Master Thesis

Developing a model to calculate the carbon footprint of refractory products

submitted by: **supervisors:**

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EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre an Eides statt, dass ich diese Arbeit selbständig verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und mich auch sonst keiner unerlaubten Hilfsmittel bedient habe.

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.

Acknowledgements

Kurzfassung

Entwicklung eines Modells zur Berechnung des CO$_2$-Fußabdruckes von Feuerfestprodukten

Die gegenständliche Masterarbeit beschäftigt sich mit dem CO$_2$-Fußabdruck von Feuerfestprodukten. Neben dem Begriff des Carbon Footprints werden auch seine Bedeutung, seine Varianten und seine derzeitigen Berechnungsansätze beschrieben. Des Weiteren wird auf die Definition von Feuerfestprodukten und ihre weitgefächerten Anwendungsbereiche eingegangen. Derzeit gibt es in der Feuerfestindustrie noch keinen einheitlichen Standard, der den Carbon Footprint von Feuerfestprodukten betrifft. Daher ist das Ziel dieser Masterarbeit ein Modell zu entwickeln, dass es insbesondere erlaubt den Carbon Footprint von geformten Erzeugnissen zu bestimmen. Neben dem analysierten System werden auch die verwendeten Daten und notwendigen Annahmen beschrieben. Das entwickelte Modell, welches unter Berücksichtigung von diversen Standards erstellt worden ist, wird in Form einer Toolbox umgesetzt. Die Toolbox ist entsprechend den Lebenszyklus- bzw. Produktionsschritten von geformten Erzeugnissen aufgebaut. Die praktische Anwendung dieses Modells wird anhand von Auskleidungskonzepten von feuerfesten Aggregaten erprobt.

Abstract

Developing a model to calculate the carbon footprint of refractory products

Present Master Thesis deals with the carbon footprint calculation of refractory products. Definitions of the term carbon footprint are given and its intent, its types as well as its calculation approaches are described. Furthermore, refractory products are characterised and their widespread application areas are exhibited. As a matter of fact, so far no standardised method exists for the calculation of the carbon footprint of refractory products. Therefore, the objective of this Master Thesis is to develop a model that enables to assess the carbon footprint of refractories, especially that of shaped refractory products (bricks). Thus, the analysed system, the applied data and the necessary assumptions made are described. This model, which considers diverse life cycle assessment and carbon footprinting standards, is arranged in form of a tool box. This tool box is structured according to the life cycle steps/production steps of shaped refractories. The practical application of this model is tested on basis of lining concepts for high temperature resistant aggregates.

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1 Introduction

Avoiding an intolerable increase in global warming is the challenge of this century and therefore discussed worldwide. Increasing industrialisation, which effects rising greenhouse gas (GHG) emissions, is the main reason for the anthropogenic caused input on climate change. [1, p. 76]

In order to achieve reduction in GHG emissions, several climate strategies have been developed. The most known of them is the Kyoto Protocol. The Kyoto Protocol is an international agreement linked to the United Nations Framework Convention on Climate Change that contains binding targets for its 37 signatories. Some industrialized countries and the European Community belong to this signatories. The aim of this agreement is to reduce the amount of GHG emissions by an average of 5 % on basis of 1990 in the period 2008-2012. The Kyoto Protocol was adopted in December 1997 and entered into force in February 2005. [2]

Thus, the European Union (EU) emission trading scheme directive (2003/87/EC) was one of the mechanisms of the Kyoto Protocol. The emission trading system (ETS) is one of the key policies introduced by the EU with the purpose to fulfil their reduction target of 8 %. [3]

However, emission trading is not only valid for the 27 EU member states. Also Iceland, Liechtenstein and Norway take part since 2008. [4, p. 5]

The member states have to develop a National Allocation Plan (NAP) where they assess their total emissions for each period. According to the NAP, which is approved by the European Committee, the member states are entitled to distribute allowances to the installations that are affected by emission trading. These installations belong to the main energy-intensive industries (e.g.: power stations, refineries, iron and steel, cement and lime, paper, ceramics, food and drink, glass, engineering, the manufacture of vehicles) or to electricity producers. One allowance is equivalent to one tonne CO_2. [3]

ETS is based on the "cap" and "trade" principle. Cap means that the total amount of GHG that can be emitted by companies is limited. Within this cap companies receive emission allowances. Trade means that companies can sell allowances or buy them from another one. At the end of each year, each company must possess enough allowances to cover its emissions or otherwise fines are imposed. [5]

It is possible to sell emission capacities, if permitted emissions are not used by the country or company itself. This is known as the carbon market, because CO_2 is the main greenhouse gas. For this reason allowances are traded like any other commodity. [1]

If a company exceeds the permitted amount of greenhouse gas emissions, it can either purchase allowances from other companies or from stock exchange. In case of late surrender (30 April of the following year) a fine has to be paid and the missing certificates have to be purchased. If a company underruns their permitted CO_2 equivalents, it can sell them or save them for the following years. [6, p. 416]; [23]

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Emission trading started in 2005 and is divided into 3 periods; 2005-2007, 2008-2012, 2013-2020. Phase I was a "learning by doing phase". Phase II, which is identical with the period of the Kyoto Protocol, includes revised monitoring and reporting rules, more stringent emissions caps and additional combustion sources. Phase III has been revised through the adoption of Directive 2009/29/EC, which brings major changes concerning harmonised allocation methodologies, additional greenhouse gases and emission sources. [7]

Harmonised allocation methodologies means that EU-wide rules are applied across all EU member states. Thus, in Phase III allowances for industry and heating sectors will be allocated based on benchmarks. These benchmarks are created on basis of the most efficient installations in the EU and are a threshold for the level of free allocation of an individual installation. Consequently, companies that meet the benchmark receive up to 100 % allowances they need. Installations that do not meet the benchmark will have a shortage of allowances and need to buy additional allowances or otherwise reduce their emissions. Benchmarks are developed per product and have to be feasible. Furthermore, benchmarks are important in order to achieve a low-carbon society. [5]

1.1 Problem identification

As a matter fact, for several industrial sectors it was not possible to develop benchmarks. Refractory industry belongs to one of them. Due to its heterogeneous manufacturing techniques and the complexity of its products, the calculation of the carbon footprint for products deriving from refractory industry is very complicated. For that reason, no standardised approach for the whole refractory industry exists so far. However, the term carbon footprint has become quite popular over the last few years and therefore the entire refractory industry is interested in developing a representative standard that is plausible and easy to use. In addition, more and more customer requests appear concerning this topic. Refractory industry has to cover a wide range of products, because of their widespread applications in industrial sectors. RHI is the world's market leader in refractories technology. This global corporate group provides solutions for more than 1,000 different aggregates. Thus, RHI offers more than 100,000 single articles and for this reason more than 1,200 individual raw materials are required to handle this. In conclusion, the carbon footprint calculation for refractory products is a challenging task.

1.2 Goal

The objective of this Master Thesis is to develop a standardised method or rather model for the calculation of the carbon footprint of refractory products, with focus on shaped refractories (bricks), manufactured on basis of the coarse ceramic production. The model to be developed should serve as basis for creating a standard work for the whole refractory industry and therefore disregards local specific aspects. The method should be simplified as far as possible, but also should ensure representative results that can be applied by the entire refractory industry. Hence, the already existing general calculation methods or rather

standards must be identified, checked and if possible applied. Then, the system to be analysed and its scope have to defined. The different types of refractory products, the production processes of their raw materials and the coarse ceramic production have to be regarded. In order to handle the large number of total products, products have to be classified into products groups. The raw materials of highest importance for manufacturing the product groups have to be identified and in addition, their emission factors have to be specified. The resulting model will be arranged in form of a toolbox. This tool box is structured according to the life cycle steps/production steps of shaped refractories. Thus, a suitable and generally acceptable approach has to be found to assess the respective CO_2 emissions of each step. Afterwards, the carbon footprint of the defined product groups can be formed by using the toolbox. Finally, the practical application of this model will be tested on basis of lining concepts for aggregates.

2 Fundamentals

This chapter provides an introduction into the greenhouse effect or global warming and the carbon footprint in general.

2.1 Greenhouse effect or global warming

The temperature of the Earth is controlled by the balance of input energy from the sun and output energy back into space. Certain atmospheric gases, known as greenhouse gases (GHG), are able to influence this balance. Due to human activities the level of GHG in the atmosphere increases. This leads to an enhanced greenhouse effect or rather global warming. [8, p. 9]

It has to be differentiated between the natural greenhouse effect and the anthropogenic caused type. The natural greenhouse effect is needed by the Earth. The atmosphere emits infrared (IR) radiation that reaches the Earth's surface and warms it. GHG in the atmosphere absorb the reflected IR radiation of the Earth's surface and thus, warm up the atmosphere. The exactly procedure is explained in Figure 1.
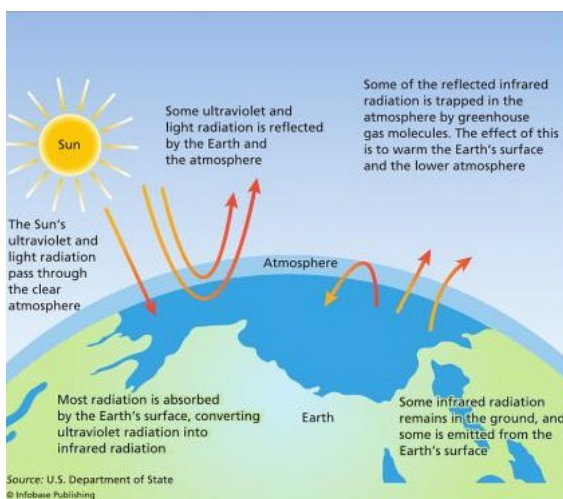
Figure 1: Greenhouse effect [9, p. 8]

GHG are trace gases located in the atmosphere that act like the glass in a greenhouse. They trap the heat energy coming from the sun close to the Earth. Additional greenhouse warming added due to human activity cause the atmosphere to overheat. [9, p. 18]

Naturally occurring GHG are:

- water vapour,
- carbon dioxide (CO_2),
- methane (CH_4),
- nitrous oxide (N_2O) and
- ozone (O_3).

They warm the Earth by 35 °C, because without them the Earth's average global temperature would be -20 °C. [8, p. 9]

These GHG capture 70-85 % of the thermal radiation emitted from the Earth's surface. Water vapour is the most common one of them and is responsible for 65 % of the natural greenhouse effect. Another 25 % of the natural greenhouse effect is generated by CO_2. Methane is the third most frequent one of them.

In addition to that, the anthropogenic greenhouse effect is caused by human activity and the age of industrialization in the 1700's was the beginning. CO_2 and other gases that stay in the atmosphere are produced due to deforestation, intensive agriculture, burning of fossil fuels, transportation, urban development, heating and cooling homes as well as industrial processes, and enforce the natural greenhouse effect. [9, p. 5-21]

The global warming potential (GWP) is a factor that describes the radiative forcing of one mass-based unit of a given greenhouse gas relative to an equivalent unit of CO_2 over a given period of time. The CO_2 equivalent is a unit that serves for comparing the radiative forcing of a greenhouse gas with carbon dioxide. GHG are converted into their CO_2 equivalents using 100-year global warming potentials defined by the Intergovernmental Panel on Climate Change (IPCC). [10, p. 2-4]

The IPCC has identified the major GHG (e.g.: CO_2, CH_4, N_2O, CCl_2F_2, $CHClF_2$, CF_4, SF_6) and their human source (see Figure 2). As a matter of fact, CO_2 is the one with the highest concentration in the atmosphere and therefore exhibits a warming potential of 1. Other GHG are low in concentration, but are much more effective than CO_2 due to their higher warming potential.

Greenhouse Gas	Chemical Formula	Pre-Industrial Concentrations	1994 Concentrations	Human Source
Carbon dioxide	CO_2	278 ppmv	358 ppmv (30 per cent increase)	Fossil fuel combustion Land use changes Cement production
Methane	CH_4	700 ppbv	1721 ppbv (240 per cent increase)	Fossil fuels Rice paddies Waste dumps Livestock
Nitrous oxide	N_2O	275 ppbv	311 ppbv (15 per cent increase)	Fertilizer Industrial processes Fossil fuel combustion
CFC-12	CCl_2F_2	0	0.503 ppbv	Liquid coolants / foams
HCFC-22	$CHClF_2$	0	0.105 ppbv	Liquid coolants
Perfluoromethane	CF_4	0	0.070 ppbv	Production of aluminium
Sulfur hexa-fluoride	SF_6	0	0.032 ppbv	Dielectric fluid

Figure 2: Major GHG and their sources [8, p. 13]

Halocarbons, like Chlorofluorocarbons (CFC's), Hydrochlorofluorocarbons (HCFC's) and sulphur hexafluoride (SF_6) are anthropogenic GHG that reach the atmosphere due to their utilisation for technical applications.

CFC's are fluorocarbons that contain chlorine atoms and are harmful to the ozone layer too. HCFC's contain fluorine atoms but do not harm the ozone layer. So they are used instead of CFC's, but they do warm the atmosphere. [9, p. 21]

SF_6 is a colourless, odorless, non toxic and non flammable gas whose molecules consist of one sulphur and six fluorine atoms. According to the IPCC, SF_6 is the most effective GHG. Thus, it has the highest GWP. [11]

2.2   Carbon footprint

In the course of increased environmental consciousness, more and more companies want to get an idea of their emitted GHG. Therefore, the carbon footprint is the appropriate tool in order to calculate them and in the next step to find measures for reducing the emissions caused. [1, p. 76]

The term carbon footprint has become quite popular over the last few years and is in widespread use across the media. Climate change topics are high up in political and corporate agenda. This is why carbon footprint calculations are in strong demand. Numerous approaches are realised, ranging from basic online calculations to sophisticated life cycle analyses and input-output-based methods or tools. However, no generally accepted definition and consistent method exists so far and confusion still dominates concerning what exactly has to be included in a carbon footprint analysis. After a literature research, this Master Thesis prefers the definition given as follows:

*The **carbon footprint** is a measure of the total amount of GHG emissions expressed as CO_2 equivalents that are produced as direct or indirect emissions caused by activities due to persons, organisations or products.* [12, p. 1-4]

*Its objective is to determine the emitted amount of GHG into the atmosphere. But in contrast, the **ecological footprint** calculates the size of the area that is required to cover the energy and raw material demand for one human.* [13, p. 6]

According to The Greenhouse Gas Protocol, direct GHG emissions are emissions that are owned or controlled by the footprinting company itself (e.g. emissions from combustion in owned or controlled furnaces). Indirect GHG occur from sources that are not owned or controlled by the company itself. On the one hand, those arise from the generation of purchased energy like electricity, on the other hand, indirect emissions appear as a consequence of several activities of the company, such as the production of purchased materials or the transportation of purchased fuel. [14, p. 25]

Biogenic CO_2, emitted due to combustion of organic substances, is considered as climate neutral, because naturally renewable raw materials can only release the same amount of CO_2 that is stored during their growth. Thus, biogenic CO_2 is not part of a carbon footprint analysis. [15, p. 47]

Generally, it is differentiated between product-, corporate- and supply chain-carbon footprint.

The CO_2 footprint of a supply chain contains all emissions generated along the value added chain and the supply chain. That includes emissions from purchasing and production, but excludes distribution. Instead, the corporate carbon footprint covers all GHG emissions produced company-wide. Direct and indirect emissions are also involved in it. [16, p. 22]

This Master Thesis deals with the product carbon footprint.

The product carbon footprint is an instrument for the determination and assessment of the climate compatibility of products and serves as basis for reducing the environmental impact of the phases of a product's life cycle. Product carbon footprints are profitable for companies, because reliable information is given about the GHG emissions associated with their products throughout the entire products' life cycle. [17, p. 7]

Product carbon footprinting offers an unique view of all GHG-emissions arising from a single product according to its life cycle, including the phases manufacturing, distribution, use and disposal or rather recycling. Product carbon footprints can support environmental consciousness of companies as well as of the public, because then consumers recognise their role in contributing to climate change and get an idea of their impact on emissions due to purchasing decisions and behaviour. [18, p. 2-3]

Motives for companies to calculate their product carbon footprint are internal and external incentives. Concerning internal incentives, the identification of possible savings is in the foreground. External compulsion is attributed to legal obligations and pressure from market, customers or investors. The results of CO_2 balances are mostly applied for public relations and marketing reasons. However, it has to be considered that a climate balance is not comparable with an all-embracing environmental balance. A climate balance only refers to GHG emissions, while other environmental aspects, like for example consumption of water or production of waste, are disregarded. [1, p. 76-78]

No international obligatory standards for the communication and assessment of product carbon footprints are known so far. However, some standards have already been developed, like The Greenhouse Gas Protocol and PAS 2050, or are under construction such as ISO 14067. [17, p. 18]

ISO 14067 Carbon Footprint of Products

The International Organisation for Standardisation (ISO) has initiated a process to create a standard for the carbon footprint analysis of products. This standard will be called "ISO 14067 Carbon Footprint of Products" and will be composed of two parts; part 1: quantification and part 2: communication of the product carbon footprint. As basis for part 1 serves ISO 14040 (Environmental management - life cycle assessment – principles and framework) and

part 2 derives from ISO 14025 (environmental labels and declarations). This standard shall be published in the middle of 2012. [17, p. 18-19]

The Greenhouse Gas Protocol - Product Accounting and Reporting Standard

The Greenhouse Gas Protocol - Product Accounting and Reporting Standard is a product-related standard for the calculation of GHG emissions from companies and other organisations. It was founded by the World Resource Institute (WRI) and the World Business Council for Sustainable Development (WBCSD). [17, p. 19]

In order to determine the emitted GHG, the emissions are divided into three scopes; Scope 1: direct GHG emissions, Scope 2: indirect GHG emissions, Scope 3: other indirect GHG emissions. [20]

The purpose of this standard, which is widespread in practice, is to create competitive advantages by enabling better product design, increasing efficiencies, reducing costs and removing risks. Also the communication of environmental information to customers shall be made easier. [21]

Publicly available specification 2050 (PAS 2050)

PAS 2050 is a British standard that was founded by the British Standards Institution (BSI) in cooperation with Carbon Trust and the Department for Environment, Food and Rural Affairs. The latest version – Specification for the assessment of the life cycle greenhouse gas emissions of goods and services - was published in 2011 and in addition supported by the Department for Energy and Climate Change (DECC) and the Department for Business, Innovation and Skills (BIS). This standard is built on ISO 14040 and ISO 14044, extended with particular principles and techniques. It provides a clear and consistent method for the assessment of life cycle GHG emissions associated with goods or services. [10, p. iii-V]

All these standards provide an orientation for the whole procedure of calculation. In case of primary data is not available, databases (e.g. GEMIS) and surveys are helpful instead to identify standard-emission factors. However, comparability of the results arising from carbon footprint calculations is still a problem. Different standards effect different ways of acting and for this reason the results can vary a lot. The development of uniform sector-specific or rather product-specific standards might solve that problem. [4, p. 96-97]

In the near future the product carbon footprint could be an instrument that serves for the purpose of product labeling, which should enable the transition of our society into a so-called "low carbon society" [1, p. 80]. The term low carbon society denotes a society that aims for a high quality of life in accordance with low GHG emissions [22, p. 3].

3   Carbon footprint calculation of refractory products

In this chapter the developed model for calculating the carbon footprint of refractory products is presented. This section also introduces refractories, gives an overview of their product categorisation and raw materials, and describes their production steps as well as the respective CO_2 calculation approaches.

3.1   Introduction in refractories

3.1.1   Description of refractory products

Not only the industrial sector is affected by refractories. Every person consumes products whose production requires the application of refractories. The annual global average consumption of refractory products is 2.3 kg per person. In Europe, annually 7.5 kg of high-grade refractory material are used per capita for producing everyday products, which means that a family of four needs an amount of 30 kg per year. [23]

International definition (DIN 51 060, ISO/R 836) characterises refractory products as nonmetallic ceramic materials, but also includes those which contain a small proportion of metallic components and moreover possess a pyrometric cone equivalent of at least 1,500 °C. The pyrometric cone equivalent is defined as end point temperature at which the tip of a pyrometric cone touches the supporting plaque. According to ISO/R 528 and DIN EN 993-12 the pyrometric cone equivalent is determined on small, slightly slanted pyramidal samples, composed of a specific mixture of ceramic materials, which are heated together with ceramic standard cones whose tips exhibit a known end point temperature for touching the supporting plaque. Generally speaking, as refractories are described products that are installed in plants and furnaces where temperatures above 600 °C dominate. [24, p. 1-2]

Products with a refractoriness below 1,500 °C are called fire resistant, above 1,500 °C refractory and above 1,800 °C super-refractory. [23]

Refractory products have to fulfil a set of requirements, like:

- high melting point,
- good mechanical properties such as compression strength, thermal shock resistance, bending strength under cold and hot conditions,
- low thermal expansion,
- low chemical reactivity against slags, gases and metallic melts,
- good ability for repair,
- good processing and
- low cost.

The purpose of refractory materials is to insulate processes operated at high temperatures from the surrounding area in an ecological and economical way. The appearing stresses may be mechanical, chemical or thermal, but nearly always a combination of these takes place. Therefore, the selection of the appropriate refractory material is adapted to the stresses of the application. [25, p. 2, 45]

3.1.2   Operational area

The types of application for refractory products are listed below:

- lining of plants for thermal processes (e.g. melting, firing and heat-treatment furnaces),

- lining of transport vessels,

- construction of fire resistant design components (e.g. functional products),

- heat recovery (e.g. regenerators, recuperators) and

- heat insulation. [24, p. 11]

More than two thirds of the total manufactured refractory products are used by the iron and steel industry. Therefore, the iron and steel industry is the largest global consumer of refractories. Further important operational areas are the nonferrous metal-, glass-, cement-, lime-, ceramic-, chemical-, petrochemical- as well as of course refractory-industry and many more applications like for example waste incineration plants. Table 1 represents the proportion of consumed refractories per sector in per cent (status: 2005). [24, p. 11]

Table 1: Refractory material consumption per sector [24, p. 12]

sector of industry	refractory material consumption [%]
iron and steel	66-69
ceramics, chemistry, petrochemistry and others	15-20
cement and lime	9-10
nonferrous metal	3
glass	2-3

The market distribution depends on the locations of the consumer industries. Another influencing factor is the degree of modernity of the manufacturing process of these industries. Especially in the iron and steel industry major regional differences still exist concerning consumption of refractories. For instance in China, the specific consumption rate is twice times higher than in Europe, Japan and the United States. [24, p. 11]

Table 2 shows the specific consumption rate of refractory material per industry in kg per tonne product.

Table 2: Specific consumption rate per industry [23]

1 tonne steel	10 kg
1 tonne glass	4 kg
1 tonne cement	1 kg
1 tonne lime	0.7 kg
1 tonne nonferrous metal	2.7 kg
1 tonne waste	5.5 kg

Annually about 20-25 million tonnes of refractory products are produced worldwide. Despite increasing production output of the consumer industries, the specific demand for refractories (in kg/t) decreases about 1-2 % per year since the 1970's due to following reasons:

- improvements of process know-how in consumer industries leads to lower refractories consumption rate,

- increase in productivity and process improvements in the area of high temperature treatment,

- enhanced production processes for refractory materials and availability of high-grade raw materials and

- improvement of existing refractory products, new developments and longer service lives.

A differentiation between the manufacturing methods for refractory products is listed as follows:

- coarse ceramic production (grain sizes up to 6 mm, in special cases up to 25 mm),

- fine ceramic production (grain sizes below 1 mm),

- manufacture by melt (fused cast products),

- manufacture of porous products (heat-insulating bricks) and

- manufacture of high temperature wools (ceramic fibres). [24, p. 13, 14, 21]

3.1.3   RHI AG (Radex-Heraklith Industriebeteiligungs AG)

RHI is a vertically integrated global provider of high-grade refractory products, systems and services. As global player RHI employs about 8,000 staff members in 32 production sites and 70 sales- and service-locations. Additionally, in Austria the headquarters (Vienna) and the technology center (Leoben: >200 employees) are placed. RHI is the world leader in refractories technology, because of close to market R&D facilities and tailor-made products. Active Management of intellectual property and more than 1,500 patents are accomplished

by international experts of the R&D team. Over 10,000 companies in more than 180 countries belong to the clientele of RHI. The world market leader focuses on manufacturing, sale, installation of complex and hard-to-replicate products. RHI is able to cover a share of its raw material demand internally due to mining of 1.3 million tonnes of magnesite and dolomite per year. As only leading full service provider for refractory products worldwide, RHI should be able to handle the complex task of this Master Thesis. Due to its world market leadership, technological progress and long-standing cooperation with several customer industries, it should be possible to gain representative data and resulting facts that are useful for the entire refractory industry. Another positive aspect is the fact that RHI has a large product portfolio, which fits a wide range of applications. Furthermore, global aspects could be involved because of locations scattered upon different continents and thus, carbon footprint analysis is enabled where locally specific manufacturing processes are disregarded and instead a worldwide valid average standard is realised. [23]

3.2 Product categorisation

As a matter of fact, refractories have to cover a wide range of applications (see chapter 3.1). Consequently, a large product portfolio is realised in refractory industry.

In general refractory products are classified into:

- functional products,

- heat-insulating materials,

- dense shaped products and

- unshaped products (monolithics). [24, p. 2]

This Master Thesis is principally dealing with the carbon footprint calculation of dense shaped products. Therefore, a description of each type of refractory product is given in this chapter as follows, but the main focus is on shaped refractories.

3.2.1   Functional products

In addition to refractoriness, a characteristic of functional products is their fast and efficient achievement of specific process objectives. Especially in the steel industry, these types of products play a vital role. Functional products include isostatically pressed products for casting steel, gas purging bricks, ceramic material for tapping and ceramic filters. [24, p. 305-344]

3.2.2   Heat-insulating materials

Heat-insulating materials are used for the refractory lining in thermal industrial plants with the purpose to reduce heat loss by utilising low thermal conductivity and thermal capacity. Thermal conductivity depends on the porosity of the material, pore size, pore shape, structure and mineralogical composition of the materials. For this reason heat-insulating materials usually have a high porosity of at least 45 %, mostly 60-90 %, and therefore a low density. Moreover, thermal shock resistance has impact on the application area. Table 3 gives an overview of heat-insulating materials and their characteristics. [24, p. 345]

Table 3: Heat-insulating materials and their characteristics [24, p. 346]

material type	bulk density [g/cm^3]	thermal conductivity [W/mK]			application area [°C]
		400 °C	800 °C	1200 °C	
heat-insulating bricks	0.35-0.7	0.12-0.23	0.19-0.30	-	750-1,000
lightweight insulating bricks	0.5-1.4	0.13-1.3	0.17-1.2	0.23-1.1	1,000-1,800
insulating castables	0.5-1.4	0.17-1.0	0.22-0.8	-	750-1,800
ceramic fibres	0.064-1.5	0.08-0.45	0.15-0.45	0.29-0.72	600-1,800
calcium-silicate minerals	0.2-0.3	0.10	0.17	-	1,000
microporous material	0.15-0.35	0.03	0.06	-	900
mineral foams	0.2-0.8	0.12-0.30	-	-	650
glass wool and mineral wool materials	0.1-0.4	0.06-0.10	0.20-0.25	-	500-700

3.2.3 Unshaped refractory products (also named monolithics)

The difference between shaped and unshaped products is that the production of unshaped products is already completed after the process of mixing and therefore mixes do not have a particular format like bricks. Unshaped products are applied directly on the place of operation and form the furnace lining after induration. [24, p. 233]

The main components for the production of unshaped products are raw materials (grained or grinding stock), binders and additives. Unshaped products are delivered in a dry condition and packaged for example in big bags, pails or sacks. Compared to shaped products, mixes are semi-finished goods, because subsequent processing is accomplished by the customer. [23]

Definition of unshaped refractory products

A general definition of unshaped products is given in the standards ISO 1927 and DIN EN 1402-1. Hence, monolithic refractories are batches consisting of additives and one or more binder that are prepared for direct use either in state of delivery or after adding one or more suitable liquids. There is a possibility of containing metallic, organic or ceramic fibres. These batches are dense or insulating. Insulating batches are those with a true porosity of more than 45 %, determined on a fired specimen according to specified conditions as indicated in EN 1094-4. [24, p. 233]

Furthermore, in DIN EN 1402-1 the different bond types are described. It is differentiated between hydraulic, ceramic, chemical and organic bonding. [24, p. 234]

Hydraulic means hydrophilic and water-resistant. Hydraulic bond is achieved by hydraulic setting at room temperature, for example with portland cement or calcium aluminate cement as binder. [23]; [24, p. 234]

Ceramic bond emerges from sintering during firing, which means that setting is arranged due to higher temperatures without adding binders or additives. Chemical bond is formed by reaction with a chemical substance such as water glass or phosphates, but at a temperature below the ceramic bond. [23]; [24, p. 234]

Organic bond is accomplished by setting at room temperature or at higher temperatures with an organic binder. [24, p. 234]

Another bond type that is important for refractory products is the carbon bond. Further information about that will be mentioned in the section of unfired bricks (see 3.2.4.2).

Hence, the prevailing bond type for mixes is the hydraulic bond, for fired bricks the ceramic bond and for unfired bricks the chemical bond.

Classification of monolithics

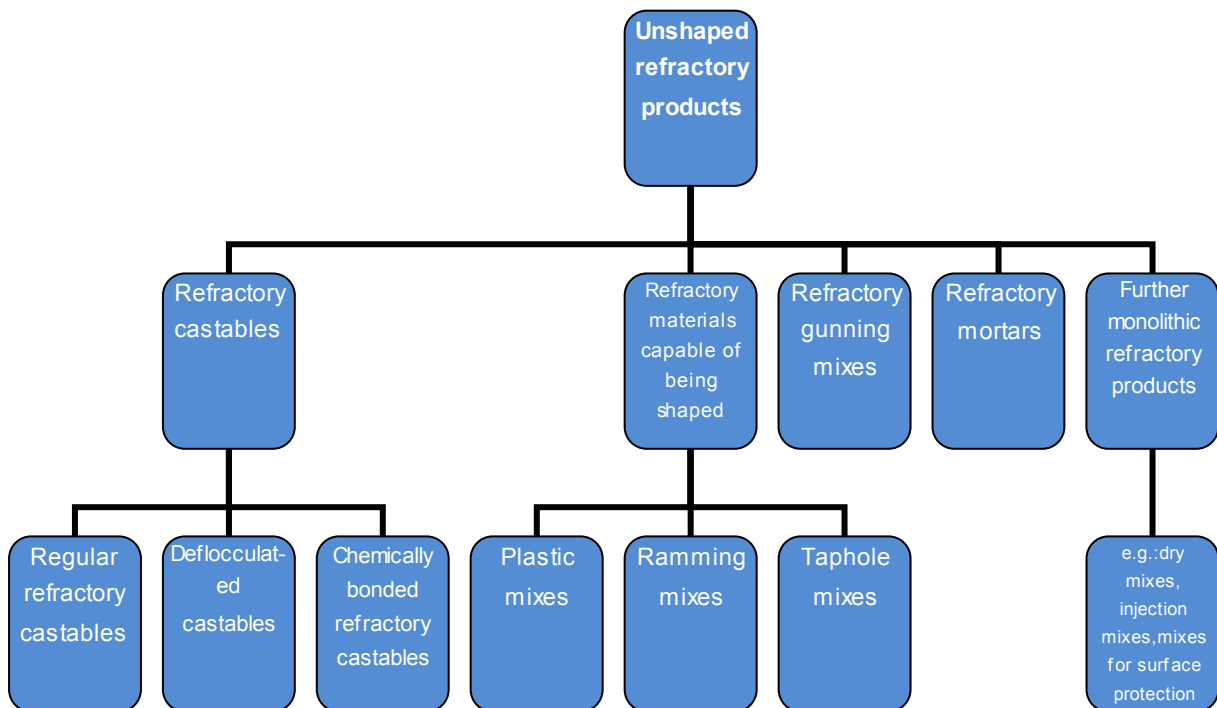The classification of unshaped refractory products is illustrated in Figure 3.

Figure 3: Classification of unshaped refractory products [24, p. 233-240]

A specification of the above mentioned terms is indicated in Table 4.

Table 4: Terms for unshaped refractory products [26, p. 3]

Mortars	Materials for bonding bricks in a lining
Castables	Refractories in which raw materials and hydraulic-setting cement or chemical binders are mixed with water, formed by casting and used to line furnaces, kilns, etc.
Plastic mixes	Refractories in which raw materials and plastic materials are mixed together with water and then formed roughly. Sometimes chemical additives are added for hardening at relatively low temperatures.
Gunning mixes	Refractories that are sprayed on the surface of walls or structured by gun.
Ramming mixes	Granular refractories, which are strengthened by formation of ceramic bond after heating, possess less plasticity and are installed by air rammer.
Taphole mixes [24, p. 237]	Refractories which are specifically used for filling and sealing blast furnace tapholes. These mixes are extruded precompacted blocks that obtain their plastic consistency from additives and organic and ceramic binders. A carbon bond is formed after firing or once in service.

The same materials that are utilised for the production of bricks are applied for the production of mixes. Therefore, another way of classification into basic and non basic unshaped products could be arranged. Basic unshaped products include construction, repair and maintaining mixes as well as mortars, joint construction and filling materials. Castables, plastic mixes, ramming mixes as well as gunning mixes and also mortars belong to the group of non basic unshaped products. [24, p. 258-302]

Examples for mixes could be seen in Figure 4.

Figure 4: Examples for mixes [23]

3.2.4 Dense shaped refractory products

A possible classification of dense shaped refractory products is accomplished by ISO 10081: Classification of dense shaped refractory products, which is divided into four parts:

- Part 1: Alumina-silica products,
- Part 2: Basic products containing less than 7 % residual carbon,
- Part 3: Basic products containing 7-50 % residual carbon and
- Part 4: Special products.

Except of part 4 that was published in 2007, all parts were released in the year 2003. [27]

For the reason that this Master Thesis focuses principally on the carbon footprint calculation of dense shaped products, the above mentioned classification is too general. Shaped refractories consists of a variety of individual products. Therefore, an appropriate method for summing them up is necessary. Hence, the relevant product categorisation is accomplished by specific product group codes of RHI (here not mentioned due to data protection reasons). The result is illustrated in Figure 5.
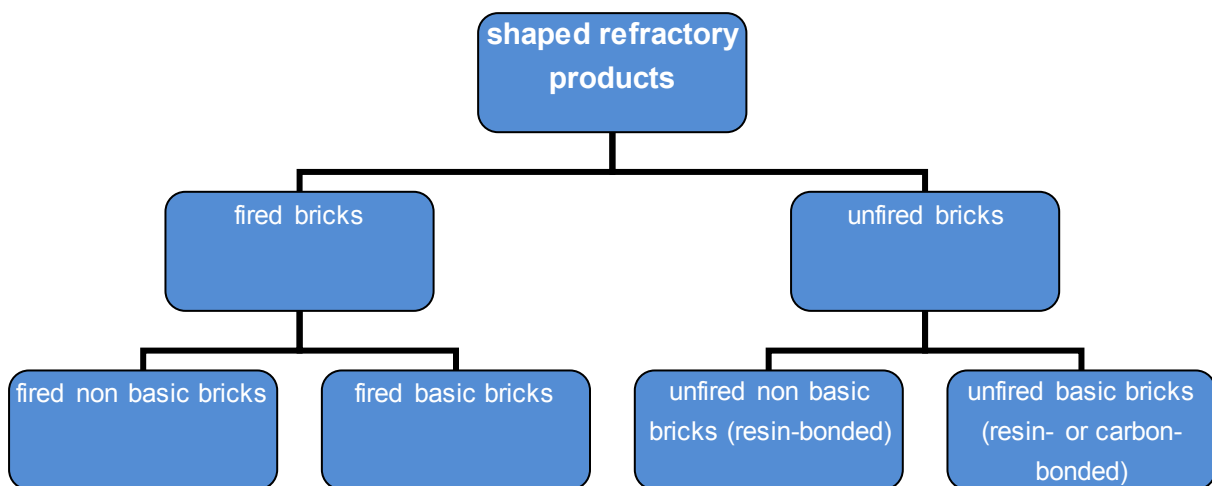
Figure 5: Classification of dense shaped refractory products

The identified four main groups, as registered below, are described in more detail in the next sections:

- fired non basic bricks,
- fired basic bricks,
- unfired non basic bricks (resin-bonded) and
- unfired basic bricks (resin-bonded or carbon-bonded).

Concerning carbon footprint calculation, a generally applicable formula for each product group or rather sub group is developed based on data from literature. In this process, the objective is to meet the requirements of the whole refractory industry in order to allow a

passable and representative result. Access to this formulas has to be denied due to data protection reasons.

3.2.4.1 Fired bricks

3.2.4.1.1 Fired non basic bricks

The group of the fired non basic bricks, also called alumina-silica bricks, includes especially materials of the SiO_2-Al_2O_3 series and other materials, which cannot be further classified in order to their chemical reaction behaviour (e.g. silicon carbide). [24, p. 51]

Concerning carbon footprint calculation the listed groups of bricks are considered to be most important:

- silica-,
- fireclay-,
- high alumina-,
- silicon carbide-,
- calcium aluminate- and
- zircon-containing bricks.

Silica bricks

Quartzite with more than 96 weight % SiO_2 is the main raw material for silica bricks. Quartz sand with a high degree of purity is also partly used as raw material. During heating and cooling of silica bricks, SiO_2 modification changes are carried out. Therefore, the mineralogical composition of fired silica bricks depends on utilised raw materials and certain manufacturing aspects. Above 600 °C these bricks are high thermal shock resistant. Premium grade silica bricks can be installed where temperatures of 1,700 °C are at work. A disadvantage is that above 1,000 °C SiO_2 is reduced to gaseous SiO by heavy reducing and H_2-containing atmosphere. The corrosion resistance to acidic slags is good, but gases and vapours containing alkalies are able to effect intensive corrosion below 1,470 °C. Major application areas for silica bricks are coke ovens, gas furnaces, hot blast stoves, roofs of electric arc furnaces and the superstructure of glassmelting furnaces. [24, p. 51-58]

Fireclay bricks

The two principal components of fireclay bricks are Al_2O_3 (10-45 %) and SiO_2 (50-80 %). Fireclay bricks could be differentiated according to their Al_2O_3 content or to the shaping process. The SiO_2 content of the bricks impacts the corrosion behaviour. A high SiO_2 content enhances the resistance to alkalies and acids. Fireclay bricks are widely-used products like

for instance in blast furnaces, hot blast stoves and steel foundries, as well as in nonferrous metal industry, glass industry and cement industry. [24, p. 66-73]

High alumina bricks

High alumina bricks are classified according to their Al_2O_3 proportion with a minimum of 45 % and a maximum of 99 %. This percentage rate influences what kind of raw materials are applied, mostly corundum, bauxite, mullite, andalusite, sillimanite and kyanite. Furthermore, the main raw material is decisive for their designation. Bricks containing 45-55 % Al_2O_3 are mainly upgraded fireclay bricks, obtained by adding high-alumina raw materials. Regarding corrosion behaviour, generally high alumina bricks have advantage over fire clay bricks. Bauxite bricks form the major part of high alumina bricks due to their low price. They are installed for example in ladles, roofs of electric furnaces and cement rotary kilns. [24, p. 74-82]

Calcium aluminate (CA) bricks

Calcium aluminate bricks are used in the tin bath bottom of float glass tanks. The main components of these bricks are 68 % Al_2O_3, 24 % CaO, 5 % SiO_2 and 0.1 % Fe_2O_3. More information about CA could be found in chapter 3.4.5.6. [23]

Silicon Carbide (SiC) bricks

SiC is seldom ever found in nature as raw material and therefore it is the outcome of the Acheson process (see chapter 3.4.5.16). The standard methods for the production of refractories are also enabled to be used for the production of SiC products, but SiC causes intensive abrasion to the pressing or molding equipment. Special properties of SiC materials are high thermal conductivity, thermal shock, abrasion and corrosion resistance to various gases, acids, slags and metal melts as well as good strength up to high temperatures. The sensitivity to oxygen and steam between 1,000 and 1,200 °C is disadvantageously. Especially, silicon carbide products are utilised for linings in plants and furnaces of the iron and nonferrous metal industry. Refractories made of SiC are also used in waste incineration plants, because they lead to improved combustion and optimised off-gas quality due to higher operation temperatures. [24, p. 98-101]

Zircon-containing bricks

The main raw material for zircon-containing bricks is zircon silicate with its theoretical composition of 67.2 % ZrO_2 and 32.8 % SiO_2, as mentioned in chapter 3.4.4.7. Zircon-containing bricks can be divided into pure zircon silicate materials and sintered alumina-zirconia-silica (AZS) materials that are manufactured out of zircon, mullite and corundum. Shaping of this materials can be arranged by hand, isostatical pressing, slip cast, uniaxially

pressing or compaction by vibration. It is differentiated between dense materials, sintered materials and ceramically-bonded materials. While ceramically-bonded materials have a volume apparent porosity of 15-24 %, the volume apparent porosity of dense and sintered materials is below 1 %, except of variants reinforced with zircon that have 5-9 %. Sintering or rather firing is accomplished by temperatures of 1,400-1,650 °C. Zircon-containing bricks exhibit high corrosion resistance to aggressive media and specifically to acidic melts. Thus, this brick type is applied most commonly in glass and steel industry. [24, p. 85-89]

3.2.4.1.2 Fired basic bricks

Magnesia (MgO) is the dominating part in fired basic bricks. Therefore, a classification on basis of the second main component is realised. [23]

The relevant groups for this Master Thesis are indicated subsequently:

- magnesia bricks,
- magnesia-chromite bricks,
- magnesia-spinel bricks,
- magnesia-hercynite bricks and
- magnesia-zircon/zirconia bricks.

Magnesia bricks

Magnesia bricks are principally made out of dead burned magnesia and secondarily out of fused magnesia. These bricks contain at least 80 % MgO and are classified according to their iron content out of magnesite. Mentionable properties of magnesia bricks are their high hot strength and resistance to basic foreign substances (e.g. steel mill slags, alkali oxides) due to the high melting point of MgO. Further advantages are the high thermal conductivity and heat storage capacity. For this reason magnesia bricks are used in heat storages and preheater plants. A disadvantage of these bricks is their sensitivity to stress caused by thermal shock due to their high thermal expansion and elasticity modulus. Applications for magnesia bricks are wear and permanent linings in steel industry, furnaces of the nonferrous metal industry, glass melting furnaces and heat storage units. [24, p. 169-182]

Magnesia-chromite bricks

The major materials for producing magnesia-chromite bricks are dead-burned magnesia and chrome ore. In refractory industry these bricks are divided into three groups that are 85/15 (10-20 % chrome ore), 60/40 (30-50 % chrome ore) and 35/65 (60-70 % chrome ore).Their relevant properties are hot erosion resistance and stress capacity capability. Magnesia-chromite bricks are also very resistant to corrosion of varying basicity. This type of fired brick is applied in steel industry (e.g. open-hearth furnace, AOD converter), nonferrous metal

industry (e.g. TBR converter), glass industry (e.g. regenerators), cement rotary kilns and lime shaft kilns. [24, p. 194-204]

Magnesia-spinel bricks

Magnesia-spinel bricks consist mainly of periclase (MgO) and spinel (MgO*Al_2O_3) with at least 40 % MgO. Due to their chemical and mineralogical composition these bricks own superb thermal shock resistance, are insensitive to reduction or oxidation change and are chemically resistant to alkali oxides. Magnesia-spinel bricks are standard products for the lining of rotary and shaft kilns to fire lime, cement, dolomite and magnesite. [24, p. 209]

Magnesia-hercynite bricks

The main materials for these fired basic products are dead burned magnesia and dense hercynite. The mechanical and thermo-mechanical behaviour is decisively influenced by an appropriate content of hercynite in grain form. Magnesia-hercynite bricks are installed in cement rotary kilns, because of their low susceptibility to cracks, excellent coating behaviour and high corrosion resistance to clinker melts. [24, p. 215-217]

Magnesia-zircon/zirconia bricks

The major materials for these types of fired basic products are premium grade sintered magnesia and/or fused magnesia. Baddeleyite, natural zircon or synthetic zircon is added. These brick types possess distinguished chemical resistance to alkalies, alkali salts and SO_2/SO_3 as well as a good thermal shock resistance. In addition, magnesia-zirconia bricks are corrosion resistant to highly basic slags and have a high endurance strength. Therefore, magnesia-zirconia bricks are installed in cement, lime, dolomite and magnesite rotary and shaft kilns. Magnesia-zircon bricks are preferably installed in regenerators of glass melting furnaces. [24, p. 213-214]

3.2.4.2 Unfired bricks

As the name suggests, the heat treatment of this kind of bricks is not achieved through firing, but the operation of tempering is applied to them (see chapter 3.7.2). The bonding is, as mentioned before, arranged chemical, because of the applied binding materials.

Attention should be paid to the fact that the required carbon carrier may act as a further CO_2 source. The added carbon of resin-bonded bricks is completely integrated in the bonding, which means that no carbon is available for forming CO_2 in the stage of thermal oxidising. But in pitch-bonded bricks 0.2 weight % of the added carbon is not integrated in the bonding, because of splitting-off volatiles. Therefore, these volatiles are converted into CO_2 in the thermal oxiliser. 0.2 weight % is equivalent to 2 kg carbon per tonne. By applying the CO_2/C ratio of 3.664 [45, p. 9], this amount of carbon transforms into 7.33 kg CO_2 per tonne. [23]

3.2.4.2.1 Unfired basic bricks

Magnesia-carbon (MgO-C) bricks belong to the group of unfired basic bricks. For the production of magnesia-carbon bricks and their carbon bond, a solid carbon carrier such as graphite or carbon black, a binder that acts as liquid carbon carrier and naturally magnesia are needed. Pitch or resin are used as carbonising binders. Premium-grade magnesia with low boron and low iron content, sintered magnesia and fused magnesia of different quality are used for this purpose. The effect of carbon is determined by wear reduction due to decreasing infiltration depth and characteristic structure flexibility. Moreover, thermal shock resistance is enhanced by increased thermal conductivity and reduced thermal expansion. In the past the bonding was generated by coal tar pitch, which is obtained by distillation of raw tar. Although coal tar pitch acts harmful to environment and nature, it was utilised because of the best performance to cost ratio of all coking binders. Nowadays, it has been replaced by pitch alternatives in accordance with health and environment protection requirements. In liquid state between 300 and 600 °C pitch forms elementary carbon accompanied by splitting-off volatiles. Phenolic resins are usually applied as synthetic resins, which are synthetic polycondensation products out of phenol and formaldehyde. Compared to pitch, pyrolysis happens in solid state. The structure of the lattice made of synthetic resin is not as good as made of pitch. [24, p. 183-189]

Metal powder (e.g. Al, Si, Mg), so-called antioxidants, may be added to influence certain properties of the brick. Mainly, antioxidants are added to resin-bonded bricks. Pitch impregnation is usually applied only to pitch-bonded bricks, but it is not needed in all circumstances. [23]

Magnesia-carbon bricks are particularly used in steel industry (e.g. as wear lining in basic oxygen furnaces, electric arc furnaces, steel casting ladles) and in functional products (e.g. taphole brick, purging brick). [24, p. 183-189]

3.2.4.2.2 Unfired non basic bricks

The group of unfired non basic bricks includes alumina-magnesia-carbon (AMC) bricks. The carbon bond is essential for a combination of raw materials with varying expansion coefficients like magnesia and corundum. AMC-bricks are bonded with phenolic resin, pressed precisely to the required format and tempered at temperatures of 150-300 °C. Concerning heat treatment, higher temperatures are not desired, because these bricks shall react during their service life in the temperature zone where they are installed. Standard AMC-bricks are manufactured with various contents of fused corundum, sintered corundum, bauxite, magnesia spinel and sintered as well as fused magnesia. Calcined alumina, graphite and antioxidants applied as additives may be added. AMC-bricks contain usually between 2-15 % carbon. According to ISO 10081-4 a classification of AMC-bricks into AMC90/N, AMC80/N, AMC70/N, AMC60/N and AMC50/N is accomplished. The number characterises the Al_2O_3 content and N corresponds to the subgroup of residual carbon. Depending on the percentage rate of Al_2O_3, the possible MgO-contents of the five groups are 5-10, 10-20, 10-

30, 30-40 and 40-50 %. Alumina-magnesia-carbon bricks are mainly installed in steel ladles due to their better services lives compared to other brick types. At temperatures of 1,600-1,750 °C these bricks have to resist turbulences of the steel bath during purging and heating-up by the electrodes and they even have to resist thermal shock during filling and emptying of the ladles. Also slight tendency to spall are advantageous properties of AMC-bricks in the ladle bottom compared to magnesia-carbon bricks. However, the slag zone of steel ladles is dominated by magnesia-carbon bricks, because of their better resistance to slags. [24, p. 107-111]

3.2.5   Fused cast bricks

To produce fused cast bricks, pure and fine grain raw materials - predominantly alumina, zircon silicate, zircon oxide, chromium oxide, chromite and special additives - are melt in an electric arc furnace and then poured into sand, graphite or metal molds. During slow cooling of the melt, the typical structure of fused cast products is formed that is a dense structure without open pores, but with intercrystalline bonds and intensive interlacing of the crystals. Products with this dense crystalline structure possess superb strength as well as corrosion and erosion resistance up to high temperatures. Fused cast bricks are used mostly in glass and steel industry. [24, p. 153-160]

3.3 System analysis

This Master Thesis is developed under consideration of DIN EN ISO 14040, PAS 2050 and The Greenhouse Gas Protocol – Product Life Cycle Accounting and Reporting Standard.

The five major principles relevance, completeness, consistency, accuracy and transparency are considered for accomplishing this carbon footprint calculation. A specification of these principles is indicated below.

- Relevance: The selected sources, data and methods should be appropriate to the studied product.

- Completeness: All greenhouse gas emissions in accordance with the system boundary should be included.

- Consistency: Meaningful comparisons in GHG-related information should be enabled.

- Accuracy: Uncertainty should be reduced as much as is practical.

- Transparency: Enough information should be disclosed in order that third parties are able to comprehend the proceeding. [28, p. 9]

According to PAS 2050 for calculating the carbon footprint of any goods or services five main steps have to be completed, which are listed as follows.

1. Constructing a process map in the form of a flow chart to identify all materials, activities and processes that contribute to the product's life cycle.

2. Defining system boundaries and prioritisation for disclosing the required inputs and outputs.

3. Collecting necessary data that allows the calculation of the footprint.

4. Determining the carbon footprint via activity data and emission factors.

5. Analysing certainty (optional) to measure precision and indicate robustness. [28, p. 9-34]

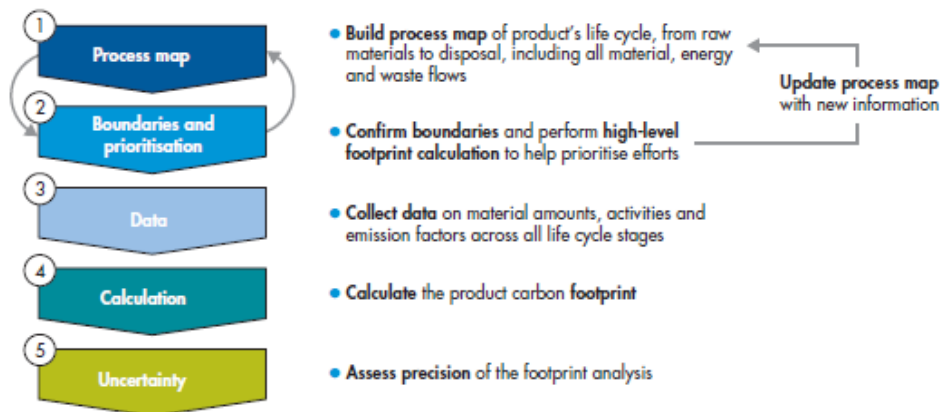Figure 6 overviews this line of action as an illustration again.

Figure 6: Steps for the calculation of the carbon footprint [28, p. 10]

However, before these steps can be carried out, a start-up and preparation phase is essential. Those include a description of the objectives, a definition of the scope, the function unit and the system being analysed.

3.3.1 Description of objectives

The goal definition is specified in chapter 1.2.

3.3.2 Scope definition

In DIN ISO 14040 is specified, which points a scope definition has to cover.

In this Master Thesis the studied products are principally dense shaped refractory products. This product category involves fired basic and non basic bricks as well as unfired basic and non basic bricks.

The target audience includes companies, which need to apply refractory products for accomplishing their production processes and especially companies that belong to the refractory industry, which want to assess their own carbon footprint.

The system boundary is selected based on the approach "cradle to gate" because, as described above, the target audience are others companies and therefore this type of analysis refers to a business-to-business (B2B) footprint.

B2B footprints capture raw materials through production up to that point where the studied product arrives at a new organisation. Distribution and transport to the customer's site are also included, while additional manufacturing steps, final product distribution, retail, consumer use, recycling and disposal are excluded. Instead the "cradle to grave" approach is applied to business-to-customer (B2C) footprints and includes the whole life cycle of the product through end of life disposal. [28, p. 11]

Figure 7 shows a comparison between the cradle to gate and the cradle to grave approach.
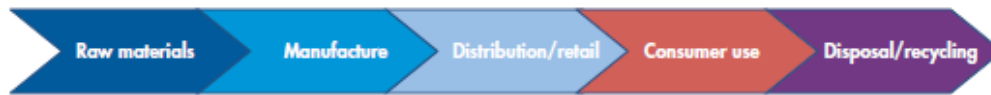
Process map steps for business-to-consumer goods

Process map steps for business-to-business goods

Figure 7: "cradle to gate" (below) and "cradle to grave" (above) [28, p. 11]

The functional unit describes the way in which the analysed product is commonly used by the customer [28, p. 7]. Here in this case, the functional unit is specified as metric tonne.

3.3.3 System description

Figure 8 represents the production processes of shaped and unshaped refractory products on basis of the coarse ceramic production. The first line shows the production of monolithics, also called unshaped refractories. The production process of unfired bricks is demonstrated in the second line, while the production process of fired bricks is illustrated in line three. For all three types of products, raw material extraction is followed by the stage of crushing. The difference between dense shaped and unshaped refractory products is that the production of unshaped refractories is already completed after the operation mixing. In addition, the production process of dense shaped refractories includes the step shaping and a certain kind of heat treatment. While heat treatment of fired bricks consists of drying and burning, tempering belongs to the heat treatment of unfired bricks. After heat treatment some bricks have to be treated by activities like drilling, sawing or grinding, what is called finishing. The last steps in the production process of refractory products are packaging and distribution.
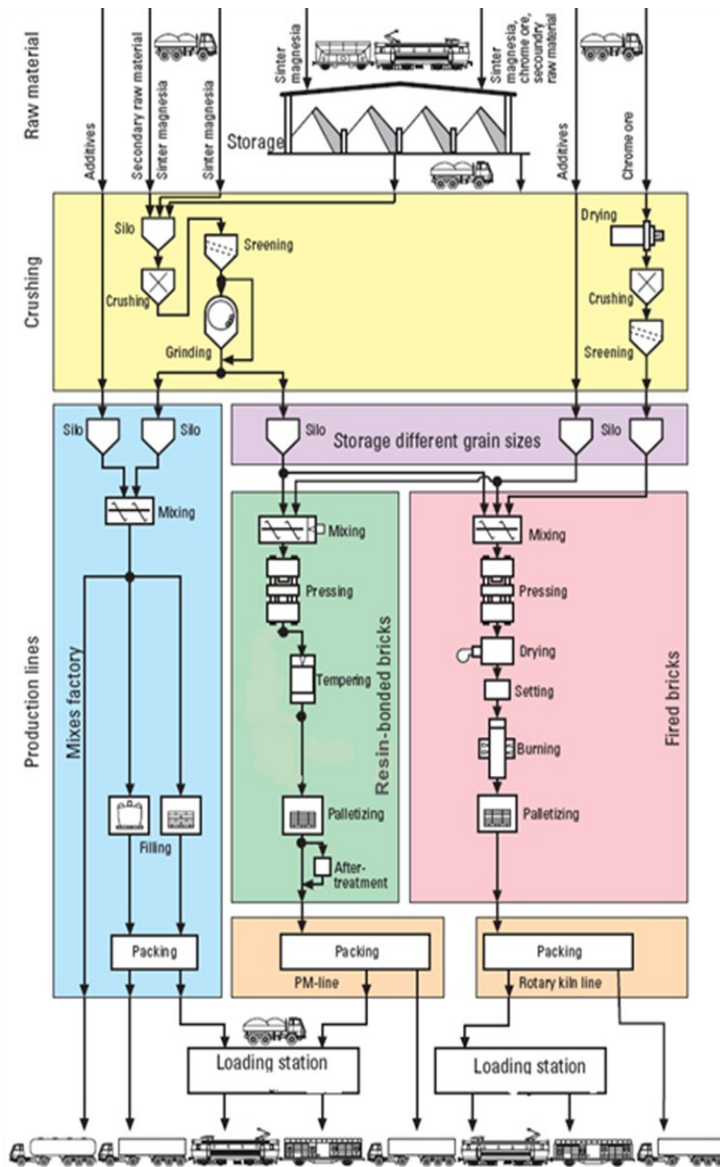
Figure 8: Process map [23]

Figure 9 sums up the main production steps again. The required raw materials are mined and produced by the footprinting company itself or another possibility is receiving them from suppliers. The ultimate raw material is prepared in order to produce the essential grain size. Preparation is followed by the steps mixing and shaping, before a necessary heat treatment is carried out. In some cases any kind of subsequent treatment takes place. After finishing, the products are packaged and dispatched to customers. A precise description of each process will be given in the individual chapters.
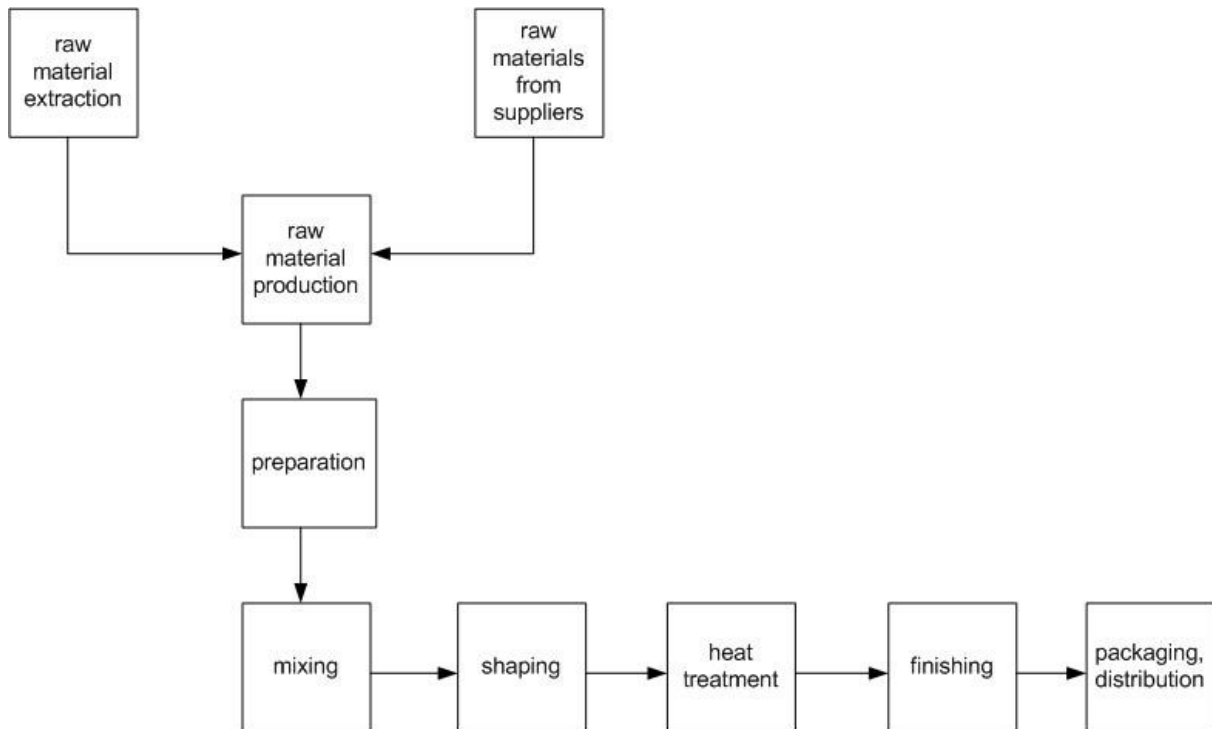
Figure 9: Major production steps

3.3.4 General assumptions

GHG

The GHG to be considered in carbon footprint calculations and their GWP are described in PAS 2050, Annex A. [10, p. 27]

The only relevant GHG for this Master Thesis is fossil CO_2.

Human inputs

This Master Thesis do not contain human inputs to processes, neither human activities in the production process (e.g. manual palletising), nor other emission sources caused by employees (e.g. business trips by plane). The reason is that the proportion of the emissions arising from human activities is negligible compared to the total carbon footprint of a refractory product.

Electricity

According to § 45 ElWOG, for electricity that derives from unknown origin the ENTSO-E-mix has to be applied, which is **413.64 g CO_2 per kWh** for the year 2010. [29]

ENTSO-E is short-term for European Network of Transmission System Operators for Electricity. This organisation represents all electric transmission operators in the EU and others connected to this network for all regions, technical and market issues. This

association was founded by the European Transmission System Operators for Electricity and intend to play an active role in the European rule setting process. [30]

"De minimis"-approach

According to EU legislation the "de minimis"-approach allows to use its own estimation method for the calculation of emissions from minor sources. [19, p. 9, 14]

Specific important assumptions that belong to individual steps of the production process for refractory products are indicated in the respective chapters.

3.3.5 Data

Data types and calculation method

Two types of data are essential for the calculation of the carbon footprint, activity data and emission factors. Activity data refers to the total quantity of material and energy that is involved in the life cycle of the product. Emission factors enable the transformation of activity data in GHG emissions. The emission factor is defined as the amount of GHG emitted per unit of activity data. Therefore, the CO_2 emissions for a certain action derive from multiplying its activity data by the appropriate emission factor. This means that the total carbon footprint is equivalent to the sum of individual carbon footprints arising from all actions that belong to the entire product life cycle. [28, p. 16-20].

The calculation formula is illustrated in Figure 10.
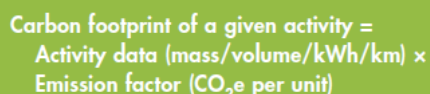
Figure 10: Calculation formula for carbon footprint [28, p. 20]

Data quality

Data quality has to meet specific requirements in order to conform to goal and scope of the life cycle analysis. Data quality includes the time-related coverage, geographical coverage and technology coverage. In this Master Thesis the time basis for data collection is year 2010, unless otherwise mentioned. The whole process of data collection lasted six months. The geographical coverage is global, because RHI is a global player. Thus, data is collected from all over the world via RHI technology center Leoben. Technology coverage means whether a specific technology or a technology mix has been applied concerning product-related technologies. In this Master Thesis the relevant technologies are considered as representative for the whole refractory industry. Furthermore, the available data is precise, complete, representative, consistent and reproducible. [31, p. 21]

According to the fact that RHI is a worldwide acting corporate group and in addition covers the entire product portfolio of refractories, it is ensured that the calculated data for this master or rather this carbon footprint calculation is considered as representative for refractory industry.

<u>Data sources</u>

Data derive from primary or secondary sources. Primary data originate from the footprinting organisation, like for example direct measurements made internally. Hence, primary activity data refer to all processes owned, operated or controlled by the footprinting company. Secondary data belong to external sources, like for instance general external measurements (not specific to the product), industry reports or literature. [28, p. 16-18]

Both types of data sources are utilised in this Master Thesis.

3.4 Raw Materials

This chapter overviews the most important raw materials of refractory industry concerning this Master Thesis. Their classification as well as production is described and their emission factors are indicated.

Most of the applied raw materials in refractory industry are naturally occurring minerals. But natural raw materials always contain slight amounts of undesirable contaminants. Thus, they have to be prepared in such a way that the proportion of impurities is as low as possible. However, synthetically produced raw materials are used more and more frequently due to increased requirements concerning purity and properties of raw materials. Synthetic raw materials are made by special manufacturers that deliver these materials in a defined grain size or crushed to a specific fine size. The utilisation of recycled materials or rather secondary raw materials, like for example refractory material broken out of furnaces or kilns, is common for premium grade refractories. But the recycling of these materials is in the majority of cases very difficult due to various contaminations. For this reason secondary raw materials are often too expensive compared to primary raw materials. [24, p. 35]

Utilised refractory products removed whilst relining a kiln can be contaminated by slags, salts, glass or metal that could influence the refractory properties of any substance to which they were added. This means that not every material is suitable for recycling due to its contaminants. [32, p. 32]

3.4.1 Classification of raw materials

As a matter of fact, a high number of different raw materials is needed in refractory industry, because of the widespread applications of refractory products. For this reason, a suitable approach has to be found to identify the most important as well as most relevant raw materials concerning this Master Thesis and in addition, an appropriate method for classifying them. The types of raw materials that are of highest importance are specified according to the total raw materials list of RHI via consumed quantity.

Concerning the classification of the specified raw materials there exist three possibilities:

1. According to the manufactured products: As already mentioned in chapter 3.2.4, the relevant product categorisation is accomplished by specific product group codes of RHI. The raw materials can be allocated to these products groups. The problem of this method is that several raw materials are needed for the production of more than one product group and therefore an explicit allocation is not possible.

2. According to the base material pyramid: The pyramid (see Figure 11) consists of the six base materials for refractory products; CaO, MgO, Cr_2O_3, Al_2O_3, SiO_2, ZrO_2. The raw materials can be allocated to these base materials. This method was not chosen, because the allocation depends on the exact composition (in weight %) of the raw materials, which is not always easy.
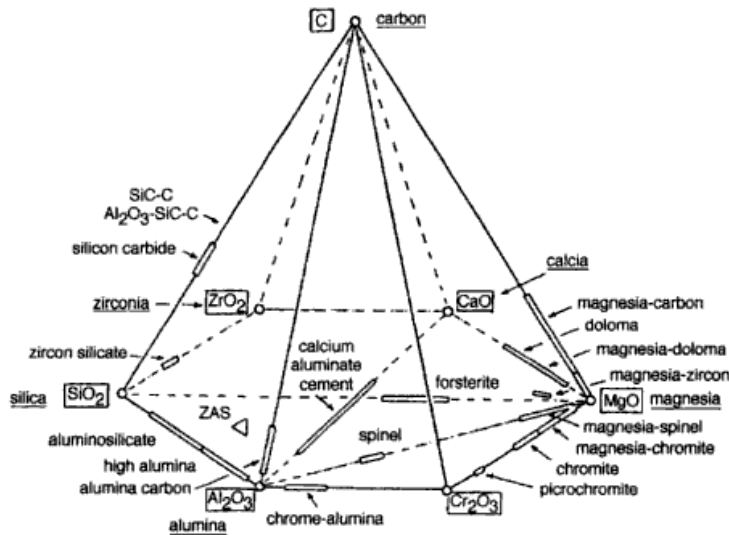
Figure 11: Base material pyramid [24, p. 3]

3. <u>According to the chemical reaction behaviour</u>: The chemical reaction behaviour characterises a refractory oxide. Raw materials can be divided in basic and non basic substances. Basic raw materials form bases when they get in contact with water, while non basic materials form acids. [23]
   This means:
   a. oxide + H_2O → base,
   b. oxide + H_2O → acid,
   c. neutral materials react neither acidic nor basic. [24, p. 6]

Table 5 overviews the specified raw materials and their classification.

Table 5: Classification of raw materials

non basic raw materials	
andalusite	kyanite
bauxite	microsilica
brown fused alumina	quartz sand
calcined alumina	quartzite
calcium aluminate	tabular alumina
fireclay (Mulcoa)	white fused alumina
fused mullite	zirconia alumina
fused quartz glass	zirconia mullite
fused silica	
basic raw materials	
calcined dolomite	fused magnesia
caustic calcined magnesia	fused magnesia chromite
chrome ore	hercynite
chromium oxide	lime
dead burned dolomite	magnesia spinel

basic raw materials	
dead burned magnesia	zircon
dolomite	zirconia
fused dolomite	
other raw materials	
carbon black	perlite
feldspar	silicon carbide
graphite	vermiculite
secondary raw materials	
fused quartz glass	mill scale
fused silica	porcelain
high alumina 55 (HA 55)	recycled MgO-C bricks
high alumina 75 (HA 75)	recycled AMC bricks
microsilica	

3.4.2 Secondary raw materials

Recycling of spent refractories is state of the art in Europe. Nowadays nearly 100 % of non-infiltrated scrap based on MgO, SiO_2, Al_2O_3, ZrO_2 and SiC is reused as secondary raw material. Selective breakout and separation of reusable materials from the infiltrated parts allows those recycling rates. The latest development is a heat treatment of the infiltrated parts that purifies the material. This step creates secondary raw material out of waste, which could not be used again. [23]

Assumption for secondary raw materials:

Secondary raw materials have already passed a production process and so the CO_2 emissions have already been counted. Therefore, they are not included in this Master Thesis. Consequently, for the calculation of the carbon footprint of secondary raw materials only preparation and transportation will be important.

Below, the most important types of recycled materials applied in refractory industry are described briefly, except of fused silica, fused quartz glass and microsilica. The description of these materials can be found in the primary material's section.

3.4.2.1 Mill scale

Principally mill scale compose of magnetite, which is chemically Fe_3O_4. Mill scale is a by-product of all hot-rolled steel products, unless processed in a protective atmosphere or descaled. The inner part of magnetite contains fine grain metal. At hot-rolling temperatures a

layer of wüstite (FeO) exists between the metal and magnetite. During the slow cooling of hot-rolled coils, FeO transforms into Fe and Fe_3O_4. [33]

3.4.2.2 High alumina (HA) 55/75

The term high alumina describes already used refractory material broken out of, for example, furnaces or kilns. The number given stands for the Al_2O_3 content. 55 means that the material contains 55 % Al_2O_3, whereas 75 means that the material is composed of 75 % Al_2O_3. In order to reuse it, the material is crushed and sorted. Then, it can be integrated in the production process again. [23]

3.4.2.3 Porcelain

Porcelain acts as a useful secondary raw material. The recycled types are sanitary porcelain and isolator porcelain. The delivered goods are crushed, then useless material is sorted out. Afterwards, it can be utilised again. [23]

3.4.2.4 Recycled MgO-C and AMC bricks

Selective breakout that is crushed and reused again. [23]

3.4.3 Binding materials and additives

The function of a binder is to stabilise the loose grain batch and to ensure sufficient strength of the batch during all steps of the production process. Additives are applied, on the one hand to improve workability and shaping, on the other hand to modify the structure of the products in order to achieve special properties. [24, p. 45]

Assumption for binders and additives:

The main proportion of the used binding materials and additives derive from organic substances (e.g. lignosulphonate), which means that the generated CO_2 emissions are of biogenic origin. As already mentioned in chapter 2.2, biogenic CO_2 emissions are not part of a carbon footprint calculation.

Moreover, only very slight quantities of binding materials and additives are added to the raw materials. For this reason, they can be considered as negligible in this Master Thesis, because the influence on the total carbon footprint would be insignificant. Regarding additives microsilica forms the exception, because of its high presence in all kind of products.

Concerning binding materials, resin and pitch are those substances that are of highest importance for the production of unfired bricks.

3.4.3.1 Phenolic resin

Phenolic resin, which is actually phenol formaldehyde resin, is the most common binder used in carbon containing refractories. Subsequently, the advantages of this binder are listed:

- easy to disperse,

- adhesive,

- high content of fixed carbon that contributes to a strong carbon bonding,

- less harmful to environment compared to coal tar pitch.

Two types of phenolic resin exist, a resol type that is thermosetting and a novolac type that is thermoplastic. The novolac type is used together with a hardening agent and is superior in terms of mixture conservation. The resol type is superior in terms of lamination resistance. The selection of the appropriate type depends on which of them has the suitable properties for the involved production facilities and processes. [26, p. 173, 306, 307]

According to GEMIS (see 3.5.2) version 4.6 the CO_2 equivalent of phenol is 2,679.37 kg CO_2/t and that of formaldehyde is 708.41 kg CO_2/t [44]. The ratio between phenol and formaldehyde in phenolic resin is approximately 1.5:1 [23]. Consequently, a value of **1,890.99 kg CO_2/t** phenolic resin results for the calculation of the specific CO_2 emissions.

3.4.3.2 Pitch

Pitch, also a typical binder for MgO-C bricks, is used in form of petroleum pitch. Chemically, pitch is a mixture of $C_{15}H_{16}$, $C_{10}H_{10}$ and $C_{18}H_{12}$, formed as distillation residue of petroleum or coal tar. [26, p. 306-307]

Assumption for pitch:

As a matter of fact, pitch is a residue of other production processes. This means that the quantity of CO_2 arising from its production has already been counted by the producing companies. For this reason those emissions are not included in this Master Thesis.

More information about this two binding materials has already been given in chapter 3.2.4.2.

3.4.4 Natural raw materials

Usually, natural raw materials have to be extracted. Mining techniques are classified into opencast mining and deep mining. In general opencast mining is preferred globally seen, because of the higher degree of mechanisation and a better performance of machinery. [34, p. 56]

Opencast mining is accomplished on the Earth's surface, while deep mining takes place underground. The term opencast mining refers to the extraction of raw materials carried out in an open cavity. The burden material of the mineral deposit is reused as mine filling material or surface cover material. Thus, this mining technique represents a temporarily time-limited usage of landscape and also a temporarily time-limited influence on environment. In order to classify opencast mining, a differentiation between loose and hard rocks is possible. Loose rocks require only one sequence of operation (loosening and loading), while hard rocks need two (loosening via blasting and then loading). Hence, continuous equipment (e.g. bucket-weel excavator) is used for extracting loose rocks and discontinuous equipment (e.g. hydraulic excavator) for hard rocks. Opencast mining is favoured, if the estimated costs are lower than that of deep mining. Opencast mining is applied, if raw materials are located near the surface and not deep within the earth [35]. [34, p. 56-59]

The relevant deep mining methods for this Master Thesis are described in the appropriate sections.

3.4.4.1 CO_2 calculation approach concerning raw material extraction

According to PAS 2050 mining or rather extracting raw materials is an essential element of a carbon footprint calculation in agreement with the "cradle to gate" approach. Furthermore, the emissions arising from any machinery used have to be included even if the impact on the total CO_2 emissions is not really crucial. [10, p. 14]

The amount of CO_2 from mining depends on the applied mining technique, because the chosen system affects the used facilities and therefore influences the energy demand. Concerning CO_2 relevance continuous equipment is nearly always electrically powered, while discontinuous equipment is diesel fuelled. [36, p. 1-3]

In order to quantify the environmental influence of mining, actual data from RHI is used. The emission factor for raw material extraction is identified on basis of data from the Austrian mining sites Breitenau, Hochfilzen and Radenthein where magnesite is extracted. For this reason, the idea is to form an average value out of the specific CO_2 emissions from the three locations. Extracting of magnesite in Hochfilzen is realised as opencast site. In Radenthein deep mining is implemented and in Breitenau both exist, opencast and deep mining. This means that the calculated average value is a combination of different mining techniques.

Breitenau:

Annually 350,000 tonnes of raw magnesite are extracted at deposit Breitenau where 150,000 tonnes of dead burned magnesia are produced out of it. In Breitenau deep mining is implemented as backfilling method. [23]

In underground mine sites backfill can be used as construction material and major ground support tool. The material that is utilised as backfill derives from the opencast mine where magnesite and backfill are extracted. [37, p. 601]

Breitenau's opencast mine is accomplished in form of sublevels with heights of 12 metres at a sea level of about 800 metres. The extraction is achieved by drilling and blasting. [23]

The underground mine starts at a sea level of 760 metres and ends at 260 metres. Bore holes are drilled via drilling jumbo and afterwards blasting follows. At one operation sequence an amount of 560 tonnes magnesite is received. [23]

Hochfilzen:

In Hochfilzen the opencast composes of sublevels with heights of 15 metres. The extraction is achieved via drilling and blasting. 180,000 tonnes of raw material are mined per year and processed to dead burned magnesia. Annually 100,000 m^3 burden material is excavated and then recultivated on-site. About 2,000 tonnes of raw material are treated each day. [23]

Radenthein:

Every year 85,000 tonnes of raw magnesite are extracted and then transported to Radenthein via cable car. For deep mining diesel-fuelled machinery is used. In Radenthein the applied deep mining technique is stope mining. [23]

A stope is an underground cavity from which the raw material is extracted. Caving of the opening is prevented by the support of mined material that is left in the stope in form of pillars and stope walls. In addition a secondary reinforcement, for instance shotcrete, is required to stabilise the rock surface adjacent to the opening. [38, p. 159]

Calculation of the emission factor for raw material extraction

The calculation of the emission factor for raw material extraction considers the specific electricity and diesel consumption of mining machines and transport vehicles based on diesel engines as well as conveyor equipment.

Assumption for mining:

CO_2 emissions due to the process of blasting and from blasting means are not taken into account, because their quantity is negligible compared to the total carbon footprint.

The following steps are accomplished in order to determine the quantity of CO_2 arising from mining raw materials.

1. Checking the annual production output [t] of the extracted raw material.

2. Identifying the annual diesel [l] and electricity [kWh] consumption for the operational area mining.

3. Multiplying the diesel consumption by a factor of 2.645 kg CO_2 per litre diesel [39, p. 12] and then dividing the result by the annual production output to obtain the specific diesel CO_2 emissions.

4. Multiplying the consumed electricity by the electricity emission factor mentioned in chapter 3.3.4 and then dividing the result by the annual production output for receiving the specific electricity CO_2 emissions.

5. Summing up the specific diesel and electricity emissions.

6. Forming the average value out of the total specific CO_2 emissions from the three mining sites.

The consumption of diesel and electricity per tonne raw magnesite and the calculated emission factors for the three Austrian mining sites are listed in Table 6. The average value of the specific CO_2 emissions for raw material extraction represents **6.70 kg CO_2/t**.

Table 6: Emission factor for mining

mining site	specific CO_2 emissions [kg CO_2/t]
Breitenau	7.68
Hochfilzen	5.04
Radenthein	7.38
average value	**6.70**

3.4.4.2 Magnesite

Magnesite, identified as magnesium carbonate ($MgCO_3$), is one of the most important magnesium minerals. This mineral forms the largest source of magnesia (MgO). When magnesite is heated, it dissociates into magnesia (47.6 %) and carbon dioxide (52.4 %). The commercially important magnesium-bearing minerals are shown in Figure 12. [40, p. 615-618]

Common Name	Chemical Composition
Brucite	$Mg(OH)_2$
Carnallite	$KMgCl_3 \bullet 6H_2O$
Dolomite	$CaMg(CO_3)_2$
Epsomite	$MgSO_4 \bullet 7H_2O$
Kainite	$MgSO_4 \bullet KCl \bullet 3H_2O$
Kieserite	$MgSO_4 \bullet H_2O$
Magnesite	$MgCO_3$
Olivine	$(MgFe)_2SiO_2$
Schoenite	$MgSO_4 \bullet K_2SO_4 \bullet 6H_2O$
Serpentine	$Mg_3(OH)_4Si_2O_5$

Figure 12: Commercially important magnesium-bearing minerals [40, p. 615]

In European deposits magnesite often occurs together with dolomite in greywacke. According to the content of Fe_2O_3 in the mineral, it is differentiated between two types of magnesite. Deposits of crystalline magnesite with at most 8 % Fe_2O_3 are found in Austria, Slowakia, Spain, Russia, China, Brazil and the United States. Microcrystalline magnesite with a Fe_2O_3 content of at least 0.5 % occurs for example in Greece, Turkey and India. [41, p. 28]

3.4.4.3 Dolomite

Dolomite is a sedimentary rock that consists of the mineral dolomite $CaMg(CO_3)_2$. Furthermore, dolomite is a useful source for producing magnesite by reaction of calcined dolomite with seawater. In refractory industry dolomite bricks are kept in back up lining, because of the lower thermal conductivity compared to magnesite. For industrial applications the mass fraction of impurities must be below 7 weight %. Apart from dolomite, dolomite rocks also contain other carbonates (e.g. siderite, magnesite and calcite) together with silica and alumina mostly in form of clays. Huge geological formations of dolomite are situated in the northeastern Italian Alps. [42, p. 610-612]

3.4.4.4 Quartz, quartzite and quartz sand

In nature quartz occurs as a major mineral in igneous (e.g. granite), sedimentary (e.g. sandstone) and metaphoric rocks (e.g. quartzite and gneiss). In case of refractories, raw quartz is essentially mined as quartz sand, which is a round silica sand, from glacial deposits, beach sands, crushed sandstones or high quality quartzite. Quartzite can be of sedimentary origin, where quartz grains are cemented by secondary silica or of metamorphic origin from sandstones. [42, p. 595]

Quartzite is a hard and brittle sediment or metamorphic rock that consists principally of quartz. It is applied for the production of non basic refractory products, because of its high melting point of over 1,700 °C and its high SiO_2 content (96 %). [43, p. 349]

A CO_2 equivalent of **29 kg CO$_2$/t** quartz sand is found on GEMIS 4.6 database. For more information about GEMIS see chapter 3.5. [44]

3.4.4.5 Bauxite

Bauxite is the major source of alumina and is a sedimentary rock with a high alumina content. Table 7 describes the chemical composition and mineralogy of bauxite. The oldest deposits were found in France, Greece and Asia. With 35 % Australia is the largest supplier of bauxite worldwide followed by South America with 25 % and Africa with 15 %. [42, p. 600-601]

Table 7: Chemical composition and mineralogy of bauxite [42, p. 601]

Oxide	Chemical composition (wt.%)	Mineralogy
Alumina (Al_2O_3)	35 to 65	Gibbsite, boehmite and diaspore
Silica (SiO_2)	0.5 to 10	Quartz, chalcedony, kaolinite
Ferric oxide (Fe_2O_3)	2 to 30	Goethite, hematite and siderite
Titania (TiO_2)	0.5 to 8	Rutile and anatase
Calcia (CaO)	0 to 5.5	Calcite, magnesite and dolomite

Data for the extraction and preparation of 1 tonne bauxite, ready for delivery to alumina plant, is given in Table 8. Data derive from a literature research. The consumption of diesel and heavy oil is transferred into the equivalent amount of CO_2 by multiplying the consumed quantity firstly by the heating value and secondly by the appropriate emission factor defined by regulation (see BGBl. 339/207). Electricity is multiplied by the emission factor for electricity, mentioned in chapter 3.3.4. The result for the emission factor of bauxite is **4.89 kg CO_2/t**.

Table 8: Extraction and preparation of 1 tonne bauxite [46, p. 23]

energy input	consumed quantity	heating value [GJ/t] [45, p. 34]	emission factor [t CO_2/TJ] [45, p. 34]	specific CO_2 emissions [kg CO_2/t bauxite]
diesel oil	1.1 kg	42.8	73.7	3.47
heavy oil	0.2 kg	40.3	78	0.63
electricity	1.9 kWh			0.79
total				**4.89**

The common form of bauxite used in refractory industry is calcined bauxite. Therefore, raw bauxite is fired in a rotary or vertical kiln. Approximately 2 tonnes of crude ore are needed to produce 1 tonne calcined bauxite. Guyana and China are the largest producers of calcined bauxite. [40, p. 241]

As a matter of fact, no data could be found concerning the consumption of natural gas for the calcination process. Therefore, a natural gas amount of 70 m^3/t is estimated according to the "de minimis"-approach (see chapter 3.3.4) [23]. 70 m^3 natural gas is equivalent to 139.61 kg CO_2 by applying a conversion factor of 1.9944, which is calculated based on the heating

value and emission factor of natural gas in Table 13. Hence, the total emission factor of calcined bauxite is **144.50 kg CO$_2$/t**.

3.4.4.6 Kyanite, andalusite and sillimanite

Kyanite, andalusite and sillimanite are naturally occurring anhydrous aluminium silicate minerals with the same chemical formula Al$_2$O$_3$*SiO$_2$, but differing crystal structures. Because of these variances in crystal structure, each of these three minerals possess unique physical properties. The largest producer of kyanite is located in the United States. Small amounts of kyanite are also produced in Australia, Brazil, China, Ukraine and India. The worldwide production of andalusite is dominated by the South African Mineral Resource Committee (SAMREC), Denain-Anzin Mineraux Refractarie Ceramique (DAMREC), the South African and French divisions of the industrial minerals conglomerate and IMERYS. Sillimanite is not as much used as andalusite and kyanite and is produced in countries like Australia, Brazil, India, Spain and the Republic of South Africa. [40, p. 553]

For the calculation of the emission factor for andalusite data could be obtained from DAMREC. The figures of 2008 and 2009 give an average value of **143 kg CO$_2$/t andalusite**. [47]

3.4.4.7 Zircon

Zirconium silicate (ZrSiO$_4$ or rather ZrO$_2$*SiO$_2$), named zircon, is a natural raw material found in granites and the weathering products of mother igneous rocks such as beach sands. Its high melting point and chemical inertness are the reasons for its importance in refractory industry. [42, p. 618]

Deposits of natural zircon are known in Australia, South Africa, Madagascar, USA, Brazil, India, China, Sri Lanka and the former Soviet Union. Its theoretical composition is 67.2 % ZrO$_2$ and 32.8 % SiO$_2$. At 1,676 °C decomposition of zircon into those both substances starts. Decomposition temperature can decline to 1,500-1,550 °C, if impurities or admixtures are contained in the zircon. [24, p. 85-88]

3.4.4.8 Chromite or chrome ore

Chromium is found in a wide variety of oxide and silicate minerals in the Earth's crust. Chromite, with its chemical formula FeO*Cr$_2$O$_3$, is a mineral that belongs to the spinel group. Another type of chromite, also part of the spinel group, is magnesiachromite (MgO*Cr$_2$O$_3$). Economic deposits contain concentrations of at least 25 % chromite mineral. The world's largest chromite resources are located in the Bushveld Igneous Complex Complex of South Africa, the Great Dyke of Zimbabwe and in the Kempersai area of Kazakhstan. [40, p. 309-311]

Chromite minerals and silicate impurities are the main components of chrome ore. The necessary ores for refractory industry (SiO_2 content as low as possible) are situated in South Africa where approximately 75 % of the known world deposits are located. [24, p. 194]

3.4.4.9 Feldspars

Feldspars are aluminium silicate minerals that consist of varying proportions of calcium, potassium and sodium. They make up the most abundant mineral group in the Earth´s crust. Feldspars are principal components in rock classification schemes. The production of feldspar is operated in more than 50 countries. European producers are Italy, Turkey, France, Germany, Spain, Czech Republic and Egypt. Significant amounts also come from China and countries in Southeast Asia. [40, p. 451, 452]

3.4.4.10   Perlite

Perlite is a natural hydrated volcanic glass formed over a few million years or by chemical weathering of obsidian at or near the Earth's surface. However, perlite is not an igneous primary rock. The formation of perlite is a very complex process where a long chain of essential events are necessary. Many deposits of perlite exist worldwide. Nevertheless, these deposits are only available, if market conditions allow or the problem is that they have not been developed yet. The largest perlite mines are located in Europe, North America and China. [40, p. 685-687]

3.4.4.11   Vermiculite

Vermiculite is a natural mineral with a similar structure to talc that belongs to the group of mica. It is formed by alteration of biotite and phlogopite. [43, p. 339]

This magnesium aluminosilicate composes of 45 % SiO_2, 31 % MgO, 13 % Al_2O_3 and 7 % Fe_2O_3. Consequently, the SiO_2-Al_2O_3 ratio is about 3:1. [24, p. 41]

3.4.4.12   Graphite

Besides diamond, graphite is one of the forms of the chemical element carbon. Graphite is usually found in metaphoric rocks often in association with feldspars, quartz etc.. Major producers of graphite are South Korea and Austria. Graphite is mostly obtained by underground mining. It has excellent heat properties due to high thermal conductivity. Moreover it is almost completely inert to all. [42, p. 623-625]

3.4.4.13   Emission factors of quartzite, dolomite, kyanite, zircon, chrome ore, feldspar, perlite, vermiculite and graphite

As a matter of fact, quartzite, dolomite, kyanite, zircon, chrome ore, feldspar, perlite, vermiculite and graphite are natural raw materials. This means that for the calculation of their emission factor only mining is relevant, because no other operations are applied for the

production of these materials. Therefore, their emission factor is **6.70 kg CO_2/t** according to Table 6.

3.4.5 Synthetic raw materials

The next section overviews the most important synthetically produced raw materials for this Master Thesis.

3.4.5.1 Magnesia

Magnesia, chemically pure MgO, serves as the main raw material in refractory industry. The reason is its high melting point of 2,850 °C. Sources for the production of magnesia are magnesite, seawater and brines. Three important modifications of magnesia exist for industrial purposes that will be described in the next paragraphs. [41, p. 30-33]; [26, p. 159]; [23]

Caustic calcined magnesia (CCM)

In principle, CCM is dissociated $MgCO_3$ or calcined magnesium hydroxide $Mg(OH)_2$. Its natural crystal structure does not change during the thermal treatment. [41, p. 31]

Usually, CCM is formed by calcination of magnesite in a rotary kiln at 800-1,000 °C. [40, p. 615].

For CCM results an emission factor of **1,093 kg CO_2/t**, derived from the average CO_2 emissions of all European magnesia producers (Ø EU–27). [41, p. 61-62]

Dead burned magnesia (DBM)

The two major sources for the production of dead burned magnesia are

- magnesite ($MgCO_3$) and
- magnesium chloride ($MgCl_2$) out of seawater, salt brines, salt deposits and industrial waste lyes.

In Figure 13 the different raw materials for DBM are indicated and the respective production processes are described. One way is out of magnesite by sintering CCM. $MgCl_2$ out of seawater, salt brines, salt deposits or industrial waste lyes is converted into magnesium hydroxide ($Mg(OH)_2$). Then, DBM is made by firing $Mg(OH)_2$. [24, p. 169-173]

raw mate-rial source	preparation, conversion	firing		production locations
		calcining	dense sintering	
magnesite	preparation [1] (after underground mining)	$MgCO_3 \xrightarrow{>1,700°C} MgO + CO_2$ in shaft or rotary kilns[2]	firing of causter briquettes[3] at 1,500 - 1,900° C[4] in shaft or rotary kilns	Austria, Slovakia, Russia, China, North Korea, Brazil, Turkey, Australia
		$MgCO_3 \xrightarrow{900°C} MgO + CO_2$ in multi-compartment kilns		
seawater	precipitation of $Mg(OH)_2$: out of $MgCl_2$:			Ireland, Japan, USA, Mexico
salt brines	$MgCl_2 + Ca(OH)_2$	$Mg(OH)_2 \xrightarrow{900°C} MgO + H_2O$ in multi-compartment kilns		
salt deposits	$\xrightarrow{RT} Mg(OH)_2 + CaCl_2$			Netherlands
waste lyes of potash salt production[5]	thermal conversion of $MgCl_2$: $MgCl_2 + H_2O$ $\xrightarrow{600°C} MgO + 2HCl$ and $MgO + H_2O \xrightarrow{RT} Mg(OH)_2$			Israel

[1] heavy liquid separation, floatation or magnetic preparation (latter also possible for sinter)
[2] direct dense firing only if there is best suited magnesite structure
[3] Very porous, active magnesia from out of the calcining or causticizing process is designated as causter
[4] Up to 2,200 °C in the production of LC sinter (chapter 4.2.2)
[5] Magnesite can, for example, also be used as raw material for spray calcining reaction

Figure 13: Production processes for DBM [24, p. 173]

DBM has a cubic crystal lattice with a density of more than 3.10 g/cm^3 and the highest melting point of all common refractory oxides. Because of these characteristics DBM is used for high temperature processes in steel industry. [41, p. 31]

The emission factor for DBM of **1,927 kg CO$_2$/t** is derived from an operation representing a synthetic DBM production in an OECD country. [41, p. 61]

Fused magnesia (FM)

Fused magnesia results from melting CCM in an electric arc furnace at approximately 3,000 °C to a molten state with a MgO content of 96-98 %. The resulting product has a density of 3.5 g/cm^3 and exhibits a high chemical stability, strength as well as resistance to abrasion. [40, p. 616]

95 % of the world's fused magnesia comes from China. [41, p. 32]

An emission factor of **2,602 kg CO$_2$/t** is calculated for fused magnesia. The composition of this value is shown in Table 9. Data concerning specific melting energy and specific electrode consumption derive from expert knowledge of RHI production sites. The emission factor 3.60 t CO$_2$/t electrode, according to 2004/156/EC (appendix VI, table 1) [63, p. 57], is applied for the determination of the CO$_2$ emissions arising from electrode consumption. Furthermore, the specific melting energy is multiplied by the emission factor for electricity, described in chapter 3.3.4, to receive the specific CO$_2$ emissions of the consumed energy.

Table 9: Emission factor for FM

emission factor CCM	specific melting energy		specific electrode consumption		total
[kg CO$_2$/t]	[kWh/t]	[kg CO$_2$/t]	[kg electrode/t]	[kg CO$_2$/t]	[kg CO$_2$/t FM]
1,093	3,300	1,365	40	144	**2,602**

3.4.5.2 Lime and synthetic raw materials out of dolomite

Lime, the common name for calcium oxide (CaO), is produced by decarbonating limestone ($CaCO_3$), which is a sedimentary carbonated rock. Calcination, according to the following chemical reaction, is carried out in a shaft furnace or a rotary kiln at 1,010-1,345 °C.

$$CaCO_3 \rightarrow CaO + CO_2$$
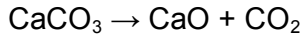
About 90 % of lime are used for chemical and industrial purposes. Major producers of lime are amongst others the United States, Canada and Mexico. [42, p. 610]

The mined mineral dolomite cannot be used directly as a refractory raw material. For this reason it must be converted into MgO*CaO by applying high temperature firing. [24, p. 165]

Calcined dolomite, also named dolime, results from the dissociation of dolomite (see chemical reaction below) into calcium oxide, magnesium oxide and CO_2 upon heating above 900 °C in a rotary.

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$$

However, the emerging dolime is too porous and reactive for most refractory applications. Therefore, calcination is carried out at higher temperatures (1,700 °C). Then, the product obtained is called dead burned dolomite. Dead burned dolomite is generally made by firing natural dolomite at high temperatures with or without additives in a rotary kiln. Dead burned dolomite can withstand temperatures up to 2,300 °C and is mainly applied in mixes. [42, p. 610-612]

The product benchmarks of lime, calcined dolomite and dead burned dolomite serve as basis for their emission factor. They are found in Annex I of 2011/278/EU "determining transitional Union-wide rules for harmonised free allocation of emission allowances pursuant to Article 10a of Directive 2003/87/EC". Table 10 summarises the mentioned emission factors.

Table 10: Emission factors for lime, calcined dolomite, dead burned dolomite [48, p. 20-21]

raw material	emission factor [kg CO_2/t]
lime	954
calcined dolomite	1,072
dead burned dolomite	1,449

Fused dolomite, consisting of 65 % raw dolomite and 35 % calcined dolomite, is a further important type of dolomite for refractory industry. In order to produce fused dolomite, the ingredients are smelt in an electric arc furnace. [23]

Data concerning specific melting energy and specific electrode consumption derive from expert knowledge of RHI production sites. The specific CO_2 emissions out of energy demand and electrode consumption are calculated in the same way like for fused magnesia. The results are shown in Table 11.

Table 11: Emission factor for fused dolomite

emission factor dolomite * 65 %	emission factor calcined dolomite * 35 %	specific melting energy		specific electrode consumption		total
[kg CO$_2$/t]	[kg CO$_2$/t]	[kWh/t]	[kg CO$_2$/t]	[kg electrode/t]	[kg CO$_2$/t]	[kg CO$_2$/t fused dolomite]
4.36	375.20	2,650	1,096	20	72	**1,547.56**

3.4.5.3 Fused silica and fused quartz glass

Fused silica is glassy solidified SiO_2. Generally, this non basic raw material results from fusing quartz sand in an electric arc furnace. The characteristic of fused silica products is their extremely low thermal expansion of 0.06 % at 1,000 °C that permits fast heating and cooling without crack formation. However, above 1,150 °C the crystallisation of cristobalite begins and this special property is lost. [24, p. 59-60]

Fused quartz glass results also from smelting quartz sand, but the only difference is that a drum-type melting furnace is used. Fused silica and fused quartz glass also appear as secondary raw materials. [23]

As a matter of fact, no data could be found concerning the production process of fused silica. Therefore, a specific melting energy of 1,500 kWh/t and a specific electrode consumption of 10 kg/t are estimated according to the "de minimis"-approach (see chapter 3.3.4) [23].

Table 12 represents the result for the emission factor of fused silica.

Table 12: Emission factor for fused silica

emission factor quartz sand	specific melting energy		specific electrode consumption		total
[kg CO$_2$/t]	[kWh/t]	[kg CO$_2$/t]	[kg electrode/t]	[kg CO$_2$/t]	[kg CO$_2$/t fused silica]
29	1,500	620,46	10	36	**685.46**

3.4.5.4 Microsilica

Microsilica, also called silica-fume, is a submicronic amorphous silica. It contains 90-98 % SiO_2 and has a low bulk density of 0.2-0.45 g/cm^3. Microsilica occurs as a by-product in the off-gases during the electrothermal production of ferrosilicon. In refractory industry microsilica is used as an additive, because it is able to form strong bonds due to its high surface area. For this reason, it enhances mechanical strength, workability, cohesiveness and flowing properties. Its worldwide produced amount is approximately 300,000 tonnes per year. The main producers are obviously ferrosilicon manufacturers in Canada and Norway. [42, p. 596]

As a matter of fact, microsilica is a by-product of the silicon and ferrosilicon production [90]. This means that the quantity of CO_2 arising from its production has already been counted by the producing company. Consequently, those emissions are not included in this Master Thesis.

3.4.5.5 Synthetic raw materials out of bauxite

Bauxite is treated in a further process, called Bayer Process. The products out of the Bayer Process, summarised in Figure 14, serve as basis for the production of the raw materials calcined alumina, tabular alumina and white fused alumina.
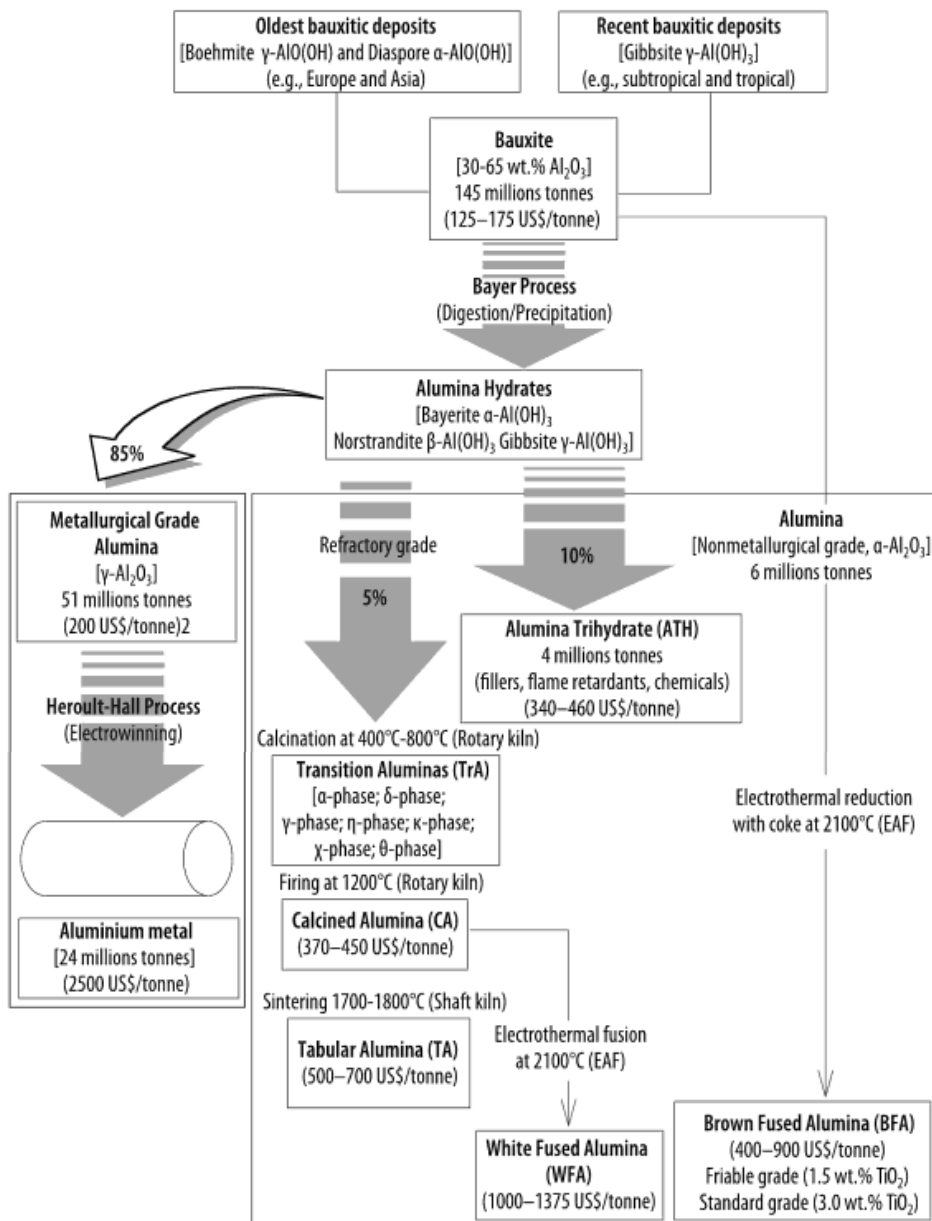
Figure 14: Bayer Process [42, p. 604]

Calcined Alumina

Calcined alumina is the final product resulting from the thermal decomposition of aluminium hydroxide. The applied aluminium hydroxide is formed in the Bayer Process. The calcination of aluminium hydroxide can be performed in rotary kilns, fluidized-bed kilns or tunnel kilns at a temperature of 1,250 °C. [42, p. 606-607]

Calcined alumina has a calculated emission factor of **716.59 kg CO_2/t**. The approach for the calculation of calcined alumina's emission factor is found due to a literature research.

Data for the production of 1 tonne calcined alumina is shown in Table 13. 2.739 tonnes of bauxite are required for producing 1 tonne of calcined alumina. [46, p. 23]

The specific emissions arising from the consumed amount of diesel, heavy oil and electricity are calculated with the same factors like for bauxite. Here, also coal is needed. The heating value and emission factor of coal and natural gas are also defined by regulation (see BGBl. 339/207). Concerning natural gas the consumed quantity in kg has to be converted first into m^3 via its density, then its heating value and emission factor could be applied.

Table 13: Emission factor calcined alumina [46, p. 23]

input	consumed quantity	heating value [GJ/t] [45, p. 34]	emission factor [t CO_2/TJ] [45, p. 34]	specific CO_2 emissions [kg CO_2/t calcined alumina]
diesel oil	0.7 kg	42.8	73.7	2.21
heavy oil	101.4 kg	40.3	78	318.74
coal	88.4	9.7	97	83.18
natural gas	92.8 kg = 123.73 m^3 density = 0.75 kg/m^3 [49]	36 [GJ/1000 m^3]	55.4	246.95
electricity	126 kWh			52.12
bauxite	2,739 kg		4.89	13.39
total				**716.59**

Tabular Alumina

Tabular alumina is produced by sintering of calcined alumina. For this reason it is also named sintered alumina. The process of sintering is usually performed in a shaft kiln, equipped with gas burners, at a operating temperature of 1,900 °C. The feed is required in form of pellets, which means that calcined alumina is crushed and then palletised. [42, p. 607-608]

The approach for the calculation of tabular alumina's emission factor is also found due to a literature research. The preparation of tabular alumina needs 0.4 kWh/kg electricity. 1 m^3 natural gas is required for sintering, which is equivalent to 1.9944 kg CO_2 (calculated based on the heating value and emission factor of natural gas in Table 13). [50]

The calculated emission factor of tabular alumina is **2,876.09 kg CO$_2$/t**. Table 14 summarises the calculation of the emission factor for tabular alumina. In this calculation the specific CO$_2$ emissions of calcined alumina have to be included, because tabular alumina is made of it.

Table 14: Emission factor for tabular alumina

input	specific consumption	specific CO$_2$ emissions [kg CO$_2$/t tabular alumina]
electricity	0.4 kWh/kg	165.5
natural gas	1 m^3/kg	1,994
calcined alumina		716.59
total		**2,876.09**

White fused alumina (WFA) and brown fused alumina (BFA)

Powdered calcined alumina is fused in an electric arc furnace in order to produce white fused alumina or corundum. White fused alumina is high purity alumina of 99.5 weight % or more and is characterised by high refractoriness and hardness. Due to its large crystal size, corrosion resistance against molten metal and slag is high. [26, p. 297]

The fused mass is slowly cooled and then crushed for producing granular alumina that is less tough, but harder than brown fused alumina and for this reason it produces less friction heat. [51, p. 17]

Brown fused alumina, also named brown corundum, occurs from fusing calcined bauxite with coke that acts as reducer in an electric arc furnace at a temperature of approximately 2,100 °C. The function of coke is to reduce iron oxide and silica to an iron-silicon slag and therefore, to separate the alumina melt from the contaminants of bauxite. Iron pieces are added to support this process, if the iron content is too low for the formation of slag. The result is a brown coloured mass, which is crushed and ground afterwards. The proportion of impurities is higher than that of WFA, which means that the alumina content of BFA is lower. [51, p. 17]

BFA contains about 95 % Al$_2$O$_3$, small amounts of SiO$_2$ and Fe$_2$O$_3$ and 1.5-5 % TiO$_2$ that is a component of bauxite. [26, p. 296-297]

Concerning the emission factor of both, WFA and BFA, a value of approximately **1,000 kg CO$_2$/t** corundum can be estimated according to information provided by Treibacher Schleifmittel GmbH. [52]

3.4.5.6 Calcium aluminate (CA)

Calcium aluminate consists of 75 % Al$_2$O$_3$ and 25 % CaO and is formed by smelting calcined alumina and lime in an electric arc furnace. [23]

According to the $CaO-Al_2O_3$ system, various phases of CA exist that are used as cement in refractory industry or for other specialised applications (e.g. bioceramics). CA is also utilised for the production of refractory castables. [53, p. 51-53]

CA in form of bricks is used in the tin bath bottom of float glass tanks. [23]

CA is a useful raw material, because of its following refractory properties:

- temperature resistance,

- thermal shock resistance,

- thermal expansion and

- de-hydration. [54]

The calculation of the emission factor for calcium aluminate is demonstrated in Table 15. Data concerning specific melting energy and specific electrode consumption derive from expert knowledge of RHI production sites. The specific CO_2 emissions out of energy demand and electrode consumption are calculated in the same way like for fused magnesia.

Table 15: Emission factor for calcium aluminate

emission factor calcined alumina * 75 %	emission factor CaO * 25 %	specific melting energy		specific electrode consumption		total
[kg CO_2/t]	[kg CO_2/t]	[kWh/t]	[kg CO_2/t]	[kg electrode/t]	[kg CO_2/t]	[kg CO_2/t CA]
537.44	238.50	1,400	579.10	8	28.80	**1,383.84**

3.4.5.7 Mullite or fused mullite

Mullite is a very rare mineral and seldom found in nature, but can also be produced artificially by heating any number of aluminium silicate minerals in certain proportions to the correct temperature. Synthetic fused mullite is produced in the United States and Asia, but its production is dominated by C-E Minerals, a division of IMERYS. [40, p. 553]

Figure 15 presents the worldwide production sites of kyanite, andalusite, sillimanite and synthetic mullite.

Figure 15: Production sites of kyanite, andalusite, sillimanite and synthetic mullite [40, p. 554]

Mullite, chemically speaking $3Al_2O_3*2SiO_2$, consists of 71.8 % Al_2O_3 and is a silicate mineral. It is an important ingredient of non basic refractory products, because of a melting point of 1,810 °C, low thermal expansion and good mechanical strength. [42, p. 600]

Fused mullite is produced by melting quartz sand and calcined alumina in an electric furnace at about 2,000 °C. Its chemical composition depends mostly on the crystallisation temperature and the cooling speed and not only on the initial composition. Electro-fused mullite exhibits a Al_2O_3 content of 77 %. [55, p. 257-260]

The calculation for the emission factor of fused mullite is demonstrated in Table 16. Data concerning specific melting energy and specific electrode consumption derive from expert knowledge of RHI production sites. The specific CO_2 emissions out of energy demand and electrode consumption are calculated in the same way like for fused magnesia.

Table 16: Emission factor for fused mullite

emission factor quartz sand * 23 %	emission factor calcined alumina * 77 %	specific melting energy		specific electrode consumption		total
[kg CO_2/t]	[kg CO_2/t]	[kWh/t]	[kg CO_2/t]	[kg electrode/t]	[kg CO_2/t]	[kg CO_2/t fused mullite]
6.67	551.77	1,550	641.10	8	28.80	**1,228.34**

3.4.5.8 Fireclay or mulcoa

Fireclay denotes a silica-rich natural clay that can withstand high firing temperatures and is mostly made of kaolinite. In practice fireclay consists of SiO_2 (50-60 %), Al_2O_3 (24-32 %) and Fe_2O_3. A good fireclay should have a plasticity of 24-26 %. Shrinkage after firing should be 6-

8 % and the Fe_2O_3 content should not be more than 25 %. According to the maximum service temperature, fireclay for refractory purposes is classified into low-duty (max. 870 °C), medium-duty (max. 1,315 °C), high-duty (max. 1,480 °C) and super high-duty fireclay (max. 1,619 °C). Hence, the higher the alumina content is in fireclay, the higher is the melting point. For industrial applications mined clay is allowed to weather for one year before producing fireclay out of it. The weathered clay is mixed with spent fireclay and comes in a mill where some water is added to ensure plasticity. After making bricks, these are dried and fired in kilns depending on the different grades of refractories. [42, p. 597]

Concerning the identification of the CO_2 emissions for the production of mulcoa (manufactured in the United States), data was provided by C-E Minerals. According to that, the figures of 2008 give an emission factor of **675 kg CO₂/t** for mulcoa. [47]

3.4.5.9 Zirconia

Pure zirconium oxide (ZrO_2) is named zirconia. Zirconia has a density of 5.85 g/cm^3 and a melting point of 2,710 °C. Chemical inertness and corrosion resistance to strong mineral acids, liquid metals and molten salts belong to its chemical properties. [42, p. 618-622]

Monoclinic zirconia occurs in form of the natural mineral baddeleyite. Cubic or rather tetragonal zirconia results from thermal decomposition of zircon silicate. [24, p. 40]

Stabilised zirconia is generated, if baddeleyite ore is fused together with a small amount of stabiliser, like CaO, in an electric arc furnace. Then it is solidified and ground to powder. Not adding a stabiliser means that monoclinic crystals are formed, which cause a significant volume change when the material is heated or cooled at temperatures of 1,000-1,100 °C. [26, p. 299]

The necessary information for the calculation of the emission factor for stabilised zirconia could be found in literature. The energy needed for the process of manufacturing stabilised zirconia is 7,000 MJ/kg [56, p. 569]. By applying a conversion factor of 1 Wh = 3.6 kJ [57], a calculated energy consumption of approximately 1,944 kWh/kg is the consequence. By multiplying this value by the emission factor for electricity, described in chapter 3.3.4, the result for the emission factor of stabilised zirconia is **804.12 kg CO₂/t**.

3.4.5.10   Zirconia mullite

Zircon sand (zircon silicate) and calcined alumina are fused in an electric arc furnace in order to create zirconia mullite. The resulting material, which exhibits the corrosion resistance of ZrO_2 and the spalling resistance of mullite, is used for high grade refractories. Zirconia mullite composes of 37 % ZrO_2, 18 % SiO_2 and 45 % Al_2O_3. [26, p. 298-299]

The calculation for the emission factor of zirconia mullite is demonstrated in Table 17. Data concerning specific melting energy and specific electrode consumption derive from expert knowledge of RHI production sites. The specific CO_2 emissions out of energy demand and electrode consumption are calculated in the same way like for fused magnesia.

Table 17: Emission factor for zirconia mulllite

emission factor zircon sand * 55 %	emission factor calcined alumina * 45 %	specific melting energy		specific electrode consumption		total
[kg CO_2/t]	[kg CO_2/t]	[kWh/t]	[kg CO_2/t]	[kg electrode/t]	[kg CO_2/t]	kg CO_2/t zirconia mullite
3.69	322.47	1,650	682,50	10	36	**1,044.66**

3.4.5.11   Zirconia alumina or zirconia corundum

Zirconia alumina or also zirconia corundum is made by fusing zirconium oxide and calcined alumina in an electric arc furnace. There exist two common types of zirconia alumina in refractory industry, one that contains 23-24 % ZrO_2 (AZ 23) and another one that consists of 40-43 % ZrO_2 (AZ 40). [23]

As a matter of fact, no data could be found concerning the production process of zirconia alumina. Therefore, the same specific melting energy (1,650 kWh/t) and the same specific electrode consumption (10 kg/t) like for zircon mullite are estimated according to the "de minimis"-approach (see chapter 3.3.4) [23]. Table 18 and Table 19 represent the results for the emission factor of AZ 40 and AZ 23.

Table 18: Emission factor for AZ 40

emission factor zirconia * 40 %	emission factor calcined alumina * 60 %	specific melting energy		specific electrode consumption		total
[kg CO_2/t]	[kg CO_2/t]	[kWh/t]	[kg CO_2/t]	[kg electrode/t]	[kg CO_2/t]	[kg CO_2/t AZ 40]
321.65	429.95	1,650	682,50	10	36	**1,470.10**

Table 19: Emission factor for AZ 23

emission factor zirconia * 23 %	emission factor calcined alumina * 77 %	specific melting energy		specific electrode consumption		total
[kg CO_2/t]	[kg CO_2/t]	[kWh/t]	[kg CO_2/t]	[kg electrode/t]	[kg CO_2/t]	[kg CO_2/t AZ 23]
184.95	551.77	1,650	682,50	10	36	**1,455.22**

3.4.5.12   Chromium oxide (Cr_2O_3)

Chromium(III) oxide is made up of positive charged chromium ions in the oxidation state +3, which is the most stable and common form. The green powder is manufactured from the

mineral chromite, which is the main component of chrome ore, as already mentioned before. [58, p. 29]

Chrome ore is crushed, dried and ground. Soda ash and lime may be added. Then, the mixture is roasted in a rotary furnace at about 1,100 °C. [59, p. 63.11]

The advantages of chromium oxide are its chemical corrosion resistance and that it increases the temperature limit of the application. However, the forming of Cr(VI), which is harmful to environment and health, is possible during the operation. Another disadvantage is the disposal costs. [23]

According to information provided by Bondex Trading Ltd., situated in Kazakhstan, for producing 1 tonne refractory grade chromium oxide about **4,000 kg CO_2** are emitted. [60]

3.4.5.13   Fused magnesia chromite

Fused magnesia chromite is produced by melting chrome ore and dead burned magnesia in an electric arc furnace at 3,000 °C. The main sector of application is the steel and non steel industry, because this material meets the demand for high hot strength and corrosion resistance. [82, p. 632]

Fused magnesia chromite composes of 40 % chrome ore and 60 % MgO. The calculation for the emission factor of fused magnesia chromite is demonstrated in Table 20. Data concerning specific melting energy and specific electrode consumption derive from expert knowledge of RHI production sites. The specific CO_2 emissions out of energy demand and electrode consumption are calculated in the same way like for fused magnesia. [23]

Table 20: Emission factor for fused magnesia chromite

emission factor chrome ore * 40 %	emission factor DBM * 60 %	specific melting energy		specific electrode consumption		total
[kg CO_2/t]	[kg CO_2/t]	[kWh/t]	[kg CO_2/t]	[kg electrode/t]	[kg CO_2/t]	[kg CO_2/t fused magnesia chromite]
2.68	1,156.20	1,950	806.60	30	108	**2,073.48**

3.4.5.14   Spinel

The spinel group is a large family of minerals with uniform crystal structure but variable composition. These minerals possess the principal chemical formula AB_2O_4, in which A may be Mg^{2+}, Fe^{2+}, Mn^{2+} or Zn^{2+}. B can stand for Al^{3+}, Fe^{3+} or Cr^{3+}, which affects that the mineral is called aluminate spinel, ferrite spinel or chrome spinel. Magnesia spinel, chemically $MgO*Al_2O_3$, belongs to the group of aluminate spinels. It has a high melting point of 2,135 °C [24, p. 206]. [23]

The emission factor of magnesia spinel is calculated on basis of data from RHI plant Radenthein. The figures of 2007, 2008, 2009 give an average value of **159 kg CO_2/t** magnesia spinel. [23]

3.4.5.15   Hercynite

Hercynite (FeO*Al_2O_3) is a part of the aluminate spinel group and exhibits a melting point of 1,780 °C. Hercynite used in refractory industry is produced by fusing calcined alumina and mill scale in an electric arc furnace. [23]

In accordance with stoichiometry, hercynite compose of 58 % Al_2O_3 and 42 % FeO. The calculation for the emission factor of hercynite is demonstrated in Table 21. Data concerning specific melting energy and specific electrode consumption derive from expert knowledge of RHI production sites. The specific CO_2 emissions out of energy demand and electrode consumption are calculated in the same way like for fused magnesia.

Table 21: Emission factor for hercynite

emission factor mill scale * 42 %	emission factor calcined alumina * 58 %	specific melting energy		specific electrode consumption		total
[kg CO_2/t]	[kg CO_2/t]	[kWh/t]	[kg CO_2/t]	[kg electrode/t]	[kg CO_2/t]	[kg CO_2/t hercynite]
0	415.62	1,450	599.80	8	28.80	**1,044.22**

3.4.5.16   Silicon carbide (SiC)

Silicon carbide is a crystalline product that is characterised by great hardness, refractability and infusibility. [61, p. 5]

The needed information for the calculation of the emission factor for SiC could be found due to a literature research.

The used silicon carbide in refractory industry is produced synthetically by the Acheson process (named by its inventor). For producing SiC, according to the following chemical reaction, a mixture of quartz sand and petrol coke is treated in the Acheson furnace where temperatures reach 1,700-2,500 °C.

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
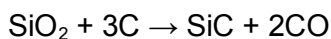
The Acheson furnace is an electrically heated resistance furnace, in which two electrodes are connected to a graphite core. Typical oven lengths are 10-30 metres and a raw material charge of 400 tonnes. [62, p. 235]

According to the chemical reaction above, 1.4 kg CO are generated during the production of 1 kg SiC, which is equivalent to 2.2 kg CO_2.

An energy demand of 7.5 kWh/kg SiC sets reaction into operation. [64, p. 27]

An electrode consumption of approximately 130 kg is required per tonne SiC. [65, p. 8]

As far as CO_2 emissions are concerned, a total of **5,770.30 kg CO_2** results per tonne SiC produced in an Acheson furnace (see Table 22).

Table 22: Emission factor for SiC

source	calculated quantity [kg CO_2/t]	calculation method
CO_2 in form of CO	2,200	1.4 multiplied by a CO_2/CO-ratio of 1.57
energy demand Acheson furnace	3,102.30	7.5 kWh/kg multiplied by the electricity emission factor in chapter 3.3.4
electrode burn-off	468	130 kg multiplied by an emission factor of 3.6 t CO_2/t electrode [63, p. 57]
total CO_2	**5,770.30**	

3.4.5.17 Carbon black

Carbon black is an amorphous solid, characterised by imperfect graphite structures. About 99 % of its composition is carbon. Hydrogen, oxygen, sulphur, nitrogen and ash are the remaining substances. Carbon black is produced by partial combustion or pyrolysis of hydro carbon liquids or gases. Carbon black is available commercially in several dozen grades. [66, p. 4-5]

Cancarb Limited, which has its plant in Cancada, provided information that **979.70 kg CO_2** are generated for producing 1 tonne of carbon black. [67]

3.4.6 Emission factors and origin of raw materials

Table 23 summarises the emission factors of the most important raw materials applied in refractory industry.

Table 23: Emission factors of raw materials

raw material	emission factor [kg CO_2/t raw material]
andalusite	143
bauxite	4.89
brown fused alumina	1,000
calcined alumina	716.59
calcined bauxite	144.50
calcined dolomite	1,072
calcium aluminate	1,383.84
carbon black	979.70
caustic calcined magnesia	1,093
chrome ore	6.70
chromium oxide	4,000

raw material	emission factor [kg CO_2/t raw material]
dead burned dolomite	1,449
dead burned magnesia	1,927
dolomite	6.70
feldspars	6.70
fireclay	675
fused dolomite	1,547.56
fused magnesia	2,602
fused magnesia chromite	2,073.48
fused mullite	1,228.34
fused silica	685.46
graphite	6.70
hercynite	1,044.22
kyanite	6.70
lime	954
magnesia spinel	159
microsilica	0
perlite	6.70
phenolic resin	1,890.99
pitch	0
quartz sand	29
quartzite	6.70
silicon carbide	5,770.30
tabular alumina	2,876.09
vermiculite	6.70
white fused alumina	1,000
zircon	6.70
zirconia	804.12
zirconia alumina (AZ 23)	1,455.22
zirconia alumina (AZ 40)	1,470.10
zirconia mullite	1,044.66

Table 24 gives an overview of the origin of these raw materials based on data from RHI. This information will be needed in chapter 4 to calculate the specific CO_2 transport emissions of the refractories arising from the delivery of the raw materials contained in the product groups.

Table 24: Origin of raw materials [23]

primary raw materials	country of origin
andalusite	South Africa, Peru
bauxite	Australia, South America, Africa (see section 3.4.4.5)
brown fused alumina	France, China
calcined alumina	Hungary, France, Germany
calcined bauxite	China, Guyana
calcined dolomite	Austria
calcium aluminate	Austria
carbon black	Canada
caustic calcined magnesia	Austria
chrome ore	China, South Africa
chromium oxide	Kazakhstan
dead burned magnesia	Austria, China, Turkey, Ireland
dead burned dolomite	Austria
dolomite	Italy
feldspars	Germany
fireclay	USA
fused magnesia	China
fused dolomite	Austria
fused magnesia chromite	South Africa, Austria
fused mullite	South Africa, USA
fused silica	China
graphite	China, Canada, Brasil
hercynite	Austria
kyanite	USA
lime	USA, Canada, Mexico
magnesia spinel	Austria
microsilica	Germany, USA, Norway
perlite	Germany
phenolic resin	China, England, Germany
pitch	Austria, England, Germany
quartzite	Slovenia
quartz sand	Germany
SiC	Germany, Belgium, Brasil
tabular alumina	Germany, Slovenia
vermiculite	Germany
white fused alumina	Germany, Austria, Hungary
zircon	Australia, South Africa, USA, China

primary raw materials	country of origin
zirconia	USA, South Africa, Ukraine
zirconia alumina	France, Austria
zirconia mullite	South Africa, USA
secondary raw materials	**country of origin**
fused quartz glass	Germany
fused silica	Germany
high alumina 55	Germany, France, Belgium
high alumina 75	Germany, France, Belgium
microsilica	Germany
mill scale	Belgium, Austria, Germany
porcelain	Germany
recycled AMC bricks	Netherlands, England, France
recycled MgO-C bricks	Belgium, France, Netherlands, Germany, Italy, Poland, Rumania, Serbia

3.5 Transportation

As a matter of fact, a high proportion of CO_2 is produced by transport. Hence, transportation is an important input of every carbon footprint calculation, because it can be a crucial factor for the overall result.

3.5.1 General aspects about transportation and corresponding CO_2 emissions

23 % of global CO_2 emissions are caused by transport actions (passenger and freight transport). It is predicted that these emissions are still growing. Typically transportation rises with increasing economic activity and gross domestic product [68, p. 6-9].

The topic transport was also one of the key sectors of the 1997 Kyoto Protocol. The dominant fuel source for transportation is oil. This dependence on fossil fuels is the reason why transport is a major contributor to GHG emissions. The impact of transport on global warming is not only limited to vehicle emissions, also the production and distribution of fossil fuels is significant. The sector road transport is the biggest producer of GHG, but aviation is considered more environmentally damaging, because GHG are released directly into the upper troposphere and stratosphere. Shipping is the dominant transport method for overseas freight and 90 % of goods are moved at low cost by shipping with cargos. There have been technological efforts to enhance fuel efficiency by developing better engines, slowing speeds and more efficient ship hulls that are enabled to contribute to a reduction of shipping CO_2 emissions by 50 %. Even the use of cleaner fuels like gas is a possibility to decrease ship emissions by as much as 90 %. Road freight by truck is the fastest growing transport method, especially in small countries where trucks are a more viable option than other modes. In contrast, transportation by rail is an attractive alternative for many long distance journeys. Rail freight is twice times more ecological efficient than road freight. Many of the run rail systems are diesel fuelled. Electric trains could be used instead, but those require a certain infrastructure. CO_2 from electricity may be minimal by using renewable energies. [69, p. 354-363]

In general, transport emissions are indicated per km and per vehicle type for a certain tonnage [28, p. 18]. Therefore, the unit tonne-km (t km) is used. Figure 16 shows a comparison of the environmental impact of freight transportation by air, water, road and rail. Airplanes are the largest emitter by far with an amount of 500-950 grams per tonne and per km. The lowest proportion of transport emissions arises from shipping with at least 10 grams of CO_2 per km. Emissions of 60-150 grams are produced by a modern truck and a modern train emits between 30 and 150 grams CO_2 per km and per tonne of freight. In conclusion, transportation by ship is the most eco-friendly mode of transport, followed by rail, road and at last by plane.
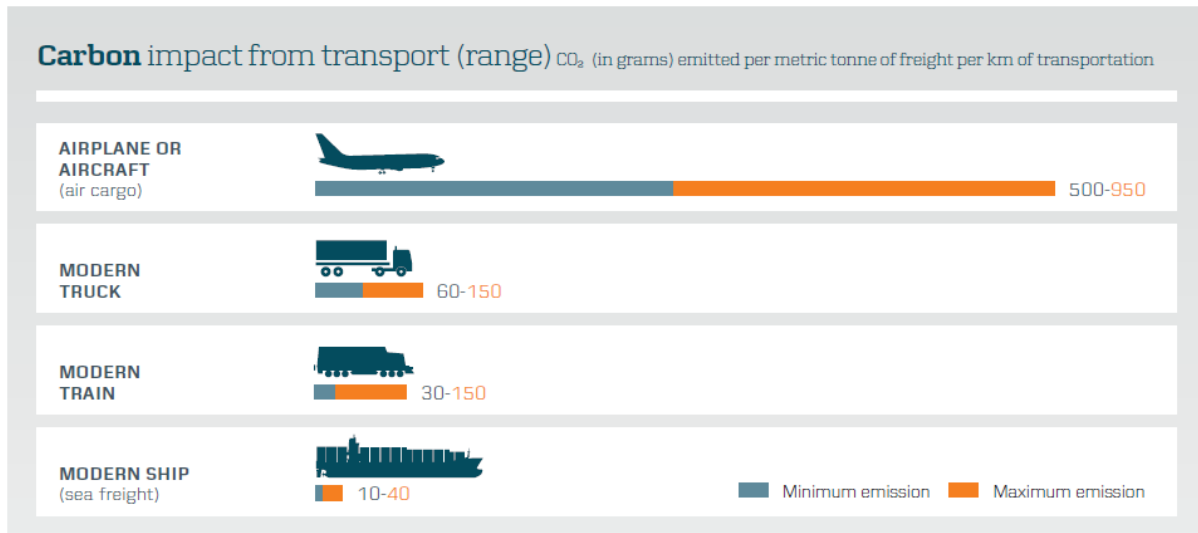
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Carbon impact from transport (range) CO₂ (in grams) emitted per metric tonne of freight per km of transportation

- AIRPLANE OR AIRCRAFT (air cargo): 500-950
- MODERN TRUCK: 60-150
- MODERN TRAIN: 30-150
- MODERN SHIP (sea freight): 10-40

Minimum emission   Maximum emission

Figure 16: Specific CO_2 emissions per transportation system type [70, p. 16]

3.5.2 CO₂ calculation approach for transports

<u>CO_2 calculation approach concerning transportation according to PAS 2050</u>

According to PAS 2050, carbon footprint assessment should include any transportation required during the product's and raw materials' life cycle. GHG emissions arising from air, road, water, rail or other transport methods (e.g. conveyor belt) form part of the life cycle and must be taken into account. When products are delivered to different locations and transport distances vary, the GHG emissions should be calculated based on the average distribution distance. In addition, transport emissions should contain the emissions associated with the entire delivery journey from source to delivery point and back, which means even the return trip of the vehicle whether it is empty or not. If return journeys are used for transporting other products, the emissions arising from those journeys should be allocated to the transported products. [10, p. 15, 23]

Here in this Master Thesis the return journeys are not needed to be considered. The carrier coordinates its return journeys in such a way that the vehicle is not empty. Therefore, the company, whose products are delivered in the course of the return trip, has to include the arising CO_2 emissions in its carbon footprint.

<u>Problematic concerning freight transportation of refractory products</u>

According to an analysis regarding the total quantity of freight transportation of the German and Austrian RHI plants, road freight and sea freight are the dominating modes of transportation in refractory industry. Freight transportation by rail is also applied, but it is often linked to shipping. Otherwise sea freight is linked to road transport. The analysis also showed that less than 1 % of the total quantity are transported by plane. This means that air cargo is negligible in this Master Thesis. [71, p. 37]

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As a matter of fact, refractory industry is a global market. The essential resources are found globally and consumers of refractory products are scattered around the world. For this reason, the radius as well as the number of transport activities in refractory industry are huge, compared to other industrial sectors. [23]

Hence, the average distribution distance is the best possible and most justified solution in order to handle the complexity of transport operations going on in refractory industry.

Data from RHI serve as basis for the calculation of the CO_2 emissions linked to freight transportation. For the reason that RHI is a global acting corporate group and the world market leader, data can be considered as representative for the whole refractory industry.

Forming the average distribution distance sounds easy, but exactly the fact that RHI acts worldwide is the reason for the difficulty of determining the emissions arising from transportation. A product can be manufactured at different plants and countless transport operations go on every year. The large number of transportation routes, different means of transportation, varying types of applied technologies (e.g. engines), human aspects (e.g. driver), high number of suppliers and the fact that a single raw material is obtained from different countries or rather continents, makes it so hard to find an appropriate CO_2 calculation approach.

The subsequent questions appeared regarding this topic:

1. What types of tools exist for calculating distances?

The best route planner for transports on road is google maps. Unfortunately, a suitable tool for the calculation of worldwide distances covered by rail could not be found. A very useful tool for shipping was found on website **http://www.searates.com/reference/portdistance/**, which offers a port to port distance calculation. The chosen route is displayed on a world map. The designation of the distance results in nautical miles. 1 nautical mile equals to 1.852 kilometres. [72]

Figure 17 demonstrates the user interface of the searates tool.
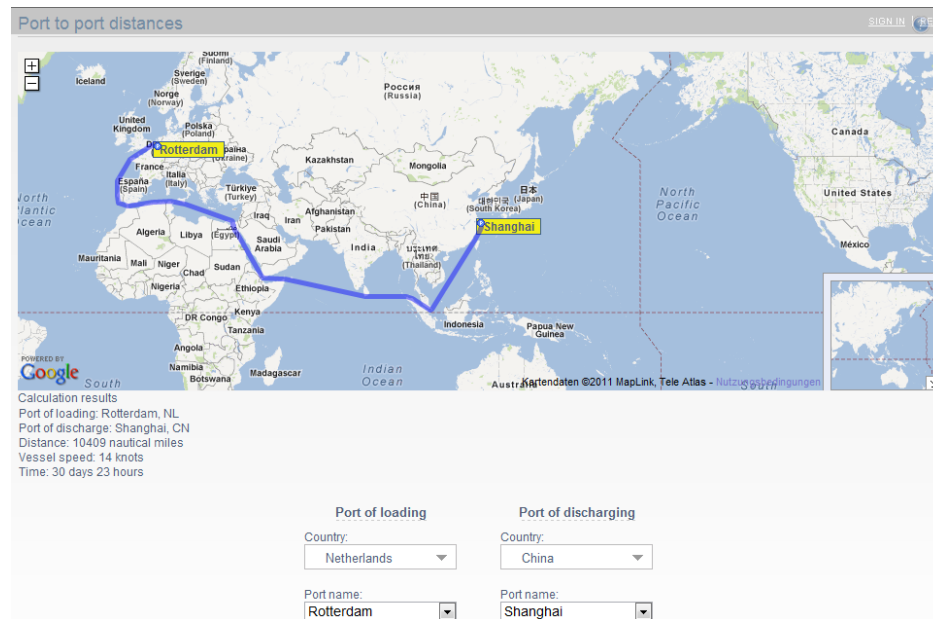
Figure 17: Tool for shipping from searates [83]

2. In what relation shall the distances be considered? (e.g. transport zones, countries or exact address)

Acting on basis of exact addresses means that every single transport activity has to be considered and analysing this seems rather impossible. Furthermore, the department for transport logistics exhibits data about quantitative material flows between the continents and so it is able to determine the most important transport routes. With this information the average distances can be assessed via the above mentioned tools.

Transportation is divided into inbound and outbound. Inbound includes delivery of raw materials from suppliers as well as internal transport (e.g. from plant Breitenau (Austria) to plant Radenthein (Austria)). Outbound is defined as distribution of finished goods to customers. [23]

A literature research is accomplished to identify appropriate emission factors for the different means of transport. In this context GEMIS, short for Global Emission Model for Integrated Systems, could be found. GEMIS version 4.7 is available on website **www.gemis.de**. GEMIS is a life-cycle analysis program and database for energy, materials and transport systems and can be copied and distributed without restriction. The latest version 4.7 is available for free as public domain software. Ökoinstitut and Gesamthochschule Kassel have created this software in close cooperation with the German Ministry for Environment and partners. The GEMIS database includes information about energy sources (fossil fuels, renewables, nuclear, biomass, hydrogen), processes for electricity and heat, materials and transports. This database also covers for each process the topics efficiency, power, capacity factor,

lifetime, direct air pollutants, greenhouse gas emissions, land use, solid wastes and liquid pollutants. [44]

The chosen emission factors for transportation by water, rail and road according to GEMIS are shown in Table 25.

Table 25: Chosen emission factor for transportation

verhicle type	emission factor [g CO_2/t km] [44]
overseas ship	7.41 (source: GEMIS 4.7, Überseeschiff 2010)
inland water vessel	20.76 (source: GEMIS 4.7, Schiff-Binnen-Diesel-DE-2010)
train	29.84 (source: GEMIS 4.7, Zug-Güter-Diesel-DE-2010)
truck	73.77 (source: GEMIS 4.7, LKW-Diesel-DE-2010)

The idea behind this approach is described in the subsequent section.

As a matter of fact, a cluster of production sites exists in Germany (6 plants) and Austria (5 plants, including the largest one). For this reason, these two countries serve as basic points for the average distance determination. A further reason is that in Europe the biggest production output is realised. Therefore, the highest number of raw materials is required there and the largest quantity of finished goods is dispatched from there. The next step is to define the most important or rather most frequented transport routes between Europe and the other continents. This is achieved in agreement with the RHI department for transport logistics. The distances for truck, rail and inland water vessel transports are specified by the transport logistics department. The remaining distances for ship transports are determined via the tool from searates, as mentioned before. Then the resulting nautical miles are converted into kilometres. Finally, the specific CO_2 emissions for the different transport routes result from multiplying the kilometres by the emission factor of the respective means of transport in Table 25. The specified routes, their calculated distances and specific CO_2 emissions are shown in Table 26.

Table 26: Transportation routes - distances and specific CO_2 emissions

transportation route	continents	distance [km]	vehicle type	specific CO_2 emissions [kg CO_2/t]
inside Austria	Europe - Europe	1000	truck	73.77
Germany - Austria	Europe - Europe	100	truck	7.38
Rotterdam (Netherlands) - Austria	Europe - Europe	800 150 150	inland water vessel rail truck	32.15
Koper (Slovenia) - Austria	Europe - Europe	400	inland water vessel	8.30
Genova (Italy) - Austria	Europe - Europe	600	inland water vessel	12.45
Russia - Austria	Europe - Europe	11,000	Trans-Siberian railway	328.24
Rotterdam - Germany	Europe - Europe	200	rail	5.97

transportation route	continents	distance [km]	vehicle type	specific CO_2 emissions [kg CO_2/t]
inside Turkey	Europe - Europe	300	rail	8.95
Derince (Turkey) - Genova	Europe - Europe	2,437	overseas ship	18.05
Derince - Koper	Europe - Europe	2,185	overseas ship	16.19
Dalian (China) - Rotterdam	Asia - Europe	20,109	overseas ship	149.00
Shanghai (China) - Rotterdam	Asia - Europe	19,277	overseas ship	142.85
Altamira (Mexico) - Rotterdam	North America - Europe	9,425	overseas ship	69.84
Montreal (Canada)- Rotterdam	North America - Europe	5,805	overseas ship	43.01
Durban (South Africa) - Rotterdam	South Africa - Europe	12,820	overseas ship	95.00
Durban - Genova	South Africa - Europe	11,081	overseas ship	82.11

Calculation of the emission factors for transportation

The determination of the CO_2 emissions will be accomplished separately for inbound and outbound, but the same transport routes will be used.

For applying this approach the following steps should be considered:

1. Depending on the raw materials origin, the appropriate transportation route according to Table 26 has to be chosen.

2. The specific CO_2 emissions of this route are multiplied by the proportion of the raw material [%] according to the composition of the refractory product in order to obtain the specific CO_2 emissions for the respective raw material and its transportation route.

3. The specific quantity of CO_2 for the total refractory product arises from summing up the specific transport emissions of all raw materials that are contained in the refractory product. The total amount of CO_2 for inbound is received by multiplying the tonnage of the refractory product by the calculated specific transport emission factor.

4. The same line of action will be applied for outbound. The first action is to determine the destination of the finished goods, then checking the transportation route and their CO_2 emissions, and multiplying them by the quantity delivered.

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3.6 Batch preparation and shaping

The following chapter introduces the operations crushing and grinding, screening and sorting, dosing, mixing as well as shaping. Finally, the approach for the carbon footprint calculation concerning these life cycle steps is described.

3.6.1 Batch preparation

Preparation is very important for the further development of the raw materials according to their application as ingredients for the resulting refractory product. Preparation includes the operations crushing, screening, sorting and grinding. In general, the required raw materials for the production of refractories are often not prepared by the companies themselves anymore. Instead they derive from other firms in the desired grain size, unless the raw materials are produced by their own. In the past only few grain sizes were used for creating a batch. But the requirements to be met by refractory products increased and so a wide range of grain sizes is needed nowadays to achieve the desired properties of a product. As a matter of fact, the characteristics of refractories are influenced by the selection of the grain structure and the variation of the grain sizes of the individual raw materials. [24, p. 22]

Table 27 demonstrates the typical grain structure of standard refractory bricks.

Table 27: Typical grain structure of standard refractory bricks [24, p. 23]

refractory product	grain-size category [%]		
	1-5 mm	0.1-1 mm	<0.1 mm
silica brick	30	40	30
fireclay brick	35	25	40
magnesia brick	45	20	35
resin-bonded magnesia brick	55	30	15

3.6.1.1 Crushing and grinding

Crushing is defined as splitting a solid in several parts due to external force effect in order to break inner bonding. The aims of crushing are to get raw materials ready for separating processes and chemical reaction processes as well as to create the required grain size for the production of the product. Concerning grain sizes, it is usually differentiated between coarse, medium and fine grain. Different types of machines are used depending on the task. They vary in the kind of stressing that is applied to the material in order to break; shear stress, compressive stress, impact stress and stress due to cutting. [23]

Thus, for the process of crushing the appropriate crushing machines have to be chosen. The selection depends on many criteria such as hardness, toughness and particle shape of the feed as well as on desired reduction ratio. [73, p. 21]

Crushing equipment can be divided in accordance with grain size of the feed, kind of stressing (mentioned above), design characteristics and application area. Coarse and medium grinding of brittle material is achieved by crushers like for instance jaw crushers, cone crushers, impact crushers, roll crushers or hammer crushers. Fine grinding is arranged by mills such as ball mills, vibration mills and roller mills. [23]

Various types of crushing and grinding equipment exist for refractory industry. A classification of crushing and grinding equipment according to the material size and the emerging grain size is given in Table 28.

Table 28: Classification of crushing and grinding equipment for refractory industry [26, p. 312]

classification	typical machines	grain size		crushing or grinding ratio
		feeding	crushed or ground	
crusher	jaw crusher, gyratory crusher	hundreds mm – 50 mm	100 mm – 20 mm	3-5
intermediate grinding mill	edge runner, roll crusher, impact crusher	50 mm – 10 mm	10 mm – hundreds µm	10–20
fine grinding mill	ball mill, rod mill	3 mm – 50 µm	1 mm – 10 µm	5-30
ultra-fine mill	vibrating mill, jet mill	hundreds µm – many µm	many µm – sub-micron	3-20

Applied crushing and grinding equipment at RHI

Jaw crusher (see Figure 18)

Crushing is carried out using a fixed and a moving jaw. Feeding is realised above and the crushed material leaves the machine at moment of the backward movement of the moving jaw. By varying the angle between the fixed and moving jaw, their gap is changed and therefore throughput and grain size can be modified. [23]
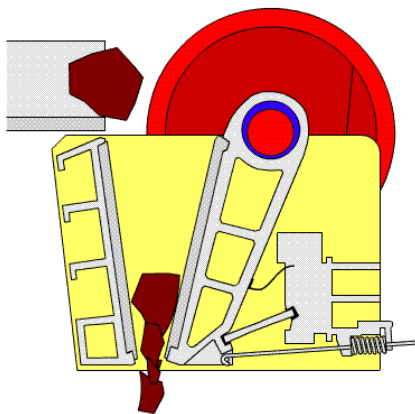
Figure 18: Schematical drawing of a jaw crusher [74]

<u>Cone crusher</u> (see Figure 19)

A rigid crushing shell and a movable cone are responsible for crushing. Crushing happens due to periodical changes of the space between crushing shell and cone. The grain size can be changed by lifting or lowering the crushing shell. [23]
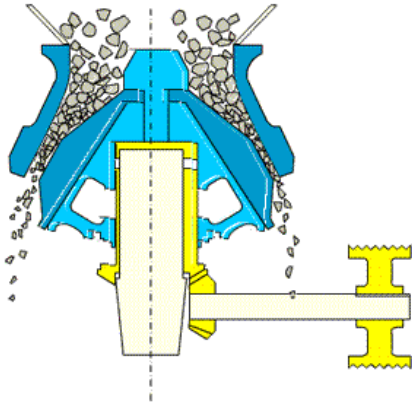
Figure 19: Schematical drawing of a cone crusher [75]

<u>Roll crusher</u> (see Figure 20)

Two counterrotated rolls, which can be driven with the same or different velocity, crush the material that is put into the processing zone. The gap between the both rolls is modifiable, because one of them is moveable. [23]
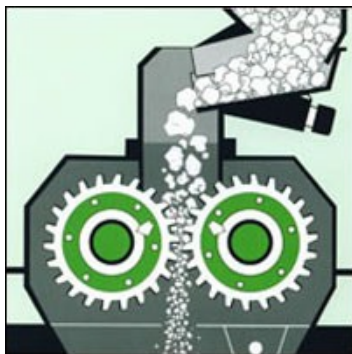
Figure 20: Schematical drawing of a roll crusher [76]

<u>Ball mill</u> (see Figure 21)

These mills are filled with a loose grinding body in form of balls. The mill can be arranged rotating or vibrating. [23]
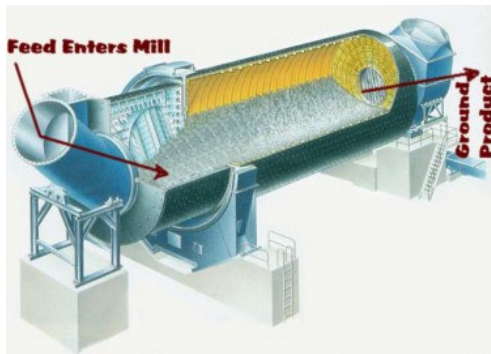
Figure 21: Schematical drawing of a ball mill [77]

The feed is crushed by the movement of the mill, causing the balls to fall onto the material effects crushing (see Figure 22). Grain size and throughput depend on fill factor of the grinding body, ball diameter, rotational speed and time for crushing. [23]
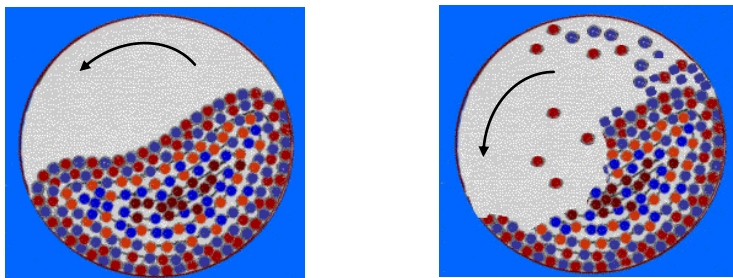
Figure 22: Principle of ball mills [77]

3.6.1.2 Screening and sorting

Screening is defined as separation according to grain size, while sorting employs physical properties to cause separation. In refractory industry sorting processes are not often utilised anymore. The separating parameters for screening are either geometry of grains or sinking speed of grains in fluids. The former is applied to coarse (>100 mm) and medium (<100 mm) grain and the second parameter to fine grain (<0.5 mm). Selection of the suitable screening process depends principally on grain size of the feed. Screening is applied in order to achieve the following objectives:

- creating a certain grain size composition,
- isolating unrequested substances,
- separating the fines from oversized material,
- protecting facilities from material that is too coarse,
- achieving separation by material type or geometry of grains (e.g. waste sorting) and
- employing quality control to products.

Sieve classification is divided into methods using either fixed screens or moving screens (screening machines). The material is transported along the screen surface where the fines go through the sieve openings due to the energy of the material. A vibrating or rotating movement of the screen supports this process. Selection of the appropriate screening machine depends on grain size of the feed, properties of the screenings, characteristics of facilities and the objective. [23]

Applied screening equipment at RHI

Mogensen Sizer (see Figure 23)

Firstly, in the upper area of the sizer the feed is loosened. Then it is transferred through several decks in free fall, while coarse material is separated from the remaining material in order to reduce the load of the upper decks. The respective grain size fractions are isolated on different decks that have their own discharge. [23]
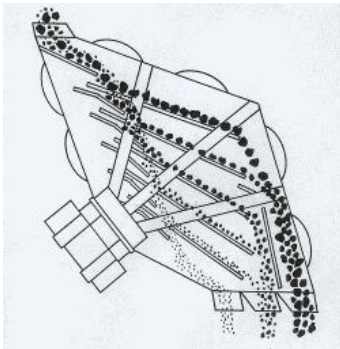
Figure 23: Schematical drawing of a Mogensen Sizer [78]

Tumbling screen (see Figure 24)

A tumbling screen consists of several screen surfaces, placed one below the other. Each one is equipped with a discharge. The feed is put onto the first screen in the middle of the surface and then is distributed from the inside to the outside due to the movement of the sizer. The fines reach the next screen, while the coarse material passes through the discharge. [23]
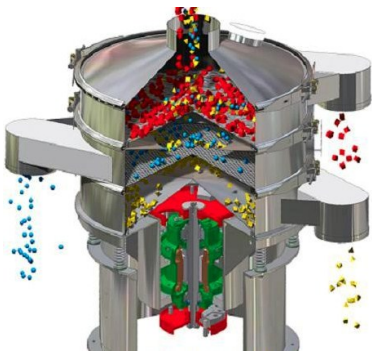
Figure 24: Schematical drawing of a tumbling screen [79]

3.6.1.3 Dosing

Dosing includes weighing and conveying. [23]

Dosing is accomplished by volume (e.g. via box feeders placed on a conveyor belt) or mass (e.g. via screw feeders linked to weigh-belts) and is mainly automated with computer control. [32, p. 18]

Weighing systems must ensure a certain accuracy. Thus, for refractory industry the most important weighing systems are weighing vessels, weighing waggons and belt weighers. Weighing vessels are vessels that are fixed on a weighing cell and are usually used for the preproportioning of additives. The term belt weigher describes that a conveyer belt, which is installed on a weighing cell, is located under a discharge of a silo, and then each component of the mixture is dosed onto the conveyor belt. However, weighing waggons are of higher importance. Vessels, equipped with weighing cells, are installed on waggons. The components of the mixture are dosed directly from the silos into the waggons. [23]

3.6.1.4 Mixing

The purpose of mixing is to distribute various components, which exhibit at least one characteristic that differs to the other components. For example, these characteristics can be chemical composition, grain size, temperature or moisture. Consequently, the aim of mixing is that the mixture becomes homogenous. This is realised by relative movements between the components. In order to perform mixing, a shaft equipped with mixing tools is installed in the vessel of a mixing machine. Various types of mixing tools exist (e. g. star-shaped) that effect the required relative movements. However, in every mixing process also segregation takes place simultaneously. Mixing can be arranged in dry or wet conditions. As a matter of fact, no possibility exists to simulate mixing processes mathematically. For this reason, trials with representative sample material have to be accomplished. [23]

Mixing time, intensity and sequence have a significant impact on the properties of the mixture and in consequence on the finished product. The prepared raw materials must be mixed in controlled proportions and homogenised to achieve the essential physico-chemical uniformity. [32, p. 18]

The composition of the mixture concerning raw materials is an essential part of the know-how of each manufacturer, except of generally known data, and therefore a well-guarded secret. [73, p. 22]

Typically utilised aggregates for this operation are intensive mixers, gravity mixers and edge runners. Mixing effectiveness and quality of intensive mixers are not surpassed by any other mixing equipment, because this type of mixer is able to optimally mix materials having a different mineralogy and grain size in one and the same batch. [24, p. 22-24]

Generally mixing machines are divided into two types, the fixed vessel type or the driven vessel type. Selection of the appropriate type of mixer refers to production output and production items. As a matter of fact, mixing is the last production step of unshaped

products. Therefore, their raw materials need rapid, uniform and high-efficiency mixing. [26, p. 314]

Regarding the production of shaped refractories the sequential arrangement of adding mixture ingredients is of highest priority, because certain components shall react with binders. Furthermore, it is differentiated between horizontal and vertical mixers. The difference is that in horizontal mixers the shaft is installed horizontal, while the shaft of vertical mixers is installed vertical. [23]

Applied mixing equipment at RHI

At RHI horizontal mixers are used for producing unshaped refractories and vertical mixers are used for producing shaped refractories. Explosion prevention and protection has to be taken into account, if explosive dusts are treated. Then, the mixer shall be made of white (non-corrosive) steel and must be earthed. [23]

Vertical mixers are purchased either from company m-tec or lödige. Figure 25 demonstrates type MR from m-tec.

Figure 25: Vertical mixer from m-tec [80]

The applied vertical mixers are made by EIRICH, because those exhibit the best application of energy. For this reason, they achieve the best mixing result. [23]

An Eirich mixing system composes of a rotating mixing pan, eccentrically arranged mixing tools and a stationary scrapper tool. The rotating pan delivers the mixture into the area of the mixing tools. Depending on the application, the mixing tools are able to create a counterflow or a cross-flow with optimised differences in speed. The scrapper tool prevents material build-up at the walls and the floor of the pan and also accelerates the emptying process at end of the mixing time. [81]

The mixing principle of Eirich is demonstrated in Figure 26.
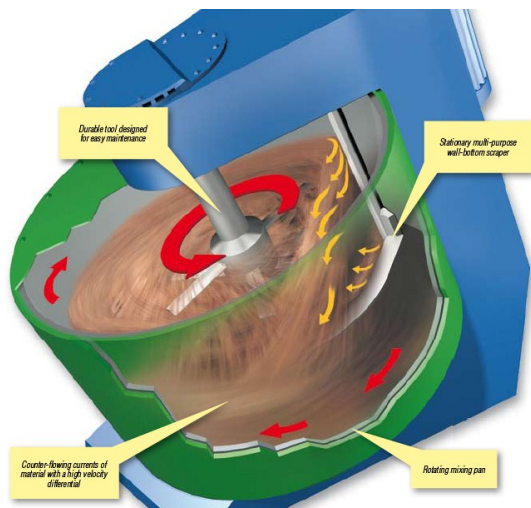
Figure 26: Mixing principle of Eirich mixers [81]

Eirich mixers of type D and R are utilised at RHI (see Figure 27). The mixing pan of type D is installed horizontal, while the one of type R is angled. This causes an additional mixing effect. However, the installation size of D is a lot bigger than that of R. The rotational speed of type R's pan is faster compared to type D and therefore also the emptying process is faster. Furthermore, type R and D have different mixing tools. [23]

Source:
[81, Folder: EIRICH Intensive-action Mixer Type D]

Source:
[81, Folder: EIRICH Intensive Mixer Type R]

Figure 27: Eirich mixers type D and R

3.6.2 Shaping [23]

The applied shaping method can have a profound impact on the ultimate characteristics of a refractory product. Stringent technical specifications are demanded, covering such properties like dimensional tolerance, density, strength, durability and refractoriness. [32, p. 19]

Selection of the shaping method depends on the mouldability of the batch (water content, plasticity), desired properties of the ultimate product, number of pieces that are manufactured and on complexity of the design of the product. The applied shaping methods in refractory industry are listed below:

- hydraulic pressing,

- vibration pressing,

- isostatic pressing,

- manual or mechanical ramming,

- extrusion pressing and

- slip-casting. [24, p. 26-27]

The most important pressing method in refractory industry is hydraulic pressing. Hydraulic pressing can be applied to high quality refractory products in all sizes, shapes and compositions worldwide. Regarding the production of shaped refractories, hydraulic presses made by the company Laeis define the state of technology, and therefore dominate the market.

Figure 28 demonstrates a model type of hydraulic presses made by Laies.

Figure 28: Laeis hydraulic press [84]

The advantages of hydraulic presses include their high compaction force, high productivity, consistency and easy adjustment. Electronic control units check the heights of the shaped goods and so the cycle is automatically adjusted to ensure size uniformity. [32, p. 19]

Size uniformity is influenced by the filling factor. The filling factor is defined as the proportion between the filling height and the brick height. Usually, the filling factor is 1.5-2.

Furthermore, this type of press ensures to meet a wide range of requirements. They are also able to form complex refractories, because even complicated press programmes can be performed. [32, p. 19]

Hydraulic presses use hydraulic systems to provide the maximum pressure along the entire press stroke. Energy transfer happens slowly in form of potential energy. In general, it is differentiated between three model types of hydraulic presses (see Figure 29):

- upstroke presses,
- downstroke presses and
- double ram presses.
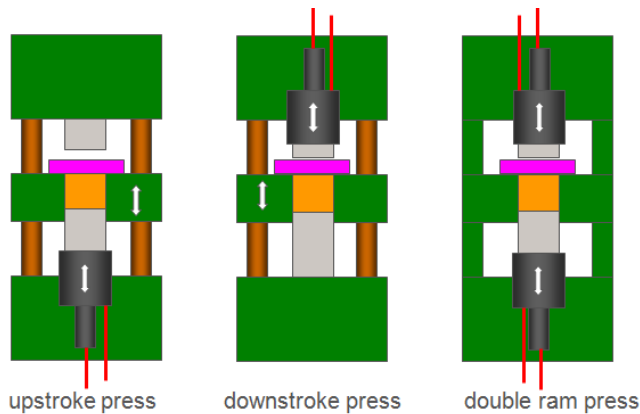
Figure 29: Model types of hydraulic presses

In upstroke presses the plunger is located at the bottom of the press, while the plunger of downstroke presses is placed at the upper part of the press. In both cases plunger and mould are moveable. The upper part of upstroke presses is fixed, instead the lower part of downstroke presses is unmoveable. Double ram presses possess one plunger at the top and one at the bottom.

In general a hydraulic press consists of the components represented in Figure 30.
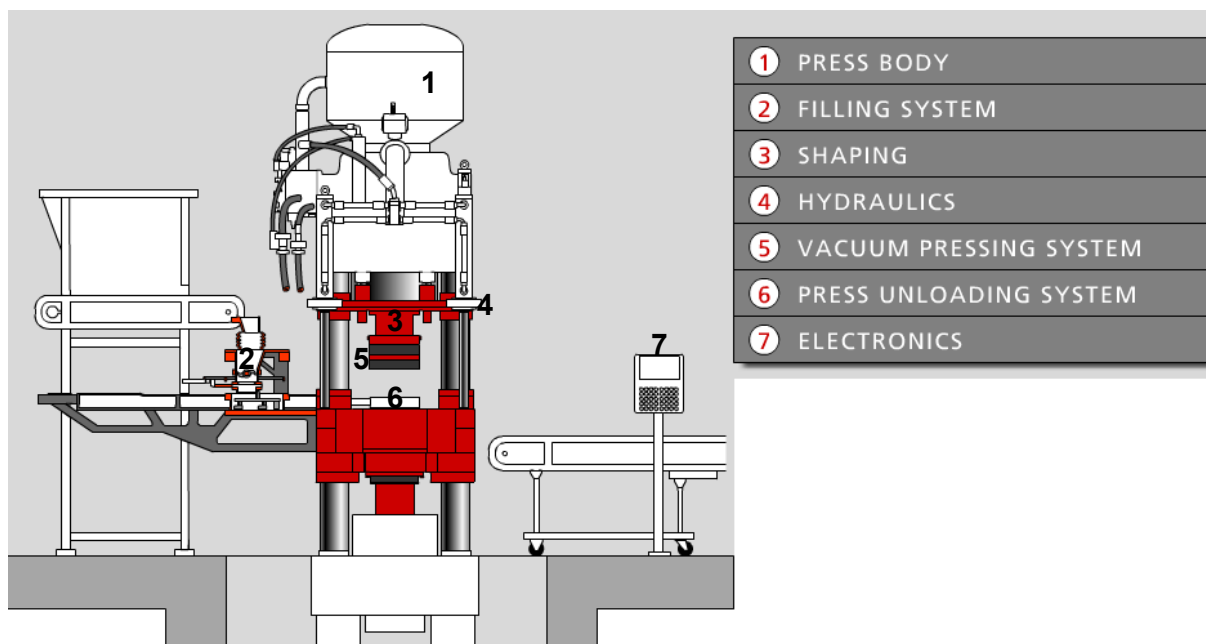
Figure 30: Components of hydraulic presses [84]

The process of pressing consists of the steps material loading, mould filling, compaction and unloading. One cycle lasts approximately 18-60 seconds. Strain gauges are used for monitoring purposes in order to check the applied pressure. The aspects that are of highest importance for the process of pressing are mixing and filling. The system may pulsate, if the material to be compacted is not mixed homogenously. Furthermore, filling has to be performed very precise in order to ensure that each unit exhibits the same density distributed along the entire brick length.

Material loading:

Transport to the pressing unit, stockage at the press and transport from the storage bin into the mould have decisive influence on the quality of the brick, because segregation and precompaction might be the effects of these actions. In order to prevent these negative aspects, material loading is arranged according to Figure 31.
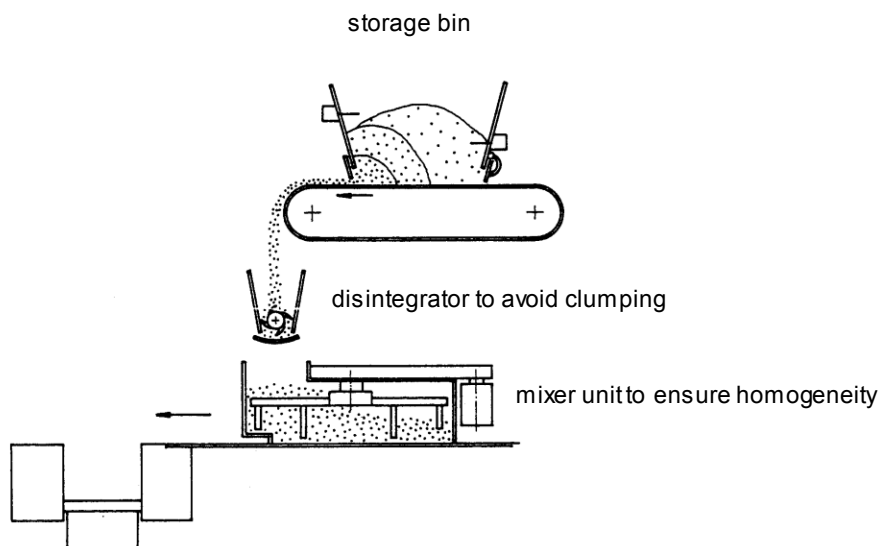
Figure 31: Material loading scheme

Mould filling:

Filling has essential impact on the density and quality of the bricks. Therefore, uniform quality is only achieved, if filling stays consistent.

Filling of the mould can be arranged either by volume or by mass. Filling by volume means that the mould is completely filled, while gravimetric filling means that a certain mass has to be achieved. In practice volumetric filling is preferred, gravimetric filling is seldom found. Actually, gravimetric filling is applied for special formats.

Mould filling is accomplished via filling shoe (see Figure 32). The material is loaded into the filling shoe, which transfers the material into the mould.
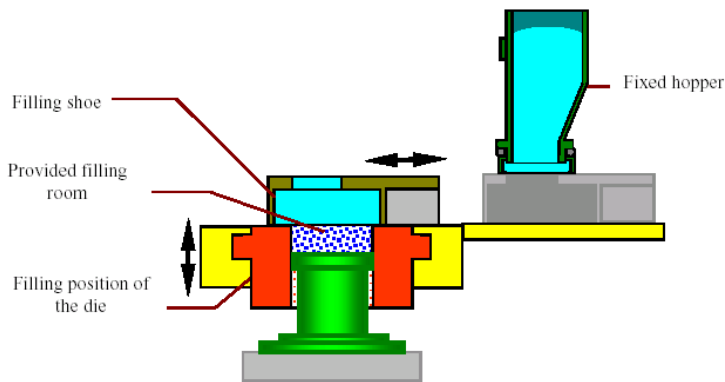
Figure 32: Mould filling

Concerning filling technique, filling can be realised either by falling or sucking (see Figure 33 and Figure 34). The difference between these two possibilities is the moment when the filling position of the mould is achieved. Filling by falling means that the filling position is achieved before the filling shoe is placed above the mould and so the material falls into it. Instead filling by sucking means that the filling shoe is placed above the mould and then the filling position is achieved. So the material is sucked out of the filling shoe and into the mould.
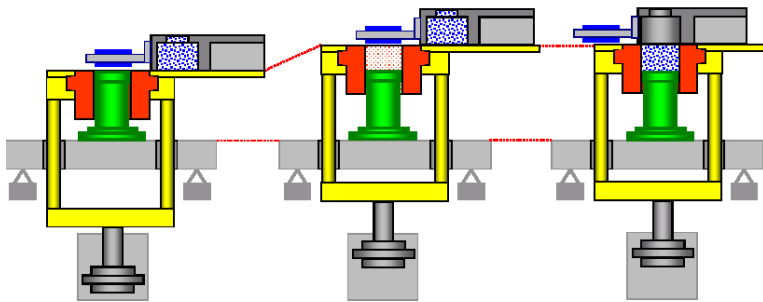
Figure 33: Filling by falling
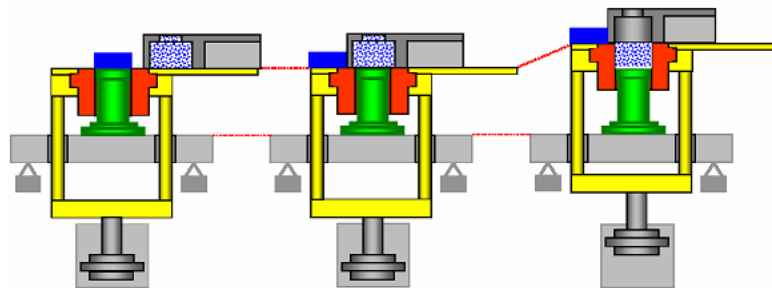
Figure 34: Filling by sucking

A correction of the filling height is necessary during the return journey of the filling shoe to ensure a constant density allocation along the whole length of the brick.

Compaction:

Pressing can be performed either one-sided or two-sided where upstroke, downstroke and double ram presses belong to. One-sided pressing means that compaction is realised only by the movement of one part of the press.

Operating speed is high at the beginning of the pressing process, but gets lower near the set pressure in order to achieve it. Then the set pressure is applied for a few seconds and after that, force decreases again slowly.

The process of pressing is finished, if either a specified pressure is achieved or the piston has covered a specified distance. A specified pressure is essential, if density is the crucial criterion. The covered distance of the piston is decisive, if the shaped product requires a certain format. Pressure and covered distance are plotted in a graph. This graph contains the minimum and maximum pressure as well as the minimal and maximal covered distance of the piston. According to this graph the tolerance limit for the desired quality of the shaped goods can be determined.

The aim of pressing is to arrange an optimised particle distribution in order to generate a certain density. Thus, the air contained in the material must be released, what is called venting. Venting is an operation where compaction is interrupted at certain pressure levels and even pressure is lowered. The number of strokes depends on the quality of the material and desired format. Venting pressure depends on the air content of the material and shall not be more than a third of the operating pressure for pressing. Working under vacuum is another method regarding venting. However, the effect lamination, which causes horizontal placed cracks in the shaped product, can appear due to entrapped air.

Unloading:

Unloading has to take place slowly and carefully, because otherwise cracks might be formed. After pressing is finished, the brick is removed out of the mould. Finally, an optical control is carried out to check, if the brick either is correct or belongs to rejections.

Pressing at RHI

At RHI downstroke presses are most commonly used. It is possible to treat up to eight blanks at the same time. Hydraulic presses up to a installation size of 3,200 tonnes and an operating pressure of 315 bar are applied.

3.6.3 Batch preparation and shaping at RHI

The flow chart below (see Figure 35) demonstrates the typical arrangement of the processes preparation, dosing, mixing and forming at RHI.
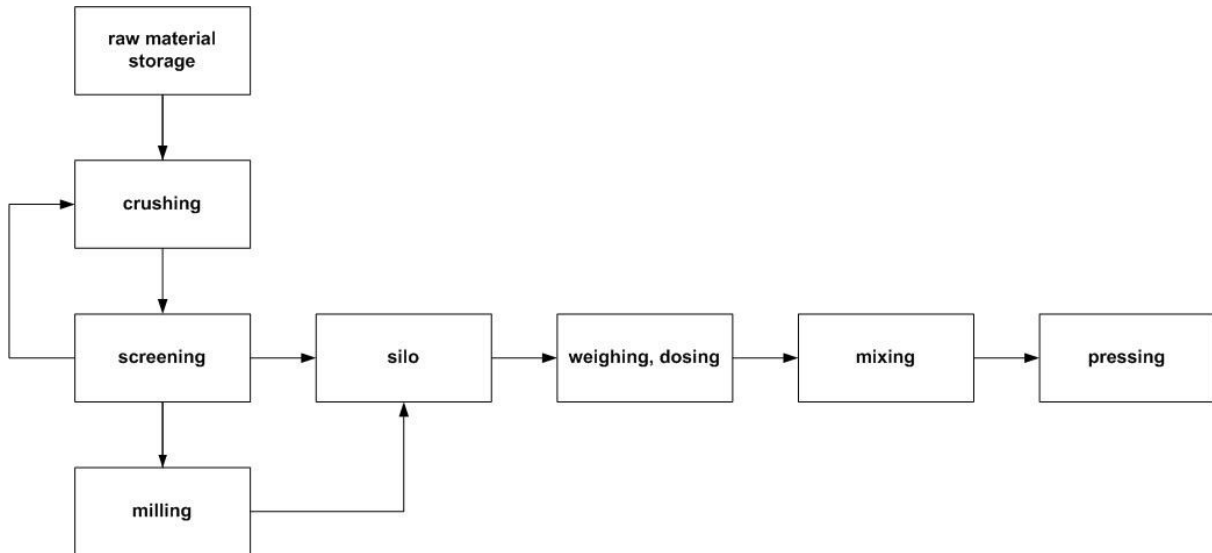
Figure 35: Batch preparation and shaping processes at RHI

The required grain fraction is achieved by crushing and screening. Oversized material has to pass crushing again to receive a limited grain size distribution. Fines are produced via ball mills. The different grain sizes and qualities are stored in silos. From there the components are dosed by weighing equipment according required recipes. As mentioned before, horizontal mixers from m-tech or lödige are used for producing unshaped refractories and vertical Eirich mixers are used for the production of shaped refractories. Unshaped products are packaged directly after mixing. For shaped products a binder is added during the mixing process. The batch is transferred immediately from the mixer to the press. Pressing is performed by Laeis hydraulic presses

3.6.4 CO_2 calculation approach for batch preparation and shaping

One and the same approach is applied in order to identify the respective emission factors of batch preparation and shaping, because these processes have in common that electricity is the only component that has an impact on their CO_2 balance. Their specific CO_2 emissions are calculated on basis of data from RHI sites located in Dalian (China), Ramos Arizpe (Mexico), Radenthein and Veitsch (both Austria). These plants are chosen, because those four represent the biggest plants in the RHI's global network. For this reason a large product portfolio of refractories is considered and consequently, a wide range of different technologies used in refractory industry is covered. Therefore, the results can be seen as representative.

The calculation approach is to determine the average energy demand for the units batch preparation, which includes crushing and grinding, sorting and screening, dosing as well as mixing, and shaping according to the above mentioned sites. In order to identify this average energy demand, the production output [t] and the electricity demand [kWh] of these processes are needed for each of the four plants. After collecting the essential data for the year 2010, the determination of the average specific CO_2 emissions for each operation could be started. For this purpose, the specific energy demand [kWh/t] per plant for each process must be calculated. Finally, the average specific energy demand of the respective process is multiplied by the emission factor for electricity according to chapter 3.3.4.

A summary of the necessary steps is indicated subsequently for determining the specific CO_2 emissions concerning batch preparation and shaping.

1. Specifying annual production output and annual electricity demand for the respective process.

2. Dividing electricity demand by production output to obtain the specific electricity demand per tonne for the respective process.

3. Performing the same steps again for each plant.

4. Calculating the average specific energy demand of all plants for the respective process.

5. Multiplying the average specific energy demand by the emission factor for electricity to calculate the average specific CO_2 emissions for the respective process.

6. The emission factor of batch preparation is the total sum of the average specific CO_2 emissions of the processes crushing and grinding, sorting and screening, dosing and mixing.

The calculated average results are mentioned in Table 29.

Table 29: Emission factors for batch preparation and shaping

process	energy demand [kWh/t]	specific CO_2 emissions [kg/t]
batch preparation	42.81	17.71
shaping	29.82	12.33
total	**72.63**	**30.04**

17.71 kg CO_2/t are generated due to batch preparation, while the process of shaping effects **12.33 kg CO_2/t**. In total a quantity of about 30 kg CO_2/t is produced by these operations.

Assumption for crushing:

The grain size of the individual raw materials is not considered in detail. As a matter of fact, the explicit impact of the different grain sizes on the required energy demand, and consequently on the arising amount of CO_2, is negligible compared to the total carbon footprint.

3.7 Heat treatment

The phases of heat treatment belong to the most important steps in the production process of a refractory product. In addition, the stage of heat treatment is also a very important part of each carbon footprint calculation. As a matter of fact, the energy consumption is high, which strongly influences the CO_2 balance. Apart from raw material production, heat treatment causes the highest amount of CO_2 in a life cycle of a refractory product. As mentioned in chapter 3.3.3, heat treatment of fired bricks contains drying and burning, while the operation of tempering is applied to unfired bricks.

3.7.1 Fired bricks

Drying

The objective of the stage of drying is to evaporate the water that was needed in the process of shaping and to prevent the incidence of dry cracks or defects after firing. Therefore, the pressed goods and in particular larger shaped parts have to be dried carefully and completely. Drying time depends on the brick shape as well as on the drying behaviour and lasts from several days to several weeks. After drying the goods are solidified and no changes in shape will be possible anymore. [24, p. 27]; [73, p. 26-28]

Drying starts in an atmosphere where the water vapour partial pressure is lower than the partial pressure of the water in the pressed goods. However, loss of water causes volume decrease. This effect is called drying shrinkage. Drying shrinkage is proportional to water loss and depends on the water content of the pressed goods and the occurrence of swellable clay minerals. Additionally, drying shrinkage increases with decreasing grain size, because then the particles are not placed as closely together. Ending of drying shrinkage is achieved at a water content of about 10 weight %. Drying strength is controlled by temperature. Above 40 °C drying strength rises, because of the reducing water content, but above 250 °C drying strength falls again. The tendency to form cracks is called sensitivity of drying. This sensitivity is proportional to drying shrinkage. But cracks can also be formed after drying due to absorption of water from ambient air humidity. [85, p. 50-56]

Assumption for drying:

No CO_2 is caused due to drying, because heat recovery is state of the art and therefore no external heating is used.

Burning

The aim of burning is to receive a mechanically solid body. A big solidity is only achieved at higher temperatures that effect sintering or a liquid phase. [85, p. 58]

In this stage the characteristic structure of a fired brick is formed as a result of various processes such as transformations, reactions in solid state, recrystallisation, melting phase formation, release and excretion processes. This characteristic structure is defined as the type, amount, size, shape, orientation and arrangement of the phases, which built the materials' composition. The structure of fired refractory materials consists of three main components; the grain, the bond matrix and the pores. During burning the grain is principally not modified significantly. The bond matrix forms first during firing. Many properties are specified by the pores. Porosity and creep in compression decrease with increasing firing temperature as well as duration, while cold and hot crushing strength, refractoriness under load, mean pore size, gas permeability and crystallite size rise. However, burning temperature is limited, because too high temperatures cause shrinkage and deformation. This influences negative the specified shape and accuracy requirements of the bricks. The combustion atmosphere is adapted to the refractory material and therefore total firing time ranges from three days to several weeks. In general, gas-heated or oil-fuelled tunnel kilns, shuttle kilns or hood-type kilns are used for the process of burning. [24, p. 27-29]

Assumption for hood-type kilns:

In case of RHI, the amount of products fired in hood-type kilns is very low compared to the total amount of fired goods. The most applied furnaces are tunnel kilns. Thus, it is assumed that this amount is included in the specific CO_2 emissions of tunnel kilns. [23]

Shuttle kilns

Shuttle kilns, as well as hood-type kilns, belong to intermittent or rather discontinuous furnaces. A single chamber is charged with the material, sealed and then subjected to a defined firing cycle. The ware, which is fired, is brought to the hearth area in a shuttle car. Usually, gas burners are employed for heating, whereby a good control of the process and the oven atmosphere is achieved. This type of kiln is mainly used for smaller scale manufacture of specialised products, such as special shaped bricks. The advantages of shuttle kilns are that they allow a good controllability of the temperature and offer flexibility, if the type of ware that should be fired changes frequently. However, intermittent kilns exhibit a lower energy efficiency. A cross-section of a shuttle kiln is shown in Figure 36. [32, p. 25]
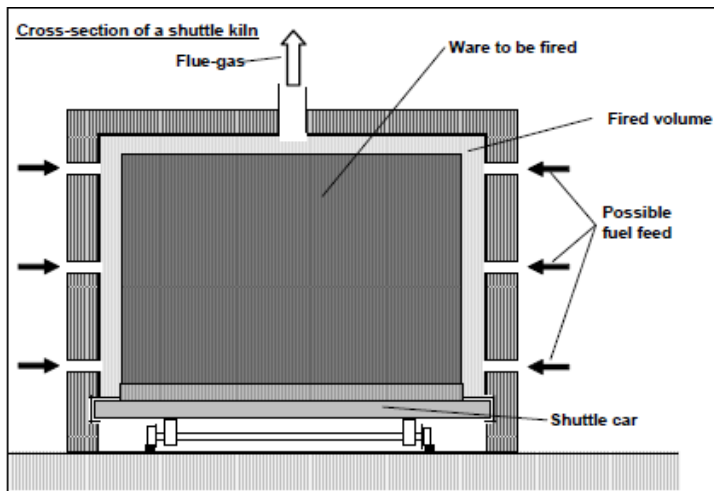
Figure 36: Shuttle kiln [32, p. 26]

Tunnel kilns

Tunnel kilns can be operated continuously and consist of a preheating, firing and cooling zone. The kiln cars, on which the ware is transported, are carried by rail tracks and are pushed through the furnace with different temperature levels at set intervals or continuously. Tunnel kilns are mostly gas-fired and operated on basis of the countercurrent principle where a flow of air is drawn by fans to an exhaust duct near the car entry zone. For this reason, the ware is preheated by hot gases from the firing zone, whilst incoming air cools the fired material. Therefore, the air itself is preheated for its combustion role. Generally, the firing chamber and kiln cars are sealed against secondary air with a sand seal in order to reduce firing time and energy demand by having a gas-tight firing chamber. [32, p. 26]

Figure 37 below shows a schematic view of a tunnel kiln.
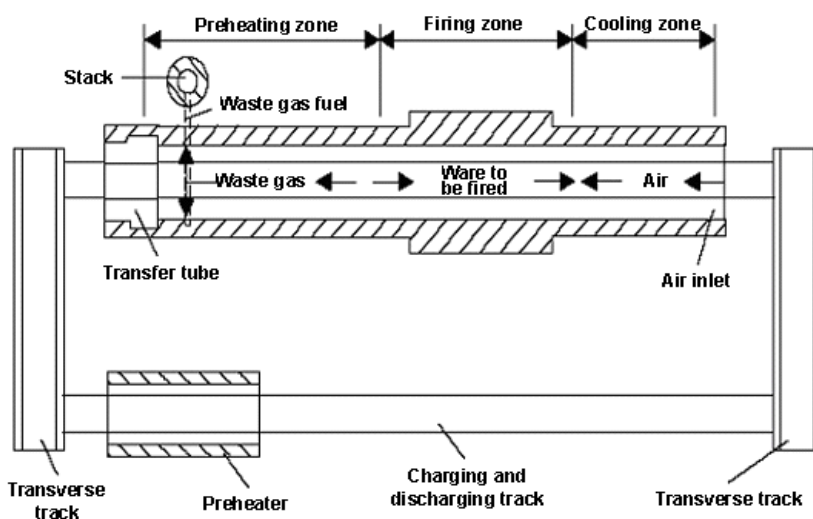
Figure 37: Tunnel kiln [32, p. 27]

The off-gas is released through the chimney with temperatures of 150-350 °C. The performance of such a kiln is determined by the tempo in which the kiln cars are pushed through the furnace. Thus, the performance is expressed as cars per day. The tunnel kilns of the corporate group RHI are operated at firing temperatures between 1,100 °C and 1,850 °C and exhibit an overall length between 50 and 160 metres. The operation mode is adapted to the treated product group. [23]

3.7.1.1 CO_2 calculation approach for fired non basic bricks

Fired non basic bricks are divided into three groups; fireclay, silica and high alumina bricks (see chapter 3.2.4.1.1). High alumina bricks include refractories made of andalusite and mullite as well as of bauxite and corundum.

In general both types of kilns are used for accomplishing the firing process.

Tunnel kilns

Concerning tunnel kilns the specific energy demand could be found in literature. As described before, tunnel kilns are usually gas-fired. In order to identify the quantity of CO_2, natural gas expressed as kJ must be transformed into the unit m^3. For this purpose the mentioned specific energy demand is divided by the factor 31,500 [23]. The conversion from m^3 into kg CO_2 is realised with a conversion factor of 1.9944 (calculated based on the heating value and emission factor of natural gas in Table 13).

The approximately specific energy demand for the firing process of different non basic bricks as well as the resulting emission factors are represented in Table 30, assuming that for burning a gas-heated tunnel kiln with an annual performance of about 20,000 tonnes is used.

Table 30: Emission factor for burning non basic bricks in tunnel kilns [24, p. 28]

brick grades	firing temperature [°C]	energy demand [kJ/kg]	emission factor [kg CO_2/t]
fireclay bricks	1,250-1,500	3,000	189.94
silica bricks	1,420-1,500	6,000	379.89
high alumina bricks	1,500-1,800	5,000	316.57

Shuttle kilns

The specific CO_2 emissions for burning different brick types made of non basic materials in a shuttle kiln with loads of about 200 tonnes are shown in Table 31. Data from RHI is used that derives from plant Niederdollendorf (Germany), which houses three shuttle kilns, in order to determine these emission factors. The specific energy demand for the gas burners expressed in kJ is transformed into m^3 natural gas and then into the equivalent amount of CO_2 with the same calculation methods as applied before. Based on all operations in year 2010 with a capacity utilisation of over 50 %, an average value for each brick grade is built.

Consequently, the quantity of CO_2 produced by shuttle kilns is a lot higher than that of tunnel kilns.

Table 31: Emission factor for burning non basic bricks in shuttle kilns

brick grade	firing temperature [°C]	specific CO_2 emissions [kg CO_2/t]
fireclay bricks	1,140	949.89
silica bricks	1,450	647.11
high alumina bricks	1,500-1,600	1,106.03

3.7.1.2 CO_2 calculation approach for fired basic bricks

Fired basic bricks are classified in accordance with their firing temperature. Products that own low heat resistance are burned under 1,500 °C, while products with high heat resistance are burned over 1,500 °C. Mainly, tunnel kilns are used for the firing process of magnesia containing bricks. [23]

The quantity of CO_2 arising from burning basic bricks in agreement with their heat resistance is calculated on basis of data from the RHI production sites Mainzlar, Niederdollendorf, Trieben, Veitsch and Radenthein that operate tunnel kilns. An average value for high heat resistant products as well as for low heat resistant products is formed out of the specific CO_2 emissions of the respective plants. An average value of **357.10 kg CO_2/t** results for high heat resistant products. The specific CO_2 emissions for products burned below 1,500 °C are **263.90 kg CO_2/t**. Concluding, CO_2 due to the burning process of high heat resistant products is about 1.4 times higher than from low heat resistant products.

3.7.2 Unfired bricks

Tempering

Unfired bricks are dried or rather heat-treated at temperatures above 150 °C to increase strength by additional chemical reactions and to remove volatile components or hydration water. [24, p. 27]

During tempering, the bricks are heated to 200-600 °C in an annealing furnace for changing their hardness and strength properties in order to make them less brittle and more workable. [23]

Tempering is followed by the stage of thermal oxidising. As mentioned in chapter 3.2.4.2, during thermal oxidising **7.33 kg CO_2/t** are produced due to splitting-off volatiles out of pitch-bonded bricks that are converted into CO_2.

3.7.2.1 CO_2 calculation approach for unfired bricks

The relevant energy inputs for the process of tempering are electricity, due to manipulation of goods and the ventilator, and the consumed gas of the burner. [23]

Concerning electricity the same CO_2 calculation approach is applied like in chapter 3.6.4 for batch preparation and shaping. An average value for electricity consumption of 17.74 kWh/t is determined on basis of data from the RHI plants Dalian, Ramos, Radenthein and Veitsch. The quantity of CO_2 results from multiplying the average electricity consumption by the electricity emission factor (see chapter 3.3.4).

For tempering resin-bonded bricks less amounts of gas (15 m^3/t) are required compared to pitch-bonded bricks (45 m^3/t), because hardening takes places at lower temperatures. Therefore, fewer CO_2 is produced as a consequence of a lower gas input. The gas consumption for pitch-bonded bricks refers to an annealing furnace with a capacity of 30,000 tonnes per year. The mentioned data derive from expert knowledge of RHI production sites. Natural gas consumption expressed in the unit m^3 must be converted into the equivalent quantity of CO_2 by applying a factor of 1.9944, as described before. Table 32 summarises the mentioned energy inputs for the process of tempering and the resulting specific CO_2 emissions.

Table 32: Emission factors for unfired bricks

input	consumption rate	specific CO_2 emissions [kg CO_2/t]
electricity	17.74 kWh/t	7.34
gas (resin-bonded bricks)	15 m^3/t	29.92
gas (pitch-bonded bricks)	45 m^3/t	89.75

3.8 Finishing [32, p. 29-30]

In some cases, but not in all, any kind of product finishing is necessary for shaped products. Machining operations such as cutting, grinding, drilling and sawing are applied to those products whose final shape or dimensional tolerance is not achieved technically or with sufficient accuracy during primary processing. This chapter introduces the most important procedures of finishing and overviews the approach for the carbon footprint calculation regarding finishing.

Cutting

The purpose of brick cutting operations is to obtain specified dimensions or non-standard shapes or to accomplish dimensional correction. For this reason machine tools equipped with diamond saw blades are used. Mostly, brick cutting is performed under wet conditions in which water or a cutting fluid are applied in order to cool the work piece, to prevent frictional heat and to remove chipped powder. [26, p. 331]

Grinding

Grinding is a batch process in which the pieces are fixed to a table that traverses under a diamond machining head. The process of grinding can be realised wet or dry. Wet grinding is utilised for the finishing of products that require the tightest dimensional tolerance. In the case of dry grinding, the whole grinding device is encapsulated or equipped with dust collectors.

In refractory industry diamond cup wheels are widely used to realise grinding. For dry grinding those diamond cup wheels are applied that are designed for electric hand tools and for wet grinding those that are designed for milling machines. [26, p. 332-333]

Drilling

Diamond core drills are used to drill holes into refractory bricks for purposes such as collecting samples, inserting measuring devices, tapping molten metal and inserting bricks of different materials. According to the variety of the brick and the function of the hole, drilling can be arranged in wet or dry conditions. [26, p. 334]

Refractory products often need to be drilled, because the accuracy for the required hole is not achieved during pressing and firing operations.

Sawing and other operations

Sawing is applied, if the final shape of a refractory brick is not effectively produced at the stage of pressing. Then oversized bricks are sawn to the necessary dimension.

Sometimes polishing is involved in the process of finishing to achieve a shiny and unglazed homogenous surface. Certain facing bricks are given an antique finish by passing them through a rubber-lined rotating inclined drum where sharp corners are removed and a softer profile is produced.

Impregnation

For certain applications the fired ware must be impregnated. The aim of impregnating bricks with pitch, resin or phosphate solution under vacuum is to enhance corrosion resistance [24, p. 29].

The presence of carbon in the final product offers advantages like increased thermal shock resistance as well as increased resistance to penetration by slag and metal, because the carbon acts as a pore filter and reduces the permeability of the product.

Pitch impregnation is a batch process. Typically the impregnation is carried out in three upright cylindrical vessels. The products being impregnated are loaded into metal baskets that fit inside the vessels. The ware is heated in the first vessel up to 200 ºC via a circulating stream of hot air. Then the basket and contents are transferred into the second vessel. The second vessel is an autoclave, equipped with a heating jacket to maintain the temperature. Next this vessel is sealed, evacuated and filled with liquid pitch that is drawn from bulk storage tanks and maintained at temperatures of around 180-200 ºC. The impregnation of the ware is achieved by releasing the vacuum and then applying nitrogen at an elevated pressure. After draining, the basket and contents are transferred into the third vessel for the purpose of cooling to a temperature below that at which volatile pitch components (complex hydrocarbons) could be evolved. The pitch volatiles have to be removed, because these may affect the working environment when the refractory products were put into service. Typically, this is achieved by transporting the impregnated ware into a furnace and to undergo a defined heating cycle. The oven has an exhaust fan that discharges the off-gas into a thermal oxidiser. The conditions for thermal oxidising are temperatures of more than 800 ºC and a dwell-time of minimum 0.5 seconds, because these conditions ensure that all pitch volatiles are completely oxidised.

However, another widespread method for impregnation exists. There, the ware being impregnated is positioned on pallets that are only used for impregnation. After that, the pallets pass through a tunnel. In this tunnel the goods are preheated, then sunk-in a vessel where impregnation happens and finally they are cooled. The pallets for impregnation are used again. [23]

The use of pitch-impregnated bricks is limited to cases where superb erosion resistance is required such as the converter mouth, frames for tap holes or purgers and ladle slide gates. [24, p. 182]

3.8.1 CO$_2$ calculation approach concerning finishing

The assessment of the specific CO$_2$ emissions occurring from the procedures of finishing is based on data of RHI plant Radenthein, because this site offers about 20,000 single articles. Therefore, Radenthein is called the refractories specialties plant in RHI's global network. This production site offers tailor-made concepts and exhibits the latest manufacturing technologies.

Regarding the specific CO$_2$ emissions of finishing, the intention is to determine an average value, formed under consideration of the entire finishing steps for the product portfolio of Radenthein in 2010. Following steps are completed in order to achieve this representative value.

1. Specifying all work stations concerning finishing.
2. Checking the processible tonnage per work station.
3. Determining the performance [t/h] per work station.
4. Defining the efficiency factor [%] that signalises the real performance per workstation.
5. Identifying the connected load [kW] of the facilities per work station.
6. Calculating the electricity consumption.
   Electricity consumption per work station [kWh] = tonnage/performance*efficiency factor*connected load
7. Summing up the electricity consumption of all work stations to obtain the total electricity consumption.
8. Dividing the total electricity consumption by the total processible tonnage for achieving the specific electricity consumption. [kWh/t]
9. Multiplying the specific electricity consumption by the emission factor for electricity to calculate the specific CO$_2$ emissions.

Here in this case, the specific electricity consumption is 15.64 kWh/t. A specific emission factor of **6.47 kg CO$_2$/t** results for the process finishing after carrying out all these steps. It is being recognized that the stage of finishing does not belong to one of the crucial factors of the carbon footprint for a refractory product.

3.9 Packaging

Regarding the "cradle to gate" approach, packaging is the last step of a refractories' production, before the finished goods are dispatched to their customers. Concerning CO_2 balance packaging would not be crucial for the overall result. This chapter informs about how packaging is arranged for shaped and unshaped products in practice. Besides, the approach for the calculation of the specific CO_2 emissions arising from packaging is mentioned.

Packaging for shaped products

A standard packaging for shaped products in refractory industry is designed in the following way. The goods are put into cardboards, positioned on wooden pallets and wrapped with a shrink film made of polyethylene (PE). Small gas burners that transfer heat to the material are applied for the effect of shrinking. [23]

A plastic hood with a size that is bigger than the pallet is sliced over it. In order to shrink, the foil needs to be heated. Due to shrinking the ware is strongly held together on the pallet. This type of packaging can be arranged automatically or manual, but then still a heater is necessary. [86]

The latest development in the area of refractory packaging films is the new stretchhood foil that is applied by RHI (see Figure 38).

Figure 38: Stretchhood packaging material [23]

At the moment this kind of packaging film conquers the market. Presently, stretchhood is the strongest, most flexible and environmentally friendly type of packaging. By using that foil a second material, which acts as an additional reinforcement, is dispensable. Thus, cost savings and environmental protection are the results.

Subsequently, some advantages of stretchhood foils are listed:

- improved safety, because tearing cannot appear and the shape stays stable under highest load and stress;

- better protection, especially from moisture and dust if the packaging has been partially opened;

- depending on the application, a multilayer film can be installed that improves the strength of the packaging;

- easier to handle and quick to open;

- simple and inexpensive disposal. [23]

Stretchhood combines the properties of shrink films and normal stretch foils and is an intelligent foil for load securing. This kind of foil is put around the pallet under tension and with the help of its memory effect, the foil tries to get back to its original shape. For this reason the pallet is kept together extremely strongly. The finished pallet is moved to the stretchhood installation. There, an electric eye records the height of the pallet and according to this measurement the correct size or rather format of foil is chosen. The foil is rolled off onto four mechanical arms and stretched out. Then the mechanical arms move downwards until the end of the pallet length is reached. When the stretchhood leaves the arms, the foil turns into its original format again. The pallet is ready for shipping after passing through this process. [86]

A pallet is a standardised transport support for all kinds of goods. Pallets are practically to apply and easy to handle due to standardisation. Pallets can be made of different raw materials. Predominantly, wooden pallets are applied in refractory industry. The CO_2 balance for one europallet is given in Table 33. [87]

Table 33: Emission factors for wooden pallets [87]

process	produced quantity of CO_2 [kg]
CO_2 emissions from harvesting and transport to pallet manufacturer (100 km)	0.40
CO_2 emissions from production	4.67
CO_2 emissions from transportation to user (200 km)	0.42
CO_2 balance	**5.49**

Depending on regional differences palletising can be accomplished by robots or by workers. At RHI for most instances palletising is arranged fully automatically. But in some plants manual palletising is still done (e.g. China). [23]

Packaging for unshaped products

Packing unshaped products is more simple. In general unshaped refractory products are weighed into bags and then palletised. [32, p. 31]

Common bags for mixes are made of PE or paper. Big bags made of plastics are also often applied. Big bags are usually available in two sizes: bigger than 1,250 kg or smaller than 1,250 kg. Normally, mortars are filled into pails made of plastics. [23]

Figure 39 demonstrates a big bag with a load capacity of maximal 1,250 kg and a possible application for paper bags.

big bag [88]
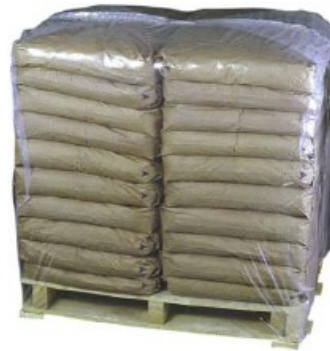
paper bags [23]

Figure 39: Common bags for mixes

3.9.1 CO_2 calculation approach for packaging

The idea for assessing the specific CO_2 emissions arising from packaging is to form an average value on basis of every single type of packaging material that was used at RHI in 2010. The resulting value is a combination of all kinds of packaging applied to refractory products (shaped, unshaped products etc.). For this purpose the total packaging material is related to the total quantity of delivered finished goods according to all RHI production sites worldwide. In order to realise this approach, the following steps have to be accomplished:

1. Identifying the total quantity [t] of packaged goods concerning all plants.

2. Checking the total number of used packaging material per type of packaging concerning all plants.

3. Multiplying the total number of used packaging material per type of packaging by the respective weight of the packing for determining the consumed quantity [kg] per type of packaging.

4. Multiplying the consumed quantity per type of packaging by the appropriate emission factor [g/kg] of the respective type of packaging in Table 34 to obtain the corresponding amount of CO_2.

5. Summing up the CO_2 emissions of all types of packaging to receive the total quantity of CO_2 [kg].

6. Dividing the total quantity of CO_2 by the total quantity of packaged goods to calculate the specific amount of CO_2 per tonne finished goods.

In case of RHI the different types of packaging materials are: cardboard, strapping (made of steel), shrink foil, paper bags, PE bags, big bags, pails (made of plastics), stretchhood foil and aluvac (packaging made of aluminium) [23]. The applied emission factors are those that are listed in Table 34.

Table 34: Emission factors of different packaging materials [89, p. 8]

packaging made of	emissions factor [g CO_2/kg packaging]
paper, cardboard	676
plastics	3,453
steel	1,095
aluminium	5,570

According to the above mentioned approach, a total amount of 18,830,144 kg CO_2 is calculated for these packaging materials and related to 1,332,781 tonnes of packaged goods. This means that for the packaging material a specific factor of **14.13 kg CO_2/t** results.

In addition to the calculated emission factor for the packaging material, in most cases the electricity consumption for palletising and the emission factor for the wooden pallet have to be considered too.

Concerning electricity consumption of palletising, the same approach is applied like in chapter 3.6.4 for batch preparation and shaping. An average value for electricity consumption of 11.09 kWh/t is determined on basis of data from the RHI plants Dalian, Ramos, Radenthein and Veitsch. The quantity of **4.59 kg CO_2/t** results from multiplying this average value by the electricity emission factor (see chapter 3.3.4).

Table 35 overviews the total specific CO_2 emissions arising from packaging, if palletising is applied too. The result is a value of **24.21 kg CO_2/t** packaged goods.

Table 35: Emission factor for packaging

parameter	emission factor [kg CO_2/t packaged goods]
packaging material	14.13
energy demand for palletising	4.59
wooden pallet	5.49
total	**24.21**

Assumption for shaped refractory products:

The slight gas consumption for shrinking the foil is negligible in this Master Thesis, because the used amount is insignificant compared to the used amount of other gas consuming facilities. Furthermore, the required gas quantity for shrinking is less than 1 % of the total consumed gas quantity in a refractory product's life cycle.

4 Practical application of the calculation model

The practical application of the calculation model developed in this Master Thesis is tested on basis of a lining concept for a reference asset in the cement industry. The asset with an oven length of 50 m, a diameter of 4.6 m and an annual output of 50,000 t clinker consists of a five-stage cyclone preheating, the calciner, the inlet chamber, the kiln hood, the rotary kiln, the grate cooler and the tertiary air duct. Table 36 represents the lining concept for this asset in detail.

Table 36: Lining concept for a reference asset in the cement industry

reference asset cement industry	refractory products	quantity [t]
cyclone preheating	alumina mixes	250
	fireclay bricks	250
calciner	alumina mixes	300
	fireclay bricks	300
inlet chamber	alumina mixes	35
	andalusite+mullite bricks	35
kiln hood	alumina mixes	90
	andalusite+mullite bricks	90
rotary kiln	magnesia-spinel bricks	350
	bauxite+corundum bricks	150
grate cooler	alumina mixes	100
	andalusite+mullite bricks	100
tertiary air duct	alumina mixes	200
	andalusite+mullite bricks	200
total		**2,450**

For this reason the found results of chapter 3 are transferred into Microsoft Excel. First of all, the specific CO_2 emissions of the product groups concerning shaped refractories and magnesia mixes as well as alumina mixes have to be calculated. They are determined for each product group on basis of the developed generally applicable recipes (mentioned in section 3.2.4). Therefore, the emission factor of every raw material contained in the product group is multiplied by its percentage rate in the recipe. The sum of them has to be formed in order to get the emission factor for the product group. The results, which only include the raw materials according to the recipes but no production procedures, are shown in Table 37.

Table 37: Emission factors for the product groups according to recipes

product group	refractory products	emission factor [kg CO_2/t]
fired non basic bricks	silica bricks (<10 % Al_2O_3)	104.30
	fireclay bricks (<45 % Al_2O_3)	507.10
	andalusite+mullite bricks (<75 % Al_2O_3)	306.54
	bauxite+corundum bricks (>75 % Al_2O_3)	1,007.41
	CA bricks	1,383.84
	SiC bricks	5,770.30
	zircon-containing bricks	14.67
fired basic bricks	magnesia bricks	1,913.56
	magnesia-spinel bricks	1,746.54
	magnesia-chromite bricks	1,467.17
	magnesia-zircon bricks	1,641.72
unfired non basic bricks	AMC bricks	1,152.87
unfired basic bricks	MgO-C bricks (resin-bonded)	1,965.23
	MgO-C bricks (pitch-bonded)	1,614.98
unshaped refractory products	alumina mixes	647.10
	magnesia mixes	1,449.00

The specific transport emissions of the product groups arising from the delivery of the contained raw materials are determined according to chapter 3.5.2. The origin of the raw materials in Table 24 serves as basis for choosing the transport route and consequently the relevant transport emission factor mentioned in Table 26. It is assumed that the products are manufactured in Austria. In order to calculate the transport emission factors for the product groups, the transport emission factor of each raw material included in the product group is multiplied by its percentage rate in the recipe and then the sum of them is formed. The results can be seen in Table 38.

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Table 38: Transport emissions for the product groups

product group	refractory products	transport emission factor [kg CO₂/t]
fired non basic bricks	silica bricks	81.50
	fireclay bricks	94.95
	andalusite+mullite bricks	120.83
	bauxite+corundum bricks	95.92
	CA bricks	7.38
	SiC bricks	73.78
	zircon-containing bricks	126.90
fired basic bricks	magnesia bricks	25.92
	magnesia-spinel bricks	12.31
	magnesia-chromite bricks	46.07
	magnesia-zircon bricks	79.66
unfired non basic bricks	AMC bricks	143.52
unfired basic bricks	MgO-C bricks (resin-bonded)	136.50
	MgO-C bricks (pitch-bonded)	86.20
unshaped refractory products	alumina mixes	91.62
	magnesia mixes	7.38

The CO_2 calculation for the reference asset starts with the lining of the cyclone preheating, which includes fireclay bricks and alumina mixes. For determining the CO_2 emissions due to their raw materials, the emission factor of fireclay bricks in Table 37 is multiplied by the quantity of fireclay bricks included in the lining of the cyclone preheating in Table 36 and the same procedure is done for alumina mixes. To calculate the transport emissions due to raw material delivery, the transport emission factor of fireclay bricks in Table 38 is multiplied by the quantity of fireclay bricks included in the lining of the cyclone preheating in Table 36 and the same action is done again for alumina mixes. The production steps of bricks consists of batch preparation, shaping, heat treatment, finishing and packaging. The production of mixes is finished after batch preparation. Afterwards, packaging is the only life cycle step that has CO_2 relevance for mixes. Consequently, the quantity of fireclay bricks is multiplied by the emission factor of batch preparation in Table 29 and the quantity of alumina mixes is also multiplied by the emission factor of batch preparation in Table 29. Next, the quantity of fireclay bricks is multiplied by the emission factor of shaping in Table 29. Then, the quantity of fireclay bricks is multiplied by the respective emission factor for heat treatment in chapter 3.7. After that, the quantity of fireclay bricks is multiplied by the emission factor of finishing in section 3.8.1. Afterwards, the quantity of fireclay bricks is multiplied by the emission factor of packaging in Table 35 and the quantity of alumina mixes is also multiplied by the emission factor of packaging in Table 35. The total CO_2 emissions comprising the lining of the cyclone preheating results from summing up the calculated CO_2 emissions out of raw materials, transport, batch preparation, shaping, heat treatment, finishing and packaging. The same line of action is done for the calciner, the inlet chamber, the kiln hood, the rotary kiln, the grate

cooler and the tertiary air duct. Finally, the carbon footprint of this reference asset in the cement industry is the total sum of the carbon footprints of its components. The calculated values are demonstrated in Table 39.

Table 39: Carbon footprint for a reference asset in the cement industry

reference asset cement industry	CO$_2$ emissions [t]
cyclone preheating	408.34
calciner	490.00
inlet chamber	83.12
kiln hood	213.73
rotary kiln	1,102.34
grate cooler	237.48
tertiary air duct	474.95
total	**3,009.96**

The carbon footprint of this reference asset in the cement industry is **3.009,96 t CO$_2$**. The rotary kiln is the most CO$_2$ intensive part of the lining concept. As expected, raw materials including their production cause the highest amount of CO$_2$ by far, followed by heat treatment and transport (see Table 40). Here in this special case the CO$_2$ emissions for the transport of the products to a customer are not included in the calculation, but if they are requested the approach concerning outbound described in chapter 3.5.2 should be applied.

Table 40: Influence of the production steps/life cycle steps on the carbon footprint of the reference asset

production steps/life cycle steps	CO$_2$ emissions [kg]	CO$_2$ emissions [%]
raw materials	1,802.51	59.89
transport (inbound)	211.60	7.03
batch preparation	43.39	1.44
shaping	18.19	0.60
heat treatment	865.42	28.75
finishing	9.54	0.32
packaging	59.31	1.97
total	**3,009.96**	**100.00**

The example shown has proven that the model developed in this Master Thesis gives plausible results and is easy to use.

5 Summary

Avoiding an intolerable increase in global warming is the challenge of this century and therefore discussed worldwide. In order to achieve a reduction in greenhouse gas emissions, several climate strategies have been developed. The most known of them is the Kyoto Protocol. The EU emission trading scheme directive (2003/87/EC) was one of the mechanisms of the Kyoto Protocol. Emission trading started in 2005 and is divided into 3 periods; 2005-2007, 2008-2012, 2013-2020. In Phase III allowances - one allowance is equivalent to one tonne CO_2 - for industry and heating sectors will be allocated based on benchmarks. As a matter of fact, for several industrial sectors it was not possible to develop benchmarks. Refractory industry belongs to one of them. Due to its heterogeneous manufacturing techniques and the complexity of its products, the calculation of the carbon footprint for products deriving from refractory industry is very complicated. For that reason, no standardised approach for the whole refractory industry exists so far. This Master Thesis meets the challenge of developing a new standardised method that is plausible, easy to use and disregards local specific production processes. The developed model may serve as basis for creating a standard work for the whole refractory industry and therefore ensure representative results.

RHI, the world's market leader in refractories technology, is interested in creating a standardised model for the calculation of the carbon footprint of refractory products, with focus on dense shaped refractories (bricks), produced on basis of the coarse ceramic production.

Per definition, the carbon footprint is a measure of the total amount of GHG emissions expressed as CO_2 equivalents that are produced as direct or indirect emissions caused by activities due to persons, organisations or products. Its objective is to determine the emitted amount of GHG into the atmosphere. No international obligatory standards for the communication and assessment of product carbon footprints are known so far. However, some standards have already been developed, like The Greenhouse Gas Protocol and PAS 2050, or are under construction such as ISO 14067.

The system being analysed is bordered according the "cradle to gate" approach and contains the extraction of the raw materials and its production, batch preparation, shaping, heat treatment, finishing, packaging and transports. The developed model is arranged in form of a toolbox, which is structured according to these life cycle steps or production steps.

Shaped refractory products are classified into fired non basic bricks, fired basic bricks, unfired non basic bricks and unfired basic bricks. A generally applicable formula for each product group or sub group is developed for the carbon footprint calculation.

The most important as well as most relevant raw materials for refractory industry are identified and classified. Their production is described and the method of calculating their specific CO_2 emissions is explicated.

Furthermore, the theoretical aspects of each life cycle step or rather production step and the corresponding CO_2 calculation approaches are presented in detail.

Finally, the practical application of the calculation model developed in this Master Thesis is tested on basis of a lining concept for a reference asset in the cement industry. The found CO_2 emission factors of the raw materials and the life cycle steps/production steps are transferred into Microsoft Excel and the way of using this model is explained. The asset with an oven length of 50 m, a diameter of 4.6 m and an annual output of 50,000 t clinker consists of a five-stage cyclone preheating, the calciner, the inlet chamber, the kiln hood, the rotary kiln, the grate cooler and the tertiary air duct. The carbon footprint of this reference asset equipped with about 2,500 tonnes of refractory material is approximately 3,000 tonnes. The example shown has proven that the model gives plausible results and is simple to use.

6 Lists

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6.2 List of abbreviations

%	per cent
°C	degree Celsius
Al	aluminium
Al_2O_3	aluminium oxide (alumina)
AMC	alumina-magnesia-carbon
AOD	argon oxygen decarburization
AZS	alumina-zirconia-silica
B2B	Business-to-Business
B2C	Business-to-Customer
BFA	brown fused alumina
BIS	Department for Business, Innovation and Skills
BSI	British Standards Institution
CA	calcium aluminate
$CaCO_3$	calcium carbonate
$CaMg(CO_3)_2$	dolomite
CaO	calcium oxide
CCl_2F_2	dichlorodifluoromethane
CCM	caustic calcined magnesia
CF_4	tetrafluoromethane
CFC's	chlorofluorocarbons
CH_4	methane
$CHClF_2$	chlorodifluoromethane
cm^3	cubic centimetre
CO	carbon monoxide
CO_2	carbon dioxide
Cr_2O_3	chromium oxide
DBM	dead burned magnesia
DECC	Department for Energy and Climate Change
DIN	Deutsches Institut für Normung
e.g.	example given
ed./eds.	editor/editors
ElWOG	Elektrizitätswirtschafts und -organisationsgesetz
EN	European standards
ENTSO-E	European Network of Transmission System Operators for Electricity
et al.	et alteri (et aliquo)
etc.	et cetera
ETS	emission trading system
EU	European Union

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Fe	iron
Fe_2O_3	hematite
Fe_3O_4	magnetite
FeO	wüstite
$FeO*Al_2O_3$	hercynite
$FeO*Cr_2O_3$	chromite
FM	fused magnesia
g	gram
GEMIS	global emission model for integrated systems
GHG	greenhouse gas(es)
GWP	global warming potential
H_2	hydrogen
H_2O	water
HA	high alumina
HCFC's	hydrofluorocarbons
IPCC	International Panel on Climate Change
IR	infrared
ISO	International Organisation for Standardisation
K	kelvin
kg	kilogramme
kJ	kilojoule
km	kilometre
kWh	kilowatt hour
l	litre(s)
m^3	cubic metre
max.	maximal/maximum
Mg	magnesium
$Mg(OH)_2$	magnesium hydroxide
$MgCl_2$	magnesium chloride
$MgCO_3$	magnesium carbonate
MgO	magnesia
$MgO*Al_2O_3$	magnesia spinel
$MgO*Cr_2O_3$	magnesiachromite
MgO-C	magnesia-carbon
MJ	megajoule
mK	millikelvin
mm	millimetre
Mn	manganese
N_2O	nitrous oxide
NAP	National Allocation Plan
O_3	ozone

OECD	Organisation for Economic Co-operation and Development
p.	page
PAS 2050	Publicly available specification 2050
PE	polyethylene
R&D	Research and Development
RHI	Radex-Heraklith Industriebeteiligungs AG
SF_6	sulphur hexafluoride
Si	silicium
SiC	silicon carbide
SiO	silicon monoxide
SiO_2	silicon dioxide
SO_2	sulphur dioxide
SO_3	sulphur trioxide
t	tonne
t km	tonne-km
TBR	Top Blown Rotary
USA	United States of America
W	watt
WBCSD	World Business Council for Sustainable Development
WFA	white fused alumina
Wh	watt-hour
WRI	World Resource Institute
Zn	zinc
ZrO_2	zirconium oxide
$ZrSiO_4$	zirconium silicate

6.3 List of tables

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6.4 List of figures

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