Excavation of a 54 MVA HC-ferrochromium furnace
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1. Abstract
A 54 MVA furnace at Elkem Rana was shut down for relining in September 1996. The interior of the furnace was investigated by a scientific excavation. This showed that most of the volume in a submerged arc ferrochromium furnace is loosely sintered burden. It reaches from the top of the furnace down to the electrode tip. The average retention time in the burden is around 24 hours, but only a small part of the reduction takes place here. The burden is heated to around 1200 °C. The main part of the required energy is probably supplied from the coke bed by circulation of Mg and SiO₂-gas. There is no liquid slag at these temperatures. Some chromite is partly reduced to solid iron rich metal prills distributed in the chromite grains. This is assumed to result in around 20 % degree of reduction.

The main part of the reduction takes place in the coke bed. It is situated below the electrode tip, is 80-100 cm high and has a width varying from the electrode diameter and upwards. It contains a surplus of coke. The materials in the coke bed have an average temperature of at least 1700 °C and an average retention time around 20-30 minutes. There are great variations among the particles due to mixing. This is caused by a high gas flow and by material flowing into the coke bed along its sides.

There is no separate slag layer. The chromite grains in the coke bed dissolve in a slag with varying composition. Some undissolved, partly reduced chromite grains occur in the tapped slag. They account for most of its chromium content. The liquid slag has a low content of dissolved chromium oxide.

2. Introduction
Theories about the reactions and temperatures inside submerged arc furnaces are usually based on measurements and observations outside the furnace. Sampling and observation from the inside of an operating furnace is extremely difficult if not impossible. A "dig out" of a furnace shut down directly from normal operation is probably the closest we may come to a direct observation. A 54 MVA furnace at Elkem Rana was shut down for relining in September 1996, and restarted in December the same year. It was sufficient time for a scientific excavation. The results are presented and discussed in this paper.

3. Description of furnace interior
The production at furnace no. 1 at Elkem Rana was shut down in September 96 after a period with very good operation. Metal with around 2 % Si and 59% Cr was produced in the furnace. The chromium source was a mixture of 75% sinter, and 25% lumpy ore, mostly Turkish. Some quartz and bauxite was added to adjust the slag composition. No special arrangements were made prior to the shutdown. The power was shut off from its normal load of 37 MW fifteen minutes after the last tapping. The furnace was then left to cool for about two weeks, before some water was sprayed on the top of the furnace burden to speed the cooling. The coke on the top of the charge was still burning even after 3 weeks cooling.

The CO-content in the off-gas dropped immediately from around 65% to around 30% after the furnace shut down. Parallel to this the N₂ and CO₂ content of the gas increased. This indicates that the CO-producing reactions ceased rapidly when the energy supply to the furnace was shut off. The off-gas temperature increased, from around 500 °C to 700 °C.
during the first 2 hours after the furnace shut down.

The furnace interior was investigated by core drilling in addition to a manual "dig out". The main purpose of the excavation was to determine the physical position and size of different zones in the furnace, and the amount and composition of ore, metal and slag in these zones. Since most of the reduction is assumed to take place below the electrode tip, the dig out focused on this part of the furnace. The main zone in this part of the furnace is the coke bed. It is defined as the part of the furnace below the electrode tip where a surplus of coke is mixed with alloy, liquid slag and partly reduced ore.

The positions and extension of the different zones found during this excavation of furnace no. 1 are shown in Fig.1.

Figure 1: Section through the centre of furnace 1. Idealised sketch based on observations from the excavation.

Most of the burden was a mixture of disintegrated material. It was not possible to distinguish between ore lumps and sinter. Between the electrodes the loose charge reached down to the metal level. The charge was sintered only a few places, mainly along the electrode leg at some length above the electrode tip. A 10-15 cm thick whitish layer composed mainly of Mg and Si oxides was localised 0.5-1 m below the top of the furnace. This was most likely reoxidised and condensed Mg and SiO-gas. The individual grains in the layer were too small to be analysed quantitatively.

Banks composed of slag, coke, ore and metal existed along the furnace walls. This zone is assumed to have been inactive during the normal operation just before shut down, and to be the result of previous periods of operational problems. There was a sharp interface between the banks and the metal below.

Below each electrode was a coke bed. The area beneath electrode B are shown in Fig 2.
The cokebed had the same diameter as the electrode, 1.5 m. The height was 50-80 cm, varying from electrode to electrode. Between the electrode tip and the coke bed was a 5-10 cm cavity. It is not known whether this cavity was present during operation or was caused by contraction during cooling.

At the top of the coke bed was a layer of "dry" coke, about 5 cm thick. Further down was a mixture of coke, slag, metal and partly reduced chromite with some lumps of undissolved quartz. 50-70% of the volume in this zone was coke. The three cokebeds were not connected. A piece from the cokebed is shown in Figure 3.

The metal below the coke beds reached higher than the metal bath in the rest of the furnaces. The interface between the coke bed and the metal below was very sharp as shown in Figure 4.

No ore layer was observed as in the pilot scale dig-outs by Yamagishi. A few slag lenses appeared along the interface.

There were no distinctive slag layer on top of the metal, but lenses of slag were found in the metal bath even below the tap hole level. A similar picture is also described by Ringdalen, from the excavation of furnace no. 2 that was shut down around one hour after last tapping. This indicates that the lack of slag layer in furnace no 1, is one of the characteristics of the process and not a result of the short time since last tapping. The metal below the coke beds was very porous as shown in Fig 5.

There were no unreacted or partially reacted ore lumps or quartz lumps in the metal bath. The metal had dissolved the 0,5 m thick carbon lining at the bottom of the furnace and metal had intruded between the refractory bricks in the bottom of the furnace.
4. Description of materials in the furnace

All zones except the pure metal zone, were mixtures of slag, metal, coke and partly reduced ore in varying quantities. Different metal occurrences are shown in Fig. 6.

The iron reduction had started high in the furnace, especially near the electrodes. The chromite grains then contained iron rich metal prills. Such partly reduced chromite grains were present in all parts of the furnace down to the metal level. Their degree of reduction varied over short distances, even between grains separated by less than one millimetre.

The original charge was a mixture of several ores that in average contained around 40% Cr₂O₃. The chromite spinels in these ores contained between 15 and 25% FeO and between 45 and 59% Cr₂O₃. Partially reduced chromite from the high temperature zones; the coke bed, and the burden close to the electrode contained less FeO than chromites from the colder parts of the furnace. There was little variation in their Cr₂O₃ content.

The bulk slag contained high levels of chromium oxide in the high temperature zones: the coke bed and close to the electrode. The slag in the colder parts of the furnace contained very little chromium oxide. It was probably a mixture of solid gangue minerals and very little chromite had dissolved in these solid phases. The chromium content of the slag in the coke bed is assumed to have varied due to the combined effect of temperature and retention time.

Most of the alloy above the metal bath was found in the coke bed, mainly as coarse metal particles. They had higher chromium content than metal particles in the loose burden. This is shown in Fig. 7. The increase was probably caused by a marked higher temperature in the coke bed than in the charge above. There was no systematic variation in the composition of the metal particles in the coke bed. The observed variation is probably a result of continuous mixing between the coke bed and less reduced charge flowing into the coke bed along its sides. Silicon is only found in the alloy in the lower part of the coke bed and in the metal bath. The metal in the metal bath contained more chromium and carbon and less silicon and iron than the metal from the last tapping. Its composition is shown in Table 1. The lower silicon content is assumed to be a result of the short time since last tapping.
The dig out showed that the interior of this furnace could be divided into four main zones, the loose burden, the coke bed, the metal bath and inactive banks. No distinctive slag layer was found.

The loose burden reaches down to the electrode tip, which is also shown in the pilot scale dig out by Yamagishi et al. When the coke beds are narrow the loose burden may reach down to the metal bath between the electrodes. The average retention time in the loose burden zone is 12-24 hours calculated from the active volume of the furnace. This is defined as the volume of loose burden that was found during the excavation. The burden is a mixture of unreduced or partly reduced chromite spinel grains, gangue minerals partly melted to a slag, fluxes, coke and metal. A small part of the iron reduction, some chromium reduction and no silica reduction takes place in the loose burden. The reduction starts near the top of the furnace.

The reduction of FeCr$_2$O$_4$ in chromite spinels with coke was shown by Katayama and Tokuda and by Hino et al. to start around 1000-1100 °C and to be completed around 1100 - 1200 °C, depending on the chromite composition. Most of the metal in the burden appears as iron rich metal prills in partly reduced chromite spinel grains. Their occurrence show that the temperature in the burden have been greater than 1000 °C.

The relatively high FeO content in many of the chromite grains shows that the FeCr$_2$O$_4$ reduction is not completed in the burden. This is either due to temperatures lower than 1200 °C or to a slow reaction. Chromite grains located close to the electrode are most reduced. They have been exposed to higher temperature than the rest of the burden, but have probably a shorter retention time in the furnace. The charge is expected to have a temperature around 1200 °C when it reaches the electrode tip. The gangue minerals, the glass phase in the
sinter and the actual alloys are solid at this temperature.

The ascending CO-gas will according to Ringdalen bring the burden temperature to around 300 °C. Currents in the charge will not create enough ohmic energy to heat the burden to 1000 °C. The additional energy is assumed to be supplied by circulation of Mg and SiO₂-gas. The MgO and SiO₂ rich condensates found in the charge supports this theory.

The degree of solid state reduction of chromite depends, according to Perry et al and Soykan et al, on the original composition of the chromite, the grain size, the reduction time, the reduction temperature and the composition of the gas phase. The differences between neighbouring grains observed during the “dig-out” may result from variations in these parameters over very short distances. Such great variations were also observed by Wedepohl and Barcza in their dig out of a 48 MVA industrial furnace. This solid state reduction is of minor importance since only a small part of the ore is reduced in the loose burden.

The main part of the reduction takes place in the coke bed. The marked difference in chromium content between the alloy in the burden and in the coke bed reflects a steep temperature gradient between these zones. The coke bed is probably the only place in the furnace where the temperature is so high that the slag is liquid and can dissolve the chromite spinels. This is assumed to be required to reduce the chromite spinels completely. Nearly all slag and metal that is produced must therefore pass through the coke bed. With a production of 9 ton/hour of metal, 5.3 m³/hour of material has to pass through the cokebeds. With three cokebeds each 1.5 m in diameter, 0.8 m high and with 60 volume % of coke, there are in total 1.7 m³ available for slag and metal in the cokebeds. The average retention time in the cokebed is then around 20 minutes. The slag has a temperature of 1600 °C to 1700 °C when it is tapped. The average temperature in the coke bed is believed to be around 100 °C higher than this. The chromite spinels must therefore be completely reduced after around 20 minutes retention time at 1700 °C to 1800 °C to achieve a high chromium yield.

Around 730 Nm³ of CO gas is produced per ton of metal. Most of it evolves in the coke bed since most of the reduction takes place here. If 80% of the gas is formed in the coke beds, the gas velocity at the top of the coke bed is 0.27 m/s at 1700 °C. This flow rate is probably high enough to mix the materials in the coke bed. Together with the variations in original chromite composition, the original grain size and inflow of material along the sides of the coke bed this can explain some of the observed variations.

There is no distinct slag layer above the metal bath. The slag in the coke bed is a mixture of melted gangue minerals, fluxes and MgO and Al₂O₃ liberated from the chromite during the reduction. Its composition varies with the degree of reduction of the ore grains and considerable variations are observed through the coke bed. The dissolution rate of the chromite grains is according to Ringdalen assumed to vary with slag composition. It will therefore be different in different locations of the coke bed. Quartz that is fed to the furnace does not dissolve until the lower part of the cokebed is reached. The silica activity in the slag is therefore expected to increase towards the bottom of the coke bed. There were no significant variations in the silicon content of the investigated samples from the coke bed.

The slag at the top of the coke bed has high chromium content. Such high chromium contents are shown by Ringdalen to occur at high temperatures after short reduction time. The chromite grains at the top of the coke bed have a low FeO content which indicate either high temperature or long reduction time. The temperature in the coke bed is therefore assumed to be highest near its top. The reduction rate and the gas evolution are then highest here.

The cokebeds contained 60 volume % coke, which is assumed to have 75 % fix C, and specific gravity 1. Each of the three coke beds will then contain 53 kmol carbon. The ore is
assumed to be a mixture of 50% MgCr₂O₄, 25% FeCr₂O₄ and 25% MgAl₂O₄. Around 18 kmol carbon is then required to reduce all the ore in each coke bed. The excess of 35 kmol coke is able to reduce 18 kmol SiO₂ and give an alloy with 63% Si. Such silicon contents are not achieved so there is a surplus of coke in the coke bed.

Some, but far from all the coarse metal particles, are believed to initially have started as rims surrounding coke grains. This indicates that the chromium oxides are most easily reduced from the slag at its point of contact with carbon. A few such metal rims are found in the coke bed. They have approximately the same carbon content as the metal particles. This is rather low and indicates carbon activities lower than unity. The activities can not be determined since the temperature is unknown.

If the carbon activity in the metal particles is lower than 1, the dissolution rate of carbon in the alloy is retarded. This can be caused by a rim of solid carbide between the alloy and the coke grain. Pet⁹ found that the reduction rate of chromium oxide in an iron free system below 1575 °C was determined by slow diffusion of carbon through a layer of Cr₃C₂ at the interface between graphite and alloy. No such carbide layer has been observed on the coke grains in the coke bed, but its existence cannot be excluded. The compositions of the few metal rims are of minor importance for the composition of the tapped alloy.

No systematic variation is found in the carbon content of the metal bath. Since the carbon lining in the bottom of the furnace had dissolved in the metal, it must at least occasionally have been unsaturated with carbon.

The silicon content of the alloy in the excavated furnace was too low and varied too little to give any information about the silica reduction.

Conclusions

The charge has a temperature around 1200 °C when it reaches the electrode tip. Some solid state reduction of chromite takes place in the burden, but this is of minor importance.

Most of the reduction takes place in the coke bed. The temperature in this zone is 1700 °C-1800 °C and the average retention time for the materials are around 20 minutes. The materials in the coke bed are continuously mixed and there are great variations over short distances in the degree of reduction of the chromite and the composition of the alloy. There is a surplus of coke in the coke bed. The produced alloy is probably not saturated with carbon. There is no slag bath and the chromite grains dissolve in slag with varying composition.

6. References


