CONTRIBUTION TO ENVIRONMENTAL SUSTAINABILITY

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Summary:
At the Paris Climate Summit in 2015, the world governments agreed to keep the global temperature rise under 2°C, if possible 1.5°C, by the end of this century to avoid the worst impacts. The steel industry is actively dedicated to meeting society's needs and advancing environmental stewardship, achieving a 40 % reduction in energy intensity and a 50 % reduction in greenhouse gas intensity since 1990, reaching an average 1.8 t CO_2/t crude steel. The contribution of the refractory industry is more limited in this fight, but necessary regarding health safety, environment and energy deployed. We will review in this paper our main innovation concerning the reduction of fumes and BaP's during installation, some way for decreasing deeply the preheating time and consequently the energy consumed as well as the development of new insulating refractories based on natural biogenic raw materials.

1. Introduction

The Paris Agreement marked a big change in the global fight against climate change. The world emits around 50 billion tonnes of greenhouse gases each year that are measured in carbon dioxide equivalents (CO_2eq). UN Intergovernmental Panel on Climate Change (IPCC), has limited the global temperature rise to 1.5°C since pre-industrial levels.
The European Union is in the process of finalizing standards for defining a Climate-Transition Benchmark (CTB) and a Paris-aligned Benchmark (PAB), both of which use absolute measures to align with a 1.5°C trajectory rather than simply a relative carbon reduction.

Emissions come from many sectors [1] (fig.1). The industry is playing a significant role for achieving the goal fixed for 2050 [2].

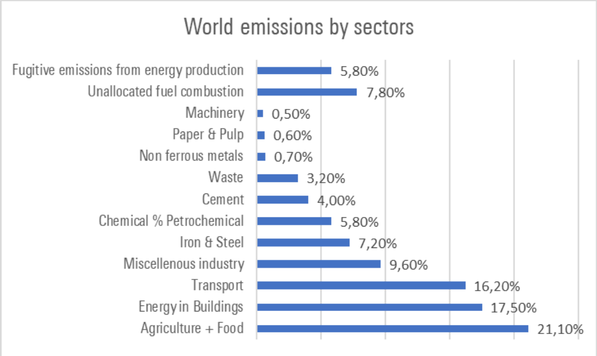

Figure 1: Energy emissions by sectors [1]

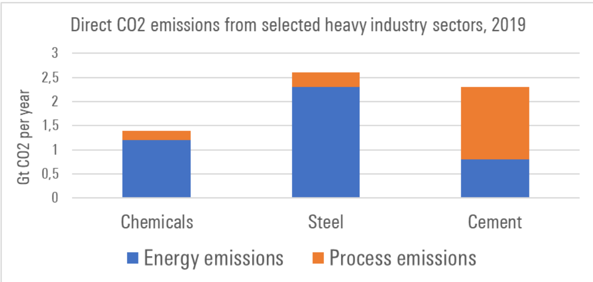

Figure 2: Direct CO_2 emissions from selected heavy industry sectors, 2019 [2]

Without targeted measures to reduce CO_2 emission the overhaul of the steel and cement production are projected to continue rising. To meet global energy and climate goals, emissions from the steel industry must fall by at least 50 % by 2050, with continuing declines towards zero emissions being pursued thereafter. Actually with a relative emission intensity of steel production close to 1.4 t CO_2/t more efficient use of energy and materials has to be proposed. Replacement of inefficient process units and introducing multiple ways of production, by using new reduction agents like hydrogen or introducing new scenario with EAF and scrap shares

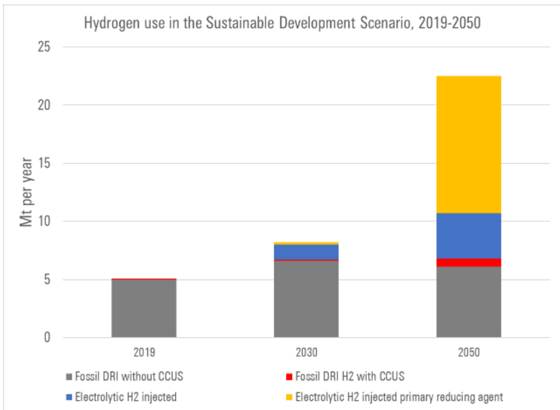

Figure 3: Hydrogen use in the Sustainable Development Scenario, 2019-2050[2)]

Hydrogen, carbon capture, use and storage (CCUS), bioenergy and direct electrification with better efficient processes are worldwide in exploration but also in existing assets by investments for the deployment of new technologies.

2. Upcoming technologies

2.1. Hydrogen introduction in the blast furnace tuyeres

TKS company aims to be carbon neutral by 2050 and to reduce emissions by 30 % by 2030. The use of hydrogen instead of carbon could theoretically save around 20 % of the CO_2. The world's first trial to supply hydrogen was carried out at the Duisburg-Hamborn site in 2019 using one of the 28 blow tuyeres on blast furnace 9.

2.2. Converting CO_2 in valuable materials:

The steelmaking gases produced during steel production, which contain large amounts of CO_2, among other things, are converted into valuable chemical raw materials. These can then be used to manufacture many useful products such as fuel, fertilizer or plastics.

2.3. Hydrogen-based DRI production

Due to the lower carbon footprint of the scrap-based EAF route, this process is clearly in advantage regarding CO_2 emissions (455 kg CO_2 / t crude steel) [3]. This can be applied in the MIDREX-DR process with possible hydrogen addition. Simulations performed by ArcelorMittal Hamburg GmbH -owner of the single DR-plant in Europe with an annual production of approximately 0.55 Mt of cold DRI- showed an overall hydrogen demand of 635 m^3_{STP} /t HBI including energy losses.

2.4. Innovative smelting reduction gas based DRI

The replacement of the BF by smelting reduction processes like the COREX or FINEX process would raise slightly the CO_2 footprint due to the high consumption of fossil coal. An ecologically favourable operation of smelting reduction processes only could be realized by the use of CCS (carbon capture and storage) or CCU (carbon capture and utilization). The use of a smelting reduction technology based on bath-smelting (HISARNA-CCS/U and EAF) in combination with CCS would reduce the CO_2 emissions by up to 80 % [4].

3. What could be the contribution of the refractories

3.1. CO_2 emissions of refractory products

The number of product used can vary considerably depending of the segment of industry. The cement industry can be covered with less than 20 products whereas the steel industry with the different aggregates needs more than 1000 products.

The specific consumption can vary a lot depending on the technological advancement of the countries. It is generally admit that annual production of refractory reach 25 Million tonnes tendency increasing. The average specific consumption by industry is shown in figure 4.

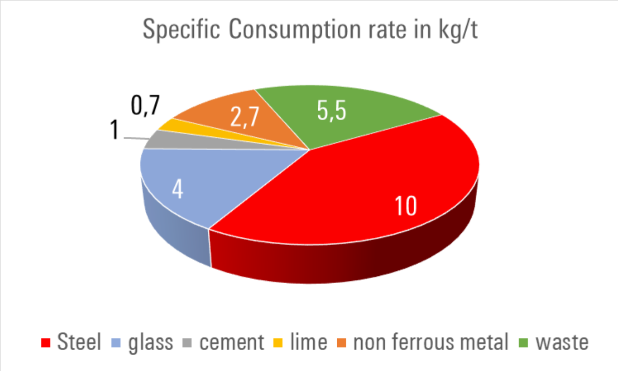

Figure 4: specific consumption by sector

The emission factors for some raw materials have been summarized in Table 1 [5]

Raw material	Emission factor [kg CO_2/t raw mat.]
Silicon carbide	5770
Chromoxid	4000
Fused magnesia	2602
Dead burned magnesia	1927
Dead burned dolomite	1449
Fused mullite	1128
Brown fused corundum	1000
White fused alumina	1000
Zirconia	804
Fused silica	685
Fireclay	675
Magnesia spinel	159
Andalousite	143
Chrome oxide	7
Graphite	7
Bauxite	5

Table 1: Emission factor from some raw materials [5]

The emission factors for major products (Table 2) could be approached after the model proposed from S. Strubel [5]

3.2. New developments

3.2.1. Hydrogen resistance of refractories

Hydrogen is a strong reduction agent enabling the reduction of SiO_2, Fe_2O_3, TiO_2, Cr_2O_3 whereas Al_2O_3 and MgO are more stable. Materials based on andalusite or mullite as well as silica containing binder should be avoided. At a temperature up to 1250°C the corrosion of mullite based refractories could be so severe that formation of silica whiskers can be

Productr group	Refractory product	Emission factor [kg CO_2/t]
Burned non basic bricks	Silica bricks	104
	Fireclays bricks	507
	Andalousite+ Mullite bricks	307
	Bauxite+ Corundum bricks	1007
Burned basic bricks	Magnesia bricks	1914
	Magnesia-Spinel bricks	1747
	Magnesia-Chromite bricks	1467
	Magnesia-Zircon bricks	1642
Unfired non basic bricks	AMC bricks	1152
Unfired basic bricks	MgO-C resin bonded bricks	1965
	MgO-C pitch bonded bricks	1615
Unshaped products	Alumina mixes	647
	Magnesia mixes	1149

Table 2: emission factor for some refractories [5)]

observed. The formation of gaseous SiO and H_2O occurs when SiO_2 reacts with hydrogen according to the equation in particular in the grain boundaries:

$$SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)$$

wehre (s) signifies a solid phase and (g) a gaseous phase.

The removal of the SiO_2 contributes to an increase in porosity near the surface

But the reaction is kinetic depending and even at 1050°C over 500 hours a porous layer can be produced.

Hervell[7] reports that in hydrogen atmospheres, the presence of calcium promotes the crystallization of the glassy grain-boundary phase bediellite at 1050°C

Therefore the resistance against hydrogen will be now become more important for determine the proper choice of refractories.

The environment of Hydrogen will also influence strongly the thermal conductivity of the products and constructions with an increasing factor close to 7. The choice of the insulation will be sometimes critical.

3.2.2. Hot abrasion MgO-C for BOF converter

Higher reduction of the hot metal ratio (HMR) will have some consequence to the wear in the impact area. A new positive experienced concept of MgO-C bricks with stainless steel fibres is still available and positively industrially implemented worldwide[6].

3.2.3. DRI/HBI furnace refractories:

There different technologies for producing DRI (or sponge iron) as shown in Figure 5 depending of the availability of gas or coal. But main process actually are MIDREX and HYL for shaft furnace and SL/RN for the rotary kiln process.

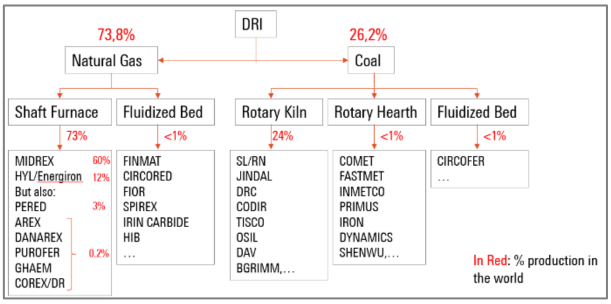

Figure 5: Main type of DRI processes

DRI/HBI will play a significant role in the future for the steel industry. All major groups are actually working in this way for reducing the actual detrimental importance of the blast furnace on the CO_2 emissions. This will be the way to reach a reduction 30% up to 2030 and being climate neutral 2050 for ArcelorMittal. Similar target for TKS will change the structure of the integrated steelshops.

DRI/HBI pellets are actually commonly used outside Europe in EAF in particular in India where the range of refractories has been optimised in last decade enabling with new developed MgO-C bricks spectacular good performance even in CONARC furnaces with tough processing.

3.2.4. Insulating material with low CO_2 emission

A new generation of high value insulating material on naturally renewable raw materials has been recently developed. Because rice husks are burned for carbon-neutral energy generation, and the resulting ash has a high melting point and low thermal conductivity this raw material with high micro-porosity is suitable for application temperature up to 1540°C. Shaped as a board the resulting material can be perfectly used for EAF, torpedo ladle or tundish insulation. This material is also available as insulating bricks and produced from Refratechnik. Apart the lower thermal conductivity these materials are alkali resistant and can resist to molten steel contact (Figure 6). The thermal conductivity reaches 0.25 up to 0.35 W/m.K at 1000°C depending of the density and material resistance of the product.

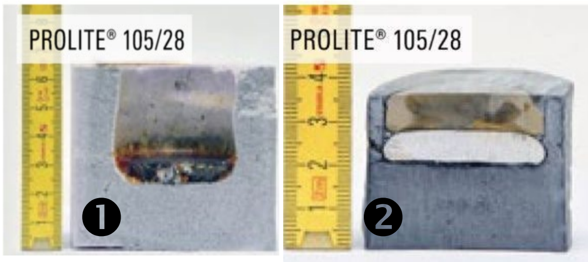

Figure 6: Alkali cup test resistance with 30 g K_2CO_3/1100°C /4 hrs (1) and against molten steel 1600°/6 hrs (2)

3.2.5. Energy savings materials

New monolithic materials based on Nanobond sol-gel technology or Hybrid technology are enabling a safe and very quick preheating of all furnaces, improving the availability and the performance without any risk of cracks or explosion. For example such a material is used as steel ladle lip ring in ArcelorMittal. (Figure 7) in an electric steel shop enabling a reduction 170 kNm³ gas/year (1100 t CO_2).

A new generation of improved sol-gel materials has been perfectly designed to be used e.g. in the lining of the runner on the blast furnace cast house. The remarkable higher mechanical strength of those hybrid materials added to the quick preheating open a wide field of applications in particular in the range of the precast pieces.

Newly developed Hybrid® range materials will deeper help the user associating a good mechanical resistance in the middle temperature range between 500 and 1000°C by

maintaining top properties at high temperature with a very good thermal shock resistance. This is opening new fields of application for example in reheating furnaces where the respect of the heating rate at lower temperature very often is difficult or illusory. This allows a preheating reduced more than 50% without consequence ion the microstructure of the refractories.
Due to their multiple advantages these materials are now standard in revamping of blast furnace shafts.

Figure 7: Cast of the lip ring in the steel ladle with Sol-Gel material

3.2.6. Recycling of materials

Recycling is a common way of reducing the carbon footprint of products. It is already used in many areas, such as MgO-C.
Material with up to 75% recycling are now available with lowest impurity levels and consistent properties.
After H.Jansen[6] an annual production of 40,000t MgO-C with a replacement of 25% of fresh material could induce an annual savings 15,848T CO_2.
Recycling despite the well-known issues like sorting, logistics and QC, recycling will definitely play a bigger role in the future.

Conclusion

Climate strategies are stepping up the existing activities in major industries to reduce emissions, stand for social responsibility and are committed to the Paris Climate Change Agreement of 2015.
Major steps for reducing the emission are focused in several innovative process ways or modification of actual assets.
The input of the refractory industry will be a contribution to the success of the new innovative ways of production by stabilizing the performance of the assets.
Reaching the very ambitious goal of Paris agreement's goals will be easier by working together to the same target in a more holistic approach to transition risk.

References:

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