CO₂ EMISSION FACTORS FOR NON-ENERGY USE IN THE NON-FERROUS METAL, FERROALLOYS AND INORGANICS INDUSTRY

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1. Introduction

The NEAT (Non-Energy use Accounting Tables) model, a material flow accounting method, has been developed to estimate CO$_2$ emissions related to non-energy use from the chemical and petrochemical sector (Patel et al., 2002). Several products from refineries, e.g. petroleum coke and pitch, are used in the non-ferrous metal, ferroalloys and inorganics industry for non-energy purposes in the form of carbon anodes or reducing agents for metal oxides. Since the use of carbon anodes and reducing agents results in CO$_2$ emissions, the calculation of this is incorporated in the NEAT model. This report gives an overview of the relevant production processes of the various metals and gives suggestions for CO$_2$ emission factors related to the non-energetic use of carbon sources.

Emission factors for the estimation of CO$_2$ emissions from the non-ferrous metal, ferroalloys and inorganics industry are to some extent also included in the IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 1996). However, IPCC Guidelines only study a limited number of products: ferrosilicon (FeSi), silicon metal (Si-metal), ferromanganese (FeMn), siliconmanganese (SiMn), ferrochromium (FeCr), calcium carbide (CaCa) and silicon carbide (SiCa). The purpose of this report is hence to extend the IPCC Guidelines with emission factors for other metals, ferroalloys and inorganics and to review the emission factors currently in use. The focus will lie with production practice within the European Union.

In NEAT, the CO$_2$ emission factors from the non-ferrous metal industry have been split in two parts, one part representing the use of carbon electrodes and another part representing the use of a carbon containing compound as a reducing agent. There is no doubt that the first emission source represents a form of non-energy use and should hence be included in NEAT. This is less clear however for the second pathway since the reductant is not only used for its reducing properties, but also as a heat source. For one production process it was not possible to distinguish between these two purposes and the overall emission factor was therefore determined (calcium carbide).

Both emission factors have been calculated using the same method. Per process the most likely consumption value for electrode or reductant consumption (in kg per kg of product) has been chosen and multiplied by the percentage of carbon that the material contains (see further for the various percentages). This is then multiplied with a factor of 3.67 based on the molecular weights of carbon dioxide and carbon (weight ratio CO$_2$/C = 3.67). If necessary, sequestered carbon in the products has been subtracted from the emission factor for the use of solid carbon (see individual emission factors).

\[
\text{CO}_2 \text{ emission factor (t CO}_2/\text{t product) = consumption electrode or reductant (t/t product) * C_{content} (%) * 3.67}
\]

For certain metals various manufacturing processes exist. The emission factors have therefore been weighted with the process mix for the total EU or total World production (if EU-data was unavailable or irrelevant). Since the NEAT model has originally been developed for the European situation, primarily European sources have been used to determine the emission factors (especially the BREF-report, 2001).

All of the emission factors and consumption of raw material is calculated for tapped material, whereas sold metal is usually reported. The amount of sold metal may be somewhat lower (1-5%), due to losses from crushing and handling (Monsen et al., 1998). Since this is only a small fraction of the total metal produced in the sector and since we are concerned with conservative estimates this has been neglected.

An excel sheet (See: emissions non-ferrous_ferroalloys_inorg.xls and Appendix B) has been constructed to calculate these CO$_2$ emission factors. The relevant electrode and reductant
consumption values are shown and the exact calculations mentioned above can be followed. If it is known for a country that the process mix for a certain product is different than indicated, the country-specific percentages for these processes can be inserted in the column “calculation final emission factor” and a more accurate country-specific emission factor can be determined. The emission factors for the following products have been calculated in detail: ferroalloys, zinc, copper, lead, nickel, magnesium and tin. Additional emission factors for primary aluminium, electric steel, titanium dioxide, white phosphorus, calcium carbide and silicon carbide can be found in Appendix A with a short explanation.

With regard to the ferroalloys only ferrochromium, ferrosilicon, ferromanganese, silicomanganese, ferrosilicocromium and ferronickel are of importance since these account for about 90% of the total production of ferro-alloys in the European Union and since the production of these ferroalloys emit the most CO$_2$ emissions. The largest European ferro-alloy producing countries are Norway, France and Spain. France and Spain are important for the production of manganese- and silicon alloys, Finland is a major producer of ferrochromium and in Sweden mainly ferrochromium and ferrosilicon are produced.

A large part of the information used in this report originates from two sources: Ullmann’s Encyclopaedia of Industrial Chemistry, 5th (edition on cd-rom, 1997) and the Reference Document on Best Available Techniques in the Non Ferrous Metals Industries (BREF, 2001). If required, more detailed information about the individual processes can be found in these sources. In addition, other documentation was used for the production structure and exact figures on electrode and reductant consumption (see References). The data from Ullmann are usually older than other sources and therefore give higher raw material use and concomitant CO$_2$ emissions. The data from BREF is based on recent European process data and is therefore considered to be most accurate if no other reliable sources were available.

The real CO$_2$ emissions differ per country for several reasons. For the processes covered in this report, it is very likely that European plants are among the most efficient in the world (since this is the case for most production processes; Euroalliages, 2002). Emissions in low-income countries may therefore be higher than determined here. Another difference is the production structure: secondary raw material may be used to a lesser extent in low-income countries (e.g. in the case of copper: only 3% compared to 36% (UN, 1996)) and processes requiring different amounts of raw material are utilized. Because of these uncertainties a conservative approach, i.e. the one that produces less CO$_2$ emissions than the average, has been chosen. Usually this was the average of the range given by the BREF-report since these values already represent a range between good and bad furnace performance (within the EU). Otherwise the most conservative estimate was taken from a different source.

The choices for emission factors in the following should therefore be regarded as an indication for Europe. If the model is applied to low-income countries it is advisable to take the production structure for the world (as indicated in the excel sheet) and use less conservative consumption values, e.g. the average consumption values indicated by Ullmann (1997). It is also possible to keep the current emission factors, keeping in mind this may underestimate the actual CO$_2$ emissions.

For the shares in production volumes a distinction has been made between high-income and low-income countries. For simplicity the division between these two groups has been done very arbitrarily with the countries belonging to economies in transition, e.g. Eastern Europe and Russia, categorized as low-income countries. High-income countries are amongst others the EU, the USA, Japan, Australia and New Zealand.
2. Raw materials and main technologies

2.1 Carbon content raw materials

To be able to calculate the emission factors, the following carbon content was taken for the raw materials used as reducing agents or electrodes:

*Reductants:*

- Coal used for coke: ± 84% (average of 80-90%; Dubbel, 1990)
- Coke from coal: ± 92% (Monsen et al., 1998)
- Petroleum coke: ± 97% (Ullmann (1997) gives a range of 85-99%; EIA (1994): 91-92%)
- Pitch (binder): 93% (Light Metals, 2001)

*Electrodes:*

- Søderberg: 97% (Monsen et al., 1998)
- Prebaked/graphite: 99% (Reuter, 2003)

When a mixture of coke and coal was used, the arithmetic mean of the carbon content of the two was taken, i.e. 88%.

2.2 Electrodes

There are three types of electrodes that are being used for the production of metals: Søderberg, prebaked and graphite electrodes.

Green paste production is the starting point for the production of all types of electrodes. The green pastes are manufactured from a mixture of calcined petroleum coke and up to 28% coal tar pitch, which acts as a binder. Petroleum coke is ground and then mixed with pitch in heated mixers. The ratio of coke and pitch is adjusted according to the application and to allow the paste to be handled.

A certain type of paste, Søderberg paste, is mainly used for electrodes in the primary aluminium industry but the paste can be processed to electrodes for other applications, for example for the production of ferroalloys in electric furnaces. A number of variants exist, such as hollow electrodes to allow continuous furnace feeding through the electrode and composite electrodes that are made to overcome production problems.

Another type of electrode is the prebaked or graphite electrode. These electrodes are also manufactured from a mixture of petroleum coke and 14 to 18% coal tar pitch and, in addition, residual material from old anodes. Electrode production involves crushing, grinding and mixing of the raw materials. The mixed materials are then formed into green electrodes. The green electrodes are then baked in ring furnaces with a large number of pits. During the baking process the coal tar pitch is converted into coke, making the material electrically conductive.

As already mentioned, the manufacture of electrodes needs a certain amount of pitch, which acts as a binder (usually coal-tar pitch). To make green pastes, about 28% of pitch is needed (rest: petroleum coke). Søderberg electrodes are made from green paste for which the raw material mix is about 28% pitch and 72% petroleum coke. Prebaked and graphite anodes are produced from an average of 16% (14-18%) pitch and 84% petroleum coke (BREF, 2001; Ullmann, 1997).
2.3 Description of the main technologies

Today, ferroalloys are principally produced either by the carbo-thermic or metallo-thermic reduction of oxidic ores or concentrates. The most important process is the carbo-thermic reduction in which carbon in the form of coke (metallurgical coke), coal or charcoal is normally used as a reducing agent. When a blast furnace is used, coke also serves as the energy source. Raw materials and energy consumption depend on the quality of the ores used (BREF, 2001).

- **Carbo-thermic reduction:**
  Metal oxide + Carbon $\rightarrow$ Metal + Carbon monoxide

- **Metallo-thermic reduction:**
  Metal oxide + Silicon $\rightarrow$ Metal + Silicon oxide
  Metal oxide + Aluminium $\rightarrow$ Metal + Aluminium oxide

There are three types of furnaces, which are primarily used for the production of ferroalloys:

- **Electric Arc Furnace (EAF)**
  An electric submerged arc furnace is any type of furnace wherein electrical energy is converted to heat energy by transmission of current between electrodes partially submerged in the furnace charge. This can be done by passing a large alternating electrical current between a series of usually three carbon electrodes (for a three phase electrical supply) to produce electrical arcs or by using a direct current (DC) and in this case the arc strikes between a number of electrodes and a carbon furnace lining (BREF, 2001). These furnaces are used for smelting a range of ferroalloys. The furnace can be operated on a batch basis or continuously with a molten charge.

  The electrodes can be Prebaked or of the Søderberg type. In the case of continuous operation with a molten charge the electrodes are "submerged" in the slag and do not strike an arc (except during start up) but operate as an electric resistance furnace or electric submerged arc furnace. The electrodes are consumed in the process and must therefore be replaced continuously. The prebaked anodes need to be replaced at certain intervals, requiring a shutdown of the furnace. To eliminate this problem Søderberg electrodes were developed. With the latter, the carbon paste is baked to a fixed electrode inside the steel casing when the electrode is heated as it approaches the warmer part of the furnace (see Figure 1), thereby allowing continuous operation. The disadvantage of the Søderberg electrodes is the higher electrical resistance (30% higher than prebaked), which reduces electrical efficiency. Carbon from the electrodes is consumed to reduce oxides to a metal or are worn away by the action of the arc. Significant concentrations of carbon monoxide can be produced. Some installations use hollow electrodes, which allow raw material to be fed into the furnace through the electrode (BREF, 2001).
The furnaces can be **open, semi-sealed** (with extraction commonly from a fourth hole in the hood) or **totally sealed** using.

The **open furnace** has a fume collection hood approximately 1 meter above the top of the furnace shell. Moveable panels or screens can be used to reduce the open area between the furnace and hood thus to improve capture efficiency. The produced carbon monoxide burns in the area between the charge surface and the capture hood and increases the volume of gas the containment system must handle. Fabric filters are typically used to control emissions. The produced CO gas escapes at the top of the furnace, where it burns to CO$_2$ in an exothermic reaction. Most of the submerged electric arc furnaces in the U.S. are open (EPA, 2003). For Europe the contribution of EAF’s has not been found.

In the case of **sealed furnaces**, all of the furnace gases are extracted and cleaned efficiently and can be used to pre-heat feed materials or as a source of fuel. The cover has feed chutes and sealing valves for charging and holes for electrodes to pass through, mechanical seals around the electrodes and sealing compounds around the outer edges. The hoods and occasionally the furnace body can be water-cooled to control the process and prevent damage. Water leaks from the cover into the furnace must be minimized as this leads to excessive gas production and unstable furnace operation. The objective of covered furnaces is to reduce air infiltration into the furnace gases, which reduces combustion of that gas. This again reduces the volume of gas requiring collection and treatment, up to a factor of 50-75 for a sealed furnace. Sealed furnaces that partially close these hood openings with charge material are referred to as "**semi-sealed**". Although these covered furnaces significantly reduce air infiltration, some combustion still occurs in the furnace itself and the reduction of the gas volume is only 10 to 20-fold. As the degree of enclosure increases, less gas is produced for capture by the hood system and the concentration of carbon monoxide in the furnace gas increases. Products with highly variable releases of process gases are typically not made in sealed furnaces for safety reasons.

Wet scrubbers are used to control emissions and the scrubbed, high carbon monoxide content gas may be utilized within the plant or flared, the former practice is growing more important (EPA, 2003). The produced metal is tapped from the bottom of the furnace.
• Electric (resistance) Furnace (EF)
This type of furnace uses a similar arrangement to the electric arc furnace. Depending on the size of the furnace, 3 to 6 Söderberg or pre-baked electrodes are immersed in the liquid raw material layer. The temperature is maintained by means of electric resistance heating. These furnaces usually operate with coke or slagging agents depending on the application. The carbon electrodes are consumed as oxides are reduced but the gas volumes produced during operation are kept to a minimum, as there are no gases produced by the combustion of a fuel. These furnaces are usually sealed and the gases are collected and treated. Where possible dust, CO and sulphur dioxide are re-used. (BREF, 2001; section 2.6.2.4)

These furnaces are used in the production of a number of metals from primary and secondary raw materials including precious metals, lead and copper and for slag cleaning. They are in competition with fuel-heated furnaces and they are primarily used in countries where the electricity prices are relatively low, e.g. Finland, Sweden and Norway.

• The Blast Furnace (BF)
This is a type of shaft furnace. It uses a heated air blast from tuyeres in the lower part of the furnace to burn coke mixed with the furnace charge of metal oxide or secondary material. The combustion of a portion of the coke raises the furnace temperature and the remainder produces CO, which along with hydrogen produced by the water gas reaction reduces the metal oxides to metal. The consumption rate of coke in blast furnaces is higher than in submerged arc furnaces,
since they also use it as a power source. The high CO content gas can be collected, cleaned and burnt to pre-heat the blast-air or may be burnt off in a separate afterburner or in an oxygen-rich part of the furnace. The metal collects on a hearth or crucible at the bottom of the furnace and may be tapped continuously or on a batch basis. When the furnace is operating batch-wise, the slag floats on top of the metal and the metal is tapped from a separate tap hole. Fume extraction and abatement is used during the tapping process.

There are two variations of the blast furnace depending on the feeding method and operating temperature:
- “hot top” where the charge material is fed via a “bell” or a conveyor via a transfer lock
- “cold top” where the furnace is charged from a hopper and the feedstock provides the top seal itself.

Blast furnaces are used for a variety of metals including precious metals, copper and lead from primary and secondary raw materials as well as high carbon (HC) ferromanganese. On a world scale 83% of the use of a BF is for the production of ferromanganese. One specific application of the blast furnace is the Imperial Smelting Furnace that is used for mixed lead/zinc concentrates. (BREF, 2001; section 2.6.2, p 89-90)

![Diagram of Blast Furnace for Copper Smelting](BREF, 2001)

Figure 3; Blast Furnace for Copper Smelting (BREF, 2001)

The most important of these furnaces are the EAF and the EF, which are used for almost 94% of the total production of ferroalloys in the world (for the year 1997; BREF, 2001).

### 2.4 Carbon monoxide gas (CO)

The process gases, mainly consisting of CO and H₂, are produced in the smelting process if carbon is used as a reducing agent. The CO can be utilized as a secondary fuel and transferred by means of pipelines within the plant area like any other fuel gas. It can be used by direct burning in the sinter-furnace, drying or preheating the furnace charge as well as for energy recovery in the form of hot water, steam and/or electricity. For example, during the production of...
HC ferromanganese in a blast furnace the CO rich top gas will be de-dusted and partly used to heat the hot stoves (BREF, 2001).

If a semi-closed submerged electric arc furnace is used for the production of ferrochromium, ferrosilicon, silicon metal, silicomanganese or ferromanganese, the CO gas from the smelting process burns between the charge surface and the capture hood by the infiltrated air thus creating a hot off-gas. Hence, the semi-closed furnaces are sometimes equipped with a waste heat boiler as an integrated energy recovery system. The waste heat boiler generates superheated steam that can be sold to neighbouring mills or used for electricity production in a backpressure turbine. During the production in a closed electric arc furnace the off-gas contains a very high percentage of CO, which is collected without being burned. This CO is a high quality fuel that can also be used for electricity production or supplied to a neighbouring industrial plant as a secondary fuel or synthesis gas serving as raw material in chemical processes. A typical composition of a CO rich gas, formed in a closed furnace producing HC FeCr, contains: 75 – 90% CO, 2 – 15% H\textsubscript{2}, 2 – 10% CO\textsubscript{2}, 2 – 5% N\textsubscript{2} and < 5% of H\textsubscript{2}O (BREF, 2001).

Summarized we can say that with an open/semi-closed furnace the produced CO is burnt off and consequently transformed into CO\textsubscript{2} with a possibility of energy recovery by a waste heat boiler. All of the CO\textsubscript{2} in this case has been non-energetic and the energy recovery is only considered to be a bonus. With a closed furnace however the CO is recovered and actually used as a secondary fuel. Since exact information on the amount of furnaces within the EU or in the world that are either open/semi-closed or completely closed is not readily available and since the principal reason for the produced carbon monoxide was non-energetic (resulting from electrode or reductant use), the assumption made here for calculating the emission factors was that all the CO is eventually turned into CO\textsubscript{2} and is regarded as non-energy use. The danger of this simplifying approach can be that the emissions are double counted if the re-used CO is also reported as fuel or as raw material for other chemical processes. (Therefore, in the statistics any CO that is re-used within the plant should not be reported since the emissions are already accounted for in the non-energy section. And any CO exported to electricity plants or elsewhere should be subtracted from the energetic use reported in that section, similarly with the CO that is used as raw material for other chemical processes.)
3. Production processes and CO$_2$ emission factor per metal

3.1 Ferromanganese

Ferromanganese (FeMn) exists in three varieties, either with a carbon content of maximum 7.5\%wt (HC), with a medium carbon (MC) content or low carbon (LC) content of maximum 1.5\%. The figure for FeMn production that is reported in statistics is most likely a combined figure for these three varieties. Of all ferromanganese (HC and MC/LC) in the world, 70\% is produced in developing countries (primarily South-Africa, Brazil and China) and Japan. The EU only accounts for 22\% of the world production with France and Norway being the biggest producers in this region. (UN Statistics for the year 1996, 1998). The USA is only a minor producer at the moment (ImnI, 2002).

Manganese ores are used for several types of products. Of the total mined manganese ore, 84\% is used for the production of ferromanganese, 13\% for the production of silicomanganese and only 2\% for the production of manganese metal. Regarding the production of ferromanganese, primarily FeMn high in carbon is made out of the manganese ores. This amounts to about 92\% of the total ferromanganese production, with the other 8\% used for the production of medium-carbon/low-carbon FeMn (Figure 6, Chapter Manganese and Manganese Alloys by D.B. Wellbeloved, P.M. Craven and J.W. Waudby in Ullmann, 1997). Different figures have been published by the International Manganese Institute (ImnI) according to which, in the year 2000, about 76\% or 3.4 million tonnes of FeMn produced was High-Carbon and the remaining 24\% was for the production of MC and LC FeMn (ImnI, 2002). Since the published figures from the ImnI are the most recent data available, this has been chosen for further calculations.

Figure 4 shows that there are four main routes for the production of materials originating from manganese ores. The two upper routes, using the EAF, produce ferromanganese or ferrosilicomanganese. The other products shown in Figure 4 are not relevant in terms of solid carbon or electrode use and are therefore not included in this report.

![Figure 4: Summary of production routes (Ullmann, 1997)]
**Pre-treatment – Sintering**

Since the FeMn process requires material of a certain size for good performance, the ore fines may be agglomerated in a separate sintering process. The use of sinter as a source of manganese is becoming increasingly popular, however the exact percentage is unclear (ImnI, 2002). In the sintering process a degree of pre-reduction is achieved, reducing the energy requirement in the furnace. For the sintering process normally about 0.1 t coke/t and 0.1 t coal/t is required (BREF, 2001) or for more efficient processes: 0.13-0.14 t/t (Monsen et al., 1998). Since the coke is primarily used for the function of energy carrier and thus for heat production the emissions concerned with this process step will not be taken into account as emissions originating from non-energy use. Partial reduction of the higher manganese oxides however may also occur during sintering and thus further discussion is required if this should be regarded as energy or non-energy use.

The chemical reactions that take place in the electric arc furnace are:

\[ \text{MnO} + 2 \text{C} \rightarrow \text{Mn} + \text{C} + \text{CO} \]
\[ \text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO} \]
\[ \text{Fe} + \text{Mn} \rightarrow \text{FeMn} \]

**High-Carbon/Standard FeMn (max 7.5% C)**

HC ferromanganese can be produced either in a blast furnace or in an Electric Arc Furnace. The choice of the use of blast furnaces over electric furnaces is based on the relative price of coke and electricity. Blast furnaces are usually used where the cost of power is high in relation to coke. In blast furnaces, coke is used both as a reductant and as the energy source. The coke rate in blast furnaces is therefore higher than in submerged arc furnaces, which use electricity as the power source.

1. **Electric Arc Furnace**

The commonly used electric arc furnaces are of the closed, semi-closed and open type, which has no or only limited consequences on the furnace itself but affects the gas composition, flow rate, recovery and de-dusting system (BREF, 2001). Usually coke is used as the reductant. However, in South Africa, where coking coal is in short supply, up to 70% of the carbon for the production of ferromanganese and siliconmanganese is supplied in the form of bituminous coal. An important feature in the design of submerged arc furnaces is the use of Søderberg electrodes. These are used because the large electrode diameters required for the production of manganese alloys make the use of prebaked electrodes uneconomic.

2. **Blast Furnace**

Ferromanganese is one of the few ferroalloys for which the blast furnace is still used regularly. The blast furnace (BF) process has been described in Section 2.3.

Due to the fact that in most countries the necessary electricity for the EAF is relatively cheaper than the consumption of coke in the BF the majority of producers use Electric Arc Furnaces to produce HC FeMn. Of the world production of HC FeMn 84% is produced with an EAF and 16% with a BF (average for 1997, BREF, 2001). In the developed world there exist only a few blast furnaces, however in Russia the majority is produced in a BF. Within the European Union France is the biggest producer of HC FeMn with a share of 46% of the total production of the EU. In France half is produced in a BF and half in an EAF (for the year 1993, BREF, 2001). The other FeMn producing countries within the EU utilize the EAF. This would mean that in the EU an average of 25% of the total FeMn produced is made in a BF. Since the NEAT model is primarily concerned with the application to Europe we take a division for the two production processes of
HC FeMn: 75% EAF and 25% BF. For other countries, e.g. Russia, this division may be completely different.

As a reducing agent in both the BF and the EAF primarily coke is used.

Medium-Carbon/Low-Carbon FeMn (with max 1.5% C):

For the production of medium carbon ferromanganese (MC FeMn) two different routes can be used, silico-thermic reduction of manganese ores or decarburisation of HC FeMn. For the production of LC FeMn only the first process is relevant.

- **Silico-thermic reduction** with an EAF. The electrodes used are made from graphite and the reduction is done by silicon. While the silico-thermic reduction process is more energy intensive than the decarburisation of high-carbon ferromanganese (see below), it has the advantage that much lower carbon content can be reached. The silico-thermic process can therefore also be used to produce low-carbon ferromanganese and industrial manganese metal (Ullmann, 1997; BREF, 2001). The chemical reaction that takes place is:

  \[ 2 \text{MnO} + \text{Si} \rightarrow \text{SiO}_2 + 2 \text{Mn} \]

- **Decarburisation of HC FeMn** is done in an Oxygen Blown Converter (OBC). For the decarburisation of HC FeMn, oxygen is blown into the molten metal, which is tapped off from the furnace. The oxidation of carbon consequently reduces the carbon content of the ferromanganese. This de-carburisation process allows the production of MC FeMn with a carbon content of about 1.3%. This process cannot be used for the production of LC FeMn (Ullmann, 1997; BREF, 2001).

Transalloys (Republic of South Africa) produces 20 kt/a of medium-carbon ferromanganese by the silico-thermic route and appears to be the only producer in the developed world to do so. In the Soviet Union, medium- and low-carbon ferromanganese are also produced silico-thermically with manganese recoveries of 59–63% (Ullmann). On the other hand, in the EU the decarburisation is the most common refining method for the production of MC FeMn (BREF, 2001), while the silico-thermic reduction process is applied to a lesser extent for the manufacture of LC FeMn. The process mix for Europe is clear, but no conclusion can be drawn on the contributions of both processes on a world scale. However, since MC/LC FeMn only constitutes about 24% of the total FeMn production this may not have a very significant impact on the emissions from FeMn.

**Calculation CO\textsubscript{2} emission factors**

Since it is assumed that the most commonly used production route for MC/LC FeMn also goes via HC FeMn (see above), the emission factors for the total ferromanganese production have been based on the emission factors for HC FeMn. The following values for electrode and solid carbon consumption will therefore only cover HC FeMn.

The amount of **electrode consumption in the EAF** given by Olsen (1998, 0.0135 t/t FeMn) is within the range that is given by the BREF report: 0.008-0.02 t/t FeMn. The electrode consumption according to Sully (1955) is many times higher, but this may be due to the fact that this is an old source, originating from 1955. With regard to the **reductant** consumption the values according to BREF (0.41-0.45 t/t FeMn) are within the range given by Ullmann, 0.13-0.65 t/t FeMn. Olsen reports even less reductant than the lowest value from BREF: 0.037-0.04 t/t FeMn. This may indicate that the production process in Norway is one of the most efficient in the EU.

For the **reductant use in the blast furnace**, the values according to BREF (1.1-1.45 t/t FeMn) are near to the bottom range given by Ullmann, 1.27-2 t/t FeMn. This is logical due to the
fact that the BREF report is based on recent information in contrast to Ullmann, which makes use of older sources.

To summarise, it was concluded from this data comparison that the average values from the BREF report represent good estimates of the actual consumption of electrode and reductant in the EU.

Since HC FeMn consists of an average of 7.5% of carbon, this amount needs to be subtracted from the CO$_2$ emissions calculated with the carbon consumption. However 24% of the HC FeMn gets further reduced to MC/LC FeMn and a part of the carbon stored is therefore eventually emitted to the air as CO$_2$. This means that not all the carbon sequestered in HC FeMn needs to be subtracted, but only the 76% that remains with a high carbon value and is not further reduced to MC FeMn. We assume here that in the EU the reduction of HC FeMn to MC/LC FeMn is primarily done by the oxygen blowing process, thus no extra emissions take place, as is the case for the EAF in the other method of producing MC/LC FeMn. In the latter case, there will be some extra emissions due to electrode use, but none from the reducing agent (achieved by silicon). Hence, for countries where the other method is predominantly used the emission factor will not differ much.

The weighted contributions of the two different processes to produce HC FeMn is taken as mentioned for Europe, i.e. 75% produced by the EAF and 25% by the BF. For the consumption of electrode and solid carbon the average BREF-value is taken. This is done for reasons mentioned above. The overall CO$_2$ emission factors, representing the situation in developed countries, are estimated at:

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<tr>
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<th>t CO$_2$/t FeMn</th>
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<tbody>
<tr>
<td><strong>Electrode use</strong></td>
<td>0.038</td>
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<tr>
<td><strong>Solid carbon use</strong></td>
<td>1.80</td>
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According to the IPCC the CO$_2$ emission factor for the production of ferromanganese should be 1.5 t/t FeMn. This means that the emission factor determined in this report is slightly higher than the IPCC value.

To improve these emission factors, several other questions will need to be answered in the course of further research. These are whether the emissions originating from the sintering process should be included or not and to what extent the coke/coal used in the blast furnace is used as a reductant. For the latter, it may be more practical to assume that all of the coke/coal consumption is regarded non-energy use (or energy use) to prevent double counting.

### 3.2 Silicomanganese

Silicomanganese is required as an alloying element in the steel industry as well as raw material for the production of MC and LC FeMn. Silicomanganese is nowadays only produced in submerged electric arc furnaces, which can be closed, semi-closed or open. The electrodes used are of the Søderberg type. The furnaces are the same or very similar to those used for HC ferromanganese production and often a furnace is operated with alternate campaigns of each alloy.

The standard grade silicomanganese contains 14-16% Si, 65-68% Mn and about 2% carbon. Lower carbon levels result when the silicon content is increased. Special grades with up to 30% Si are produced for use in the manufacture of stainless steel. The world production of silicomanganese was about 3.5 million tonnes in 2000, similar to the quantity of ferromanganese produced (see also 3.1; ImnI, 2002)
The chemical reaction that takes place is:

\[
\begin{align*}
\text{SiO}_2 + 2 \text{C} & \rightarrow \text{Si} + 2 \text{CO} \\
\text{MnO} + 2 \text{C} & \rightarrow \text{Mn} + \text{C} + \text{CO} \\
\text{Si} + \text{Mn} & \rightarrow \text{SiMn}
\end{align*}
\]

In general three production routes exist:

- Reduction of manganese ores and silica with coke and coal
- Reduction of MnO-rich slags from ferromanganese production and quartzite with coke and coal
- Reaction of high-carbon ferromanganese and quartzite with coke

The first two processes are used for the production of alloys containing 15–25% Si and can be carried out in the same furnaces used for ferromanganese production. The third method is used to produce alloys containing 30–35% Si and is generally performed in smaller furnaces (Ullmann). Afterwards siliconmanganese can be further refined into medium- or low-carbon ferromanganese as well as manganese metal. The share of these processes in the process mix for the EU or worldwide is not known, but since the consumption values in the next section do not refer to any particular production method it would not be possible to take this into account.

**Calculation CO\(_2\) emission factors**

As just mentioned, it is not known which production method the following values represent.

The consumption of **electrodes** is about the same (0.02-0.03 t/t SiMn) for three sources found (BREF, 2001; Ullmann, 1997; Olsen, 1998). The average value of the BREF report is therefore taken to calculate the emission factor.

In the case of the consumption of **reducing agent** the range given by BREF (0.4-0.6 t/t SiMn) is again within the range by Ullmann (0.14-0.84 t/t SiMn), whereas the value of Olsen et. al. (1998) is less than the lowest value of BREF (0.33-0.38 t/t SiMn). This suggests that the production processes in Norway is one of the most efficient in the EU. Since SiMn contains about 2% of carbon this was subtracted from the final emission factor.

The emission factors for the production of SiMn are thus based on the average reductant and electrode use given by the BREF report:

- **Electrode:** 0.089 t CO\(_2\)/t SiMn
- **Solid carbon use:** 1.54 t CO\(_2\)/t SiMn

The emission factor given by the IPCC (1996), 1.7 t CO\(_2\)/t SiMn, is almost identical to the sum of these values, 1.66 t CO\(_2\)/t SiMn, and is also within the range of the overall emission given by the BREF report, 1.1-1.8 t CO\(_2\)/t SiMn (column K in excel file). More accurate emission factors can be calculated if the share of the processes and the concomitant consumption figures were known.

### 3.3 Ferrochromium

Ferrochromium is largely produced in low-income countries (almost 85% of the total world production) with South Africa accounting for almost half of the world production. The EU only accounts for ± 14% of the world production; in absolute terms this is 525 kt (all values for 1996; UN, 1998). The total world production of FeCr was 3,400 kt in 1994, of which HC FeCr accounted for about 3,100 kt. This means that approximately 92% of the FeCr production is for High-Carbon FeCr (UN, 1998)
Pre-treatment – Sintering
For the production of HC FeCr, the ore first goes to a Sintering plant. Here the chromium ore is mixed with coke fines and heated to produce sinter (0.13-0.14 t/t FeCr in Norway according to Olsen (1998) or 0.08-0.12 t/t pellets in Finland acc. to Riekkola-vanhanen (1999)). Burning of the coke powder provides the necessary heat for sintering. Since this is the use of coke primarily for energy purposes the resulting CO₂ emission from this production step will not be taken into account in this calculation (see also FeMn section). Afterwards the sinter goes into the EAF to produce HC FeCr. For this type of FeCr approximately 7-8% of the material is stored carbon and thus has to be subtracted from the final CO₂ emissions.

All of the Ferrochromium is produced by carbo-thermic or silico-thermic reduction in Electric Arc Furnaces. Only Søderberg electrodes are used in the processes and for the production of HC and MC FeCr metallurgical coke is the most common reducing agent, although coal and charcoal are used as well. When chromium oxide is reduced with carbon it will always produce HC FeCr (4-10% carbon) alloys, rather than low- or even-medium carbon grades.
The chemical reaction that takes place during reduction is (Riekkola-vanhanen, 1999):

\[
\text{Cr}_2\text{O}_3 + 3 \text{ C} \rightarrow 2 \text{ Cr} + 3 \text{ CO}
\]

High-Carbon FeCr (± 4-10% C)
High-carbon Ferrochromium (HC FeCr) is produced almost exclusively by direct carbo-thermic reduction of chromite ore in three-phase submerged electric arc furnaces (EAF) with continuous operation. The smelting charge can be pre-heated in a shaft or rotary kiln by using the CO gas from the smelting process. Pre-reduction in a rotary kiln is also possible. In both cases the specific consumption of electrical energy will be reduced. Closed, semi-closed or open submerged electric arc furnaces including three-phase AC (Alternating Current) operation and single-phase DC (Direct Current) plasma furnaces are used. The DC arc furnace uses a single hollow graphite electrode.

![Diagram of HC FeCr production](image)

Figure 5: HC FeCr production by using a closed furnace (BREF, 2001)
**Medium-Carbon FeCr (± 0.5-4% C):**

For the production of MC FeCr there are three possibilities:

- **Silico-thermic reduction** of chromite ore and concentrates. The reducing agent is ferrochromiumsilicon (FeCrSi).
- **Aluminothermal.** The reducing agent is a finegrained powder of primary or secondary aluminium.
- **De-carburisation** of HC FeCr in an oxygen-blown converter.

The silico-thermic route is more economic and thus more important nowadays for producing MC FeCr. The reason for this route being more economic may be that only a small amount of MC FeCr is needed on the market compared with the high demand of HC FeCr together with the fact that the same process can produce low-carbon ferrochromium as well. Since the silico-thermic route is the most important process for MC FeCr and only ferrochromiumsilicon is used as the reducing agent no CO\(_2\) emissions occur for the production of MC FeCr (BREF, 2001). CO\(_2\) emissions may occur however due to the use of carbon electrodes, but since the production of MC FeCr is very small compared to HC FeCr this will not be taken into account.

**Low-Carbon FeCr (± 0.01-0.5%)**

In order to get the desired low carbon content in low-carbon ferrochromium a carbo-thermic process cannot be used. The most commonly used processes are therefore metallo-thermic (here: silico-thermic) reductions known as the Duplex, Perrin or Simplex processes:

- **Silico-thermic reduction:** ferrochromium-silicon and ferrosilicon are used as reductants and therefore no CO\(_2\) is emitted in this process due to non-energetic use. CO\(_2\) emissions may occur however due to the use of carbon electrodes. For the same reason mentioned above for MC FeCr this will not be taken into account.

**Calculation CO\(_2\) emission factors**

Since 90% of the world production is for HC FeCr the emission factors for the total production of ferrochromium are based on the electrode and reductant consumption of this type of FeCr. The **electrode consumption** given by the Finnish Environmental Institute (Riekkola-Vanhanen, 1999a), 7-9 kg/t FeCr, and by Olsen et al.(1998) for Norway, 20 kg/t FeCr, are within the range given by the BREF-report (2001), 7-25 kg/t FeCr. Since Norway (165 kt; UN, 2000) and Finland (222 kt; UN, 2000) account for two-thirds of the production of chromium alloys in Europe the average consumption of the BREF-report was taken to calculate the emission factor from electrode use. For other countries the electrode consumption may be somewhat higher. This is expected to be small however and will not make a large difference in the final emission factor.

Regarding the **consumption of reducing agent** the Finnish report (Riekkola-Vanhanen, 1999a), 0.5-0.55 t/t FeCr, and the report by Olsen et al.(1998) for Norway, 0.44 t/t FeCr are rather on the low side of the range given by BREF, 0.55-0.7 t/t FeCr. This again suggests a higher efficiency of the furnaces in these countries. Since most of the production in Europe comes from these countries and since we use conservative estimates the lower value of the BREF report is taken to calculate the CO\(_2\) emissions from solid carbon use. Another source (Jones, 2003) gives a value also within the range stated by BREF, 0.6-0.7 t/t FeCr, but this is more an average for the production of FeCr worldwide and not especially for the situation of Europe. As stated above the consumption of reducing agent will be different in other countries. A larger reductant consumption, e.g. 0.65 t/t FeCr, will have a bigger impact on the overall emission factors than in the case of electrode consumption because the quantities are several times larger. For countries
using processes with a higher reductant use the emission factors may therefore need to be corrected.

On this basis the following emission factors have been estimated:

<table>
<thead>
<tr>
<th></th>
<th>CO₂/t FeCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode:</td>
<td>0.057</td>
</tr>
<tr>
<td>Solid carbon use:</td>
<td>1.57</td>
</tr>
</tbody>
</table>

The sum of these values, 1.63 t CO₂/t FeCr, is high compared to the emission factor suggested in the IPCC Guidelines (1996), 1.3 t CO₂/t FeCr. The factor of the IPCC is based on a material balance from Sintef (1991) in Norway and probably uses a value for the reductant consumption that is closer to the value for Norway mentioned in Olsen et al. (1998). This shows that the right value for the reductant consumption is essential. Since South Africa accounts for almost half of the world production it is suggested that information about raw materials consumption for plants in this country be used to estimate an emission factor for FeCr that is representative of the whole world. If these are not available the average of BREF could be taken, for the article by Jones (2003) also supports this.

### 3.4 Ferrochromium-silicon

This can be produced in the same kind of three phase submerged electric arc furnaces as used for HC FeCr production. The reduction of SiO₂ to Si by **metallurgical coke** is accompanied by the generation of huge amounts of CO gas. The high generation rate of CO makes it important to use a porous burden (e.g. gas coke) and a semi closed or closed furnace with an appropriate energy recovery system. The CO gas is usually burned at the top and then scrubbed. Compared to the production of FeCr the production of ferrochromiumsilicon worldwide is negligible (50 kt to 4500 kt, only 1%; BREF, 2001). The composition of FeCrSi depends largely on the type and can range from 20-55% Cr and 18-60% Si (Chromium and Chromium alloys by Downing J.H, Deeley P.D, Fichte R.M. in Ullmann, 1997). The carbon content can range from 0.03-6%. FeCrSi with a high silicon content and low carbon content are most commonly used (Ullmann, 1997). The chemical reaction is as follows:

\[
\text{SiO}_2 + 2 \text{C} + [\text{Cr, Fe}] \rightarrow \text{FeCrSi} + 2 \text{CO}
\]

**Calculation CO₂ emission factors**

Ullmann (1997) is the only source found with information about raw materials consumption for the production of FeCrSi. Therefore the average values for electrode and reductant consumption from this source are taken to calculate the CO₂ emission factors:

<table>
<thead>
<tr>
<th></th>
<th>CO₂/t FeCrSi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode:</td>
<td>0.114</td>
</tr>
<tr>
<td>Solid carbon use:</td>
<td>2.71</td>
</tr>
</tbody>
</table>

The IPCC does not give a value for this ferroalloy.
3.5 Chromium metal

The production of chromium metal can be done by the following reduction methods, performed in an EAF or by electrolysis of a chromium solution:

- **Alumino-thermic reduction**
  Aluminium is the most important reducing agent for producing Cr from \( \text{Cr}_2\text{O}_3 \).
  \[
  \text{Cr}_2\text{O}_3 + 2 \text{Al} \rightarrow 2 \text{Cr} + \text{Al}_2\text{O}_3
  \]

- **Carbo-thermic reduction**
  With this method the chromium oxide is reduced by carbon in an electric arc furnace. The chromium metal produced contains high amounts of carbon.
  \[
  \frac{2}{3}\text{Cr}_2\text{O}_3 + 2 \text{C} \rightarrow \frac{4}{3}\text{Cr} + 2 \text{CO}
  \]

- **Metallo-thermic/Silico-thermic reduction**
  The silico-thermic reduction is not sufficiently exothermic to be self-sustaining and must therefore be performed in an electric arc furnace. As the name already suggests, the reduction occurs with a silicon alloy as reducing agent.

- **Electrolytic**
  In the electrolytic process normally high carbon ferrochromium is used as the feed material, which is then converted into chromium by dissolution with sulphuric acid at temperatures at about 200ºC and subsequent electrolysis. This is not a very efficient process and is primarily used for plating (Chromium and chromium alloys by Downing J.H, Deeley P.D, Fichte R.M. in Ullmann, 1997)

**Calculation CO\(_2\) emission factors**

Since alumino-thermic is worldwide the most commonly used method for the production of chromium metal (no exact percentages could be obtained, Maliotis, 1996; Lyakishev, 1998), no CO\(_2\) emissions resulting from electrode use nor from solid carbon use occur. The amount of CO\(_2\) originating from the carbo-thermic reduction method can be regarded as negligible.

More accurate emission factors could be obtained if the exact shares of the various processes and the carbon consumption of the carbo-thermic reduction process (if it were to have a significant share) were known.

3.6 Ferrosilicon

China, the US, Norway and the Ukraine are the biggest producers of ferrosilicon in the world. The developing world accounts for about 70% of the total world production. The EU produced about 18% of the total world production in 1996, with the major share being produced in Norway (UN, 1998).

Ferrosilicon (silicon content less than 95%), silicon metal (silicon content more than 95%) and calcium silicon (CaSi) are used as additives in different industrial activities. As an alloying element, ferrosilicon increases the strength of steel and is therefore used for steel that is needed to produce for instance wire-cords for tyres or ball bearings. High purity FeSi is used to produce high permeability steel for electric transformers. Silicon metal is important as alloying element in
aluminium and for the production of chemicals and electronic equipment. The major user for calcium silicon is also the steel industry.

Ferrosilicon is produced with varying percentages of silicon content. This can range from 10% up to 95% of silicon in the alloy, however the BREF-report only mentions FeSi75 (with 75% Si content). Ullmann (Silicon by W. Zulehner, B. Neuer and G. Rau in Ullmann, 1997) mentions also FeSi 45 and the IPCC has three different emission factors for the various types of FeSi, i.e. containing 90%, 75% and 50% Si. In Norway only FeSi with a silicon percentage higher than 66% is produced. Since Norway is the biggest producer in Europe and the contribution of FeSi75 in the total European production is not exactly known it is assumed that the production of FeSi75 is a good representative for the total production of FeSi in this region and the total emission factor is therefore based on this production process. Of the total FeSi production in Iran, 80% is for FeSi75 and 20% for FeSi45 (Iran Ferroalloy Industries Co., 2003). In the USA the division is 50% FeSi75 and 50% FeSi45 (EPA, 2001). The division may hence be different in other countries and will need adjustment if the emission factors were to be applied to other countries.

Ferrosilicon is produced with varying percentages of silicon content; this can range from 10% up to 95% of silicon in the alloy. Ferrosilicon, silicon metal and calcium silicon are commonly produced in low-shaft three-phase submerged electric arc furnaces. The electric arc furnaces can be of the open or semi closed type. Norway, which is the biggest FeSi producer in the EU, uses primarily furnaces that are semi-open. In low-income countries FeSi is manufactured in open furnaces. The furnace normally rotates about once a week, in order to connect the reaction areas around each electrode tip. This homogenises the molten metal in the furnace and saves 5 to 10% of electric energy. The rotation gives rise to some difficulties in obtaining good capture efficiency of the fugitive emissions at the tap-hole as the location of the tap-hole will rotate with the furnace. A typical electric arc furnace for the production of ferrosilicon is shown in figure.2 in Section 2.3 It is the same type of furnace as for the production of calcium carbide and FeSi is also a by-product of this process. The consumption of solid carbon varies with the performance of the furnace operation (BREF, 2001).

The raw material is fed from storage bins above the furnace, through feeding tubes into the smelting zone around the electrodes. For the production of FeSi and CaSi Söderberg electrodes are used and as the reducing agent metallurgical coke, petroleum coke or coal can be used. The electrodes normally supply about 5–10% of the total requirement of reducing agent.

The chemical reaction is as follows:

\[ \text{Fe}_2\text{O}_3 + 2 \text{SiO}_2 + 7\text{C} \rightarrow 2 \text{FeSi} + 7\text{CO} \]

**Calculation CO\textsubscript{2} emission factors**

Since at present time the division of FeSi75 and FeSi45 is not exactly known for Europe, only the values of FeSi75 are used to calculate the emission factors for the total Ferrosilicon production.

The **electrode consumption** is from all sources (BREF, 2001; Ullmann, 1997; Monsen, 1998; Iran Ferroalloy Industries Co., 2003) more or less the same, ranging from 0.04 to 0.07 t/t FeSi. The value for Iran (2003) is higher than the BREF value, but this seems plausible in view of the level of technology applied. Since the BREF value is the same as the value for Norway this is regarded as representative of the electrode consumption in Europe, 0.05 t/t FeSi, and therefore used to calculate the emission factor for electrode use.

In the case of the use of **reductant**, BREF gives a value of 0.85 t/t FeSi, which lies within the range given by Ullmann, 0.7-0.9 t/t FeSi. Monsen et al. (1998) and Iran Ferroalloy Industries Co. (2003) indicate a value much higher than this, 1.175-1.2 t/t FeSi, but it is not completely clear why this is the case. Since the BREF-report gives the most conservative estimate this value is used.
For ferrosilicon, the following emission factors have been estimated:

<table>
<thead>
<tr>
<th>Type</th>
<th>CO₂ emission (t/t FeSi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>0.178</td>
</tr>
<tr>
<td>Solid carbon use</td>
<td>2.75</td>
</tr>
</tbody>
</table>

The total emission factor according to the IPCC (3.9 t CO₂/t FeSi) is much higher than the sum of the above-mentioned values (2.93 t/t FeSi). The former is based on a work from Streibel (1974) and is equal to the value for FeSi75 calculated in the more recent paper by Monsen et al. (1998). The discrepancy between the values originates in the higher reductant consumption according to Monsen et al.(1998). The BREF report also gives a total emission: 4.4 t CO₂/t FeSi. Unfortunately, the report does not give any sources or assumptions that were taken for the determination of this value and hence we cannot conclude why the value is much higher than the value of this report and even higher than the value of the IPCC.

The discrepancy between the emission factors could be solved if more information from different sources (preferably directly from manufacturers) were available on the reductant consumption for this process. More data are also required on the production shares between the various types of FeSi. For now, we assume these emission factors to be correct and are in line with the conservative approach we have adopted for this report.

### 3.7 Silicon metal

The main producing countries for metallurgical-grade silicon are Norway, the United States, France, Canada, South Africa, the CIS, Italy, Spain, and Yugoslavia (UN, 1998). The world production of silicon metal is normally about one third of the production of ferrosilicon.

There are two ways of producing silicon metal (pure silicon, silicon content above 95%):

- **Carbo-thermal**

  \[
  \text{SiO}_2 + 2 \text{C} \rightarrow \text{Si} + 2 \text{CO}
  \]

  1. **EAF**. The same furnace as for the production of FeSi is used (see description above), but **graphite/prebaked electrodes** are used instead of Søderberg electrodes. The reducing agent can be **petroleum coke** or **coal**. The purity of the silicon produced depends primarily on the purity of the materials used and secondarily on the purity of the graphite electrodes and the furnace lining.

  2. **DAR**, direct arc reactor. An improved arc furnace by Dow Corning to produce purer silicon.

- **Alumino-thermal**

  \[
  3 \text{SiO}_2 + 4 \text{Al} \rightarrow 3 \text{Si} + 2 \text{Al}_2\text{O}_3
  \]

  Reduction takes place with aluminium as the reducing agent.

The **carbo-thermal** reduction in an EAF is the method most commonly used (Silicon by W. Zulehner, B. Neuer and G. Rau in Ullmann, 1997; BREF, 2001).

### Calculation CO₂ emission factors

The values for the **electrode consumption** given by BREF (2001), Monsen et al. (1998; values for Norway) are both 0.1 t/t Si and very close to those given by Ullmann (0.12-0.14 t/t Si). The slightly consumption in Ullmann can be explained with older and less efficient processes than currently used in Europe. The value of BREF and Monsen et al. is therefore taken to determine the emission factor from the use of electrodes.

Regarding the **consumption of reducing agent**, the values of Monsen et al. (1.39 t/t Si) and Ullmann (1.2-1.4 t/t Si) lie within the range given by BREF: 1.15-1.5 t/t Si. The only difference between Monsen et al. and the BREF report is that the former states only coal as a reductant.
(with an increasing use of charcoal) and the BREF mentions besides coal also the use of petroleum coke and amorphous carbon as reducing agents. The difference in carbon content between petroleum coke and coal results in 0.45 t CO₂/t metal higher emissions in the case of use of petroleum coke. Since we have chosen to take a conservative approach when estimating emissions and since Norway is a large producer of silicon metal in Europe we have used the consumption of coke for Norway to calculate the emission factor. The emission factors are:

<table>
<thead>
<tr>
<th></th>
<th>CO₂/t Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>0.363</td>
</tr>
<tr>
<td>Solid carbon use</td>
<td>4.49</td>
</tr>
</tbody>
</table>

The resulting emission factor of 4.49 t CO₂/t Si is somewhat higher than the value given by the IPCC: 4.3 t CO₂/t Si. According to Monsen et al. this is due to the fact that the work on which the IPCC emission factor is based (Streibel, 1974) assumed a little higher consumption of wood chips, improved silicon yield and lower fix C consumption. The emission factor suggested by the work of Monsen et al. is expected to be more representative, a mean value for excellent and bad furnace performance, and this is therefore taken for the NEAT model.

More exact emission factors could be determined if the exact share of the carbo-thermal process were known.

### 3.8 Calcium silicon

Calcium silicon has a silicon content of about 60 – 65% and a calcium content of 30 – 35%. It is produced in the same type of furnace as FeSi and Si-metal (see description above). Söderberg electrodes are used and the reductant is either coke or coal. The chemical reaction is given by:

\[
\text{CaO + 2 Si + C} \rightarrow \text{CaSi}_2 + \text{CO}
\]

**Calculation CO₂ emission factors**

Only Ullmann data were found for the production process of this metal. Therefore the average value from this source, 0.09 t electrode/t CaSi and 0.74 t reductant/t CaSi, was used to estimate the CO₂ emission factors:

<table>
<thead>
<tr>
<th></th>
<th>CO₂/t CaSi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>0.320</td>
</tr>
<tr>
<td>Solid carbon use</td>
<td>2.39</td>
</tr>
</tbody>
</table>

### 3.9 Lead

Europe and the US are the largest producers of lead in the world. Europe accounted for 1,850 kt and the US for 1,410 kt lead production in 1999. In 1996 the EU accounted for 25% and the low-income countries for about 34% (UN, 1998). Lately China has been increasing its production substantially (Lead-zinc, 2000). In the EU France, Italy, UK, Germany and Belgium are the main producers.

An average of 50% of the total lead production comes from primary raw material and the other 50% from secondary raw material (BREF). According to other sources the contribution of secondary raw material is even more, i.e. 59% of the production in high-income countries (Siegmund, 2001) and 61% of the total production in the world (Hassal et al., 2000). In the USA there is even mention of 85% from secondary raw material (RSR Corporation website, 2003). UN statistics report lower values for the production from secondary raw materials (UN, 1998). Approximately 44% of the total world production is from secondary raw materials and specifically
for **developing countries** this figure is 23%. These are however values for the year 1996 and it is expected that the contribution of secondary raw material has increased over the last few years.

### 3.9.1 Primary lead

There are two basic pyrometallurgical processes that are available for the production of lead from lead sulphide or mixed lead and zinc sulphide concentrates: sintering/smelting or direct smelting. The processes may also be used for concentrates mixed with secondary raw materials.

**Smelting with a Blast Furnace**

Before smelting, a sintering step is always incorporated. Lead concentrates are blended with recycled sinter fines, secondary material and other process materials like limestone and silica and pelletised in rotating drums. Sulphur is oxidised to sulphur dioxide during the process and the reaction generates enough heat to fuse and agglomerate the pellets.

The charge to the blast furnace comprises:
- Sinter, which incorporates the roasted concentrate and fluxes
- Other oxygen-containing lead materials such as oxides and silicates
- Metallurgical coke in the Blast Furnace has two functions: reducing agent and heating fuel

In the combustion zone, atmospheric oxygen blown in through the tuyeres reacts with the coke to form carbon dioxide with extensive release of heat. This hot gas ascends through a coke-rich layer (arch) and is reduced to carbon monoxide, the main reductant. The rates of coke combustion and conversion of carbon dioxide to carbon monoxide (Boudard reaction equilibrium) must be in accordance with the rate of reduction in the reaction zone and with the rate of heat transfer. If the combustion rate exceeds the rate of heat transfer to the charge, the coke burns more rapidly than the charge melts causing the melting zone to rise in the furnace. If the combustion rate is lower than the rate of heat transfer, the coke burns so slowly that it prevents the charge from descending and slows down the performance of the furnace. Slag and lead collect in the furnace bottom and are tapped out periodically or continuously. The slag is quenched and granulated using water, or allowed to cool and is then crushed, depending on its destination or further use (BREF, 2001; IZA, 2003; Ullmann, 1997).

For smelting bulk lead and zinc concentrates and secondary material, a specially designed blast furnace is used, i.e. the **Imperial Smelting Furnace** (see also section 2.3). In this furnace, hot sinter, pre-heated coke and hot briquettes are charged. Together with these raw materials, hot air or enriched oxygen is injected. The reduction of the metal oxides not only produces lead and slag but also zinc, which is volatile at the furnace operating temperature and passes out of the ISF with the furnace off-gases. Lead is more or less a by-product of the production of primary zinc.

Since zinc and lead are simultaneously produced in an ISF an allocation has to be made on the amount of coke used for the two products. An allocation on mass is chosen since this reflects the reduction process the best. For the production of 100 t of zinc and 35 t of lead bullion an amount of 1 t coke is required. This means that 26% of the coke needs to be allocated to the production of lead bullion, i.e. 0.26 t coke/t lead bullion. And 74% needs to be allocated to the zinc production, i.e. 0.74 t coke/t zinc (Lead-Zinc, 2000).
Direct Smelting

With these processes it is also possible to mix primary lead with secondary material. The sintering stage is not carried out separately with these processes. Lead sulphide concentrates and secondary materials are charged directly to a furnace and are then melted and oxidised. Sulphur dioxide is formed and is collected, cleaned and converted to sulphuric acid. Carbon (coke or gas) and fluxing agents are added to the molten charge and lead oxide is reduced to lead, a slag is formed.

Bath Smelting:
- *Isasmelt-Ausmelt;* This furnace uses a steel lance for the injection of fuel gas, oil or coal and oxygen or air into a cylindrical bath furnace. The lance is submerged in the molten bath and relies on the formation of a coating of slag to prevent rapid deterioration. Other raw materials are fed into the furnace by sealed conveyor where they react at a high rate and are melted. The submerged combustion lance stirs the bath and produces a slag along with the desired metal or matte. Slag reduction is done by coal.
- *QSL-furnace* (Queneau-Schumann-Lurgi) This furnace consists of a horizontal cylinder with oxidation and reduction zone. Tuyeres supply a mixture of air and coal dust to the slag reduction zone. Raw material can be moist and sized from large lumps to fine material. They are fed into the top of the furnace mixed with coal and fluxes. The oxidation zone produces lead bullion, sulphur dioxide and a lead rich slag. This flows into the reduction zone so that a further quantity of lead bullion is produced; this flows in the reverse direction to the lead tap hole. Slag is tapped from the reduction end and then granulated. Lead bullion is tapped from the oxidation end and then refined. Slag reduction is done by submerged combustion of oxygen fuel in gas shrouded tuyeres. Coal is used as the main reductant.
- *Kaldo* This is a rotating and tilting furnace that uses lances for heating and blowing purposes. The furnace is small and is usually housed in an enclosure to contain secondary emissions, which are treated. Rotation of the furnace promotes good mixing of the charge and complete reaction of the components but can lead to abrasion of the refractory lining. Oxygen and fuel are added via the lances, which blow on to the surface of the melt. The use of oxygen results in the production of low off-gas volumes and high sulphur dioxide.
when sulphides are smelted. The process is normally carried on a batch basis and it is common to use a number of these furnaces for smelting, converting and slag cleaning. (BREF, 2001)

**Flash Smelting:**
- Kivcet (KSS)
  With this furnace the charge is ignited as it enters the reaction shaft, temperatures up to 1400 °C are reached and complete de-sulphurisation takes place immediately. The coke breeze is only heated as it falls down the shaft. The coke floats on the slag bath and reduces PbO. Partly reduced slag and bullion flow under a submerged partition wall into the reduction section of the furnace, which is electrically heated and where additional coke or coal is added for final reduction. Lead bullion is sent for refining, the slag may be sent to a Waelz kiln. This process is also used for copper production.

A survey among primary smelters in the Developed World, representing approximately 86% of the total primary lead production, had the following result: 6% QSL, Kaldo 4%, Kivcet 12% and the BF/ISF 78%. Two smelters produced lead with the Ausmelt method, but did not participate in the survey. This would probably constitute about 5% of total production (Dutrizac et al., 2000). These percentages indicate that 78% is done with the **Blast Furnace/Imperial Smelting Furnace** (including sintering) and about 22% is done with the **direct smelting** method.

### 3.9.2 Secondary Lead

Scrap batteries are the major source of secondary lead. This dominance of battery scrap allows for a standard recovery process. There are three ways of processing these batteries:
- **Battery recovery with desulphurisation**
- **Battery recovery without desulphurisation**
- **Whole battery smelting**

Smelting can be carried out using the following vessels: BF (blast furnace), EF (electric resistance furnace), EAF (electric arc furnace) or the Isasmelt furnace. The electric resistance furnace is used for complex secondary materials. It can be operated on a campaign basis alternating with secondary copper production in a copper smelter. Petroleum coke is used as the reducing agent.

In the US the majority of domestic battery scrap is processed in blast furnaces or reverberatory furnaces. Newer secondary recovery plants use lead paste desulphurisation to reduce sulphur dioxide emissions and waste sludge generation during smelting (EPA, 2002).
- **Reverberatory Furnace**
  The reverberatory furnace is used for smelting concentrates and secondary material. Two general types exist, a simple bath furnace for smelting of calcine or concentrates and a reverberatory hearth furnace for melting or refining. Furnaces can sometimes be tilted to pour or blow metal. Tuyeres can be used for the injection of treatment gases or for the addition of fine material.

The new processes QSL, Kivcet and Isasmelt also allow the treatment of primary and secondary material. Despite this trend the **majority of secondary lead** is produced **pyrometallurgically** in an Imperial Smelt Furnace (Siegmund, 2001). In Europe a few smelters apply blast furnace operation treating the entire, unbroken battery. The smelters in the US use reverberatory furnaces coupled with either a BF or EF. Some newer plants desulphurise the batteries (Robert et al., 2001)
Refining of primary and secondary lead

- **Electrolytic.**
  An electrolytic cell is used consisting of a cast anode of de-copperised lead bullion and a cathode, placed in an electrolyte containing the metal solution. The cathode is either a thin blank of pure metal (starter sheet) or a former sheet made from stainless steel (permanent cathode plate). This is a high cost process and is used infrequently.

- **Pyrometallurgical.**
  A pyrometallurgical refinery consists of a series of kettles, which are indirectly heated by oil or gas. This process does not use any electrical methods nor reducing agents and therefore does not have CO₂ emissions from non-energy use.

Of the world production 90% is refined via pyrometallurgical methods (EPA, 2002).

**Calculation CO₂ emission factors**

Electrodes are not used in the production of lead, therefore only emissions from the use of a reducing agent occur.

For the emission factor of reductant use, a weighted average is taken. Approximately half of the production comes from primary material (BREF, 2001) and of this 80% is produced with Imperial Smelt Furnaces (ISF) while the rest is done with the direct smelting processes: Kivcet, Ausmelt and QSL (Dutrizac et al., 2000). Since the majority of secondary lead is also smelted with an ISF (after pre-treatment), the overall division in processes for primary and secondary lead together is estimated at 80% ISF and 20% other.

For the ISF the coke consumption is taken from the article of Waquier and Bendixer (0.18 t coke/t Pb) since this is quite a recent value (1998) for a plant in France. This is also the most conservative estimate compared with the other sources (Morris, 1983; Dutrizac et al., 2000; Ullmann, 1997). For the direct smelting processes the average is taken of the three processes (0.25 t CO₂/t Pb) since the contributions of the three to the total production is very similar in magnitude.

For the production of lead from secondary raw materials the CO₂ emissions originating from the battery treatment (a conservative value of 0.2 t CO₂/t is taken) is added to the total emission factor with a weight of 50%. With this an overall emission factor can be calculated:

Reductant use: 0.64 t CO₂/t Pb

No IPCC emission value exists for the production of lead. More accurate emission factors could be determined if the consumption of reductant for the ISF and the direct smelting processes would be more in accordance with each other. At the moment the values differ a lot and it is uncertain what the best value is. In addition, the emissions for secondary material are only based on values from the BREF report, other sources would be useful to give a more representative figure.

### 3.10 Zinc

Canada, China, Japan and the EU are the most important producers of zinc. In 1996 Europe was the largest with about 33% of the world production (UN, 1998). According to the International Zinc Association (IZA, 2003) 60% of the production in Europe is primary zinc while 40% is secondary zinc (recycled zinc) In the USA the total recycling rate ranged between 24.2% (1995) to 27.5% (1998) (USGS 1999). The shares for worldwide production could differ substantially depending on the production structure in China and Japan. In the developing world almost all of the zinc is produced from primary raw material (UN, 1998).
3.10.1 Primary Zinc

The production route for primary zinc is as follows:
- Calcining
- Leaching or Sintering
- Smelting or Purification
- Final Refining

The primary production of zinc begins with the reduction of zinc concentrates to metal (the zinc concentration process consists of separating the ore, which may contain as little as two percent zinc, from waste rock by crushing and flotation, a process normally performed at the mining site. Zinc is found in the earth’s crust primarily as zinc sulphide, ZnS. Zinc reduction is accomplished in one of two ways: either pyrometallurgically or hydrometallurgically by electrowinning (EPA, 1995, 2002). According to a recent report of the IZA (2002) the contribution of the various production processes representative for the European industry is as follows: 85% hydrometallurgical (= electrolytic) and 15% pyrometallurgical (Imperial Smelting Furnace). In other countries this can be slightly different, e.g. in the USA 80% is manufactured hydrometallurgically and 20% pyrometallurgically (EPA, 2002; Fugleberg, 1999).

![Schematic flow diagram of the principal operations leading to the production of SHG zinc ingots from virgin raw materials. The left-hand side of the diagram relates to electrometallurgical processing and the right-hand side relates to pyrometallurgical processing.](Figure 7: Schematic flow diagram of the zinc production routes (IZA, 2002)

There are three principal methods of producing zinc (BREF, 2001; Ullmann, 1997), i.e. the electrolytic (or hydrometallurgical) process and two pyrometallurgical processes (ISF plant and electro-thermic distillation):
1. Electrolytic (hydrometallurgical)

- **Roasting or calcining**
  Roasting is a high-temperature process that converts zinc sulphide concentrate to an impure zinc oxide called calcine. Roaster types include multiple-hearth, suspension, or fluidized-bed. In general, calcining begins with the mixing of zinc-containing materials with coal. This mixture is then heated, or roasted, to vaporize the zinc oxide, which is then moved out of the reaction chamber with the resulting gas stream. The gas stream is directed to the bag-house (filter) area where the zinc oxide is captured in bag-house dust. Roasting is an exothermic process and no additional fuel is used, the heat generated is recovered. The following reactions occur during roasting:

\[
\begin{align*}
2 \text{ZnS} + \text{O}_2 & \rightarrow 2 \text{ZnO} + \text{SO}_2 \\
2 \text{SO}_2 + \text{O}_2 & \rightarrow 2 \text{SO}_3
\end{align*}
\]

- **Leaching**
  Leaching refers to the dissolving of the captured calcine in a solution of sulphuric acid to form a zinc sulfate solution. The calcine may be leached once or twice. In the double-leach method, the calcine is dissolved in a slightly acidic solution to remove the sulfates. The calcine is then leached a second time in a stronger solution, which dissolves the zinc. This second leaching step is actually the beginning of the third step of purification because many of the iron impurities (such as goethite and hematite) drop out of the solution as well as the zinc. The following reaction takes place:

\[
\text{ZnO} + \text{SO}_3 \rightarrow \text{ZnSO}_4
\]

- **Liquor purification**
  After leaching, the solution is purified in two or more stages by adding zinc dust. The solution is purified as the dust forces deleterious elements to precipitate so that they can be filtered out. Purification is usually conducted in large agitation tanks. The process takes place at temperatures ranging from 40 to 85°C, and pressures ranging from atmospheric to 2.4 atmospheres. The elements recovered during purification include copper as a cake and cadmium as a metal. After purification the solution is ready for the final step, i.e. electrowinning.

- **Electrolysis**
  The purified solution passes to a cell house where zinc is electrically won using lead-silver anodes and aluminium cathodes (IZA, 2003). Zinc of high purity (>99.995%) is deposited on the negative cathodes.

No CO₂ emissions are released in any of these production processes since no carbon is used.

2. Imperial Smelting Furnace (pyrometallurgical)

The ISF process (Imperial Smelting Furnace) is the only pyrometallurgical method that is still used today in the EU and it is still of importance because it enables complex lead-zinc concentrates and secondary material to be treated simultaneously, yielding saleable lead and zinc. The overall process for the production of primary zinc metal (slab zinc) is very similar to that for copper and lead, albeit with minor differences. The reaction that takes place is:

\[
\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}
\]

The ores are usually first treated by a sinter plant (see also Section 3.1). In the Imperial Smelting Furnace, lead and zinc are produced together in a single blast furnace operation. This is basically
a zinc production process in which lead is also obtained. The zinc to lead ratio in the sinter mixture is usually 2:1. Coke or coal is used as the reducing agent in this furnace.

Since zinc and lead are simultaneously produced in an ISF an allocation has to be made on the amount of coke used for the two products. An allocation on mass is chosen here. For the production of 100 t of zinc and 35 t of lead bullion an amount of 1 t coke is required (Dutrizac et al., 2000). This means that 26% of the coke needs to be allocated to the production of lead bullion, which is equivalent to 0.26 t coke/t lead. And 74% needs to be allocated to the zinc production, which is equivalent to 0.74 t coke/t zinc.

3. Electro-thermic distillation (pyrometallurgical)

The electro-thermic distillation retort process, the only pyrometallurgical technique utilized by the US primary zinc industry and some Japanese plants (Okura et al., 2002), was developed by the St. Joe Minerals Corporation in 1930. The principal advantage of this pyrometallurgical technique over electrolytic processes is its ability to accommodate a wide variety of zinc-bearing materials, including secondary items such as calcine derived from electric arc furnace (EAF) dust. Electro-thermic processing of desulphurised calcine begins with a downdraft sintering operation, in which grate pallets are joined to form a continuous conveyor system. The sinter feed is essentially a mixture of roaster calcine and EAF calcine. Combustion air is drawn down through the conveyor, and impurities such as lead, cadmium, and halides in the sinter feed are driven off and collected in a bag filter. The product sinter typically includes 48 percent zinc, 8 percent iron, 5 percent aluminum, 4 percent silicon, 2.5 percent calcium, and smaller quantities of magnesium, lead, and other metals. (EPA, 1995)

Product sinter and, possibly, secondary zinc materials are charged with coke to an electric retort furnace. The charge moves downward from a rotary feeder in the furnace top into a refractory-lined vertical cylinder. Paired graphite electrodes protrude from the top and bottom of this cylinder, producing a current flow. The coke serves to provide electrical resistance, producing heat and generating the carbon monoxide required for the reduction process. Temperatures of 1400°C are attained, immediately vaporizing zinc oxides according to the following reaction:

\[ \text{ZnO} + \text{CO} \rightarrow \text{Zn} \text{ (vapor)} + \text{CO}_2 \]

The zinc vapour and carbon dioxide pass to a vacuum condenser, where zinc is recovered by bubbling through a molten zinc bath. Over 95 percent of the zinc vapour leaving the retort is condensed to liquid zinc. The carbon dioxide is regenerated with carbon, and the carbon monoxide is recycled back to the retort furnace. (EPA, 1995)

3.10.2 Secondary Zinc

The process route used to recover zinc from secondary raw materials depends on the form and concentration of zinc, the final use and the degree of contamination. Over 40 possible technologies (hydro- and pyrometallurgical) are available. A possible process route is: concentration (Waelz Kiln), Sintering, Imperial Smelting and finally Refining (BREF, 2001).

The following processes are used to fume volatile metals such as lead or zinc, from a substrate. The process uses high temperatures and a source of carbon to produce an inert slag by fuming or volatilising metals from the material. This allows the metals to be recovered usually as a zinc oxide for further processing in an ISF. Waelz kilns (= Rotary Kiln) and slag fuming furnaces are used. Fuming is also achieved during batch converting processes when volatile metals are removed during the process.
1. **Waelz Kiln**

This process is designed to separate zinc (and lead) from other materials by reducing, volatilising and oxidising zinc (and lead) again. The Waelz kiln process is a commonly used to enrich secondary raw materials i.e. slags, flue dusts and sludges and Pb/Zn materials to a product with >45% Zn. In total, the Waelz kiln process does not lead to metal reduction as the following formulae show:

\[
\begin{align*}
\text{ZnO} + \text{C} & \rightarrow \text{Zn (vapour) + CO} \\
\text{Zn (vapour) + CO + O}_2 & \rightarrow \text{ZnO + CO}_2
\end{align*}
\]

The only purpose of the Waelz process is hence separation of ZnO for further processing.

Figure 8 shows the elements of a *Waelz Kiln plant*. The dust, other secondary raw materials and coke fines are loaded into silos. The materials are mixed and can also be pelletised. The mixture is then sent directly to the kiln feeding system or for intermediate storage. Weighing equipment can be used to control the quantity of reduction materials (coke) according to the zinc content of the raw materials and of fluxes for the desired slag quality. The normal operating temperature inside a Waelz kiln is about 1200°C. Inside the kiln solid materials are first dried and then heated up by the counter current flow of hot gas and contact with the refractory lined walls. Depending on the inclination, length and rotation speed, the material has an average residence time between 4 and 6 hours in the kiln. In the strongly reducing atmosphere of the solid bed, zinc, lead and other heavy metals are reduced. Zinc and lead are evaporated into the gas atmosphere; chlorides and alkalis (depending on the slag basicity) are vaporised together with the heavy metals. As there is a surplus of air in the kiln, the metal vapours are oxidised. The mixed oxides are drawn from the kiln with the process gases and separated in the gas treatment system. (BREF, 2001)

![Figure 8: Waelz Kiln plant (BREF, 2001)](image_url)

The Waelz oxide that is produced can be processed in a number of ways. The most basic process is hot briquetting or sintering for sale to pyrometallurgical zinc plants e.g. *Imperial Smelting Process*. If the lead oxide content is high, a calcination step can also be used to volatilise the lead. Waelz oxide can also be leached in a two-stage process using sodium carbonate in the first stage and water in the second stage to remove chloride, fluoride, sodium, potassium and sulphur. The purified final product is dried and can be used as a feed material for the zinc *electrolysis* process.
In Waelz kiln, heating is done principally by the combustion of hydrocarbons. The intermediate reduction is brought about by the partial burning of added coke, and mixing is effected by the rotation of the furnace.

Since the Zinc is not really reduced with the carbon in the end (a Waelz oxide is the product, see second formula above), we consider heat raising to be the ultimate purpose of hydrocarbon and coke use. In other words, since the final product is identical with the original product (in both cases ZnO), we do not allocate any of the carbon input to the reduction process. This is a convention and other approaches would also be possible. As a consequence of the convention chosen here, the CO₂ emissions released from the Waelz kiln process are regarded as emissions from fuel combustion and not from non-energy use (feedstocks). For this reason no emission factors have been determined for this process.

2. Slag reduction (slag fuming)

This process is only used for the liquid slag, which comes from Lead and Copper smelting. The Zinc oxide, which is the product of the slag reduction process, is processed further and is converted to metallurgical zinc. Electric arc furnace dust, most of the slags from lead smelting operations and other residues from zinc reduction contain lead and zinc that would be lost without further treatment. These materials may be fumed with a source of carbon such as coal, to recover lead and zinc and to raise heat for the process. In the slag fuming process a mixture of coal dust as a reductant and air is injected through tuyeres into liquid blast-furnace slag at 1150–1250 °C in a water-jacketed furnace. In contrast to the Waelz kiln method, with which a range of raw materials can be treated, the slag fuming process is only used to remove zinc from molten slags from lead and copper smelting. (BREF, 2001)
**Calculation CO₂ emission factors**

*Primary zinc.* Since the ISF is currently the only pyrometallurgical method used in Europe we will solely discuss the reductant consumption in this process. In other countries it may be necessary to take into account the electro-thermic distillation process (e.g. Japan) where the use of electrodes will also cause emissions from this category. Then it will also be required to use a different weighing factor for the process mix (exact shares for this process have not been found) to also include the emissions from this process. No consumption of carbon takes place in the electrolytic process.

For the Imperial Smelting Furnace (ISF) three different values for the reductant consumption are available from three different sources (Ullmann, 1997; Vereecken, 1991; Kola, 1995), ranging from 0.77-0.95 t/t Zn. The most recent source is from 1995 (Kola) and gives a value of 0.85 t/t Zn. Since this is in between the other two values and since it is the most recent this was used to determine the CO₂ emission factor for solid carbon use. To determine the CO₂ emission factor it was taken into account that the ISF process accounts for 15% of the total primary Zinc production in Europe.

*Secondary zinc.* No information was found on the material flows and energy use for the production processes used in secondary zinc production. As discussed above there are good
reasons not to take into account the non-energy carbon use and the resulting emissions of the Waelz kiln process. It is assumed that the same share of pyrometallurgical methods can be assumed here as for primary zinc production. If we take the production split for the total zinc production (primary and secondary) the same as for the primary zinc production, we can calculate a weighted average of 15% for the CO$_2$ emissions reflecting solid carbon use. Then we come to the following emission factors:

- **Electrode use:** 0 t CO$_2$/t Zn
- **Solid carbon use:** 0.43 t CO$_2$/t Zn

More accurate emission factors could be estimated if the exact process mix for secondary zinc production were known and if more sources were available.

### 3.11 Magnesium

Canada, China, the US, Russia and Norway are the biggest producers of magnesium in the world. The EU does not have a primary magnesium producer anymore, since the Pechiney plant in France shut down in July 2002. However, as the NEAT model calculates emissions reaching back to 1990 this plant still needs to be taken into account.

Magnesium can be produced either by electrolysis or a thermal reduction process. The raw materials used are dolomite, magnesite, carnalite, brines or seawater depending on the process. Magnesium can also be recovered and produced from a variety of magnesium containing secondary raw materials. Each of the processes practiced at these facilities uses a different means of feed preparation and this in turn causes the electrolytic cell end of the processes to be different also.

The Pechiney plant in France used the thermal reduction process Magtherm. In Norway the electrolysis method is still in use. The United States has only one producer, the Magnesium Corporation, which also uses electrolysis for its production. Also in Russia and a part of the magnesium production in Canada is produced with electrolysis. China supplies about one-third of the world’s magnesium needs at the moment and they use primarily the thermal process. In total about 60% of the world’s magnesium metal is produced by electrolysis. (IMA, 2002; Noranda, 2003).

#### 1. Electrolysis of molten magnesium chloride

The two main routes for the production of dehydrated magnesium chloride cell feed are (Ullmann, 1997):

- **Chlorination** of magnesia (MgO) or magnesite (MgCO$_3$) in the presence of carbon or carbon monoxide. Two processes are used industrially: IG-Farben (Norway) and the MagCan process (Canada). The consumption of carbon is 0.45 t/t and 0.51 t/t respectively according to Shekhovtsov et al. (2000) and 0.45 t/t and 0.55 t/t according to Ullmann (1997). The carbon is usually added in the form of petroleum coke. For the MagCan process the main reactions are:

  \[
  \begin{align*}
  \text{MgCO}_3 + \text{CO} + \text{Cl}_2 & \rightarrow \text{MgCl}_2 + 2 \text{CO}_2 \\
  \text{CO}_2 + \text{O}_2 + 3 \text{C} & \rightarrow 4 \text{CO}
  \end{align*}
  \]

- **Dehydration** of aqueous magnesium chloride solutions (brines) or hydrous carnalite (MgCl$_2$·KCl·6 H$_2$O). The former process is used by NorskHydro in
Over half of the world's magnesium metal is produced by molten salt electrolysis, with magnesium metal produced at the steel cathodes and chlorine gas generated at carbon anodes. The anodes react with residual oxygen in the electrolysis cell to form carbon dioxide gas. The reaction slowly consumes the anode and results in an ever-increasing anode-to-cathode distance, leading to increased voltage and increased energy use in the cell. In addition, chlorine gas reacts with residual hydrocarbons in the carbon anode, resulting in the formation of chlorinated hydrocarbons (CHCs).

The cell electrolyte is a molten mixture containing about 25% MgCl$_2$ - 15% CaCl$_2$ - 60% NaCl, and the cell is operated between 700°C and 750°C. The cell electrolytic reaction is:

\[ \text{MgCl}_2 \rightarrow \text{Mg}(l) + \text{Cl}_2(g) \]

The magnesium produced is about 99.9% pure as it comes from the cell, since neither sodium nor calcium is reducible more easily than is magnesium. The chlorine produced in the cell is converted to HCl for use in the acidification process by reaction with natural gas and steam or in a hydrogen/chlorine burner. (Ullmann, 1997)

There are various types of electrolytic cells in use (Ullmann, 1997):
- IG-cell. This is used in Russia, Norway and the USA.
- Sovjet-Union cell. This is used in Russia and the USA.
- Alcan-cell. This is used in Canada, Japan and the USA.

2. Silico-thermic: Thermal reduction of magnesium oxide

Magnesium oxide is reduced with Ferrosilicon and therefore no CO$_2$ emissions occur due to non-energy use of carbon.

\[ 2 \text{CaO} + 2 \text{MgO} + \text{Si} \rightarrow 2 \text{Mg} + \text{Ca}_2\text{SiO}_4 \]

Two thermal processes currently are in use to recover magnesium metal from dolomite—the Pidgeon process and the Magnetherm process. Both use the same basic chemistry, but the Pidgeon process uses an external heat source, and the Magnetherm process uses heat generated by the electrical resistance of the reactants. In the Pidgeon process, dolomite and ferrosilicon are formed into briquettes and heated in a retort under a vacuum. Magnesium oxide in the dolomite reacts with the ferrosilicon to produce magnesium vapor, which is cooled and condensed in a separate section of the retort. In the Magnetherm process, calcined dolomite, ferrosilicon, and alumina are heated under a vacuum. Alumina reduces the melting point of the slag produced by the dolomite-ferrosilicon reaction to make resistance heating practical. Magnesium vapour is cooled and condensed in a condensing chamber. The Magnetherm process is used in plants in Brazil, Serbia and Montenegro, and the United States.

**Calculation CO$_2$ emission factors:**

From the information above it can be concluded that it is not necessary to have an emission factor for magnesium for the European Union, and specifically for Norway the emission factor can be calculated by only taking into account the electrolysis process. Before the closure of the Pechiney plant in France, the European production of Magnesium was done by the Magnetherm process, hence no emission factor is required. If an emission factor for the world production would be needed, it is suggested to use a weighed emission factor with 40% of the world production using the thermal processes and 60% using the electrolytic methods.
The electrode consumption values differ a lot between the different cells, 0.015-0.07 \text{ t CO}_2/\text{t Mg} (Ullmann, 1997; Shekhovtsov et al., 2000). Although many others exist, Ullmann (1997) only gives consumption figures regarding the IG and Dow cells and the BREF report (2001) does not make any reference to electrode consumption. Since the value of Shekhovtsov et al. (2000) is most recent and since it is within the range of the figures from Ullmann, we assume this one for the electrode consumption. With this value and the information that about 60\% of the world production is done via the electrolysis method the CO$_2$ emission factor from electrode use can be calculated.

For the use of solid carbon for the preparation of cell feed, Ullmann (0.45-0.55 t CO$_2$/t Mg) and Shekhovtsov (0.45 – 0.51 t CO$_2$/t Mg) give values. The lower value is for the IG process, the latter for the MagCan process. Due to a lack of data, it is uncertain what the share of chlorination and dehydration exactly is for the world production. We have therefore assumed that both processes cover half of the production of cell feed for the electrolysis process. Multiplying this 50\% with the average value of the carbon consumption from both available sources and weighing this with 60\%, the emission factor can be determined. The emission factors for the world in total are:

- Electrode use: 0.038 t CO$_2$/t Mg
- Solid carbon use: 0.53 t CO$_2$/t Mg

More information is required on the exact share of the chlorination and dehydration process.

### 3.12 Nickel

The world's primary nickel production in 1996 was approximately 950 kt. In Europe the production capacity is approximately 200 kt, about 20\% of the world production. In Europe Norway, UK, Finland, France and Greece are the biggest producers of Nickel. Of the total world production, Canada and Australia have by far the largest production. Developing countries accounted for about 26\% of the world production in 1996 (UN, 1998).

Much of the nickel used in metal products (e.g., stainless steel, nickel plate, various alloys) is recycled, resulting in the fact that 32\% of nickel consumption in 1988 was derived from secondary scrap.

Nickel is produced from oxidic (laterite and saprolite) or sulphidic ore, about 60\% of the nickel comes from sulphide deposits and about 40\% from oxide deposits (Terry, 2001). The oxidic ores are used to make nickel mattes or ferronickel and the sulphidic ores are used to produce nickel metal. The primary extraction processes can be defined as the processes that receive nickel concentrate or prepared ore to produce final metal products, ferronickel and nickel oxide, as well as intermediate products such as matte and liquor. Nickel primary extraction is comprised of two main methods:

1. Pyrometallurgical methods
2. Hydrometallurgical methods

Over 90\% of the world's nickel sulphide concentrates are treated by pyrometallurgical processes, e.g. reverberatory furnace or flash smelting, to form nickel-containing mattes (Riekkola-vanhanen, 1999c; Lembgen et al., 2001). In several modern operations the roasting step has been eliminated, and the nickel sulphide concentrate is treated directly in the smelter.
Oxidic ores:

The ore is pre-treated and calcined in a rotary kiln and afterwards usually smelted in an EAF (BREF). Lateritic ore is processed by pyrometallurgical or hydrometallurgical processes. In the pyrometallurgical process, sulphur is generally added to the oxide ore during smelting, usually as gypsum or elemental sulphur, and an iron-nickel matte is produced. The smelting process that does not include adding sulphur produces a ferronickel alloy, containing less than 50% nickel, which can be used directly in steel production (see the Ferronickel section above). This is done by most laterite nickel producers. Hydrometallurgical techniques involve leaching with ammonia or sulphuric acid, after which the nickel is selectively precipitated. Alloys, such as stainless steels, are produced by melting primary metals and scrap in large arc furnaces and adjusting the carbon content and concentration of alloying metals to the desired levels. (BREF, 2001; Ullmann, 1997; Riekkola-Vanhanen, 1999c).

In Inco’s process for the production of nickel matte from laterite ores, reduction is accomplished by adding coal to the kiln feed and by lancing high-sulphur oil into the ore bed. The hot calcine is then smelted in an electric furnace. Most of the nickel and a large portion of the iron are reduced and sulphurised to form a low-sulphur matte phase. Iron removal can then be accomplished by fluxing and selective oxidation of the iron in a converter to produce a nickel matte containing over 75% Ni, 20 – 22% S, and less than 1% Fe (BREF, 2001; Ullmann, 1997; Riekkola-Vanhanen, 1999c).

Sulphidic ores:

*Flash smelting* is the most common process in modern technology, but electric smelting is used for more complex raw materials when increased flexibility is needed. Both processes use dried concentrates. Electric smelting requires a roasting step before smelting to reduce sulphur content and volatiles. Only the Outukumpu flash furnace is used in Europe. The INCO flash furnaces and electric or shaft furnaces are used elsewhere in the World. Conventional smelting processes are used to remove iron and other gangue materials from sulphide concentrates to produce nickel matte. In the world there are about 6 flash smelting furnaces (Outokumpu), 6 EAF’s and 3 reverberatory furnaces (Terry, 2001).

In flash smelting, dry sulphide ore containing less than 1% moisture is fed to the furnace along with preheated air, oxygen-enriched air (30–40% oxygen), or pure oxygen. Iron and sulphur are oxidized. The heat that results from exothermic reactions is adequate to smelt concentrate, producing a liquid matte (up to 45% nickel) and a fluid slag. Furnace matte still contains iron and sulphur, and these are oxidized in the converting step to sulphur dioxide and iron oxide by injecting air or oxygen into the molten bath. Thus no CO₂ emissions take place as a cause of non-energy use. Oxides form a slag, which is skimmed off. Slags are processed in an electric furnace prior to discard to recover nickel. Process gases are cooled, and particulates are removed by gas-cleaning devices (BREF, 2001; Ullmann, 1997; Riekkola-Vanhanen, 1999c).

Smelting:

- **Reverberatory furnace**: No electrode and no reductant is used in this process. Only fossil fuel for the energy supply.
- **Flash smelting**: This furnace is primarily used for the production of nickel from sulphidic ores (approximately 90% of total production). No electrode and no reductant is used in this process.
- **Electric furnace**: Carbon electrodes are used and can be of the Søderberg or prebaked type. Coke is additionally used as a reductant and constitutes about 2.5% wt of the concentrate. This furnace is mostly used for the production of FeNi (see previous section).
Nickel refining:

Various processes are used to refine nickel matte (BREF, 2001; Riekkola-Vanhanen, 1999c):

- **Fluid bed roasting and chlorine-hydrogen reduction** produce high-grade nickel oxides (more than 95% nickel).
- Vapour processes such as the carbonyl process can be used to produce high-purity nickel pellets. In this process, copper and precious metals remain as a pyrophoric residue that requires separate treatment. Nickel will react with carbon monoxide to form a gaseous nickel compound called nickel carbonyl. The nickel is removed in the vapour phase, leaving behind all of the copper, cobalt, and other metals. The nickel carbonyl is heated to a higher temperature, where it becomes unstable and decomposes into metallic nickel and carbon monoxide. The metallic nickel forms round pellets, and the carbon monoxide is recycled to refine more nickel. The nickel carbonyl can also be used to coat things with nickel, such as graphite fibres. The only problem is that nickel carbonyl is very poisonous, so your process controls and containment have to be very, very good.
- **Electrowinning**, in which nickel is removed from solution in cells equipped with inert anodes, e.g. lead or titanium anodes, and cathodes is the more common refining process. The cathode is either a thin blank of pure metal (starter sheet) or a former sheet made from stainless steel or aluminium (permanent cathode plate). By controlling the chemistry of the plating bath along with the voltage, fairly high purity nickel can be produced. Up to this point, the methods for producing copper and nickel are almost the same. Sulphuric acid solutions or, less commonly, chloride electrolytes are used.

**Calculation CO₂ emission factors:**

Since most of the nickel metal is produced from sulphidic ores and since about 90% of the production of nickel is done by flash smelting, no emissions of CO₂ from the use of electrodes or solid carbon occur. The main gas, which is emitted during production of nickel, is SO₂.

### 3.13 Ferronickel

**Japan** is the largest producer of ferronickel in the world with almost half of the world production. The **EU** produces only about **11% of the total world production** (UN, 1998).

The *carbo-thermic* reduction process of ferronickel from primary raw material is carried out exclusively by the **EAF**. The first step is drying. The next process step is homogenisation where the different ores are mixed with coal and pelleted dust, which is recycled from the main process. The hot pre-reduced calcine can be introduced directly to the smelting furnace or by insulated containers. The containers may be used for two reasons, first to conserve the heat and second to add coke or coal required for complete reduction before they are discharged into the electric furnace, where melting and final reduction occurs. The reductant is either coke or coal and in the EAF Søderberg electrodes are used. (BREF, 2001)

FeNi can also be produced from secondary raw materials, such as spent catalysts and sludge from the galvanising industry. This is also done in a submerged EAF.

**Calculation CO₂ emission factors:**

Since ferronickel from primary and secondary material is both produced in an EAF it does not matter for the CO₂ emissions which percentage of the raw material is recycled. Information on electrode and solid carbon use was only found in Ullmann and therefore this is used to calculate the emission factors:
The IPCC does not give any value for this process. The BREF report gives a CO$_2$ emission factor for the whole process: 1.2-1.5 t CO$_2$/t FeNi. The sum of the two values calculated above with the carbon consumption corresponds very well with the average value of the range given by the BREF emission factor. The former value is therefore assumed to be representative for the ferronickel production in Europe and very likely also for many other countries with comparable technology levels, e.g. Japan. However, it is recommended to take information from several plants in Japan (since this is the largest producer) to determine the emission factor more precisely making it more representative for the total world production.

### 3.14 Tin

China, Indonesia, Malaysia and the US are the biggest producers of tin. In low-income countries it is almost entirely primary tin that is produced, whilst the developed world almost completely relies on secondary production. In the EU only 3% of the tin is produced and in non-developed countries almost 92% (UN, 1998), the US accounts for the remaining 5%.

The production of tin is mostly done by pyrometallurgical methods. The dominant reduction furnace used is the reverberatory furnace. This has taken the place of the blast furnace, which was used in the past. The rotary kiln is only used in Indonesia and Bolivia at the moment (Robilliard et al., 2000).

The electric furnace is another important furnace for the reduction of Sn and is used in various countries, e.g. in France, Germany, Italy and Canada. It uses 3 graphite electrodes and consumes about 0.01 t electrodes per tonne of tin. The reduction material can be coal, coke or charcoal and is usually about 11-21% of the mass of the concentrate. This amounts to approximately 0.33 t of reductant per tonne of tin. There are various other ways of producing zinc, e.g. the TBRC-Converter in the USA, the Siromelt in Australia and electrolysis (hydrometallurgical), but these have only a very limited contribution to the overall production (Ullmann, 1997).

The chemical reaction that takes place inside the furnace is:

$$\text{SnO}_2 + 2\text{CO} \rightarrow \text{Sn} + 2\text{CO}_2$$

**Calculation CO$_2$ emission factors:**

To calculate the emission factor we assume that about one third of the production is done in electric furnaces and about two-thirds in reverberatory furnaces (very rough estimate). This is done due to lack of data of the exact contribution of the various processes to the overall tin production. The only information available is that the reverberatory furnace is the dominant production method in the world (Robilliard et al., 2000), but that in Europe also the EF is used in several countries.

Only Ullmann has been found to give a figure for electrode consumption and this is therefore used to determine the emission factor after assuming that only 33% of the production is done in an EF. For the consumption of reducing agent it is assumed that the reverberatory furnace uses the same amount of reducing agent as the EF since the tin-oxide needs to be reduced anyway. The value given by Ullmann is about the average of the range of consumption given by another source (Robilliard et al., 2000). The former is hence used to calculate the emission factor from solid carbon use. The emission factors are:
Electrode use: 0.012 t CO₂/t Ni
Solid carbon use: 1.08 t CO₂/t Ni

As explained above these emission factors may be subject to uncertainties since only two sources were found. The IPCC also does not mention an emission factor for this process. In addition, no information was available on the reductant consumption in the reverberatory smelter or on the exact percentage of use of the reverberatory smelter and EF.

3.15 Copper

The largest producer of refined copper is the US (2,480 kt in 1998), followed by Chile (2,335 kt), Japan (1,277 kt), China (1,150 kt), Germany (696 kt) and Russia (625 kt) (USGS, 1999). The EU only represents 16% of the total production, whereas the production from non-developed countries, e.g. Chile and China, is about 53% of the world production (UN, 1998). In the EU the division primary-secondary copper is about 50-50, but on a worldwide scale primary copper production is about 70% of the total (ICSG, 1997).

Copper can be produced either pyrometallurgically or hydrometallurgically depending upon the ore-type used as a charge. The ore concentrates, which contain copper sulphide and iron sulphide minerals, are treated by pyrometallurgical processes to yield high purity copper products. Oxide ores, together with other oxidized waste materials, are treated by hydrometallurgical processes to yield high purity copper products. Approximately ±85% of the world primary and secondary copper production is now manufactured by pyrometallurgical techniques. However this is decreasing and the hydrometallurgical method of producing copper is gaining popularity (Riekkola-vanhana, 1999b). At the moment about ±15% of the copper worldwide is produced with leaching processes, i.e. hydrometallurgical (pers. comm. Vroonhof, 2003). The production structure can be summarised as follows (pers. comm. Vroonhof, 2003):

The type of smelters used for the pyrometallurgical method are:

- **Worldwide.** The Outokumpu flash smelter is worldwide the most common with approximately 50% of world production using this smelter, the reverberatory smelter contributes about 25% and 25% other smelters.
- **Europe.** In Europe the Outokumpu flash smelter has a share of about 60%, the reverberatory smelter about 8% and others 32%.

3.15.1 Primary Copper

The technology choice depends on the specific characteristics of the concentrate feed. Sulphide ores go to a concentrating stage, whereas oxide ores are routed to leaching tanks immediately. Afterwards there are two options (Riekkola-vanhanen, 1999b; Ullmann, 1997; EPA, 2002):
1. Leaching and electrowinning (SX/EW) – hydrometallurgical process

In the hydrometallurgical process, the oxidized ores and waste materials are leached with sulphuric acid from the smelting process. Leaching is performed in situ, or in specially prepared piles by distributing acid across the top and allowing it to percolate down through the material where it is collected. Once the copper-rich solutions are collected they can be processed by either of two processes - the "cementation" process or the "solvent extraction/electrowinning" process (SXEW). The cementation process is rarely used today (EPA, 2002).

In the SXEW process, the leach solution (PLS) is concentrated by solvent extraction. In solvent extraction, an organic chemical that extracts copper but not impurity metals (iron and other impurities) is mixed with the PLS. The copper-laden organic solution is then separated from the leachate in a settling tank. Sulphuric acid is added to the pregnant organic mixture, which strips the copper into an electrolytic solution. The stripped leachate, containing the iron and other impurities, is returned to the leaching operation where its acid is used for further leaching. The copper-rich strip solution is passed into an electrolytic cell known as an "electrowinning" cell. An electrowinning cell differs from an electrorefining cell (see second process below) in that it uses a permanent, insoluble anode. The copper in solution is then plated onto a starting sheet cathode in much the same manner as it is on the cathode in an electrorefining cell. The copper-depleted electrolyte is returned to the solvent extraction process where it is used to strip more copper from the organic. The anodes are inert (Pb-Sn-Ca). (EPA, 2002; BREF, 2001). The chemical reaction occurring in the cell is:

\[ \text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu} + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 \]

No carbon is used for non-energy purposes in this process.

2. Smelting and fire refining/electrolytic refining – pyrometallurgical process

Several stages of melting and purifying result in matte, blister and finally: 99% pure copper. There is an additional stage for the treatment of slag, a rest product of the smelting and converting stage. Recycled (secondary) copper begins its journey by re-smelting. Carbon (in the form of coke or natural gas) and fluxing agents are added to reduce metal oxides if required. Apart from fuel, smelter inputs include silica (800 kg/t of copper) and limestone (250 kg/t). 80% of the heat introduced to the process comes from carbon, the rest from oil.

- **Smelting.** The copper ore first goes to the smelter. During smelting the concentrates are dried and fed into one of several different types of furnaces. There the sulphide minerals are partially oxidized and melted to yield a layer of "matte," a mixed copper-iron sulphide, and "slag," an upper layer of waste.

- **Converting.** Following smelting, the copper matte is fed into a converter. Lime and silica are added to the copper matte to react with the iron oxide produced in the process to form slag. Secondary copper may also be added to the converter. Air is blown into the molten matte causing the remainder of the iron sulphide to react with oxygen to form iron oxide and sulphur dioxide. Following the "blow," the converter is rotated to pour off the iron silicate slag. During a second blow the remainder of the sulphur is oxidized and removed from the copper sulphide. The converter can then pour off the molten copper, which at this point is called "blister" copper (so named because if allowed to solidify at this point, it will have a bumpy surface due to the presence of gaseous oxygen and sulphur). Sulphur dioxide from the converters is collected and fed into the gas purification system together with that from the smelting furnace and made into sulphuric acid. Due to its residual copper content, slag is recycled back to the smelting furnace (EPA, 2002).

- **Refining.** Blister copper, 98.5% copper, is refined to high purity copper in two steps. The first step is "fire refining," in which the molten blister copper is poured into a cylindrical furnace,
similar in appearance to a converter, where first air and then natural gas or propane are blown through the melt to remove the last of the sulphur and any residual oxygen from the copper. The molten copper is then poured into a casting wheel to form anodes pure enough for "electrorefining." (EPA, 2002). Natural gas or propane are used as reducing agents to reduce any copper oxide formed. (Ullmann, 1997; BREF, 2001; EPA, 2002)

Carbon emissions can come from the use of coke, natural gas or propane as reducing agents. However, precise consumption figures have not been found. Coke is mainly used as a fuel, 30-50 kg/t Cu (Riekkola-vanhanen, 1999b). Reported emission of CO$_2$ in a copper refinery plant was 2.7 kg/t Cu in 1997 (Table 8, p 316, Riekkola-vanhanen, 1999b). Probably this is only from energy use, but this is not certain.

- **Slag cleaning.** The slag produced in the smelting and converting stage of the pyrometallurgical process can be cleaned either in an electric furnace or in a slag concentration plant.

**Electric furnace**
Slag, coke and reverts are injected into the electric furnace. The produced matte from the electric furnace is periodically tapped through tapping holes and launders into ladles and transferred by cranes to the above-mentioned converters for further treatment. The additional slag from this process is tapped into granulation or cast in blocks and sold or transported to the slag storage area.
There are three or six electrodes in the electric furnace to supply energy into the furnace. Electric power is needed for the reduction reactions, heat losses and smelting of reverts. The reductive agent is coke. Electric furnace off-gases are first burned in an incinerator, then cooled and taken through a bag filter or a scrubber to the stack (Riekkola-vanhanen, 1999b).

**Slag concentration.**
With slag concentration neither electrode nor reductant is consumed.

### 3.15.2 Secondary copper

The process route used to recover copper depends tremendously on the type of copper, the final use and the degree of contamination.
The primary processes involved in secondary copper recovery are scrap metal pre-treatment and smelting. Pre-treatment includes cleaning and concentration to prepare the material for the smelting furnace. Pre-treatment of the feed material can be accomplished using several different procedures, either separately or in combination. Feed scrap is concentrated by manual and mechanical methods such as sorting, stripping, shredding, and magnetic separation. Pyrometallurgical pre-treatment may include sweating, burning of insulation (especially from scrap wire), and drying (burning off oil and volatiles) in rotary kilns. Hydrometallurgical methods include flotation and leaching with chemical recovery. After pre-treatment the scrap is ready for smelting. Though the type and quality of the feed material determines the processes the smelter will use, the general fire-refining process is essentially the same as for the primary copper smelting industry. (EPA, 2002)

**Calculation CO$_2$ emission factors:**

More information is required to calculate an emission factor for the production of copper. It is necessary to determine the amount of coke, natural gas or propane used for the reduction of copper oxides in the pyrometallurgical process and to what extent coke is still used nowadays. Also, the amount of slag produced, cleaned and redirected into the process is not known, neither is the share of the EF or slag concentration process, nor the consumption of carbon containing materials.
4. Summary of CO₂ emission factors and recommendations

In this report CO₂ emission factors were estimated for ferroalloys, inorganics and other metals. For all emission factors we have chosen a conservative approach as to not overestimate the emissions taking place during production. For the emissions can differ significantly per country depending on the process and production practices used. The geographical focus of the study has been primarily the region of the European Union.

The emission factors are based on the average consumption of carbon agents (electrode or reductant) per tonne of product used. Then, the stoichiometric relationship was used to estimate the final CO₂ emissions. It was assumed that all the CO gas simultaneously produced in various processes reacts with oxygen to form carbon dioxide gas. The principal sources for the consumption figures were the BREF report (2001), Ullmann's Encyclopedia (1997), various scientific articles and producer data. These figures primarily represent production practices in Europe, but in several cases data for Europe were unavailable or not relevant. In that case, the consumption data mainly represent production practice elsewhere.

In the tables below the specific CO₂ emissions and input of carbon containing raw materials are shown for all processes that were described in detail in the preceding chapters. Additionally, in the third table of this chapter, the emission factors as determined in this report are compared with the emission factors currently recommended by the IPCC.

4.1 Emissions from electrode use

<table>
<thead>
<tr>
<th>Input raw materials (%)</th>
<th>Specific CO₂ emissions (t CO₂/t product)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pet coke</td>
</tr>
<tr>
<td>Primary aluminium</td>
<td>84</td>
</tr>
<tr>
<td>Electric steel</td>
<td>70</td>
</tr>
<tr>
<td>White phosphorus</td>
<td>72</td>
</tr>
<tr>
<td>Ferrosilicon</td>
<td>72</td>
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<tr>
<td>Silicon metal</td>
<td>85</td>
</tr>
<tr>
<td>Calcium silicon</td>
<td>85</td>
</tr>
<tr>
<td>Ferromanganese</td>
<td>72</td>
</tr>
<tr>
<td>Siliconmanganese</td>
<td>72</td>
</tr>
<tr>
<td>Ferrochromium</td>
<td>72</td>
</tr>
<tr>
<td>Ferrochromiumsilicon</td>
<td>72</td>
</tr>
<tr>
<td>Magnesium</td>
<td>85</td>
</tr>
<tr>
<td>Ferronickel</td>
<td>72</td>
</tr>
<tr>
<td>Tin</td>
<td>85</td>
</tr>
<tr>
<td>Calcium carbide</td>
<td>72</td>
</tr>
</tbody>
</table>

Values printed in italics represent first estimates and may need to be revised in the course of further work.
### 4.2 Emissions from solid carbon use

<table>
<thead>
<tr>
<th>Input raw materials (%)</th>
<th>Specific CO₂ emissions (t CO₂/t product)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pet coke</td>
</tr>
<tr>
<td><strong>White phosphorus</strong></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Titanium dioxide</strong></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ferrosilicon</strong></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Silicon metal</strong></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Calcium silicon</strong></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ferromanganese</strong></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Silicomanganese</strong></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ferrochromium</strong></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ferrochromiumsilicon</strong></td>
<td>100</td>
</tr>
<tr>
<td><strong>Lead</strong></td>
<td>100</td>
</tr>
<tr>
<td><strong>Nickel</strong></td>
<td>-</td>
</tr>
<tr>
<td><strong>Ferronickel</strong></td>
<td>100</td>
</tr>
<tr>
<td><strong>Magnesium</strong></td>
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</tr>
<tr>
<td><strong>Tin</strong></td>
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</tr>
<tr>
<td><strong>Zinc</strong></td>
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</tr>
<tr>
<td><strong>Copper</strong></td>
<td>-</td>
</tr>
<tr>
<td><strong>Chromium</strong></td>
<td>-</td>
</tr>
<tr>
<td><strong>Calcium carbide</strong></td>
<td>15</td>
</tr>
<tr>
<td><strong>Silicon carbide</strong></td>
<td>100</td>
</tr>
</tbody>
</table>

Values printed in italics represent first estimates and may need to be revised in the course of further work.

1. This estimate is taken from the IPCC and represents solid carbon use and electrode use.
2. This estimate is taken from the IPCC.

### 4.3 Comparison total CO₂ emission factors NEAT - IPCC

<table>
<thead>
<tr>
<th></th>
<th>Specific CO₂-emissions (t CO₂/t product)</th>
<th>Absolute CO₂-emissions (kt CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IPCC</td>
<td>NEAT¹</td>
</tr>
<tr>
<td><strong>Primary aluminium</strong> ²</td>
<td>1.5</td>
<td>1.55</td>
</tr>
<tr>
<td><strong>Electric steel</strong> ³</td>
<td>-</td>
<td>0.011</td>
</tr>
<tr>
<td><strong>White phosphorus</strong></td>
<td>-</td>
<td>4.36</td>
</tr>
<tr>
<td><strong>Titanium dioxide</strong></td>
<td>-</td>
<td>0.49</td>
</tr>
<tr>
<td><strong>Ferrosilicon</strong></td>
<td>95% Si: 4.8-6.5</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>75% Si: 3.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45% Si: 2-2.7</td>
<td></td>
</tr>
<tr>
<td><strong>Silicon metal</strong> ⁴</td>
<td>4.3</td>
<td>4.85</td>
</tr>
<tr>
<td><strong>Calcium silicon</strong></td>
<td>-</td>
<td>2.71</td>
</tr>
<tr>
<td><strong>Ferromanganese</strong> ²</td>
<td>1.5</td>
<td>1.79</td>
</tr>
<tr>
<td><strong>Silicomanganese</strong> ⁵</td>
<td>1.7</td>
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<td><strong>Ferrochromium</strong></td>
<td>1.3</td>
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<td><strong>Ferrochromiumsilicon</strong></td>
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<tr>
<td><strong>Nickel</strong></td>
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</tr>
<tr>
<td><strong>Ferronickel</strong></td>
<td>-</td>
<td>1.36</td>
</tr>
</tbody>
</table>

CO₂ emission factors for non-energy use in the non-ferrous metal, ferroalloys and inorganics industry
The emission factors of the IPCC and NEAT could only be compared for several products, as the IPCC does not give factors for half of the products shown in the table above. The absolute CO₂ emissions have been determined with NEAT emission factors and UN statistics for production values for the year 2000 (UN, 2000). This gives some insight into whether the absolute amount of CO₂ emissions really warrants an adjustment of the emission factors currently in use by the IPCC.

The IPCC gives emission factors for several products, but none for example for lead, ferronickel zinc and electric steel, whereas these products do give a contribution in the order of million tonnes (8.7 Mt) to worldwide absolute CO₂ emissions. For a complete picture it is therefore recommended that these values be included. In addition, NEAT emission factors for ferrosilicon, pure silicon, ferromanganese and ferrochromium give significantly different CO₂ emissions compared to the IPCC value. The changes in absolute worldwide annual emissions if the factors in this report were used are -25% (-2.6Mt) for ferrosilicon, +13% (+0.5Mt) for silicon, +19% (+0.2Mt) for ferromanganese and +25% (+2.4Mt) for ferrochromium (including also the annual production of ferrochromiumsilicon). Except for the case of ferrosilicon, adjustment of these particular factors should hence be considered. For ferrosilicon further research is necessary on the actual reductant consumption, because of large diverging values between sources. For the other products, e.g. magnesium and tin, the annual production quantity is so minimal that it does not warrant the inclusion of these emission factors to greenhouse gas inventories.

The emission factors for aluminium, electric steel, white phosphorus and titanium dioxide have not been researched thoroughly (see Appendix A) and these should hence be considered as a rough first estimate. Especially the accuracy of the emission factor of aluminium is, due to its large production volumes, of great importance for the annual CO₂ emissions. The emission factor suggested here would give an increase of 3% in the annual worldwide CO₂ emissions (for the year 2000). Since this is relatively large (1.5 Mt), further research is required to estimate a more accurate emission factor for aluminium.

Several issues were encountered during the course of this work, which require additional discussion:

- Should the emissions due to sintering (pre-treatment) be included in the total CO₂ emissions of the production process?
- How should one deal with the fact that carbon monoxide, produced by non-energetic carbon consumption, is used as a fuel or as a chemical feedstock in other production processes?
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_**CO₂ emission factors for non-energy use in the non-ferrous metal, ferroalloys and inorganics industry**_
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CO₂ emission factors for non-energy use in the non-ferrous metal, ferroalloys and inorganics industry 47

Appendices

A: Emissions from other metals and inorganics

1. Primary Aluminium

Primary aluminium is produced in an electric arc furnace, using Søderberg or prebaked electrodes for the necessary reduction. One third of the aluminium used worldwide is produced from recycled aluminium scrap (IAI, 2002). The chemical reaction that takes place is:

\[
\text{Al}_2\text{O}_3 + \frac{3}{2} \text{C} \rightarrow 2 \text{Al} + \frac{3}{2} \text{CO}_2
\]

Primarily prebaked anodes are used in the production of Aluminium. A recent estimate by the International Aluminium Institute (IAI, 2002) indicates that of the IAI members 18% of the production is done by Søderberg electrodes and the remaining 82% by prebaked anodes. No other solid carbon source is used for the reduction of aluminium oxide.

For the raw materials used to manufacture the electrodes for the aluminium production the values of the BREF report (2001) for prebaked electrodes have been taken. Of the possible percentages of binder (coal tar pitch), 14-16%, used for the production of the electrodes the highest value has been taken since a small part of the electrodes produced are of the Søderberg type, which slightly more binder than the prebaked anodes. The split in raw materials is therefore: 16% coal tar pitch and 84% of petroleum coke.

**Calculation CO\(_2\) emission factors:**

The emission factors for electrode use calculated with consumption values according to the BREF report (2001), 1.53 t CO\(_2\)/t Al with prebaked anodes and 1.92 t CO\(_2\)/t Al with Søderberg anodes, are higher than the emission factor that is given by the IPCC (1996), 1.5 t CO\(_2\)/t Al for the use of prebaked anodes and 1.8 t CO\(_2\)/t Al for the use of Søderberg electrodes. Since we are making conservative estimates the CO\(_2\) emission factor for electrode use was taken from the Revised IPCC guidelines 1996. If these values are combined with the split in use of Søderberg and prebaked electrodes according to the IAI (2002), 82% prebaked and 18% Søderberg of total production IAI members, a weighted average is obtained of:

**Electrode use:** 1.55 t CO\(_2\)/t Al

The IPCC emission factors are based on a Norwegian and Canadian report: Sintef (1991b) and Ortech (1994) and give total emissions from electrode consumption. The emission factor given by the IAI is: 1.7 t CO\(_2\)/t Al and is higher than the value calculated with the consumption values of the BREF report. The BREF report also gives a different split in the use of prebaked and Søderberg anodes, 60% and 40% respectively, which would result if these values were used for the weighted average in a higher emission factor. The emission factor chosen is thus a very conservative estimate.

2. Electric Steel

Electric steel is produced in an EAF. In a modern EAF, 1.3 to 1.7 kg electrodes are consumed per tonne of steel (Heinen, 1994). From a different source consumption values of 1.5-4.5 kg of graphite electrodes per tonne of electric steel have been obtained (BREF, Iron and Steel Industry, 2000, pg.281). Other sources indicate even higher consumption of electrodes, 3-14 kg per tonne.
of steel (Ullmann, 1997; De Beer, 1998). The raw material consumption of 30% binding agent (coal tar pitch) and 70% petroleum coke was based on Pawlek (1995, pers. comm.).

For reductant consumption the several sources give very different values. The BREF report does not make any mention of reductant use, Ullmann (1997) gives a value of 0.04 t/t steel and Worrel (1994) has a range of 0.115-0.37 t/t steel.

**Calculation CO₂ emission factors:**

The average BREF value has been taken since this represents Europe the best. The BREF value is also on the low side of the value given by Ullmann, which is understandable, since the sources used for Ullmann are generally older than the ones used by BREF. The resulting emission factor is:

**Electrode use:** 0.011 t CO₂/t Steel

More information is required on the use of reductant in this process. No emission factor has been calculated since the values that were actually found diverge significantly. The IPCC does not provide any emission factor.

### 3. White Phosphorus

White phosphorus is also produced in an electric furnace. In general dried metallurgical coke is used as a reducing agent. The maximum moisture content should be 1 %, and the ash content as low as possible. It is possible to replace a large proportion of this coke by cheaper petroleum coke. In this case, a higher proportion of organic impurities in the phosphorus must be accepted (Ullmann, 1997). The chemical reactions taking place are:

$$\text{Ca}_3(\text{PO}_4)_2 + 5 \text{CO} \rightarrow 3 \text{CaO} + 5 \text{CO}_2 + 2 \text{P}$$

$$5 \text{CO}_2 + 5 \text{C} \rightarrow 10 \text{C}$$

The CO off gas is used for drying and sintering the pelletized raw materials.

The assumed split in use of raw material between pet coke and coke is a rough estimate since the exact values differ greatly per producer. To produce 1 t of phosphorus, 1.25 t of coke and 0.05 t electrode material is required (Ullmann, 1997). A manufacturer of which consumption values were obtained uses slightly less solid carbon: 1.2 t coke/t of phosphor (confidential).

**Calculation CO₂ emission factors:**

The value for electrode consumption was taken from Ullmann (1997) since this is the only source found with figures on this. The carbon consumption given by Ullmann is slightly higher than what was reported by the manufacturer and since we are making conservative estimates the latter value was taken to determine the emission factor. This results in:

**Electrode use:** 0.178 t CO₂/t phosphorus

**Reductant use:** 4.18 t CO₂/t phosphorus
4. Titanium Dioxide

Titanium dioxide is the most important inorganic pigment in terms of quantity, 3 Mt were produced in 1989 (Ullmann, 1997). The raw materials for TiO₂ production include natural products such as ilmenite, leucoxene, and rutile, and some very important synthetic materials such as titanium slag and synthetic rutile. For the production of titanium slag an EAF is used with carbon electrodes. In 1987 titanium slag was mainly produced in South-Africa (650 kt/a), Norway (200 kt/a) and Canada (1000 kt/a). The other raw materials seem to be produced in larger quantities: ilmenite (3060 kt/a), natural rutile (490 kt/a) and synthetic rutile (470 kt/a), (Ullmann, 1997).

Over 95 % of the total quantity of titanium minerals extracted worldwide is used to produce TiO₂ pigment, and only ca. 4 % for titanium metal. There are two methods of producing titanium dioxide, the chloride and the sulphate method. At present, approximately one-half of the TiO₂ world production (2.1 Mt/a) is produced by the chloride process. The sulphate method is the oldest method and its use has been decreasing constantly over the last decades (Inorganic pigments, Ullmann, 1997).

The sulphate method does not use any reducing agents. For the chloride process the coke consumption per tonne of TiO₂ is 250–300 kg. If CO₂-containing chlorine from the combustion of TiCl₄ is used, the coke consumption increases to 350–450 kg. The titanium in the raw material is converted to titanium tetrachloride in a reducing atmosphere. Calcined petroleum coke is used as the reducing agent because it has an extremely low ash content and, due to its low volatiles content, very little HCl is formed. The titanium dioxide reacts exothermically as follows (Ullmann, 1997):

$$\text{TiO}_2 + 2 \text{Cl}_2 + \text{C} \rightarrow \text{TiCl}_4 + \text{CO}_2$$
$$\text{TiCl}_4 + \text{O}_2 \rightarrow 2 \text{Cl}_2 + \text{TiO}_2$$

**Calculation CO₂ emission factors:**

The assumption taken in the model is that the emissions due to electrode use are negligible. This is primarily done because of lack of data and may need further work. The lack of data is due to the fact that the amount of electrode consumption for the production of titanium slag is unknown for the EAF and because the amount of titanium slag used as a raw material is not exactly known. Figures from 1987 show that it was about 32% then, however since the chlorine process has gained in popularity considerably since then, it is unclear which percentage it would be at the moment.

For the reductant consumption the average value of Ullmann was taken weighted with 50% since half of the world production uses the chloride process. The other process does not use any carbon source. This results in the emission factor:

**Reductant use:** $0.49 \text{ t CO}_2/\text{t TiO}_2$

5. Calcium Carbide

The majority of today’s carbide furnaces (EAF) are operated with a three-phase current. The consumption of Söderberg material is about 12 kg per tonne of carbide and the consumption of coke about 0.55 t/t CaC₂. Carbon monoxide gas from open furnaces burns directly at the surface.
of the feed material to harmless carbon dioxide (Ullmann, 1997). The percentages of raw material used represent a rough estimate.

According to a report from the EPA about 0.99 t of lime, 0.68 t of coke (petroleum or metallurgical), and 17-20 kg of electrode paste are required to produce 1 t of calcium carbide (EPA, 2003).

The percentages of raw material used represent a rough estimate.

According to a report from the EPA about 0.99 t of lime, 0.68 t of coke (petroleum or metallurgical), and 17-20 kg of electrode paste are required to produce 1 t of calcium carbide (EPA, 2003).

The chemical reaction that takes place is:

\[ \text{CaO} + 3 \text{C} \rightarrow \text{CaC}_2 + \text{CO} \]

The factor \( \frac{\text{CO}_2}{3\text{C}} = 1.22 \) (2/3 is stored in the product and 1/3 is emitted) instead of 3.67.

**Calculation CO\(_2\) emission factors:**

The IPCC Revised guidelines 1996 give these values for the required raw material: 550 kg of coke and 20 kg of electrode material per tonne of calcium carbide. The guidelines also give a total emission factor for coke consumption and electrode use: 1.1 t CO\(_2\)/t CaC\(_2\). Emissions during product use (1.1 t CO\(_2\)/t CaC\(_2\)) or from limestone use (0.7 t CO\(_2\)/t CaC\(_2\)) are not included in this factor. If one calculates the emissions using the given carbon consumption and the stoichiometric factor for the reaction a result of 0.69 t CO\(_2\)/t CaC\(_2\) is obtained. The reason why this differs significantly from the value of 1.1 t CO\(_2\)/t CaC\(_2\) given by the IPCC is unknown.

The values of Ullmann are the most conservative estimate of the emissions. This would give:

- **Electrode use:** 0.014 t CO\(_2\)/t CaC\(_2\)
- **Solid carbon use:** 0.59 t CO\(_2\)/t CaC\(_2\)

However, in the calculations we have kept the IPCC factors as uncertainties still exist regarding the actual calculation done by the IPCC and as there was not sufficient time to solve this.

**6. Silicon Carbide**

Commercial SiC is produced in an electric furnace from a mixture of coke and silica sand. Electrodes and a graphite core produce the required temperature. Another method used to form SiC pieces is by vapour deposition of silicon onto a heated graphite or carbon surface. Three main types are produced commercially: green, black and metallurgical SiC. The reaction that takes place is:

\[ \text{SiO}_2 + 3 \text{C} + \text{O}_2 \rightarrow \text{SiC} + 2 \text{CO}_2 \]

Dutch producers only use petroleum cokes and therefore this is taken as raw material. A certain manufacturer of which data was obtained produces 62 kt of silicon carbide. The total petroleum coke consumption is 82.6 kt and the final use non-energetic reported is 45.8 kt. Based on these numbers the consumption is: 1.3 t coke/t SiC (total input of petroleum cokes) and 0.74 t coke/t SiC (non-energy use reported). According to Ullmann (1997) 1-2 t coke or coal is required for the production of 1 tonne of SiC. This is probably energy and non-energy use since the sum of coke consumption for energy and non-energy use according to the manufacturer (see above) is about 2 t coke/t SiC.

**Calculation CO\(_2\) emission factors:**
The expected pet coke consumption theoretically is 0.9 ton coke/ton SiC \((\text{SiC}/3\text{C} = 40/36 = 0.9)\) equal to 3.2 ton CO\(_2\)/ton SiC with 2/3 of this CO\(_2\) being emitted and 1/3 being stored in the product. This would give a theoretical emission factor of 2.14 t CO\(_2\)/t SiC. According to the non-energetic coke consumption reported by the manufacturer the emission factor would be: 1.8 t CO\(_2\)/t SiC, much lower than in theory. According to the IPCC (1996), the emission factor for SiC should be: 2.3 t CO\(_2\)/t coke and thus with a theoretical coke consumption this would mean an emission factor of: 2.07 t CO\(_2\)/t SiC and with the non-energetic coke consumption reported by the manufacturer the emission factor would be: 1.7 t CO\(_2\)/t SiC.

The non-energetic coke consumption according to the manufacturer is lower than what would be required theoretically for the reduction of silicium oxide. It is therefore probable that the producer allocates too much coke consumption to the energetic use. Since the process will not be perfect there will be more coke consumption than in theory thus more than 0.9 t coke/t SiC will be consumed, therefore the lowest value of coke consumption according to Ullmann, 1 t coke/t SiC has been taken to determine the emission factor for reductant use. If this is multiplied by the emission factor given by the IPCC an emission factor per tonne of SiC can be determined:

**Reductant use:** \(2.3 \text{ t CO}_2/\text{t SiC}\)
## B: Furnaces used for metal production

*Metal production and process control techniques (Source: BREF, 2001):*

<table>
<thead>
<tr>
<th>Metal</th>
<th>Type furnace likely to be encountered</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Molten Electrolyte Cells. Reverberatory Furnaces. Rotary and Shaft Furnaces. Induction Furnaces.</td>
<td>• Molten electrolyte cells only for primary.</td>
</tr>
<tr>
<td>Lead</td>
<td>Imperial Smelting Furnace (ISF) Flash Furnace (Kivett). Bath Furnace (OSL, ISA Smelt/Ausmelt). Short rotary Furnace. Heated Kettle Sinter machine.</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>ISF and New Jersey Distillation Fluidised bed roaster, sinter machine. Induction and crucible furnace. Slag fuming furnaces</td>
<td>• Temperature control of melting is vital.</td>
</tr>
<tr>
<td>Precious Metals</td>
<td>Electric Furnace. Blast Furnace Crucible Furnace. Rotary and Static Incinerator. Cupel and BBOC. Vacuum distillation</td>
<td>• A variety of applications depending on the raw material and process stage.</td>
</tr>
<tr>
<td>Refractory Metals</td>
<td>Pusher Furnace. Band Furnace Batch Furnace Rotary Furnace Electron Beam Furnace. Vacuum Induction Furnace.</td>
<td>• Pusher, band, batch and rotary furnaces are used for powder production.                • Electron beam furnace is used for ingot smelting</td>
</tr>
<tr>
<td>Ferro Alloys</td>
<td>Blast Furnace Electric Arc Furnace. Electric Furnace. Reaction Crucibles. Herreshoff Furnace Metallo-thermal reactors</td>
<td>• The electric arc furnace is used as an open, semi-closed and closed furnace. • Herreshoff furnace is only used for Mo-roasting</td>
</tr>
<tr>
<td>Alkali Metals</td>
<td>Molten Electrolyte Cells. Electric Furnaces. Induction Furnaces.</td>
<td>• Induction furnaces are mostly used for re-melting.</td>
</tr>
<tr>
<td>Carbon and graphite</td>
<td>Pit Furnaces, Vacuum Furnaces. Electric Furnaces.</td>
<td></td>
</tr>
</tbody>
</table>
(Source: BREF, 2001)

### Process steps for pyrometallurgical operations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reactor</th>
<th>Metals</th>
<th>Energy source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed preparation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drying</td>
<td>rotary kiln</td>
<td>different</td>
<td>hydrocarbons</td>
</tr>
<tr>
<td>Calcining</td>
<td>fluidized bed, rotary kiln</td>
<td>Al</td>
<td>hydrocarbons</td>
</tr>
<tr>
<td>Roasting of sulfides</td>
<td>fluidized bed</td>
<td>Zn</td>
<td>autogenous with air</td>
</tr>
<tr>
<td></td>
<td>multiple hearth</td>
<td>Mo</td>
<td></td>
</tr>
<tr>
<td>Sinter roasting of sulfides</td>
<td>DL-sintering machine</td>
<td>Pb, PbZn</td>
<td>autogenous with air</td>
</tr>
<tr>
<td>Sintering of oxides</td>
<td>DL-sintering machine</td>
<td>Fe</td>
<td>coke</td>
</tr>
<tr>
<td>Enrichment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matte smelting</td>
<td>flash smelter</td>
<td>Cu, Ni</td>
<td>autogenous with air</td>
</tr>
<tr>
<td>Slag reduction</td>
<td>electric furnace</td>
<td>Cu, Pb</td>
<td>electric and coke</td>
</tr>
<tr>
<td>Slag fuming</td>
<td>fuming furnace</td>
<td>Pb, Zn</td>
<td>coal</td>
</tr>
<tr>
<td>Waez process</td>
<td>rotary kiln</td>
<td>Pb, Zn</td>
<td>coal</td>
</tr>
<tr>
<td>Metal production</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reduction with carbon</td>
<td>shaft furnace</td>
<td>Fe, Pb, PbZn</td>
<td>coke</td>
</tr>
<tr>
<td>Metallothermic reduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxides</td>
<td>various reactors</td>
<td>V, Mg, Cr</td>
<td>Al, FeSi</td>
</tr>
<tr>
<td>Chlorides</td>
<td>retort furnace</td>
<td>Ti, Zr</td>
<td>Na, Mg</td>
</tr>
<tr>
<td>Reduction with hydrogen</td>
<td>retort furnace</td>
<td>Mo, W</td>
<td>H₂-heating</td>
</tr>
<tr>
<td>Electrochemical reduction</td>
<td>electrolytic cells</td>
<td>Al, Mg</td>
<td>electrical</td>
</tr>
<tr>
<td>Conversion of sulfides</td>
<td>converters</td>
<td>Cu, Ni, Pb</td>
<td>autogenous</td>
</tr>
<tr>
<td></td>
<td>flash smelter</td>
<td>Pb, Cu</td>
<td>autogenous</td>
</tr>
</tbody>
</table>

**CO₂ emission factors for non-energy use in the non-ferrous metal, ferroalloys and inorganics industry**