GREENHOUSE GAS EMISSIONS FROM FERROALLOY PRODUCTION

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ABSTRACT

The authors are lead authors for chapter 4.3 "Emissions from Ferroalloy Production" in "2006 IPCC Guidelines for National Greenhouse Gas Inventories, Volume 3".

The paper discusses the methods to calculate and report emissions from the production of ferrosilicon, silicon-metal, ferromanganese, silicomanganese and ferrochromium alloys, as well as the basis for the methods and choice of emission factors.

CO_2 *is the main greenhouse gas emission from ferroalloy production, accounting for about 95 % of the total* CO_2*-equivalents. The most accurate method of determining emissions is to base the calculations on reported amounts and analyses of reducing agents and carbonate ores used in the process. If analyses are not available, typical* CO_2 *emission factors for the different reducing agents are recommended. If neither reliable amounts nor analyses of all reducing agents are known, default generic* CO_2 *emission factors for the type of ferroalloy multiplied with amount produced, can be used.*

The CO_2 *produced from bio-carbon (charcoal and wood chips) should be reported but will not be accounted for in national emissions. If any bio-carbon is used, the default generic* CO_2 *emission factors cannot be applied.*

CH_4 *accounts for less than 1 % of the total emission of* CO_2*-equivalents.*

Default emissions factors for CH_4 *are given for the production in open or semi-closed furnaces of silicon-metal and ferrosilicon. In the production of FeMn, SiMn and FeCr in closed furnaces the gas containing CO,* CO_2 *and volatiles can be combusted in boilers and* N_2O *may be formed. While reporting is not required, IPCC Guidelines recommend that the* N_2O*-content in the off-gas is measured.*

1. INTRODUCTION

In 2003, the International Panel on Climate Change (IPCC) started a process to improve the Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories [1]. This task engaged several hundreds of experts from around the world and has resulted in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories [2]. This collaborative effort has resulted in improved methodologies for estimating greenhouse gas emissions. In particular, Volume 3, Chapter 4, Metal Industry Emissions, provides an updated methodology for ferroalloys in section 4.3.

The production of ferroalloys results in emission of greenhouse gases. In ferroalloy production, raw ore, carbon materials and slag forming materials are mixed and heated to carbon sources. Since charcoal and wood are biologically based from renewable sources, they are not accounted for as an emissions source for the purpose of the greenhouse gas inventories.

Under the revised guidelines, greenhouse gas emissions inventories are organized to avoid double counting of emissions. Thus greenhouse gas emissions (CO_2 and CH_4) from coke production are reported within the Energy Sector.

Ferroalloys are most commonly produced by electric submerged arc furnaces with graphite electrodes or consumable Søderberg electrodes. Some ferroalloys, and especially ferromanganese, are also produced in blast furnaces. In addition to emissions originating from reducing agents and electrodes, the calcination of carbonates in ores and fluxes such as limestone or dolomite, contribute to the emission of CO_2. Primary emissions in covered arc furnaces consist almost entirely of CO, due to the strong reducing environment. This CO is either utilised for energy production in boilers, or it is flared. The energy produced is assumed to be used internally at the site and the carbon content of the CO subsequently converted to CO_2 in-plant. The CO gas produced in open or semi-closed furnaces is burnt to CO_2 above the charge level. Any CO emitted to the atmosphere is assumed to be converted to CO_2 within days afterwards.

While CO2 is the main greenhouse gas from ferroalloy production, recent research has shown that CH_4 and N_2O account for an equivalent greenhouse gas emission of up to 5 % of the CO2 emissions from ferrosilicon (FeSi) and silicon-metal (Si-metal) production. Methodologies are presented for N_2O and CH_4 emissions. These emissions should be better investigated for all ferroalloy production, and more measurements of these emissions should be carried out at ferrosilicon and Silicon-metal plants.

2. METHODOLOGY FOR INVENTORY OF CO_2 EMISSIONS

The 2006 IPCC Guidelines outline several approaches for calculating CO_2 emissions from ferroalloy production. For practical purposes, this chapter adopts a mass balance approach where all CO emitted is reported as emitted CO_2. Tier 1 method calculates emissions from general emission factors applied to a country's total ferroalloy production. The Tier 2 method calculates emissions from a known consumption of reducing agents, preferably from plant-specific consumption data, but alternatively from industry-wide data using emission factors similar to those used to estimate combustion emissions. The Tier 3 method is based on facility-specific emissions data.

Tier 1 Method: Production-based Emission Factors

When the only data available are national ferroalloy production statistics, the guidance recommends the use of default emission factors. However, because of very different practice and types of ferroalloy production, it is necessary to determine how much tonnage is produced by which method and then to sum up the product of the factors shown in Table 1 and the appropriate production tonnages. These factors are calculated using typical practice for the ferroalloy production scenarios listed. If any bio-carbon, except some woodchips for FeSi and Si-metal production, is used, the factors cannot be employed. The factor for FeSi90 and Si-metal is based on a Fix C consumption of 110 % of the stoichiometric amount needed for reduction of SiO_2. For the other FeSi-alloys the factor is based on 114 % of the stoichiometric amount of Fix C. These default emission factors were assessed by Olsen [3] for the manganese alloys and Lindstad [4] for the silicon alloys. A report from SINTEF and DNV on greenhouse gas emissions from the Norwegian process industry based on confidential data on raw materials consumption and production reported for each plant [9] was also taken into account. These reports updated previous reports by Monsen and Olsen [5] on CO_2-emission factors for the manganese and chromium alloys and by Monsen [6] for the silicon alloys. These previous reports were presented in papers by Olsen, Monsen and Lindstad [7] and by Monsen, Lindstad and Tuset [8] at the Electric Furnace Conference in 1999. Examples showing the calculations for FeSi75 and HCFeMn are given in the appendix. In these calculations the emission factors for the reducing agents are used. How they are calculated is shown in the chapter on Tier 2 method.

$$E_{CO2} = \sum MP \times EF \tag{1}$$

Where:

E_{CO2} = CO_2 emissions, tonnes
MP = specific ferroalloy production, tonnes
EF = generic emission factor, tonnes CO_2 per tonne specific ferroalloy product.

Table 1: Generic CO_2 Emission Factors for Ferroalloy Production (tonne CO_2/tonne product)

Type of Ferroalloy	*Generic Emission Factor*
Ferrosilicon 45 % Si	2.5
Ferrosilicon 65 % Si	3.6
Ferrosilicon 75 % Si	4.0
Ferrosilicon 90 % Si	4.8
Ferromanganese (7% C)	1.3
Ferromanganese (1 % C)	1.5
Silicomanganese	1.4
Silicon metal	5.0
Ferrochromium	1.3 (1.6 with sinter plant)

It should be stressed that these emission factors are calculated for tapped metal, whereas solid metal normally is reported. The amount of solid metal may be somewhat lower, due to losses from crushing and handling.

For FeMn alloys the emission factors are based on production where the manganese-containing raw materials are a mixture of oxide ores, carbonate ores and imported Mn-sinter. If the sinter is produced abroad it will not give any contribution to the national greenhouse gas inventory. Emission from sinter production must be reported where the sinter production is located.

Default emission factors are not given for other ferroalloys. For ferroalloys not listed, one would use at least the tier 2 method based on consumption of reduction materials.

Tier 2 Method: Production-based, Raw Material Specific Emission Factors

A less uncertain approach is to use emission factors for the reducing agents. For the other raw materials and products the procedure is the same as in Equation 6.

$$
\begin{aligned}
E_{CO2} &= \sum \textit{(Mass of reducing agent i)} \bullet \textit{(Emission factor of reducing agent i)} \\
&+ \sum \textit{(Mass of ore h} \bullet \textit{C-content in ore h)} \bullet 44/12 \\
&+ \sum \textit{(Mass of slag forming material j)} \bullet \textit{(C-content in slag forming material j)} \bullet 44/12 \\
&- \sum \textit{(Mass of product k)} \bullet \textit{(C-content in product k)} \bullet 44/12 \\
&- \sum \textit{(Mass of non-product outgoing streams)} \bullet \textit{Associated C-contents} \bullet 44/12 \qquad (2)
\end{aligned}
$$

Definitions:

Content means weight-fraction in all equations.

The constant 44/12 is the multiplication factor for the mass of CO_2 emitted from each mass unit of total carbon used. Remember to use the net amounts of all input materials and gross amounts of all products.

Emission factors for reducing agents

The factors were assessed in 2004 for production of silicon alloys [4] and manganese alloys [3], based on a vast amount of analyses of samples of coal and coke received from coal and coke suppliers and the ferroalloy industry. These works represented updates of earlier assessments referred to in the preceding sub-chapter.

Typical compositions of reducing agents (coal and coke) used in the Norwegian production of ferrosilicon and silicon metal are presented in the Tables 2 and 3. The tables also give the CO_2 emission factors (e_{ra}), which have been calculated using Equations 3 - 5. Typical composition of coke used in the production of manganese alloys is shown in Table 4.

$$C+O_2=CO_2 \qquad \text{(weight ratio } CO_2/C=3.665\text{)} \qquad (3)$$

$$C_{tot} = C_{fix} + C_{VM} \qquad \text{(tonne C/tonne raw material)} \qquad (4)$$

$$e_{ra} = 3.665 \times C_{tot} \qquad \text{(CO2 emission factor)} \qquad (5)$$

The fixed C content in the tables, called C_{fix} in Equation 4, is an average measure for typical materials in use. The amount of carbon in volatile matter (VM), called C_{VM} in Equation 4 is an estimate.

Table 2: Typical compositions of coal (%) used for ferrosilicon and silicon-metal and calculated CO_2 emission factors (tonne CO_2/tonne coal)

Fix C	60.0
VM	38.5
% C in VM	65
% C total	85.0
CO_2 emission factor, e_{ra}	**3.12**

Table 3: Typical composition of coke for ferrosilicon, and calculated CO_2 emission factor (tonne CO_2/tonne coke)

	Coke for: *FeSi66% FeSi75% FeSi90%*
Fix C	84.0
VM	9.5
Sulphur	0.5
Ash	6.0
% C in VM	80
% C total	91.6
CO_2 emission factor , e_{ra}	3.36

Table 4: Typical composition of coke for manganese alloys and calculated CO_2 emission factor (tonne CO_2/tonne coke)

Fix C	87- 88
VM	≈ 1
Ash	11-12
SUM	100
% C in VM	90
% C total	87.9 – 88.9
CO_2 emission factor, e_{ra}	**3.22 – 3.26**

Söderberg electrodes are used in the production of the ferrosilicon alloys, while prebaked electrodes are used in the production of silicon metal and manganese alloys. Table 5 shows typical compositions of these materials, and the corresponding emission factors, which are 3.51-3.54 tonnes CO_2/tonne electrode and 3.36 tonnes CO_2/tonne electrode paste.

Table 5: Typical compositions of electrode materials (%) and calculated emission factors (tonne CO_2/tonne electrode or paste)

	Electrode paste	*Prebaked electrodes (Si)*	*Prebaked electrodes (Mn)*
Fix C	85.0	96.0	95
VM	9.5	0.7	1
Sulphur	0.5	0.3	
Ash	5.0	3.0	4
SUM	100	100	100
% C in VM	70	80	80
% C total	91.7	96.6	95.8
CO_2 emission factor, e_{ra}	3.36	3.54	3.51

On the basis of these assessments the following emission factors were recommended for the guidelines.

Table 6: CO_2 Emission factors for reducing agents

Reducing agent	*e_{ra} tonne CO_2/tonne reducing agent*
Coal for FeSi and Si-metal	3.1
Coal for other ferroalloys	*)
Coke for FeSi and Si-metal	3.3-3.4
Coke for FeMn and SiMn	3.2-3.3
Coke for other ferroalloys	*)
Petroleum coke	3.5
Prebaked electrodes	3.54
Electrode (Søderberg) paste	3.4

Note: Inventory compilers are encouraged to use producer-specific values based on average blend of coal and/or coke for each ferroalloy producer.

Tier 3 Method: Calculations Based On Amounts and Analyses of Reducing Agents

The producers use coal and coke with different contents of ash, fixed carbon and volatiles. Further, the amounts of carbon in carbonate ores and slag forming materials will vary. The most accurate method is therefore to calculate the CO_2 emissions from the total amount of carbon in reducing agents, electrode paste, ores, slag forming materials and products, and deduct any carbon in products, solid and liquid wastes. This calculation is carried out for each ferroalloy produced.

$$
\begin{aligned}
E_{CO2} = {} & \sum \textit{Mass of reducing agent } i \bullet \textit{Total C-content in reducing agent } i \bullet 44/12 \\
& + \sum \textit{Mass of ore } h \bullet \textit{C-content in ore } h \bullet 44/12 \\
& + \sum \textit{Mass of slag forming material } j \bullet \textit{C-content in slag forming material } j \bullet 44/12 \\
& - \sum \textit{Mass of product } k \bullet \textit{C-content in product } k \bullet 44/12 \\
& - \sum \textit{Mass of non-product outgoing streams} \bullet \textit{Associated C-contents} \bullet 44/12 \qquad (6)
\end{aligned}
$$

The constant 44/12 is the multiplication factor for the mass of CO2 emitted from each mass unit of total carbon used. The calculation will have very low uncertainty if analyses of total carbon in all reducing agents and other materials are available. Thus it is necessary to determine the total carbon content of the reducing agents used in the production processes. Most ferroalloys producers analyse only on the basis of percentage of ash and volatiles, and calculate:

$$\textit{Fix C \%} = 100\ \% - \%\ \textit{Ash} - \%\ \textit{Volatiles} \qquad (7)$$

Then the total C-content of reducing agents is calculated by Equation 8.

$$\textit{Total C-content in reducing agent } i = \textit{Fix C in } i + \textit{Content of volatiles in } i \bullet Cv \qquad (8)$$

Where:

Cv = Carbon content in volatiles. Unless other information is available, Cv = 0.65 is used for coal and Cv = 0.80 for coke.

3. METHODOLOGY FOR CH_4 AND DISCUSSION OF N_2O EMISSIONS

The heating of carbon materials in the furnace releases volatiles including methane. With open or semi-covered furnaces – predominantly used for FeSi and Si ferroalloy production - most of the volatiles will burn to CO_2 above the charge, in the hood and off-gas channels, but some will remain un-reacted as CH_4 and non methane volatile organic compounds (NMVOC). The amounts depend on the operation of the furnace. Sprinkle-charging will reduce the amounts of CH_4 compared to batch-wise charging. Increased temperature in the hood (less false air) will reduce the content of CH_4 further. The IPCC Guidelines outline several approaches for calculating CH_4 emissions from FeSi- and Si- ferroalloy production. The Tier 1 method calculates emissions from general emission factors applied to a country's total ferroalloy production. The Tier 2 method calculates emissions from operation-specific emission factors. The Tier 3 method uses facility-specific emissions data.

The errors associated with estimates or measurements of N_2O emissions from the ferroalloys industry are very large and thus, a methodology can not be provided at present time. N_2O is formed in combustion processes, but it is difficult to validate the amount of N_2O formed in the combustion of gases in ferroalloy furnaces based on measurements of N_2O from various other combustion processes. The emissions given as CO_2-equivalents may be in the order of magnitude of 1 % of the emissions from the carbon contents.

Tier 1 Method: FeSi and Si-metal Production-based Emission Factors

When the only data available are national ferroalloy production statistics, the guidance recommends using default emission factors. However, because of very different practice and types of ferroalloy production, it is necessary to determine how large tonnage is produced by which method and then to sum up the product of the factors shown in Table 7 and the appropriate production tonnages. These default emission factors for CH_4 are based on the averages of a small number of operation-specific measurements, see Tier 2 method. Total emissions are calculated according to:

$$E_{CH4} = \sum MP \times EF \tag{9}$$

Where:

E_{CH4} = CH_4 emissions, tonnes

MP = specific Si-alloy production, tonnes

EF = generic emission factor, tonnes CH_4 per tonne specific Si-alloy product.

Table 7: Default emission factors for CH_4

Alloy	*Emission Factor (kg CH_4/tonne product)*
Si-metal	1.2
FeSi 90	1.1
FeSi75	1.0
FeSi 60	1.0

These default emission factors for CH_4 are based on the averages of a small number of operation-specific measurements, see Tier 2 method.

Tier 2 Method: FeSi and Si Alloy Production-based, Operation Specific Emission Factors

The Tier 2 method is also based on emission factors but unlike the Tier 1 method, these factors are operation specific. The procedure is otherwise the same as given in Equation 6, but using the values in Table 8. These default emission factors for CH_4 is based on a small number of operation-specific measurements carried out by SINTEF and DNV mainly in 1995 and 1998 and assessed by FFF [10].

Table 8: Operation-specific emission factors for CH_4(kg emission/tonne product)

Alloy	*Operation of furnace*		
	Batch-charging	Sprinkle-charging 1)	Sprinkle-charging and > 750 °C 2)
Si-metal	1.5	1.2	0.7
FeSi 90	1.4	1.1	0.6
FeSi 75	1.3	1.0	0.5
FeSi 65	1.3	1.0	0.5

1) Sprinkle-charging is charging intermittently every minute.
2) Temperature in off-gas channel measured where the thermocouple cannot “see” the combustion in the furnace hood.

Tier 3 Method: Direct Measurements

Tier 3 is based on measurements rather than emission factors. The inventory compiler should consult guidance on plant-level measurements outlined in Volume 1, Chapter 2, and on QA/QC of measurements in Volume 1 [2]. Inventory compilers are strongly encouraged to measure CH_4 emissions where emissions from ferroalloys industry are a key category.

4. COMPLETENESS AND DOUBLE-COUNTING

In estimating emissions from this source category, there is a risk of double-counting or omission in either the Industrial Processes or the Energy Sector. Since the primary use of carbon sources (coal, coke, limestone, dolomite etc.) is to produce ferroalloys, the emissions are considered to be industrial process emissions and are reported as such. The risk of double counting is particularly high for the Tier 1 approach. Any deviation from reporting emissions as originating from an industrial process should be explicitly mentioned in the inventory, and a double-counting/completeness check should be performed.

5. CHOICE OF ACTIVITY DATA

The Tier 1 method requires only the amount of ferroalloy produced in the country by product type. These data may be available from governmental agencies responsible for manufacturing statistics, business or industry trade associations, or individual ferroalloy companies. These tonnages can then be multiplied by the corresponding emission factors in Table 1 to estimate CO2 emissions from the sector and Table 7 to estimate CH_4 emissions from the sector.

The Tier 2 method requires the total amount of reducing agent and other process materials used for ferroalloy production in the country, and knowledge of processes used. These data may be available from governmental agencies responsible for manufacturing or energy statistics, business or industry trade associations, or individual ferroalloy companies. These amounts can then be multiplied by the appropriate generic emission factors in Tables 6 and 7 and summed to determine total CO_2 and CH_4 emissions from the sector. However, activity data collected at the plant-level is preferred.

The Tier 3 method requires collection, compilation, and aggregation of facility-specific emissions data. These data may be available from national environmental agencies or directly from the ferroalloy producers.

6. UNCERTAINTIES

Uncertainties for ferroalloy production result predominantly from uncertainties associated with activity data, and to a lesser extent from uncertainty related to the emission factor. CO_2-emissions from wood or other biomass used in ferroalloy production should not be counted, because wood-based carbon is of biogenic origin.

Emission Factor Uncertainties

For Tier 3, actual emissions data would be expected to have less than 5% uncertainty. For Tier 2, the material-specific emission factors would be expected to be within 10%, which would provide less uncertainty overall than for Tier 1. Emission factors would be expected to be within 10% or less than 5% if plant-specific carbon content data are available. The default emission factors used in Tier 1 may have an uncertainty of more than 25 %.

Activity Data Uncertainties

For Tier 1 the most important type of activity data is the amount of ferroalloy production by product type National statistics should be available and likely have an uncertainty less than 5%. Tier 2 applied with plant-specific information on the amounts of reducing agents and process materials as applied in Tier 2 method should not exceed 5% uncertainty.

7. ACKNOWLEDGEMENT AND FUTURE WORK

We thank the ferroalloy industry in Norway for their co-operation in providing basic data and the IPCC working group on greenhouse gas inventories for permission to publish the present paper, some of the text written for the 2006 guidelines.

It is extremely important that the emission inventories should be as correct as possible. When world-wide inventories become available they should also be used to improve the methodology and correct emission factors.

For ferroalloys, CO_2 is the primary greenhouse gas, whereas CH_4 and N_2O are only a few percent of the CO_2-equivalents emitted. Present emission factors for CH_4 are based on a very limited number of measurements, and it was impossible to recommend emission factors for N_2O. Hopefully funding will be available for researchers wanting to study the relation between operating conditions and emission of CH_4 and N_2O.

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APPENDIX CALCULATION OF PRODUCTION BASED EMISSION FACTORS

Table A1: Typical reducing agents consumption producing FeSi 75%, and calculation of CO_2 emission factor [3]

	Consumption dry basis kg/tonne metal	*CO_2 emission factor*	*CO_2 emission tonne/tonne metal*
Coal	650	3.12	2.03
Coke	420	3.36	1.41
Electrode/ paste	50	3.4	0.17
CO_2 Emission factor			3.61

Table A2: Calculated CO_2 emission factor for HC FeMn based on consumption of carbon containing raw materials [4]

	Consumption (kg/ton)	*CO_2 emission factor*	*CO_2 emission ton /ton metal*
+ Carbonate Mn-ore	270	0.35	+ 0.095
+ Dolomite/ Limestone	11-31	0.47	+ 0.005-0.015
+ Coke	326-359	3.24	+ 1.056-1.163
+ Electrode paste	14-16	3.51	+ 0.049-0.056
- C in the product	70	3.67	- 0.26
= Emission factor			0.945 – 1.069