

#### LEHRSTUHL FÜR THERMOPROZESSTECHNIK

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# Diplomarbeit

# Heat Balance of a Continuous Galvanizing Line

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# AFFIDAVIT

I declare in lieu of oath that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. Je remercie toutes les personnes qui m'ont donné la possibilité d'effectuer ce travail et qui m'ont supporté dans sa réalisation.

Ich bedanke mich bei allen, die mir diese Diplomarbeit ermöglicht und mich bei ihrer Erstellung unterstützt haben.

# Abstract

# Heat Balance of a Continuous Galvanizing Line

Metal-working industries traditionally require high energy inputs for their various processes. Aware of the finiteness of natural fuel deposits, efforts are undertaken to reduce the fuel input and to increase the efficiency in order not to waste precious natural resources. In the present work the heat distribution and energy efficiency is examined for the Continuous Galvanizing Line 4 at voestalpine Stahl GmbH in Linz.

In the first part a literature survey gives an overview on the principles and developments in thermal treatment and galvanization of steel strips. Thereafter the process for the Selas' furnace in Linz is described in detail, including the visualization of mass and energy flows during the operating of the line. These flow diagrams are the basis for a heat balance of the two furnace sections DFF (direct-fired furnace) and RTH/RTS (radiant tube heating/ soaking). The quantification for each flow entering and leaving the 2 sub-systems is done by temperature and flow measurements. The majority of them are installed permanently to monitor and control the process; others were added for the purpose of a heat balance.

The primary aim of the heat balance is to calculate to what extent the spent energy does account for the heating of the steel strip and what amount of energy is lost via waste gas, conduction losses through furnace walls etc.

The results are presented for different kinds of steel strips varying in size, material and heat cycle. Analysis evidence a lack of correlation between entering and leaving energy flows, which leads to the conclusion that some of the applied measurements are apparently not working properly. A sensitivity analysis points out which of them have the greatest impact on the results.

Finally possibilities for the optimization of the Continuous Galvanizing Line are presented, including the consideration of a more accurate temperature and volume-monitoring and approaches to gain a higher energy efficiency of the process.

# Kurzfassung

# Energiebilanz einer kontinuierlichen Feuerverzinkungsanlage

Betriebe der metallverarbeitenden Industrie sind traditionell mit einem hohem Energieeinsatz bei ihren Prozessen konfrontiert. Im Hinblick auf eine schonende Nutzung der nicht regenerativen Energiequellen kommt der Reduzierung des Ressourcenverbrauchs und einer Erhöhung der Energieeffizienz eine ständig wachsende Bedeutung zu.

In dieser Arbeit wird die Energieverteilung für die kontinuierliche Feuerverzinkungsanlage für Kaltband (FVZ4) der Voestalpine Stahl GmbH in Linz untersucht. Der erste Teil gibt einen Überblick über die grundlegenden Prinzipien und Entwicklungen in der thermischen Behandlung und Verzinkung von Stahlband. Danach wird der Prozess der FVZ4 im Detail beschrieben. Die Masse- und Energieströme werden anhand von Flussdiagrammen veranschaulicht. Diese Diagramme stellen gleichzeitig die Basis für die Energiebilanz der beiden Ofensektionen DFF (direkt befeuerter Ofen) und RTH/RTS (Strahlrohrofen) dar. Die Quantifizierung sämtlicher Ströme, welche in die beiden Subsysteme eintreten und selbige wieder verlassen, erfolgt mittels Temperatur- und Volumensstrommessungen. Ziel der Energiebilanz ist die Berechnung desjenigen Anteils der eingesetzten Energie, welche im Ofen zur Erwärmung des Stahlbandes genutzt werden kann, und die Erhebung der Verluste im Abgas, durch Wärmeleitung in den Ofenwände, etc.

Die Ergebnisse der Bilanz werden für unterschiedliche Stahlbänder, verschiedene Formate und Glühzyklen präsentiert. Die auftretende Unstimmigkeit zwischen den Energieströmen, die in das System eintreten und jenen, die es wieder verlassen, lässt darauf schließen, dass eine oder mehrere Messungen nicht exakt sind. Eine Sensitivitätsanalyse zeigt, welche der verwendeten Messungen den größten Einfluss auf die Ergebnisse haben.

Ausgehend davon werden einerseits Möglichkeiten zu einer verbesserten Temperatur- und Volumensstrommessung und andererseits Potentiale zur Steigerung der Energieeffizienz diskutiert.

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ANNEX I Enthalpy of air,  $CO_2$ ,  $H_2O$ ,  $N_2$ ,  $O_2$  and  $H_2$ 

ANNEX II Steel enthalpy

# 1 Introduction

# 1.1 Aim of this work

The aim of this work is the calculation of a heat balance for the two furnace sections of Andritz Selas' Continuous Galvanizing Line CGL4 at Voestalpine Stahl in Linz. In a first step, the system boundaries have to be defined. Then all the flows that enter and/ or leave the system are qualified. The quantification of each single flow is done by the use of measurements taken on site. The knowledge of energy flows in the furnace section does not only identify the main process flows but allows also the determination of the energy distribution: What part of the spent energy does apply for the main process aim (the heating or holding of the temperature of steel strips) and what amount of energy is lost. This analysis should lead to considerations about possible optimization.

# **1.2 Definition of the problem**

Metal-working industries are traditionally confronted with high energy inputs for their processes. In times of the shortening of natural resources and an increase of their prices an efficient use of these resources is aimed at. Efficiency can be described as the

"degree to which a system or component performs its designated functions with a minimum consumption of resources." [1]

The main function of the two furnace sections DFF and RTH/RTS of the continuous galvanizing line is the heating of steel strips to their annealing temperature and the holding of this temperature in the soaking zone. This is achieved by the energy that is released during the combustion of natural gas and combustion air. The major part of this energy enters the strip, the remainder leaves the furnace via waste gas, through furnace walls and losses in general.

At the moment heat balances for the furnace are based on theoretical values. In this work the real ongoing in the furnace should be examined. The values that enter the heat balance are monitored on site and display the actual situation. Therefore the heat balance is able to deliver more detailed information and exceeds any theoretical calculation.

The knowledge of energy distribution can further lead to a more precise vision of each furnace section and may offer valuable information on how to increase the energy efficiency.





# 2 Theoretical considerations

The following chapter gives an overview of the theory behind balances and the basic aspects in thermal treatment of steel. Later the element zinc, its production, use and toxicology is reviewed. Finally the process of the Continuous Galvanizing Line CGL4 is described in detail.

# 2.1 Heat Balance

Heat balances have to comply with the following requirements:

- Defined control volume
- Consideration of all entering and leaving flows
- Common reference condition
- Standardised units

The choice of the control volume for any balance can have a strong effect on the result. Therefore it should be chosen with care. According to the objective the control volume can be a

- Differential volume (dV)
- Finite volume (V)
- Unit operation
- Process [1]

Working with differential volumes leads to differential equations that describe the time- and space-dependent behaviour of the variable. This is not the objective of the present work, a finite volume is dealt with. Two furnace sections of the continuous galvanizing process are studied; the boundaries of the system are described in 4.1.1 and 4.2.1.

Figure 1 shows a very simple scheme of a technical process. The characteristic of any process is the transformation from an input to an output. In real processes incoming flows can be resources, electrical energy, water, e.g. Output flows can be the products of the process, heat losses, waste water etc.



Figure 1: Technical process

Balances comprise all entering and leaving flows: Figure 2 depicts a process with several mass/ energy flows across its boundaries. According to the complementarity principle of mass and energy the following formula has to be fulfilled.





Mass and energy can neither be created nor destroyed during the process; entering and leaving flows have to match.

In the case that mass or energy flows are stored during the process or when stored energy/ mass flows are freed, the change of this stock has to be regarded, too.

$$\sum \dot{m}_{input} = \sum \dot{m}_{output} + \Delta \dot{m}_{stock} \tag{1}$$

$$\sum \dot{E}_{input} = \sum \dot{E}_{output} + \Delta \dot{E}_{stock}$$
(2)

Transfer coefficients describe the distribution of entering goods: For the system in Figure 2 the transfer coefficients k are calculated to the following formulas. The sum of all transfer coefficients has to be equal to 1. All entering flows have to be transferred to one of the flows that leave the system.

$$k_1 = \frac{x_{o1}}{x_{i1} + x_{i2}} \tag{3}$$

$$k_2 = \frac{x_{o2}}{x_{i1} + x_{i2}} \tag{4}$$

$$k_3 = \frac{x_{o3}}{x_{i1} + x_{i2}} \tag{5}$$

$$\sum_{i=1}^{n} k_i = 1 \tag{6}$$

| Xi1   |         | X <sub>01</sub>  |
|-------|---------|------------------|
| V:0   | PROCESS | X 02             |
| ^   Z | TROCESS | X <sub>0</sub> 3 |
|       |         |                  |

Figure 2: Process with incoming and outgoing mass/ energy flows





# 2.2 Thermal treatment of steel

Thermal treatment of steel is nowadays used in many different industry sectors. The aim is an improvement of the mechanical properties of steels. In the manufacturing technology the basic processes are annealing and thermal treatment. They are usually followed by a mechanical process to produce serviceable goods. Annealing and thermal treatment focus on different objectives:

- Annealing is the heating up of the material in order to make it accessible for further deformation. It seeks the softening of one (e.g. jointing) or of all of the constituent elements (e.g. milling, forging), which at the same time represents an advance regarding quality.
- Thermal treatment however focuses strictly on quality issues, it requires certain temperature-time-cycles, often in combination with carburization or nitration. Due to the presence of alloys in the steel, the crystal formation and structure of the steel can vary significantly. The final mechanical properties depend on the heating cycles in the thermal treatment. Apart from the heating cycle, also soaking time and cooling rate have a significant effect on the steel properties after the treatment.

Thermal treatment plants are usually operated under protective atmospheres. This prevents surface alterations and reactions on the surface. Due to the large number of demands in steel structure and quality there is a big variety in thermal treatment plants. Still, the principle of thermal treatment is similar for all processes, it is either a recristallisation process, a dissolution or an elimination of an alloy element. Thermal treatment plants basically use the same constituent devices such as heating devices, fans, conveying system, but are specialized in one particular thermal treatment. Process control and automation play a major role. [1]

The background of thermal treatment is the temperature-dependent occurrence of ferrite and austenite. From 25 to 910°C iron exists as the body-centered cubic structure BCC, up to 1.400°C it occurs in its face-centered cubic struct ure FCC (see Figure 3). The lower-temperature form is called  $\alpha$ -ferrite or just ferrite, the FCC-form of iron is called austenite. [1]







Figure 3: Austenite (FCC, left) and ferrite (BCC, right) [4]

The time-dependent occurrence of ferrite and austenite is displayed in Figure 4. When pure iron is heated from 25 to 910°C, the decrease in length is almost linear. At 910°C a sudden decrease in length is noted, indicating the change from the BCC to the FCC form. The two types of atomic packing have a different specific volume (or density), the BCC has two, the FCC has 4 atoms in it. Supposing the iron atoms are spheres of the same diameter and mass for both structures, the volume difference for the two types of packings can be calculated. The change from BCC to FCC results in a decline of volume (or length) of 9%. The abrupt increase in length at 1.400°C is due to a changing back from the FCC to the BCC. [4]



Figure 4: Length changes v. temperature for pure iron [4]

Ferrite and austenite have dissolving power regarding carbon (see Figure 5). Therefore it is possible to change steel properties in a certain range. The amount of carbon in steels is usually lower than 2%. For this percentage, only the left part of the Fe-C-phase diagram is of interest here. In this area austenite will be built at higher temperatures.







Figure 5: Fe-C phase diagram [4]

The isothermal time-temperature-transformation diagram in Figure 6 depicts the kinetics for the transformation of carbon steel. If the cooling from the austenitizing temperature is very fast, martensite will be built. This leads to a significant increase in hardness. Martensite has a lower dissolution power of carbon than austenite. When rapidly cooled, carbon atoms can not diffuse through the  $\gamma$ -grid. This leads to a steadying of the  $\alpha$ -grid and to increased hardness.



Figure 6: Isothermal TTT-diagram for an eutectoid, plain carbon steel [4]





In order to get a high amount of martensite also in the core of thicker workpieces, fast cooling is required. Martensite is very brittle, therefore steel has to undergo another treatment, the so-called annealing. According to the steel grade and its purpose, annealing temperatures vary between 300 and 600°C. Low annealing temperatures result in diminished brittleness at constant hardness, medium annealing temperatures lead to a significant increase of toughness while hardness decreases. High annealing temperatures form a grid with good toughness and high strength durability. Theses properties are required for e.g. construction materials. [4]

#### 2.2.1 Galvanizing

Non-alloyed or low-alloyed steel is nowadays used for a various number of applications because of its hardness and formability. It is applied for the manufacturing of housetops, walls, electric devices and above all in the automotive industry. For many of the applications of steel, a protective coating is necessary so that steel will not corrode. Steel that is used for the packing of alimentary good is usually coated with tin, for other utilization purposes the coating element is zinc. The process of applying a coating of zinc to steel is called galvanizing. The two main processes are electro-galvanizing (see 2.2.1.1) and hot dip-galvanizing (see 2.2.1.2). [1]

The protective nature of a galvanized coating is due to two effects. On the one hand the zinclayer represents a physical barrier between the steel strip and the corrosive atmosphere; on the other hand electrochemical effects prevent exposed steel surfaces (as e.g. cut edges or scratches on the surface) from being corroded. Studies documented the corrosion behavior of galvanized steel strip to depend on the thickness of the protective layer, its micro-structure and the coating adherence. The more continuous, cohesive and adherent corrosion layers are, the longer lifetime steel will show. [5]

Figure 7 displays the effect of the coating thickness, respectively coating weight, on the corrosion resistance. Electro-galvanized (EG, see 2.2.1.1), galvannealed (GA) and hot dip-galvanized (GI, see 2.2.1.2) steel sheets were exposed in an unpainted condition to the atmosphere at 10 km from the shoreline in Okinawa (Japan). [6] The results show a decline in corrosion occurrence in thicker protective layers. The thickness of the zinc coating varies according to the coating process. Heavy layers of zinc can be produced at low cost by hot-dip proceedings.







Figure 7: Effect on coating weight on corrosion resistance [6]

#### 2.2.1.1 Electro-galvanizing

In an electro-galvanizing plant the steel strip is cleaned in a first step, afterwards it is electroplated and further post-treated. In the main section it passes a zinc bath at a temperature of 30 to 60°C (see Figure 7). The zinc in the electrolyte is deposited on the steel surface. The greatest percentage of steel processed in continuous steel strip plating lines is electrodeposited with one of the following metallic coatings: zinc, tin, chromium, and alloys of zinc with either nickel or iron. Several other metallic coatings such as copper, nickel, brass (Cu-Zn), and terne (Pb-Sn) are also applied by continuous steel strip plating but on a relatively smaller scale and production volume. Typical layer thicknesses are between 0.13 and 0.49 mm. [7]



Figure 8: Principle of electrogalvanizing [9]





#### 2.2.1.2 Hot dip-galvanizing

Hot dip-galvanizing is a very old process where the strip is immerged into a bath of molten zinc. Both strip and zinc are at a temperature of 450 to 480°C. During the galvanizing, the zinc reacts with the iron in the steel and forms several layers of zinc/iron-alloys.

The top layer consists of pure zinc (see Figure 9). In order to adjust the thickness of the zinc layer, air or gas knifes are installed just above the zinc bath (see Figure 10).



Figure 9: Surface of galvanized steel [8]

Figure 10: Hot dip-galvanizing [9]

Apart from galvanizing with pure zinc, strips can also be coated with zinc alloys. The alloy elements are in the majority of cases iron (Fe), aluminium (AI), lead (Pb) and nickel (Ni). The most commonly used alloys are

- Galfan: 90% Al, 10% Zn
- Galvalume: 60% Al, 40% Zn

Different coatings lead to different properties. The most convenient coating has to be found in accordance to the demands. Table 1 andTable 2 give an overview on the characteristics of different coatings on steel strips.

 Table 1: Properties of electro-galvanized steel [10]

|                      | Coating | Characteristics  |  |  |
|----------------------|---------|--|--|--|
|                      |         | smooth, attractive surface                               |  |  |
|                      | pure Zn | excellent forming of coating                             |  |  |
| Electro-galvanizing  |         | same mechanical properties as base metal                 |  |  |
| Liecti 0-gaivanizing |         | good weldability   |  |  |
|                      | Zn-Ni-  | 3 to 5 times corrosion resistance than that of pure zinc |  |  |
|                      | alloy   | superior formability and weldability                     |  |  |





#### Table 2: Properties of hot dip-galvanized steel [10]

| Coating Characteristics |           |   |  |  |  |  |
|-------------------------|-----------|---|--|--|--|--|
|                         | nure 7n   | light coated products: good weldability and formability |  |  |  |  |
|                         | pule ZII  | heavy coated products: superior corrosion resistance    |  |  |  |  |
|                         | Galfan    | excellent formability                                   |  |  |  |  |
| Hot din galvanizing     |           | good adhesion and ductility of coated layer             |  |  |  |  |
| not dip galvanizing     |           | good paintability                                       |  |  |  |  |
|                         | Galvalume | heat resistance and heat reflection due to Al           |  |  |  |  |
|                         |           | corrosion resistance due to Zn                          |  |  |  |  |
|                         |           | attractive white silver surface                         |  |  |  |  |

In the automotive industry, mainly hot dip-galvanized steels were used until 15 years ago. Their application in the automotive body reduced corrosion and improved the appearance of the automobile's outer body. From the beginning 1990's, the amount of electro-galvanized sheet increased constantly. Robert E. Socia, manager of ferrous metals for General motors Corp., explained that electro-galvanized steel

"is providing us with more consistent application of zinc over hot-dip" [11]

However, nowadays both methods are applied to provide suitable steel strips for the automotive sector. Electro-galvanized steel is used rather on the outer parts, the cheaper hot dip-galvanized steel is used in the inner body parts where appearance is not as obvious as on the outer skin. [11]

#### 2.2.2 Historical development of Continuous Galvanizing Lines

Hot dip-galvanizing of steel is an old process. In the beginning the steel plates were dipped into the zinc bath manually, in the 1950's the first continuous process was developed by T. Sendzimir (see Figure 11). The strip was processed through a horizontal furnace and heated up to  $600^{\circ}$ C in order to evaporate the oil coating. In the reduction section an atmosphere of 30% H<sub>2</sub> and 70% N<sub>2</sub> was maintained, the strip was heated to 700°C. It travelled through a soaking and a cooling section before passing the zinc bath at a temperature of 460°C.

Due to the horizontal arrangement, the heat from the reduction section could be transferred to the oxidation section to pre-heat the strip. The production was limited to 15 t/h; mainly corrugated iron sheet was processed. [1]







Figure 11: Sendizmir process

The transition to bigger productions was due to 2 innovations: the development of a nonoxidizing furnace and a vertical arrangement of the furnace.

The non-oxidizing furnace (NOF) was developed in the 1960s. The strip was pre-heated in a direct-fired furnace (DFF) in under-stoichiometric conditions in order to evaporate the oil layer on its top and in order to clean the surface. Afterwards the heating cycle was continued under a protective atmosphere. It consists of a mixture of 5% H<sub>2</sub> and 95% N<sub>2</sub>, the dew point is about -20°C. This guarantees a strip surface cle an of oxidation products and cuttings. The strip was heated up to the annealing temperature, cooled down to the zinc bath temperature and passed through the zinc pot. [1]

The typical components of a continuous galvanizing line are dealt with in detail in 2.4, the basic scheme is presented in Figure 12.



Figure 12: Vertical furnace with direct-fired section (DFF)





# 2.3 Zinc

The word "zinc" was first mentioned in the 16<sup>th</sup> century. However it has been known since 1.500 B.C. by the Chinese and Indians. It is not precisely known when zinc was first produced. Coins made of zinc were cast during the Ming Dynasty (1368-1644), remains of zinc smelting operations were found in India that date back to the 13<sup>th</sup> century. The meaning of the word "zinc" is not clear, it is assumed to derive from the German "Zinke" which itself is a derivation of "Zacke" (jagged peak). It may hint at the jagging appearance of the ore in the furnace. [12]

Zinc has a low boiling point of 906°C. It can be worked at temperatures of 120°C and has a remarkably good deformability which is the basis for some of its uses. Due to its lower position in the electrochemical series than iron, Zinc coatings protect it from corrosion. This is due to the formation of a passivating protective coating of basic zinc carbonate by reaction with the atmosphere. [1]

In all its compounds zinc has an oxidation state of 2. Complexes are formed with ammonia, amines, cyanide and halide ions. In mineral acids zinc dissolves under the formation of hydrogen, whereas dissolution in nitric acid leads to the formation of  $NO_x$ . Zinc is resistant to air due to a protective coating that is formed in contact with the atmosphere. It is also resistant to halogens, but is corroded rapidly by HCI gas. [1]

Zinc is a natural component of the earth crust, average abundance is assumed to be 65 g/t. Zinc appears only in a chemically combined state, usually as the sulfide. Native zinc does practically not exist. The primary ore is zinc blende (sphalerite, ZnS, see Figure 13), a light yellow to black mineral that consists of 67.09% Zn and 32.91% S. Zinc blende has impurities, among them the most important is iron sulfide (FeS). It occurs at concentrations between 0.3 and 20%. Zinc blende can further contain Pb, Cd, Mn and Cu-sulfides. [1]



Figure 13: Zinc blende [13]

Worldwide zinc reserves are estimated to  $185.3 \times 10^6$  t. This figure does not include the Chinese deposits where no information is available. The biggest deposits in Canada, North and South America account for almost half of the known reserves.





Western Europe's deposits represent 17% of the total deposits, the biggest sources are found in Ireland, Sweden and Yugoslawia (Kosovo). The ten biggest zinc deposits are listed in Table 3. [1]

| Country                | Proven            | Reserves | Potential Reserves |      |  |  |
|------------------------|-------------------|----------|--------------------|------|--|--|
| Country                | 10 <sup>6</sup> t | %        | 10 <sup>6</sup> t  | %    |  |  |
| Canada                 | 37560             | 20,3     | 6620               | 5,6  |  |  |
| United States          | 31800             | 17,1     | 32200              | 27,3 |  |  |
| GUS and Eastern Europe | 30000             | 16,2     | 10000              | 8,5  |  |  |
| Australia              | 17560             | 9,5      | 27950              | 23,7 |  |  |
| Japan                  | 9150              | 5        | 6100               | 5,2  |  |  |
| Ireland                | 8820              | 4,8      | 350                | 0,3  |  |  |
| Peru                   | 7150              | 3,8      | 1500               | 1,3  |  |  |
| Spain                  | 5060              | 2,7      | 1200               | 1    |  |  |
| Sweden                 | 4000              | 2,2      | 2000               | 1,7  |  |  |
| Yogoslawia             | 3500              | 1,9      | 2000               | 1,7  |  |  |

Table 3: Worldwide zinc deposits [1]

#### 2.3.1 Zinc production

In order to produce zinc, the sulfidic raw material has to be pretreated in order to get the oxide ZnO. The two possibilities to remove sulfur as  $SO_2$  and to convert ZnS to ZnO are roasting and pyrometallurgical concentration processes. For the roasting, the two most common processes are fluidized-bed and sinter roasting. They allow not only the conversion of zinc into its oxidic form but also the recovery and use of  $SO_2$  in the waste gas. [1]

The Waelz kiln process is a pyrometallurgical concentration process to treat secondary raw materials from zinc metallurgy (e.g. slags, flue dusts and sludges). The zinc is gained from the oxide product by a thermal process. In a strictly reducing  $CO/CO_2$  atmosphere the following reactions take place:

$$ZnO + C \to Zn(g) + CO \tag{7}$$

in the solid charge and

$$Zn(g) + CO + 0_2 \rightarrow ZnO + CO_2 \tag{8}$$

in the gaseous phase.

After the pretreatment the oxidic zinc can be treated either by electrolytic or pyrometallurgical processes. In the pyrometallurgical retort process zinc is reduced by carbon according to the following equation.

$$ZnO + C \Leftrightarrow Zn + CO \tag{9}$$





This reaction is highly endothermic, the enthalpy  $\triangle H = 353$ kJ.

This means that 5.4 MJ of heat are required to produce 1 kg of zinc. The process temperature lies between 1.100 and  $1.300^{\circ}$ , zinc is consequently produced in its vapor state and has to be condensed into its liquid state. This reduction can take place in horizontal or vertical retorts. Apart from the retort process, zinc can be produced in a shaft furnace. There, the demanded heat for the reduction is provided from the oxidation of carbon to CO and CO<sub>2</sub>. [1]

Another option to gain elemental zinc from its oxidic form is the electrolysis of aqueous solutions and molten salts. So far only aqueous electrolytes have been in industrial use. In the so-called electrowinning process zinc is produced from solutions of zinc sulfate in sulfuric acid. In the recent decades this process has grown significantly, today about 80% of the world-wide production derives from this process. Figure 14 gives an overview of the electrowinning process.



Figure 14: Zinc electro-winning [14]





In the first step zinc blende is roasted to obtain zinc in its oxidic form, the so-gained calcine is leached. In the leaching and the following liquor purification, the iron and other impurities such as As, Sb, Ge, Ni and Co must be separated from the zinc in order not to interfere with the electrolytic process. Their presence during the electrolysis would otherwise lead to

- Lower current efficiency
- The presence of impurities in the cathodically deposited zinc
- Adverse effects on anode and cathode [1]

The standard electrode potential of Zn is -0.763V. Therefore hydrogen is supposed to be liberated during electrolysis instead of zinc being deposited on the cathode. However, due to the hydrogen overvoltage at the zinc cathode, zinc deposition is possible. Nowadays typical process parameters are current densities of  $400 - 600 \text{ A/m}^2$  and a temperature below  $40^{\circ}$ C.

## 2.3.2 Use of zinc

Today zinc is used in a large variety of applications. The two properties that account for the vast use are

- the standard electrical potential more positive than that of iron
- the relatively low melting point

#### 2.3.2.1 Zinc as a chemical product

Zinc based chemicals account for 12-15% of the total chemical consumption. The most important product is zinc oxide, followed by zinc dust, zinc sulphate and zinc chloride. The main consumer of zinc oxide is the rubber industry. Zinc activates the vulcanization process and the filling. Zinc can be further found in

- formulations in the glass and ceramic industry
- face powder, lipsticks, creams in the cosmetics industry
- lubricants, adhesives, dying agents [15]

#### 2.3.2.2 Zinc as construction material

The use of zinc as a construction material has increased in the past 40 years after the development of low-alloy zinc grades based on Zn-Ti-Cu. These alloys assure sufficient creep resistance and allow together with zinc's fairly good strength properties its use in various applications.





The material can be rolled to zinc plate or sheet and is used in the manufacturing of roof drainage components or for covering buildings. [16]

#### 2.3.2.3 Galvanizing

The importance of galvanizing has increased during the last decades. In order to preserve the use of commercial metals over a long period of time and to assure its performance, steel has to be protected against corrosion, bearing in mind that the atmosphere is becoming more and more corrosive. Two mechanisms ensure the lasting corrosion protection for zinc layers:

- CO<sub>2</sub>, air moisture and zinc form a protective layer on the steel surface, leading to a low corrosion rate
- In areas of small defects zinc prevents the occurrence of corrosion due to its electrochemical property of providing cathodic protection. [17]

The galvanizing process is described in detail in 2.2.1.

#### 2.3.3 Toxicology

Zinc is one of the heavy metals, being called like that because of a density higher than 5 kg/dm<sup>3</sup> [18]. The growing concern with all heavy metals (pointed out in Figure 15) is related to the exhibition to human beings. Heavy metals provoke renal dysfunction, disturbances in the reproductive system and in the liver, to name only some of their negative effects on the human health.

| н   |     |    |     |     |     |     |     |     |     |      |      |    |     |     |     |     | He |
|-----|-----|----|-----|-----|-----|-----|-----|-----|-----|------|------|----|-----|-----|-----|-----|----|
| LI  | Be  |    |     |     |     |     |     |     |     |      |      | в  | с   | N   | 0   | F   | Ne |
| Na  | Mg  |    |     |     |     |     |     |     |     |      |      | AI | SI  | Р   | s   | СІ  | Ar |
| к   | Ca  | Sc | TI  | v   | Cr  | Mn  | Fe  | Co  | Ni  | Cu   | Zn   | Ga | Ge  | As  | Se  | Br  | Kr |
| Rb  | Sr  | Y  | Zr  | Nb  | Мо  | Tc* | Ru  | Rh  | Pd  | Ag   | Cd   | In | Sn  | Sb  | Te  | I   | Xe |
| Cs  | Ba  | Lu | Hſ  | Та  | w   | Re  | 0s  | lr  | Pt  | Au   | Hg   | TI | Pb  | Bi  | Po* | At* | Rn |
| Fr* | Ra^ | ư  | Rf* | Db* | Sg* | Bh* | Hs* | Mt^ | Ds* | Uuu* | Uubʻ |    |     |     |     |     |    |
|     |     |    | La  | Ce  | Pr  | Nd  | Pm* | Sm  | Eu  | Gd   | ТЬ   | Dy | Ho  | Er  | Tm  | Yb  |    |
|     |     |    | Ac* | Th* | Pa* | U*  | Np* | Puŕ | Am* | Cm*  | Bk*  | Cf | Es* | Fm* | Md* | No  | -  |

Figure 15: Heavy metals in the periodic table [19]





However, zinc is one of the least toxic heavy metals. The toxicity of its salts does not generate from the element itself but depends mainly on the anionic part of the component. The high toxicity and carcinogenicity of zinc chromate  $ZnCrO_4$ , for example, is due to  $CrO_4^{2-}$  and not due to the cation  $Zn^{2+}$ . Zinc is even an essential element for human being and plants. The body of a 70 kg man contains about 2.3 g of zinc, 64% are found in muscle tissues, 28% in bones [20].

For humans zinc is necessary for growth, skin integrity and function, testicular maturation, wound healing and for a variety of metabolic processes. Zinc intoxications occur rarely, symptoms being diarrhea, nausea and abdominal pain [21]. The main exposure route is the oral one, zinc can be taken up by ingestion of food or drinks that were prepared or stored in galvanized containers. Another possibility is the inhalation of zinc or zinc oxide fumes. The symptoms are rapid breathing, cough, fever, shivering, sweating, metallic taste and may occur in welding, galvanizing or smelting operations. They are known as 'metal fume fever'.

The established MAK-value for such zinc fumes is 5 mg/m<sup>3</sup> in Austria [22]. The same value has been set by the WHO in Hungary, Japan, Poland and Sweden. Finland established a limit value of 15 mg/m<sup>3</sup>, in Bulgaria, Romania and Pennsylvania (USA) the limit value is 20 mg/m<sup>3</sup> [20]. Zinc chromate is classified in group A1 of Appendix III of the MAK list and is therefore considered to be a proven human carcinogen [22].

# 2.4 Process description of Continuous Galvanizing Line CGL4

The basis of any heat or mass balance is a profound knowledge of the process. All relevant mass flows have to be identified. On the following pages Andritz Selas' Continuous Galvanizing Line is presented, the explications go along with the visualization of the mass/ energy flows in flow diagrams.

## 2.4.1 Pre-heating section (PH)

Prior to its entrance into the direct-fired furnace, the strip travels through a waste gas preheater where its temperature is increased from ambient air temperature (around  $25^{\circ}$ ) up to 280°C. The final strip temperature depends on the temperature of the waste gas after the post-combustion (PC) and the ability of the steel strip to take up heat from the gas flow. The oxidation of the strip in the PH is avoided by a short exposure to the waste gases. In this context it is also necessary to guarantee low oxygen contents in the flue gas.

The combustion gases of the direct-dired furnace are exhausted at the top of the furnace and directed through 2 fiber refractory lined post-combustion chambers. The air-gas ratio  $\lambda$  in the PC usually is about 1.01. After the complete burning of the waste gases, they travel counter flow to the strip movement in the pre-heater and heat the strip. Afterwards they are collected at the entrance of the pre-heater.





Downstream the pre-heater, a recuperator is located. In this heat exchanger the waste gas pre-heats the combustion air of the burners in the direct-fired furnace. It is protected against excess of waste gas temperature (maximum 900°C) by a controlled air dilution inlet. After the recuperator, the exhaust gas is directed to the exhaust blower and then to the stack. To avoid overheat damage to the exhauster at waste gas temperatures above 300°C, dilution air is admitted to the flue gas stream before the exhauster (see Figure 16).

Under normal operating conditions the first dilution valve is closed, waste gas temperatures at the exit of the PH do not exceed 900°C. After the recuperator, the dilution is generally applied to guarantee a temperature lower than  $300^{\circ}$ C at the exhauster.

Figure 16 describes the mass flows in the pre-heating and direct-fired section of the continuous galvanizing furnace.



Figure 16: Flow diagram pre-heating section and DFF







Figure 17: Drawing of pre-heating section and DFF

#### 2.4.2 Direct-fired furnace

The strip exits the pre-heating section and passes through a crossover chamber where its temperature is checked by a pyrometer. It is directed downward into the vertical direct-fired furnace DFF.

The fiber lined furnace chamber of the DFF is divided into 5 vertically arranged heating zones. Before the first zone the strip travels through a recuperative zone without burners, in the following zones it is heated by different burner types. Zone 1, 2 and 3 are fired with Selas nozzle mix duradiant burners (see 2.4.2.1). They are equipped with an integrated combustion control to accommodate chamber atmosphere requirements. The bottom zones (zones 4 and 5) are fired with Selas premix type duradiant burners (see 2.4.2.2). These burners create a chamber atmosphere with a high reducing potential in order to clean the surface of the strip completely.

The waste furnace gases from the DFF are removed by two flue ports at the top of the chamber.





Due to their content of unburned CO and  $H_2$ , flue gases can not be sent into the atmosphere without further treatment. Flue gases are directed into two symmetrical post-combustion chambers to complete the combustion. Oxygen burns the gases for about one second.

The post-combustion air flow is calculated according to equation 10. A Lambda-value of 1.01 is desired.

$$\dot{V}_{air} = \dot{V}_{gasDFF} * Va * (1 + 5 * SP_{O2}) - \dot{V}_{airDFF}$$
 (10)

| $\dot{V}_{air}$    | Calculated post-combustion air flow set-point  |
|--------------------|--|
| $\dot{V}_{gasDFF}$ | Total DFF gas flow                             |
| Va                 | Stoichiometric air/gas ratio                   |
| SP <sub>02</sub>   | After post-combustion oxygen content set-point |
| $\dot{V}_{airDFF}$ | Total DFF air flow                             |

It is necessary to keep the  $O_2$ -level in the flue gas as low as possible to avoid any oxidation of the strip in the pre-heating section. The oxygen content is measured after the post-combustion by an  $O_2$  analyzer. The result is used to correct the post-combustion air flow set-point to compensate for the lack of accuracy of the flow measurements.

#### 2.4.2.1 Duradiant burners for DFF

Duradiant burners are cup-shaped precision combustion tools which radiate heat to work pieces without flame impingement. Due to their uniform heat distribution and the lack of a flame outside the cup, these burners can be placed close to the work piece.

In the Direct Fired Furnace two different types of duradiant burners are used.

#### 2.4.2.2 Nozzle-mix DN burners

The three top zones of the DFF are fired with nozzle-mix burners that are fed with natural gas and pre-heated air. The combustion takes places at the burner nozzle. The air/gas mixture sweeps radially across the cup in such a way that the refractory cup surface is always washed by the hottest part of the flame. The incandescent surface acts as an ignition device and flame holder. Stable combustion is maintained within the cup at all times, a controllable heat flow is produced.

Each zone consists of 2 (width) x 3 (height) burners on each side of the strip, being a total of 12 burners per zone.





#### 2.4.2.3 Premix KB burners

The bottom zones of the DFF (zones 4 and 5) are fired by premix burners. Natural gas and pre-heated air are mixed before the combustion. The mixture passes through the tip's refractory orifices, is distributed radially and burns within the refractory cup in a petal-shaped formation. The inner contour of the cup is always washed by hot combustion products at their highest temperature and becomes incandescent. Combustion is always carried out within the cup. For  $\lambda$ -values below 1 there is no more free oxygen outside the cup. This avoids the oxidation of the strip by maintaining a highly reductive atmosphere.

Each zone consists of 6 rows of alternatively 5 and 6 burners on each side of the strip (66 burners per zone). In order to avoid overheating at the strip edges, four vertical rows of premix burners (one of each edge and each side of the strip) can be trimmed low when the strip width passes a certain limit. Zone 4 and zone 5 can be trimmed independently (see Table 4).

|                              | Strip width | Burners in operation |        |       |  |  |
|------------------------------|-------------|----------------------|--------|-------|--|--|
| Nr. of trimmed vertical rows | (mm)        | Zone 4               | Zone 5 | Total |  |  |
| 0                            | 1500-1750   | 66                   | 66     | 132   |  |  |
| 1                            | 1250-1500   | 54                   | 54     | 108   |  |  |
| 2                            | 1000-1250   | 42                   | 42     | 84    |  |  |
| 3                            | 750-1000    | 30                   | 30     | 60    |  |  |

 Table 4: Trimming of premix burners

#### 2.2.2 Strip temperature control

Strip temperature is measured by a radiation pyrometer in the boot area after the DFF. The process value is sent to the strip temperature controller which generates a control signal. Basically the strip temperature control is in cascade. Power is fed from the bottom zone to the top zone. For low-temperature heat cycles it may be sufficient to use only the bottom premix burners. The higher strip exit temperature is demanded, also the top zones will be fired on top of their power level (see Table 5). This regulation provides the adjustment of the heat input according to the format and the heat cycle of the processed steel strip.

 Table 5: Cascade mode for burners' power adjustment

| Power level<br>(%) | Zone | Power level of each burner<br>(%) |
|--------------------|------|-----------------------------------|
| 16-20              | 5    | 80-100                            |
| 20-40              | 4    | 30-100                            |
| 40-60              | 3    | 20-100                            |
| 60-80              | 2    | 20-100                            |
| 80-100             | 1    | 20-100                            |





#### 2.4.3 Radiant Tube Heating/ Radiant Tube Soaking

The strip is transferred from the DFF to the Radiant Tube Heating (RTH) via a crossover section that is heated by electrical heaters. The temperature at the exit of the DFF will be maintained by electrical heating devices and controlled by pyrometers.

Radiant Tube Heating consists of a vertical chamber of radiant tubes divided into 2 zones of regulation (RTH1, RTH2). Each radiant tube (outer diameter 244 x 186 mm) is made of 3 mm thick rolled refractory steel sheets that are connected with 180° bends of the same material. The assembly resembles a double-P (see Figure 18) and faces the strip in order to provide maximum heat uptake of the strip.



Figure 18: Double P-tube and burner arrangement

Heat is supplied by gas fired recuperative burners with low NO<sub>x</sub>-emissions (usually lower than 300 mg/Nm<sup>3</sup>/hrs at 3% O<sub>2</sub>). For energy saving purpose, the combustion air is preheated to approx. 600°C. The heat is recovered from waste gases by an individual recuperator located in the burner assembly itself. Each burner has individual valves on air and gas entry and can thus be controlled independently. The temperature of the tubes and the zone is measured by thermocouples (see 3.1.1.1).

The chamber is divided into 3 vertical zones for temperature control purposes. Zone 1 and 2 heat the strip via indirect heating (RTH), in Zone 3 the temperature of the strip is maintained but usually not further increased (Radiant Tube Soaking RTS) (see Figure 19). There are 25 burners in each of the two heating zones and 15 burners in the soaking zone. Each of them has a capacity of 140.000 kcal/h and is fired by natural gas.







Figure 19: Flow diagram RTH/RTS

The wall between RTH and RTS consists of a fiber lining suspended by stainless steel tubes. It is covered with INCONEL 601, a nickel-chromium-iron alloy (see Table 6). INCONEL 601 is an engineering material used for applications that require heat resistance and resistance to high-temperature corrosion. The composition is a face-centered-cubic solid solution with a high degree of metallurgical stability. A substantial chromium content based on Nickel provides resistance to many corrosive media and high-temperature environments. The oxidation resistance is enhanced by the aluminum content. [25]

| Table 6: Limiting chemical compo | osition of INCONEL 601 [25] |
|----------------------------------|-----------------------------|
|----------------------------------|-----------------------------|

| Compound  | %          |
|-----------|------------|
| Nickel    | 58-63      |
| Chromium  | 21-25      |
| Iron      | remainder  |
| Aluminium | 1-1.7      |
| Carbon    | max. 0.1   |
| Manganese | max. 1     |
| Sulfur    | max. 0.015 |
| Silicon   | max. 0.5   |
| Copper    | max. 1     |

## 2.4.4 Slow Jet Cooling/ Rapid Jet Cooling

After the RTH the strip passes a crossover section where its temperature is maintained by electrical radiant tubes.





During Slow Jet Cooling (SJC) the temperature of the strip is smoothly decreased from maximum 850 to 620 °C. Average cooling rates are between 2 and 15°C/s. The chamber consists of 6 modules, five in the first leg of the cooling and one in the upper part of the second leg (see Figure 20).

Each module contains both heating and cooling devices in order to properly adjust the desired strip temperature. Heating is provided by electrical radiant tubes. The cooling part of each module consists of a jet cooler with eight cooling tubes, having its own blower and heat exchanger. Therefore the modules can be operated independently to achieve the desired cooling curve. The cooling power is adjusted by the blower motor speed. Several pyrometers are installed in the SJC to control the cooling progress.



Figure 20: Flow diagram SJC/RJC

In the Rapid Jet Cooling (RJC) section the strip is cooled to the temperature specified by the thermal cycle for the particular product that is processed. RJC occupies the second pass of the cooling system and consists of two modules. In each of them the protective atmosphere is drawn backwards through banks on each side of the strip. It is collected in a plenum. Further the flow is divided and sent to three primary and secondary heat exchangers (see Figure 20). The cooled atmosphere gas is led to five separated banks disposed along the strip width. The strip temperature is read by a scanner. In the case of an inhomogeneous temperature profile along the strip width the blowers can be adjusted to blow more or less.

## 2.4.6 Overaging Furnace

The purpose of the Overaging Furnace (OA) is to hold the strip temperature at a defined level. This section is equipped with heating and cooling advices to adjust both strip and chamber temperature. The heating is done by 45 electrical radiant tubes (ELRAD).





In order to cool the strip, the atmosphere gas is collected in the bottom chamber and sent to a heat exchanger. A bypass is installed to separate one part of the flow before the heat exchanger and add it afterwards to the cooled atmosphere gas (see Figure 21). So the temperature of the atmosphere flow that is directed into the OA can be regulated.

Cooling and heating devices are regulated in a way that the strip temperature is stable.



Figure 21: Flow diagram Overaging furnace

#### 2.4.7 Final Heating Holding

The purpose of this chamber is guiding the strip to the zinc pot and adjusting the temperature to the value required for entering the zinc bath, usually around 460°C. The chamber is heated by ELRADs (see Figure 22).



Figure 22: Flow Diagram Final Heating Holding





#### 2.4.8 Hot Bridle and Snout (HB&S)

This section is equipped with ELRADs to maintain the strip temperature before the strip enters the zinc bath. During the heating and cooling of the strip in all chambers prior to the zinc bath, it is surrounded by a protective gas atmosphere HNX (mixture of  $H_2/N_2$ ). The average Hydrogen-Nitrogen proportion is 5%  $H_2$  and 95%  $N_2$ . During operation, furnace chambers are ventilated with HNX at a rate of approximately half the furnace volume per hour (600 Nm<sup>3</sup>/h). This guarantees the renewal of the atmosphere every second hour. The atmosphere gas is delivered to each furnace chamber in order to maintain a positive pressure in each of them.

HNX is entered before the zinc pot and travels through the furnace by a pressure gradient. After the pre-heating section it is directed to the post-combustion, diluted and released through the stack (see Figure 16).

The application of a  $N_2$ - $H_2$ -mixture in processes where a protective atmosphere is required is wide-spread. It is estimated that more than 50% of the hydrogen that is used outside the chemical and refining industry is used in heat treatment applications. The amount of hydrogen in the protective gas varies according to the processed good; it can be in a range from 2 to 100 % [23]. Table 7 gives an overview of typical atmosphere compositions for the heat treatment of different materials.

In recent years the trend goes towards reducing the hydrogen content as much as possible while guarding its unique properties. Hydrogen is on the one hand an excellent reducing agent, on the other hand it has good heat transfer properties. As reducing agent it either prevents adventitious oxygen that enters the system through leaks from oxidizing the material, or actively reduces oxides. In Andritz Selas' Continuous Galvanizing Lines the HNX is applied to avoid the oxidation of the steel strip in the furnace. The pre-cleaning of the strip occurs in the DFF where the burners operate in under-stoichiometric conditions and provide a reductive atmosphere. At the exit of the DFF all impurities are removed from the strip, a further reduction via hydrogen is not necessary. Therefore the H<sub>2</sub>-content can be decreased from 15% for fully cleaning the steel surface to 5%. This incline in H<sub>2</sub> minimizes at the same time the danger of explosions. [23] [24]

Table 7: H<sub>2</sub>-N<sub>2</sub>-atmospheres in heat treatment applications [23]

| Material             | Hydrogen<br>% | Nitrogen<br>% |
|----------------------|---------------|---------------|
| Copper               | 2             | 98            |
| Mild steel           | 2 to 4        | 96 to 98      |
| Bronze               | 5             | 95            |
| Brass                | 25            | 75            |
| Stainless steel      | 50            | 50            |
| High chromium alloys | 100           | 0             |





# 2.4.9 Zinc bath

The strip is processed through a zinc bath at a temperature of about 460°C. The zinc bath is kept at a temperature higher than the melting point of the element (419.5 °C). During this process diffusion processes cause a layer of iron-zinc alloys on the surface of the steel which provides good adhesion of the zinc coating. [25]

The bath is equipped with a measurement of the zinc level and an automated machine to feed the bath with zinc in the same proportion as it is dragged-out by the strip.

After the zinc bath an air knife is installed to adjust the thickness of the zinc layer to a maximum weight of  $138 \text{ g/m}^3$ .

## 2.4.10 After Pot Cooling (APC)

After the zinc bath the strip is cooled to ambient air temperature in three steps.

The first step provides smooth cooling to optimize the zinc solidification. Cold air from inside the building is used, the exit temperature of the strip is below the zinc melting point (zone 1 and 2). In a second step fresh air from outside the building is used (zone 3 to 10) in order to reach a strip temperature of 120°C.





The final cooling consists of a water quench. Before and after passing through demineralised water at 32 - 38°C, some of it is sprayed on the surface on the strip. Finally the water that does not run down to the quench due to gravity is removed by 2x2 wringer rolls.





The water in the quench is reused after being cooled in a heat exchanger (see Figure 24).



Figure 24: Flow diagram Water Quench





# **3** Practical work

#### 3.1 Measurements

The present heat balance is based on on-site measurements. In the following chapter the applied measuring devices are presented.

#### 3.1.1 Temperature measurement

The three major temperature measurement systems in use are thermocouples, RTDelements and radiation pyrometers.

#### **3.1.1.1 Thermocouples**

Thermocouples measure the temperature of the zones and the temperature of fluids. According to the expected temperature range, different types of thermocouples are employed (see Table 8). The measuring principle is based on the thermoelectric effect named after Seebeck. When a conductor is subjected to a thermal gradient, it generates voltage. In order to measure this voltage another conductor is connected to the "hot end", suffering the same temperature gradient (see Figure 25).

Table 8: Temperature ranges for different thermocouples

| Туре | Max. temperature<br>℃ | Wire 1           | Wire 2          |
|------|-----------------------|------------------|-----------------|
| J    | 700                   | iron             | copper-nickel   |
| K    | 1100                  | nickel-chrome    | nickel-aluminum |
| R    | 1600                  | platinum-rhodium | platine         |



Figure 25: Thermocouple arrangement





According to the metals in use voltage will differ. The voltage difference increases with increasing temperature. Typical values are between 1 and  $80 \text{ mV/}^{\circ}$  in available metal combinations. A thermocouple generates voltage as a function of 2 temperatures and its nature. For standard thermocouples, the electromotive force (EMF) can be found in reference tables. The values can also be displayed as shown by Figure 26.



Figure 26: EMF as a function of the type of thermocouple and of temperature [27]

#### 3.1.1.2 RTD-elements

For temperatures lower than  $300^{\circ}$ , Pt100-elements are used. These resistance thermometers exploit the change in electrical resistance of a material at temperature variations. They are made of platinum because of its inertness and its linear relationship between resistance and temperature.

#### 3.1.1.3 Optical pyrometers

Pyrometers are used in the furnace to read the temperature of the steel strip. They allow the monitoring of temperatures without contact to the moving strip (see Figure 27). The optical system focuses the thermal radiation.





The output signal of the detector is related to the thermal radiation of the object through the Stefan-Boltzmann law

$$\dot{q} = \boldsymbol{\sigma} \cdot T^4$$
 black body (11)

$$\dot{q} = \varepsilon \cdot \sigma \cdot T^4$$
. grey body (12)

| ġ | $\frac{W}{m^2}$                            | Radiant flux              |
|---|--|---------------------------|
| σ | $5.67 \cdot 10^{-8} \frac{W}{m^2 \cdot K}$ | Stefan-Boltzmann constant |
| Т | К  | Temperature               |
| ε | -  | Emissivity                |

The energy flux density is proportional to the fourth power of the temperature. As the strip is not a black body that absorbs the full amount of radiative flux, the emissivity  $\varepsilon$  is not 1 but between 0 and 1. For the temperature measurement of the steel strip, the emissivity has to be adjusted to the correct  $\varepsilon$ -value. The pyrometers in the installation are adjusted to an emissivity value of about 0.4.



Figure 27: Pyrometer arrangement

## 3.1.2 Flow measurement

The flow of natural gas, combustion air, hydrogen, nitrogen and water is measured by orifice plates. A differential pressure transmitter reads the pressure before and after the orifice plate (see Figure 28) and converts the differential pressure into an electrical (or numerical) signal.





The actual flow is calculated according to the following formula, considering the actual pressure p and the actual temperature T of the medium.

$$\dot{Q} = K \cdot \sqrt{(p_2 - p_1) \cdot \frac{T_0}{T_0 + T} \cdot \frac{p_0 + p}{p_0}}$$
(13)

- $\dot{Q}$  Nm<sup>3</sup>/h Actual flow
- *K* Orifice plate constant
- T<sub>0</sub> 273.15 K Reference temperature
- $p_0$  1013 mbar Reference pressure



Figure 28: Orifice plate for flow measurement

# 3.2 Calculations

#### 3.2.1 Strip enthalpy

The enthalpy of steel strips that are processed in the continuous galvanizing line is found in a table that is also used for Selas' dimensioning of its furnaces. An outline of the table for the temperature-dependent steel enthalpy is added in annex II.

Figure 29 displays the relation between steel temperature and its enthalpy. It is linear in the range from 0 to  $500^{\circ}$ . At higher temperature the relation is not linear anymore.







Figure 29: Steel enthalpy

#### 3.2.2 Natural gas

The combustible for the heating sections DFF and RTH/RTS is natural gas, its main component being  $CH_4$ . Apart from methane it contains traces of higher hydrocarbons, carbon dioxide ( $CO_2$ ) and nitrogen ( $N_2$ ). Table 9 displays the composition of the fuel.

Table 9: Composition of natural gas

| Component      | Content<br>m³/m³ |         |
|----------------|------------------|---------|
| Methane        | $CH_4$           | 0.98100 |
| Ethane         | $C_2H_6$         | 0.0051  |
| Propane        | $C_3H_8$         | 0.0004  |
| Butane         | $C_4H_{10}$      | 0.0002  |
| Pentane        | $C_5H_{12}$      | 0.0004  |
| Hexane         | $C_6H_{14}$      | 0.0001  |
| Carbon dioxide | C0 <sub>2</sub>  | 0.0058  |
| Nitrogen       | N <sub>2</sub>   | 0.007   |
| Total          |                  | 1.000   |





#### 3.2.2.1 Lower heating value

The lower heating value (LHV) is calculated based on the composition of the fuel depicted in Table 9. The chemical equation for the complete combustion of methane is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \qquad (14)$$

$$C_n H_{2n+2} + \frac{3n+1}{2}O_2 \to nCO_2 + (n+1)H_2O$$
 (15)

for the higher hydrocarbons, respectively.

The constants of the equations above and the calculation of the LHV can be seen on Table 10. Due to the composition of natural gas and the lower heating values of the constituents a LHV of 35.681 kJ/Nm<sup>3</sup> was determined. The higher heating value of 39.640 kJ/Nm<sup>3</sup> does not enter the further calculations because it takes into account the latent heat of water vaporization in the combustion products; heat that can not be actuated in the combustion itself when the water is in its vapour form.

#### 3.2.2.2 Waste gas flow

The waste gas flow is calculated based on the flow of fuel and combustion air. Both parameters are measured in Nm<sup>3</sup>, the mass balance gives the waste gas flow as the sum of fuel and combustion air flow.

Equation 16 and 17 shows the calculation of the waste gas flow for the exemplary case of the combustion of  $1 \text{ Nm}^3 \text{ CH}_4$ .

$$CH_4 + 2O_2 + (\frac{2}{0.21} - 2)N_2 \rightarrow CO_2 + 2H_2O + (\frac{2}{0.21} - 2)N_2$$
 (16)

$$1Nm^3 + 2Nm^3 + 7.54Nm^3 \to 10.54Nm^3$$
(17)

The same principle is applied to all calculations concerning waste gas flow, the flow is determined as the sum of fuel and combustion air flows.





#### 3.2.2.3 Waste gas composition

The composition of waste gas varies with the air/gas ratio. At stoichiometic conditions, when

$$\lambda = \frac{\dot{V}_{air}}{\dot{V}_{air,stoich}} = 1, \qquad (18)$$

 $\lambda$  - Lambda-value

 $\dot{V}_{air}$  Nm<sup>3</sup>/h Actual air flow

 $\dot{V}_{air,stoich}$  Nm<sup>3</sup>/h Stoichiometric air flow

the carbon present in the fuel reacts with the oxygen in the combustion air and forms  $CO_2$ . In ideal conditions there is no free  $O_2$  left in the waste gas. Waste gas is composed of  $CO_2$ ,  $H_2O$  and  $N_2$  only. Further air components such as sulphur ( $S_2$ ), inert gases and traces of  $CO_2$  are neglected in the further calculations.

In over-stoichiometric conditions there is an excess of  $O_2$  that does not take part in the combustion. The waste gas is composed of  $CO_2$ ,  $H_2O$ ,  $N_2$  and the excess  $O_2$ .





Table 10: Calculation of heating value of natural gas

| Gas Components                |                 | Stoïchiomatr Air CO.              |                   |   | Water Vapor   |         | Density com-   |              | Heating Value |         |                            |          |                            |         |
|-------------------------------|-----------------|-----------------------------------|-------------------|---|---|---------|--|--------------|---------------|---------|----------------------------|----------|----------------------------|---------|
|                               |                 | Content                           | Storen            |   |   |         |  | pared to Air |               | High    |                            | Low      |                            |         |
| Components (m <sup>3</sup> /r |                 | (m <sup>3</sup> /m <sup>3</sup> ) | V <sub>a</sub> (m | ı <sup>3</sup> air / m <sup>3</sup><br>gas) | V <sub>CO2</sub> (m <sup>3</sup> CO <sub>2</sub> / m <sup>3</sup><br>gas) |         | V <sub>H2O</sub> (m <sup>3</sup> H <sub>2</sub> O / m <sup>3</sup><br>gas) |              | d             |         | HHV (kWh/Nm <sup>3</sup> ) |          | LHV (kWh/Nm <sup>3</sup> ) |         |
|                               |                 | Α                                 | В                 | A x B                                       | С   | AxC     | D  | A x D        | E             | AxE     | F                          | AxF      | G                          | AxG     |
| Methane                       | $CH_4$          | 0.98100                           | 9.54              | 9.3587                                      | 1   | 0.981   | 2  | 1.962        | 0.555         | 0.54446 | 11.08                      | 10.86948 | 9.97                       | 9.78057 |
| Ethane                        | $C_2H_6$        | 0.0051                            | 16.84             | 0.0859                                      | 2   | 0.0102  | 3  | 0.0153       | 1.048         | 0.00534 | 19.58                      | 0.09986  | 17.88                      | 0.09119 |
| Propane                       | $C_3H_8$        | 0.0004                            | 24.37             | 0.0097                                      | 3   | 0.0012  | 4  | 0.0016       | 1.557         | 0.00062 | 28.22                      | 0.01129  | 25.94                      | 0.01038 |
| Butane                        | $C_4H_{10}$     | 0.0002                            | 32.41             | 0.0065                                      | 4   | 0.0008  | 5  | 0.001        | 2.096         | 0.00042 | 37.41                      | 0.00748  | 34.49                      | 0.00690 |
| Pentane                       | $C_5H_{12}$     | 0.0004                            | 40.87             | 0.0163                                      | 5   | 0.002   | 6  | 0.0024       | 2.671         | 0.00107 | 47.11                      | 0.01884  | 43.52                      | 0.01741 |
| Hexane                        | $C_6H_{14}$     | 0.0001                            | 46.81             | 0.0047                                      | 6   | 0.0006  | 7  | 0.0007       | 3.072         | 0.00031 | 55.06                      | 0.00551  | 51.02                      | 0.00510 |
| Carbon dioxide                | C0 <sub>2</sub> | 0.0058                            | 0                 | Х   | 1   | 0.0058  | 0  | Х            | 1.529         | 0.00887 | 0                          | Х        | 0                          | Х       |
| Nitrogen                      | $N_2$           | 0.007                             | 0                 | Х   | 0   | Х       | 0  | Х            | 0.968         | 0.00678 | 0                          | Х        | 0                          | Х       |
| Total                         |                 | 1.000                             |                   | 9.48188                                     |   | 1.00160 |  | 1.98300      |               | 0.56786 |                            | 11.01246 |                            | 9.91154 |





Table 11 shows an exemplary calculation of the waste gas composition for the combustion of  $1 \text{ Nm}^3$  of CH<sub>4</sub> under non-stoichiometric conditions. At Lambda-values superior to 1 oxygen excess and the according nitrogen amount in the combustion air will be present in the waste gas. They have to be taken into account in the calculation of the specific enthalpy of the waste gas.

Table 11: Composition of waste gas for the combustion of  $1 \text{ Nm}^3$  of  $CH_4$  for overstoichiometric conditions

|      | Fuel                                 | Combust                                    | ion Air                                  | Composition of Waste Gas           |                                     |                                   |                                   |                          |  |
|------|--------------------------------------|--|--|------------------------------------|-------------------------------------|-----------------------------------|-----------------------------------|--------------------------|--|
| λ    | V <sub>fuel</sub><br>Nm <sup>3</sup> | V <sub>air,stoich</sub><br>Nm <sup>3</sup> | V <sub>air,real</sub><br>Nm <sup>3</sup> | CO <sub>2</sub><br>Nm <sup>3</sup> | H <sub>2</sub> O<br>Nm <sup>3</sup> | N <sub>2</sub><br>Nm <sup>3</sup> | O <sub>2</sub><br>Nm <sup>3</sup> | total<br>Nm <sup>3</sup> |  |
| 1.00 | 1                                    | 9.54                                       | 9.54                                     | 1                                  | 2                                   | 7.54                              | 0.00                              | 10.54                    |  |
| 1.05 | 1                                    | 9.54                                       | 10.02                                    | 1                                  | 2                                   | 7.92                              | 0.10                              | 11.02                    |  |
| 1.10 | 1                                    | 9.54                                       | 10.49                                    | 1                                  | 2                                   | 8.29                              | 0.20                              | 11.49                    |  |
| 1.15 | 1                                    | 9.54                                       | 10.97                                    | 1                                  | 2                                   | 8.67                              | 0.30                              | 11.97                    |  |
| 1.20 | 1                                    | 9.54                                       | 11.45                                    | 1                                  | 2                                   | 9.05                              | 0.40                              | 12.45                    |  |
| 1.25 | 1                                    | 9.54                                       | 11.93                                    | 1                                  | 2                                   | 9.43                              | 0.50                              | 12.93                    |  |
| 1.30 | 1                                    | 9.54                                       | 12.40                                    | 1                                  | 2                                   | 9.80                              | 0.60                              | 13.40                    |  |

#### 3.2.2.4 Waste gas enthalpy

The enthalpy of a gas mixture is the sum of the enthalpy of its components; hence the enthalpy of the waste gas is determined according to its composition and the enthalpy of  $CO_2$ ,  $H_2O$ ,  $O_2$  and  $NO_2$ . An extract of enthalpy values for these gases is added to this report in annex I.

# 3.2.3 Heat losses through walls

The walls of the furnace are supplied with insulation material in order to prevent heat from the inside to be transferred to the outer surface of the installation. Depending on the temperatures in the different sections the walls are covered with layers of different composition and thickness. Table 12 lists the Lambda-values for all materials that are used for the insulation.

The thermal conductivity  $\lambda$  is a function of the temperature. This relation is visualized in Figure 30. At higher temperatures Lambda-values increase, indicating a higher heat flow through the layer. In the calculation for the heat balance heat losses through walls were calculated using the Lambda-value of the mean temperature.

See the calculation of the heat losses in an exemplary case on the following pages.





|                  | Lambda in W/(mK) |          |                     |          |          |         |  |  |  |  |  |
|------------------|------------------|----------|---------------------|----------|----------|---------|--|--|--|--|--|
| Temperature<br>℃ | Group 28         | Group 24 | Calcium<br>Cilicate | Group 30 | Group 26 | CALOR A |  |  |  |  |  |
| 400              | 0.32             | 0.14     | 0.12                |          | 0.27     | 0.24    |  |  |  |  |  |
| 500              | 0.33             | 0.15     | 0.13                |          | 0.28     | 0.26    |  |  |  |  |  |
| 600              | 0.34             | 0.16     | 0.14                | 0.44     | 0.29     | 0.28    |  |  |  |  |  |
| 700              | 0.35             | 0.17     | 0.15                | 0.45     | 0.3      | 0.3     |  |  |  |  |  |
| 800              | 0.36             | 0.18     | 0.16                | 0.46     | 0.31     | 0.32    |  |  |  |  |  |
| 900              | 0.37             | 0.19     |                     | 0.485    | 0.32     | 0.345   |  |  |  |  |  |
| 1000             | 0.38             | 0.2      |                     | 0.51     | 0.33     | 0.37    |  |  |  |  |  |
| 1100             | 0.395            |          |                     | 0.545    | 0.34     |         |  |  |  |  |  |
| 1200             | 0.41             |          |                     | 0.58     | 0.35     |         |  |  |  |  |  |

Table 12: Thermal conductivity for different insulation material

|                  | Lambda in W/(mK) |                |        |                |                                   |                      |  |  |  |  |  |
|------------------|------------------|----------------|--------|----------------|-----------------------------------|----------------------|--|--|--|--|--|
| Temperature<br>℃ | Module<br>1150   | Module<br>1250 | KALFEU | Module<br>1400 | CFB 1260<br>128 Kg/m <sup>3</sup> | CFB 1260<br>96 Kg/m³ |  |  |  |  |  |
| 400              | 0.1              | 0.11           | 0.1    | 0.11           | 0.1                               | 0.11                 |  |  |  |  |  |
| 500              | 0.12             | 0.13           | 0.12   | 0.135          | 0.125                             | 0.135                |  |  |  |  |  |
| 600              | 0.14             | 0.15           | 0.14   | 0.16           | 0.15                              | 0.16                 |  |  |  |  |  |
| 700              | 0.175            | 0.185          | 0.18   | 0.195          | 0.175                             | 0.195                |  |  |  |  |  |
| 800              | 0.21             | 0.22           | 0.22   | 0.23           | 0.2                               | 0.23                 |  |  |  |  |  |
| 900              |                  | 0.255          | 0.29   | 0.27           | 0.235                             | 0.275                |  |  |  |  |  |
| 1000             |                  | 0.29           | 0.36   | 0.31           | 0.27                              | 0.32                 |  |  |  |  |  |
| 1100             |                  |                |        | 0.35           |                                   |                      |  |  |  |  |  |
| 1200             |                  |                |        | 0.39           |                                   |                      |  |  |  |  |  |



