ΣIDERWIN project: electrification of primary steel production for direct CO₂ emission avoidance

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Summary
ΣIDERWIN project proposes to develop a breakthrough innovation compared to the present-day steel production process by applying electrochemical technique to iron metal production. The electrolysis process using renewable energies will transform any iron oxide, including those inside the by-products from other metallurgies, into steel plate with a significant reduction of energy use. This process decomposes under mild conditions but at intense reaction rate naturally occurring iron oxides such as hematite into iron metal and oxygen gas. By developing a low-COsteel production process, the project could contribute to the reduction of the total greenhouse gas emissions. Compared to traditional steelmaking plants, this innovative technology has several positive impacts such as: a reduction by 87% of the direct CO2 emissions; a reduction by 31% of the direct energy use; the ability to produce steel from by-products rich in iron oxides from non-ferrous metallurgy residues; an increased integration with renewable energies with a more flexible process.

Key Words
Iron making, Electrification, Electrowinning, Carbon neutral

Introduction

The steel industry generates between 7 and 9% of direct emissions from the global use of fossil fuel [1]. It operates highly efficient processes and is considered difficult to decarbonize. However, the competitive deployment of renewable electricity might provide an opportunity for the decarbonisation of a portion of the industry, through the direct use of electricity. Deep electrification of iron production could provide a contribution to the abatement of the overall Green House effect Gases emissions [2].

To these regards, H2020-ΣIDERWIN project proposes to develop a breakthrough innovation compared the present-day steel production process by applying electrochemical technique to iron metal production. By assuming that no genuine environmental improvement is possible without significant reduction of the amount of energy exchanged, the electrolytic process is designed and engineered to follow the thermodynamic route of least energy involvement between the starting iron oxide to the final iron metal.

This process has been gradually up scaled from workbench experiments at Technical Readiness Level1 to laboratory pilot at TRL4 during the ULCOS project (2004-2010) and later projects such as RFCS-IERO, ANR-ASCoPE and ADEME-VALORCO. It is based on the electrowinning of iron in alkaline solution at 110°C [3]. Now in the ΣIDERWIN project, a pilot of TRL6 is being built to address the development of the key components of the technology and to operate in a relevant environment.

Thermodynamics

The first step of process development is to consider the production of iron in its most general way regardless of the intermediate steps. The starting component is hematite as a representative of iron oxide from natural resources and the final product is iron metal and the accompanying oxygen. The chemical transformation is considered at room temperature and pressure (1).

$$\tfrac{1}{2}Fe_2O_3 \text{ (s, 25ºC)} \leftrightarrows Fe \text{ (s, 25ºC)} + \tfrac{3}{4}O_2 \text{ (g, 1atm, 25ºC)} \qquad (1)$$
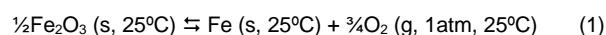
The energy need of the forward transformation is calculated from the thermodynamics properties of the involved compounds [4]. The overall energy demand, *i.e.* the enthalpy variation ΔH, is 2.1 MWh.t_{Fe}^{-1} or 7.4 GJ.t_{Fe}^{-1}. This energy amount is the addition of two forms of energy, the first is work, determined by free enthalpy variation ΔG, and the second is heat, deduced as the complementary energy need $\Delta H - \Delta G$. Heat represents 10% of the overall energy need and at room temperature heat can be considered in free supply from the surrounding atmosphere. Conversely, work represents most of the overall energy need with 1.9 MWh.t_{Fe}^{-1} or 6.7 GJ.t_{Fe}^{-1} and must be supplied from a source of work which is not a spontaneous phenomenon. There is a limited number of energy forms that can supply work. Here

four are considered as mechanical, thermal, chemical and electrical.

If work is supposed to be supplied only by the mechanical form of energy, then a vacuum of gas pressure of $P_{O2} = 10^{-87}$ atm or a centrifugal velocity exceeding v=500 km.s^{-1} must be applied. These figures are extreme and cannot be technically envisioned.

As mention earlier, the reaction of iron oxide decomposition is endothermic and therefore favoured by high temperature. Indeed, heating Wüstite to a temperature higher 3414°C could decompose it. The high level of this temperature compromises material properties needed to maintain these conditions and separation of gaseous iron from oxygen is a challenging task. Nevertheless, conventional processes rely on the application of high temperature as it favours thermodynamically and kinetically chemical reaction and because it is an adjustable parameter that helps to control processes.

The general application of chemical energy is to introduce a reactant "X" with hematite according to the reaction (2):

$$\tfrac{1}{2}Fe_2O_3 \text{ (s, 25°C)} + X \leftrightarrows Fe \text{ (s, 25°C)} + XO_{3/2} \quad (2)$$
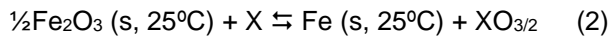
The supply of work from a panel of reactants is represented on an Elligham type diagram, cf. Figure 1. Some of them can reduce hematite into iron at low temperature, here below 300°C. Hydrazine does not evolves carbon dioxide but it reacts far from the conditions of equilibrium [5]. Formic acid [6], formaldehyde, acetylene, ketene and methanol could be candidate for hematite reduction but none of them is carbon neutral, they all oxidise by evolving carbon dioxide.
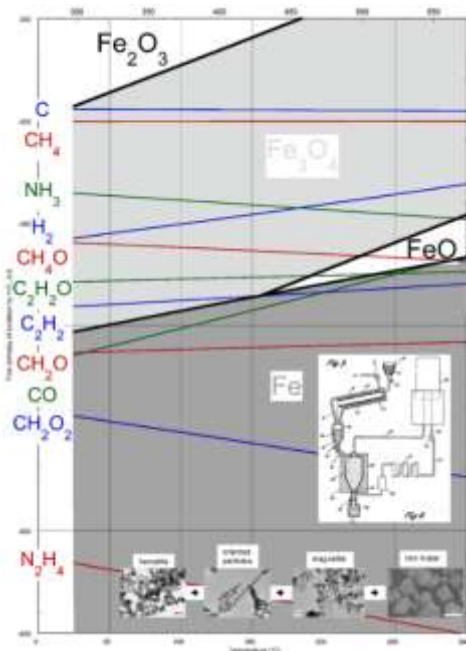

Figure 1: Ellingham diagram.

If work is provided from electrical energy, then a voltage of 1.28V is necessary. This condition is easily applied due to the large variation of electrical resistivity among materials, *i.e.* it is easy to find good conductors and good insulators [7]. Thanks to this advantage, electrical energy can be channeled efficiently through cables and grids, thus gaining in flexibility and controllability that explain to a large extend why electricity is an established energy vector. Furthermore, electricity can be produced from any kind of primary energy resource, either fossil fuels, nuclear or renewables and these energy sources can be mixed and their respective share may change in time.

All the iron producing processes are a combination of these energy forms that can be represented in a tetrahedra cf. Figure 2.
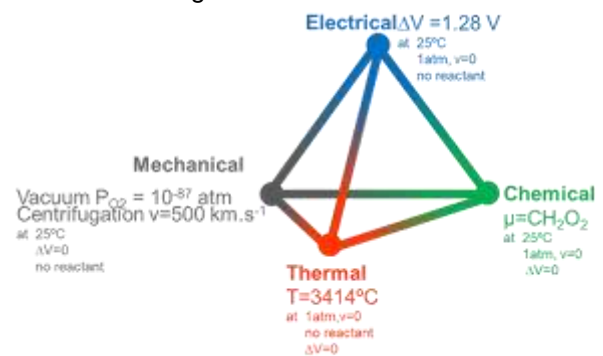

Figure 2: Parameters for iron making processes.

Electric based decomposition of iron oxides

Although convenient, electricity as an energy form is impossible to apply directly on iron oxides dues to the absence of electrical charges born by the constituting elements. Hematite is an electrical insulator and application of the 1.28 V would not produce any change. To overcome this shortcoming, an electrolyte is necessary that separates iron and oxygen as distinguished ions. Among the different options, the most straightforward is water that has the additional property to transfer oxygen. The equilibrium diagram drawn by Pourbaix [8] shows that there exist two domains one in the acidic condition and the other in the alkaline condition, cf. Figure 3.
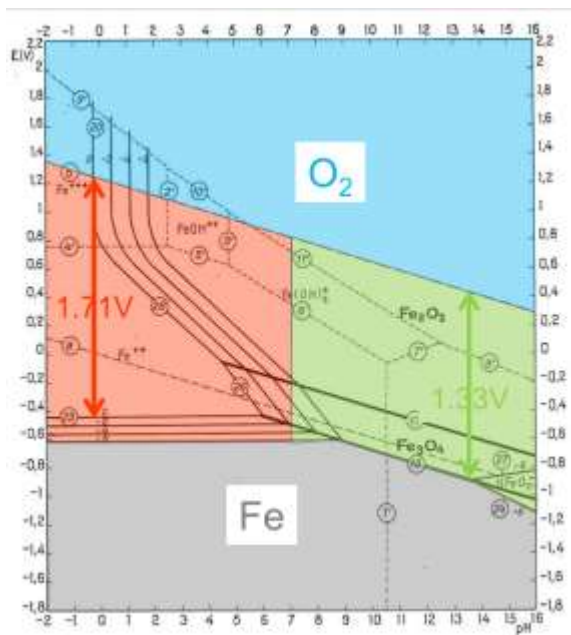
Figure 3: Pourbaix diagram of iron.

In the acidic condition, hematite dissolves spontaneous into ferric iron and water as high soluble salts. However, two limitations can be noticed, firstly soluble cations are stabilised as hydrated species which increases the thermodynamic need to 1.71 V and worse iron has a second cation valence as ferrous iron. These two valences produce an electrical loop where ferric iron can be reduced as ferrous iron at the cathode with the reverse reaction at the anode. Introduction of process components to counter acting this short circuit, as membranes for example, would compromise the energy efficiency of the process. Conversely, in the alkaline domain, iron is hardly soluble, with a single soluble specie as ferrous iron. This seems detrimental for a potential process operating at high production rate. However, an extensive series of experimental work as shown that an electrochemical route is possible, it involves a three steps scheme [9] [10] [11] [12]:
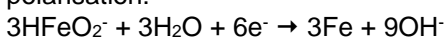
❶Chemical reaction of hematite with soluble ferrous iron:
$Fe_2O_3 + HFeO_2^- \rightarrow Fe_3O_4 + OH^-$
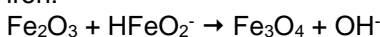
❷Galvanic coupling of magnetite with iron:
$Fe_3O_4 + Fe + 4OH^- \rightarrow 4HFeO_2^-$
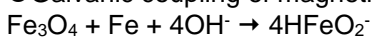
❸Electrocrystallisation of iron under cathodic polarisation:
$3HFeO_2^- + 3H_2O + 6e^- \rightarrow 3Fe + 9OH^-$

This succession of reactions relies on the reactivity of magnetite made possible by its high electronic conductivity, magnetite being the most conductive oxide thanks to the multivalent iron cations in octahedral sublattice of its inverse spinel structure. The resulting thermodynamic voltage corresponds to magnetite reduction which incurs a low penalty with a cell voltage of 1.33 V. The electrical form of energy provides not only the thermodynamic need but also the activation of the electrochemical reactions and it is easily adjustable.

Design of an electrolysis route for steel production

To apply the electrochemical conditions for high production rate a dedicated process unit must be designed. The approach followed is to limit the energy involved by thermodynamic optimisation. Firstly, the energy supply is made accurate in terms of amount, of form and of intensity. The unit operates close to thermodynamic reversibility and includes a ratchet effect to orientate the progress of reaction (1) in the forward direction. The temperature and pressure conditions of operation are chosen as close as possible to surrounding conditions, to minimise heat and pressure losses. The energy and material flows are straight or "once through" flows to minimise the number of loops and of internal recirculations. The process has few chemical mixing, dissolution or dispersion steps. The transfer resistances are minimised, particularly ohmic voltage between electrodes. The conditions of transfer are uniform in space which means no hot spots or not dead zones. This uniformity is maintained steadily in time, which means that transients are minimised.

To fulfil these prescriptions a new concept of electrochemical cell has been engineered. It is based on parallel plate electrodes for uniform current distribution. The anode is chosen to be positioned at the top to separate oxygen by spontaneous buoyancy. The supply of solid particles on the cathode surface is obtained by moderate electrolyte flow rate. Anode geometry is chosen to act as a gas-electricity exchanger, it has maximum openness for gas bubbles to flow upward and minimum inter electrodes gap distance. The gas is collected and its residence time is minimized with an overall 45° inclination of the cell [13] [14] [15] [16].

These concepts have been tested on a pilot operated during the ULCOS (2004-2010) and IERO projects (2010-2014). It could have been possible to check that steady state operation is obtained either thermally, hydraulically or electrically. Electrolysis does not require separators between electrodes such as membrane or diaphragm. The distance between electrodes could be reduced down to 1 cm. The production rate can reach 1000 A.m^{-2}. Self-standing, stiff, compact and conveyable metal plates were produced under low voltage of $\Delta V=1.7V$. The oxygen gas was fully recovered. Cheap construction materials were chosen for the construction of the cell [17]. The integration of these functions into a single cell corresponds to a TRL4.

Figure 4: TRL4 Pilot and iron plate.

ΣIDERWIN project

To progress further toward a solution for carbon neutral steel production by 2050, a new project has been launched [18]. The H2020 -ΣIDERWIN has started in 2017 for five years. Its main purpose is to develop a breakthrough innovation compared to the actual steel production process by producing iron metal with an electrochemical processing route. The process unit is designed to operate at high energy efficiency, to be flexible in production rate and to be supplied with iron oxides from residues of non-ferrous metallurgies. It will result in the design, construction and operation of an experimental pilot cell, cf. Figure 5.

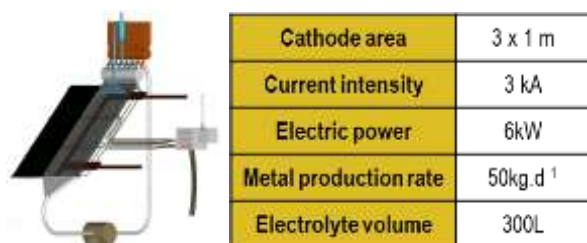| Cathode area | 3 x 1 m |
Current intensity	3 kA
Electric power	6kW
Metal production rate	50kg.d^{-1}
Electrolyte volume	300L

Figure 5: Main objectives of the ΣIDERWIN pilot.

During this project the main key components of the technology will be addressed. The cell will be developed to evaluate the potential of the design for the size of the final industrial cells. The cell will incorporate an oxygen gas collecting system. The harvesting of the metal plates requires a dedicated development that will be tested. The continuous supply of iron oxide according to its consumption will be developed. Furthermore, this process is intended to be integrated in the electrical grid and to contribute to the integration of Renewable Energy Sources. For that purpose, the production rate flexibility will be

developed by studying growth of metal deposit at low temperature and with variable rates. Fine, concentrated and alkaline sources of iron oxide are produced by other metallurgies than iron, they represent a cheap feedstock particularly well suited for ΣIDERWIN.

From such a technology a significant reduction of the specific energy need is expected with 3.6 MWh. t_{Fe}^{-1} or 13 GJ. t_{Fe}^{-1} for the overall process from iron ore to liquid steel. This could achieve a reduction by 87% of the direct CO_2 emissions.

First results of ΣIDERWIN project

During the first months of the project an industrial plant concept has been proposed. It is based on a plant architecture where cells are assembled in series in bipolar configuration with permanent electrical connections. Stacks of cells are made interruptible with vacuum switches. The confinement of electrolyte, gas and electrical circuits is the main contribution to the safety. The maintenance of the plant is facilitated by involving static components which assumes *in-situ* harvesting. The state variables of the process have been identified and the corresponding probes to measure them.

The basic engineering of the pilot has been completed, cf. Figure 6. The P&IDs of the electrolyte, electric, gas circuits have been drawn incorporating the studied main key components.

Figure 6: ΣIDERWIN pilot.

Conclusion

Carbon dioxide emission from steel plants are process-related, they are produced from chemical reactions other than combustion. It represents a major engineering difficulty [19]. However, an electrochemical route to decompose iron oxide in mild conditions represents a considerable advantage for steel to achieve lower carbon emissions. The corresponding process is currently developed at an engineering level and the main technological

components are being addressed. High energy efficiency could be possible thanks to conditions close to reversibility, additional economic advantages can be obtained from flexibility and participation to Demand Side Response. ΣIDERWIN is a possible technology for steel production in an energy environment which contains a high share of RES.

Abbreviations

GHG	Green House effect Gases
TRL	Technical Readiness Level
RES	Renewable Energy Sources
DSR	Demand Side Response

Acknowledgments

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