

FORMATION, CHARACTERISTICS AND UTILISATION OF CO-GAS FORMED IN FERROCHROMIUM SMELTING

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ABSTRACT

High carbon ferrochromium is produced by carbon reduction. No replacement for carbon as reductant has yet been developed. The reduction creates a considerable amount of CO-gas. In open and semi-closed furnaces the gas is burned when leaving the burden. In closed furnaces the formed gas is sucked out by a fan, washed and utilised as fuel.

The formation of carbon monoxide is presented briefly starting from thermodynamic considerations up to solid and liquid state reduction. The volume, composition and energy content of the furnace gas are discussed, focusing on the raw materials and pre-treatment processes of the furnace feed as well as on the process equipment and control.

Outokumpu has been using closed and sealed furnaces and utilising the CO-gas in its Tornio Ferrochrome Works since 1968. Today in Tornio with an annual ferrochromium production of 260 000 t CO-gas production is 186 million m³, representing 68 MWh an hour. At the same time the furnace power input is 95 MW. About 98 % of the CO-gas is utilised, whereof 30 % in the ferrochrome production itself.

This paper focuses on the characteristics and utilisation of CO-gas. CO-gas is secondary energy, which on one hand saves primary electric and fossil fuel energy in ferrochromium production and, on the other, replaces other fossil fuels at the adjacent steel works. The characteristics of the fuel, requirements for utilisation as well as health and safety aspects are discussed. Utilisation of the gas has a high impact on the total dust and gaseous emissions and on the energy optimisation at the ferrochromium and steel works.

1. INTRODUCTION

The conventional ferrochromium smelting processes are open furnaces, in which the formed reduction gas is burned over the burden. The off-gas is cooled either wholly with excess air or partly with diluting air and finally in trombone coolers. The gas is cleaned in baghouses. The off-gas volumes are high, depending on the cooling method from 4 000 to 13 000 Nm³/h per MW of furnace power or from 15 000 to 55 000 Nm³ per tonne of FeCr. The heating value of the gas is wasted.

Semiclosed furnaces were developed in the 1950's for FeSi production with increasing size. In semiclosed furnaces the hood consists of movable panels. The diluting air flow is limited and the off-gas is cooled in a boiler. In a semiclosed FeCr furnace the gas volume is from 2 500 to 4 000 Nm³/h per MW or from 10 000 to 15 000 Nm³ per tonne of FeCr.

The early development of FeSi furnaces is presented in Figure 1. The trend in the gas volumes in different gas systems are the same for FeSi, FeCr and other ferroalloys.

In closed smelting furnaces the gas can be cleaned and utilised. Closed furnaces were used already in the 1930's for pig iron production and were developed for ferroalloys in the 1950's.

Closed furnaces are restricted by the raw material quality, in that only lumpy materials can be used. However, the reduction gas from the furnace can be cleaned in scrubbers and utilised. The corresponding gas volumes to be treated are generally from 220 to 250 Nm³/h per MW of furnace power or from 650 to 850 Nm³ per tonne of FeCr depending on the leakage air.

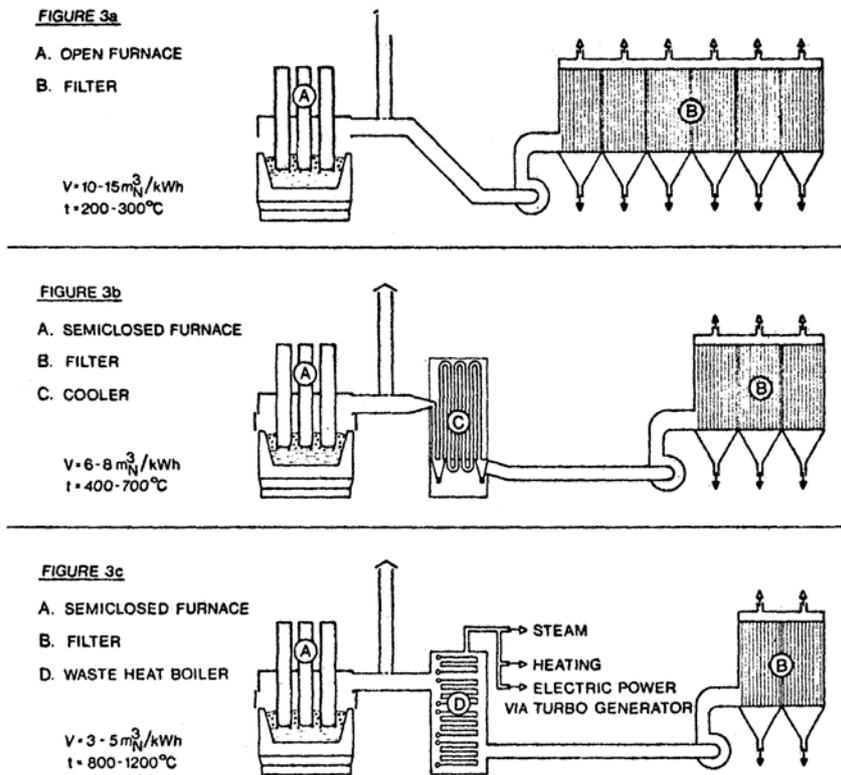


Figure 1. The development stages of gas treatment in FeSi production [1].

Outokumpu's ferrochromium production started in 1968 using even at the beginning a closed furnace and gas scrubbers. CO-gas was used from the start for the heating of ladles and some in the pre-heating kiln burner, but very soon also in the sintering furnace. The existing process, since developed in many ways is presented in Figure 2.

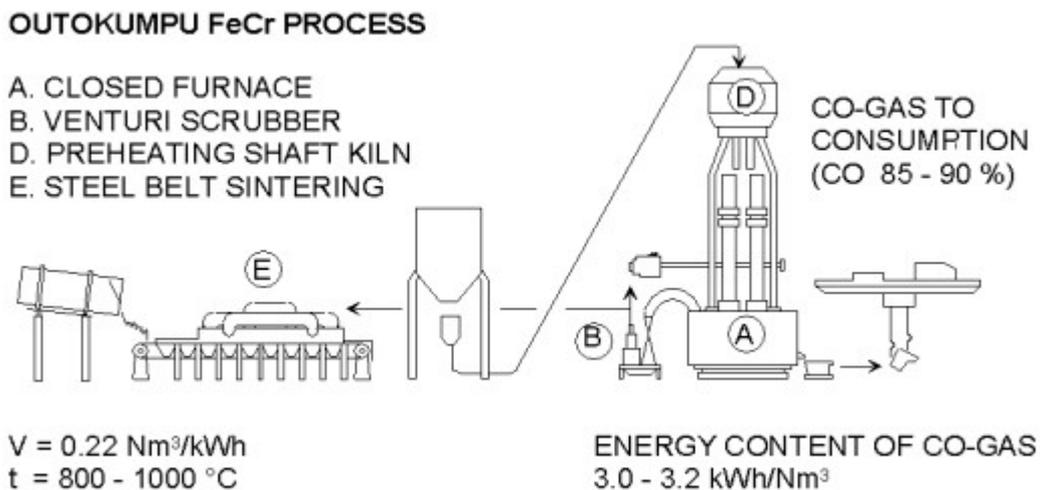
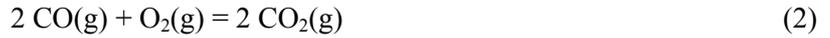


Figure 2. Outokumpu ferrochromium process.

2. FORMATION OF CO-GAS IN CLOSED SUBMERGED ARC FURNACE

2.1 Theoretical Considerations

The formation of carbon monoxide is studied by the reduction in the solid and molten stages in the production of ferrochromium in a submerged electric arc furnace. The stability of oxides is compared to each other according to the Ellingham diagram. The calculations are based on the equilibrium software of HSC Chemistry [2]. The reduction of oxides is based on solid carbon and carbon monoxide gas. The reduction reactions are:



Solid carbon acts kinetically in an effective way with molten phases. The molten phases appear in the lower part of the bed and in the adjacency of the electrodes. The carbon monoxide gas acts effectively in the solid stage in the upper part of the bed.

The general study of reduction is divided into three categories:

- Metals reduced from oxides (Fe, Cr)
- Reduction of slag components (SiO_2 , TiO_2 , Al_2O_3 , MgO , CaO , including gaseous Mg and SiO)
- Alkalis

Free energy - temperature relationships for metal oxides are shown in Figure 3.

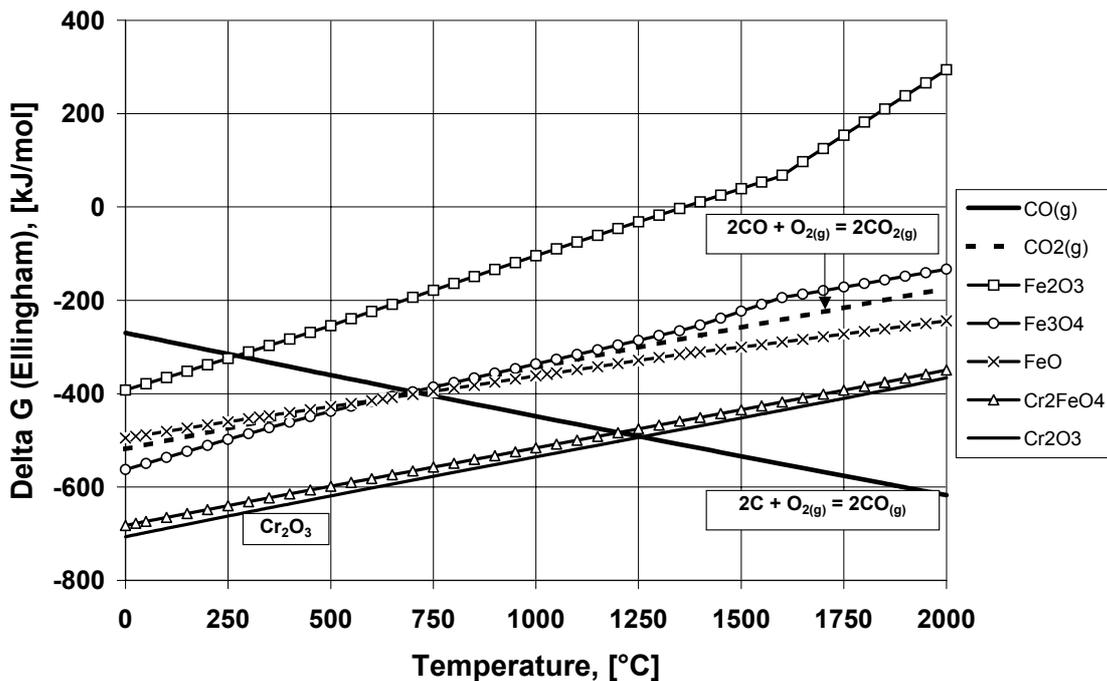


Figure 3. Standard free energies of reduction of metal oxides with carbon and carbon monoxide.

Solid carbon effectively reduces metal oxides. Wüstite is reduced at low temperatures, but the reduction of chromium oxide occurs at higher temperatures. Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) reduces at a lower temperature than chromium oxide.

Carbon monoxide reduces hematite to magnetite over the whole calculated temperature range. The higher the reduction degree of iron oxides, $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, the higher the CO/CO_2 ratio needed. The reduction of magnetite to wüstite occurs kinetically at higher temperatures. The reduction of wüstite to metallic iron occurs at over 710°C in the high CO/CO_2 ratio. Reduction of chromium oxide and chromite is not possible with carbon monoxide. Free energy - temperature relationships for slag components and for alkali oxides are shown in Figures 4. and 5., respectively.

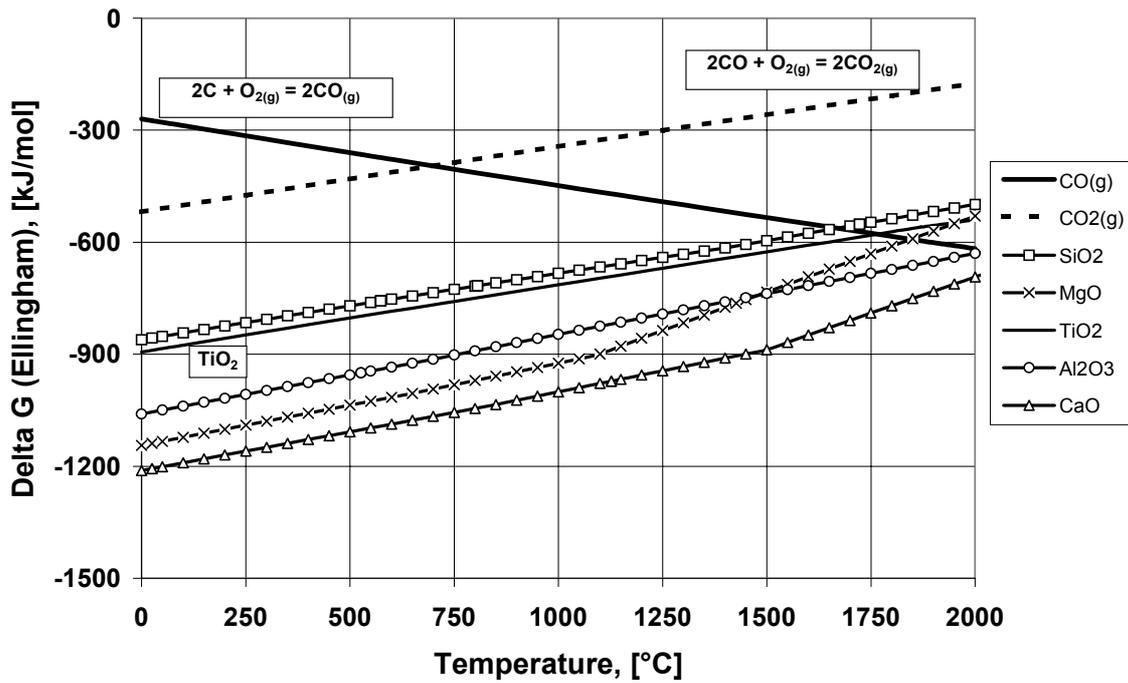


Figure 4. Standard free energies of reduction of slag components with carbon and carbon monoxide.

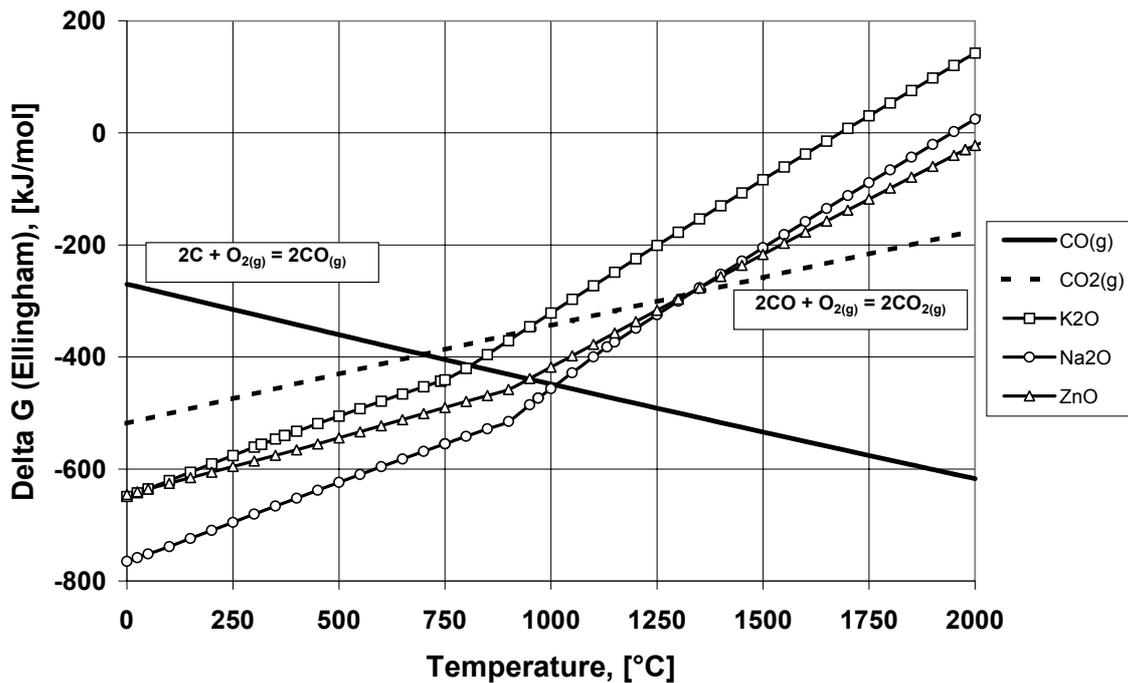


Figure 5. Standard free energies of reduction of alkali oxides with carbon and carbon monoxide.

Slag components are very stable, but solid carbon reduces them at very high temperatures. The most instable oxide is silica. These components can not be reduced even with pure carbon monoxide gas.

Carbon monoxide reduces potassium oxide at about 900 °C and sodium and zinc oxides at about 1300 °C. Solid carbon reduces the alkali oxides. The reduction of these oxides occurs mostly before the molten stage.

Free energy - temperature relationships for gaseous magnesium and silicon oxide are shown in Figure 6.

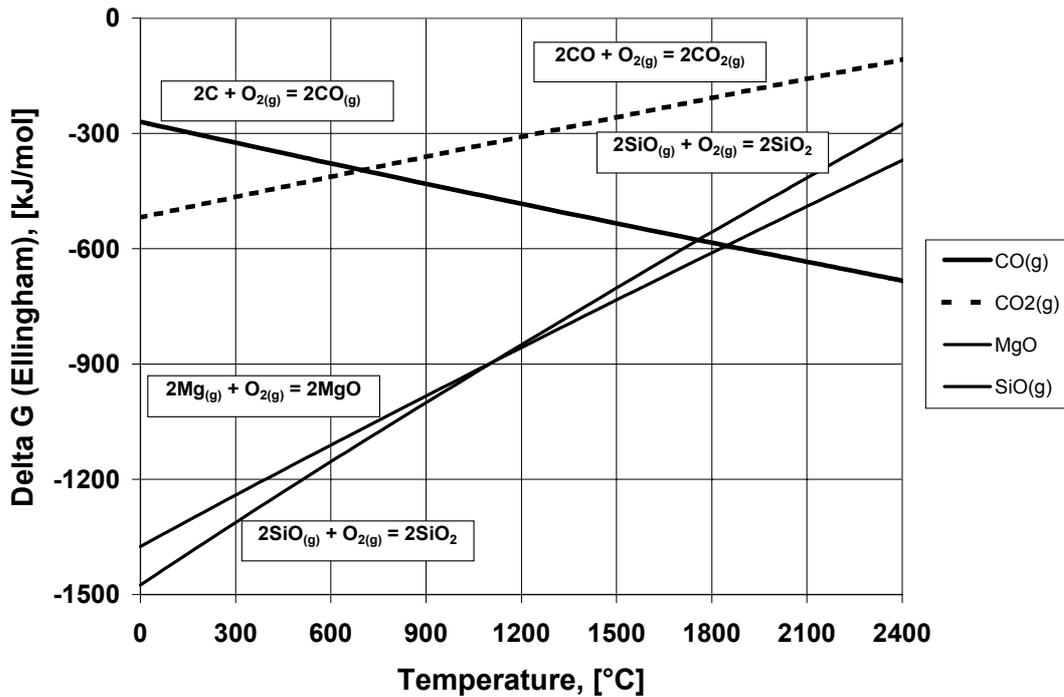


Figure 6. Standard free energies of gaseous magnesium and silicon oxide.

The reduction of magnesium oxide with solid carbon occurs at over 1800 °C in the adjacency of the electrode tips. Gaseous magnesium is oxidised very easily back to magnesium oxide by carbon monoxide gas. Silicon dioxide is also reduced with solid carbon to silicon oxide gas at very high temperatures, but carbon monoxide gas oxidises it back to silicon dioxide.

2.2 Formation of CO-gas in Practice

Ferrochromium smelting in the good sealed submerged electric arc furnace generates 650-750 Nm³ CO-gas per tonne of production. The volume and composition of the gas depends on the feed materials and their pre-treatment methods, on the construction of the smelting furnace and on the furnace controls. The gas production varies both in time and place. It is affected by e.g. different temperatures, furnace electrical values, material flows, segregation, position of electrodes and the time to tapping. The process equipment and control of the process gas is presented in Figure 7.

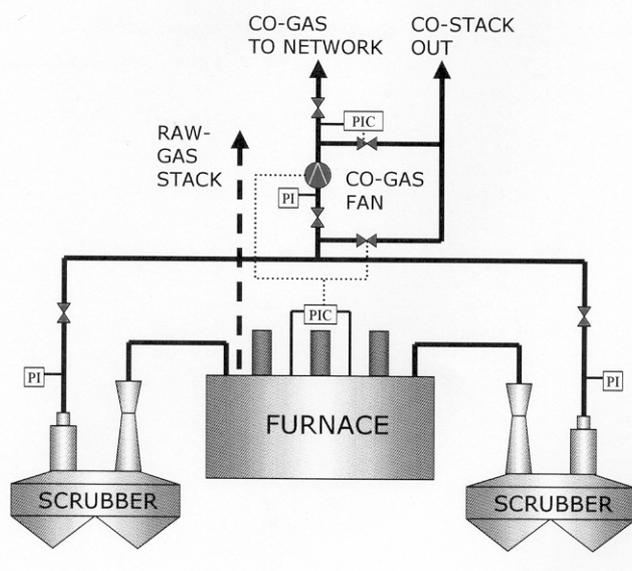


Figure 7. Process equipment and gas control.

The roof of the furnace is water cooled and as gas tight as possible, e.g. the electrode seals. The formed CO-gas is conducted typically through two water-cooled goose necks to be cleaned in two ejector-venturi scrubbers. In rare abnormal cases the gas can be conducted directly out from the furnace through a raw gas stack.

The pressure in the furnace is measured by the connections through the roof and it is controlled by the CO-gas fan to close to 0 Pa so that the furnace is not over-pressurised or under-pressurised. Over-pressure causes blowing from the furnace and under-pressure causes leaking of air into the furnace. The CO and H₂ contents and possibly also the CO₂ and O₂ contents are measured from the gas for reason of furnace control and for the utilisation of the CO-gas. Valves are required in the equipment after the scrubbers for further CO-gas handling. The valves can be pinch, plug, ball or butterfly type. The gas lines are flushed through the ventilation lines during maintenance work. The required 8 to 14 kPa pressure for the utilisation of the gas in the usage points is attained with the CO-gas fan. Separate blowers or compressors are used after that so that the required pressure can reach 30 to 35 kPa depending on the usage point. If all the formed gas cannot be utilised, the gas is conducted out after the CO-gas fan or in some cases directly after the scrubbers. The excess gas is burned in a stack.

The CO-gas from the submerged electric arc furnace contains generally 75-90 % CO, 2-15 % H₂, 2-10 % CO₂ and 2-7 % N₂. The burning components are CO and H₂ and depending on the gas composition the burning energy is 10.1 – 11.5 MJ/Nm³ i.e. 2.8-3.2 kWh/Nm³, which then means 7200 – 8280 MJ/t FeCr i.e. 2.0-2.3 MWh/t FeCr.

A high CO-content is achieved by pellets in the melting batch, by good pre-heating, a gas-tight furnace and functional pressure control. The contents of H₂O and CO₂ increase when using lumpy ore because of carbonates and hydroxides. Feed materials affect the gas composition in many ways: The volatile matter in the raw material decomposes into the gas. The moisture of the batch evaporates into the gas also, but in the cold batch the moisture and the hydroxides of the feed also react with the carbon and form hydrogen through water gas reaction, $\text{H}_2\text{O} + \text{C} = \text{H}_2 + \text{CO}$. CO₂ from carbonates can react with carbon through the Boudouard reaction, $\text{CO}_2 + \text{C} = 2\text{CO}$, which is a highly endothermic reaction. Both decomposition reactions consume coke and energy. The reduction behaviour of the decomposition reactions affects the coke utilisation and the amount and analysis of the gas.

The pre-treatment methods also have an effect. The feed materials can be pre-dried, pre-heated or as in some solutions, pre-reduced. Every step decreases the amount of gas formed in smelting and affects the analysis by reducing gas components from evaporation, decomposition and reduction reactions. The concentrate can be pelletised and sintered at high temperatures. The characteristics of sintered pellets due to Fe³⁺ combined with the preheating of the smelting charge has the effect that reduction starts in the smelting burden in the upper part of the burden by the CO-gas coming from the lower parts. The carbon dioxide in the off-gas increases, decreasing the carbon monoxide correspondingly. The nitrogen content tells us however, that the increased carbon dioxide comes from the batch and not due to leakage air. Leakage air into the furnace increases both the CO₂ and N₂ content.

The temperature of the CO-gas from the furnace is 600 to 700 °C with cold and 800 to 1000 °C with the pre-heated batch with good electrode lengths. In gas scrubbing the temperature decreases to the level of 5 to 40 °C.

The smooth constant active power of the submerged electric arc furnace and pre-heated furnace charge eases furnace pressure control. A pre-heated furnace charge, furnace pressure control and good furnace sealing decrease the amount of gas per production tonne.

3. USE OF CO-GAS AS FUEL

CO-gas is formed as result of reduction processes and, from a closed furnace, is an unburned secondary energy to be utilised later in different processes for replacing other fuels. The gas must be scrubbed for utilisation, dry cleaning cannot be used. The gas at the same time cools down, but for practical reasons the latent heat of the gas is not utilised. Generally there are different low pressure and high pressure scrubbers for cleaning of CO-gas. The specific water consumption varies on a large scale depending on the scrubber type.

In Outokumpu's ferrochrome process the gas coming from the furnace is washed in the ejector-venturi scrubber, see Figure 8. The scrubber is the result of long research and development work. The water is sprayed at 30 bar pressure through the nozzle and the fast speed jet sucks the gas from the furnace. The water spray consists of very small water droplets, which collect the dust efficiently. The slurry and the gas are separated in the bottom part of the scrubber and the gas is conducted through the droplet separator to the CO-gas line. The scrubber is designed taking safety aspects into account. The amount of water and the scrubber itself are dimensioned so that the pressure in the gas line after the scrubber is above atmospheric pressure. Typical pressure after the scrubber is 3 to 7 kPa. The specific water consumption is 5 to 7 litres per m³ gas.

The solid content in the furnace gas varies depending on the operation conditions in the furnace and is typically 35 to 45 g/Nm³. The separation degree of the scrubber is close to 99.9% after which the produced CO-gas contains 50 to 100 mg/Nm³ dust. The dust remaining in the gas is very fine. A fraction smaller than 1 µm is even theoretically very difficult to separate from the gas with a venturi scrubber. By filtering the gas after the scrubber with a sintered plate filter the residual dust level of 1 mg/Nm³ is achieved.

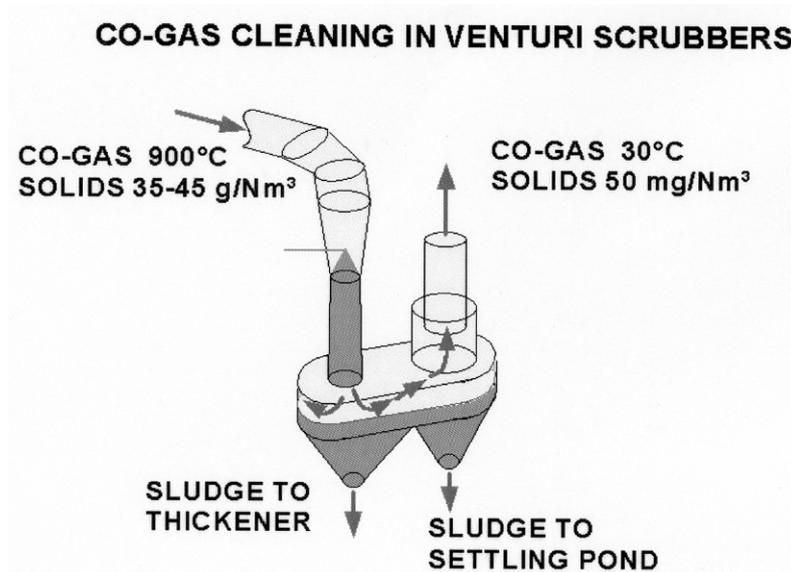


Figure 8. An ejector-venturi scrubber.

The heating value of the CO-gas is high, at close to 60% of the primary energy of the reductant, and on the other hand about 70% of the primary electric energy required for smelting. Because of the high energy content the use of CO-gas for replacing other fuels is very economical and with respect to net CO₂ emissions significant.

The CO-gas utilisation in the AvestaPolarit Tornio Works complex is shown in Figure 9 as an example. With an annual 260 000 t FeCr production, 186 million Nm³ of CO-gas is formed. That means 21 300 Nm³/h of gas with a total active power of 95 MW. As burning energy the heating value of the CO-gas is 243.5 GJ/h, i.e. 67.7 MWh/h. About 98% of that is utilised. The portion used in the ferrochrome works for coke drying, sintering, pre-heating and heating of ladles is 30 to 35%. About 45% of the gas is used in steel production in the smelter, hot and cold rolling mills and 20% in the central heating plant for heat and steam production. In the ferrochromium works the use of CO-gas for pre-heating decreases the specific energy consumption in smelting and increases the production capacity by 15 to 20%. Burning of the gas takes place with an air coefficient of about 1 to avoid burning of coke in the preheating shaft kiln. The right gas temperature to the shaft kiln is controlled by oxygen free circulating gas. In other utilisation points in the ferrochromium works CO-gas replaces LPG or oil and burning takes place with extra air. In steel production and the Central Heating Plant CO-gas is used instead of LPG and oil.

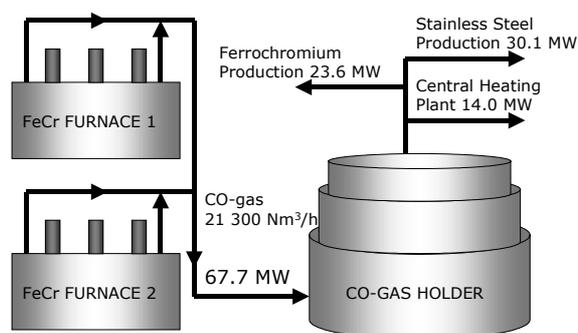


Figure 9. Use of CO-gas in the AvestaPolarit Tornio Works complex.

CO-gas is easily ignited and combustible. In burning with air high adiabatic combustion gas temperature of over 2200 °C is achieved. The flame is long, e.g. compared to that of LPG, which is favourable for the linings, especially in the steel belt sintering furnace. Burning of CO-gas is easy and compared to other fuel with regard to flow controls. Because of its characteristics the use requires care and the burning logics and safety interlocks must be functional. Under-pressure is not allowed in the gas lines. The process equipment must be strong and air-tight. Pressure losses must be minimised in the gas lines.

The CO₂ content in the combustion gas is high, about 2.5 fold compared to oil and LPG. On the other hand, H₂O content is less than half and also the N₂ content is low. The composition of the combustion gas is of significance in operating conditions in which the water-gas reaction is possible. On the other hand, the higher CO₂/CO ratio favours the Boudouard reaction, $\text{CO}_2(\text{g}) + \text{C}(\text{s}) = 2 \text{CO}(\text{g})$

4. SAFETY ASPECTS

Carbon monoxide is a very poisonous gas. It is colourless, odourless and tasteless. Its physical characteristics are like nitrogen. CO is little lighter than air and is easily blended with it. Its solubility in water is little greater than that of air. CO creates an explosive gas mixture with air at a content of 12-75 %. The characteristics of CO are presented in Table 1.

Table 1. Characteristics of carbon monoxide.

Density	1.19-1.26	kg/Nm ³
Igniting temperature with air	>630	°C
Igniting temperature with oxygen	>590	°C
Heating value	12636	KJ/Nm ³
Theoretical burning temperature with air	2250	°C
Melting point	-205	°C
Boiling point	-192	°C
Solubility to water	3.3-2.3	ml/100 ml
Compressibility	ca. 1	
Explosiveness with air	12-75	% CO

Carbon monoxide is poisonous when breathing, because it displaces oxygen in the haemoglobin of the blood. Its ability to bind in haemoglobin, responsible for the transport of oxygen, is 200 to 250 times greater than that of air. Even a content of 1000 ppm in breathing air is life-threatening. The direct symptoms are headache, dizziness, general weakness, lack of ability to concentrate and difficulty in breathing. In severe poisoning the blood pressure first rises and starts then finally to drop, the patient becomes unconscious and may start to have seizures.

The mixtures of gaseous fuel with air are explosive. The precondition is that the composition of the mixture is inside what are termed the lower and higher explosion limits. Ignition takes place even with a very small energy spark, < 1 mJ, like the static electricity felt by man. The explosion creates locally a very high pressure, up to a kilobar. The H₂ content in the CO-gas from the furnace does not in practice increase the explosion risk in the furnace or gas handling after that. To avoid the explosive gas mixture before the process

starts the oxygen content of the gas mixture should be <3.5%. In practice the use of nitrogen has continuously increased as a pooling gas in connection with maintenance work on the gas lines. The carbon dioxide produced in the process is also used as an alternative.

In practice a CO - water emulsion is formed during scrubbing of the furnace gas. The construction of the scrubber must be as simple as possible to avoid the formation of gas locks in the scrubber. The scrubber is equipped with special water-lock tanks to form an air sealed construction from the scrubber and to avoid settling of the solids and thus possible blockages. CO vaporises in time from the water. This may cause an explosive gas mixture to be created in closed spaces like pump tanks and drains, if they are not correctly ventilated. In practice these kinds of drains and canals are separated from others. Theoretically CO-gas should always rise upwards from the leaking point, but in certain conditions, such as low pressure or channelling of the wind, the gas can go downwards. To ensure work safety the ventilation ducts from the gas treatment equipment have to be constructed high enough.

The working environment is equipped with an alarm system for possible CO leakages. Ceramic gas probes control the CO content in selected points. Two different alarm limits are normally used, 150 and 300 ppm, which give an alarm both locally and to the control rooms. In addition, personal portable meters are used, in which the normal alarm limit is 50 ppm. In alarm cases the working safety instructions are to be complied with.

5. EMISSIONS

Conditions in the submerged electric arc furnace are too reducing for the formation of NO_x or Cr(VI), but are favourable for the formation of cyanide. The formed CO-gas contains very little sulphur. Burning of CO-gas in the usage points and outside generates CO₂ emissions. Because the gas amount from the closed furnace is small and the gas is cleaned the solid discharges out are kept small. With efficient water treatment the solid discharges from the process to the waters are also small.

Sample taking and analysing from the closed furnace has proved that Cr(VI) contents are smaller than the assay limit. The Cr(VI) content in the solids has been less than 0.01% both in the samples from the gas space and in the dust accumulated in the goose neck. In process water samples collected after the gas scrubbing the Cr(VI) contents have been under the assay limit, <0.01 mg/l. 70-85% of the sulphur in the smelting feed materials goes to slag and 5-15 % to the ferrochromium. The sulphur content in the solids in the CO-gas is less than 5 % and the solid content after scrubbing is 50-100 mg/Nm³. After cleaning the burning of CO-gas does not generate appreciable SO₂ emissions. The lack of sulphur in the gas has been an important fact.

High carbon ferrochromium is produced by carbothermic reduction of metal oxides. No replacement for carbon as reductant has been yet developed. Burning of the formed CO-gas generates CO₂ emissions [4]. Ferrochromium production generally generates 1200-2000 kg and with preheated pellet batch 1400 kg CO₂ per tonne of FeCr. CO-gas is secondary energy and 25-30 % of it is needed in the pre-treatment and by-processes of the production itself. If the excess gas is used outside, e.g. in the Ferrochrome – Steel complex, the specific CO₂ emission from the ferrochrome works is 600 kg/t FeCr. The specific emission coefficient per energy unit is about double compared to LPG or oil. From the environmental aspect utilisation of CO-gas as much as possible is significant.

The smelting raw materials contain nitrogen and alkalis, which in a closed submerged electric arc furnace form cyanides 30-70 mg/Nm³ [5]. The cyanides dissolve in scrubbing water. Granulation of ferrochromium slag offers good conditions for the decomposition of cyanides from the scrubbing waters. 70 % of cyanides are removed to the gas atmosphere in granulation and the removal continues in the settling ponds. After process water treatment the cyanide discharge to seawater is 0.5-1.0 g/t FeCr, which has no ill effects for the environment.

In the cleaning of CO-gas about 25 kg of solids is separated per tonne of ferrochromium by venturi scrubbers. After that clarifiers and sand filters are used in the scrubber water treatment. Settling is intensified by flocculants. The slurry is not suitable for recycling. The solid discharges after water treatment to the sea from the whole ferrochrome production are 10-15 g/t FeCr.

6. CONCLUSION

Efficient utilisation of CO-gas is an important environmental aspect. The utilisation decreases significantly the primary specific energy consumption in ferrochrome production. External use decreases in different ways the total emissions to air. With an annual production of 260 000 tonnes ferrochrome the energy value of produced CO-gas is in total 593 GWh. This is equal to over 50 000 tonnes of oil.

CO-gas filtering with a sintered plate filter after scrubbing creates new possibilities for utilisation of the gas even in demanding user points. The use of gas as fuel is the most economical and efficient alternative especially combined with the ferrochrome-steel complex. CO-gas can be utilised also for external heat and steam production, or for power production. CO can be used as raw material for methanol and formic acid production. However, substitutive use as raw material for the chemical industry requires a higher price for the gas compared to fuel.

Energy recovery is one significant part of the best available technology (BAT) [6] in ferrochromium production. It will become more and more important in the future. Flaring of CO-gas is only acceptable in the case where customers inside or outside the plant are temporarily not available.

7. REFERENCES

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