ArcelorMittal
Centro de desarrollo tecnologico
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Training report

Energy and exergy analysis of a basic oxygen furnace

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From March to July 2011

Charging of hot metal in a basic oxygen furnace

Tutor: Rocío Llera Traviesa

Special thanks

First I would like to express my gratitude to the team of Avilés research center for welcoming me and giving me the opportunity to work with them on this project. I especially thank my tutor, Rocío Llera Traviesa, and Sara Villalobos Fernández for their help and support.

I also thank Michel Feidt, teacher at the ENSEM, for helping me understand the concept of exergy, for his presence and for his answers to the questions I had during my training.

I address my final greetings to all the other members of the Energy group, for their support and precious help.

Summary

Lexicon

CO: Coke Oven.
BF: Blast Furnace.
BOF: Basic Oxygen Furnace.
NG: Natural Gas.
Nox, Sox: components principally used for the combustion of fossil fuels.
Hot metal = Pig iron

Introduction

Nowadays, the rational use of energy has become a priority all around the world because of environmental concerns and the rising cost of energy. All these reasons lead to the research for the improvement of plants performances, especially steel plants, because of the large amount of energy involved.

In this type of industries, it has become crucial to specifically determine the exact amount of energy needed and produced within the plant. The concept of exergy, imagined in 1889 by Georges Gouy, includes the First and Second laws of thermodynamics and has been proved to be a tool that can precisely assess the thermodynamic losses of a system along with the thermodynamic efficiency of it. It thus seems to be a good concept to work with for the analysis of steel plants.

In this report we are going to study one of the processes involved in steel making, the basic oxygen furnace process.

First we're going to present the company ArcelorMittal with whom we worked with on this project, then in a first part we will detail the steps of steel making, in a second part present the energy analysis of the process and then finish with a third part on the exergy analysis of it.

Because of the large number of documents consulted during this training, the assertions made in this report are not always directly referenced to the specific document from where we quoted it. Sometimes we can find reference into the text presented between brackets. This corresponds to the articles we didn't have at our disposal and they do not figure in the references of this report but are important to understand the part where they appear.

Training goal: Energy and exergy analysis of the basic oxygen furnace process.

The company ArcelorMittal

I) Profile of ArcelorMittal

ArcelorMittal is the world's leading steel production company, with operations in more than 60 different countries and more than 300 000 employees.
It is the leader in all major global steel markets, including automotive, construction, household appliances and packaging, with leading R&D and technology, as well as sizeable captive supplies of raw materials and important distribution networks.
With an industrial presence spanning four continents, the Company covers all of the key steel markets, from emerging to mature and wishes to develop its position on the Chinese and Indian markets, reputed for their important growth rates.

In 2010, ArcelorMittal had revenues of $78.0 billion and crude steel production of 90,6 million tons, representing approximately 8 per cent of world steel output.

ArcelorMittal's infrastructures all around the world.

II) History of ArcelorMittal

ArcelorMittal is a successor to Mittal Steel, a business founded in 1989 by Mr. Lakshmi N. Mittal, the Chairman of the Board of Directors and Chief Executive Officer of ArcelorMittal.

Mittal Steel made its first acquisition in 1989, leasing the Iron & Steel Company of Trinidad and Tobago. Some of its principal acquisitions since then include Thyssen Duisburg (Germany) in 1997, Inland Steel (USA) in 1998, Unimetal (France) in 1999, Sidex (Romania) and Annaba (Algeria) in 2001, Nova Hut (Czech Republic) in 2003, BH Steel (Bosnia), Balkan Steel (Macedonia), PHS (Poland) and Iscor (South Africa) in 2004, ISG (USA), Hunan Valin (China) and Kryvorizhstal (Ukraine) in 2005, and three Stelco Inc. subsidiaries (Canada) and Arcelor in 2006.

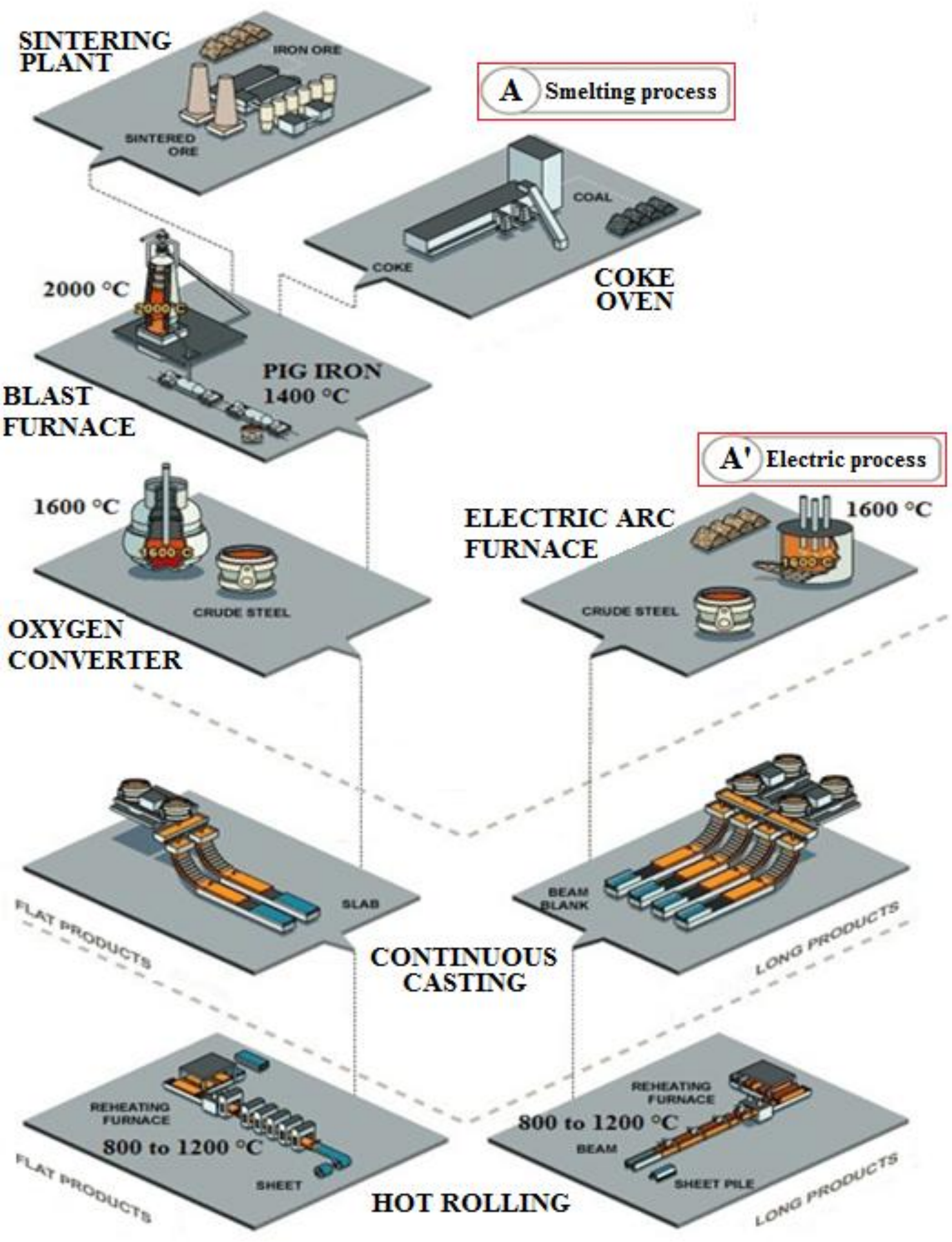
Arcelor was created in February 2002 by the combination of three steel-making companies: Aceralia (Spain), Arbed (Luxembourg) and Usinor (France), to create a global presence in the steel industry. At the time of its acquisition by Mittal Steel in 2006, Arcelor was the second largest steel producer in the world in terms of production, with 2005 production of 46,7 million tons of steel and 2005 revenues of €32.6 billion. In 2006 on January 28th Mittal Steel offers publically to buy Arcelor for €18,6 billion. The company vigorously defends its position, until the end of February 2006 when both companies’ market capitalizations are almost the same. The fusion of both groups gives birth to ArcelorMittal.

In 2007, ArcelorMittal continued to pursue a disciplined growth strategy, with a total of 35 transactions all around the world, and numbers of them were completed in 2007. During 2007, ArcelorMittal also announced or completed buy-out offers for minority interests in certain of its subsidiaries in Argentina, Brazil and Poland. ArcelorMittal also initiated development plans for its greenfield projects in India, Liberia and Senegal and announced new prospective development projects in Mauritania, Mozambique, Nigeria, Russia, Saudi Arabia and Turkey.

During the first eight months of 2008, ArcelorMittal continued making investments, with significant transactions announced in Australia, Brazil, Canada, Costa Rica, France, Russia, South Africa, Sweden, Turkey, United Arab Emirates, the United States, and Venezuela, the majority of which have been completed. More recently, ArcelorMittal's acquisitions are focused on raw material producers and production sites.

Part 1: The process of steel making

I) General description of steel making



General diagram of the steel making process

Steel, because of its versatile properties and its recycling possibilities, is the basic material for sustained development in modern industrial society. It enjoys a broad range of uses in almost all important sectors of industry, such as apparatus and machinery manufacture, bridge building, steel-framed building construction, power and

environmental engineering, transportation, and the packaging industry, to name just a few.
Raw materials for steel production are coal and iron (imported predominantly from Brazil, Canada, Australia and Sweden). The coal is transported from the storage to the coke plant, where metallurgical coke is obtained. The iron ore is sintered and taken to the blast furnace where it is mixed with coke, lime and blown air to produce pig iron. The pig iron is conveyed to the reduction oven or as we can also name it the basic oxygen furnace where pure oxygen is injected to reduce pig iron in steel. Steel is then molded into sheets, blocks and other forms through continuous casting and hot rolling.
Continuous casting consists in producing steel products such as rails, beams or slabs through the use of molds. We are not going to describe this process because we are more interested in the hot rolling process, which takes the slabs, heat them and flatten them into coils. Coils can be used to build cars, cans, household appliance … It is thus the main product of any steel plant, that’s why we are going to focus on describing this process instead of the continuous casting one.

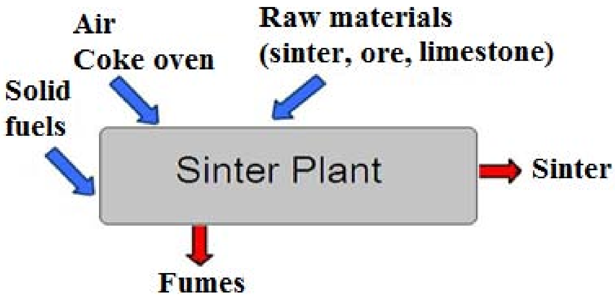
As we can see on the general diagram of steel making there are two ways to produce steel, A and A’. In our study we are going to work with the A way because it is the one that was used in the Avilés steel plant.
We are thus going to describe the following processes within the steel plant:

- The sintering plant
- The coke oven
- The blast furnace
- The basic oxygen furnace (object of our study) also called oxygen converter
- The hot rolling

With the A’ way we use an electric arc furnace to produce steel by using steel and iron scrap. The electric arc furnace allows us to transforms electrical energy into melting heat by using electrodes to conduct the electrical current and create the arc to the metallic charge. Nowadays this process is less used than the one we are going to work on.

The description of the basic oxygen furnace process is obviously going to be more detailed than the other processes in this study.

II) The sintering plant



Matter flows in the sinter plant

Sintering is the welding together of small particles of metal by applying heat below the melting point.

In a steel-sintering plant a bed of powdered iron ore, mixed with coke or anthracite, is humidified to allow gas to flow easily through it during the roasting. The mixture is then ignited by a gas burner and moved along a travelling grate. Air is drawn down through the grate to produce downdraft combustion (the combustion spreads from the top to the bottom of the layer of particles). As the bed moves forward, a very high heat (1325–1500° C) is generated, converting the tiny particles into lumps about 2,5 cm in diameter suitable for burning in the blast furnace. The layer of particles is then cooled down.

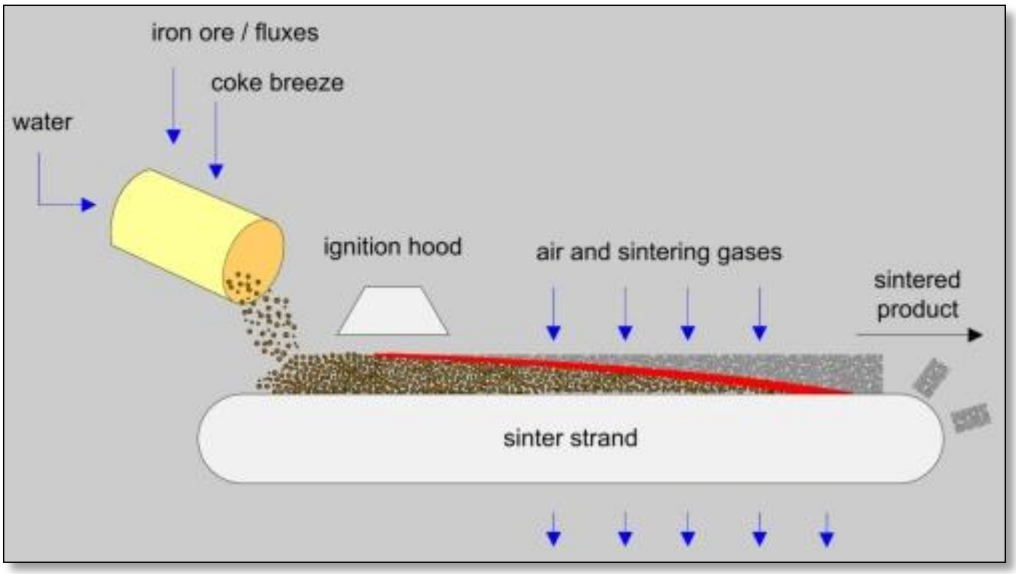


Figure: The sintering process

III) The coke oven

Coke is obtained by heating up coal to 1000°C in silicon furnaces. During the pyrolysis the coal releases gas, tar and water. The gas is purified before its reuse and the water treated before being released in the environment.
The heart of the process is the coking battery comprising a number of tall, narrow ovens. Coking is a dry distillation process, i.e., combustion without access to oxygen. The coal is charged by “coal machines” above the oven battery.

The ovens have brick partitions in which the heating wall channels are heated by the gas generated in the coking battery itself, possibly mixed with blast furnace gas. The coal is heated in the narrow, airtight ovens until it is in an almost flowing, plastic form.

The elements that are to be removed will then be gasified. The process takes about 18 hours. The temperature is above 1,000°C, and the coal is converted to 75 percent coke and 25 percent gas. The coking plant has a number of processes in which the gas is cleaned in several stages and many raw materials are recovered.

The most important is the cleaned gas that supplies energy to the processes of the coking plant itself and to other users, such as the blast furnace. But raw materials are also recovered for the chemical process industry, such as sulphur in desulphurizing, fertilizers for agriculture, tar and asphalt. The end customers of the coking plant include manufacturers of perfumes and pharmaceuticals.

Photograph of the Schwelgern coke oven plant in Duisburg, Germany

IV) The blast furnace

The purpose of the blast furnace is to produce hot metal by bringing fuel and ore through the top of the furnace while air is blown into the bottom of the chamber, thus allowing the chemical reactions to take place throughout the furnace as the material moves downwards. In the end we obtain hot metal, slag phases taped into the bottom and gases exiting from the top of the furnace.

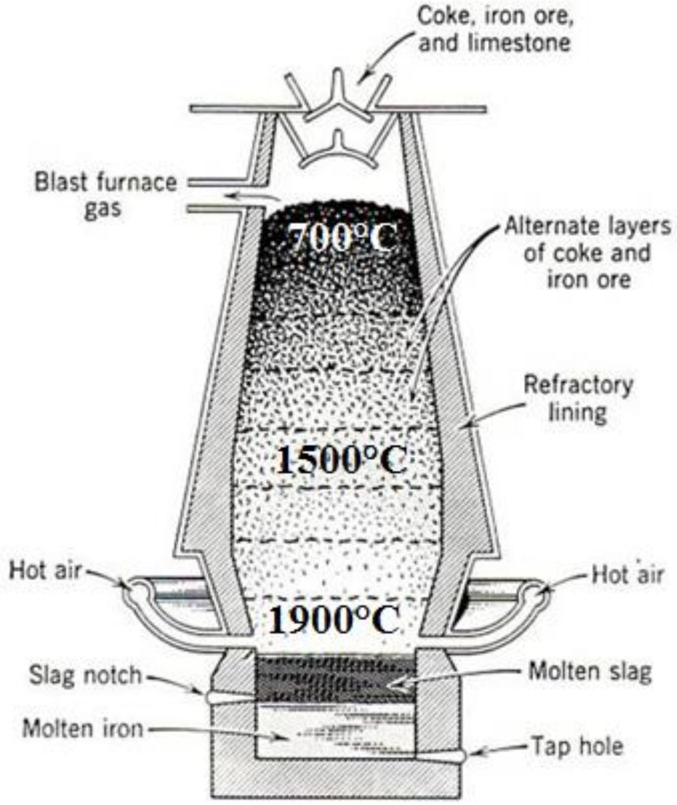


Figure: Inside of the blast furnace

The blast furnace is charged continuously from the top with ore pellets, coke and additives.

The particle size of the coke allows the molten hot metal to trickle down and the gas to rise through the blast furnace. The blast air is supplied at high pressure though a number of large tuyeres under the broad belly of the blast furnace, where pulverized coal is injected at the same time.

Limestone is added to the blast furnace process in order to collect silicon and other undesired substances to form a slag. The slag floats on top of the molten hot metal and is separated by the skimmer.

The reduction process takes place inside the refractory-lined blast furnace, where the temperature is 2,200°C in the hottest zone. The melting point of iron is 1,535°C, but the carbon lowers the melting point to below 1,200°C.
When the iron has been reduced by the carbon and melted, it trickles down and is collected in the bottom of the blast furnace. The blast furnace is tapped at a uniform

rate. Tapping takes place during about 2 hours and is then interrupted for 40-50 minutes before the next tapping.

The released gas is composed with carbon monoxide CO and carbon dioxide CO_2, which is discharged from the blast furnace through large gas pipes to a gas treatment plant. The carbon monoxide is rich in energy, and the blast furnace gas is recovered as energy for the processes of the blast furnace itself and for other energy customers in the steelworks, and also for power generation and for district heating (see the section on Energy).

V) The basic oxygen furnace

1) General description

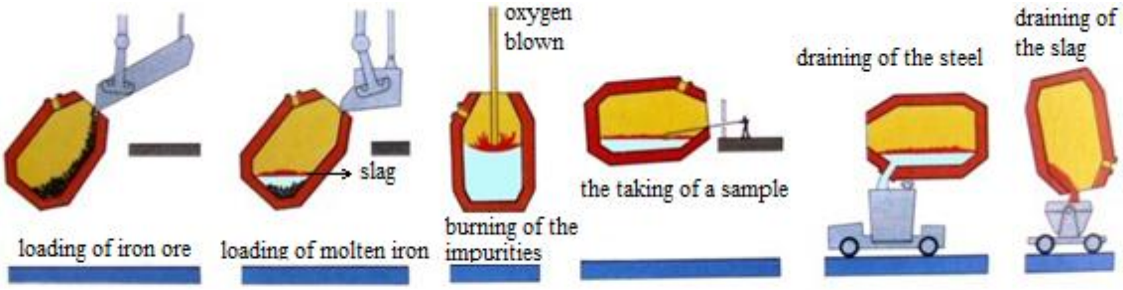


Diagram of the steel making steps into the basic oxygen furnace

The basic oxygen furnace is a device producing steel from hot metal (pig iron) with a high content of carbon.
Pressurized oxygen is blown in the melting hot metal with a lance, raising the temperature to 1700°C. At this level of temperature, the scrap metal melts, and the content of carbon and of some other undesirable chemical elements decreases. Other fluid components are added to form at the surface of the mixture the slag absorbing the process impurities.

The transformation of pig iron into steel is called “conversion” and corresponds to the oxidation of certain elements contained in the materials used to produce the pig iron (C, Si, Mn, Ti, P and S). The conversion technique aims to reduce the amount of these elements into predefined ranges. The reactor where these refining operations occur is called a converter
The converter holds up to 400 t crude steel. Added along with hot metal and scrap are lime, for slag forming purposes, and alloying agents. The blowing process takes some 20 minutes.

Here is the representation of a converter:

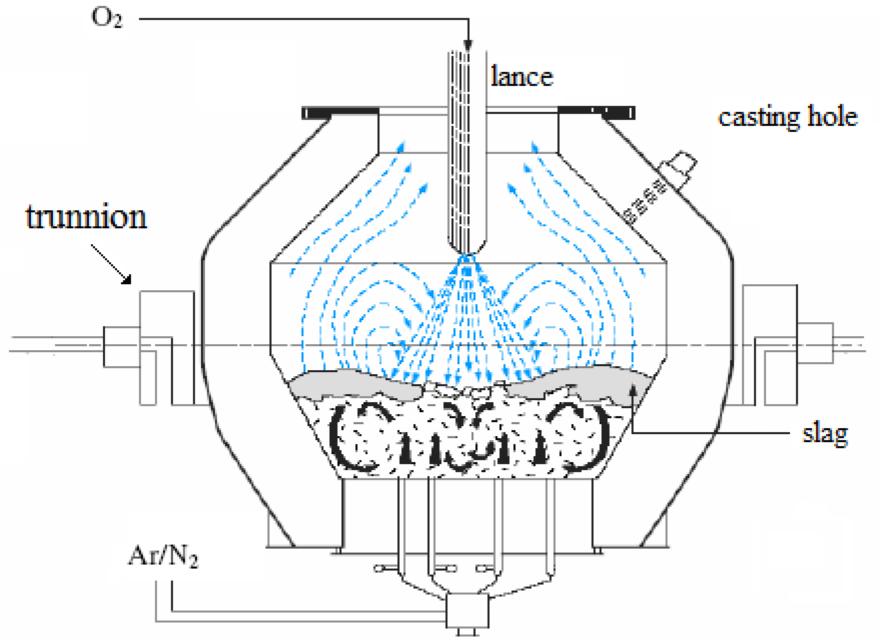


Figure: Scheme of a converter (Astier, 1998)

The converter is essentially constituted by a steel shell with firebricks on the inside and its volume is 7 to 12 times larger than the volume occupied by the pig iron inside it. It is designed this way to confine most of the spitting occurring during the oxygen blowing part or the swelling of the slag.

The vessel consists of three parts: spherical bottom, cylindrical shell and upper cone. The vessel is attached to a supporting ring equipped with trunnions. The supporting ring provides stable position of the vessel during oxygen blowing. The converter is capable to rotate about its horizontal axis on trunnions driven by electric motors. This rotation (tilting) is necessary for charging raw materials, sampling the melt and pouring the steel out of the converter.

There are different ways to blow the oxygen inside the converter:

- Blowing from the top
- Blowing from the bottom
- Mixed blowing (from the top and the bottom)

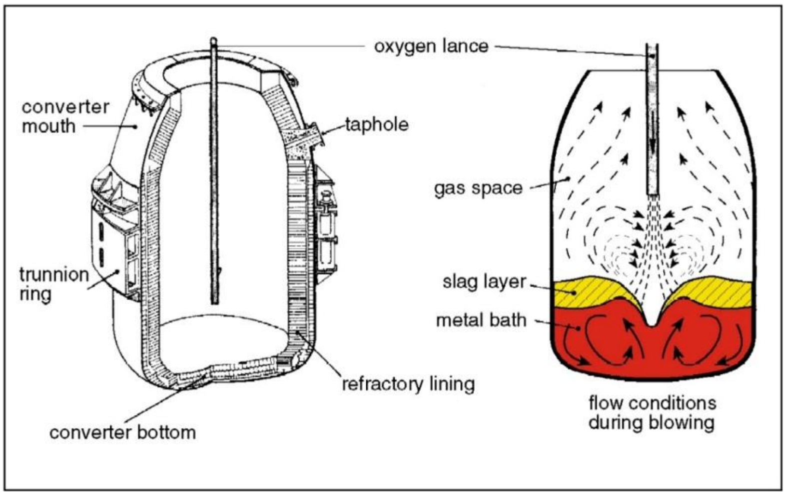


Figure: Illustration of an oxygen top-blowing converter

Inert gas (nitrogen with argon) is injected from the bottom of the converter to help with the mixing.

The basic oxygen furnace uses no additional fuel. The pig iron impurities (carbon, silicon, manganese and phosphorous) serve as fuel. Indeed, iron and its impurities oxidize evolving heat necessary for the process. The heat produced by these refining reactions compensates the thermal losses, heats up and melts all the necessary inputs added and to bring the pig iron to a higher temperature than the one when it enters the converter.

The raw materials introduced inside the converter are:

- Pig iron: It is put inside the converter at the approximate temperature of 1370°C.

- Additions containing iron: It can be minerals, scrap, solid pig iron... They are generally introduced at ambient temperature as cooling agents, since the oxidation process generates a strong amount of heat. These additions are thus used to adjust the thermal balance and obtain the liquid steel temperature aimed.

- Additions to constitute the slag and adjust its composition: The first addition is the lime (CaO), which is used to help with the transfer of Si and P of the steel into the slag. The amount of P inside the steel is, along with the amount of C, a quality factor for the steel produced. The lime also helps controlling the basicity of the mixture by reacting with the silica SiO_2, thus affecting the oxidation reactions occurring inside the converter.
  The second addition is the dolomite, which helps saturate the slag with magnesia to limit the deterioration of the firebricks.

- Oxygen: It is injected into the mixture through a water-cooled lance or through immersed tailpipes. The necessary quantity of oxygen is determined trough the steel composition and the priority rules of oxidation.

- Nitrogen: The injection of nitrogen helps mixing the content of the converter. A portion of this inert gas can be dissolved into the liquid mixture and the rest goes into the gas leaving the converter, also called BOF gas.

Three principal products are indentified at the end of this process:

- Liquid steel: It is the main product of the process and of the steel plant. The steel composition is characterized by a high amount of iron and a reduced amount of carbon compared to the amount contained in the pig iron entering the converter. Its temperature is generally around 1650°C.

- Slag: The slag is located on top of the liquid steel at the end of the process. It is thus collected at the very end after all the liquid steel is retrieved. The slag is mainly composed of lime and silica.

- Gas: The gas leaves the converter at a temperature between 1600 and 1800°C through a hood and is leaded to a cooling and dust removal installation. In this process the collected dust can be partially or totally recycled.

The ratio pig iron/scrap put in the oven changes from a plant to another, following the economic circumstances.
All the oxidation reactions are strongly exothermic, and the energy produced is higher than the one necessary to heat up the pig iron (1350-1400°C) to the temperature wanted for the steel (1650-1665°C) and to heat up and dissolve into the slag the lime and the dolomite. The remaining energy is used to melt the scrap and/or reduce and melt the iron ore.

2) Physico-chemical characterization of the conversion

The reactions occurring inside the converter are the refining reactions on the pig iron. The refining reactions correspond with the oxidation reactions. They happen very quickly and are triggered by the contact between the oxygen and the liquid metal. Whatever the way of blowing the oxygen, as soon as they both interact the dissolved elements (C, Si, Mn, P) are oxidized until there is no oxygen left (iron is also consumed with the oxygen in this process because its initial amount is very high).

It is the FeO created that oxidizes the silicon, the manganese, the phosphorus and the carbon (Sollac, 1976). Due to its reduced solubility into the metallic bath, the FeO remaining goes to the surface, helping form the slag.

The silicon contained in the pig iron is irreversibly oxidized and after a few minutes its amount in the metal is already really low. The main part of the silica formed goes in the slag and the rest reacts with the lime to form Ca_2SiO_4.

The oxidations of manganese and silicon occur simultaneously. One part of the MnO produced goes into the slag and the rest is decomposed and the manganese returns back into the bath.

The formation of P_2O_5 is only possible in the presence of CaO and gives for example $P_2O_5(CaO)_3$.

When almost all of Si is consumed the oxygen contained in FeO reacts with the carbon to give CO. This reaction is the one consuming the bigger part of the oxygen. When the lance used to blow the oxygen is submerged, some of the CO produced is oxidized into CO_2. This reaction is called post combustion and only a part of the energy supplied is retrieved by the gas.

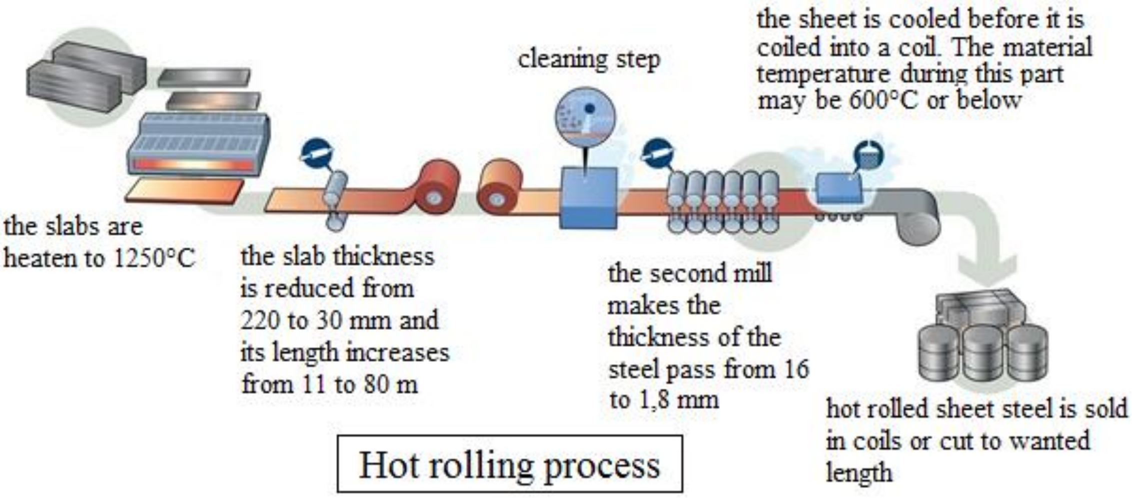
The sulfur is principally brought into the converter via the pig iron. At high temperatures (1600-1800°C) and when the slag is basic, it is possible to realize a desulfurization of the pig iron. The more basic the slag is, the better this operation works.
The reduction of the iron oxide Fe2O3 contained in the iron ore is supposedly managed by the carbon (Huber, 2005).

Usually the refining part is studied by simplifying the chemical reactions occurring inside the converter. Here are the reactions we are going to work on:

$$Fe + 1/2\ O_2 \rightarrow FeO$$
$$Si + O_2 \rightarrow SiO_2$$
$$Mn + 1/2\ O_2 \rightarrow MnO$$
$$2\,P + 5/2\ O_2 \rightarrow P_2O_5$$
$$C + \ 1/2\ O_2 \rightarrow CO$$
$$CO + 1/2\ O_2 \rightarrow CO_2$$

The oxygen converter (basic oxygen furnace) we chose to study is the one used in the steel factory of Avilés (Spain), where this internship took place.

VI) The hot rolling



Hot rolling is a metalworking process that occurs above the recrystallization temperature of the material.

The starting material is usually large pieces of metal, like semi-finished casting products, such as slabs, blooms, and billets. If these products came from a continuous casting operation the products are usually fed directly into the rolling mills at the proper temperature. In smaller operations the material starts at room temperature and must be heated. This is done in a gas- or oil-fired soaking pit for larger workpieces and for smaller workpieces induction heating is used.

As the material is worked the temperature must be monitored to make sure it remains above the recrystallization temperature (usually 50 to 100 °C above it).

While the finished product is of good quality, the surface is covered in mill scale, an oxide that forms at high-temperatures. It is usually removed via pickling or the smooth clean surface process, which reveals a smooth surface.

Hot rolling is used mainly to produce sheet metal or simple cross sections, such as rail tracks.

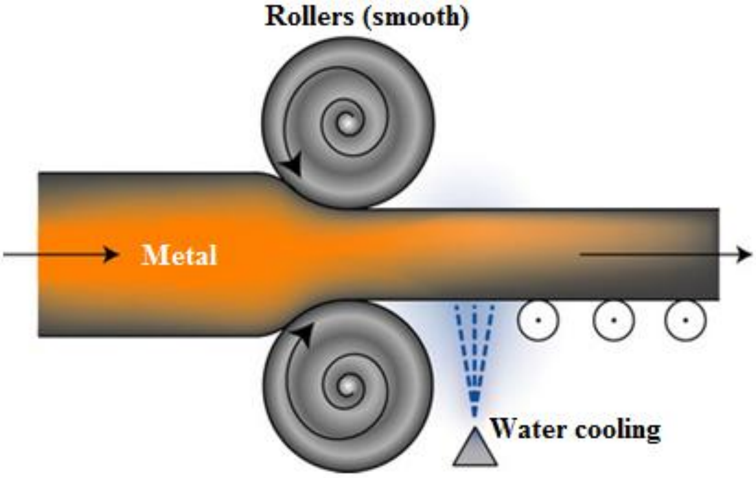


Figure: Principle of the rolling mill

Part 2: Energy analysis of the basic oxygen furnace

In the basic oxygen furnace the only energies involved are thermal energy (associated with a change in temperature of the different inputs or outputs of the process) and the energy associated with the reactions occurring inside the converter.

I) Calculation of the thermal energy

As mentioned before, the thermal energy is associated with a change in temperature. When the different inputs of the process get inside the converter and the oxygen is blown up, some reactions occur, raising the temperature of these inputs and thus creating energy.
This energy is calculated with the formula:

$$En_{thermal} = \int_{T_i}^{T_f} mc_p dT = m \int_{T_i}^{T_f} c_p dT$$

With En being the amount of energy in J, T_i and T_f respectively being the initial and final temperature of the input considered in K, m being the mass of the input in kg and c_p being its heat capacity in J/(kg.K).
As we know the heat capacity of the elements changes with the temperature so we looked for the $c_p$formulas of all the elements involved in steel making process(more details in the appendix section):

It is important to precise that we used the average amount of every input and output on this process based on the data gathered during one year in the oxygen converter of Avilés. Then we adapted all the values for a production of one ton of liquid steel.

II) Calculation of the energy of reaction

To calculate the energy associated with a reaction we used the following formula:

$$En_{reaction} = m * \Delta Hr_{reaction}(T)$$

With $\Delta Hr(T)$ being the enthalpy of reaction associated with the reaction considered in J/kg and m being the mass of reactant consumed in the reaction. This value represents the mass energy associated with a reaction. If this amount is positive it means that the reaction is endothermic and needs energy to occur but if it’s negative, it means that the reaction is exothermic and produced energy (heat).

It is pretty hard to determine precisely the mass of reactant consumed in each reaction because we are not really sure of what's happening inside the converter. It is said that the iron contained in the hot metal and in the scrap is oxidized by the oxygen blown in the converter through a lance. The FeO produced then reacts with the other components of the hot metal (Si, Mn, P and C) to produced oxides going in the slag. This information was found in the reference:

- Chapitre V. Modélisation physico-chimique du convertisseur à oxygène et du laminoir à chaud pour l'analyse de l'ICV.

Here are the reactions considered:

$$Fe + 1/2\ O_2 \rightarrow FeO$$
$$Si + O_2 \rightarrow SiO_2$$
$$Mn + 1/2\ O_2 \rightarrow MnO$$
$$2\,P + 5/2\ O_2 \rightarrow P_2O_5$$
$$C +\ 1/2\ O_2 \rightarrow CO$$
$$CO + 1/2\ O_2 \rightarrow CO_2$$

To determine the enthalpy of reaction $\Delta Hr(T)$ we use the formula:

$$\Delta Hr(T) = \Delta Hf(T_0) + \int_{T_0}^{T} c_p dT$$

With $\Delta Hr(T)$ being the enthalpy of reaction of one of the elements involved in the reaction, $\Delta Hf(T_0)$ being the enthalpy of formation in J/kg of the component considered at the environment temperature $T_0 = 298{,}15\ K$ and T being the temperature inside the volume where the reaction occurs. In our study the temperature inside the converter is $T = 1600°C = 1873{,}15\ K$.

We determine $\Delta Hr(T)$ for every element involved in the refining reactions and then we obtain $\Delta Hr_{reaction}(T)$ by subtracting $\Delta Hr(T)$ of the reactants of the reactions to $\Delta Hr(T)$ of the product of the reaction considered (not forgetting to take into account the stoichiometric factors of the reaction).

We suppose the reactions are total and balanced. Let us study all the reactions to calculate the mass of reactant consumed for each one and thus be able to calculate the enthalpies of reaction:

<u>$Fe + 1/2\ O_2 \rightarrow FeO$</u>:

For this reaction we want to know how many Fe reacted to produce FeO. As mentioned before, the elements Si, P and Mn are not oxidized by O_2 directly but by FeO. So we can suppose that all the oxygen reacted with Fe to form FeO because Fe is in excess compared to the oxygen. Looking at the equation of the reaction we know that:
$n_{Fe}(used) = 2 * n_{O2}(used)$ but n_{O2} is the number of moles of O_2 introduced with the lance inside the converter.

$Si + O_2 \rightarrow SiO_2$:
In this reaction we can see that all the Si contained in the hot metal is consumed and there is no Si left in the liquid steel so we can use the mass of Si inside the hot metal to determine the energy associated with this reaction.

$Mn + 1/2\ O_2 \rightarrow MnO$:
Here it is the same thing than the reaction before except that there is still Mn left in the liquid steel so we determined the mass of Mn consumed by subtracting the mass of Mn In liquid steel to the mass of Mn in hot metal.

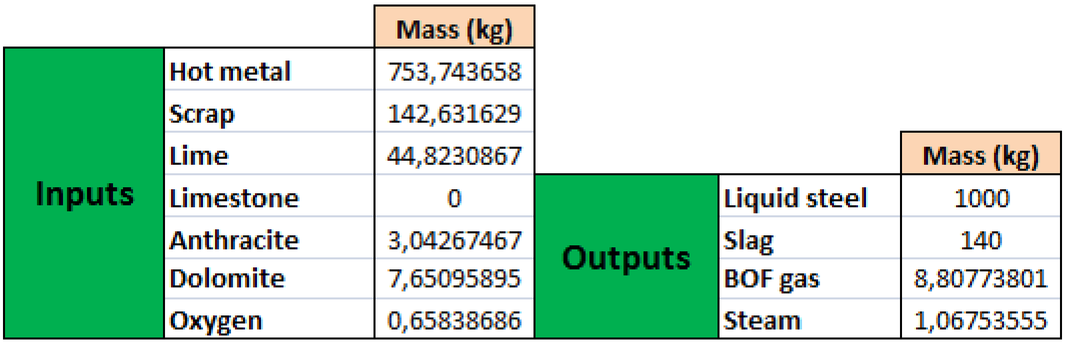
$2\ P + 5/2\ O_2 \rightarrow P_2O_5$:
With this reaction we used the same method that we used in the previous one.

$C +\ 1/2\ O_2 \rightarrow CO$:
With this reaction we used the same method that we used in the two previous ones.

$CO + 1/2\ O_2 \rightarrow CO_2$:
Based on the last reaction we know that $n_{CO}(produced) = n_C(used)$ so we can find the mass of CO produced. Since we know what mass of CO remains in the BOF gas, we can determine what mass of CO reacted to produce CO_2.

III) Results of the energy analysis

Here are the results of the energy analysis. But first we present in a first table the mass balance of the basic oxygen furnace process for the steel plant of Avilés. The data are evaluated for a production of 1 ton of liquid steel.

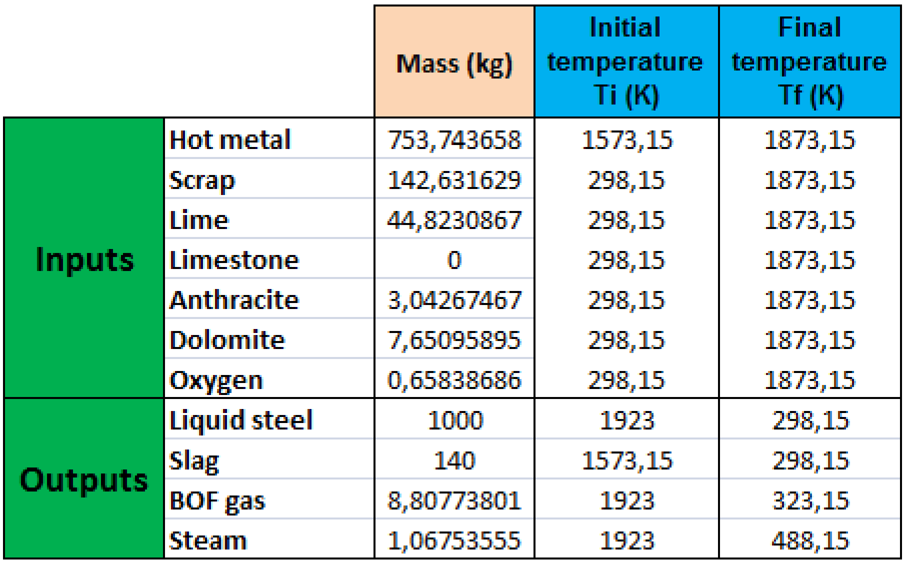


		Mass (kg)
Inputs	**Hot metal**	753,743658
	Scrap	142,631629
	Lime	44,8230867
	Limestone	0
	Anthracite	3,04267467
	Dolomite	7,65095895
	Oxygen	0,65838686

		Mass (kg)
Outputs	**Liquid steel**	1000
	Slag	140
	BOF gas	8,80773801
	Steam	1,06753555

Figure: Mass balance of the basic oxygen furnace (Avilés, Spain, 2010)

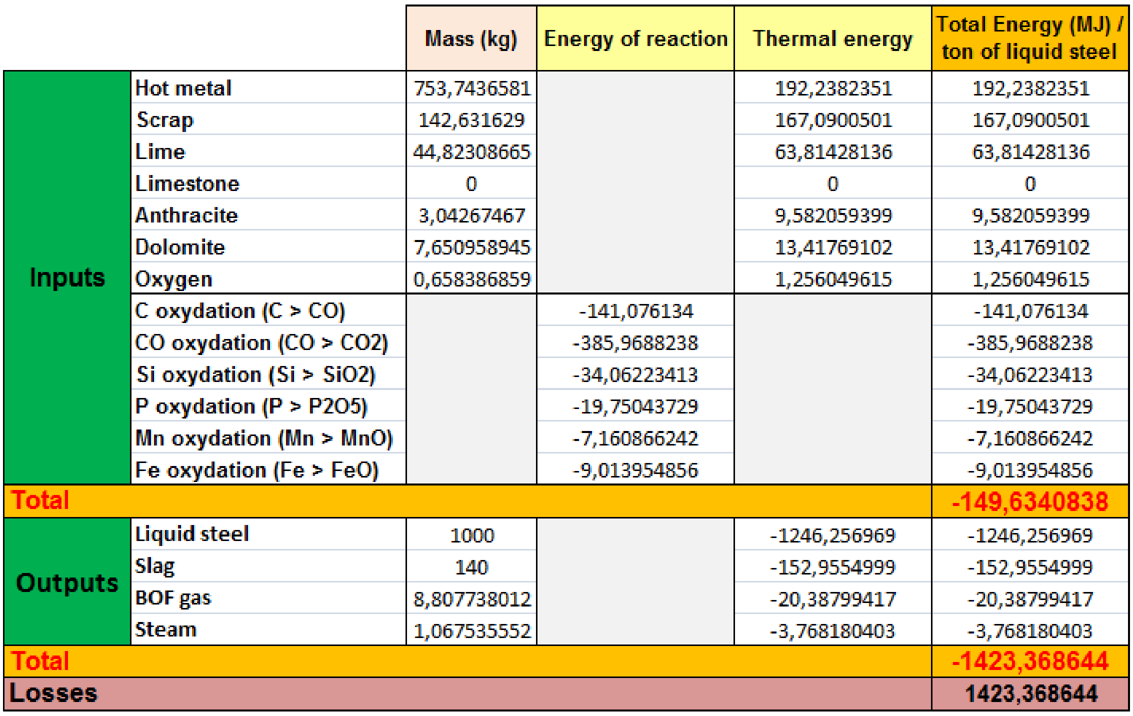
Let us also present the initial and final temperatures for all the inputs and outputs of the process (these temperatures are approximate and we added 273,15 to put them in Kelvins):



		Mass (kg)	Initial temperature Ti (K)	Final temperature Tf (K)
Inputs	**Hot metal**	753,743658	1573,15	1873,15
	Scrap	142,631629	298,15	1873,15
	Lime	44,8230867	298,15	1873,15
	Limestone	0	298,15	1873,15
	Anthracite	3,04267467	298,15	1873,15
	Dolomite	7,65095895	298,15	1873,15
	Oxygen	0,65838686	298,15	1873,15
Outputs	**Liquid steel**	1000	1923	298,15
	Slag	140	1573,15	298,15
	BOF gas	8,80773801	1923	323,15
	Steam	1,06753555	1923	488,15

Figure: Initial en final temperatures of the inputs and outputs of the BOF process (Avilés, Spain, 2010)

Here are now the results of the energy balance. In the category inputs we put the chemical reactions occurring inside the converter, and as they are all exothermic, all the energies associated are negatives. In the category outputs we can as well observe that the energies are negatives, and that is explained by the fact that the temperature of all the outputs decreases, contrary to the temperature of all the inputs.
To find the calculation details of the energy balance, it is necessary to refer to the EXCEL file associated with this study.



		Mass (kg)	Energy of reaction	Thermal energy	Total Energy (MJ) / ton of liquid steel
Inputs	Hot metal	753,7436581		192,2382351	192,2382351
	Scrap	142,631629		167,0900501	167,0900501
	Lime	44,82308665		63,81428136	63,81428136
	Limestone	0		0	0
	Anthracite	3,04267467		9,582059399	9,582059399
	Dolomite	7,650958945		13,41769102	13,41769102
	Oxygen	0,658386859		1,256049615	1,256049615
	C oxydation (C > CO)		-141,076134		-141,076134
	CO oxydation (CO > CO2)		-385,9688238		-385,9688238
	Si oxydation (Si > SiO2)		-34,06223413		-34,06223413
	P oxydation (P > P2O5)		-19,75043729		-19,75043729
	Mn oxydation (Mn > MnO)		-7,160866242		-7,160866242
	Fe oxydation (Fe > FeO)		-9,013954856		-9,013954856
Total					**-149,6340838**
Outputs	Liquid steel	1000		-1246,256969	-1246,256969
	Slag	140		-152,9554999	-152,9554999
	BOF gas	8,807738012		-20,38799417	-20,38799417
	Steam	1,067535552		-3,768180403	-3,768180403
Total					**-1423,368644**
Losses					**1423,368644**

Figure: Energy balance of the basic oxygen furnace (Avilés, Spain, 2010)

In the section “Conclusion and perspectives” we are going to analyze further these results.

Part 3: Exergy analysis of the basic oxygen furnace

I) Presentation of the exergy concept

The first and second laws of thermodynamics are incontrovertible “laws” in the resolution of problems concerning energetic. The first law enunciates the equability of diverse forms of energy (thermal, mechanical, electrical…) and allows us to examine the energy flows to which the diverse systems are submitted.

However, we remark that even if there is quantitative equality of the diverse forms of energy, the quality of these forms changes from one to the other, even inside one given form, and also changes with the situations considered. Thereby, one MJ of thermal energy at 1000°C doesn’t represent the same energetic “potential” that one MJ of the same thermal energy at 20°C. Similarly, the potential of use of one MJ of mechanical energy quickly appears to be different from the one of one MJ of thermal energy. Indeed, if mechanical energy can be spontaneously transformed into thermal energy (through “deterioration” for example), the reversed transformation, non spontaneous, needs to proceed according a very specific scheme.

All these elements, linked with the energy quality and with the transformation of energy constitute the second law of thermodynamics, also considered as an evolution law.

The physical quantity associated with this evolution is entropy whose creation we observe for processes occurring outside of strict equilibrium, that is to say for all the industrial operations which necessarily have to present a certain kinetic to occur in a limited time. Thereby, the bigger the unbalance is in a process (heat transfer in a heat exchanger for example) the bigger the power necessary is. But there is a drawback to this observation: an important kinetic of transfer can be obtained by an important deterioration of the energy (spontaneous and irreversible transformation of an energy known to be “noble” in heat) and an important creation of entropy.

Thereby, since a long time, entropy creation was used by scientists to measure the deterioration of energy caused by the irreversibilities of the energetic transfers and transformations. However, for the engineer, who is used to think in energetic terms in J, MJ or kW.h, or in terms of power in watts, kW or MW, this measure isn’t practical. Indeed, entropy, or its evolution in time, is measured in energy unit, or power unit, per Kelvin ($J.K^{-1}$; $W.K^{-1}$).

This fact is at least one of the reasons why it is interesting to use the notion of exergy to treat these problems of energy deterioration.

The exergy (unit: J), is the part of the energy amount for a specific transformation that can be potentially retrieved in the form of work or electrical energy (these are equivalently directly usable in a process). It is thus the maximum theoretical useful work obtainable as the system interacts with the ambient. The rest of the energy amount is called anergy and it's the part of energy that cannot be retrieved.

So we can write the energy of a system as following:

Energy = Ex + An

With Ex being the exergy of the system and An being the anergy or non useful exergy of the system.

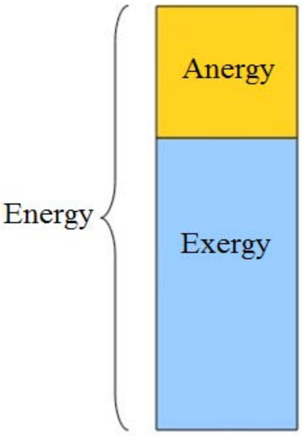


Figure: Representation of the energy and anergy part within a certain amount of energy (the proportions are totally random)

Important remarks:

- A high amount of exergy is an indication of quality for the energy concerned in terms of potentially extractible work.
- The exergy losses have two origins and are irreversible: technological imperfections like dissipation or friction and irreversibilities of the system because of the second law of thermodynamics.

II) General calculation of exergy

Let's consider the system of the figure bellow which is initially in any state. This system is defined by its energy En, its entropy S, its volume V, its temperature T, its pressure P and its chemical potential μ. This system is not in balance with the ambient environment (thermally, mechanically and chemically) so heat, work and matter exchanges will occur.

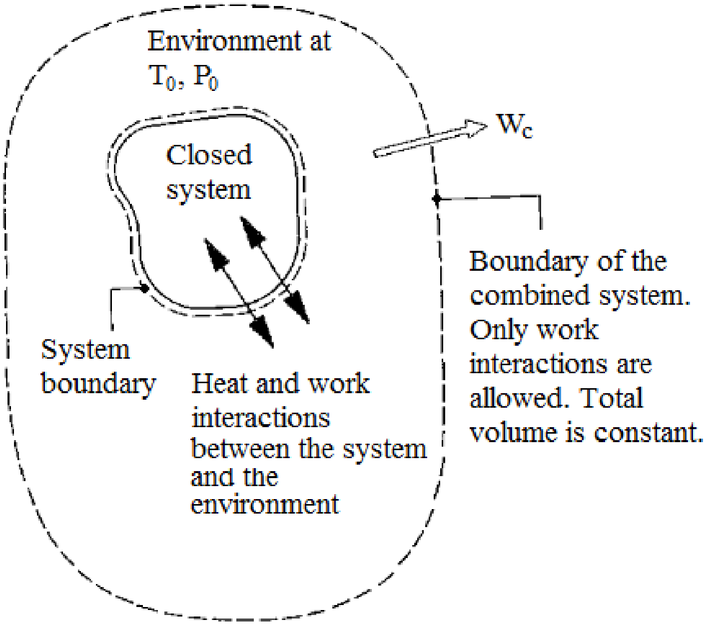


Figure: Combined system of closed system and environment

We want to evaluate the maximum work W_c that could be developed by the combined system. The boundary of the combined system allows only energy transfers by work ensuring that the work developed is not affected by heat transfers to or from the combined system. We are thus going to express the work (or mechanical energy) that this supersystem (system with the ambient environment) can produce when the system changes from its initial state to a dead state (non forced balance state with the ambient environment where the thermal, mechanical and chemical balance conditions are satisfied).

$$\Delta En_c = Q_c - W_c$$

With ΔEn_c being the variation of energy of the combined system (or supersystem) and Q_c being the heat developed by the combined system. We know that $Q_c = 0$ because only work interactions are allowed concerning the combined system (see figure).

ΔU_c is the internal energy change of the supersystem and $\Delta U_c = \Delta En_c = \Delta En - \Delta En°$ with ΔEn being the variation of energy of the system and $\Delta En°$ the variation of energy of the environment. Let's also define U as being the initial internal energy of the system and U_0 its final internal energy (internal energy of the environment).

We know that U changes with the entropy S, the volume V and the number of moles of each specie N_i.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_i} dV + \sum_i \left(\frac{\partial U}{\partial S}\right)_{V,S,N_{j\neq i}} dN_i$$

But we know that for a .0closed system: $dU = TdS - PdV$

So for an open system: $dU = TdS - PdV + \sum_i \mu_i dN_i$ with $\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j}$ being the chemical potential of the specie i.

Since U is an homogeneous function of the first degree with S, V and N_i we can write:

$U = TS - PV + \sum_i \mu_i N_i$ so for the environment: $U° = T_0 S° - P_0 V° + \sum_i \mu_i° N_i°$

(the exponent "°" refers to the environment while the index "0" refers to the system when it is in equilibrium with the environment).

And for a system of constant chemical composition: $U = TS - PV$

So $\Delta U° = T_0 \Delta S° - P_0 \Delta V° + \sum_i \mu_i° \Delta N_i°$

And so $W_c = \Delta En - T_0 \Delta S° + P_0 \Delta V° - \sum_i \mu_i° \Delta N_i°$

- We know that the volume of the environment is really big compared to the volume of the system so $\Delta(V + V°) = 0$ and we can replace $\Delta V°$ with ΔV.
- Likewise, $\Delta(N_i + N_i°) = 0$ so we can substitute $\Delta N_i°$ with ΔN_i.
- We can say that $\Delta S \sim \Delta S°$ because we want to express the maximum amount of work (exergy) so we neglect the entropy production.

We also have:

$$\left.\begin{array}{l} - \quad \Delta En = U_0 - En \\ - \quad \Delta S = S_0 - S \\ - \quad \Delta V = V_0 - V \\ - \quad \Delta N_i = N_{i,0} - N_i \end{array}\right\}$$

All the different variations concerning the system between its initial state and the balanced state with the environment (described with the index "0")

So: $\Delta Ex = W_{c\,(optimal)} = U_0 - En - T_0(S_0 - S) + P_0(V_0 - V) - \sum_i \mu_i°(N_{i,0} - N_i)$

With ΔEx being the variation of exergy of the supersystem.

But we know that $U_0 = T_0 S° - P_0 V° + \sum_i \mu_i° N_i°$

And that for a system balanced with the environment:

- $T = T_0 = T°$
- $P = P_0 = P°$
- $S = S_0$
- $V = V_0$
- $\mu_i = \mu_{i,0} = \mu_i°$

So: $\Delta Ex = -En + T_0 S - P_0 V + \sum_i \mu_i° N_i = Ex° - Ex = -Ex$

With $Ex°$ being the exergy of the environment (always null), and Ex being the exergy of the system (which we are trying to evaluate).
$Ex_{system} = Ex = En - T_0S + P_0V - \sum_i \mu_i°N_i$ but $En = U + Ec + Ep$

So the exergy of a system can be calculated using the following general formula:

$$\boxed{Ex = U - T_0S + P_0V - \sum_i \mu_i°N_i + \frac{c^2}{2} + gz}$$

In conclusion, in the absence of nuclear, magnetic, electrical and surface tension effects the total exergy of a system Ex can be divided into the four following components:

- Physical exergy
- Kinetic exergy $Ex_{kn} = \frac{c^2}{2}$
- Potential exergy $Ex_{pt} = gz$
- Chemical exergy

These are going to be determined further.

III) Exergy calculation of the basic oxygen furnace

In a steel plant the kinetic and potential energies and thus exergies are not taken into account because we suppose that the speed factor is negligible and that the different products used and produced are at the same altitude $z = 0$.

The only exergies left to consider are thus the physical and the chemical exergies.

The chemical exergy

The chemical exergy of a system is defined as the exergy of this system when it is mechanically and thermally balanced with the environment.

So: $Ex_{ch} = U_0 - T_0S_0 + P_0V_0 - \sum_i \mu_i°N_{i,0}$

$$Ex_{ch} = T_0S_0 - P_0V_0 + \sum_i \mu_{i0}N_{i,0} - T_0S_0 + P_0V_0 - \sum_i \mu_i°N_{i,0}$$

So the chemical exergy of a system can be calculated with the formula:

$$\boxed{Ex_{ch} = \sum_i N_{i,0}(\mu_{i0} - \mu_i°)}$$

With $\mu_i°$ being the chemical potential of the specie i within the environment (at T_0 and P_0) and μ_{i0} being the chemical potential of the specie i within the closed system in equilibrium with the environment.

In most studies the chemical exergy is not taken into account because it is hard to calculate and not really representative. In our study we chose to only consider physical exergy because of these facts and also because in our energy analysis we only had energies related with temperature changes and we wanted to do a direct comparison between exergy and energy, which seemed simpler without the chemical exergy factor.
However, it is important to precise that it would be very interesting to learn more about chemical exergy, how to evaluate it and what it exactly represents.

The physical exergy

To calculate the physical exergy we use the formula demonstrated before:

$$Ex_{ph} = H - T_0S = U + P_0V - T_0S$$

With the different terms being:

- U: Internal energy
- V: Volume
- H: Enthalpy
- S: Entropy
- P: Pressure
- P_0: Reference pressure
- T: Temperature
- $T_0 = T_{ref}$: Reference temperature (298,15)

So we have: $dEx_{ph} = dU + P_0dV - T_0dS$

So: $dEx_{ph} = \delta W + \delta Q + P_0dV - T_0dS$

$$dEx_{ph} = -PdV + \delta Q + P_0dV - T_0dS = -(P - P_0)dV + \delta Q - T_0dS$$

If $P = P_0$ then: $dEx_{ph} = \delta Q - T_0dS$ but: $dS = \delta S_e + \delta S_i$ (with δS_e being the outdoor part of entropy and δS_i being the indoor part of entropy).

If $\delta S_i = 0$ then: $dS = \delta S_e = \frac{\delta Q}{T}$ and $dEx_{ph} = \delta Q - T_0\frac{\delta Q}{T} = \delta Q(1 - \frac{T_0}{T})$
So we obtain: $dEx_{ph} = \delta Q\left(1 - \frac{T_0}{T}\right) = \delta Q\theta$ with $\theta = \left(1 - \frac{T_0}{T}\right)$ being the Carnot factor.
So we can conclude that the physical exergy can be determined generally as following:

$$dEx_{ph} = \delta Q\left(1 - \frac{T_0}{T}\right)$$

So: $$Ex_{ph} = \int_{T_0}^{T} \delta Q\left(1 - \frac{T_0}{T}\right)dT = \int_{T_0}^{T} \delta Q\theta dT$$

With δQ being the thermal energy (heat) and τ being the Carnot factor.

1) Exergy of a heat reservoir with a constant temperature T

If the variable T is constant we have:

$$Ex_{ph} = Q\left(1 - \frac{T_0}{T}\right)$$

This formula can be used for the chemical reactions inside the converter because they produce heat at a fixed temperature. The temperature T will be replaced with the temperature inside the converter in that case.

We name this type of exergy the exergy of the heat losses:

$$Ex_{heat\ losses} = Q\left(1 - \frac{T_0}{T}\right)$$

2) Exergy of a heat reservoir with a changing temperature T

If the temperature T changes, the formula of physical exergy gives:

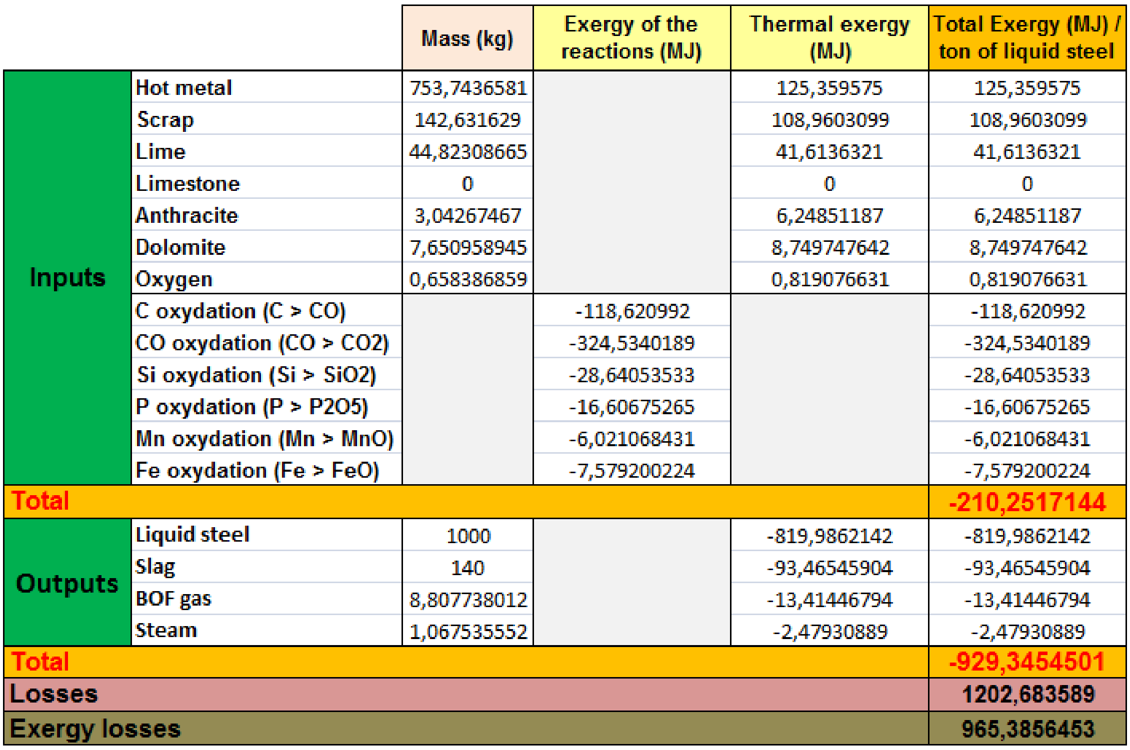
$$Ex_{ph} = \int_{T_0}^{T_f} \delta Q\left(1 - \frac{T_0}{T}\right) dT \; = mc_p \int_{T_0}^{T_f} \left(1 - \frac{T_0}{T}\right) dT = mc_p\left(T_f - T_0 - T_0 ln\frac{T_f}{T_0}\right)$$

$$Ex_{ph} = mc_p\left(T_f - T_0\right) * \left(1 - \frac{T_0}{T_f - T_0} ln\frac{T_f}{T_0}\right)$$

We call this type of exergy the thermal exergy:

$$Ex_{thermal} = mc_p\left(T_f - T_0\right) * \left(1 - \frac{T_0}{T_f - T_0} ln\frac{T_f}{T_0}\right)$$

IV) Results of the exergy analysis

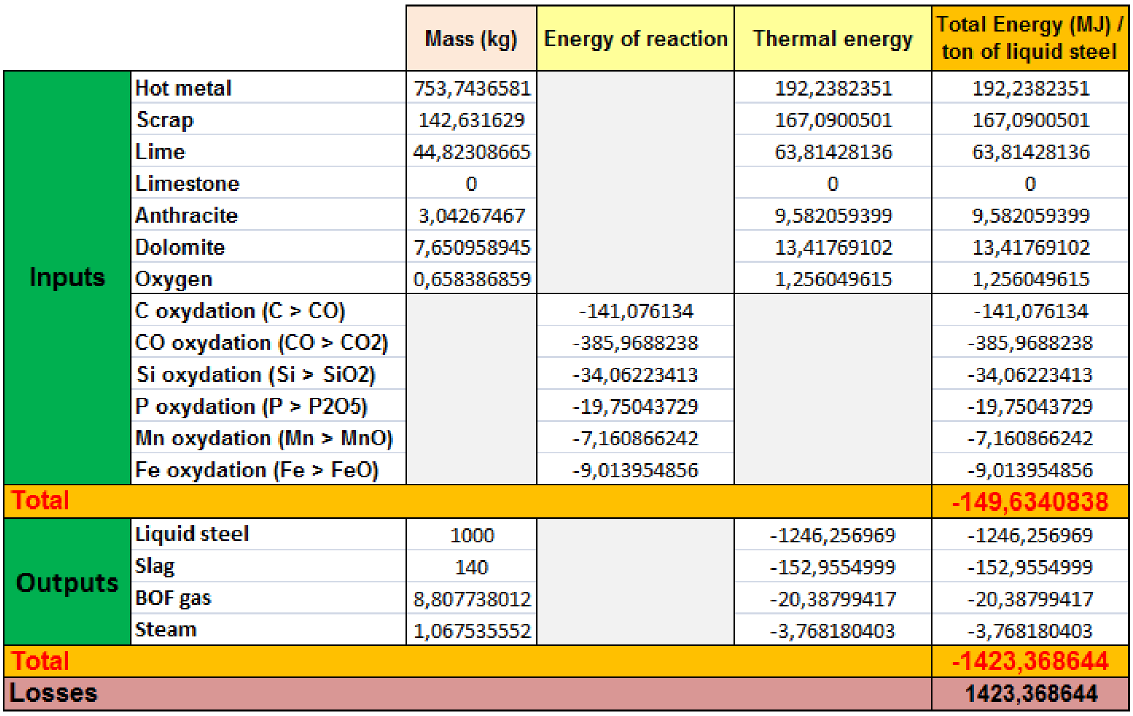


		Mass (kg)	Exergy of the reactions (MJ)	Thermal exergy (MJ)	Total Exergy (MJ) / ton of liquid steel
Inputs	Hot metal	753,7436581		125,359575	125,359575
	Scrap	142,631629		108,9603099	108,9603099
	Lime	44,82308665		41,6136321	41,6136321
	Limestone	0		0	0
	Anthracite	3,04267467		6,24851187	6,24851187
	Dolomite	7,650958945		8,749747642	8,749747642
	Oxygen	0,658386859		0,819076631	0,819076631
	C oxydation (C > CO)		-118,620992		-118,620992
	CO oxydation (CO > CO2)		-324,5340189		-324,5340189
	Si oxydation (Si > SiO2)		-28,64053533		-28,64053533
	P oxydation (P > P2O5)		-16,60675265		-16,60675265
	Mn oxydation (Mn > MnO)		-6,021068431		-6,021068431
	Fe oxydation (Fe > FeO)		-7,579200224		-7,579200224
Total					**-210,2517144**
Outputs	Liquid steel	1000		-819,9862142	-819,9862142
	Slag	140		-93,46545904	-93,46545904
	BOF gas	8,807738012		-13,41446794	-13,41446794
	Steam	1,067535552		-2,47930889	-2,47930889
Total					**-929,3454501**
Losses					**1202,683589**
Exergy losses					**965,3856453**

Figure: Exergy balance of the basic oxygen furnace (Avilés, Spain, 2010)

In the section “Conclusion and perspectives” we are going to analyze further these results.

Presentation and interpretation of the results



		Mass (kg)	Energy of reaction	Thermal energy	Total Energy (MJ) / ton of liquid steel
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Total					**-1423,368644**
Losses					**1423,368644**

Figure: Energy balance of the basic oxygen furnace (Avilés, Spain, 2010)

In the inputs section we can see the energies needed to heat up these inputs, followed by the study of the different refining reactions. It is very important to precise that the energy consumed to heat the different inputs comes from the chemical reactions and that no other source of energy is used for this purpose.

The biggest amount of energy consumed is for the heating of the hot metal with 192,24 MJ per ton of liquid steel produced. Considering the mass of hot metal involved we could think that the energy consumed to heat it up should be more important. The reason comes from the fact that this input is just heated from 1573,15 to 1873,15 K (see page 18) because it comes directly from the previous process, the blast furnace, so it didn’t have time to cool down to the room temperature. Processing it directly into the basic oxygen furnace saves a lot of energy.

The other inputs are heated up from 298,15 to 1873,15 K but their respective masses are less important than the mass of hot metal. We can however observe that the energy needed to heat up the scrap is close to the one necessary to heat the hot metal despite the different gaps of temperature.

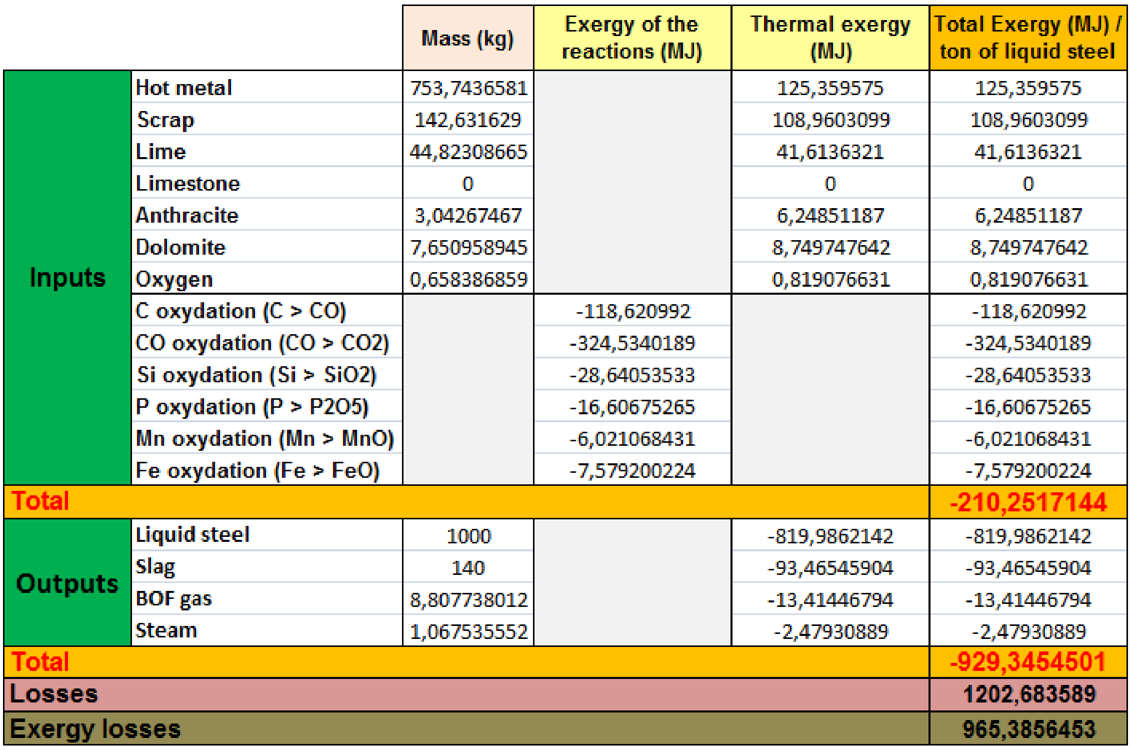
Concerning the chemical reactions we see that all the reactions are exothermic and that the ones producing the more energy are the CO oxidation and then the C oxidation. The energy produced by these reactions is used to heat the different inputs of the process.

In the Total line we have -149,63 MJ. This negative result means that the energy produced by the chemical reactions was sufficient and even too important to heat up the different inputs so in the inputs section there is more energy produced than there is energy consumed.

Now when we take a look at the outputs of the process we see that the biggest amount of energy produced comes from the liquid steel with 1246,26 MJ produced per ton of liquid steel. Such an amount can be explained by the important gap between its initial and final temperature and its important mass. All the outputs produce energy by releasing heat while their temperatures decrease that's why all the energies are negative. With the result of -1423,37 MJ in the Total line we can see that the outputs section produces a lot of energy for one ton of liquid steel produced and produces in fact more energy than the inputs section.

In the Losses line we put, in absolute value since it is a loss, the amount of energy produced by the outputs because the energy produced by the inputs remains inside the converter (the system is supposed to be adiabatic in our study) and is contained in these 1423,37 MJ of losses. We suppose that this energy is not recovered (it is more than probable that it is at least partially recovered in reality) and that's why we put it in the Losses line.

Remark: Even if there is no limestone added during the year 2010 it is considered to be an input of the BOF process so we chose to figure it on the different tables.



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	Limestone	0		0	0
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	Dolomite	7,650958945		8,749747642	8,749747642
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Total					**-210,2517144**
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	Slag	140		-93,46545904	-93,46545904
	BOF gas	8,807738012		-13,41446794	-13,41446794
	Steam	1,067535552		-2,47930889	-2,47930889
Total					**-929,3454501**
Losses					**1202,683589**
Exergy losses					**965,3856453**

Figure: Exergy balance of the basic oxygen furnace (Avilés, Spain, 2010)

Comparing the results of the energy analysis with the ones of the exergy analysis we can see that the exergy amount of each quantity of energy is as expected inferior to the amount of energy.

Concerning the inputs and the outputs sections the results are almost in the same range than before so the previous remarks on the different amounts are still available.

The Total line is not really interesting because it is not relevant to know what amount of exergy is associated with the energy needed to heat up hot metal (for example) because this exergy is consumed for the process and not released. What's more interesting is to

know what amount of exergy can be retrieved from an amount of energy produced. Here is the amount of exergy retrievable (in absolute value) on the inputs of the BOF process:
$Ex_{retrievable}(inputs) = 118{,}62 + 324{,}53 + 28{,}64 + 16{,}61 + 6{,}02 + 7{,}58 = 508\ MJ.$
Concerning the chemical reactions, taking for example the amount of energy produced by the oxidation of the carbon, we now know that on the 141,08 MJ of energy produced only 118,62 MJ is pure exergy and can thus be retrieved. The rest of it, as mentioned before, is lost and is called anergy.

In the outputs section the Total line represents the exergy retrievable on the outputs (calculation we did before on the inputs part). The results of the exergy analysis show that most of the exergy can be retrieved from the liquid steel and that the biggest the energy is, the biggest the anergy is as well. We can thus now determine the real amount of exergy we can hope to retrieve from the BOF process:

$$Ex_{retrievable}(BOF) = 508 + 929{,}35 = 1437{,}35\ MJ$$

The losses are evaluated to be occurring at a temperature around 1873,15 K (temperature inside the converter) so we determined the exergy associated with them using this temperature and the formula of the exergy of the heat losses. We had no information on the real temperature of the heat losses that's why we had to make a supposition. It is however easy to recalculate this result by referring to the exergy calculation part (page 25) and by simply changing the temperature.

Finally the exergy losses represent the sum, in absolute value of all the anergies of the process, also called exergies lost. This part cannot be retrieved and is definitively lost (the origin of these losses is explained page 20).

Here is now a presentation in absolute values of the results under the form of histograms. The red part representing anergy is definitively lost and the blue part represents the exergy.

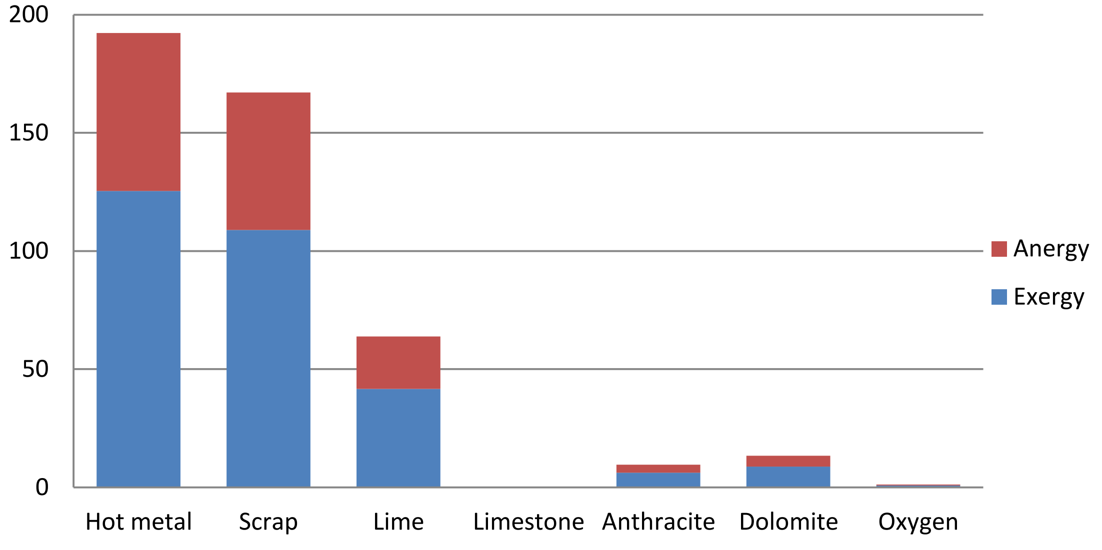


Figure: Histogram of the ratio between anergy and exergy for all the inputs of the BOF process (Avilés, Spain, 2010)

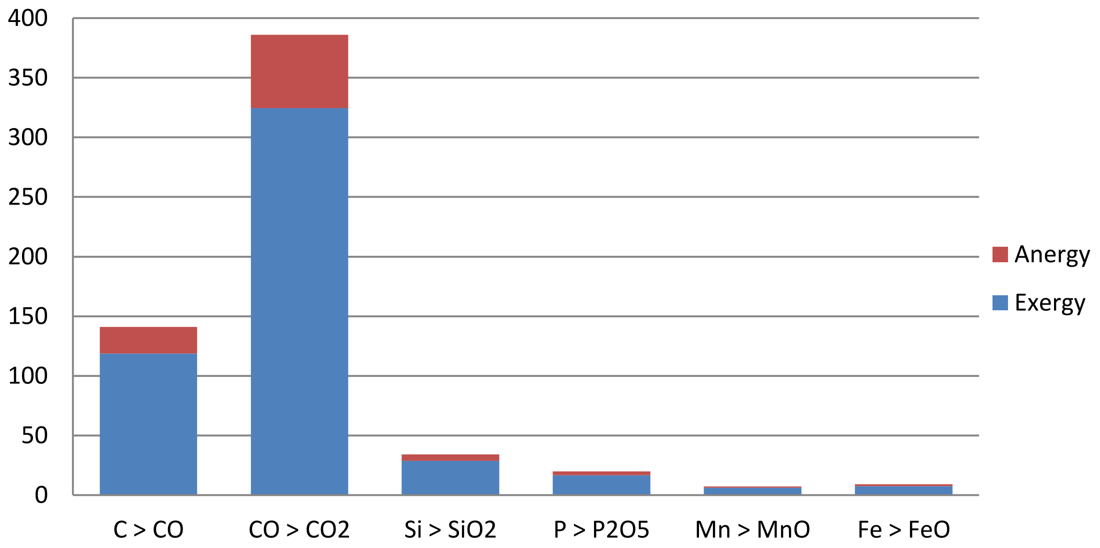


Figure: Histogram of the ratio between anergy and exergy for all the chemical reactions occurring in the BOF process in absolute values (Avilés, Spain, 2010)

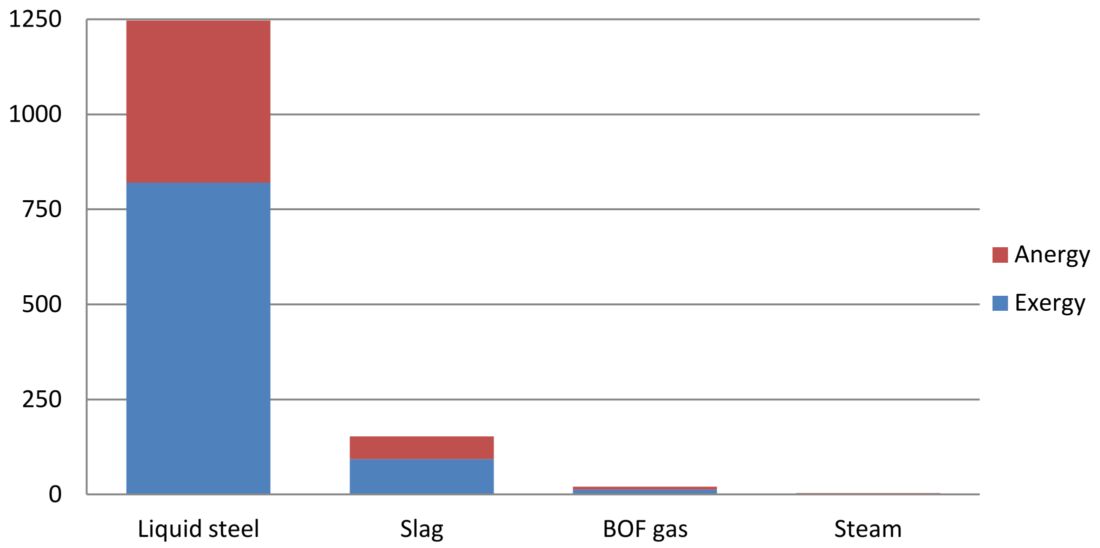


Figure: Histogram of the ratio between anergy and exergy for all the outputs of the BOF process in absolute values (Avilés, Spain, 2010)

In all these histograms, every bar represents the amount of energy ($En = Ex + An$).

Conclusions and perspectives

Conclusions of the analysis of the basic oxygen furnace:

This analysis was designed to compare energy and exergy analysis on the BOF process. The results showed us the importance of the different streams within the process and helped us quantify the real amount of retrievable energy (exergy) and its origin.

On this process we can conclude that there is more energy released than there is consumed. We can thus imagine that the BOF process can be a good source of improvement within the plant concerning exergy recuperation.

The exergy study is very interesting because it only takes into account exergy, so it fully determines the real streams of usable energy in presence. It also helps us identify the location and importance of the thermodynamic losses (exergy losses) and thus allows the comparison of the different processes between them and with the environment (by this mean we can then classify them in the order of their potential of improvement).

Regarding all these points it seems obvious that exergy analysis provides additional information compared to a simple energy analysis because it can really identify where we should really put the effort to retrieve energy and by this mean, economize it.

A good advantage of exergy analysis is that it can be used in different ways: an environmental impact analysis will focus more on resource consumption and harm caused by waste streams, whereas technical improvement of the process will be achieved by pinpointing the main exergy losses and low exergy efficiencies.

Perspectives:

If this project is pursued, one important goal would be to study the other processes within the steel plant and compare them to evaluate the most important losses and their locations. This could be very interesting for the company in economical terms.

We can hope that it will be possible to analyze the different streams within the plant in order to reduce the losses or to limit the impact of the plant on the environment.

Another goal to achieve in this work would be to fully determine what is called “chemical exergy” and how to calculate it.

In conclusion, we can say that there's still a lot of work to accomplish concerning the exergy analysis but that it seems to be an interesting concept to pursue studying.

Appendix

I) Cp formulas of the elements involved in steel making processes

Here are the formulas of the heat capacities of most of the elements involved in steel making.

cp formulas of the elements (unit: cal/K.mol):

- Al2O3 – c: (298 – 1800): $27{,}43 + 0{,}00306\,T - 847000/T^2$
- Ar – g: (all temperatures): $4{,}97$
- C – c: (298 – 2300): $4{,}1 + 0{,}00102\,T - 210000/T^2$
- CO – g: (298 – 2500): $6{,}79 + 0{,}00098\,T - 11000/T^2$
- CO2 – g: (298 – 2500): $10{,}55 + 0{,}00216\,T - 204000/T^2$
- CH4 – g: (273 – 1200): $5{,}34 + 0{,}0115\,T$
- CaO – c: (298 – 1800): $11{,}67 + 0{,}00108\,T - 156000/T^2$
- CaCO3 – c: (273 – 1033): $19{,}68 + 0{,}01189\,T - 307600/T^2$
- Cu – c: (273 – 1357): $5{,}44 + 0{,}01462\,T$
  Cu – l: (1357 – 1573): $7{,}5$
- Cr – c: (273 – 1823): $4{,}84 + 0{,}00295\,T$
  Cr – l: (1823 - 1923): $9{,}7$
- Fe – c, α: (298 – 1033): $3 + 0{,}00758\,T + 0{,}6.\,10^5/T^2$
  Fe – c, β: (1033 – 1183): $11{,}13$
  Fe – c, λ: (1183 – 1673): $5{,}8 + 0{,}002\,T$
  Fe – c, δ: (1673 – 1810): $6{,}74 + 0{,}00164\,T$
  Fe – l: (1810 – 2973): $9{,}77 + 0{,}0004\,T$
- FeO – c: (298 – 1650): $11{,}66 + 0{,}002\,T - 67000/T^2$
  FeO – c: (1650 – 1873): $16{,}3$
- Fe2O3 – c: (273 – 1097): $24{,}72 + 0{,}01604\,T - 423400/T^2$
- Fe3O4 – c: (273 – 1065): $41{,}17 + 0{,}01882\,T - 979500/T^2$
- H2 – g: (273 – 2500): $6{,}62 + 0{,}00081\,T$
- H2O – g: (300 – 2500): $8{,}22 + 0{,}00015\,T + 0{,}000000134\,T^2$
- H2S – g: (300 – 600): $7{,}2 + 0{,}0036\,T$
- K2O, Al203, 3 SiO2 – c, orthoclase:
  (273 – 1373): $69{,}26 + 0{,}00821\,T - 2331000/T^2$
  K2O, Al203, 3 SiO2 – v, orthoclase:
  (273 – 1373): $69{,}81 + 0{,}01053\,T - 2403000/T^2$
  K2O, Al203, 3 SiO2 – c, microclinic:
  (273 – 1373): $65{,}65 + 0{,}01102\,T - 1748000/T^2$
  K2O, Al203, 3 SiO2 – v, microclinic:
  (273 – 1373): $64{,}83 + 0{,}01438\,T - 1641000/T^2$
- Mn – c, α: (273 – 1108): $3{,}76 + 0{,}00747\,T$
  Mn – c, β: (1108 – 1317): $5{,}06 + 0{,}00395\,T$

Mn – c, λ: (1317 – 1493): $4{,}8\ +\ 0{,}00422\,T$
Mn – l: (1493 – 1673): 11

- MnO – c: (273 – 1923): $7{,}43\ +\ 0{,}01038\,T - 0{,}00000362\,T^2$
- Mg – c: (273 – 923): $6{,}20\ +\ 0{,}00133\,T - 67800/T^2$
  Mg – l: (923 – 1048): $7{,}4$
- MgCO3 – c: (290): $16{,}9$
- MgO – c: (298 – 2100): $10{,}18\ +\ 0{,}00174\,T - 148000/T^2$
- Na2O, Al2O3, 3 SiO2 – c, albite:
  (273 – 1373): $63{,}78\ +\ 0{,}01171\,T - 1678000/T^2$
  Na2O, Al2O3, 3 SiO2 – v:
  (273 – 1173): $61{,}25\ +\ 0{,}01768\,T - 1545000/T^2$
- N2 – g: (300 – 3000): $6{,}5\ +\ 0{,}00100\,T$
- Ni – c, α: (273 – 626): $4{,}26\ +\ 0{,}00640\,T$
  Ni – c, β: (626 – 1725): $6{,}99\ +\ 0{,}000905\,T$
  Ni – l: (1725 – 1903): $8{,}55$
- NO – g: (300 – 5000): $8{,}05\ +\ 0{,}000233\,T - 156300/T^2$
- O2 – g: (298 – 3000): $7{,}16\ +\ 0{,}001\,T - 40000/T^2$
- P – c, yellow: (273 – 317): $5{,}5$
  P – c, red: (273 – 472): $0{,}21\ +\ 0{,}0180\,T$
  P – l: (317 – 373): $6{,}6$
- P2O5 (P4O10) – c: (273 – 631): $15{,}72\ +\ 0{,}01092\,T$
  P2O5 (P4O10) – g: (631 – 1371): $73{,}6$
- S – c, rombic: (273 – 368): $3{,}63\ +\ 0{,}0064\,T$
  S – c, monoclinic: (368 – 392): $4{,}38\ +\ 0{,}0044\,T$
- SO2 – g: (300 – 2500): $7{,}7\ +\ 0{,}0053\,T - 0{,}00000083\,T^2$
- Si – c, α: (298 – 523): $4{,}28\ +\ 0{,}02106\,T$
  Si – c, β: (523 – 1995): $17{,}39\ +\ 0{,}00031\,T - 990000/T^2$
- SiO2 – c, quartz, α: (273 -848): $10{,}87\ +\ 0{,}008712\,T - 241200/T^2$
  SiO2 – c, quartz, β: (848 -1873): $10{,}95\ +\ 0{,}00550\,T$
  SiO2 – c, cristobalite, α: (273 -523): $3{,}65\ +\ 0{,}024\,T$
  SiO2 – c, cristobalite, β: (523 -1973): $17{,}09\ +\ 0{,}000454\,T - 897200/T^2$
  SiO2 – v: (273 -1973): $12{,}8\ +\ 0{,}00447\,T - 302000/T^2$
- Sn – c: (273 – 504): $5{,}05 + 0{,}00400\,T$
  Sn – l: (504 – 1273): $6{,}6$
- Ti – c: (273 – 713): $8{,}91\ +\ 0{,}00114\,T - 433000/T^2$
- TiO2 – c: (273 – 713): $11{,}81\ +\ 0{,}00754\,T - 41900/T^2$
- Zn – c: (273 – 692): $5{,}25\ +\ 0{,}00270\,T$
  Zn – c: (692 – 1122): $7{,}59\ +\ 0{,}00055\,T$

II) Explanation of the EXCEL file

The goal of my internship was to establish the energy and exergy balance of the basic oxygen furnace process used in the steel industry. This brief report is designed to explain the calculation I did in the excel file containing the energy and exergy balances.

In a first part I am going to explain how I established the energy balance of the process, then in a second part I will present briefly the concept of exergy and its calculation to finally conclude with the exergy balance of the process considered.

1) The energy balance

Calculation of the thermal energy

We have:

$$En_{thermal} = \int_{T_i}^{T_f} mc_p dT = m \int_{T_i}^{T_f} c_p dT$$

With En being the amount of energy in J, T_i and T_f respectively being the initial and final temperature of the input considered in K, m being the mass of the input in kg and c_p being its heat capacity in J/(kg.K).

We used these two references to find the $c_p$of all the elements involved in steel making process:

- O. Kubaschewski and C. Alcock; Metallurgical Thermochemistry, 5th edition, 1989
- Manual del ingeniero químico sexta edición (TOMO 1) Mc Graw Hill

We used in priority the formulas of the first reference because they had been used before in other studies. Here are all the formulas we used in the excel file. They appear in a table named “Heat capacity formulas” in the sheet “Reference” of the excel file.

For the calculation of thermal energy we created a sheet called “cp calculation” where the term $\int_{T_i}^{T_f} c_p dT$ is determined for every input and output by taking into account the composition of each one. This composition comes from the sheet “Mass balance” of the excel file. In this sheet, you can also find the data from the BOF of the steel factory of Avilés.

Calculation of the energy of reaction

$$En_{reaction} = m * \Delta Hr_{reaction}(T)$$

With $\Delta Hr(T)$ being the enthalpy of reaction associated with the reaction considered in J/kg and m being the mass of reactant consumed in the reaction.

Let’s remind the reactions considered:

$$Fe + 1/2\ O_2 \rightarrow FeO$$
$$Si + O_2 \rightarrow SiO_2$$
$$Mn + 1/2\ O_2 \rightarrow MnO$$
$$2\,P + 5/2\ O_2 \rightarrow P_2O_5$$
$$C +\ 1/2\ O_2 \rightarrow CO$$
$$CO + 1/2\ O_2 \rightarrow CO_2$$

To determine the enthalpy of reaction $\Delta Hr(T)$ we use the formula:

$$\Delta Hr(T) = \Delta Hf(T_0) + \int_{T_0}^{T} c_p dT \qquad (*)$$

With $\Delta Hr(T)$ being the enthalpy of reaction of one of the elements involved in the reaction, $\Delta Hf(T_0)$ being the enthalpy of formation in J/kg of the component considered at the environment temperature $T_0 = 298{,}15\ K$ and T being the temperature inside the volume where the reaction occurs. In our study the temperature inside the converter is $T = 1600°C = 1873{,}15\ K$.

We found the values of $\Delta Hf(T_0)$ for all the elements of the reactions considered in the reference (These values are stored in the sheet “Reference” under the name “Formation quantities (at 298,15 K)”):

- Manual del ingeniero quimico (sexta edicion) Tomo 1 Mc Graw Hill

Then we calculate the second term of the equation (*) in the sheet “Chemical reactions” and thus we obtain $\Delta Hr(T)$ for every element involved in the chemical reactions.
Finally we built the table in the top of the sheet “Chemical reactions” to determine the energy associated with each reaction. In the first column we put $\Delta Hr(T)$ of the first reactant, then in the second column, $\Delta Hr(T)$ of the second reactant and in the third one $\Delta Hr(T)$ of the product of the reaction considered. We can thus determine in the fourth column the enthalpy of the reaction considered for 1 kg of reactant consumed.
To find the energy of each reaction we just need the masses of the reactants (calculation explained in the report in the energy balance part). All of the calculation are realized in the sheet “Chemical reactions”.

2) The exergy balance

Calculation of the physical exergy

$$Ex_{ph} = \int_{T_0}^{T} \delta Q \left(1 - \frac{T_0}{T}\right) dT \ = \int_{T_0}^{T} \delta Q \tau dT$$

With δQ being the thermal energy (heat) and τ being the Carnot factor.

This general formula can be used for two cases:

- *<u>Exergy of a heat reservoir at a fixed temperature T:</u>*

We name this type of exergy the exergy of heat losses:

$$Ex_{heat\ losses} = Q\left(1 - \frac{T_0}{T}\right)$$

- *<u>Exergy of a heat reservoir with a declining temperature T:</u>*

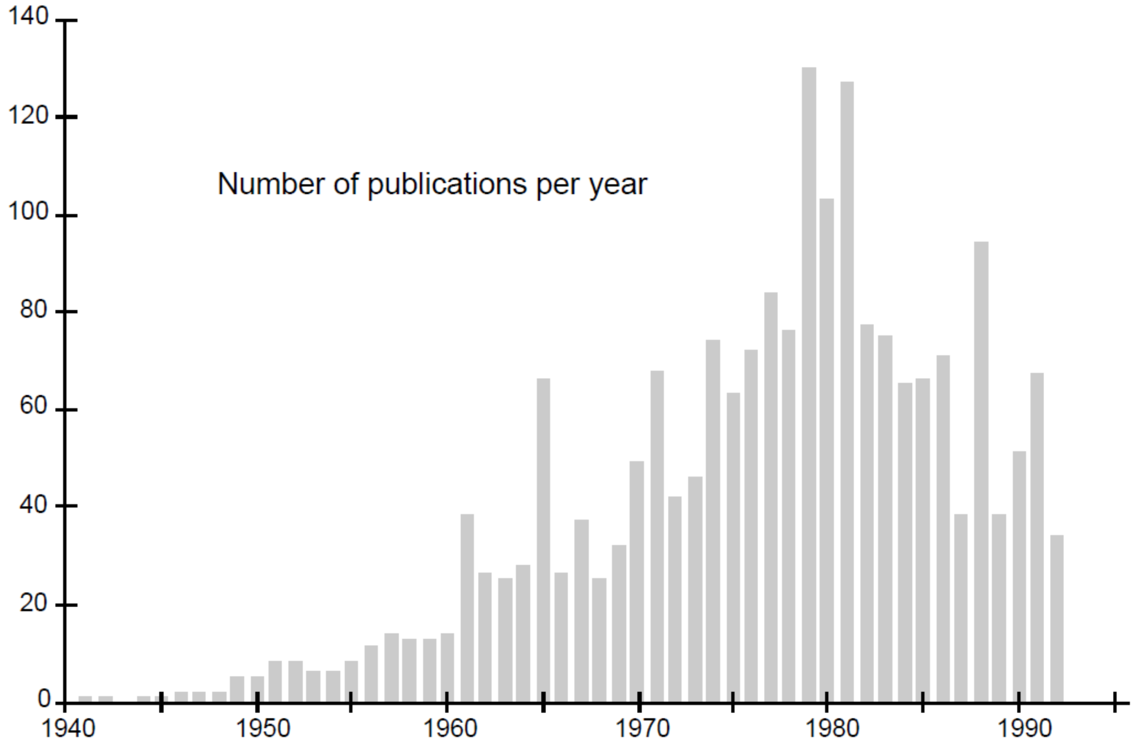
We call this type of exergy the thermal exergy:

$$Ex_{thermal} = mc_p\left(T_f - T_0\right) * \left(1 - \frac{T_0}{T_f - T_0} ln \frac{T_f}{T_0}\right)$$

In the sheet “Exergy balance” we calculated the term $\left(1 - \frac{T_0}{T_f - T_0} ln \frac{T_f}{T_0}\right)$ and then multiplied it with $mc_p\left(T_f - T_0\right)$ which is the heat energy determined in the sheet “Energy balance”.

References

Many articles have been written about exergy throughout the last decades. The figure below shows the number of publications per year during the period from 1940 to 1992.



Obviously the articles I am going to present here are those I used for my study but I'd like to mention the article of Göran Wall, "Bibliography on exergy", where about 2034 documents about exergy are listed. I will put this article in my references and for those who are interested I can transfer it to them.
Certain articles are confidential documents of ArcelorMittal so they don't have an editor and sometimes the edition year isn't available.

Some references figuring within the report itself do not appear in this references part because we weren't able to find them. We chose to put them in the report anyway because maybe some professionals working in the energy field can have access to these references and thus better understand our work.

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