crucible in an argon atmosphere and then reduced using a hydrogen-argon gas mixture. The energy consumption and the gas flow are measured continuously and the composition of the exhaust gas is continuously monitored using a mass spectrometer. The water - cooled furnace chamber is pressure sealed and the crucible is cooled via its walls. The current and the reducing gas are fed into the furnace via an adjustable-height, hollow electrode made from graphite or tung-

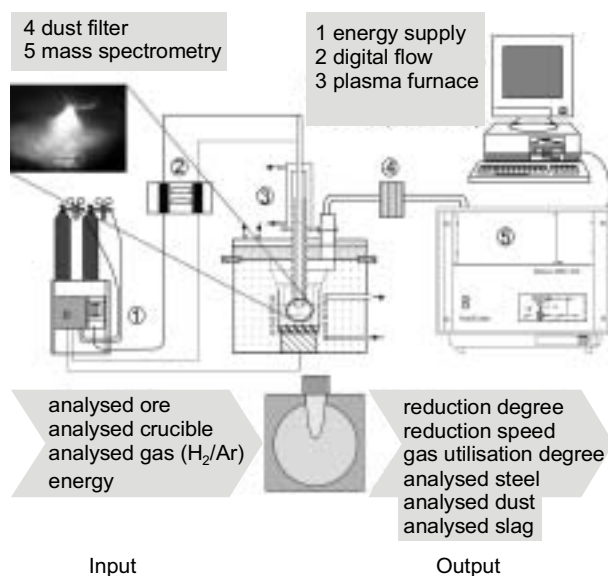


Figure 4. **Laboratory furnace**
Slika 4. **Laboratorijska peč**

sten. The electrical circuit is completed at the anode at the bottom of the crucible. This results in plasma being formed. The melt can be observed and the temperature measured optically through a window. The continuous analysis of exhaust gases documents the progression of the reduction and the utilisation of the gas, i.e. how much of the hydrogen added to the system is converted to water vapour. When the reduction is finished, the furnace is cooled with argon, the crucible containing the solidified metal is weighed and the metal and slag are analysed. The plasma arc results in a large temperature difference within the melt, as illustrated by the 3-zone model in Figure 5. [13].

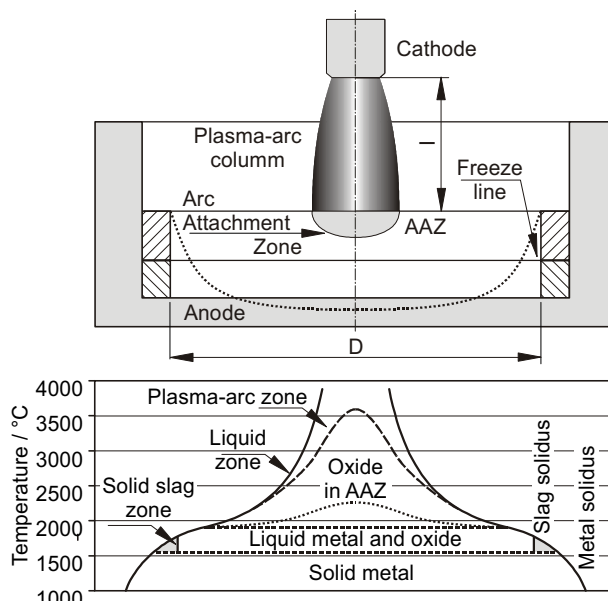


Figure 5. **Three-zone-model [14]**
Slika 5. **Trodimenzalni model [14]**

The temperature of the melt in the arc attachment zone (AAZ) is over 3000 °C, and the atomised and partially ionised plasma gas is hotter still. Oxides and reduced metals are vaporised and condense in colder zones. The temperature gradient at the water-cooled wall and base of the crucible is so large that a solid layer forms at the walls and protects the crucible. On the other hand, the liquid metal around the anode slowly melts the base of the crucible away. The temperature difference and the stirring action of the plasma arc cause a current in the AAZ, where the rate of reaction is very fast. The reduced heavier metal atoms collect at the base of the crucible.

The structure of a molten ore consists of cations, anions and anion-complexes in a particular short-range order, whereby the simple Fe^{2+} and O^{2-} ions account for approx. 95 %. Figure 6. illustrates this schematically for an advanced reduction stage with flow lines and the surface area where the molten oxide comes into contact with the gas.

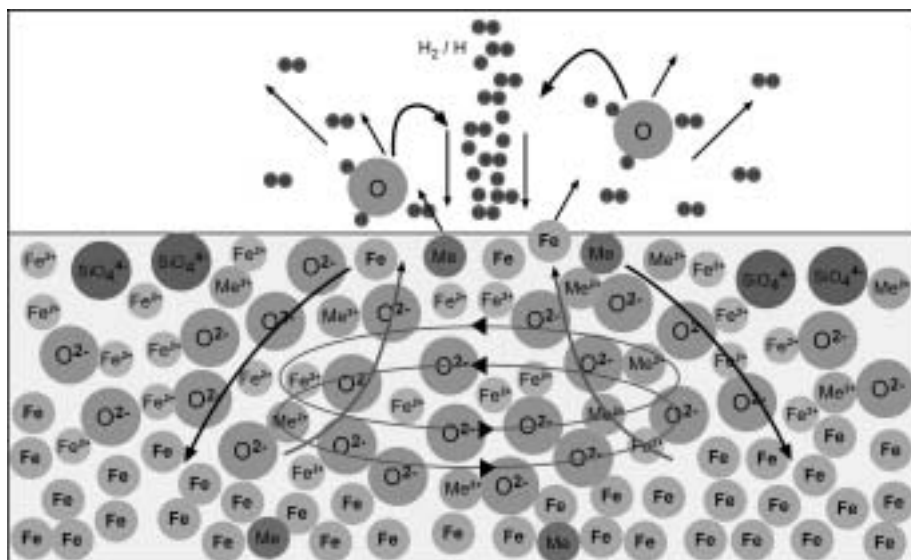


Figure 6. Gas-oxide surface reaction model
Slika 6. Model reakcije na medipovršini plin/oksid

The $\text{H}_2/2\text{H} + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ reaction occurs here and especially in the AAZ at a high rate. Water vapour escapes and promotes the reduction. The electrons neutralise Fe^{2+} to Fe, which then falls to the base of the crucible due to gravity. The same procedure occurs for the divalent Mn and Cr cations. Silicon and aluminium oxide from the acidic gangue in the ore form anionic complexes SiO_4^{4-} , AlO_3^{3-} and PO_4^{3-} which agglomerate. This makes them more difficult to reduce than the simple oxygen ions and they are therefore pushed out to the colder outlying areas of the melt and become even more inactive. At the end of the reduction the acidic, highly viscous slag can be found mainly at the crucible edge. Fe, Mn and SiO also vaporise in the AAZ. These elements and suboxides are

partially reoxidised by the water vapour and can be found in the dust of the exhaust gases. A fraction of the rising gases are sucked in by the plasma arc and reduced again.

In the laboratory tests the ore is melted in an argon atmosphere. Weight is lost in the form of water vapour and perhaps CO_2 or other volatile components and by the loss of oxygen as Fe_2O_3 and Fe_3O_4 are converted to liquid FeOx.

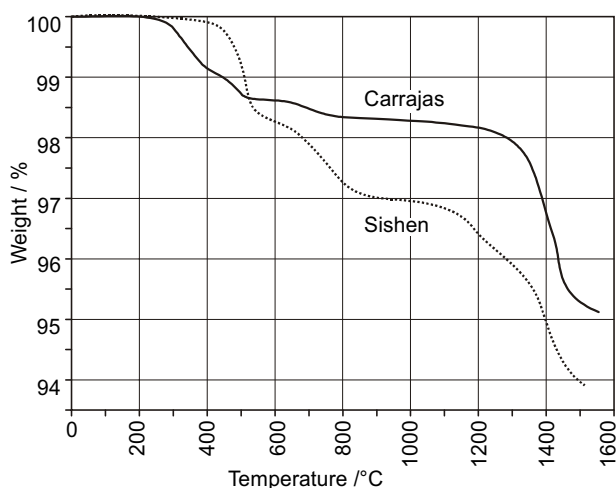
As an example, Figure 7. shows the weight loss of two ores when heated to melting point using the thermo balance. Approx. 3 % by weight is lost as oxygen when hematite ores (sinter feed) are melted, in accordance with the FeO phase diagram (see Figure 1.).

Hydrogen reduction begins at this liquid oxide phase in the laboratory tests. Figure 8. shows the progression of the reduction reaction with time, which is similar in principle for all high grade ores. Numerous tests with different ores have shown this to be true. Even the type of gangue has no significant influence in the usual quantities of up to 5 %.

At the start, Fe^{3+} is primary reduced. This reaction proceeds at the highest rate and with the highest degree of gas utilisation. The Fe^{2+} reduction phase is characterised by a constant rate of reaction until the melt becomes less rich in O^{2-} and the transport in the AAZ controls the reaction rate at a degree of reduction of about 90 %. In this final phase manganese, phosphorous and, to a lesser degree, silicon is increasingly reduced. The degree of utilisation of the gas decreases continuously to about 40 to 50 %, that means 50 to 60 % H_2 in an $\text{H}_2/\text{H}_2\text{O}$ mixture and agrees with the equilibrium calculations (see Figure 3.). Dur-

ing the final phase the degree of reduction is driven to 97 to 99 % in order to keep iron losses below 3 %. Towards the end of the reduction the plasma arc forces the molten oxides, which are becoming increasingly viscous, outwards and reacts direct with the iron melt. The hydrogen content in the exhaust gas increases sharply. Specific tests showed that a deoxidation of the iron to less than 100 ppm O could be achieved during this phase [7, 14]. The remaining slag has a glass-like structure and is primarily made up of silicon, aluminium and manganese oxides. The filter dusts contain mainly iron oxide, manganese oxide and SiO_2 as well as lower levels of metallic iron formed by vaporising and successive partial reoxidation.

H_2 -Ar mixtures containing 15 to 60 % H_2 were tested in laboratory experiments. An increase in the H_2 content of the mixture leads to an increase of the reduction speed, but a decrease in the degree of utilisation of the H_2 . The

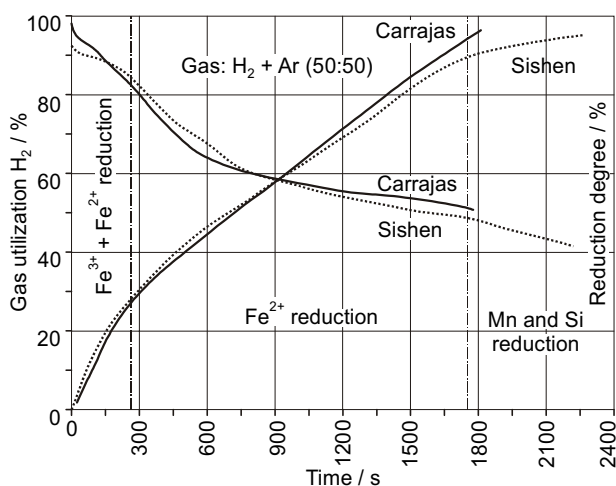


Iron Ore	Fe _{ges}	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	P	S
Carrajas	67,66	0,56	0,84	0,01	0,02	0,31	0,037	0,010
Sishen	65,78	3,45	1,71	0,04	0,02	0,02	0,049	0,015

Figure 7. Loss of weight during heating in argon atmosphere
Slika 7. Gubitak mase tijekom zagrijavanja u atmosferi argona

rate controlling reaction is that at the surface interface between the plasma arc and the oxide melt.

The liquid iron is a mixture of the reduced iron form oxides and molten crucible material. This is why the tramp element content of samples which were allowed to solidify in the crucible and later analysed (analysis in Figure 8.) shows a concentration gradient from the crucible wall towards the centre of the melt. Liquid iron is always cleaner than the crucible material. The C-content, for example, is



Iron from	Fe	Si	Mn	P	Cr	S*	S**
Carrajas	99,73	0,0068	0,0793	0,0091	0,023	0,0085	0,0244
Sishen	99,75	0,0121	0,0550	0,0158	0,024	0,0120	0,0214

* from crucible

** from crucible and C-electrode

Figure 8. Example for test results
Slika 8. Primjer rezultata ispitivanja

always lower in the sample than would be expected from calculations, even though a graphite electrode was used. This means that carbon is being oxidised by the oxide melt or takes part in the reduction reaction. The CO and CO₂ contents of the exhaust gas confirm this. Trials with a tungsten electrode resulted in a C content of < 0,005 % at the surface of the sample: a value at the limit of that which the spectrometer is capable of detecting.

Sulphur, which can come from the ore, the crucible and/or the graphite electrode, is also mostly removed from the melt via the gas phase.

Manganese, phosphorous and silicon are reduced at the end of the process. Dependent on the degree of reduction (< 99 %) and their activities, manganese can be reduced by up to 70 % and P up to 60 % in the sample. Silicon is not significantly reduced but rather vaporises and can be found as a white SiO precipitate in the furnace and the exhaust gas.

A comparison of Carrajas ore and Sishen ore, which was reduced further, showed higher Si and P contents in the sample where the P content before reduction was about the same range and the end slags were similar. Since the degree of reduction is calculated by analysing the exhaust gas, the reoxidation of reduced iron can cause the degree of reduction measured to be low by 1 to 1,5 %, so that the curve never reaches 100 %.

HPSR TECHNOLOGY ASSESSMENT

The mass and energy balance, the way in which the reactions proceed and the metallurgical aspects of the HPSR process can be adequately described and evaluated based on the results of laboratory tests.

The concept behind an HPSR plant for the continuous production of 75 t liquid steel per hour is shown in Figure 9.

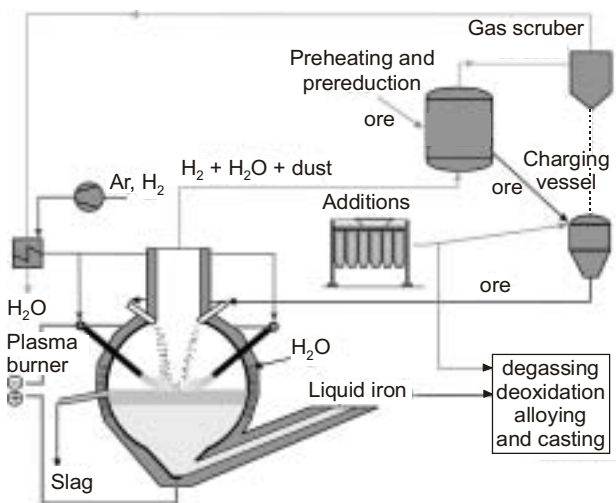


Figure 9. Concept of HPSR-process
Slika 9. Koncept HPSR procesa

This equates to 1,2 million t per year. Ore fines with a particle diameter of between 0,1 and 10 mm are pre-heated in the hot exhaust gas of the furnace and pre-reduced to wustite. This pre-reduction reaction is not of significant importance in comparison to that in the direct reduction processes, since the rate of reduction is much faster and the degree of utilisation of the H₂ gas much higher in the subsequent liquid-state reaction.

The preheated fine ore is transported continuously into the HPSR reactor with any small amounts of lime or dolomite added to achieve a suitable slag viscosity. Six obliquely positioned hollow electrodes, via which the reducing gas and the direct current are brought into the melt, ensure a high-energy concentration. A continuous 82 MW electricity supply and H₂ gas supply of 100.000 Nm³/h are required. Hot exhaust gas from the reactor is mixed with cold gas to achieve the temperature required to pre-heat the ore. The gas is subsequently cleaned and dried, and additional H₂ and Ar are added to make up the required concentration before the gas is recycled back into the process. The degree of reduction is set at least 97 %. This allows the iron losses to be kept to under 3 % and the reduction of phosphor to be kept to under 50 %. Slag (max 6 t/h) is forced to the wall of the reactor, where it acts as a protective layer, and is tapped off in a controlled manner. The degree of reduction can be controlled by the holding time.

The liquid iron is continuously tapped off by the siphon and undergoes degassing to remove hydrogen before it is deoxidised and alloyed to the required grade.

A full-scale version of this concept can only be realised following several years of research work on a pilot plant. The following problems must be addressed:

- continuous pre-heating of the ore fines and transport into the HPSR reactor,
- design of the reactor and control of the high-energy concentration,
- control of the necessary large volumes of gas,
- refractory lining and cooling of the reactor.

In the assumption that these problems can be suitably solved and that an HPSR plant can be built as described, an economic comparison of current and possible future manufacturing routes for steel was carried out. [8,15].

The costs for the 18 most important production factors, including factors such as throughput and credits, were incorporated into a calculated model. In order to more easily interpret the results, the production factors have been grouped together into five cost groups and only the two best of the 14 production processes considered are shown in comparison with a cost-optimised integrated steel mill with a yearly capacity of 3,2 million tonnes (coking, sintering, BF, BOF, ladle metallurgy, CC, hot rolling).

In Figure 10. the current costs per tonne of hot strip produced by this process have been assigned a value of 100

%. The comparison shows that HPSR is the best choice, with a cost reduction of 21 %, and the FINMELT process the next best with a cost reduction of 15 %. FINMELT is a further development of the FINMET process [16] (reduction of ore fines using natural gas) in which the hot DRI is continuously charged into the EAF in a similar way to HPSR. For both process, the yearly capacity needed for cost-effective production is about 1,2 million t / year. A variation in the costs of the different factors of +/- 40 %, based on the current costs of those factors, was also simulated in the calculations and the effect of this variation on the individual cost groups and total costs investigated.

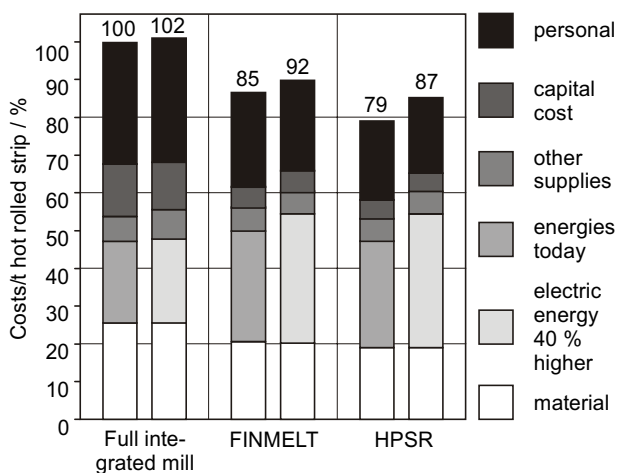


Figure 10. Production costs for different steel making technologies
Slika 10. Proizvodna cijena različitih tehnologija izrade čelika

An increase in the cost of electrical energy - the largest influencing factor for HPSR and required to produce H₂ and for melting - of 40 %, results in the production cost of hot strip increasing by 8 % per tonne. Even then the costs lie approx. 13 % lower than for the current optimised costs of an integrated steelworks.

The other cost groups are significantly lower due to the one-step, continuous nature of the process. This is similar for the two-step FINMELT process.

Figure 11. shows a comprehensive evaluation of the potential of each of the three production routes. A decision on a large development and financial investment cannot be made based on production costs alone. In addition to the quantifiable or partly quantifiable values there are a number of factors which can only be judged subjectively, relative to each other: the smaller the value or the smaller the area on each of the six axes, the more advantageous the process.

The "investment price" (axis I) includes the costs and capital required as well as the revenue from product sales. It indicates the subjective value of a process for each production unit [17, 18]. Since an integrated steelworks is only cost effective as a long process chain of large units

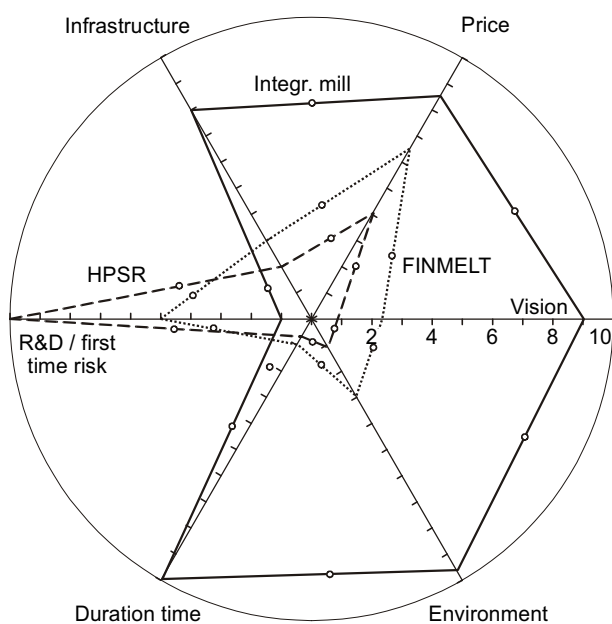


Figure 11. **Technology assessment for different processes**
Slika 11. **Tehnološki trošak za različite procese**

(e.g. 3,2 million t/year), the necessary costs of plant push the “investment price” above that of the simpler and smaller FINMELT and HPSR production lines (1,2 million t/year).

Future possibilities and development potential, relative values, which cannot be calculated but only given subjective, are shown under the heading “vision” on axis II. The development potential (quality and price of the products, energy consumption, flexibility, new processes, infrastructure etc.) of the integrated steelworks, already extensively technically and economically optimised, is low. FINMELT has significant potential for the future in combination with the pre-reduction of ore fines, which has already been tested on a production scale, and the continuous hot feed of DRI into the EAF, which has yet to be developed. The continuous casting of strip fits well in this picture with respect to capacity. The one-step HPSR process has the highest potential for development on all points, in particular the quality of the new product.

Environmental considerations (axis III) also indicate HPSR as a first choice, as long as the energy used does not come from fossil fuel sources. CO_2 , SO_2 and NO_x emission are reduced to a minimum, since they are only generated in heating processes (ladles, tundish etc.). The volumes of slag and dust produced are also low and justifiable. Wastewater contamination is unlikely.

Throughput times and flexibility are considered on axis IV. In a well-organised steelworks it takes approximately 40 hours to get from raw materials to hot strip, and the process has associated cooling losses and interim storage needs (coke, sintered product, pellets, slabs). The estimated throughput time for FINMELT is 5 hours, and that for HPSR 3 hours. This results in a high degree of flexibility

of customer service and in the quantities produced, and a low level of interim storage for products in progress and consequently lower capital lockup.

The research and development needs and the investment risk (axis IV) are highest for the HPSR process and lowest for a conventional steelworks. Experience has shown that new ore reduction technologies require around €100 - 200 million in investment and a development period of around 10 years between conception and the first industrial plant [15]. In addition, it takes about 18 months for that first plant to come into normal production. The first plant risk is highest for HPSR. FINMELT is less risky due to the fact that the direct reduction of ore fines is already proven.

Infrastructure criteria (axis VI) are particularly important when a new steelworks is built. Factors such as the distance to the customer, consistent quality and delivery times, flexibility, simple logistics and the cooperation in development between those who make the steel and those who use it will become increasingly important in the future. Steel users, such as the automotive industry, are based in highly populated, highly industrialised areas. In such areas production facilities can typically only be built if their impact on the environment is small and they require only a small site. An HPSR plant, which is cost effective at a capacity of just 0,8 to 1,2 million t/year in conjunction with a thin strip continuous casting facility, fulfils these requirements ideally. The smaller production units allow specialised production for particular customers and the erection of plants local to those customers. The flexibility to react to customer requests in quality and quantity with short transport distances and no need for warehousing is an unbeatable advantage. In comparison to an integrated steel works the fixed costs such as investment, infrastructure and personnel costs are lower due to the smaller plant size. In addition to the lower costs required running the plant at full capacity, lower fixed costs are advantageous if the plant must be run under nominal capacity. Smaller units also benefit production synergy and are easier to manage.

In the evaluation of all criteria, the small area for HPSR show that it has the greatest potential for the future but also high development costs. FINMELT could be a stepping-stone to what is basically a new, more environmentally friendly steel manufacturing technology for the 21st century, but is limited to use in certain locations due to the need for natural gas. The necessary development work on continuous melting with hot charging of DRI would also be advantageous for the development of HPSR.

CONCLUSION

A new steel making technology based on iron ore with hydrogen as reducing agent and electric energy has been shown. The basic scientific work and technological solutions have been carried out. The results of experiments

have led to the development of a concept for HPSR plant on industrial scale with the capacity to continuously produce an iron melt free of carbon and sulphur in a single stage using ore fines. A technology assessment has shown that HPSR, if it were available today, could result in steel production up to 20 % cheaper than by conventional steel making routes but with higher product quality, flexibility and in an absolutely environmental friendly way.

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