CO_2-Emissions and the Ferroalloys Industry

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Abstract

CO_2-emissions connected with the production of ferrosilicon, silicon-metal, silicomanganese and ferromanganese are discussed. The specific CO_2-emission is given for different ways for generating electric power; hydro-/nuclear, natural gas, coal and a European mix of energy sources. CO_2-emissions connected to coke production are included. Otherwise the paper has not taken into account the contribution to CO_2-emissions from mining raw material, or transport of raw materials and products. The use of bio-carbon as a source for carbon is discussed. Present and possible contributions to the global CO_2-balance by using by-products and recovering energy from off-gases are discussed.

Introduction

In the sixties, both the public and politicians became more aware of environmental issues. New laws were passed in many countries, new regulatory agencies were established and public control of emissions and effluents were increased. Since then solving environmental problems caused by our industry has been an essential part of the metallurgist's work. One example is the silica fumes evolved in production of ferrosilicon and silicon-metal. After some years of research a process using bag filters to collect the silica dust was developed. The large quantities of dust collected represented however a major disposal problem. A heavy research was started in the seventies to find applications for this waste product [1]. As we know many applications have been found, the main one being the use as an additive to cement. To collect the silica dust in the off-gas it is necessary to cool the gas. This gives us the opportunity to recover huge amounts of energy, which directly has relation to the CO_2-problem.

We might say that until the last 5 years the industry's main environmental challenges have been to remove local and regional pollution, dispose of waste products and use energy and other raw materials in a reasonable way. The focus on greenhouse gases, CO_2 in particular, changes dramatically the conditions for the ferroalloys industry.In this paper we will try to take a closer look on how the industry can contribute, directly or indirectly to reduce CO_2 - emissions.

Thermodynamical Premises

Metal oxides are the only raw materials for ferroalloys, except that scrap iron is often used to supply the iron part. The Gibbs energy needed to decompose the oxides to metal and oxygen are so high that only solid carbon or electrolysis can be used to break the binding between the metal atom and oxygen, as the case is for aluminium and silicon. For manganese and chromium oxides, part of the oxygen (in the higher oxides) can also react with carbon monoxide or hydrogen.

Breaking the metal-oxygen binding by electrolysis is the process used for production of aluminium, but is also theoretically possible for silicon and is used for the production of manganese metal. We will take a closer look on electrolysis as a possibility to reduce CO_2 emissions.

CO_2-emissions from the ferroalloys industry. Status

The sources for carbon dioxide - emissions are the reduction materials (coal and coke) and the power generation (if coal, oil or gas is used). If coke is used, we should also include the emission of CO_2 from the coking process. Carbon dioxide generated from renewable carbon sources like charcoal is not included. The amount of emissions depends on the processes and the technical standards. The numbers chosen for efficiency of the power plant, electric energy and carbon consumption per tonne ferroalloy are open for discussion. The numbers in this paper are believed to represent good efficiencies.

Power generation

Table 1. Power generation

Energy source	Process	Thermal efficiency, %	CO_2 - emissions kg CO_2/kWh
Natural gas	Combined cycle	50	0,40
Coal	Steam turbine	33	0,98
UCPTE-mix*)			0,40
Nuclear			0
Hydroelectric			0

*)UCPTE is abbreviation for " Union pour la co-ordination de la production et du transport de électricité". The union consists of Belgium, Germany, France, Greece, Italy, Ex-Yugoslavia, Luxembourg, The Netherlands, Portugal, Switzerland and Spain. UCPTE-mix is 36.2 % nuclear power, 15.2 % hydroelectric power, 9.5 % from gas, 9.6 % from oil and 29 % from coal [10].

Coke production

A typical coke for ferroalloys production contains 90 % C (78 % fix C). Assuming the content of volatiles in the coals to be 35 % and in the coke to 12 % we have calculated the CO_2 - emissions from production of coke to be 1,0 kg CO_2 per kg coke.

Ferroalloys production

The relative amount of coal or coke used will vary from plant tc plant. If we, however, include the carbon dioxide emissions from coke production, the specific CO_2 -emissions will be fairly constant for each type of ferroalloy, when good efficiencies are presumed for all. This way of thinking will be correct on a global base, but is difficult when national quotas for emissions are on the agenda.

Table 2. CO_2- emissions per tonne ferroalloy from electric furnace, including coke production

Ferroalloy	From reduction materials, kg CO_2	From electrodes, kg CO_2	From ore and flux, kg CO_2	Total kg CO_2
FeSi75	4200	180		4380
Si-metal	4100	450		4550
SiMn	1800	100	150	2050
FeMn	1800	50	150	2000

To evaluate the total carbon dioxide emissions caused by ferroalloy production we add the emissions caused by power generation (Table 3) times the power consumption, to the emissions from the furnace including the coking process (Table 2) and get Table 4.

The figures in Table 4 are visualised in Fig. 1, where the total CO_2-emissions are plotted.
In Fig. 2 we have compared the different ways for power generation by plotting the total CO_2 - emissions relative to the total emissions where coal is used for power generation (100 %).

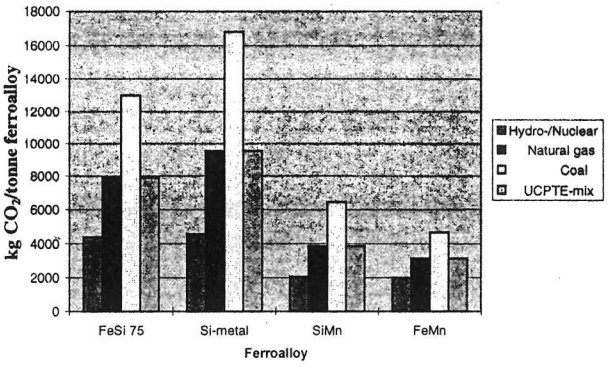

Figure 1 Total CO_2-emissions

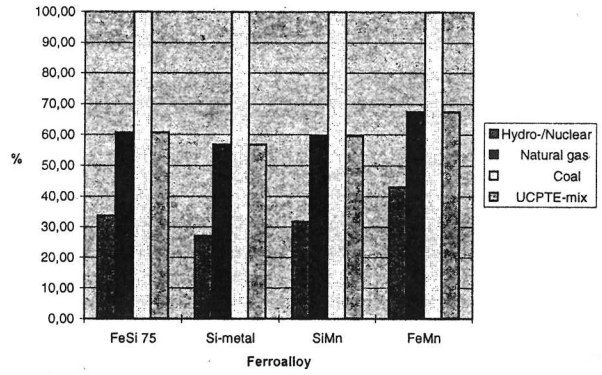

Figure 2 CO_2-emissions as % of emissions with coal-power

Table 3. CO_2-emissions from the generated power used per tonne ferroalloy.

Ferroalloy	Electric energy consumption kWh	Electric power generated by: Hydro-/Nuclear	Natural gas	Coal	UCPTE-mix
FeSi 75	8800	0	3520	862	3520
Si-metal	12500	0	5000	12250	5000
SiMn	4500	0	1800	4410	1800
FeMn	2700	0	1080	2646	1080

Table 4. Total CO_2-emissions per tonne ferroalloy

Ferroalloy	Electric energy consumption kWh	Electric power generated by: Hydro-/Nuclear	Natural gas	Coal	UCPTE-mix
FeSi 75	8800	4380	7900	13004	7900
Si-metal	12500	4550	9550	16800	9550
SiMn	4500	2050	3850	6460	3850
FeMn	2700	2000	3130	4646	3130

Methods or ways to reduce CO_2-emissions

In this discussion we will include credits the industry should have, if our industry's efforts to recover energy or by-products contributes to a reduction of CO_2 - emissions in other areas of activity.

1. More efficient production will of course contribute to a reduction, connected to both the use of less carbon and less electrical energy. Strong economic incentives support this trend, and are not necessary to comment further. In ferrosilicon production the typical electric energy consumption has been reduced from 9800 kWh per tonne in 1977 to 8800 kWh per tonne in 1997.

2. Electrolysis is a possibility, but much more electrical energy is needed than in the submerged arc furnace. How the electricity is produced is important.

3. Bio-carbon. It is accepted that using carbon from natural sources does not contribute to the greenhouse effect, because carbon dioxide formed by the oxidation of endogenous carbon are assimilated by new plants and trees.

4. Recovery of by-products. Silica dust can replace some of the cement in concrete. Since much CO_2 also is emitted in cement production, such a replacement might give a total reduction in CO_2-emissions, and should consequently be recognised in an EPI-indicator.

5. Energy recovery. We will discuss how energy recovered as heat or electrical energy should be assessed in an environmental performance indicator (EPI) for the plant.

Electrolysis

Manganese

Manganese metal is produced in an aqueous electrowinning process. Its standard reduction potential is 1.18 volts more negative than hydrogen. Manganese electrolysis is made possible by the high hydrogen overvoltage on manganese. The current efficiency for manganese is low, of the order of 65 %. Since rather high cell voltages are used, about 5 V, the energy consumption is so high as 8.5 kWh/kg [2]. The costs for electrolytic manganese are substantially higher than for manganese in ferromanganese. According to Metal Bulletin [3], the prices on June 12/13 1997 were:

Table 5. Prices for manganese in electrolytic manganese and ferromanganese

	% Mn	%C	$/tonne	$/tonne Mn
Electrolytic manganese	99.7		1280-1380	1284-1384
Ferromanganese standard	78	7.5	480- 500	615- 640
Ferromanganese medium C	80	<1.5	947- 991	1184-1238

These differences in prices tell us why ferromanganese and not manganese metal is used for alloying steel. At least that is the case when standard ferromanganese can be used.The next question is: Will a transition from ferromanganese to electrolytic manganese give a reduction in CO_2 -emissions? The answer to this question depends on the way the electricity is generated.The electric energy consumption for the production of ferromanganese is 2700 kWh/tonne FeMn (see previous chapter), which is equivalent to 3460 kWh/tonne Mn. If the energy in the off-gases is recovered and used for the production of electric energy, about 15 % of the input electricity can be recovered (see chapter Energy Recovery). This reduces the net electric energy consumption to 2295 kWh/tonne FeMn, being equivalent to 2940 kWh/tonne Mn.

Table 6 shows the changes in electricity consumption and CO_2 - emissions for a transition from ferromanganese to electrolytic manganese.

The conclusion is that unless one has a lot of available hydroelectricity, it is not even from an environmental point of view a good idea to change from ferromanganese to electrolytic manganese.

Table 6. CO_2 -emissions for the production of ferromanganese and electrolytic manganese. All values given for a production of 1000 kg (1 tonne) Mn

FeMn:				
Electricity generated by:	Hydro-	Natural gas	Coal	UCPTE-mix
Electric energy, kWh:	2940	2940	2940	2940
CO_2 emissions from el.gen., kg:	0	1176	2881	1176
CO_2 emissions from C-red., kg:	2000	2000	2000	2000
CO_2 emissions sum, kg:	2000	3176	4881	3176
Electrolytic Mn:				
Electricity generated by	Hydro-	Natural gas	Coal	UCPTE-mix
Electric energy, kWh:	8500	8500	8500	8500
CO_2 emissions from el.gen., kg:	0	3400	8330	3400
CO_2 emissions sum, kg:	0	3400	8330	3400
Change in CO_2 emissions, kg:	-2000	224	3449	224

Silicon

Several authors have shown that it is possible to extract silicon by electrowinning in a process like that for aluminium. Many have studied the production of aluminium-silicon alloys by the electrolysis of aluminosilicates. These papers have been referred by Stubergh and Liu /4/, which recently have developed a process for electrowinning of pure silicon from a bytownite-cryolite molten mixture at about 970 °C. In the electrolysis cell, the bottom of a graphite crucible was used as the anode. The cathode was also made of graphite. Their experiments were conducted as a batch process, the melt consisted at start of 12 % bytownite (a solid solution of anorthite and albite) and 88 % of cryolite. It was possible to extract almost all silicon as a pure metal (99.8-99.98 % Si) before any aluminium was deposited. The overall reaction is:

$$SiO_2 + C = Si + CO_2 \qquad (1)$$

Thonstad has estimated the consumption of electric energy to be about 20000 kWh per tonne Si for the electrowinning process using consumable carbon anodes [5]. The electric energy consumption for the production of silicon in the electric furnace is 12500 kWh/tonne Si. If the energy in the off-gases is recovered and used for the production of electric energy, about 20 % of the input electric energy can be recovered (see chapter Energy Recovery). This gives a net electric energy consumption of 10000 kWh/tonne Si. Table 7 shows the difference in electricity consumption and CO_2- emissions changing from production of silicon metal (99 % Si) in an electric arc furnace to an electrolytic process, for various alternatives for the generation of electric power.

Table 7. CO_2 -emissions for the production of silicon metal
All values given for a production of 1000 kg (1 tonne) Si

Silicon metal (99 % Si)

Electricity generated by:	Hydro-	Natural gas	Coal	UCPTE-mix
Electric energy, kWh:	10100	10100	10100	10100
CO_2 emissions from el.gen., kg:	0	4040	9898	4040
CO_2 emissions from C-red., kg:	4550	4550	4550	4550
CO_2 emissions sum, kg:	4550	8590	14448	8590

Electrolytic silicon (99.8 % Si)

Electricity generated by	Hydro-	Natural gas	Coal	UCPTE-mix
Electric energy, kWh:	20000	20000	20000	20000
CO_2 emissions from el.gen., kg:	0	8000	19600	8000
CO_2 emissions from anodes, kg:	1570	1570	1570	1570
CO_2 emissions sum, kg:	1570	9570	21170	9570
Change in CO_2- emissions, kg:	-2980	980	6722	980

The conclusion is the same as for manganese. Unless there is a lot of available hydroelectricity, it is not from an environmental point of view a good idea to change production from the electric furnace to an electrolytic process. For the production of high purity silicon, however, the development of an electrolytic process is interesting.

Bio-carbon

The use of bio-carbon,which is a general term for all possible reducing agents from raw biological materials as haulm and wood, and processed biological materials as roasted wood and charcoal will not contribute to the greenhouse effect, because the carbon dioxide formed from these sources is reckoned to be assimilated by new plants and trees. Peat will probably not be counted as a biological raw material, but considered like coal to supply extra carbon dioxide to the atmosphere. A precondition for excluding bio-carbon as a source for greenhouse CO_2 is that at least the same amount of plants and trees are grown or planted, as we have used. In addition to adding to the greenhouse effect a deforestation caused by an increased demand for charcoal will cause other severe damages to the environment like increased watersheds and erosion.

Looking back in the metallurgical history, we have several examples of overexploitation of forests to produce charcoal for the production of copper and iron.

In most regions charcoal is a more expensive carbon material than coal or coke. Brazil is an exception, more than 95 % of the carbon material used is charcoal made from eucalyptus [6]. About 15000 km^2 of homogeneous forests supplies the Brazilian production of 1 million tonnes of ferroalloys and silicon metal.

In other regions some chips of wood and charcoal are used, especially for the production of silicon-metal. Up to now this has been done only because it has been advantageous for the process. The threat of possible restrictions on CO_2-emissions has resulted in a report about bio-carbons for the ferroalloys industry for The Norwegian Ferroalloy Producers Research Association (FFF) [7]. Today about 10 % of the Fix Carbon used in the Norwegian production of silicon-metal and ferrosilicon is from bio-carbon. There are sufficient bio-materials (deciduous woods and thinning wood) available in the neighbourhood of the ferroalloys plants to make a substantial increase (double or triple) in the use of bio-carbon. The price for charcoal from these sources can be estimated to be in the same price range as imported charcoal (about 400 $/tonne Fix Carbon). FFF has started a research project aimed at bringing the costs down for charcoal produced in temperate regions, and this project is supported by the "KLIMATEK"-programme in The Norwegian Research Council. The project covers all aspects of using bio-carbon; felling, transportation, pyrolysis, use of volatiles and finally using it in the ferroalloy process. But the ferroalloys industry will be only one of the interested parties to bio-carbons. The industry will have to compete among others with district heating.

Recovery of by-products

When the development of bag filters to collect silica dust started in the early seventies, the specific emissions from silicon and ferrosilicon plants were considerably higher than what is obtained by good practise today. Typical silicon yields now are 90 % for ferrosilicon and 85 % for silicon-metal giving respectively 0.24 and 0.38 kg SiO_2 per kg Si. The huge amount of silica dust collected in the baghouses, in Norway alone more than 100 000 tonne per year, presented a major disposal problem. But many applications have been found for this waste product, addition to cement in concrete

being the major application. The addition of silica dust (10-30 % of the cement weight) will increase the strength (compressive and tensile) of the concrete. It has even been found that part of the cement can be replaced by silica dust and still the concrete will gain strength. 1 kg silica dust can replace 3 kg cement.
In cement production the CO_2 - emissions are 0.8 - 1.0 kg CO_2 per kg cement. Thus the replacement with 1 kg silica dust will remove 2.5 kg of CO_2 - emissions. Giving ferrosilicon and silicon-metal production the credit for this means that we can deduct 800 kg per tonne in the specific CO_2 - emission for FeSi and 950 kg per tonne for silicon-metal *).

*) For FeSi: (0.24*2.5/0.75) *1000 kg = 800 kg
For Si: (0.38*2.5) * 1000 kg = 950 kg

Energy recovery

Ferromanganese and silicomanganese

The use of sealed furnaces and removal of the dust by wet scrubbing (Venturi scrubbers) was an established practice already in the sixties [8]. The clean gas containing 50 to 70% CO can be used as a synthesis gas or for heat generation. If there is no other uses for this energy the solution will be to produce electric energy. Typically we can expect to recover up to 15 % as electric energy of the input electric energy.

Using the gas for heat generation or electric power generation instead of natural gas is equivalent to removing the following CO_2 - emission per tonne ferroalloy:
SiMn-production, 70 % CO in off-gas: 450 kg CO_2/tonne SiMn
FeMn-production, 50 % CO in off-gas: 250 kg CO_2/tonne FeMn

Using the gas instead of coal is equivalent to removing the following CO_2 - emission per tonne ferroalloy:
SiMn-production, 70 % CO in off-gas: 650 kg CO_2/tonne SiMn
FeMn-production, 50 % CO in off-gas: 350 kg CO_2/tonne FeMn

Ferrosilicon and silicon-metal

The bag filters, which collect the silica dust, cannot be exposed to temperatures above 250 °C. Cooling the off-gas from the open furnace by mixing it with huge amounts of air is possible, but gives a gas flow of 16 Nm^3/kWh [8]. As the capital requirement for the baghouse is roughly proportional to the volumetric gas flow, minimisation of the gas volume is highly wanted. This has led to the development of semiclosed furnaces where the off-gas is reduced to 4 - 6 Nm^3/kWh and the gas-temperature in the off-gas channels is as high as 800 °C. Cooling this gas down to an acceptable temperature for the bag filters releases vast amounts of heat . The off-gas from a ferrosilicon furnace has an enthalpy of approx. 36 GJ per tonne FeSi produced, and from a silicon-metal furnace approx. 54 GJ per tonne Si. The most economical use of the energy is for heat generation, as a substitute for natural gas, oil or coal. If the energy is used for generation of electricity, we can expect to recover about 20 % of the input electrical energy.

Using the off-gas for heat generation or electric power generation instead of natural gas is equivalent to removing the following CO_2-emissions:

Ferrosilicon production : 2000 kg CO_2/tonne FeSi
Silicon-metal production : 3000 kg CO_2/tonne Si

Using the off-gas instead of coal is equivalent to removing the following CO_2 - emission per tonne ferroalloy:
Ferrosilicon production : 2800 kg CO_2/tonne FeSi
Silicon-metal production : 4200 kg CO_2/tonne Si

Adding up possible contributions

We will sum up the different contributions the ferroalloys industry can make to reduce CO_2 - emissions and greenhouse effects.

Table 8. Possible reductions in CO_2 - emissions

Situation where present and possible contributions are not included:				
Ferroalloy	Hydro-/Nuclear	Natural gas	Coal	UCPTE-mix
FeSi 75	4380	7900	13004	7900
Si-metal	4550	9550	16800	9550
SiMn	2050	3850	6460	3850
FeMn	2000	3130	4646	3130
Using 20 % bio-carbon in production of FeSi and Si-metal				
FeSi 75	-876	-876	-876	-876
Si-metal	-910	-910	-910	-910
SiMn	0	0	0	0
FeMn	0	0	0	0
Recovery of silica dust:				
FeSi 75	-800	-800	-800	-800
Si-metal	-950	-950	-950	-950
SiMn	0	0	0	0
FeMn	0	0	0	0
Energy recovery				
FeSi 75	-2000	-2000	-2800	-2000
Si-metal	-3000	-3000	-4200	-3000
SiMn	-450	-450	-650	-450
FeMn	-250	-250	-350	-250
Net CO_2 – emissions:				
FeSi 75	704	4224	8528	4224
Si-metal	-310	4690	10740	4690
SiMn	1190	2990	5400	2990
FeMn	1350	2480	3896	2480

In Fig. 3 the net CO_2-emissions are plotted for different electric power sources taking credit for present and possible contributions to reduce CO_2-emissions.

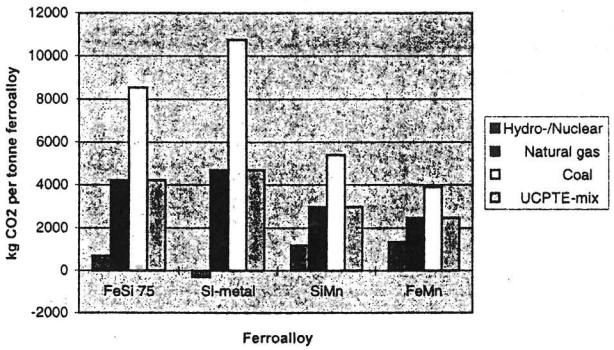

Fig. 3 CO_2-emissions with different power sources including present and possible CO_2-contributions

Comparing Figs. 1 and 3, we see that by using partly (20 %) bio-carbon in the furnace and recover by-product (silica-dust) and energy from the off-gas it is possible to get a substantial reduction in the total CO_2-emissions caused by ferroalloy production.

Acknowledgement

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