Steel and CO_2 – the ULCOS Program, CCS and Mineral Carbonation using Steelmaking Slag

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Abstract

Over the past 40 years the European steel industry has reduced its CO_2 emissions with approximately 50 to 60%: this is the highest level of energy conservation achieved by any industrial sector. This is due to several decades of cost management, as high energy prices have driven the industry to optimise its processes as close as possible to physical (thermodynamic) limits. Cutting CO_2 emissions further, to the level that post-Kyoto policies require, raises therefore specific challenges: it is indeed necessary to uncouple energy savings and CO_2 reduction in the Steel sector. There is no simple process, available off-the-shelf, that can accomplish this. Deep paradigm shifts in the way steel is produced have to be imagined and the corresponding breakthrough technology designed and developed. The largest R&D program, called ULCOS (Ultra Low CO_2 Steelmaking) has been running in the EU since 2004 to progress in this direction. The present paper gives the current status of the various ULCOS options. In particular, attention is drawn to the use of CCS and mineral carbonation within new ULCOS technologies. CCS has been identified from the start as a powerful solution. Mineral carbonation has also been assessed, showing that it can only result in moderate, albeit important, overall emissions reductions. Therefore, mineral carbonation, in particular, needs more detailed elaboration before it can be considered as an option compared to geological CCS.

Introduction

Steel is among the major structural materials in the world, with its production coming second only to that of cement. Iron and steel have been used for several thousands of years, either to make artifacts, from buildings to automobiles and from guns to cans, but also tools and machines from which all other artifacts are made. Steel is ubiquitous. The history of mankind is completely interwoven with that material. Behind the name of steel hide several thousands of different alloys, the largest family of materials ever. The Steel industry, which produces steel, is a sophisticated, modern and capital intensive industry. It features some of the most impressive engineering reactors, such as the blast furnace, which is unique and probably as powerful and complex as a nuclear reactor or a large rocket used to raise heavy payloads to orbit.

Steel production in 2007 amounted to 1.342 Gton and in 2008 to 1.329 Gton. Anthropogenic emissions of GHGs, which amounted to 49 Gton of CO_2 equivalent worldwide in 2004,[1)] are traditionally split among economic sectors, among which industry represented 19.4%. The Steel Industry represents 6 to 7% of global anthropogenic CO_2 emissions according to the IPCC,[1)] but only 4-5% according to the IEA,[2)] *i.e.* one fourth to one third of the whole industry sector. These estimates include direct emissions by the steel mills themselves and indirect ones, generated by the energy sector to produce the electricity that the mills consume. This accounting method leaves out a life-cycle presentation, where the benefits of using steel, in terms of CO_2 emissions that can be allocated to using it, would be taken on board: this would account for avoided emissions at least an order of magnitude larger than the emissions of the steel mills. But in a traditional analysis, this scenario modeling of a society that uses steel, against an hypothetical one that would not, is usually not considered.

The carbon dioxide intensity of the steel sector today is 1.9 $t_{CO2}/t_{crude\ steel}$. The Steel Industry comes out as a small emitter compared to the energy sector (25.9%), transport (13.1%), forestry (17.4%) or agriculture (13.5%). However, the CO_2 stream is generated by a relatively small number of large emitters, each one spouting out between 1 and 10 Mton per year.

CO_2 emissions of the Steel Sector

Why does the Steel Industry generate CO_2? There are two main reasons: on the one hand, energy is needed to produce steel, more often than not generated from fossil fuels, while on the other hand, reducing agents are necessary to produce steel from iron ores, the cheapest, most easily available reductant being the carbon of coal. Figure 1 shows the various production routes used today to make steel and their share in the world and in France. The Blast Furnace (BF) route produces steel from primary raw materials, *i.e.* iron ore and requires both energy and reducing agents in the form of coke and pulverised coal; it is called an Integrated Steel Mill. The Electric Arc Furnace (EAF) route produces steel from secondary raw materials, *i.e.* iron scrap, and needs mainly energy, in the form of electricity, along with some coal and oxygen. The DR route is based on ore and uses natural gas as the reducing agent and fuel, along with electricity for subsequent processing in an EAF. The carbon dioxide intensity of the three routes is respectively 1.97, 1.10 and 0.45 $t_{CO2}/t_{crude\ steel}$.

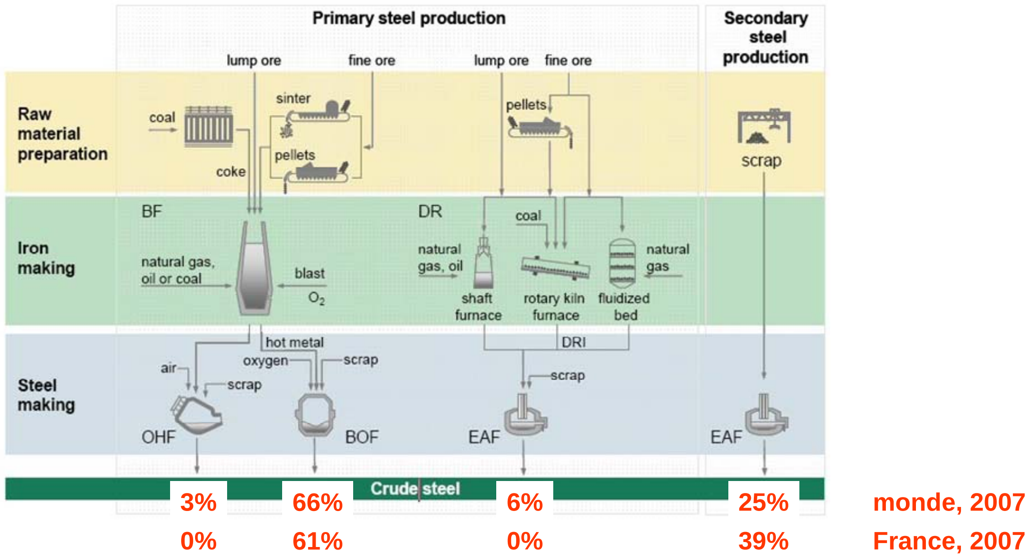


Figure 1: Production routes to make steel today, with production shares in the world and in France (BF: Blast Furnace; OHF: Open Hearth Furnace; BOF: Basic Oxygen Furnace; EAF: Electric Arc Furnace; DR: Direct Reduction)

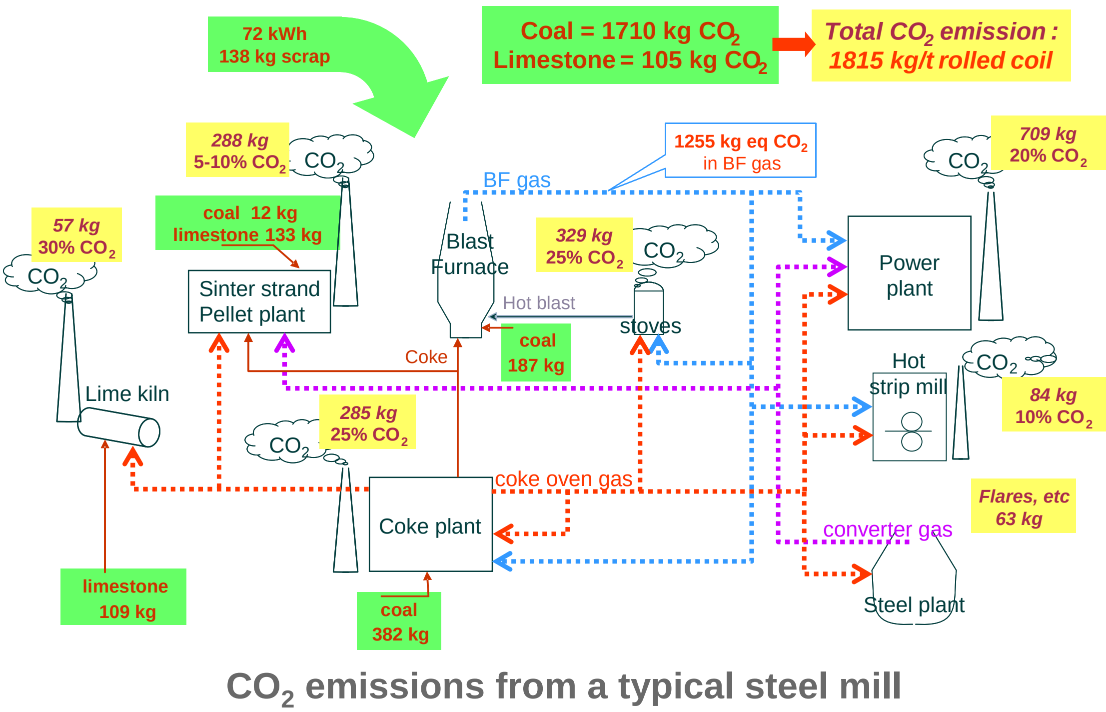


Figure 2: Simplified flow sheet of an Integrated Steel Mill, showing carbon-bearing material input (green boxes, highlighted), CO_2 emissions, expressed in volume (kg/t of hot rolled coil) and concentration in the flue gas (volume %).

An Integrated Steel Mill (ISM) is a complex series of interconnected plants, where CO_2 comes out from many stacks (10 or more). Figure 2 gives a simplified carbon balance, showing the major entry sources (coal and limestone) and the stack emissions, in volume (kg/t of hot rolled coil) and concentration of CO_2 (volume %). The major CO_2 stream comes out of the blast furnace and accounts for 69% of all Steel Mill emissions to the atmosphere. This is indeed where most of the reduction takes place and where most of the energy is needed. The top gas of the blast furnace is composed of roughly 25% of CO_2, the rest being CO at a similar concentration with a complement of nitrogen. The other stacks all together account for 31% of the emissions: they exhibit rather low CO_2 concentrations, typical of the flue gas in a conventional boiler, combustion chamber or power station. Of course, the BF top gas never ends up directly in a stack, as the embedded energy is recovered in a power plant, which is part of the Mill complex. A Direct Reduction steel mill generates CO_2 in lesser quantities at the stack of the DR plant - as well as downstream at the steel shop and rolling mills, like in the ISM. An EAF mill generates even smaller amounts of CO_2, from the steelshop on: most of its emissions are actually due to electricity production needed to power the EAF.

Strategies to control CO_2 emissions from the Steel Sector

A state of the art Steel Mill is a very optimised system in terms of consumption of fuels and reducing agents. The Blast Furnace itself operates 5% away from thermodynamic limits and the whole mill has a potential of energy savings of roughly 10% only. This is due to several decades of cost management, as high energy prices have driven the industry to optimise its processes as close as possible to physical limits. The Industry rightfully claims energy savings and, correspondingly, CO_2 cuts which range between 50 and 60% over the last 40 years, depending on the local conditions: this is the highest level of energy conservation achieved by any industrial sector. Cutting CO_2 emissions further, to the level that post-Kyoto policies require, raises therefore specific challenges: it is indeed necessary to uncouple energy savings and CO_2 reduction in the Steel sector – an original feature compared to other sectors.

First, a more or less obvious fact that ought to be stated anyway, is that the usage of steel scrap should be kept at the high level that it has reached today. It is estimated that the collecting rate of obsolete scrap is around 85% today, which forms the basis of a strong recycling economy, complete with scrap dealerships and a specific steel production route based on the EAF. In simple words, value is created by the recycling of virtually all available scrap. In the long term, this situation will continue. It should also be pointed out that the indirect emissions related to electricity production will evolve with time. For example, ULCOS has shown that, under a strong carbon constraint, the carbon intensity of the European electricity grid will drop from 370 g_{CO2}/kWh in 2006, to 144 g in 2050, a specific drop of 55% which will be translated at the same level in indirect emissions.[3)]

The major source of CO_2 emissions from steel mills still remains the ore-based route, which will retain an important role in the long term, at least until a recycling society can replace the 20th and 21st century economy of production growth that is mainly driven by population growth – probably some time in the next century or at the very end of the present one.

Solutions to curtail emissions from the ore-based route have to be exhibited and it is clear from the previous sections that there is no simple process, available off-the-shelf, that can accomplish this. Deep paradigm shifts in the way steel is produced have to be imagined and the corresponding breakthrough technology designed and developed, by strong R&D programs. The largest such program called ULCOS, for Ultra Low CO_2 Steelmaking, has been running in the EU since 2004 to progress in this direction.[3,4] The analysis that ULCOS has proposed in terms of Breakthrough Technologies is shown in

Figure 3, which explains how reducing agents and fuels have to be selected from three possibilities: carbon, hydrogen and electrons, mostly in the form of electricity.

The present steel production technology is based on coal, *i.e.* mostly on carbon, on natural gas, a mix of carbon and hydrogen and on electric arc furnaces. To identify CO_2-lean process routes, 3 major solution paths stand out and three only: either (1) a shift away from coal, called decarbonising, whereby carbon would be replaced by hydrogen or electricity, in processes such as hydrogen reduction or electrolysis of iron ore, or (2) the introduction of CCS technology, or (3) the use of sustainable biomass.

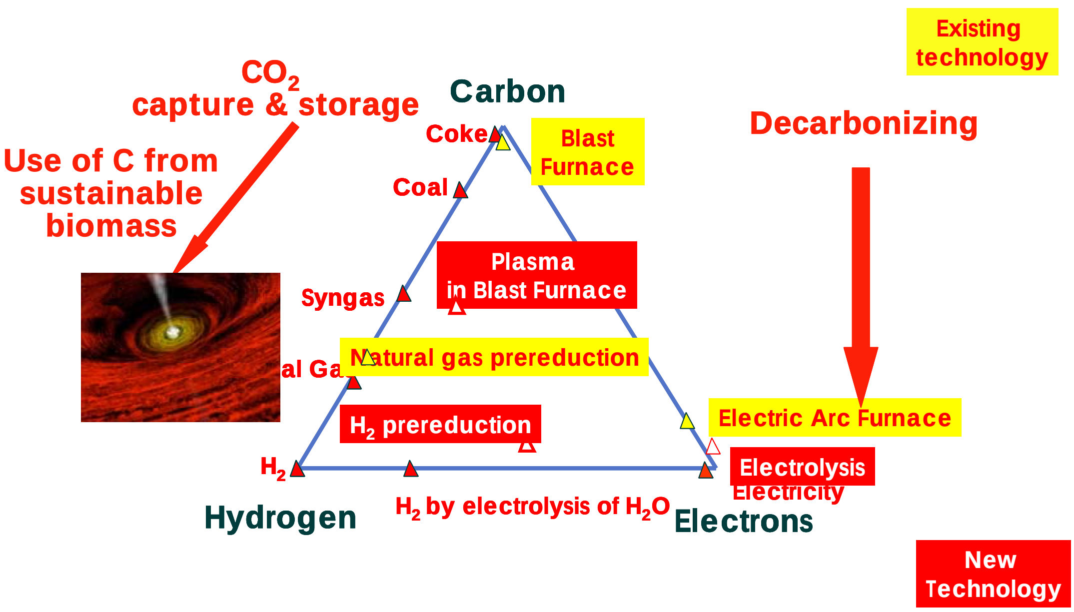


Figure 3: pathways to breakthrough technologies for cutting CO_2 emissions from the ore-based steel production routes

ULCOS has investigated about 80 different variants of these concept routes in the initial phase of its research program, using modeling and laboratory approaches to evaluate their potential, in terms of CO_2 emissions, energy consumption, operating cost of making steel and sustainability.[3,4] Among all of these, six broad families of process routes have been selected within the ULCOS program for further investigation and eventual scale up to a size where commercial implementation can take over:

- a *blast furnace* variant, where the top gas of the Blast Furnace goes through CO_2 capture and the remaining reducing gas is reinjected at the base of the reactor, which is moreover operated with pure oxygen rather than hot blast (air). This has been called the Top Gas Recycling Blast Furnace (TGR-BF). The CO_2-rich gas stream is sent to storage (cf. Figure 4);
- a *smelting reduction process* based on the combination of a hot cyclone and of a bath smelter called HIsarna and incorporating some of the technology of the HIsmelt process.[5] The process also uses pure oxygen and generates off-gas which is almost ready for storage (cf.
- Figure 5);
- a *direct reduction process*, called ULCORED, which produces DRI in a shaft furnace, either from natural gas or from coal gasification. Off-gas from the shaft is recycled into the process after CO_2 has been captured, which leaves the DR plant in a concentrated stream and goes to storage (cf. Figure 6);
- two *electrolysis variants*, ULCOWIN and ULCOLYSIS, which respectively operate slightly above 100°C in a water alkaline solution populated by small grains of ore (electrowinning process), or at steelmaking temperature with a molten salt electrolyte made of a slag (pyroelectrolysis);
- *two more options* are available: one consists in using hydrogen for direct reduction, when and if it is available without any carbon footprint; the other is based on the use of sustainable biomass, the first embodiment of which is charcoal produced from eucalyptus sustainable plantations grown in tropical countries.

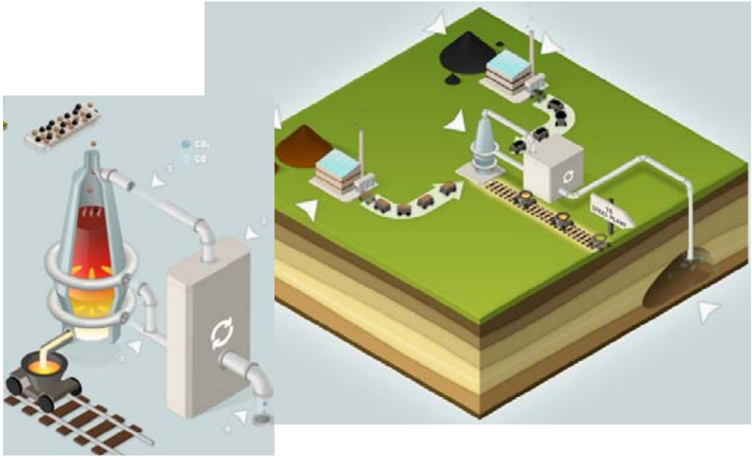


Figure 4: Schematics of the TGR-BF process

In the nearer term, the TGR-BF seems the most promising solution, as existing Blast Furnaces can be retrofitted to the new technology and thus extensive capital expenditures that would be necessary to switch over to the Breakthrough Technologies are maintained under some control. Moreover, the very principle of the process delivers energy savings because the capture of CO_2 and the recycling of the purified gas displaces high temperature chemical equilibria (Boudouard reaction) and uses coke and coal with a higher efficiency inside the BF than is possible with conventional operation. This balances the extra costs incurred by the capture and storage, to some extent. The concept has in addition been tested on a large scale laboratory blast furnace in Luleå, with a positive outcome.

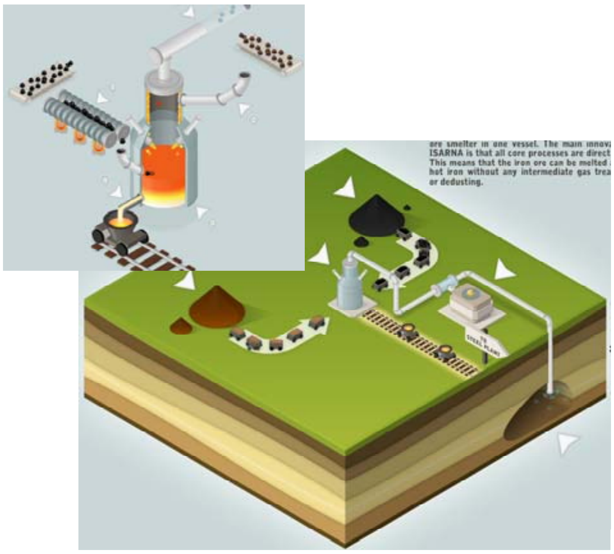


Figure 5: Schematics of the HIsarna process

Where natural gas is available, ULCORED is an attractive option. A 1 t/h pilot is planned to be erected in Luleå in the next few years by LKAB, an ULCOS partner, to fully validate the concept. Somewhat later and probably for greenfield steel mills, the

HIsarna process will also be an option. An 8 t/h pilot is to be erected and tested in the course of the ULCOS program. The electrolysis processes have been developed from scratch within the ULCOS program and, therefore, are still operating at laboratory scale. Although they hold the promise of zero emissions, if they have access to green electricity, time is required to scale them up to a commercial size (10 to 20 years).

Hydrogen steelmaking will depend heavily on the availability of green hydrogen, while the use of charcoal, far way from growing countries, would require the set up of complex logistics, including heavy infrastructure across several continents. The discussions have been centered until now on the major sources of CO_2, which allows to cut emissions for the whole steel mill by more than 50%. It is possible to cut emissions further, by treating the other stacks of the steel mill: the cost of abatement would of course be higher. With this rationale, though, zero emissions could be achieved.

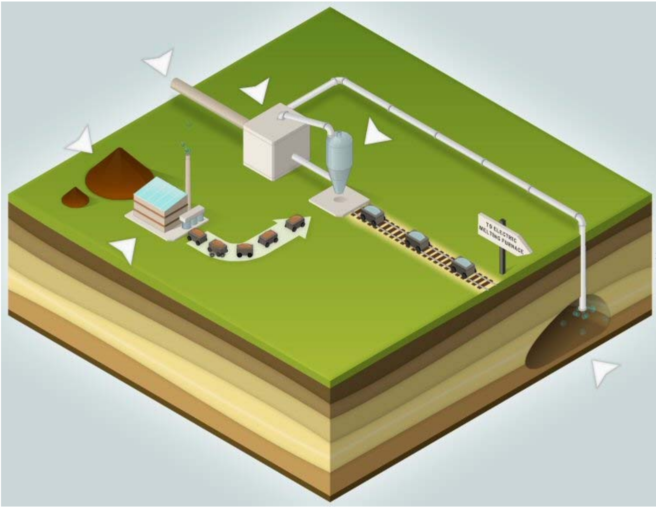


Figure 6: Schematics of the ULCORED process

In parallel to ULCOS, other programs have been launched under the umbrella of the worldsteel CO_2 Breakthrough Program.[6)] Their rationale is similar to the one of ULCOS. They are less advanced in terms of making Breakthrough Technologies available. This long development on Breakthrough Technologies shows that there is no simple recipe for cutting the present CO_2 emissions of the Steel Industry by 50% or more (the objective of the ULCOS program): new technologies have to be developed, which means a high level of risk, incompressible development time, large budgets for R&D and then large capital expenditures to convert steel mills to the Breakthrough processes. Moreover, the economic viability of these solutions, which definitely are not no-regret, will depend on the price of CO_2 and on the implementation of a level playing field for climate policies all around the world that avoid “carbon-havens” and therefore carbon leakage, especially out of Europe. With all these caveats, the Steel Industry can cut its emissions significantly and continue to provide a material that the world needs to ensure a good life to its citizens and cut CO_2 emissions in other sectors.

CCS for the Steel Sector

This section will refocus on CCS for the Steel sector, because implementing CCS seems to be the quickest way – in the 2020s – to delivering significant cuts in the CO_2 emissions of the sector. The first point is that CCS will be implemented in the Steel Industry without matching any of the existing CCS categories, which have been defined with the context of energy generation in mind. Indeed, in the Steel sector, the major part of the generation of CO_2 is related to the reduction of the iron oxides that constitute iron ore. Oxyfuel combustion, pre- or post-combustion capture chemical looping do not mean much in an industrial context where there is no combustion and no oxidation either – except very locally inside the reactors.

Figure 7 presents the various CCS concepts applied to the steel industry and to a combustion process.

The proper concept to apply to the TGR-BF is that of *in-process CO_2 capture, with oxygen operation*. The oxygen part is similar, but not identical to oxyfuel operation. The recycling part is original and is the key reason why some energy savings and the corresponding cut in operating cost are gained. The same concept applies to the ULCORED process, which also includes the use of pure oxygen and in-process recycling of the shaft top-gas, in addition to other features like a series of shift reactors in the recycling loop.

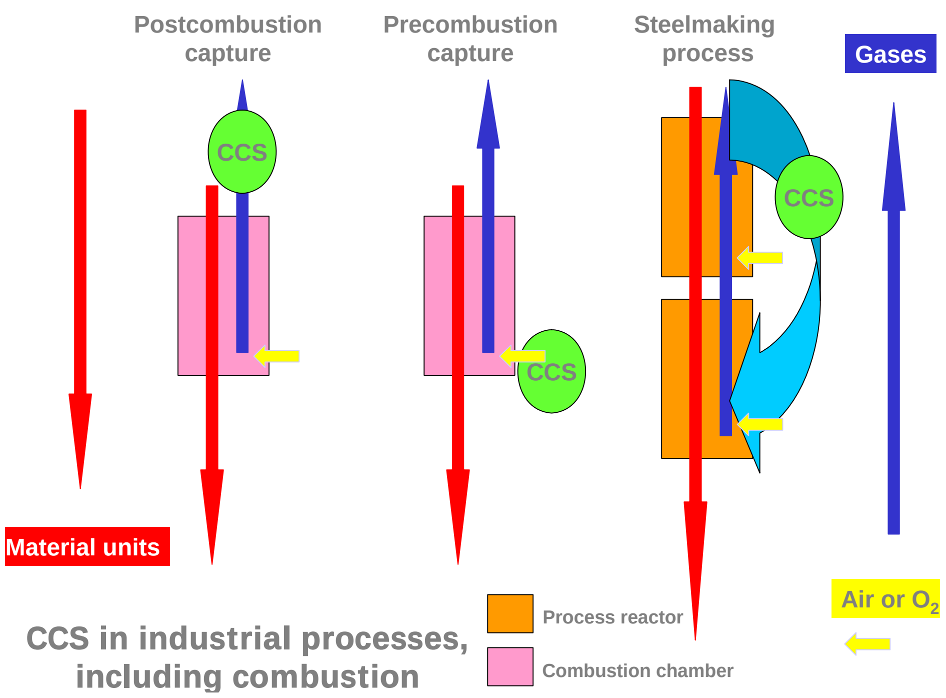
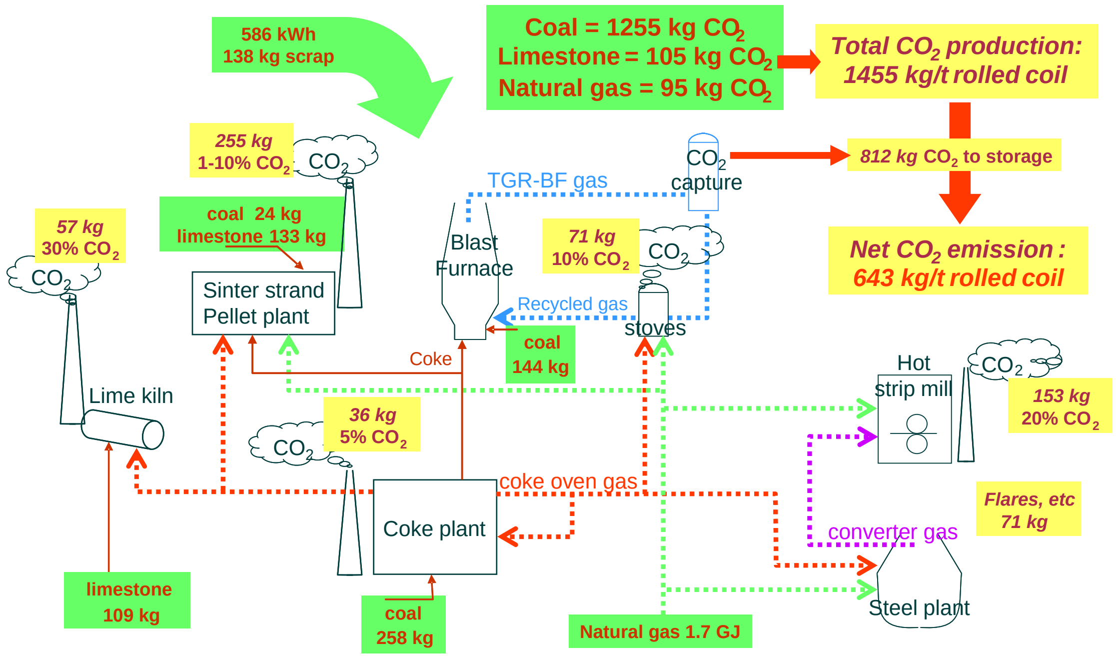


Figure 7: Implementation of CCS in process industries including combustion

The HIsarna process is slightly different from the two other processes as it does not involve a recycling loop for the gas: the smelter gas is oxidised at the cyclone level, where some reduction is carried out along with combustion to preheat and melt the ore. There is a counter current flow of the gas against the iron stream, in which its chemical energy is fully exhausted.



CO_2 emissions from a TGR-BF steel mill

Figure 8: Simplified flowsheet of an Integrated Steel Mill operating with a TGR-BF, showing carbon-bearing material input (green, highlighted boxes), CO_2 emissions, expressed in volume (kg/t of hot rolled coil) and concentration in the flue gas (%).

Figure 8 show the carbon and CO_2 mass balances of a steel mill operating with TGR-BF. Emissions are cut by 65% compared to the non-ULCOS benchmark steel mill of Figure 2 (and by 56% in the steel mill itself, due to the carbon saving introduced by the process). Capturing the flue gas of an extra stack, like that of the sinter plant, would bring the reduction at the level of 75%. The most striking feature of the top gas stream from which CO_2 is recovered is the high concentration of CO_2, around 35%, which is significantly more than in the top gas of the conventional blast furnace.

CO_2 storage for the steel sector

Storage of CO_2 can take place in geological reservoirs (geostorage), in the ocean or by the mineralisation of some other compounds, chemical reactants or rocks (*ex situ* storage). In the context of the present Symposium, we now focus on mineral sequestration (mineral carbonation).

Mineral sequestration

Mineral sequestration is an option which has been seriously examined in the ULCOS program (for example in ref.[7]) and also in the world of steel. The concept is simple: some minerals such as magnesium-rich ultramafic rocks (peridotites, serpentines, gabbros, *etc.*) can react spontaneously (negative enthalpy of reaction) with CO_2 and form carbonates, which stand below CO_2 on the oxido-reduction scale:[8] the compounds are usually stable and the only difficulty of these schemes is to master the kinetics of reactions, which naturally take place in the realm of geology, with the corresponding time scales. Some of the reactions may involve lime or magnesia and bicarbonates may also be formed. A scheme specific to the steel industry proposes to use slag, especially steelmaking BOF slag, as the reactant that will be used to absorb CO_2 by a chemical reaction: there is a phase in that slag, called larnite (Ca_2SiO_4) and present at the level of 30 to 40%, which can react with CO_2:

$$\tfrac{1}{2}\,Ca_2SiO_4 + CO_2 \rightarrow CaCO_3 + \tfrac{1}{2}\,SiO_2 \qquad (1)$$

with an enthalpy of - 22 kcal. In addition to larnite, slag may contain as much as 6% free lime (CaO), which also reacts with CO_2 to form the same calcium carbonate. The use of slag has been studied in the ULCOS program,[7] where it was shown that the reaction can proceed at moderate temperatures (90°C), high pressures (100 bar), and moderate times of reaction (90 min) if the slag is ground (50 µm) to liberate the calcium silicate, mixed with water to produce a slurry and kept agitated during the reaction process. 70% of carbonation is achievable under these conditions, with means that 1 ton of slag can capture 250 kg of CO_2.

Comparing this amount of stored CO_2 with the Steel Mill emissions and the amount of slag which is generated in parallel, shows that only 1.3% of the total CO_2 generated by the Steel Mill (0.1 CO_2 Mt compared to total emissions of 7.2 Mt/y) can be sequestered in this way. The ULCOS program conclusion was that this was not measuring up to the level of the challenge and did not match in any way the 50% mitigation target that was its goal.

Now, if mineral carbonation was to provide more sequestration, then more reactant would have to be used, roughly 100 times more. This shows the level of the logistics involved, as it would amount to 25 times the mass of steel produced. Proponents of mineral carbonation do not suggest to move the rocks to the Steel Mil, but rather the gas to the mine. This, however, is a proposal that needs more detailed elaboration before it can be considered as an option compared to geostorage. (*See also other contributions on mineral carbonation in these Proceedings, which focus on improved, accelerated carbonation*.)

Conclusions

The Steel Industry has been aware of the Climate Change threat since the late 1980s and started to propose solutions early.[9] CCS has been identified from the start as a powerful solution to deal with this issue. Cooperative programs have been launched in Europe and in the rest of the world to tackle the issue at various scales and commercial-size demonstrator experiments are now under way, which may lead to implementation and deployment from the 2020s onwards. This is a long term agenda, full of promises but also of risks and traps, a situation which is probably similar to what other sectors are experiencing. Risks are related to the complexity of the issue, which calls on the development and the implementation of breakthrough technologies under time constraints which are very short. The message is not that CCS is unlikely to happen in the Steel Industry, quite the opposite. But we believe that the optimism which prevails in many policy-driven publications is overrated. Some researchers are actually becoming aware of this situation.[10]

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