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Upgrading and Utilisation of Residual Iron Oxide Materials for hot metal production

URIOM

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Abstract

For reuse of residual iron oxides from stainless steelmaking within the steelworks itself, two new technologies have been developed. One technology is the inductively heated coke bed reactor, which is coupled either with a cupola furnace or a flash reactor as premelting unit. Further, a new briquetting technology using vegetable binders for briquette utilisation in the EAF has been developed.

The first step of the investigations is a characterisation and selection of suitable residual iron oxide materials to be processed by the new technologies. For both technologies comprehensive process concepts have been developed based on laboratory- and technical scale trials. Further, a software process model has been developed for the coke bed reactor in order to support the development of the process concept. Finally, as a base for assessing economic aspects and metal yield, energy and material balances have been set up and the composition of products has been measured or calculated for both technologies.

Project overview table

CATEGORY OF RESEARCH:	**STEEL**
TECHNICAL GROUP:	**TGS 2**
REFERENCE PERIOD:	**01.07.2007 – 31.12.2010**
GRANT AGREEMENT N°:	**RFSR-CT-2007-00010**
TITLE:	**Upgrading and Utilisation of Residual Iron Oxide Materials for hot metal production**
BENEFICIARIES:	**Co1: VDEh-Betriebsforschungsinstitut GmbH (BFI),** **BEN2: Böhler Edelstahl GmbH & Co KG (BEGMBH),** **BEN3: Centro Sviluppo Materiali S.p.A. (CSM),** **SC: Tribovent Verfahrensentwicklung GmbH (TRIBOV)**
COMMENCEMENT DATE:	**01.07.2007**
COMPLETION DATE:	**31.12.2010**
WORK UNDERTAKEN:	**WP 1** Chemical and physical characterisation of waste iron oxides from the iron and steel industry (All). Thermochemical calculations for selection of a suitable type and amount of slag forming additives concerning the carbothermic reduction of chromium oxide containing residuals (BFI). Selection of suitable residual iron oxides and briquetting mixtures for briquette production (CSM). **WP 2** Characterisation of coke bed reactor melt flow (residence time) and gas permeability (pressure drop) by use of a transparent cold model (BFI). Lab scale investigation of carbothermic chromium oxide reduction kinetics within a representative model slag (BFI). Lab scale investigation of carbothermic zinc oxide reduction kinetics (BEGMBH). Briquetting investigations concerning the use of vegetable binders. Pressure and binder/mixture content are varied and resulting briquettes are characterised in terms of density and mechanical stability (CSM). A technology concept concerning slag melt reduction in a coke bed reactor is developed, which covers geometry of the reactor, suitable coke size and inductor power (BFI, BEGMBH).

WORK UNDERTAKEN:	**WP 3** A concept for melt charging into the inductively heated coke bed reactor is developed (BEGMBH). Lab scale reduction trials (coupled trials) have been carried out with residuals from stainless steelmaking at BEGMBH. A suitable coke feeding and preheating concept for the inductively heated coke bed reactor is selected by evaluation of four different concepts (BEGMBH). A gas reforming unit for treatment of the zinc vapour in the coke bed reactor off gas is designed by thermochemical calculations and finally tested by use of a technical scale unit (BEGMBH). Selection of suitable briquetting procedure with vegetable binders by briquette melting tests in a VIM furnace in Ar atmosphere (CSM). **WP 4** Based on the software FactSage and HSC, a process model for carbothermic reduction of molten stainless steel residues in an inductively heated coke bed reactor is developed and validated for prediction of coke consumption, composition of products and necessary heat supply (BFI). In order to simulate pre melting of stainless steel residues in a cupola furnace as an upstream process for a following coke bed reactor, a cupola process model has been developed based on operational cupola furnace parameters (BFI). Prediction of heat and material balances and chemical composition of products for processing of stainless steel residues in a combined cupola furnace / coke bed reactor process by use of combined process model (BFI). **WP 5** A process concept, process optimisation and productivity analysis for the CSM briquetting process is developed based on operational trials in a technical scale EAF. A process concept for the combined cupola furnace/coke bed reactor process is developed by BFI by modelling various scenarios of operational conditions. BEGMBH has developed an optimised process concept for a two stage flash smelter/coke bed reactor process by taking into account economic and environmental aspects. Finally, by all partners a comparison of all new developed processes has been performed.

MAIN RESULTS:	**Inductively heated coke bed reactor process (BFI, BEGMBH)** Basic design of the inductively heated coke bed reactor - including geometry, coke size, inductor power and induction frequency by use of flow model investigations and laboratory trials. For coke feeding and preheating a vertical feeder concept has been selected and for off gas treatment of the inductively heated coke bed reactor, a steam reforming process is tested successfully (optimum temp.: 800°C). Further, an overall concept for coupling the flash reactor and the inductively heated coke bed reactor (Metal yield 92 % to 96 %) has been developed by BEGMBH. BFI has developed a software based process model for the inductively heated coke bed reactor coupled with a cupola furnace for premelting and pre-reduction of the residues. Electric energy consumption and coke consumption have been determined for economic assessment; heat and material balances for two reference residues have been predicted as well as the chemical compositions. **Briquetting with vegetable binders and briquette utilisation in EAF (CSM)** Selection of iron oxides residuals and vegetable binders to produce suitable briquettes for pilot plant scale tests. Main briquetting process parameters, as forming pressure and humidity content, have been defined. The melting behaviour of different briquettes has been tested, in a VIM furnace and in a 1 ton capacity electric furnace. High iron/alloy yield of > 90 % was achieved. No significant difference of chemical compositions and energy consumption has been found between briquette use and standard EAF melting practice. In order to optimise iron recovery, it is suggested to introduce briquettes together with the second (or/and third) bucket. From economic point of view, the briquette production is favourable (about +130€/t of residue).
FUTURE WORK TO BE UNDERTAKEN:	-
ON SCHEDULE :	**YES**
PROBLEMS ENCOUNTERED:	Tribovent (TRIBOV) has left the project consortium as a beneficiary. The project has been re-arranged, so that BEG has taken over part of the TRIBOV work, and TRIBOV acts as subcontractor of BEG

CORRECTION – ACTIONS *(USE OF A TABLE IS RECOMMENDED)*:	As long as the TRIBOV subcontract had not been clarified and approved by the EC, the project was suspended from 01.05.2008 until 17.10.2008.
PUBLICATIONS – PATENTS	**None**

BUDGET INFORMATION PER BENEFICIARY: Based on overall costs (independently from EU financial contribution)		
BENEFICIARY (incl. coordinator)	***Total amount spent to date (€)***[*]	***Total allowable cost (€) as foreseen in Grant Agreement***
CO1: BFI	416.881	416.083
BEN2: BEGMBH	438.825	719.415
BEN3: CSM	438.301	428.000
SC: TRIBOV (SC of BEGMBH)	76.200	

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[*] Mandatory for Mid-term Reports

1. Final Summary

Within the URIOM reserach project two new technologies for recovery of iron and chromium containing residues from stainless steelmaking are developed and assessed based on modelling results or lab scale and technical scale experiments. Finally, the different processes and process variants are evaluated and compared. The following processes have been investigated:

- **Inductively heated coke bed reactor process**:
  - Variant 1 (BEGMBH): Coupled with a flash smelter as preceding process step for premelting of the oxidic residues.
  - Variant 2 (BFI): Coupled with a cupola furnace as preceding process step for melting and pre-reduction of the oxidic residues.
- **New briquetting technology using vegetable binders (CSM)**. The produced briquettes are directly recycled to the electric arc furnace (EAF).

Both technologies are key processes for economic and environmentally friendly on-site recycling of stainless steelmaking residues with a complete recovery of alloying elements for steelmaking, zinc for non ferrous metal use and a product slag usable for building applications. As follows, the work and results concerning each of the new recycling technologies are summarised according to the different tasks of the research project.

1.1 Data collection and compilation

1.1.1 Chemical / physical characterisation of waste iron oxides (Task 1.1)

All partners carried out an extensive characterisation of various representative waste iron oxides in order to obtain representative data for the further process development.
BFI carried out analyses of a set of representative high chromium EAF dusts and of hot rolling scale from stainless steel production. **CSM** analysed stainless steelmaking residues, which are divided into two groups: hot and cold collected wastes. The first group includes EAF and AOD slags, whereas the second group includes oil containing materials, refractory materials, scale, dust and sludge. The waste materials rich in metals are sludge, scale and dust, whereas EAF and AOD slags and refractory materials are low metal materials. **BEGMBH** carried out a comprehensive study of electric arc furnace dust properties.

Significant variation of the chemical composition of the dust appears especially with regard to Fe_3O_4, Cr_2O_3, ZnO, CaO, MgO and SiO_2. Investigations with a high-temperature heating microscope to characterize the melting behaviour of the dust showed good correlation with the results of the thermochemical melting point calculations. Under oxidizing conditions it was almost impossible to melt any of the samples below a temperature of 1650 °C, even when significant amounts of slag-forming agents (SiO_2) were added. However, under (strong) reducing conditions – as we find them in the InduCarb – the main dust components Fe_3O_4, Cr_2O_3 and ZnO are reduced to the metal and now either the slag formers or the formed alloy mainly determine the melting point.

A grain size analysis revealed that the dust is very fine (57 % < 1 µm; 100 % < 12 µm). and has a low bulk density (0.70 and 0.91 g/cm^3), which indicates that the dust is formed via evaporation and condensation/sublimation processes.

WDX investigations revealed that Fe, Cr and Zn – the main dust components – mainly appear as combined, complex oxides (likely in the form of $(Fe, Zn)O\cdot(Fe, Cr)_2O_3$ compounds). Nevertheless we also find Fe and Cr (as well as Mn and Ni) partially in metallic form, but always surrounded by an oxide layer.

1.1.2 Selection of slag forming additives (Task 1.2)

BFI has carried out initial calculations with FactSage thermochemical software for selection of suitable slag forming additives, which ensure liquid slag and metal phases during chromium oxide reduction. The calculations based on a typical high-Cr EAF slag, from which Cr recovery is a suitable option.

The untreated high-Cr EAF slag is not sufficiently liquid at 1600°C, due to the high fraction of solid compounds. The addition of SiO_2 has been found to increase the proportion of liquid phase in the slag starting at lower temperature. For the typical high-Cr EAF slag with addition of 15 weight-% SiO_2 ($CaO:SiO_2 = 1.1$), a sufficient fraction of liquid slag phase was already obtained at a relatively low temperature of 1400°C. As a main conclusion, for a low viscosity of slag at 1600°C, the mass relation of $CaO:SiO_2$ should be in the range of 1.

1.1.3 Selection of reference waste iron oxides for briquette production (Task 1.3)

In order to produce suitable briquettes for iron recovery, all the materials, composing the briquettes, have been analysed: iron residues, vegetable binders and reducing agent.
Concerning vegetable binders different materials have been taken into consideration: starch, sawdust, flour. It is important that vegetable binders have characteristics of filling agent and absorbent of eventual oily residues. Between them, flour has been selected for CSM briquettes preparation due to its good binder characteristics determined by both starch gelatinisation and gluten formation.
Finally, in order to select the appropriate reducing agent, calculation has been done in order to establish the chemical and energy balance, as a function of the percentage of the constituents of the mixtures, involved in the chemical reactions and energy exchange. FeSi has been used as reducing agent.

Used materials and corresponding quantity were:

- *waste materials*: residual iron oxides in a variable percentage of 80-90 %,
- *binding agent*: expired wheat flour, in a variable percentage of 8-10 %,
- *water*, in a variable percentage of 2-3 %.

Wheat flour has been selected as binding agent because its components, in presence of water, could lied waste materials through two mechanisms: starch gelatinisation and gluten formation. Both mechanisms help stability and compactness of briquettes.

1.2 Development of inductively heated coke bed reactor process

1.2.1 Melt flow investigations (Task 2.1)

For investigations of the melt flow of an inductively heated coke bed reactor, the BFI has constructed and built a full scale physical coke bed model reactor. The dimensions of the reactor model (diameter: 600 mm; height: 1200 mm) have been calculated for an estimated slag input of 300 kg/h.
By use of the model reactor the pressure loss of a coke bed reactor was estimated, the (model) slag flow was visualised and the mean residence time of the slag (as well as dead time, max. tracer concentration) was measured in dependency of different varied parameters. The following parameters have been varied: Gas flow, coke (ball) diameter, slag flow rate, way of slag feeding (point feeding; circumferential feeding) and model slag viscosity.
By the model trials, the pressure loss of a coke bed reactor pilot plant (T=1600°C) was determined. Further, the trials revealed that the mean residence time decreased with increasing slag flow rate and viscosity. The mean residence time was nearly independent from model coke (ball) diameter and gas flow rate, while the mean residence time was increasing when circumferential slag feeding was applied in comparison to point feeding. Circumferential slag feeding to the coke bed reactor is the reference state when a cupola furnace is the preceding process. Point feeding refers to liquid slag charging e. g. from a flash reactor.

1.2.2 Kinetic investigations (Task 2.2)

Based on the results of the melt flow investigations (Task 2.1), kinetic investigations on carbothermic chromium oxide reduction have been performed by **BFI** in a high-temperature laboratory furnace. These investigations are performed for assessment of the chromium oxide reduction performance of the new designed coke bed reactor according to the dimensions of the cold reactor model.
For this purpose a high-chrome EAF stainless steel slag was heated up in the furnace to 1600°C. In order to simulate the slag flow conditions on the coke surface inside a coke bed reactor, a rotating graphite rod was immersed in the slag acting as reductant for chromium oxide. The rotational speed of the graphite rod was varied for simulation of different flow velocities the coke bed reactor. Slag samples have been taken frequently for chemical analysis.
Based on the results of the melt flow investigations within Task 2.1, the chromium oxide reduction capability of the new designed coke bed reactor is estimated to around 4 to 7 kg/Cr_2O_3 per minute depending on the coke size. Taking into account typical input slag flows, between 100 and 300 l/h and a chromium oxide mass percentage of 14 %, for all investigated operational parameters of the coke bed reactor a complete chromium reduction is ensured because the chromium oxide reduction capability in any case is significantly higher than the amount of chromium oxide in the slag.

Within this work package **BEGMBH** investigated the reduction kinetic of zinc and iron in the InduCarb. At the operating temperature of the InduCarb reactor (ca. 1600 °C), ZnO reduction is thermodynamically preferred to that of FeO and Cr_2O_3 , so a fast ZnO reduction kinetic is expected. For investigation of the reduction kinetics, trials in a laboratory high-temperature muffle furnace as well as in a laboratory InduCarb have been performed.
The ZnO reduction was found to be significantly faster (about twice as fast) than the Fe reduction. The reduction kinetic is accelerated by use of smaller coke size. For the InduCarb development the following conclusions are drawn from these investigations: 1) The ZnO reduction is very fast and immediately starts, when the slag gets in contact with the hot coke; 2) The ZnO reduction is accompanied by the sudden formation of a large gas volume (Zn, CO), which emerges directly at the top of the InduCarb (because of the fast reduction kinetics). This has to be considered when charging the InduCarb, since the evolving gases may cause ejections of slag and dust.

1.2.3 Smelting technology (Task 2.4)

To generate basic lay-out data for an InduCarb pilot plant and built a testing facility which aimed to generate data for the InduCarb geometry (diameter, height), the design of the induction coil, the required generator power and design, the required induction frequency, the electric – thermal conversion efficiency and for characterisation of the induction-heating behaviour of different coke types. During an intensive test campaign the described experimental set-up was used to investigate the influence of coke grain size and induction frequency on the heating behaviour of the coke The trials were characterized by a systematic testing procedure where 3 coke grain size classes (10 - 20 mm, 20 - 40 mm, 40 - 60 mm) were systematically tested with three different frequencies (75, 105, 150 kHz). The main findings from the trials are summarized as follows:

- The induction heating of coke allows very fast up-heating velocities of 25 - 45 K/min (max. 55 K/min)
- The conversion efficiency of electric energy to coke heat is about 60 %
- The achievable temperature levels are very high and mainly limited by the refractory materials.
- Since the induction shows a small penetration depth into the coke and the coke itself has a bad thermal conductivity a sharp skin effect is observable, which results in a large temperature gradient between the margin and the centre of the coke bed.
- Lower frequencies and larger grain sizes cause reduced temperature gradients in the coke bed.
- The required induction frequency for heating of coke lies between 75 and 105 kHz.

1.2.4 Construction of the interface for melt charging and –carry-over into the inductively heated coke bed reactor (Task 3.1)

The RecoDust process for pyrometallurgical treatment of steel mill dusts consists of 2 main process steps. The first is flash-melting of steel mill dust under oxidizing conditions in order to evaporate impurities like Pb, alkalis and halogens as well as to produce a pre-melt, containing Zn, Fe, Ni, V, W, Cr, Ca, Si, Al in oxidic form. The second step is a reduction of the pre-melt on the inductively heated coke bed (InduCarb reactor).

Since the pre-melt is very corrosive on the refractory-material due to its high content on dissolved iron oxide and its relatively high temperature (1600 °C), the interface between the Flash Reactor and the InduCarb requires special focus. Further, the interface must prevent slag freezing and should guarantee an optimal melt distribution on the coke bed. There is a need to separate the gas phases from the Flash Reactor and the InduCarb for getting a high purity ZnO from the InduCarb reduction process. So, extensive experimental work has been carried out on a continuously working and gas tight tapping system for the Flash Reactor pre-melt. The only system, which proofed to be successful was an indirectly water cooled tuyere (tapping hole), installed at the bottom of the Flash reactor.

Apart from the tilting concept of the Flash Reactor also an appropriate InduCarb feeding concept had to be found. In total the following concepts were investigated in detail: **Cold feeding, Tundish feeding, Spray feeding and Snorkel feeding.** Although each of the introduced feeding and interface concepts has its particular advantages and disadvantages the spray feeding system seems to fulfil the requirements in the best way and is preferred because it allows dispersing the melt into fine droplets and directly feeding them into the energy rich area of the coke bed cross section. In addition to this the generation of fine droplets also accelerates reduction kinetics.

1.2.5 Coupled trials – Flash reactor – InduCarb (Task 3.2)

The coupled trials of **BEGMBH** had the aim to generate basic data to set-up a rough mass and energy balance for treating EAFD originating from stainless steel production with the RecoDust process. In the coupled trials the Flash Reactor demo-plant was used to smelt the stainless steel mill dust under oxidizing conditions at a temperature of 1600 °C, in order to be able to supply a liquid pre-melt to the InduCarb reactor, which was placed directly underneath the Flash Reactor. Several test runs have been performed for calculation of the mass balance.

In the Flash reactor a significant amount of material carry over by the filter dust was observed (up to 9,5 %), mainly due to partly reduction of ZnO, Zn vaporisation and finally reoxidation. Apart from the zinc also Pb, F and Mo are concentrated in the filter dust.

The reduction of oxides in the InduCarb reactor was almost complete. The product slag is almost free of reduceable metals – the remaining 1,5 % of Cr_2O_3 and 1,2 % of FeO just amount to 3,7 and 0,5 % of the amount contained in the EAFD. Also for Co, Mn, Ni, V, W and Cu, the reduction rate was above 90 %. So, the slag is almost free from heavy metals and thus shows a very good leaching behaviour.

The produced iron alloy is rich in carbon and high in copper, apart from this also the amount of chromium (10,2 %) and manganese (7,6 %) is high. The mixed composition makes it difficult to use the iron alloy as scrap substitute (even for high alloyed steels) although it contains a lot of expensive alloying elements.

The combination of the Flash reactor with the InduCarb is able to process the flue dusts from stainless steelmaking and transfer them from a hazardous waste into valuable products. The tests proofed that both the Flash reactor as well as the InduCarb prototype work fine and that the technical concept is capable to process these dusts.

1.2.6 Coke feeding and pre-heating (Task 3.3)

The coke feeding and pre-heating system, which was developed by **BEGMBH** within this work package, uses the sensible heat from the CO-Zn InduCarb off gas for preheating the coke required as reductant in the InduCarb. In order to avoid Zn-condensation within the pre-heater it is important that the gas is not cooled below 1000 °C in the system. In a first step several coke charging and preheating concepts have been developed and evaluated. A concept with a horizontal coke pushing unit and an inclined coke feeding tube was estimated to fulfil the requirements in the best way.

To check the functionality of the equipment and to gain lay out data for the industrial pilot plant a laboratory scale prototype of this system was built and tested. Investigated parameters were the influence of inclination angle, coke grain size and interface design on the coke distribution in the InduCarb. The best results were achieved without using any interface for distributing the coke in the reactor at an inclination angle of the coke feeding tube of 60 °.
Due to the high required pushing force the feeding unit was redesigned into a vertical feeder with a horizontally moving feeding plate.
Apart from the development and testing of the mechanical feeding unit also a thermal engineering of the pre-heater was performed. The essential parameters and presettings for the thermal engineering were that the CO and Zn vapor containing off-gas enters the pre-heater with a temperature of 1600 °C and can only be cooled down to 906 °C – the boiling point of Zn – in order to avoid condensation of zinc on the coke in the pre-heater. By heat balance calculations the maximum length of the pre-heater was determined to around 0.5 m under these specifications. If the pre-heating zone is longer, the off-gas cools below 900 °C and problems due to zinc condensation would arise.

1.2.7 InduCarb off gas treatment (Task 3.4)

The InduCarb off gas mainly consists of gaseous Zn and CO. The gas leaving the coke preheater with a temperature of around 1000 °C has to be further processed to recover the zinc contained in it. To recover the zinc a reforming concept was selected, by which water is injected into the Zn-CO off gas so that H_2 and ZnO are formed. For this reaction thermochemical equilibrium calculations have been performed in order to predict the amount of the reaction products. With the findings from these thermochemical considerations a laboratory scale testing facility for the treatment of a Zn-CO containing off-gas, as evolving form the InduCarb reactor, was designed, constructed and put into operation by **BEGMBH**.
The aim of the tests performed with the experimental set-up was to determine the optimal reforming temperature in order to maximize the conversion degree of Zn to ZnO. Besides this it was also of interest to which degree the CO was transferred to CO_2 and whether the amount of water added has an influence on the experimental results. The range of parameters investigated covered reforming temperatures from 700 - 1000 °C, Zn-contents in the CO-Zn mixture of 10 - 20 % and steam in an amount of 3 - 9 times the stoichiometric amount of Zn contained in the off-gas.
During the trials, a good conversion efficiency of > 90 % was obtained in the temperature range from 700 to 950 °C, proving that there is a wide process window for the operation of the process in which good are obtained. The amount of water and the zinc content of the off-gas have been found to be of minor importance with respect to the achieved conversion degree. The same is for the amount of CO transferred into CO_2 which always varies between 16 and 18 % of the original CO volume.
Since the reforming simultaneously allows to generate a marketable ZnO product on the one hand and to conserve the chemical energy of the off-gas during the cooling process on the other hand it’s a nearly perfect solution for the process chain Flash Reactor-InduCarb. While the ZnO can be sold as valuable raw material to hydrometallurgical zinc winning, the cold CO and H_2 rich gas from the reforming unit can be perfectly used as fuel in the Flash Reactor. Since the optimal reforming temperature lies around 800 °C also the link with the coke pre-heater, where the off-gas leaves with about 900 °C, is an ideal solution.

1.2.8 Development, Optimisation and validation of process model for carbothermic reduction of molten stainless steel waste in inductively heated coke bed (Task 4.1, 4.2)

In a first step an initial one stage process model for carbothermic reduction of molten stainless steel waste in inductive heated coke bed has been modelled by **BFI** by use of the Fact Sage Software. The model bases on the thermochemical equilibrium calculation in one single reaction volume. Since results of inductive heating trials (BEGMBH) revealed a concentric heat distribution in the inductively heated coke bed with the highest temperature at the outer part near the induction coil and the lowest temperature in the centre of the coke bed, this fact has been taken into account for the model optimisation.
Consequently, an optimised mass and energy balancing model for the coke bed reactor has been developed by use of FactSage and HSC software, which is divided into two main reaction units, representing different reaction temperatures. The temperature in the outer area is defined to 1600°C and in the inner area 1400°C. The distribution of input components and phases between the reaction units is user defined.

The element distribution in the main reaction units is calculated according to different element distribution models, which have been developed by thermochemical equilibrium calculations with reference residual materials by use of the FactSage Software.

1.2.9 Adaptation of cupola process model for Waste oxide melting (Task 4.3)

Based on initial calculations by the SimuSage software and on the existing BFI cupola furnace model, a new element and component distribution model including heat and material balances has been developed by use of the HSC software. This model is able to predict successfully the chemical composition and the amount of the products at given input materials for the cupola furnace process.
By use of this model the specific amount of the different materials streams and the composition of the output streams have been calculated for a standard cupola furnace process. Since the results of the calculation are similar to operational cupola furnace process data, the applicability of the new cupola furnace process model is proven. The adapted cupola furnace model is the basis for the combination with the inductively heated coke bed reactor model.

1.2.10 Combining inductively heated coke bed model with adapted cupola process model (Task 4.4)

For combining the inductively heated coke bed reactor and the cupola furnace, the respective models (Tasks 4.1, 4.2, 4.3) have been linked together by the BFI. The cupola furnace is used for premelting and pre-reduction of the residues (quantity of 15 % of the metallic input). The product slag of the cupola furnace undergoes a final reduction of metal oxides in the coke bed reactor.
For the model calculations, two different high chromium residues have been considered: A spray roasting residue and a high-Cr EAF slag. For processing of both residues overall material balances and the chemical composition of the final product slag and product iron has been calculated. In any case the final slag is (nearly) free from chromium oxide and iron oxide and to a large extent only contains slag formers. The product metal is a cast iron (C and Si: ca. 3 %) with elevated content of chromium (around 2,5 %) and Ni in case of the spray roasting residue (Ni: 1,1 %).

1.2.11 Process concepts and cost optimisation (Task 5.1)

The **BFI** has modelled two different scenarios of operational conditions concerning processing of oxidic residues by a coupled process of cupola furnace and iductively heated coke bed reactor, involving the processing of a spray roasting residue and a high-Cr EAF slag from stainless steelmaking. By comparison of the required energy and consumables demand for processing of both types of residues, an economic assessment for the processing of these very different residues is performed.
For processing of 1 t residue, the coke consumption of the coke bed reactor unit is 2,5x higher for the high-Cr EAF slag compared to the spray roasting residue. Also the thermal energy feed and the electric energy consumption is significantly higher for processing of the EAF slag compared to the spray roasting residue (factor: 1,8). The reason is the higher input slag amount when processing the EAF slag. Generally, the electric energy consumption of the coupled process is high with 2905 kWh respectively 1635 kWh for processing 1 t of the EAF slag respectively spray roasting residue.
The electric power demand of the coke bed reactor unit related to 300 kg input slag per hour, is higher for the spray roasting residue (962 kW) than for the high-Cr EAF slag (677 kW), because the spray roasting residue contains a higher amount of iron- and Ni-oxide, thus the energy demand for oxide reduction increases.

For evaluation of the coupled Flash reactor and InduCarb process for treating stainless steel residuals a mass and energy balance of the whole process chain has been calculated by **BEGMBH** based on the results of the coupled trials as well as on a few theoretical and thermochemical calculations. Since the treatment of the EAF dust is the main aim of the investigated process, the calculated mass and energy balances of Flash reactor and InduCarb reactor are referred to 1 ton of EAF dust.

The main products of the coupled process are 185 kg of (an inert) slag, 455 kg of liquid metal phase and 171 kg of zinc vapour. By addition of 176 kg of water in the gas reforming step, the off-gas is turned from CO and gaseous Zn into 213 kg of (pure) ZnO as well as into 203 Nm^3 of CO and 100 Nm^3 of H_2 (and 42 Nm^3 of CO_2). Since the slag doesn't contain any harmful heavy metals and shows stable elution behaviour it is not a waste product but a raw material for further applications. In the end this means that the coupled Flash reactor – InduCarb process is able to turn the EAFD in to valuable products without generating any harmful side products.
Based on the calculated energy balance including possible energy saving measures, a simplified process flow-sheet for the treatment of stainless steel residuals by a combined Flash reactor / coke bed reactor process is proposed.

1.3 Briquetting with vegetable binders and briquette utilisation in EAF

1.3.1 Briquetting investigations (Task 2.3)

In order to identify principal operational parameters, preliminary briquettes have been produced in a laboratory apparatus. At first, it has been decided to analyse the binding behaviour, therefore in these tests no reducing agent has been added. In view of an industrial use, the most important characteristics of briquettes are: suitable density value (2.7-3.1 g/cm^3, so as to prevent floating on slag surface) and mechanical resistance to handling (without fragmentation or pulverisation).

The main steps for briquette preparation were:

- mixing of the solid components to facilitate the homogenization of the materials,
- water addition to activate the binding effect,
- charging of the mixture into the cylindrical shape mould, selected with specific dimensions (height and diameter),
- mechanical pressing,
- drying and storage of the obtained briquette.

Mechanical pressing reinforced the bonds between the different materials. The supposed mechanism could be lied to the increasing of the surface contact among the units, made by gel surrounded particles, that reinforces mutual entangle of molecules.
In addition, pressure compacts briquette structure, reducing the ways for water entry. This means that the briquette is protected by high humidity content of the environment.
The briquetting procedure has been tested with residual iron oxides. Three different types of iron residuals have been utilised in order to have a suitable quantity of briquettes for pilot plant tests (about 15 for each type).
Briquettes named A were made packing the "blast grinding" residual coming mainly from austenitic steel; B briquettes were packed using the "fine metals" residual from the slag treatment and the C briquettes were build-up using very fine residual "blast grinding" coming mainly from ferritic stainless steel.
Only A and B briquettes have resulted to be sufficiently compact and solid after fall test and long storage. For these reasons, only these type of briquettes have been used in melting tests.

1.3.2 Determination of optimised process parameter for industrial pre-treatment and recovery processes (Task 3.5)

The determination of melting behaviour of the obtained briquettes has been performed during pilot plant tests. The behaviour at the melting of *A* and *B* briquettes have been tested in a VIM furnace (Vacuum Induction Melting - 10 litre crucible) in argon atmosphere. A maximum pressure value of 350 mbar has

been set up during the melting phase in order to hamper bubble formation in the metal bath. Melting temperatures have been measured by both pyrometer and thermocouple.
In case of *A* briquettes, no problems have been observed during the melting test. On the contrary, in case of *B* briquettes a dense black fume has been generated, suddenly at their melting starting. At the end of the trial, carbon residues have been detected on the wall and a pungent odour has been smelt at the opening of the furnace. These phenomena could be lied to the binder reaction in reducing atmosphere. *A* briquettes contained high concentration of metal oxides (in particular Fe and Cr) which oxygen has been used by the wheat flour carbon to produce CO/CO_2. B briquettes contain almost not oxidised metal forms and slag residues (the measured oxygen comes, mainly, from calcium silicate that is the major component of the slag. In this case the oxy-reduction reaction could not take place and the binder pyrolised/gasified.
A new melting test has been performed with *B* briquettes in air atmosphere for better simulation of the EAF conditions. Within this test a high metal yield (> 90 %) has been achieved from the briquettes.

1.3.3 Process concepts and cost optimisation (Task 5.1)

Preparation of a suitable quantity of briquettes for a pre-industrial experimentation, has been carried out. Wheat flour and water content quantity have been optimised during the briquettes production operations. In particular, encountered problems were lied to the water quantity in the final product.
During the preparation of the first group of briquettes, the machine showed operative difficulty. The performed maintenance procedure on the briquettes machine showed presence of a plastic water-flour-iron residual mixture that blocked part of the machine. Moreover, obtained briquettes were weak, wet and with a high tendency of crumbling. The reason has been identified in the too high water content of the utilised iron residual (H_2O > 5 %).
This phase of the project has been fundamental to evaluate the difference between laboratory and pilot plant scale briquettes production. Moreover the importance of a dry environment, for briquettes storage, has been confirmed.

1.3.4 Productivity analysis of EAF briquette utilisation (Task 5.2)

CSM has tested the behaviour at the melting of stainless steel briquettes during pre-industrial trials in a 1 ton capacity furnace. CSM has conducted two different trials, in order to test the modality of briquettes charging in the EAF. The *first test* has been carried out charging briquettes, in a preformed bath of scrap, in continuous charge whereas the *second test* has been carried out charging in batch together a suitable quantity of briquettes and scrap. Chemical analysis of the melted bath showed that the Fe yield is more than 90% in both cases.
Fume analysis (temperature value, CO, NO_2, O_2 and dioxins concentration) has been done during the experimentation. There are some peaks of CO due to the partial oxidation of the carbon within the briquettes.

1.3.5 Comparison of the different technologies of briquette utilisation in EAF (Task 5.3)

During this project CSM has been developed a technology for briquetting iron oxides residues from stainless steelmaking in order to reuse the high iron part (>70 %).
CSM has selected both iron oxides residues and vegetable binders to produce suitable briquettes for pilot plant scale tests. In particular, concerning vegetable binders, wheat flour has been chosen due to its easy availability and lower cost (especially in case of expired flour). Main briquetting process parameters, as forming pressure and humidity content, have been set up and correlate with the briquettes density. Conclusion on the briquettes preparation are:

- excess of water content (higher than 3%) causes weak and crumble briquettes,
- a content of wheat flour higher than 13%, although has the function to absorb excess of iron residual water, results in a lack of briquettes mechanical resistance,
- briquettes, at the exit of the machine, need a storage in aerated and dry location, so as to favour the drying of the binding agent (flour) and the obtainment of a material more resistant to traction and flexion.

Thermal capacity and diffusivity of briquettes have been determined in order to properly design pilot plant test. Melting tests were carried out both in a VIM furnace and in a 1 ton capacity furnace. Results have shown:

- preservation of briquettes characteristics for long time (>3 months) if stored in a dry environment,
- briquettes capability to remain in the interface slag/steel due to their suitable density value,
- high iron/alloy yield (>90%),
- generation of fumes (from the vegetable binder) in case of low oxygen concentration to be used for generating CO/CO_2,
- relation between melting time and chemical composition of iron residues (minor melting time when iron residues are essentially metallic and not oxides).

Comparison of the different briquette technologies utilisation, *from a chemical point of view*, has not shown significant differences between the continuous injection or the charging in batch of briquettes. In fact, in both cases:

- gases compositions, temperature values and dioxins concentration have similar value,
- leaching of produced slags respected Italian Law limits for inert materials,
- iron recovery reached value higher than 90%.

Also energy consumption, compared with the melting of a standard bath done by CSM during previous tests, has not showed a significant increase.
From a process management point of view, in order to optimise iron recovery, it is suggested to introduce briquettes together with the second (or/and third) bucket so to have the better melting conditions. Briquettes are more heavy than the slags so, during the charge of the second bucket, they go directly in the melted bath. In addition, being the second bucket added to melted bath at ambient temperature, this procedure avoid dioxins formation during the pre-heating, normally performed with the first bucket.
A preliminary economical evaluation of the developed process has been done in order to estimate the advantages in the internal reuse of iron residue by means of briquettes preparation and utilisation. The economical evaluation, considering only the briquettes production, seams to be favourable (about +130€ for each ton of used iron residues, table 21). Nevertheless, it is important to define costs lied to additional energy consumption and slags disposal.

1.4 Conclusions - Overall evaluation, Process comparison (Task 5.4)

Inductively heated coke bed reactor process (BFI, BEGMBH)

As a first step of the investigations for development of the inductively heated coke bed reactor process, for selection of suitable residues, data have been collected on physical properties and chemical composition of the residues. Suitable slag forming additives have been selected. A basic design of the inductively heated coke bed reactor - including geometry, coke size, inductor power and induction frequency - has been worked out by BFI and BEGMBH by cold flow model investigations and laboratory trials concerning carbothermic chromium reduction kinetics and inductive heating trials.
Further, a concept and design of the peripheral equipment of the inductively heated coke bed reactor has been developed by BEGMBH. For coke feeding and preheating a vertical feeder concept has been selected. For off gas treatment of the inductively heated coke bed reactor, a steam reforming process of the zinc and CO-containing off gas has been investigated by thermochemical calculations and finally tested in technical scale trials. The optimum temperature for off gas treatment has been determined to 800°C.
BEGMBH has developed an overall concept for coupling the flash reactor and the inductively heated coke bed reactor. The overall concept includes a tapping concept for the flash reactor. Trials have been performed to analyse the composition of product slag and product metal phase and the element distribution (metal yield): For the three valuable metals Cr, Fe and Ni a very high yield of 92 % to 96 % was achieved. Finally, mass and energy balances for the coupled process have been calculated for economic assessment.

BFI has developed a software based process model for the inductively heated coke bed reactor and a coupled process of a cupola furnace for premelting and pre-reduction of the residues and a coke bed reactor for final reduction. By use of the model, heat and material balances for two reference residues have been predicted as well as the chemical composition of the products slag and metal. Independently from the residue, the slag is free of valuable metals and the product metal is a cast iron (high Cr and Si) with elevated content of Cr (and Ni, depending on residue). As a base for economic assessment of the coupled cupola furnace/coke bed reactor process, the electric energy consumption and the coke consumption have been determined.

Briquetting with vegetable binders and briquette utilisation in EAF (CSM)
CSM has selected both iron oxides residuals and vegetable binders to produce suitable briquettes for pilot plant scale tests. Main briquetting process parameters, as forming pressure and humidity content, have been defined. Optimal briquetting parameters are: Water content < 3 %, Content of wheat flour < 13 %. The melting behaviour of different briquettes has been tested, in a VIM furnace and in a 1 ton capacity electric furnace. Results of melting test in VIM furnace have shown that briquettes are durable for long time (>3 months) if stored in a dry environment; Briquettes are capable to remain in the interface slag/steel; High iron/alloy yield of > 90 %.
Comparison of the different briquette utilisation technologies in the pre-industrial test, *from a chemical point of view*, has not shown significant differences between the continuous injection and the batchwise charging of briquettes. Also energy consumption has not significantly increased, compared with standard melting procedure. *From a process management point of view*, in order to optimise iron recovery, it is suggested to introduce briquettes together with the second (or/and third) bucket so to have better melting conditions. A preliminary economical evaluation of the developed process has been done in order to estimate the advantages in the internal reuse of iron residue by means of briquettes preparation and utilisation. From economic point of view, the briquette production is favourable (about +130 €/t of residue).

1.5 Exploitation and impact of the research results

As a result of the investigations concerning the **inductively heated coke bed reactor** process, the industrial applicability of a coupled process (flash reactor/coke bed reactor) is proven by lab scale and technical scale trials. Further, the basic design of the inductively heated coke bed reactor including coke feeding system and off-gas treatment is available. Thus, a following step for dissemination of the new developed process would be the industrial implementation of a pilot or demonstration plant. For the combined process of coke bed reactor and cupola furnace a software based process model is available, which will be used as a tool for supporting industrial implementation of the new recycling process. Potential customers for application of the new process variants are stainless steel producers respectively . foundries or smelters operating a cupola furnace.

Experiments on a **new briquetting technology using vegetable binders and direct recycling in the EAF**, concerning the analysis of the briquettes melting behaviour, conducted during this project, both in VIM furnace and in pilot plant scale, have shown an iron recovery higher than 90 %.
Results of the analysed process, however, need to be confirmed and validated with industrial tests in a EAF, possibly utilising briquettes prepared with different iron residues. In particular, during real scale trials, it is important to analyse energy consumption, quality of slag (also by means of leaching test) and dioxins production along the fume duct.
In following industrial trials, a more detailed economical evaluation of the whole process (from the briquettes production until their complete melting in EAF) could be done so as to verify the convenience of internal iron residues recycling by means the briquettes utilisation.

In the course of the project, no patents have been filed and no publications or conference presentations resulted from the project.

2. List of deliverables

	Deliverable	**Status**
D1.1	Residual iron oxides chemical / physical characteristics	fulfilled
D1.2	Type and amount of slag forming additives for carbothermic reduction process	fulfilled
D1.3	Reference waste iron oxides mixture for briquetting investigations	fulfilled
D2.1	Melt flow characterised by residence time distribution, flooding limit for the packed bed, slag distribution - tundish concept	fulfilled
D2.2	Kinetic data for carbothermic reduction of molten residuals from stainless steelmaking	fulfilled
D2.3	Reference briquettes made of the selected waste, produced with different mixture techniques	fulfilled
D2.4	Basic lay-out for inductively heated coke bed reduction technology	fulfilled
D3.1	Interface solution, hot tested	fulfilled
D3.2	Documented results and interpretation of the trials, Dimensioning data for inductively heated coke bed process	fulfilled
D3.3	Dimensioning data for coke feeding and preheating unit	fulfilled
D3.4	Reformer Unit, safety concept	fulfilled
D3.5	Process parameter for optimised industrial pre-treatment and recovery process	fulfilled
D4.1	Carbothermic reduction model	fulfilled
D4.2	Optimised carbothermic reduction model	fulfilled
D4.3	Adapted cupola furnace-model for calculation of stainless steelmaking residuals processing, taking into account the specific influence of briquetted stainless steelmaking residuals melting in a cupola process	fulfilled
D4.4	Adjusted process model for carbothermic reduction treatment of oxidic stainless steel waste, consisting in a smelting-module (adapted BFI-cupola furnace model) and a carbothermic reduction module	fulfilled
D5.1	Process concepts for processing of stainless steel residuals	fulfilled
D5.2	Productivity data for briquette operation	fulfilled
D5.3	Suitable briquetting technology	fulfilled
D5.4	Process comparison and recommendation	fulfilled
D6.1	Progress reports	fulfilled
D6.2	Midterm Report, Final Report	fulfilled

3. Scientific and technical description of results

3.1 Objectives of the project

Within the URIOM reserach project, concepts of the two following new technologies for recovery of iron and chromium containing residues from stainless steelmaking have been developed: The **inductively heated coke bed reactor process** has been developed by BEGMBH and BFI and a **new briquetting technology using vegetable binders and direct recycling in the EAF,** developed by CSM .
Both technologies are key processes for economic and environmentally friendly on-site recycling of stainless steelmaking residues with a complete recovery of alloying elements for steelmaking, zinc for non ferrous metal use and a product slag usable for building applications.
BEGMBH has developed a concept for an inductively heated coke bed reactor process coupled with a flash smelter as preceding process step for premelting of the oxidic residues. In this process, iron and the valuable alloying components are contained within the produced hot metal, while zinc is contained in a separate zinc oxide product obtained at the inductively heated coke bed reactor.
In addition to this, the BFI worked out a concept of inductively heated coke bed reactor process coupled with a cupola furnace as preceding process step for melting and pre-reduction of the oxidic residues. Here, the main product is hot metal, which contains the valuable alloying components (Cr etc.).
For development of the process concept, BEGMBH has performed extensive lab scale and technical scale experiments, while the work of BFI was focused on liquid flow modelling, carbothermic reduction trials and on development of a software based process model for simulation of the overall process. The basic design of the coke bed reactor unit was carried out in cooperation of BEGMBH and BFI.
Finally, the different processes and process variants are evaluated and compared. The intention of all developed processes is to enable an economic and environmentally friendly way for internal recycling of the stainless steelworks residues.

3.2 Comparison of initially planned activities and work accomplished.

All the work accomplished within the research project has been carried out as initially planned.

3.3 Description of activities and discussion

3.3.1 Data collection and compilation

3.3.1.1 Chemical / physical characterisation of waste iron oxides (Task 1.1)

The main objective of this work was to generate data about the chemical and physical properties of the dust, required for the InduCarb process development and plant lay-out (e.g. theoretical mass- & energy balancing). Especially the dust composition and its variation seriously affect the melting point of the dust as well as of the resulting InduCarb slag. For the correct selection of slag forming additives this information is therefore essential.

BEGMBH carried out a comprehensive study of electric arc furnace dust properties from stainless steel production throughout a period of six months. The performed investigations included chemical analysis, particle size analysis (laser granulometry), bulk density measurements, melting point determinations with a high-temperature heating microscope, elution tests, thermo gravimetric measurements and XRD (X-ray diffraction) analysis. In addition to this also optical SEM (scanning electron microscope) characterizations combined with both EDX (energy dispersive X-ray spectroscopy) and WDX (wavelength dispersive X-ray spectroscopy) phase mappings of selected samples were performed.

The average dust composition calculated from more than 40 samples as well as the detected minimum and maximum concentrations shows **Table 1**:

Table 1: Average dust composition as well as minimum and maximum concentrations

	Fe_3O_4	Cr_2O_3	ZnO	Pb	Al_2O_3	CaO	MgO	SiO_2	C
average [%]	40.35	8.33	24.10	0.14	0.87	8.63	3.00	6.11	1.02
minimum [%]	29.71	2.47	6.72	0.02	0.23	2.77	0.58	2.10	0.11
maximum [%]	62.81	24.99	43.81	2.56	1.78	20.12	6.90	8.64	3.68

	F	Cu	Mn	Co	Mo	Ni	V	W
average [%]	0.26	0.18	3.24	0.12	1.43	0.76	0.14	0.44
minimum [%]	0.06	0.07	0.73	0.02	0.27	0.15	0.04	0.14
maximum [%]	0.90	0.42	13.73	0.54	2.92	5.26	0.78	1.22

Significant variation of the dust composition appears especially with regard to Fe_3O_4, Cr_2O_3, ZnO, CaO, MgO and SiO_2. In order to be able to supply the correct amount of reductant (for Fe_3O_4, Cr_2O_3, ZnO reduction) and to control the slag melting point (CaO, MgO, SiO_2) by suitable flux addition, either a homogenisation of the dust or/and an extensive monitoring of the dust composition is necessary.
Figure 1, which shows the variation of the main slag forming components – CaO, MgO, SiO_2 – in the corresponding phase-system, additionally underlines this fact.

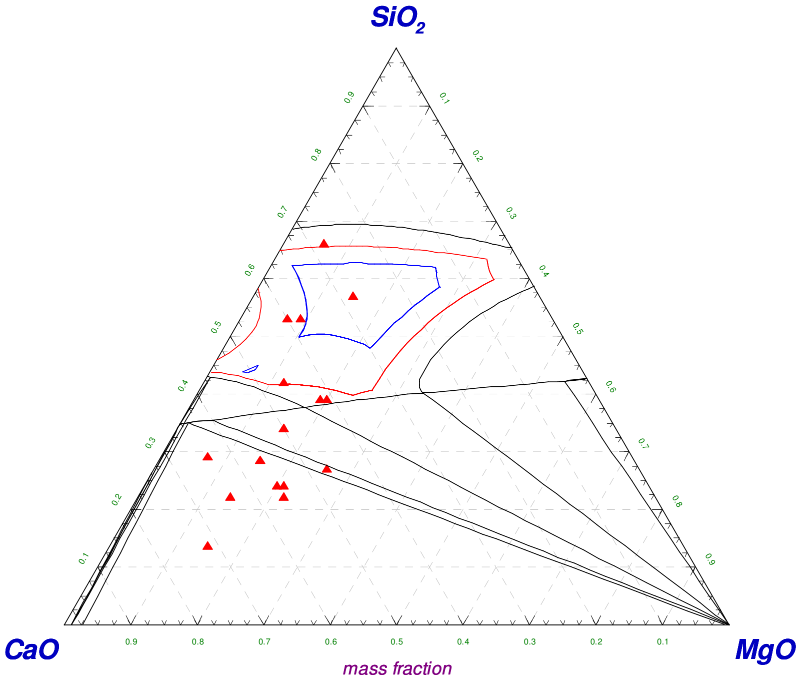
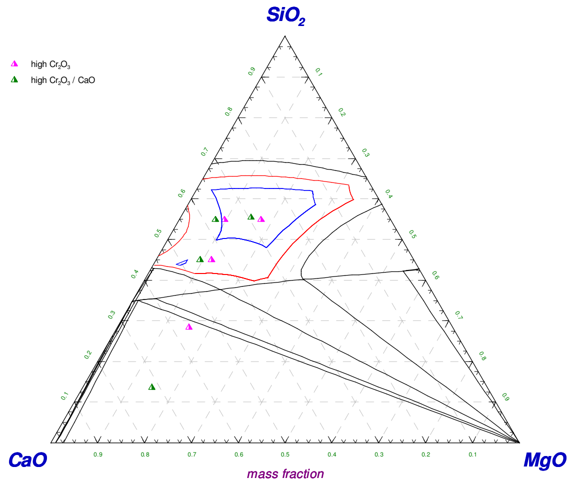


Figure 1: Variation of main slag forming dust components, displayed in the SiO_2-CaO-MgO system

Investigations with a high-temperature heating microscope to characterize the melting behaviour of the dust showed good correlation with the results of the thermochemical melting point calculations, displayed in Figure 1. Under oxidizing conditions it was almost impossible to melt any of the samples below a temperature of 1650 °C (max. temperature of the high-temperature heating microscope), even when significant amounts of slag-forming agents (SiO_2) were added. The reason for this is that the main dust components are not the slag formers, but Fe_3O_4, Cr_2O_3 and ZnO. Since especially the latter ones are characterized by very high melting temperatures, they are responsible for increasing the melting point of the whole mixture. However, under (strong) reducing conditions – as we find them in the InduCarb – Fe_3O_4, Cr_2O_3 and ZnO are reduced to the metal and now either the slag formers or the formed alloy mainly determine the melting point. With suitable flux addition it is possible to adjust the InduCarb slag melting point in a way so that there is no risk of slag-freezing anymore. For two selected dust samples **Figure 2** shows the variation of the dust melting point in dependence of the amount of slag forming additives under reducing conditions. It is obvious that without additions, there is no chance to melt the mixture below a temperature of 1650 °C. With suitable additions it is not the slag anymore that determines the overall melting point but it is also the formed FeCr-alloy.



additions	high Cr_2O_3	high Cr_2O_3/CaO
31.8 % SiO_2, 7.5 % MgO		1454 °C
31.8 % SiO_2		1480 °C
19.8 % SiO_2		1460 °C
-		> 1650 °C
18.3 % SiO_2, 4.4 % MgO	1530 °C	
18.3 % SiO_2	1552 °C	
9.4 % SiO_2	1585 °C	
-	> 1650 °C	

Figure 2: Melting points of 2 selected dust samples with various additions of slag forming components under reducing condition

An also performed grain size analysis revealed that the dust is very fine. The grain size distribution (exemplarily shown for one dust sample in **Figure 3** shows that about 57 % of the dust has a grain size which is smaller than 1 micron, while nearly 100 % are below 12 microns. This low particle size indicates that the dust is formed via evaporation and condensation/sublimation processes. The low bulk density of the dust, which ranges between 0.70 and 0.91 g/cm^3, can also be explained by this fine grain size.

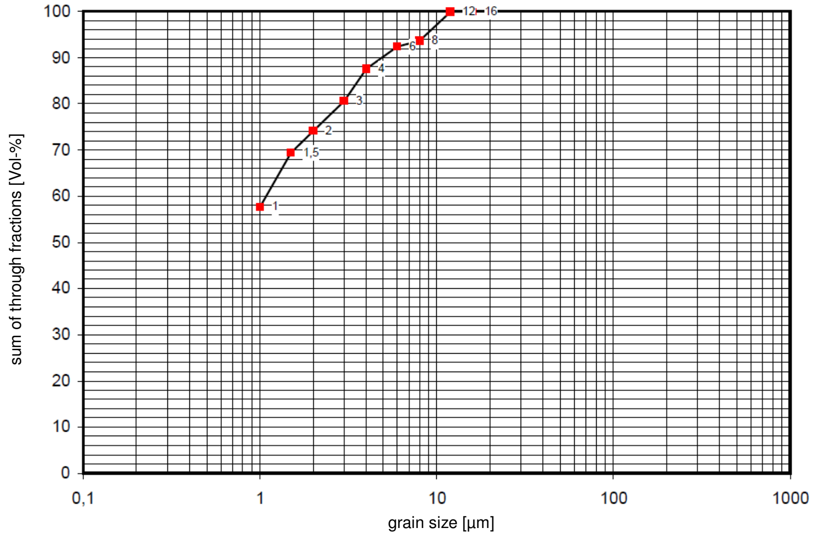


Figure 3: Grain size distribution of EAF-dust

A chemical-morphological dust characterisation was done by SEM, EDX and WDX analysis. The found results were all similar, but – because of its high resolution – the WDX investigations delivered the best results. As an example **Figure 4** shows such a WDX-picture. It is obvious that Fe, Cr and Zn – the main dust components – mainly appear as combined, complex oxides (likely in the form of (Fe, Zn)O·(Fe, Cr)$_2$O$_3$) compounds). Nevertheless we also find Fe and Cr (as well as Mn and Ni) partially in metallic form, but always surrounded by an oxide layer.

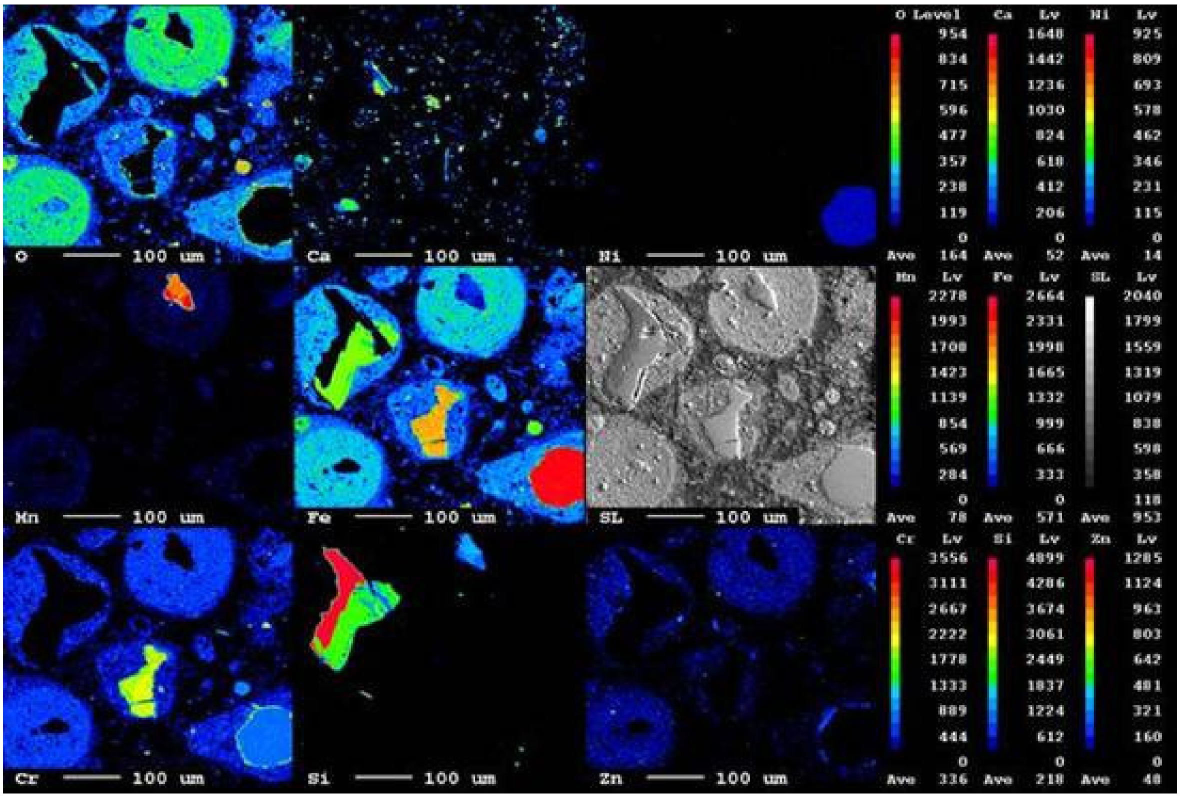


Figure 4: WDX analysis of an EAFD sample

BFI carried out analyses of a set of representative high chromium EAF dusts from steel production, on high chromium EAF slag and on a residue from a spray roasting process, which is used for recovery of spent acids from a pickling line. The chemical composition of the selected high-Cr residues is given in **Table 2**.

Table 2: Chemical composition of selected high-Cr residues (average values)

Component (Mass fraction in %)	SiO_2	Cr_2O_3	Al_2O_3	CaO	MgO	MnO	Fe_{tot}	FeO	Fe_2O_3	ZnO	NiO	TiO_2
high-Cr EAF dust	4	14	1	9	6	4	23	-	-	24	-	< 0,1
high-Cr EAF slag	21	25	5	40	6	2	-	1	-	-	-	-
Spray roasting residue (pickling line)	-	25	-	-	-	-	-	-	65	-	10	-

Different types of residual iron oxides have been analysed by **CSM**. Analysed stainless steelmaking residues are divided into two groups: hot and cold collected wastes. The first group includes EAF and AOD slags, whereas the second group includes oil containing materials, refractory materials, scale, dust and sludge. The analysed waste materials rich in metals are sludge, scale and dust, whereas EAF and AOD slags and refractory materials are low metal materials. The compositions of different selected residual iron oxides are listed in **Table 3**.

Table 3: Composition of different residual iron oxides

	EAF stainless steel "dusts"		**EAF carbon special steel "dusts"**		**AOD and Ladle furnace "sludges" ***		**CC oxy-slab cutting "scale"**		**HRC Hot rolling mill "scale"**		**Slab grinding "dusts"**		**Slab grinding "shavings"**		**Hot rolling "Grit blasting" "dusts"**		**Pickling "sludges"**	
N° samples	**4**		**5**		**17**		**7**		**6**		**2**		**1**		**17**		**3**	
Substance	**Average**	std.dev.	**Average**	std.dev.	**Average**	std.dev.	**Average**	std.dev.	**Average**	std.dev.	**Average**	std.dev.	**Average**	std.dev.	**Average**	std.dev.	**Average**	std.dev.
C	**-**	-	**0,29**	0,29	**2,12**	0,54	**0,22**	0,08	**0,15**	0,06	**2,5**	-	**0,1**	-	**0,65**	0,65	**0,90**	0,28
S	**-**	-	**0,50**	0,50	**0,27**	0,05	**0,02**	0,01	**0,02**	0,01	**0,1**	0,1	**0,048**	-	**0,02**	0,02	**29,10**	10,92
SiO_2	**6,02**	0,96	**1,90**	1,90	**2,36**	0,84	**5,37**	2,19	**1,51**	0,23	**10,4**		**0,1**	-	**0,67**	0,67	**0,39**	0,15
Cr_2O_3	**14,61**	2,53	**1,03**	1,03	**12,52**	2,50	**17,70**	2,65	**3,03**	1,03	**18,6**	6,9	**13,45**	-	**12,41**	12,41	**2,79**	0,92
Al_2O_3	**-**	-	**0,46**	0,46	**1,08**	1,07	**1,90**	0,73	**0,23**	0,05	**-**	-	**0,01**	-	**0,70**	0,70	**<0,010**	-
CaO	**6,61**	0,77	**3,93**	3,93	**12,75**	2,72	**5,72**	2,35	**0,27**	0,08	**-**	-	**0,01**	-	**0,24**	0,24	**25,65**	0,64
MgO	**0,29**	0,25	**1,83**	1,83	**1,44**	0,43	**0,34**	0,28	**<0,010**	0,00	**-**	-	**0,01**	-	**0,05**	0,05	**0,01**	0,00
MnO	**3,17**	0,93	**1,85**	1,85	**2,95**	0,52	**1,55**	0,24	**0,62**	0,16	**0,5**	0,7	**0,06**	-	**1,05**	1,05	**0,18**	0,08
Fe_{tot}	**22,87**	4,66	**21,81**	21,81	**31,16**	5,95	**55,56**	7,96	**74,02**	7,90	**48,6**	40,2	**64,5**	-	**74,87**	74,87	**17,72**	6,15
MoO_3	**1,65**	-	**0,01**	0,01	**0,89**	1,19	**0,23**	0,10	**0,01**	0,00	**0,2**	0,1	**0,01**	-	**0,03**	0,03	**0,02**	0,02
NiO	**1,47**	0,85	**0,15**	0,15	**2,40**	0,79	**6,49**	2,04	**0,28**	0,22	**5,9**	0,8	**8,85**	-	**1,37**	1,37	**1,02**	0,61
ZnO	**25,13**	6,52	**49,70**	49,70	**13,19**	8,07	**0,08**	0,05	**<0,005**	0,00	**<0,100**	-	**<0,010**	-	**0,06**	0,06	**0,06**	0,06
Cl	**-**	-	**1,01**	1,01	**0,11**	0,24	**-**	-	**<0,010**	0,00	**0,5**	-	**<0,010**	-	**-**	-	**0,37**	0,29
CdO	**<0,010**	-	**0,06**	0,06	**0,03**	0,01	**<0,005**	-	**<0,005**	0,00	**-**	-	**<0,010**	-	**<0,002**	-	**<0,005**	-
CuO	**-**	-	**-**	-	**0,16**	0,02	**0,11**	0,02	**0,06**	0,02	**<0,050**	-	**0,15**	-	**0,17**	0,17	**<0,050**	-
TiO_2	**-**	-	**-**	-	**0,08**	0,03	**0,22**	0,05	**0,10**	0,01	**<0,050**	-	**0,2**	-	**0,66**	0,66	**1,93**	1,25
Pb_3O_4	**0,66**	0,33	**1,61**	1,61	**1,33**	1,14	**0,15**	0,03	**-**	-	**<0,100**	-	**<0,010**	-	**-**	-	**0,06**	0,06
sum (1)	**89,00**	19,12	**92,35**	16,57	**93,75**	6,72	**95,67**	5,95	**101,44**	9,13	**101,28**	25,25	**105,97**	-	**92,95**		**80,25**	18,71
Note	(2)		(2)		(2)		(3)		(2)		(2)		(2)		(3)		(3)(4)	
Humidity	**dry (at origin)**		**dry (at origin)**		**53,6**	4,7	**11,43**	3,47	**3,32**	1,05	**<0,100**	**-**	**<0,100**	**-**	**dry (at origin)**		**63**	11,10

Notes

(1) When the sum exceeds 100% means that the substance is not fully oxidised; - (2) Fe_{tot} (as FeO); - (3) Fe_{tot} (as Fe); - (4) S (as SO_4^{-2})

*** sludges generated in the fume treatment line**

3.3.1.2 Selection of slag forming additives (Task 1.2)

VDEh-BFI has carried out initial calculations with FactSage thermochemical software for selection of suitable slag forming additives, which ensure liquid slag and metal phases during chromium oxide reduction. The calculations based on a typical high-Cr EAF slag, from which Cr recovery is a suitable option. In **Table 4**, the chemical composition of the high-Cr EAF slag, taken as basis for the thermochemical calculations, is presented.

Table 4: Chemical composition of high-Cr EAF slag, taken as basis for thermochemical calculations

Component	CaO	SiO_2	MgO	Al_2O_3	MnO	Cr_2O_3	FeO
Mass fraction in %	40	21	6	5	2	25	1

The thermochemical calculations revealed the phase composition of the high-Cr EAF slag in dependence of temperature. At 1600°C the fraction of solid compounds is ca. 50%, this means, the slag is not sufficiently liquid at this temperature. At 1700°C, the slag is supposed to be sufficiently liquid, since the fraction of solid compounds is only about 25% at this temperature.

In order to obtain a sufficiently liquid slag for processing in a coke bed reactor at ca. 1600°C, several slag foaming additives have been taken into account for calculation of the resulting phase composition and the remaining percentage of solid compounds. Especially the addition of SiO_2 has been found to increase the proportion of liquid phase in the slag starting at lower temperature.

Figure 5 shows the main phase fractions of the high-Cr EAF slag with addition of 15 weight-% SiO_2 in dependence of temperature.

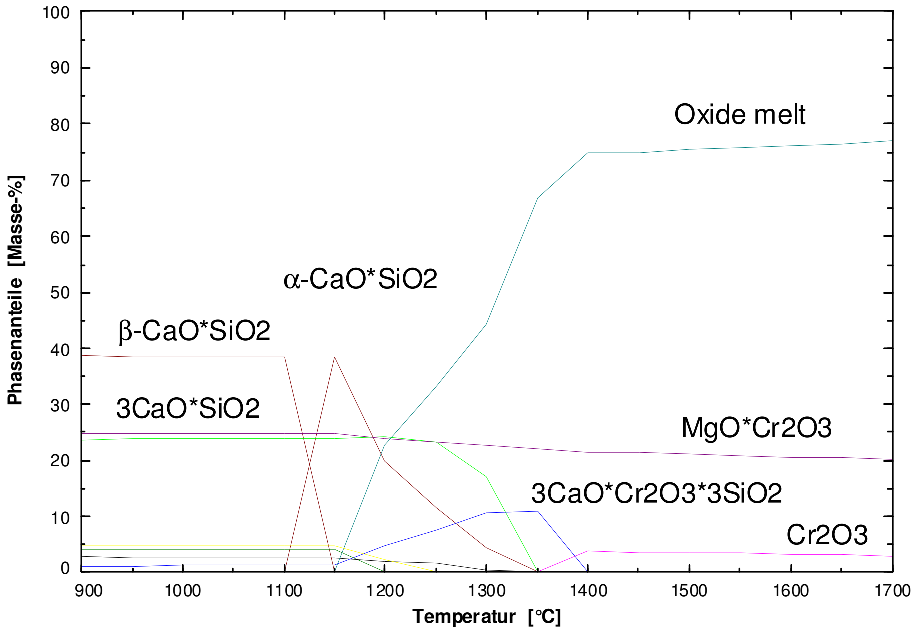


Figure 5: Main phase fractions of the high-Cr EAF slag with addition of 15 weight-% SiO_2.in dependence of temperature

For the typical high-Cr EAF slag with addition of 15 weight-% SiO_2 ($CaO:SiO_2 = 1.1$), a sufficient fraction of liquid slag phase was already obtained at a relatively low temperature of 1400°C. At this temperature, a fraction of solid compounds of about 25 % remained in the slag. This fraction did not change considerably when temperature increases. Main conclusion is that for a low viscosity of slag at 1600°C, the mass relation of $CaO:SiO_2$ should be in the range of 1.

3.3.1.3 Selection of reference waste iron oxides for briquette production (Task 1.3)

The direct use of residual iron oxides (dusts, scales, sludges) in EAF shows a very low yield and the specific electrical consumption increases, due to the following two reasons:

- granulometry: normally scales, dusts and dried sludges are very fine (<10mm) and the surface active tension (relatively to the slag) is high. This fact hinders the materials submerging and the contact with the metal for the solubilisation. Furthermore, the charging is complicate: if introduced together the scrap in the basket, the great part is carried out from the exhauster, if blown trough the lances it can induce the clogging of the pipe,
- oxidation state: often in the residues iron is about totally oxidised; the residues addition in an oxidising process (as the EAF steelmaking) hampers the possibility of the FeO reduction and thus results only in the FeO rising in the slag and any Fe recovery occurs.

The following remarks can be made:

- the iron oxides can be reduced by means of a reducing agents, but these compounds must be neighbours
- the reduction occurs mainly when the oxide remains in a not oxidised atmosphere (i.e. at metal/slag interface)
- a reducing atmosphere can be generate also in a local area.

Therefore, to obtain the optimal iron oxides reduction, the idea is to press them together with a vegetable binders and to prepare briquettes.

In fact, it is very difficult to prepare briquettes utilising only the iron residues because, also in case of applied elevated pressures (2000-4000 kg/cm^2), this not guarantee a not-deformable briquette shape during the transport and feeding into the EAF furnace. To this reason a binder addition, that is able to guarantee the shape maintaining without fines dispersion, is of extreme importance.

The carbon of the binder can reduce the oxide at high temperature, but not the electrical consumption. So, at the briquette components, it is important to add a reducing agent that supply energy during the FeO chemical reduction. Such a briquette can be defined “self reducing and self thermal”.

Advantages of such briquettes are:

- the bulk density is higher than the slag bulk density (2.7 - 3.1 kg/dm^3). So, the briquettes penetrate the slag and float, partially immersed, in the steel, below the slag layer and protected from the air,
- the SiO_2 formation that creates a protective film on the briquette surface slowing down the action of the FeO contained in the slag.

Concerning vegetable binders different materials have been taken into consideration: starch, sawdust, flour. In order to prepare suitable briquettes, it is important that vegetable binders have also characteristics of filling agent and absorbent of eventual oily residues.

Table 5 reports chemical composition of starch and sawdust whereas composition of corn and wheat flour have been summarised in **Table 6**.

Table 5: Chemical composition of starch and sawdust

Parameter	*Starch*	*Sawdust*
C (%)	44	48-50
H (%)	7.3	5-7
O (%)	48.7	42-44
N (%)	-	2-2.5
Ash (%)	-	1-3*

* Ca = 20-25%, K = 2-10%, P = 0.5-1.5%

Table 6: Principal components of corn and wheat flour

	Lipids (%)	Proteins (%)	Carbohydrates (%)
Corn flour (yellow):			
- enriched	3.78	9.34	76.27
- unenriched (degermed)	1.39	5.59	82.75
Wheat flour (white):			
- enriched	0.98	10.33	76.31
- self rising	0.97	9.89	74.22
- type 0	1.0	11.5	76.2

Starch is composed by amylase and amylopectine: both are polymers of glucose ($C_6H_{12}O_6$). Glucose is lied $\alpha(1\rightarrow4)$ in a linear structure that rearranges in helix, in the amylopectine the glucose is lied $\alpha(1\rightarrow6)$ in a macro structure composed by 24-30 units.

Sawdust is dry wood that is composed principally by organic substances (about 84 %). These organic substances are cellulose (i.e. glucose lied $\beta(1\rightarrow4)$ in a macro structure of 1500-1600 units) and lignin.

Flour components are mainly consisting of proteins, lipids and carbohydrates. In particular, more than 82 % of the carbohydrates is starch.

The amount of exothermal reducing agents (like FeSi), to be added to the mixtures, has been defined by means of thermodynamic considerations. Calculation has been done in order to establish the chemical and energy balance, as a function of the percentage of the constituents of the mixtures, involved in the chemical reactions and energy exchange. To carry out the calculations, metals (Fe, Cr, Mn,…), reducible at 1600°C by means of carbon, have been considered (**Figure 6**).

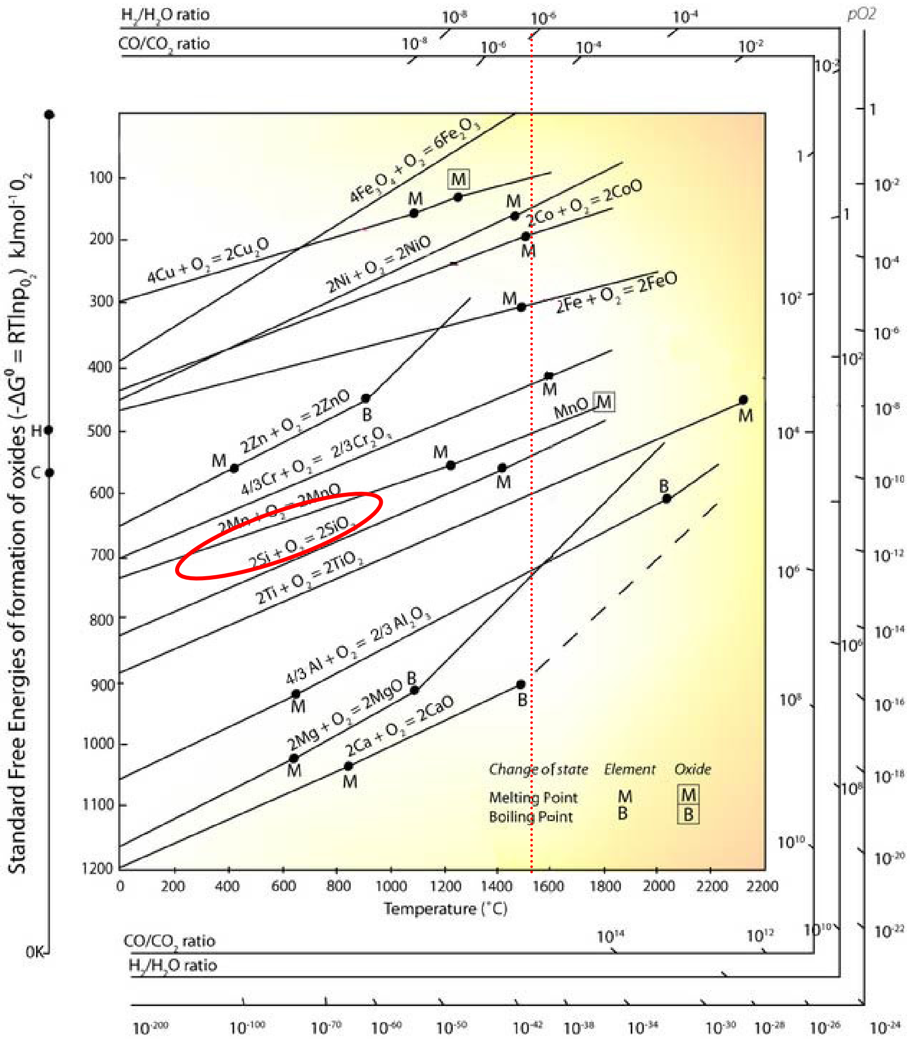


Figure 6: Ellingham diagram

As exothermal reducing agent silicon has been selected.

Taking into consideration the iron oxide, the model used for the calculation is the following:

$$FeO + C \rightarrow Fe + CO \qquad \Delta H_{FeO/C}\ (>0);$$

$$2FeO + Si \rightarrow 2Fe + SiO_2 \qquad \Delta H_{FeO/Si}\ (<0);$$

$$\textit{solid briquette} \Rightarrow \textit{liquid briquette} \qquad \Delta H_{fus}\ (>0);$$

Regarding the overall energy balance, three main conditions for briquettes mixture preparation have been considered on the basis of silicon addition:

1. self reducing briquettes: silicon amount reduces only the oxides residues generated by the reduction of the binding agent carbon,
2. self thermal briquettes: silicon is balanced in order to generate a quantity of energy sufficient to satisfy condition 1 and to melt the briquette,
3. powered briquettes: silicon amount is balanced in order to generate a quantity of energy sufficient to satisfy both conditions 1 and 2 and to have an additional quantity of energy.

The selection and preparation of the different types of briquettes depends on the different plant situation and economical evaluation (i.e. Fe-Si cost):

1. the self-reducing briquettes can used when the productivity of the furnace is generally higher than the production line (the energy is supplied by means of the furnace devices: electrode and lances),
2. the self-thermal briquettes can be used when any lime is necessary to compensate the slag basicity index. In this case the productivity isn't altered,
3. the powered briquettes (exothermal reaction) can be used if it is necessary to add lime into the furnace. Also in this case the productivity isn't altered.

Regarding points 2 and 3, oxides are exploited to supply the additional energy. **Table 7** shows the range of waste material, silicon and binders amounts, for the three conditions calculated, (binder carbon content of about 30%). It results that the silicon amount varies between a minimum of 8 % and a maximum of 33%.

Table 7: Range of compositions of the briquettes after energy balance calculations

	Self reducing briquettes	Self thermal briquette	Powered briquette
Waste (%)	79÷84	64÷74	62÷72
Silicon (%)	6÷13	19÷30	21÷33
Binder (%)	7,9÷8,5	6,4÷7,4	6,2÷7,2

Selected materials for briquettes preparation, and corresponding quantity, were:

- *waste materials*: in a variable percentage of 80-90 %, in addition to residual iron oxides coming from "hot rolling mill scale" and "grit blasting dust"[1], other residues have been selected due to their high iron content (such as scale and fine metals, see **Table 8**),
- *binding agent*: expired wheat flour, in a variable percentage of 8-10 %,
- *Fe-Si*: in a variable percentage of 6-8 %,
- *Water*: in a variable percentage of 2-3 %.

Table 8: Composition of other residuals iron oxides useful for briquettes

	C	S	SiO_2	Cr_2O_3	Al_2O_3	CaO	MgO	MnO	Fe_{tot}	MoO_3	NiO	P_2O_5	Na_2O
Ingot reheating scale	0.01	0.01	0.34	4.01	1.60	0.01	0.60	1.55	89.6	0.21	1.58	0.08	0.35
CC slab surface scale	0.01	0.01	3.99	6.3	8.04	4.02	0.49	0.32	72.3	0.01	1.94	0.10	0.4
Fine metals	0.01	0.01	5.89	2.05	1.12	7.24	0.78	0.41	77.6	0.01	0.09	0.02	0.13

Waste materials: residual iron oxides composition depends from a series of parameters going from the kind of raw materials to the quality of produced steels on the kind of steel refined. Despite of the expected variability in chemical analysis of residuals, during a typical production programme of the steel plant, it is no practicable to analyse each sample of wastes to be used for briquetting. Moreover, it is no practicable a procedure that foreseen to modify the ratios of the briquettes constituents in function of each iron wastes. For this reason, the relative percentage of briquette components has been defined on the basis of the average values.

In particular, to give an idea of the great inhomogeneity of iron residues, samples of grit blasting dust have been considered as example. Depending on the granulometry, there are two types of these residues:

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[1] Dust arising from blasting is produced by the removal of the surface layer of oxides present on the hot strip surface by blasting, or through a mechanical action which does not generate chemical transformations

“granular” or round and “flakes” or fine (**Figure 7**). These types of grit blasting dusts have also different bulk density value: respectively granular dust has the high density value of 4.52 kg/dm^3 and fine dust has a density value in the range of 1.3-2.5 kg/dm^3. Moreover, more than 90 % of granular residues particles have a size between 125 and 250 microns, whereas the fine residues have a maximum size of large particle lower than 125 microns. CSM has collected samples of fine grit blasting dust having dimensions lower than 60 micron (about 50 % of particle size lower than 32 micron) or dimensions lower than 90 micron (about 98 %).

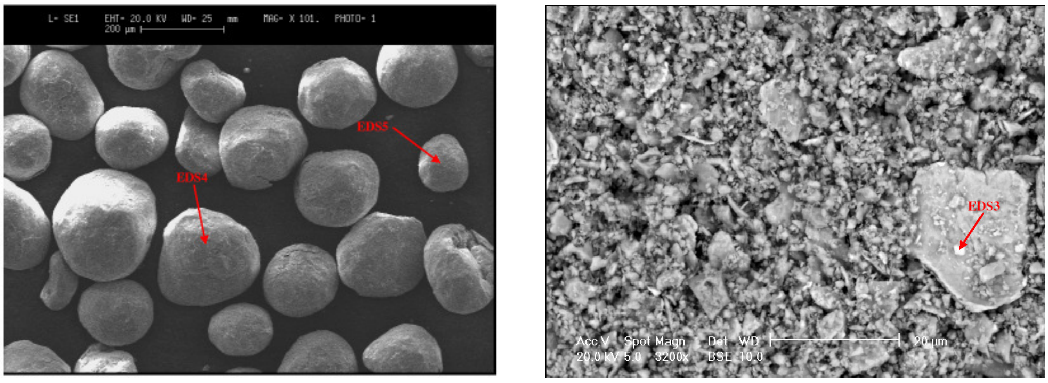

Figure 7: SEM images of granular (left) and fine (right) grit blasting dust

Binding agents: wheat flour has been selected as binding agent because its components, in presence of water, could lied waste materials through two mechanisms (**Annex 1**):

- **starch gelatinisation**: starch is a polysaccharide macromolecule, made by combination of glucose units in macrostructure as amylase and amylopectine, that are not soluble in water on the contrary of glucose. When polysaccharides come in contact with water they are prone to disarrange its original, ordered, structure. Therefore, starch undergoes a transition process, known as gelatinization, during which is produced a mixture of polymers-in-solution, that increases viscosity. The gel units fill the briquette empty spaces, avoiding the loss of finer particles. Also, during gel development and swelling of starch granules, finer particles could be trapped, and so blocked, into the gel units. The gel activation temperature depends on the kind of polysaccharide composition and structure. Wheat starch has the lower temperature of gelatinization respect to other type of starch (T = 52°-54°C);
- **gluten formation**: in the presence of water, glutenin and gliadin (the most abundant proteins of wheat) relax from their tangled state. Water molecules form hydrogen bond with the protein chain favouring their deployment and stretch during the amalgamation: cross-links are formed that stabilise the new structure, the gluten. Gluten is an elastic and plastic network of proteins that has the ability to stretch into a very thin film without tearing, and spring back into its original form.

Wheat flour has been selected for CSM briquettes preparation due to its good binder characteristics determined by both starch gelatinisation and gluten formation. In addition, wheat flour compared to pure starch is cheaper and it is possible to use expired flour, which is not useful anymore for food purposes[2].

Water: water, fundamental for the gelatinisation process and gluten formation, causes also an electrolytic environment in which the exothermic iron oxidation takes place, for example of rolling mill scales:

$$3FeO + 1/2O_2 \rightarrow Fe_3O_4 \qquad \Delta H° = -75 \text{ kcal / kmol}$$

$$2Fe_3O_4 + 1/2O_2 \rightarrow 3Fe_2O_3 \qquad \Delta H° = -60 \text{ kcal / kmol}$$

The resulting increase of temperature favours the starch/gluten swelling that captures metallic particles and blocks them into the briquettes. Obviously, the internal heating is not enough to accomplish the con-

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[2] The use of expired flour could be considered a “turning residue into valuable material” operation.

solidation of briquettes, specially in case of high water content of scales ($H_2O > 4$ %) or humid environment, caused for example by the rain.

3.3.2 Development of inductively heated coke bed reactor process

3.3.2.1 Melt flow investigations (Task 2.1)

The physical model reactor was built by BFI in full scale. **Figure 8** shows a photo of the model test rig.

Figure 8: Physical model test rig

The transparent reactor is made of acrylic resin. The packed bed is simulated by semi-transparent plastic balls. The model coke size can be varied by the use of plastic balls with different diameters (60 mm and 38 mm). The simulated slag can be fed through a central nozzle (point feeding). For the simulation of circumferential feeding a perforated plate, which is blocked in the central part, is inserted above the packed bed to distribute the simulated slag over the whole reactor circumference in order to simulate the phenomena in a cupola furnace. The slag is tapped through an opening at the bottom of the reactor. The model is equipped with two gas inlets on the top of the reactor and three outlets at the lower shaft. So gas and simulated slag flow are co-current. The exhaust flow rate can be varied. The residence time distribution of the simulated slag was measured by tracer injection (constant amount) at the top and determination of the time-dependent tracer concentration at the tap hole with the help of a colorimeter. From the residence time distribution the mean residence time and the dead time are calculated. The equipment was tested with air simulating the gas flow and water as simulated slag. In succeeding trials the viscosity of the simulated slag was varied by addition of saccharose.

With the measurement of the pressure loss in the packed bed the gas permeability is determined. **Figure 9** shows the pressure loss measured in the model for different ball diameters in the packed bed.

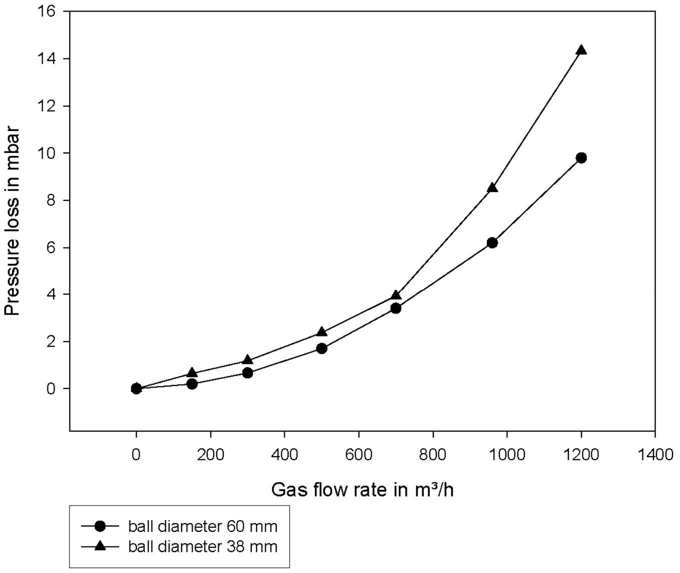


Figure 9: Pressure loss in the packed bed of the model

The results of the model trials are transferred to estimated plant conditions considering the Euler number ($Eu = \Delta p / \rho u^2$). In **Figure 10** the calculated pressure loss depending on the gas flow rate at standard conditions for the industrial plant is given. The pressure loss values for the relevant range of gas flow rate (up to 120 m³/h STP) are similar for both studied coke diameters.

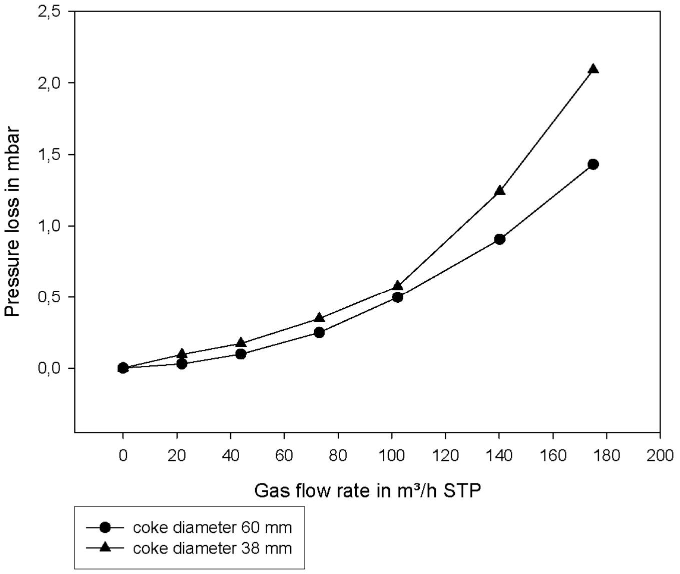


Figure 10: Calculated pressure loss in the packed bed of the pilot plant

In the first trials the slag was simulated by water. The simulated slag flow was visualized by adding dye to the fluid. **Figure 11** shows the packed bed with pure water and coloured water during point feeding in comparison. Obviously the circumferential part of the packed bed is not in contact with the slag during point feeding.

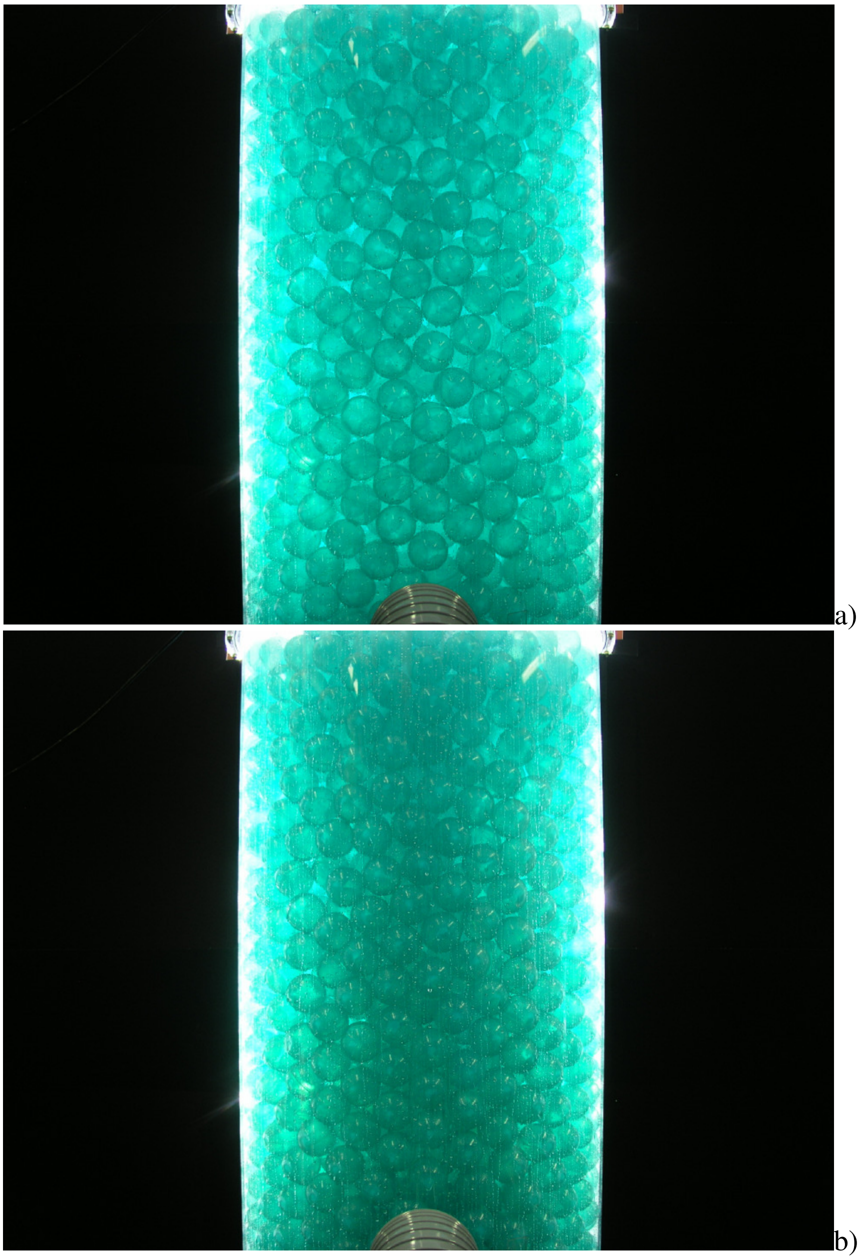


Figure 11: Visualized slag flow in a packed bed of balls with 60 mm diameter during point feeding; slag flow is simulated by
a) pure water
b) coloured water

Figure 12 shows the measured mean residence time depending on simulated slag flow rate for a packed bed of balls with 60 mm diameter and point feeding. The slag was simulated with water. It was assumed that a gas volume of 40 m³ STP is produced per 100 l of slag. A corresponding gas flow rate depending on the simulated slag flow rate was assumed and similar gas velocities in model and plant were realized. The mean residence time is decreasing with increasing slag flow rate, because the mean fluid velocity increases with increasing slag flow rate. For the same reason also the dead time decreases with increasing slag flow rate, see **Figure 13**.

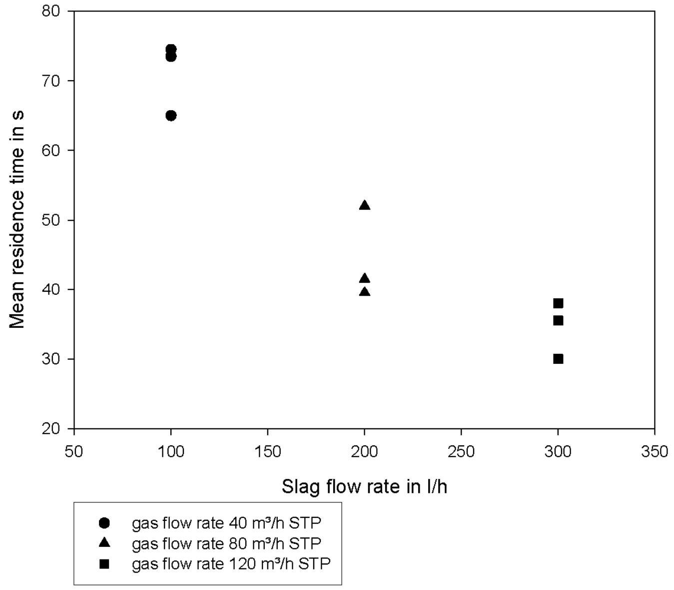


Figure 12: Measured mean residence time depending on liquid flow rate (water) in the physical model for a packed bed of balls with 60 mm diameter and point feeding

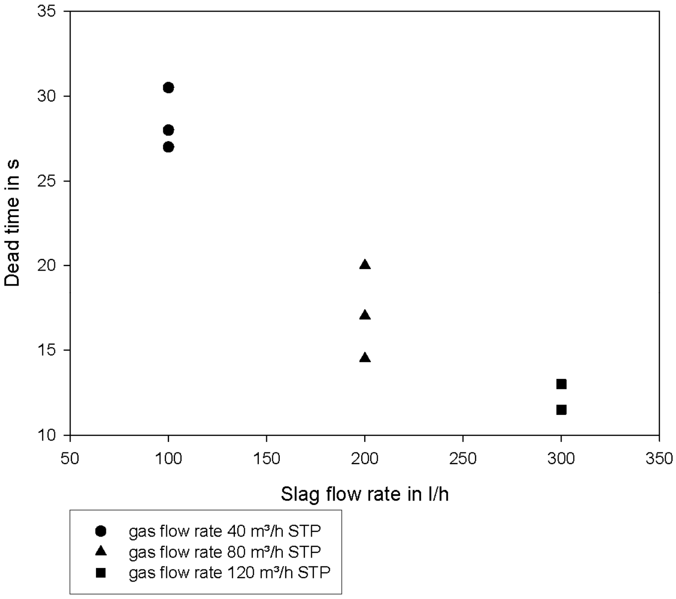


Figure 13: Measured dead time depending on liquid flow rate (water) in the physical model for a packed bed of balls with 60 mm diameter and point feeding

The normalized maximum tracer concentration increases with increasing slag flow rate, because the available time for mixing is reduced with decreasing residence time, see **Figure 14**.

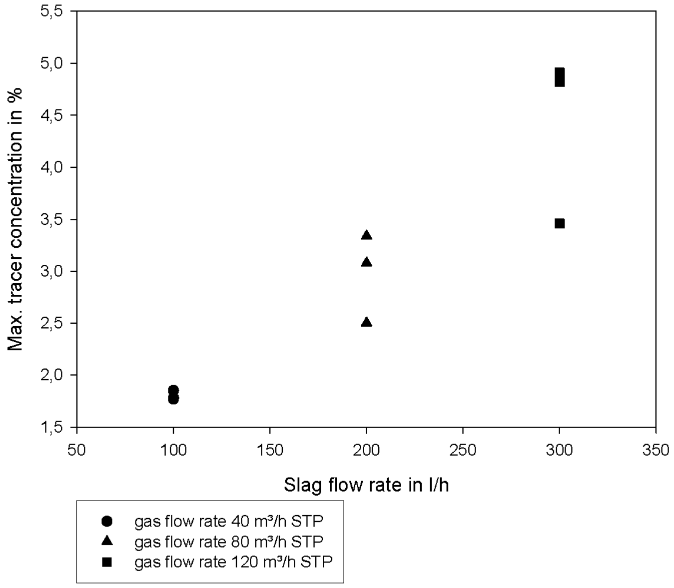


Figure 14: Measured normalized maximum tracer concentration depending on liquid flow rate (water) in the physical model for a packed bed of balls with 60 mm diameter and point feeding

The influence of the gas flow on the residence time, dead time and maximum tracer concentration of the liquid in the packed bed is low. Only at high gas flow rate (120 m³/h) the variation of the mean residence time for different single measurements increases, due to splashing of the liquid, which therefore is entrapped for a longer time in dead volumes of the reactor. Exemplary, **Figure 15** shows the measured residence time for a packed bed of balls with 60 mm diameter and point feeding.

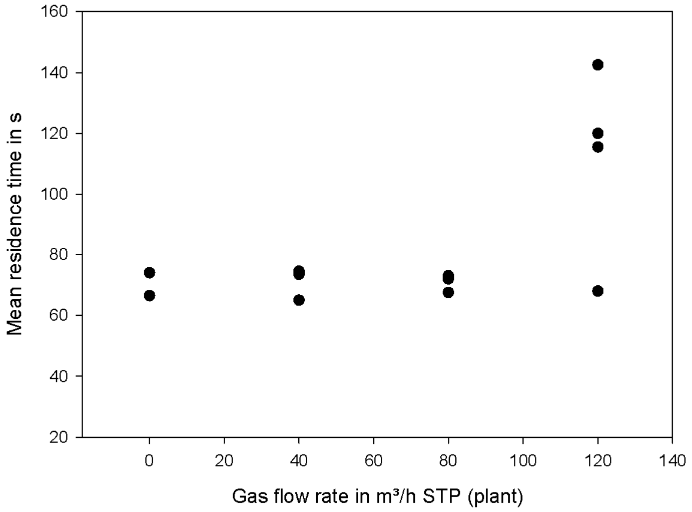


Figure 15: Measured mean residence time depending on gas flow rate in the physical model for a packed bed of balls with 60 mm diameter and point feeding

Figure 16 - **Figure 18** show the measured residence time, dead time and maximum tracer concentration depending on gas flow rate for a packed bed of balls with 38 mm diameter and point feeding. The results are similar to those with a packed bed of balls with 60 mm. So it can be concluded that the influence of the coke diameter on the residence time of the liquid in the packed bed is low.

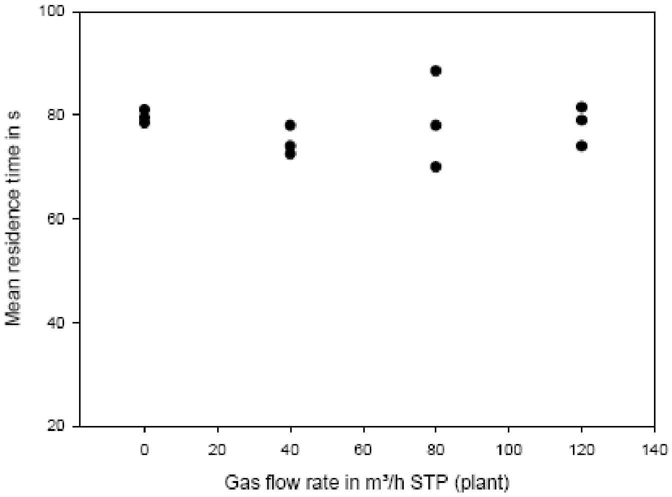


Figure 16: Measured mean residence time depending on gas flow rate in the physical model for a packed bed of balls with 38 mm diameter and point feeding

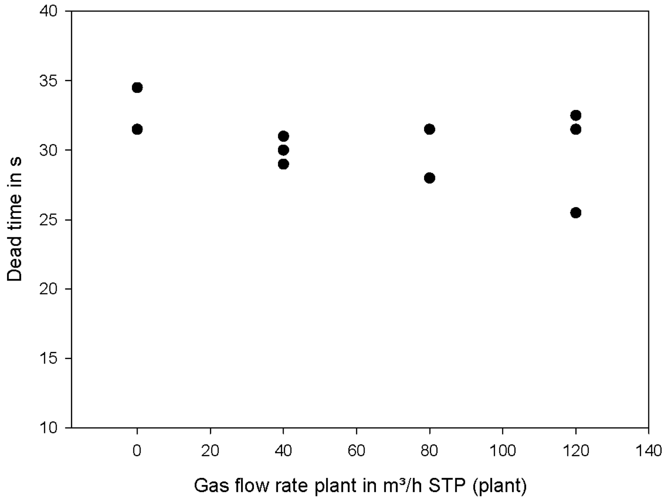


Figure 17: Measured dead time depending on gas flow rate in the physical model for a packed bed of balls with 38 mm diameter and point feeding

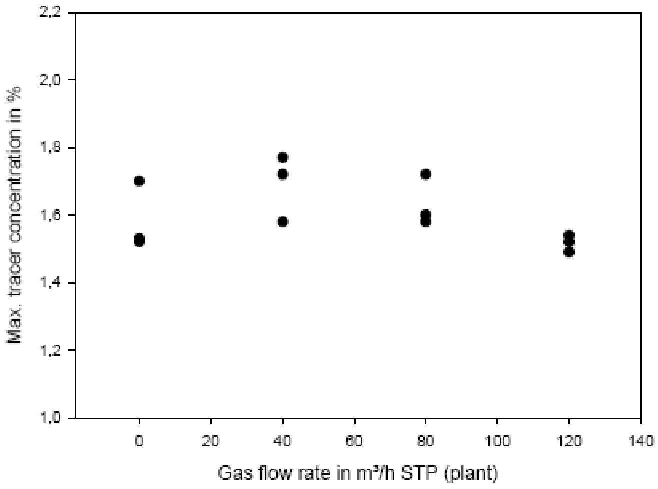


Figure 18: Measured normalized maximum tracer concentration depending on gas flow rate in the physical model for a packed bed of balls with 38 mm diameter and point feeding

Within the range of measured residence times of 30 to 80 s (point feeding; 38 mm balls), the average flow velocity of slag in the coke bed reactor was calculated. For this reason a tortuocity factor of 1.5 was considered. The average flow velocity results from the bed height x 1.5 divided by the mean residence time. The resulting average flow velocity of the slag is in the range of 0.023 to 0.06 m/s depending on the slag flow rate.

For the simulation of circumferential feeding a perforated plate, which is blocked in the central part, was inserted above the packed bed to distribute the simulated slag over the whole reactor circumference in order to simulate the phenomena in a cupola furnace. The blockage was achieved with a plate of 400 mm diameter in the centre of the perforated plate. The residence time of the simulated slag was measured by dye injection at the top and determination of the time-dependent tracer concentration at the tap hole with the help of a colorimeter. In the first trials the slag was simulated by water.

Figure 19 shows the measured mean residence time depending on simulated slag flow rate for a packed bed of balls with 38 mm diameter and point feeding and circumferential feeding in comparison. The slag was simulated with water. No gas flow was assumed. The mean residence time is higher than in the case of point feeding, because the slag is distributed over a larger area of the reactor cross-section the mean fluid velocity decreases.

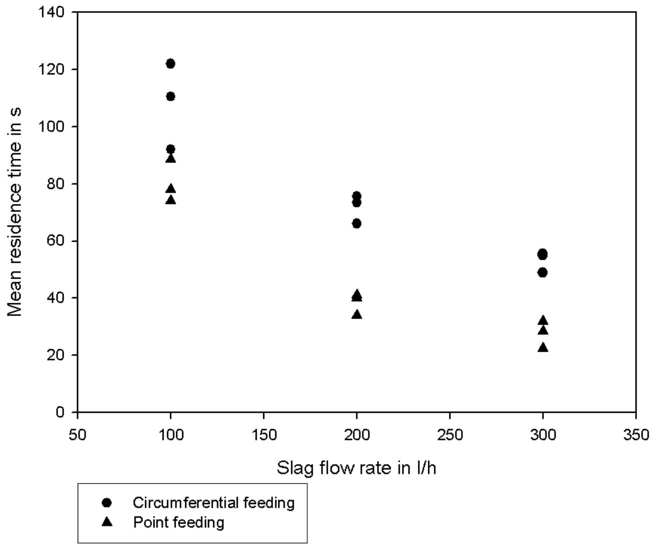


Figure 19: Measured mean residence time depending on liquid flow rate (water) in the physical model for a packed bed of balls with 38 mm diameter for point and circumferential feeding in comparison

For the same reason also the dead time is higher than in the case of point feeding, see **Figure 20**.

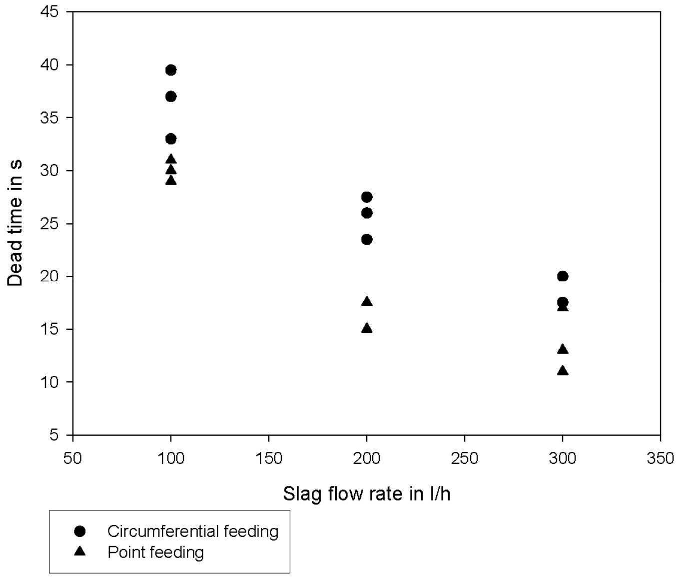


Figure 20: Measured dead time depending on liquid flow rate (water) in the physical model for a packed bed of balls with 38 mm diameter for point and circumferential feeding in comparison

The normalized maximum tracer concentration is lower for the case of circumferential feeding, because the available time for mixing is higher with increasing residence time, see **Figure 21**.

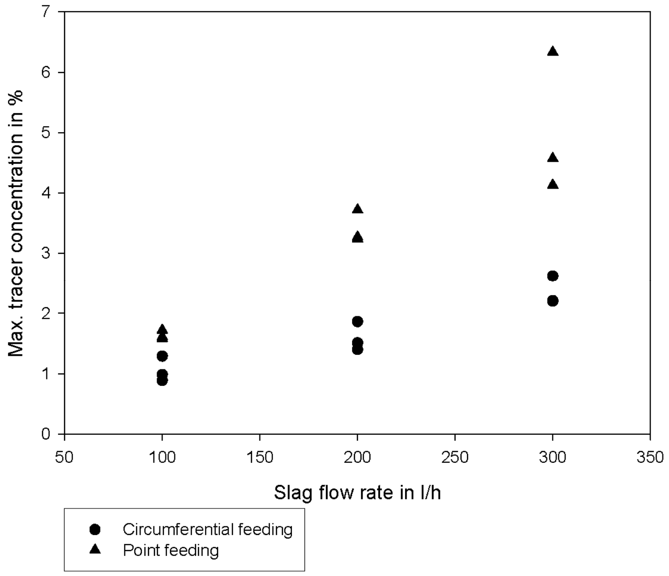


Figure 21: Measured normalized maximum tracer concentration depending on liquid flow rate (water) in the physical model for a packed bed of balls with 38 mm diameter and circumferential feeding

In succeeding trials the viscosity of the simulated slag was varied by addition of saccharose. The simulated slag was fed through a central nozzle (point feeding).

Figure 22 shows the measured mean residence time depending on liquid viscosity for a packed bed of balls with 38 mm diameter and point feeding. The residence time is decreasing rapidly with increasing viscosity of the liquid. The reason could be that splashing is reduced with increasing liquid viscosity. Moreover the density of the liquid increases with increasing saccharose concentration. So the formation of compact rivulets with high flow velocity is promoted.

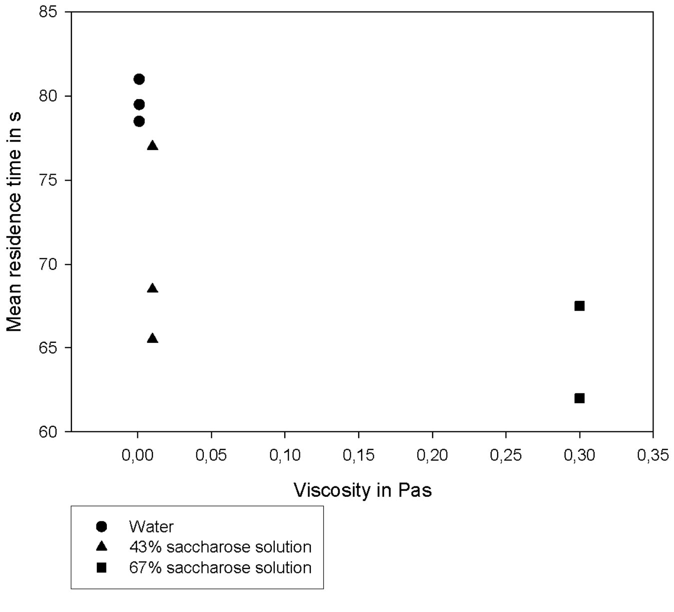


Figure 22: Measured mean residence time depending on liquid viscosity in the physical model for a packed bed of balls with 38 mm diameter and point feeding

For the same reasons the dead time decreases with decreasing liquid viscosity, see **Figure 23**.

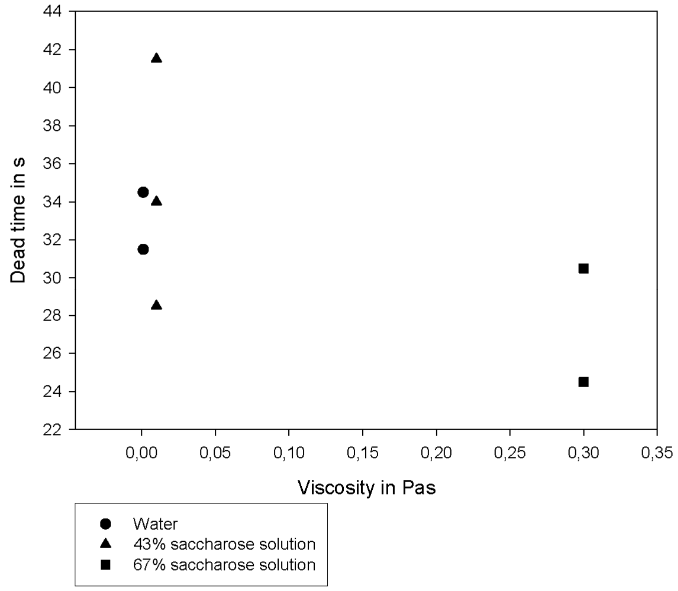


Figure 23: Measured dead time depending on liquid viscosity in the physical model for a packed bed of balls with 38 mm diameter and point feeding

Mixing is impeded by the viscous behaviour of the fluid. Therefore the maximum tracer outlet concentration is increasing with increasing liquid viscosity, see **Figure 24**.

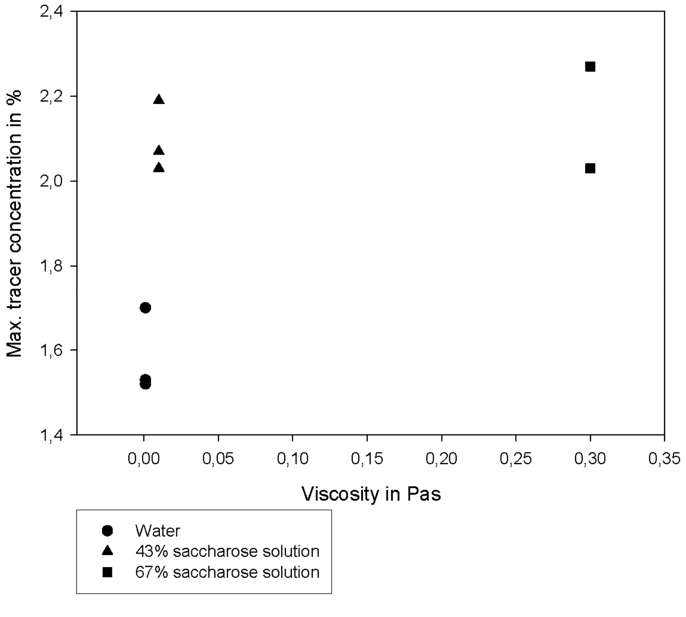


Figure 24: Measured normalized maximum tracer concentration depending on liquid viscosity in the physical model for a packed bed of balls with 38 mm diameter and point feeding

3.3.2.2 Kinetic investigations (Task 2.2)

BEGMBH

Within this work package **BEG** investigated the reduction kinetic of zinc and – for the purpose of comparison – iron in the InduCarb. From the thermodynamic point of view zinc is at lower temperatures (below ~ 1200 °C) more ignoble than iron while at higher temperatures this turns and zinc then becomes the more noble metal (as the Richardson-Ellingham-Diagramm in **Figure 25** indicates). At temperatures around 1600 °C, where the InduCarb reactor is operating, ZnO reduction is thermodynamically preferred to that of FeO (and of course to that of Cr_2O_3). This is also why a faster reduction kinetic for the ZnO reduction can be expected. The fact that the product of the reduction reaction

$$ZnO(s) + C(s) \Rightarrow Zn(g) + CO(g)$$

is vaporous zinc that immediately leaves the place of reaction – the product is continuously withdrawn – should further accelerate the kinetic of this reaction.

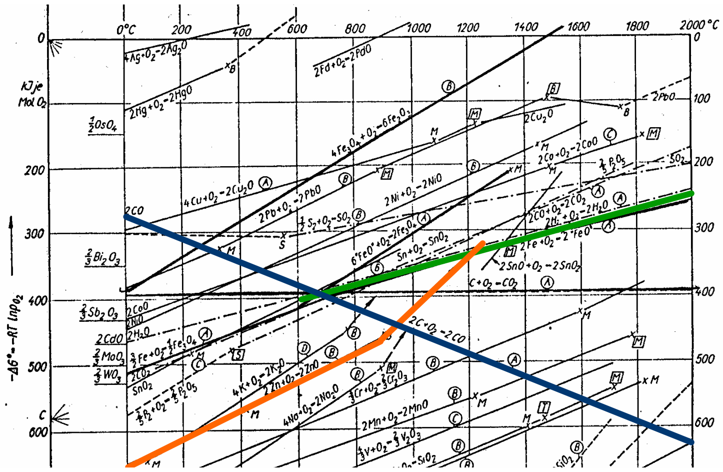


Figure 25: Detail of the Richardson-Ellingham-Diagramm

BEG's experimental investigations covered trials in a laboratory high-temperature muffle furnace as well as in a laboratory InduCarb reactor – shown in **Figure 26**. In case of the muffle furnace water granulated, pre-molten dust (in a laboratory EAF) was charged together with coke in a hot clay graphite crucible and then put back into the furnace for a specific reaction time. After this time the crucible content was cooled in water and the slag was then analyzed for its Fe and Zn content. Although this experimental set-up in general worked very well, there were some limitations. One major was that due to temperature losses during the charging of the material it took some time until the final reaction temperature was reached. Because of that it was difficult to generate repeatable data for reaction times shorter than 5 minutes. Here the trials in the laboratory InduCarb had the advantage that the reactions immediately started. Unfortunately there was no chance in the laboratory InduCarb for an exact temperature measurement. Also a periodic sampling/quick cooling was not possible, so the reaction progress could only be visually observed and the slag was analyzed after the trials, when the crucible was fully cooled.

Figure 26: Laboratory InduCarb (left) and muffle furnace (right), used for kinetic investigations

The diagrams in **Figure 27** show that – as expected – the ZnO reduction is significantly faster (about twice as fast) than the Fe reduction. Since a smaller coke grain size offers a larger reaction surface, the reduction kinetic can be accelerated if a smaller coke is chosen, as the right diagram in Figure 27 shows. For the InduCarb development the following conclusions can be drawn from these investigations:

1) the ZnO reduction is very fast and immediately starts, when the slag gets in contact with the hot coke
2) especially the ZnO reduction is accompanied by the sudden formation of a large volume of gaseous phases (Zn, CO), which emerge directly at the top of the InduCarb (because of the fast reduction kinetics). This has to be considered when charging the InduCarb, since the evolving gases may cause ejections of slag and dust.

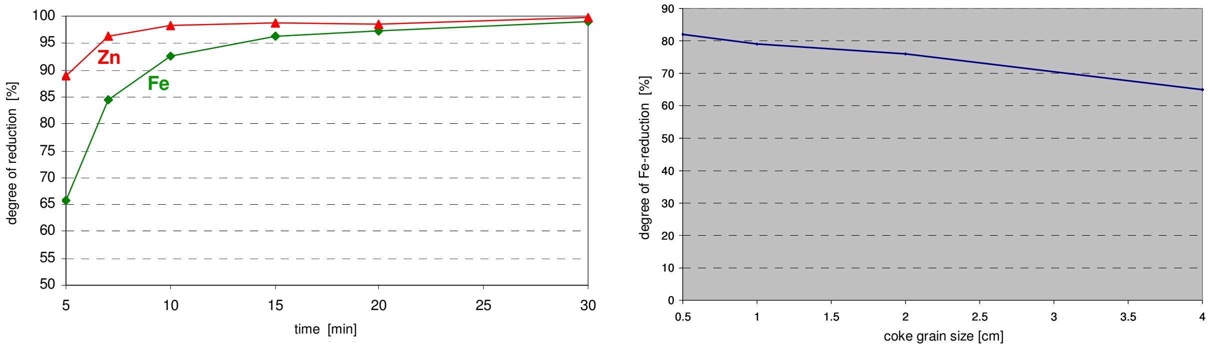


Figure 27: Zn and Fe reduction degree in dependence of time (T = 1600 °C) – left, influence of coke grain size on the Fe reduction degree (T = 1600 °C, t = 5 min) – right

BFI

Based on the present results of the melt flow investigations (Task 2.1), kinetic investigations on carbothermic chromium oxide reduction have been performed by BFI in a high-temperature laboratory furnace. These investigations are performed for assessment of the chromium oxide reduction performance of the new designed coke bed reactor according to the dimensions of the cold reactor model (Task 2.1).

For this purpose a chromium containing EAF stainless steel slag (approx. 9,6 % Cr, 14 % chromium oxide) was heated up in the furnace to 1600°C. The amount of the slag is approx. 900 g. In order to simulate the slag flow conditions on the coke surface inside a coke bed reactor, a rotating graphite rod (diameter: 2 cm) was immersed in the slag acting as reductant for chromium oxide. The rotational speed of the graphite rod was varied in two steps (30 1/min; 60 1/min). These speeds correspond to circumferential velocities of 0,031 respectively 0,063 m/s, which is exactly the range of flow velocities calculated from the coke bed reactor cold model in Task 2.1. Slag samples for chemical analysis (especially chromium) have been taken in 10-minutes intervals during a total time of 1 hour. **Figure 28** shows the sampling procedure at the high-temperature furnace. In **Figure 29** the outer part of the rotating graphite rod during a carbothermic chromium oxide reduction trial is illustrated.

Figure 28: Sampling procedure at the high-temperature furnace

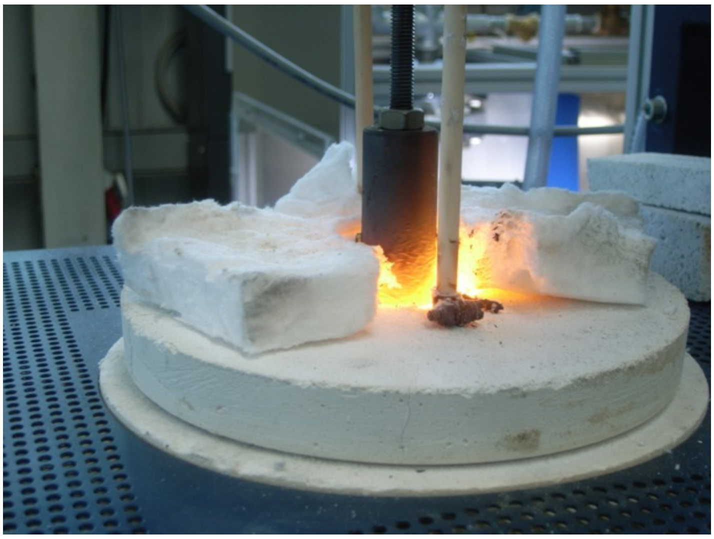


Figure 29: Outer part of the rotating graphite rod during a carbothermic chromium oxide reduction trial

The resulting chromium content of slag as a function of time for a rotational speed of the graphite rod of 30 1/min at 1600°C is shown in **Figure 30**. The chromium content decreases with the time, which indicates the carbothermic reduction of chromium oxide.

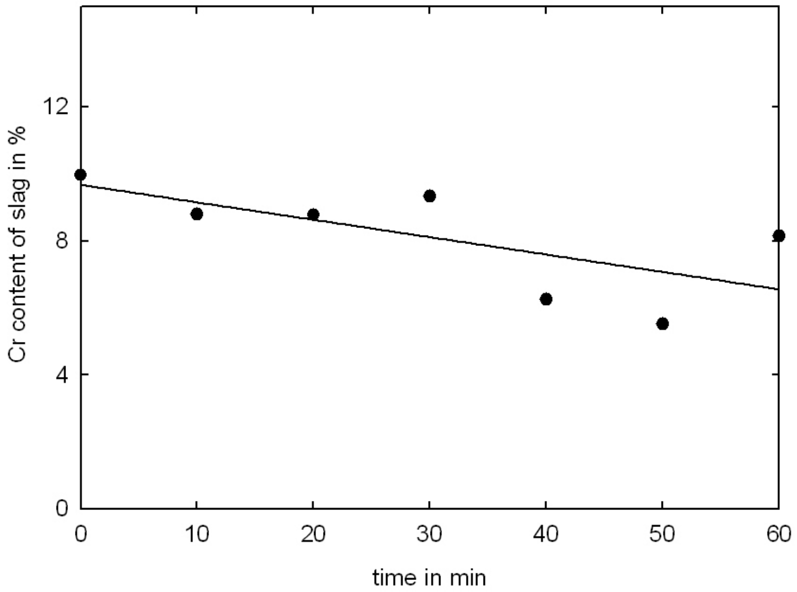


Figure 30: Chromium content of slag as a function of time for a rotational speed of the graphite rod of 30 1/min at 1600°C

The mass percentage of chromium in the slag decreases from 9,6 % to 6,6 % within 60 minutes (as calculated by linear regression). Supposing that Cr in the slag is present only as Cr_2O_3, the chromium oxide content in the slag decreases from 14,1 % to 9,6 %. In consideration of the immersed surface area of the graphite rod and the slag mass, the mass of reduced chromium oxide related to the graphite (carbon) surface is calculated to 0,128 kg Cr_2O_3/m^2*min. Increased rotational speed of the graphite rod (60 1/min) did not lead to increased chromium reduction, so these results are not reported here. Based on the results of the melt flow investigations within Task 2.1 (point – and circumferential feeding of slag; variation of model coke size, variation of viscosity by use of water and saccharose solution as model slag) as follows, the chromium oxide reduction capability of the new designed coke bed reactor is estimated.

The (ideal) inner surface area of the coke bed reactor is calculated based on the assumption that the model coke balls are arranged in a cubic closest packing. The space filling degree of this packing is 74 %. Based on this, the total mass of potentially reduced chromium oxide per time is calculated. The ideal inner surface of the reactor filled with 38 mm balls (coke size) amounts to 39,6 m², while the surface with 60 mm balls is 25,1 m². The resulting mass of chromium oxide, which is potentially reduced by the coke/carbon, is 5,1 kg/min (38 mm coke size) respectively 3,2 kg/min (60 mm coke size).

For an input slag flow into the coke bed reactor of 100 l/h and 300 l/h (slag density: 3.000 kg/m³) and a chromium oxide mass percentage of 14 %, the chromium oxide mass flow is 0,7 kg/min respectively 2,1 kg/min. This means, for the low slag flow (100 l/h) the relation factor of the reduction capability to the contained chromium oxide is 7,2 (38 mm coke size) respectively 4,6 for 60 mm coke size. The same relation factor for the high slag flow (300 l/h) is 2,4 (38 mm coke size) respectively 1,5 for 60 mm coke size.

As calculated from the measured mean residence time of the slag in the coke bed reactor, the average filling degree of the free reactor volume (cubic closest packing) is in the range between 2 % (min.) and 6 % (max.). For low residence times (mainly for point feeding) also the filling degree is low, while the filling degree is high for higher residence times (mainly for circumferential feeding). The influence of the slag input flow on the average filling degree of the reactor is low, since for increasing slag flow, the residence time decreases.

For the mentioned design parameters of the coke bed reactor and input slag flows (and slag composition) the results of the kinetic investigations indicate, that a complete chromium reduction is achieved because the chromium oxide reduction capability in any case is higher (at least by factor 1,5) than the amount of chromium oxide in the slag. The results also show, that the input slag flow rate into the coke bed reactor is limited to about 300 l/h (respectively 900 kg/h). With higher slag flow rate, complete chromium reduction may not be achieved.

It is to be pointed out that the kinetic investigations have been performed with relatively low reactive graphite as carbon source in the laboratory furnace. For industrial application, more reactive coke will be used as reductant, which may result in a higher reduction capability. On the other hand, reduction capability may decrease when only part of the carbon surface in the reactor has slag contact, and thus is available for chromium oxide reduction. The slag contact area was not measured during the investigations.

3.3.2.3 Smelting technology (Task 2.4)

To generate basic lay-out data for an InduCarb pilot plant and build a testing facility which aimed to generate data

- for the InduCarb geometry (diameter, height)
- for the design of the induction coil,
- to the required generator power and design
- to the required induction frequency
- to the electric – thermal conversion efficiency and
- to characterize the induction-heating behaviour of different coke types.

In addition to this the design of the pilot plant also allowed (with small modifications) its use for the coupled trials of Flash-Reactor and InduCarb. However, since the coupled trials were intended as demo-trials without a systematic variation of parameters, the design just allowed a very limited number of trials, which had to be stopped when major damages at the testing facility were observable (especially at the refractory lining, which was not optimized for a longer testing campaign). A schematic illustration and a photo of the testing facility is shown in **Figure 31** and **Figure 32**. Its main components are:

- the high frequency generator
- the induction coil with the associated capacitors and cooling devices
- a heat sink, placed in the coke bed and called “cooling finger”
- the mechanical construction holding the refractory lining and
- the instrumentation.

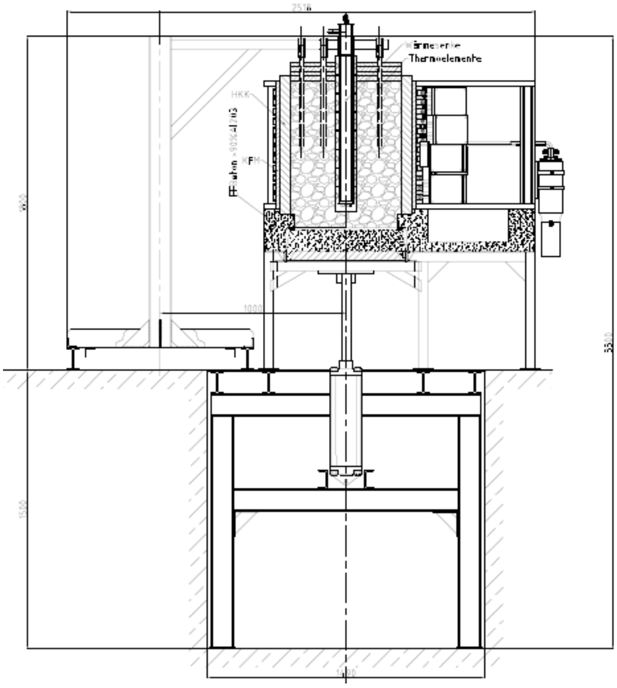


Figure 31: Structural design of the testing facility

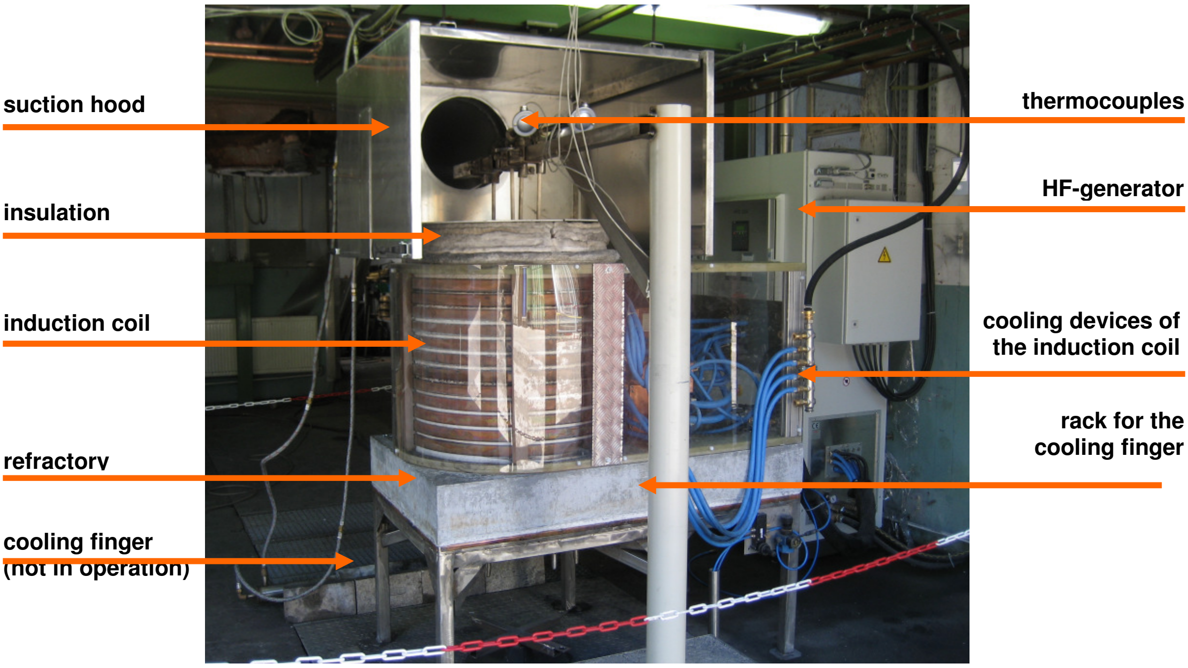


Figure 32: Testing facility

As follows, an overview of the plant components is given and their main characteristics are described.

The **high frequency generator** (type: Eldec HFG200) is electronically power regulated and offers a maximum power output of 200 kW (at a main capacity of 240 kVA), which is infinitely variable between 2 and 100 percent. The connection between the generator and the directly compensated induction coil is realized via water cooled, flexible power cables. Operating frequency of the generator can be changed within a range of 50 to 200 kHz by adjusting the capacities at the induction coil.

The **framework** bearing the InduCarb-reactor was manufactured from austenitic stainless steel which was partially plated with copper. This was necessary in order to avoid an inductive heating of the metal parts by stray fields originating from the coil. To protect the metal construction against the heat, generated in the coke bed, the InduCarb-reactor itself was placed upon a refractory block, lying on the framework (see **Figure 33**). In order to be able to quickly remove (hot) coke from the InduCarb reactor, a pneumatically operating bottom discharge unit was integrated into the construction. The InduCarb-reactor itself had an inner diameter of 600 mm and a height of 800 mm, which corresponds to a volume of about 225 litres. Depending on charging level, type, humidity and grain size of coke this volume is equal to 85 and 150 kg of coke respectively. To minimize heat losses during the tests it was tried to insulate the reactor as good as possible. This was realized by the use of bubble alumina for the InduCarb cylinder and additional fibre blankets for the insulation between the InduCarb cylinder and the induction coil.

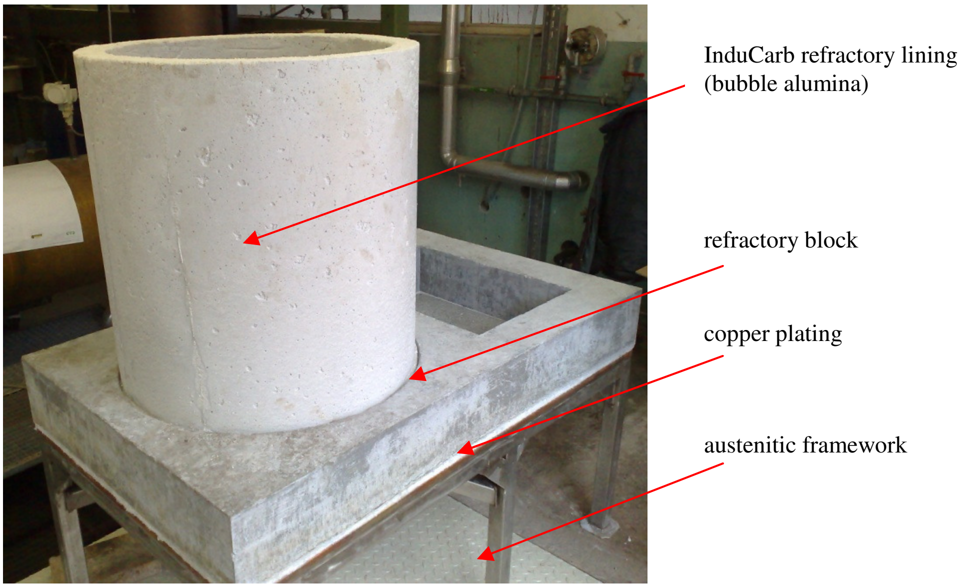


Figure 33: Mechanical framework with refractory block and InduCarb refractory-lining

The **induction coil** (see **Figure 34**) was manufactured from hollow, water cooled, rectangular (40 x 15 mm) copper profiles. From the 12 turns of the whole coil always 4 turns were connected in parallel and these 3 parallel linked groups of turns were then connected in series (the coil had 3 x 4 turns). The coil itself was supported by a fibreglass construction.

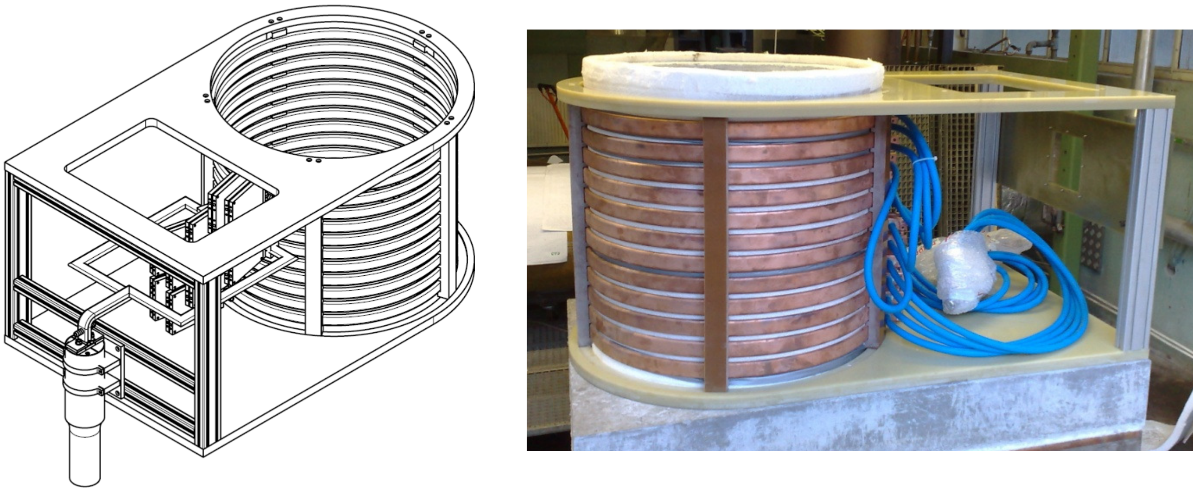


Figure 34: Construction of the induction coil

A cross section of the **heat sink** is illustrated in Figure 31 – it is essentially a water cooled austenitic stainless steel cylinder that is equipped with a protective refractory layer (outer diameter: 116 mm) and placed axially in the centre of the coke bed. The idea behind the cooling finger is to simulate an energy consuming process (e.g. smelting of dust, energy for reduction of Fe, Ni, Cr, . . .) within the coke bed. This in turn gives an indication which temperature gradients can be expected during a continuous dust-processing and whether or to which extent energy is transferred from the outside margin of the coke bed (where it is expected to mainly be induced) to the centre. Depending on coke bed temperature the heat sink is able to remove between 10 and 15 kWh of energy.

In addition to these key components also a **cooling water system**, the **instrumentation** and the **PLC** for a central data logging and monitoring were installed.

During an intensive test campaign the described experimental set-up was used to investigate the influence of coke grain size and induction frequency on the heating behaviour of the coke The trials were characterized by a systematic testing procedure where 3 coke grain size classes (10 - 20 mm, 20 - 40 mm, 40 - 60 mm) were systematically tested with three different frequencies (75, 105, 150 kHz). As an example for the testing procedure **Figure 35** shows the data of a trial with a frequency of 150 kHz and a medium coke grain size that was performed as follows:

1. preheating of coke and thermocouples with 20 % of power
2. first heating period to target temperature 1600 °C with 70 % of power
3. temperature equalisation period with 25 % of power
4. power cut off – cooling phase (with T_3 target temperature 1400 °C)
5. heating period with 90 % of power (with T_3 target temperature 1600 °C)
   Step 4 and 5 were then repeated with heating powers of 80, 70, 50 and finally again 90 % of power. Temperature T_3 was always oscillating between 1600 and 1400 °C during heating and cooling periods respectively.
6. power cut off and cooling down to room temperature

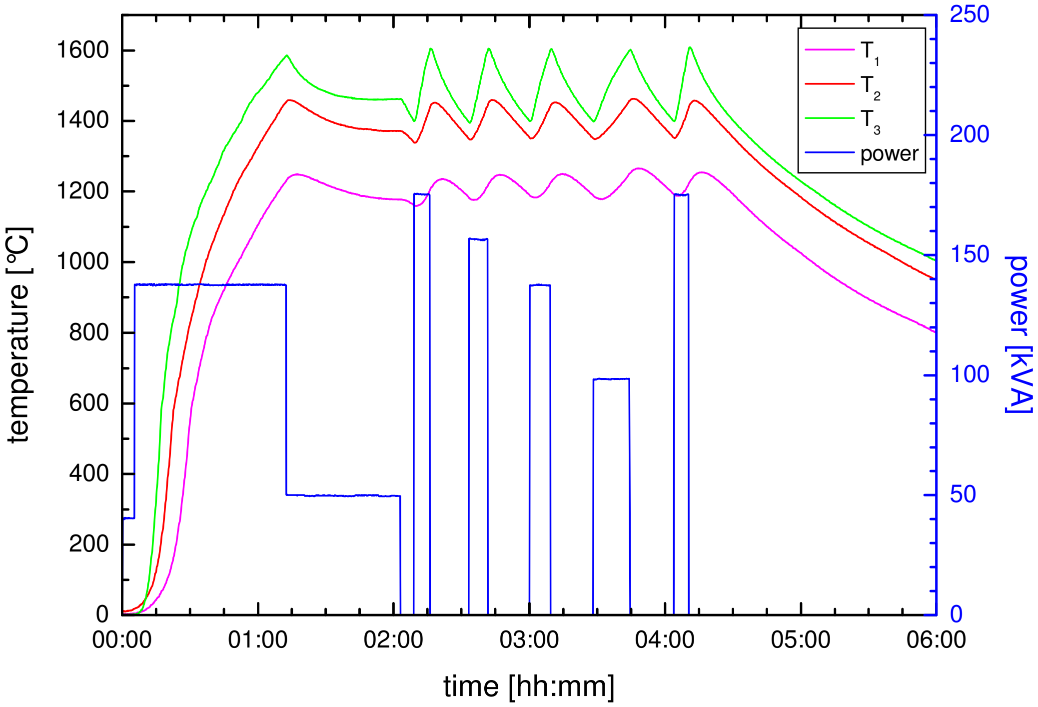


Figure 35: Time-temperature graph of trial nr. 5

The 3 temperature graphs of the diagram show coke-bed temperatures at three different, horizontal positions. As **Figure 36** displays, T_1 is placed close to the heat sink with a distance of 21 cm from the outside margin of the coke bed. T_2 and T_3 are placed in a distance of 15 and 7.5 cm respectively from the margin.

All thermocouples normally have the same depth of immersion into the coke bed and are positioned at the transition of the upper to the middle third of the induction coil – more exactly between the 4th and 5th turn of the coil (which has 12 turns). In addition to the temperature graphs, the diagram also shows the generator power on a second y-axis.

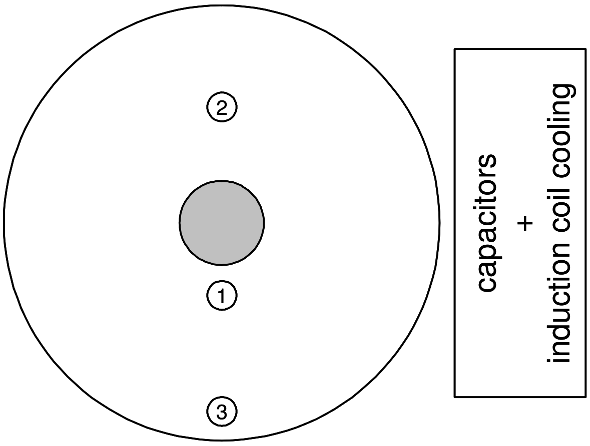


Figure 36: Schematic diagram to the positioning of the thermocouples in trials 1 – 11

The experiments turned out that one of the most critical issues concerning an industrial InduCarb reactor is a homogenous temperature distribution in the coke bed. Unfortunately the trials clearly showed that even with moderate heat removal from the coke bed centre through the heat sink (10 - 15 kW) major horizontal temperature gradients appear. **Table 9** shows the measured temperature gradients from several trials with different coke types and induction frequencies at the beginning (min.) and at the end (max.) of the last heating period of each trial. The corresponding diagrams to the data in Table 9 are displayed in **Figure 37** and **Figure 38**. The graphs show the following tendencies:

- Independent of frequency the smallest coke grain size class 1 shows considerably larger temperature differences than coke grain size class 2 and 3, which just marginally differ.
- During heating periods temperature differences between the outer (T_3) and inner thermocouple (T_1) of about 350 °C are typical. Considering that the distance between T_1 and T_3 is just 15 cm, these extremely high gradients indicate a very inhomogeneous temperature distribution.
- The temperature difference between T_2 and T_1 is noticeably higher than those between T_2 and T_3.
- Different frequencies have only small influence on the measured temperature gradients. Nevertheless there is a slight tendency that with lower frequency also the temperature gradients become smaller. A possible and logical explanation for this is an increased penetration depth of induction with lower frequency.
- During cooling periods all temperature differences clearly decrease, especially the difference between T_3 and T_2 is minimized to around 30 – 40 °C.

Table 9: Temperature differences before and after the last heating period of each trial

	coke 1		**coke 2**		**coke 3**	
	min.	max.	min.	max.	min.	max.
150 kHz						
$T_2 - T_1$	245	283	160	215	144	153
$T_3 - T_2$	145	306	47	164	33	178
$T_3 - T_1$	390	589	207	379	177	331
105 kHz						
$T_2 - T_1$	-	-	163	226	139	212
$T_3 - T_2$	-	-	35	141	39	137
$T_3 - T_1$	-	-	198	367	178	349
75 kHz						
$T_2 - T_1$	245	292	152	214	123	188
$T_3 - T_2$	161	310	29	114	44	122
$T_3 - T_1$	406	602	181	328	167	310

Although frequency seems to have only a small influence on the measured temperature differences, there is strong effect regarding the coupling behaviour. In all trials with a frequency of 75 kHz the maximum power output of the generator was limited to 70 % since above this value an overvoltage alarm occurred. The same problem occurred during the group 1 trials when the small coke grain size class (coke type 1) was tested with a frequency of 105 kHz. This is also the reason why coke grain size class 1 was not tested with a frequency of 105 kHz. The other coke grain size classes (2 + 3) didn't show any problems at 105 kHz – the same is for a frequency of 150 kHz where even coke grain size class 1 worked well.

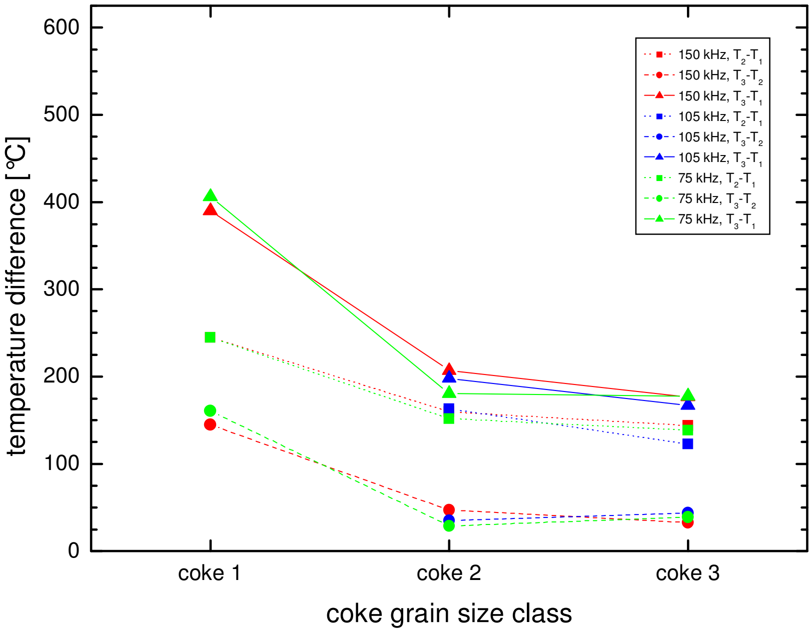


Figure 37: Temperature differences after cooling period

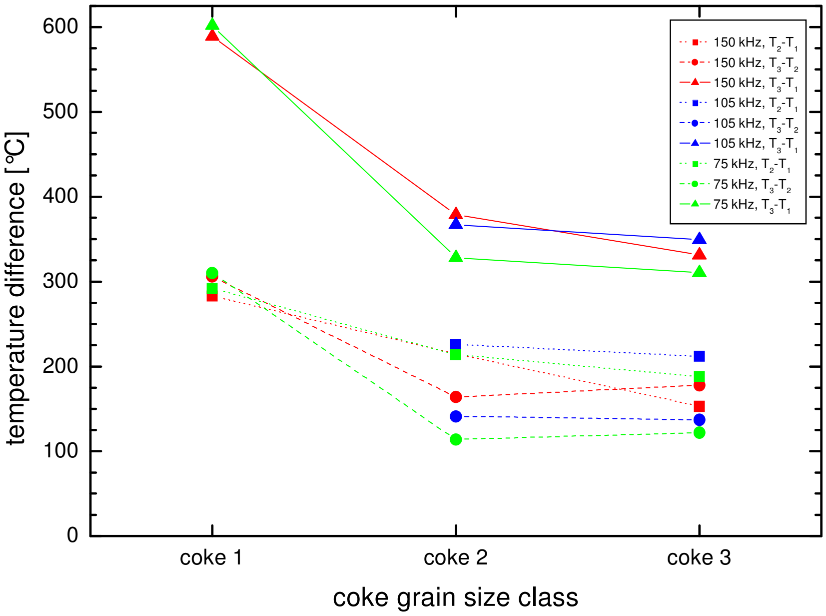


Figure 38: Temperature differences after heating period

The main findings from the trials can be summarized as follows:

- The induction heating of coke allows very fast up-heating velocities of 25 - 45 K/min (max. 55 K/min)
- The conversion efficiency of electric energy to coke heat is about 60 %
- The achievable temperature levels are very high and mainly limited by the refractory materials.
- Since the induction shows a small penetration depth into the coke and the coke itself has a bad thermal conductivity a sharp skin effect is observable, which results in a major temperature gradient between the margin and the centre of the coke bed.
- The required induction frequency for heating of coke lies between 75 and 105 kHz.
- Lower frequencies and larger grain sizes cause reduced temperature gradients in the coke bed.

3.3.2.4 Construction of the interface for melt charging and –carry-over into the inductively heated coke bed reactor (Task 3.1)

The RecoDust process for pyrometallurgical treatment of steel mill dusts consists of 2 main process steps. The first is flash-melting of steel mill dust under oxidizing conditions in order to evaporate impurities like Pb, alkalis and halogens as well as to produce a pre-melt, containing Zn, Fe, Ni, V, W, Cr, Ca, Si, Al in oxidic form. The second step is a reduction of the pre-melt on the inductively heated coke bed (InduCarb reactor).

Since the pre-melt is very corrosive on the refractory-material due to its high content on dissolved iron oxide and its relatively high temperature (1600 °C), the interface between the Flash Reactor and the InduCarb requires special focus. Additional problems are that the interface must prevent slag freezing and that it should guarantee an optimal melt distribution on the coke bed.

There is a need to separate the gas phases from the Flash Reactor and the InduCarb for getting a high purity ZnO from the InduCarb reduction process. As an important consequence there must not be a direct connection between the Flash Reactor tapping and the InduCarb feeding system. Extensive experimental work has been carried out on a continuously working and gas tight tapping system for the Flash Reactor pre-melt. Several refractory materials have been evaluated, e.g. high Alumina, MagCarbon, MagChrome, graphite, etc. but none of them has performed satisfactorily due to the highly corrosive character of the pre-melt. The only system, which proofed to be successful was an indirectly water cooled tuyere (tapping hole), installed at the bottom of the Flash Reactor as shown in **Figure 39** in a general (left) and a more detailed view (right)

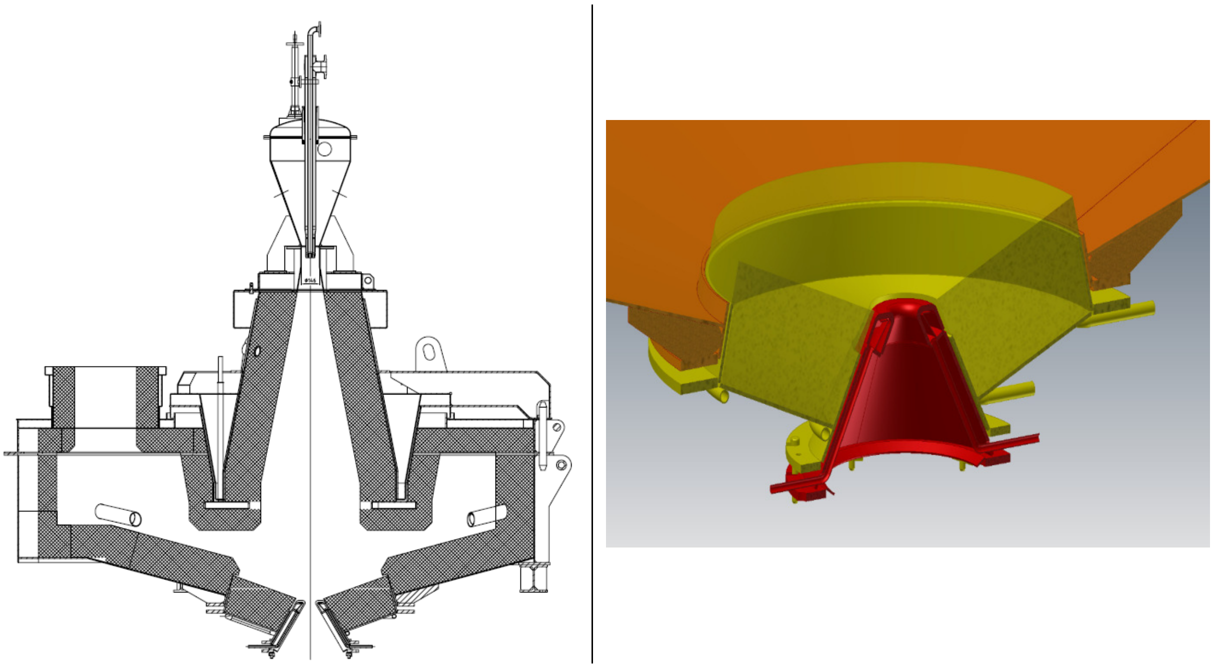


Figure 39: Indirectly water cooled Flash Reactor tap hole

After intensive experimental and optimization work, the final concept of the tapping system for a Flash Reactor with a throughput of 1.5 t/h is as shown in **Figure 40**. Cooling water energy demand was determined with about 25 kWh to get the pre-melt frozen on the surface of the tuyere (self protecting melt layer) on the one hand but to prevent a complete freezing of the tap hole on the other hand. The melt transfer from the tap hole of the Flash Reactor to the InduCarb-Feeding system is suggested to perform via a moveable, preheated pipe made of refractory similar to that of a LD-converter (MagCarbon). Optionally the melt flow area can also be indirectly water cooled (self protecting melt layer) to avoid refractory corrosion.

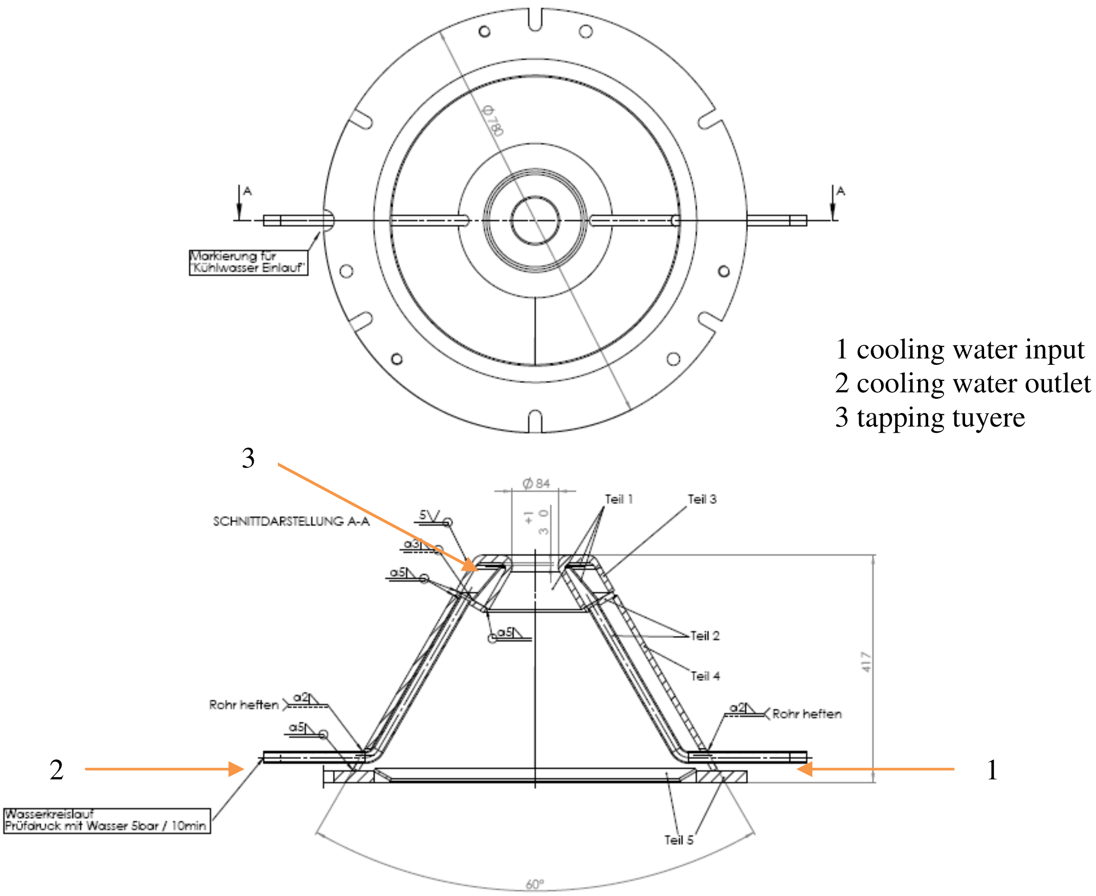


Figure 40: Detailed drawing of water cooled Flash Reactor tap hole

Apart from the tilting concept of the Flash Reactor also an appropriate InduCarb feeding concept had to be found. In total the following 5 concepts were investigated in detail:

Cold feeding

The simplest way of feeding is the water quenching of the pre-melt into small, solid granules, which are subsequently charged onto the inductively heated coke bed. This was experimentally investigated at the testing plant. As the schematic drawing of the experimental set up in **Figure 41** shows, the feeding of the pre-melt granules on the inductively heated coke bed of the InduCarb reactor was performed in parallel flow with the gas-stream (suction into the hot coke bed).

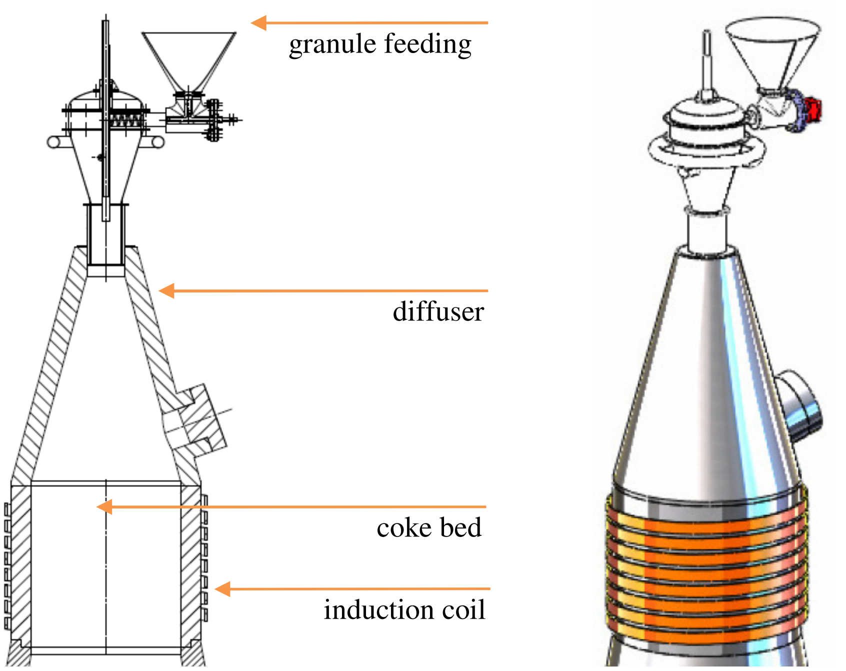


Figure 41: Schematic drawing of the experimental set-up for cold charging of the InduCarb reactor with pre-melt granules

A big disadvantage of this system is the loss of heat of about 460 kWh per ton of pre-melt. Furthermore also the production and the handling of the granules represent additional, cost and labor intensive process steps. According to test trials, the size of the granules should not succeed 3-4 mm. Disintegration of the granules to this grain size can be easily achieved by mechanical crushing. Crushing energy demand was determined with 2-7 kWh/t.

Advantages of this feeding concept are the disconnection of 2 totally newly developed processes (Flash Reactor, InduCarb) and that the feeding concept is based on the development of the well proven Flash Reactor burner system. As carrier gas for the feeding of the granules oxygen (burning of coke bed decreases electrical energy demand but increases coke demand as well as CO production) or natural gas (decreases specific coke consumption due to reductive behavior of CH_4 but increases the electrical energy demand due to the required energy for decomposing methane) is proposed. A big advantage that comes along with the use of a carrier gas is that the gas equalizes the temperature distribution over the coke bed cross section. Because of the diffuser also a very homogenous distribution of the material on the coke bed is achieved. Without this transportation effect too much heat would be required in the upper region of the coke bed, leading to “melt-pulsation” within the coke bed which then results in a non controllable operation of the entire InduCarb reactor.

Tundish feeding

A very simple way to feed the liquid pre-melt into the InduCarb reactor is to use a tundish with a bottom tuyere that ensures a compact, continuous and good controllable melt flow into the subsequent InduCarb reactor (**Figure 42**). The tundish concept has the advantage, that the tundish serves as a melt buffer between the Flash Reactor and the InduCarb that is able to compensate short interruptions in one of those two reactors. Additionally, by keeping a melt sump in the tundish, it is possible to separate the oxidizing Flash Reactor and the reducing InduCarb atmosphere from each other. Another advantage is that the InduCarb reactor itself can either be operated with a co-current or a counter-current gas flow.

The disadvantage of this concept mainly lies in the fact that a compact melt stream is fed in the centerline of the InduCarb reactor. Due to the high induction frequency, required for heating the coke bed, a major “skin effect” can be observed. As a consequence the main power (=heat) input is concentrated to the out part of the coke bed, so that in the coke bed a hot “hollow cylinder” with a cold “dead man” in the centre is formed. After the basic trials on the experimental InduCarb it is assumed, that only about 40 % of the coke bed radius is active. Since the melt stream coming from the tundish directly feeds into the centre of the coke bed, there is the risk that not enough energy can be supplied to the centre and as a consequence the melt starts to "freeze" there. However this problem can be overcome by the addition of oxygen, which will drastically increase the active coke bed volume. The injection of the oxygen into the InduCarb reactor can be done via radially distributed oxygen tuyeres or lances as known from the Cupola furnace. However in this case it would be necessary to run the InduCarb with a co-current gas and material flow in order to ensure a full transformation of the formed CO_2 to CO by passing through the coke bed.

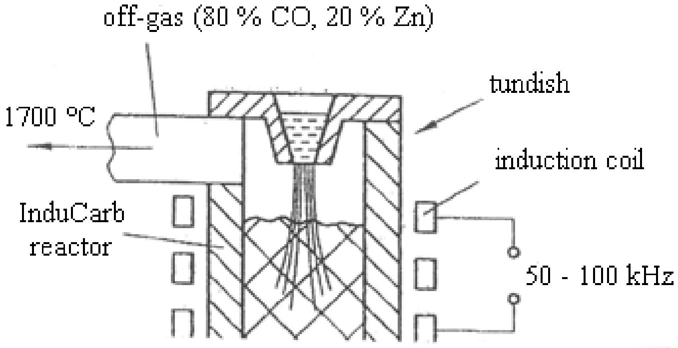


Figure 42: Schematic drawing of tundish feeding

Spray feeding

To overcome the disadvantage of the centreline feeding known from the tundish concept with the simple bottom tuyere the spray feeding concept is introduced. It also uses a tundish for the pre-melt but to guarantee a more uniform melt distribution over the cross-section of the coke bed, the melt does not simply leave the tundish through a bottom tuyere but is atomized with either a reactive (O2, CH4) or an inert gas (N2) through the bottom tuyere directly on the coke bed, as schematically shown in **Figure 43**.

The nozzle is designed in a way so that the pre-melt film running out of the nozzle forms a "hollow cylinder". The thickness of this film can be controlled by the axial position of the moveable protection pipe (5 + 7). Now by blowing gas into the "hollow cylinder" of pre-melt, the pre-melt is atomized into a cone of small droplets which splash on the inductively heated coke bed. Due to the cone form of the droplet stream, the highest droplet density can be found at the outer margin of the coke bed – where also the energy input has its maximum.

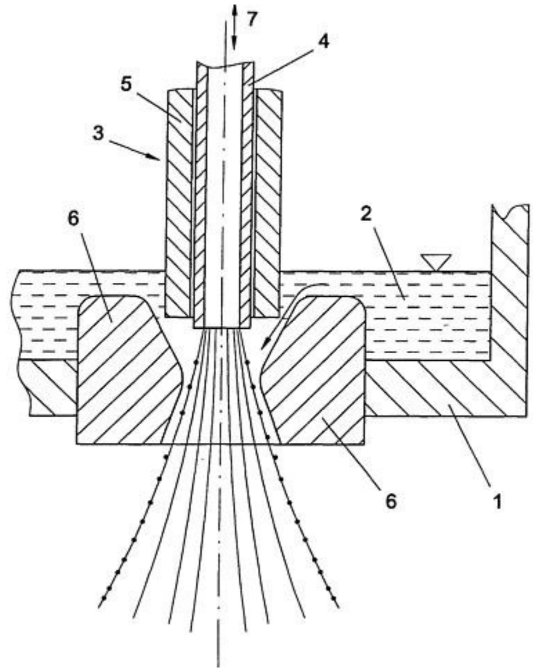


Figure 43: Schematic drawing of spray feeding concept

1 = tundish, 2 = pre-melt, 3 = atomizing lance, 4 = gas pipe, 5 = protection pipe, 6 = nozzle, 7 = vertical adjustment of atomizing lance

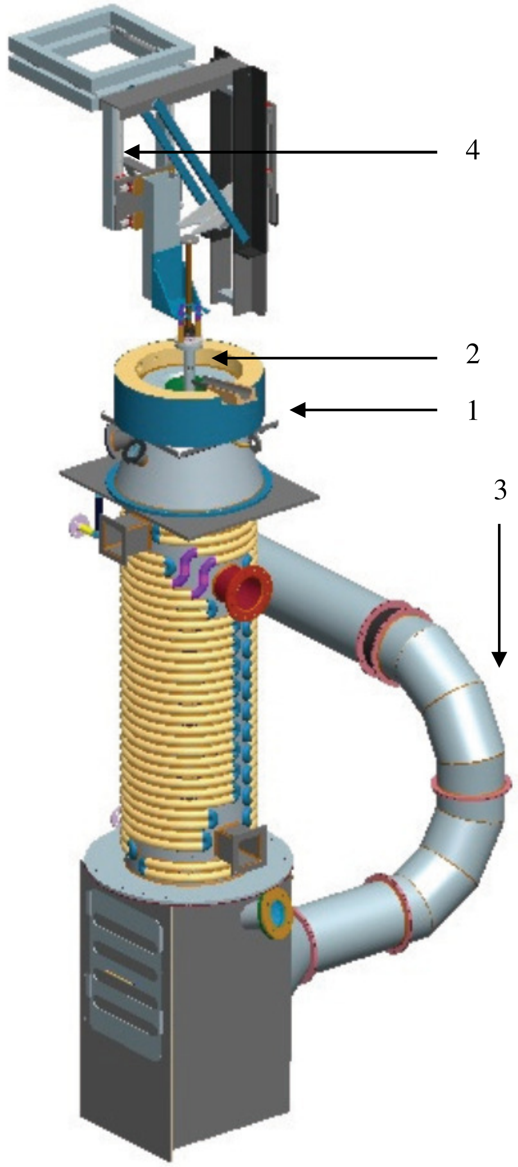
According to the specific gas flow, gas pressure (gas velocity) and position of the protection pipe one can control:

- droplet diameter,
- droplet distribution on the surface of the "hollow cone" and the
- final diameter (cross section) of the hollow cone, penetrating the coke bed.

As intensive hot tests with blast furnace slag and investigations on a water model have shown, it is possible to generate a droplet cone with very fine droplets. This however leads to a significantly increased reaction surface as well as to an accelerated reaction kinetics (droplets instead of a compact melt flow) which is further improved, since the melt droplets mainly hit the coke bed in its hot, energy-rich area.

The final size of the atomized droplets depends on viscosity, density and surface tension of the melt. In case of Flash Reactor pre-melt originating from steel mill dusts the parameters are comparable with those of blast furnace slag. However, due to its high iron oxide content the intermediate melt has an even lower viscosity, which additionally simplifies the atomizing process, which was originally developed for atomizing blast furnace slag melts to powders for subsequent cement production.

In **Figure 44** a schematic drawing of the experimental set-up for testing the atomizing process is given. In the right part of the picture additionally the main experimental parameters are listed.



1 tundish
2 gas pipe
3 suction pipe
4 movable carrier for spraying device
(gas pipe + protection pipe)

Experimental Parameters

melt viscosity:	0,3-0,5 Pa x s (1540 C)
specific weight of melt:	2,5 - 3,2 kg/dm³
droplet size:	165 - 260 µm
melt : gas ratio:	1 kg : 0.6-1.2 Nm³
gas:	pressurized air
gas pressure:	1.2 – 1.,9 bar

Figure 44: Schematic drawing of experimental set-up for slag atomizing

Snorkel feeding

Another investigated opportunity was the feeding of the liquid pre-melt via a central pipe (“snorkel”) on “free fall mode” directly from the Flash Reactor deeply into the coke bed. As the concept in **Figure 45** shows, this concept requires a counter current gas and melt flow. By charging the coke with a bell system this interface design also allows a pre-heating of the coke within the InduCarb reactor by the ascending off-gases.

The advantage of this concept is based on the fact, that the highly aggressive pre-melt has no contact with any device of the InduCarb feeding system like a tundish, a protection pipe or a nozzle, since the melt is directly fed to the coke bed without any contact to refractory materials.

The disadvantage is that - as in case of the tundish system - a central feeding of the pre-melt to the cold “dead man” zone of the InduCarb reactor happens. To minimize this cold area the cross section of the InduCarb reactor may be changed to a more oval or rectangular shape.

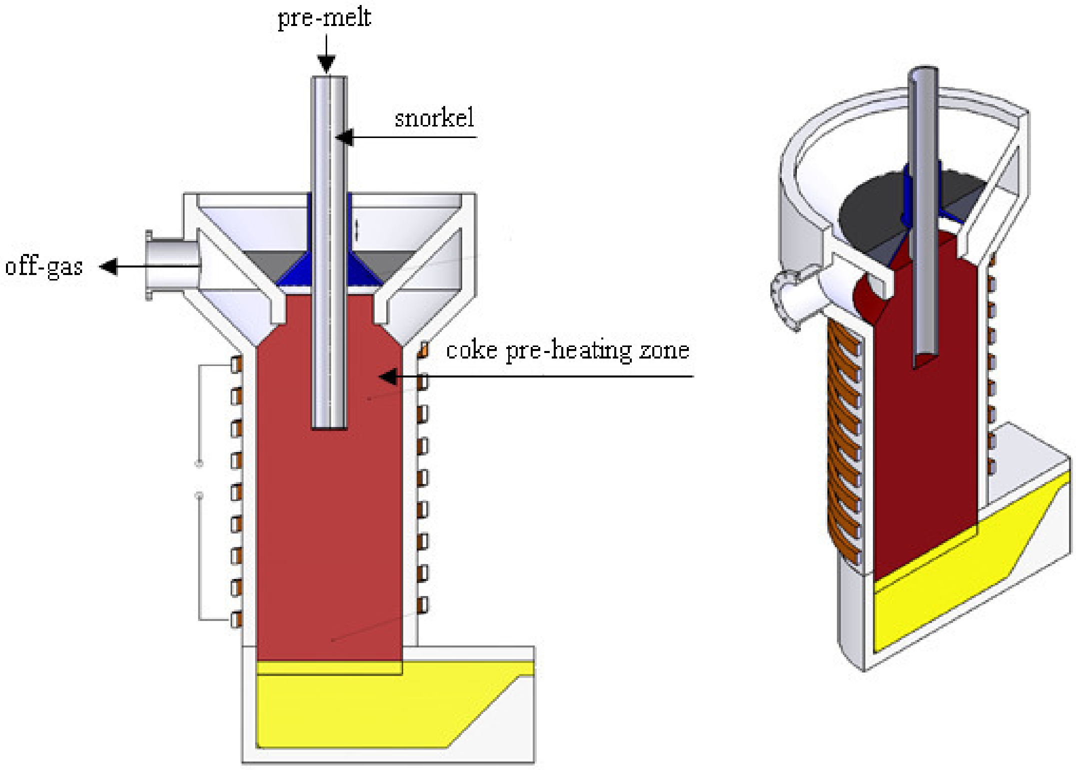


Figure 45: Schematic drawing of snorkel feeding system

Although each of the introduced feeding and interface concepts has its particular advantages and disadvantages the spray feeding system seems to fulfil the requirements in the best way and should be preferred. This is especially because it allows dispersing the melt into fine droplets and directly feeding them into the energy rich area of the coke bed cross section. In addition to this the generation of fine droplets also accelerates reduction kinetics. The possibility to use a reactive gas for the spraying process is another interesting option. Finally the system is already experimentally well tested and proofed to be successful in hot tests.

3.3.2.5 Coupled trials – Flash reactor – InduCarb (Task 3.2)

The coupled trials had the aim to generate basic data to set-up a rough mass and energy balance for treating EAFD originating from stainless steel production with the RecoDust process. Since the experimental devices used for these trials are mainly those, being developed within work package 2.4 “smelting technology”, there is close connection of these work packages. The same is for tasks 5.1 (process concepts) and 5.4 (overall evaluation), since the results of the coupled trials build the basis for the mass and energy balancing being done in those two work packages.

The Flash Reactor demo-plant has a maximum smelting capacity of 300 kg/h and consists, as schematically shown in **Figure 46**, of the burner, the burning chamber with the water cooled tapping tuyere, an off-gas line with water injection to cool the off-gases, a separator for coarse particles and a dust collection chamber (not included in the drawing anymore). In the coupled trials this plant was used to smelt the stainless steel mill dust under oxidizing conditions at a temperature of 1600 °C, in order to be able to supply a liquid pre-melt to the InduCarb reactor, which was placed directly underneath the Flash Reactor.

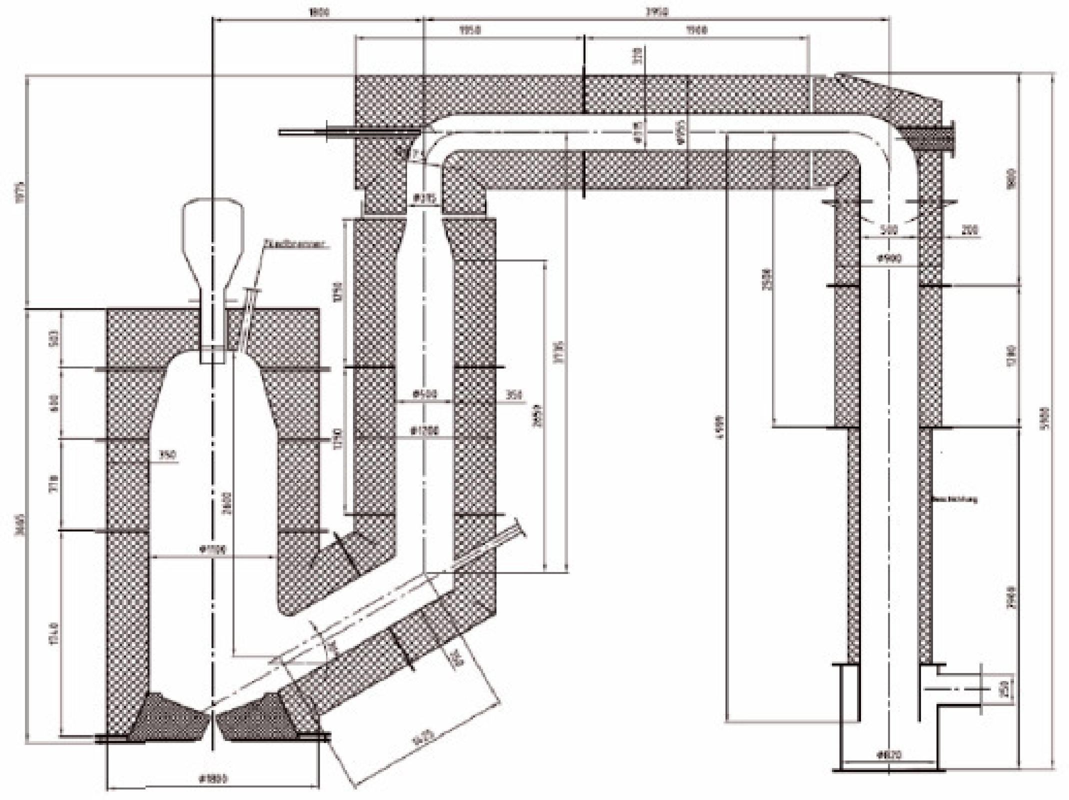


Figure 46: Schematic drawing of the Flash Reactor demo-plant

For reasons of simplicity and to be able to control the costs of the trials, the tests were done without using an interface between the Flash Reactor and the InduCarb. For the same reason also the InduCarb off-gases were not reformed as described in WP 3.4 as well as no coke pre-heater was installed. Instead of this coke was charged batch-wise for each trial and the off-gases were simply sucked off with a strong fan and burnt as the photo from the trials in **Figure 47** shows.

Figure 47: InduCarb reactor and the Flash Reactor tapping during the coupled trials

Although the InduCarb testing facility, described in detail in WP 2.4, was not originally built for the coupled trials, it was suitable - with a few small modifications - to perform a small number of those coupled tests. The modifications were essentially the installation of a refractory cladding for the induction coil (see Figure 47) and the installation of a continuous bottom tapping in form of a nozzle brick instead of the removable coke discharging unit.

In total it was possible to run 9 tests with a material throughput of between 113 and 344 kg. Three of these 9 tests were running so smooth, that it was possible to set up a mass balance of the tests. The measured input and output streams of these tests are shown in **Table 10**. It is also these data which was taken to calculate the full mass and energy balance shown in WP 5.

To avoid zinc losses in the Flash Reactor, the burner ran at λ = 1,1 – 1,15. The addition of SiO_2 to the dust was necessary to ensure a moderate liquidus temperature of the final slag in the InduCarb reactor, so that slag freezing in the reactor or at the tapping could be avoided. The weight difference between the input materials (EAFD and SiO_2) and the output materials (carry over, Fe alloy, slag) can be traced back to some (unavoidable) material losses, but is mainly caused by the oxygen removal (during the reduction), which leaves the system as CO through the off-gas, and by the zinc-losses, because Zn leaves the system as vapour with the InduCarb off-gas as well. Since the off-gas volume could not be measured during the tests, this weight loss can only be calculated on a theoretical basis (as done in the mass and energy balancing in WP 5).

The amount of carry over in the Flash reactor is a little high with 8,4 to 9,5 %. As the analysis of the dust in **Table 11** shows, one reason for the increased carry over is an enrichment of ZnO in the flue dust. This enrichment was observed in nearly all flue dust samples. It is assumed that, although the Flash reactor is run at lambda 1,1, a part of the ZnO is reduced within reducing parts of the flame. These areas appear since it is not possible to fully mix the CH_4 with the oxygen before the burning so that the flame has some reducing areas where the ZnO is reduced, the zinc is then vaporized and finally reoxidized in the off-gas line. As a consequence about 15 % of the zinc is lost with the flue dust. Apart from the zinc also Pb, F and Mo concentrate in the flue dust. While the enrichment of Pb and F was expected the enrichment of Mo was a little surprising. Investigations with the SEM and EDX analysis turned out that the Mo forms MoO_3 which is volatile at the temperatures of the Flash reactor and thus goes into the flue dust.

Table 10: Measured input and output streams of the coupled trials 4, 7 and 8

	unit	trial 4	trial 7	trial 8
Input – Flash Reactor				
EFAD	[kg]	154	213	302
SiO_2	[kg]	7,7	10,7	15,1
CH_4	[Nm^3]	26,9	35,2	55,1
O_2	[Nm^3]	59,3	78,14	127,3
Output – Flash Reactor				
dust (carry over)	[kg]	13,6	21,2	28,3
Output - InduCarb				
Fe alloy	[kg]	69,5	94,4	136,3
slag	[kg]	28,7	40,2	54,2

As the analysis of the InduCarb slag and the iron alloy in Table 11 as well as the calculated recovery rates in **Table 12** show, the reduction in the InduCarb reactor works very good. As a consequence of this, the slag is almost free from reduceable metals – the remaining 1,5 % of Cr_2O_3 and 1,2 % of FeO just amount to 3,7 and 0,5 % of the amount contained in the EAFD, indicating that the reduction was almost complete.

Very similar is the situation with Co, Mn, Ni, V, W and Cu, which all showed a reduction rate being higher than 90 % (see Table 12).

As a consequence from the excellent reduction results the slag is almost free from heavy metals and thus shows a very good leaching behaviour, which allows its application for typical slag uses. The quality of the iron alloy is a little bit difficult to evaluate, because it's an uncontrolled mixture of all the metals contained in the EAFD. So it is rich in carbon and high in copper, apart from this also the amount of chromium (10,2 %) and manganese (7,6 %) is significantly high. It is this mixture which makes it difficult to use the iron alloy as scrap substitute (even for high alloyed steels) although it contains a lot of expensive alloying elements.

Table 11: Analysis of the input materials and products of trial 8

	EAFD	**carry over**	**slag**		**Fe alloy**	
	[%]	[%]		[%]		[%]
ZnO	24,77	45,31				
Pb	0,05	0,56				
Cr_2O_3	7,23	2,68	**Cr_2O_3**	1,53	**Cr**	10,20
FeO	45,16	23,37	**FeO**	1,18	**Fe**	73,50
F	0,14	1,37				
Al_2O_3	0,23	-	**Al_2O_3**	1,22		
CaO	5,16	3,73	**CaO**	25,80		
Co	0,03	-			**Co**	0,06
C	0,73	-			**C**	4,71
Cu	0,09	-			**Cu**	0,19
MgO	0,93	0,24	**MgO**	4,71		
MnO	4,87	3,12	**MnO**	0,18	**Mn**	7,60
Mo	2,00	16,70			**Mo**	1,33
Ni	0,21	-			**Ni**	0,45
SiO_2	6,87	0,93	**SiO_2**	62,90	**Si**	0,31
V	0,04	-			**V**	0,09
W	0,25	0,14			**W**	0,52
sum	**98,76**	**98,15**		**97,52**		**98,97**

Table 12: Recovery rates of the different metals and compounds into the different output streams (trial 8)

	carry over	**slag**		**Fe alloy**	
	[%]		[%]		[%]
ZnO	15,7				-
Pb	94,4				-
Cr_2O_3	3,2	**Cr_2O_3**	3,7	**Cr**	91,9
FeO	4,4	**FeO**	0,5	**Fe**	93,4
F	83,3				
Al_2O_3	-	**Al_2O_3**	95,4		
CaO	6,2	**CaO**	88,6		
Co	-			**Co**	95,5
C	-			**C**	287,7
Cu	-			**Cu**	94,1
MgO	2,2	**MgO**	89,9		
MnO	5,5	**MnO**	0,7	**Mn**	89,9
Mo	70,8			**Mo**	29,6
Ni	-			**Ni**	95,5
SiO_2	0,7	**SiO_2**	94,2	**Si**	2,5
V	-			**V**	93,3
W	4,8			**W**	92,7

However the coupled trials clearly showed that the combination of the Flash reactor with the InduCarb is able to process the flue dusts from stainless steelmaking and transfer them from a hazardous waste into valuable products. The tests proofed that both the Flash reactor as well as the InduCarb prototype work fine and that the technical concept is principle capable to process these dusts. Also the flow of the slag through the coke bed (no freezing, etc.) and the slag and metal separation worked very well, so that from an process engineering point of view the concept proofed as successful as from the chemical point of view (reduction degree, slag composition, etc.). With throughputs between 113 and 344 kg of EAFD and a duration of the single trials between 55 and 110 minutes also the scale of the trials was in a range that allows to gain representative results and get a reliable impression whether the process can also successfully work on an industrial scale, which is definitely the case.

3.3.2.6 Coke feeding and pre-heating (Task 3.3)

The coke feeding and pre-heating system, which had to be developed within this work package, should use the sensible heat from the CO-Zn InduCarb off gas for preheating the coke required as reductant in the InduCarb. In order to avoid Zn-condensation within the pre-heater it is important that the gas is not cooled to below 1000 °C in the system. In a first step several coke charging and preheating concepts have been developed and evaluated. The coke charging and pre-heating system concept shown in **Figure 48** was estimated to fulfil the requirements in the best way. To check the functionality of the equipment and to gain lay out data for the industrial pilot plant also a laboratory scale prototype (see **Figure 49**) of this system was built and tested.

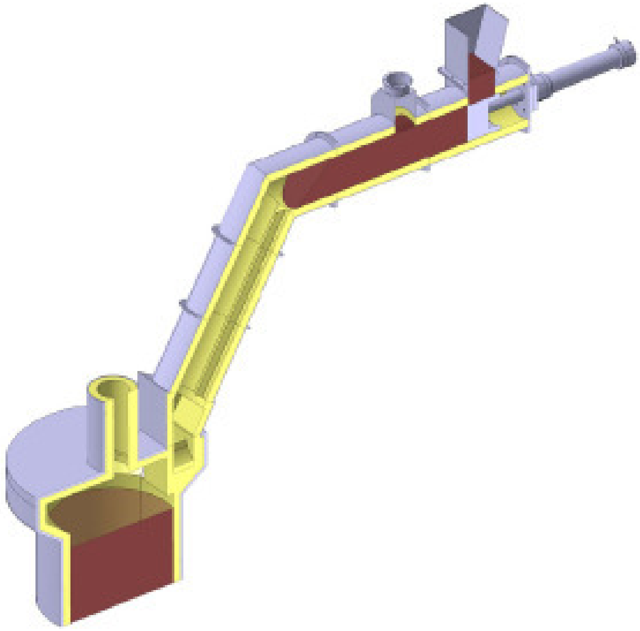
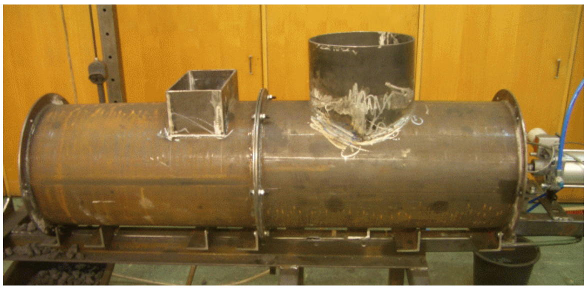
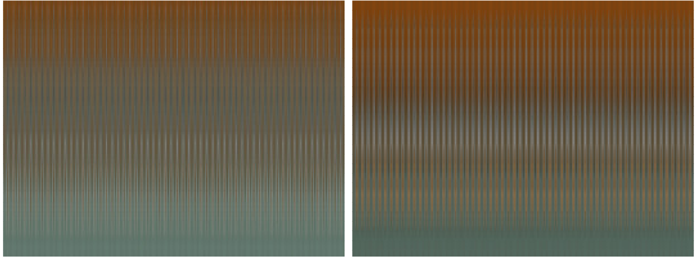


Figure 48: Concept of a coke charging and pre-heating system for the InduCarb reactor

coke feeding tube



coke pushing unit (pre-heater)



type A

type B

Figure 49: Coke charging testing facility

Investigated parameters were the influence of inclination angle, coke grain size and interface design on the coke distribution in the InduCarb. The best results were achieved without using any interface for distributing the coke in the reactor at an inclination angle of the coke feeding tube of 60 °. A photo of the achieved distribution shows **Figure 50**. In comparison to this, **Figure 51** shows the coke distribution at an inclination angle of 40 ° and with the type A coke distributing interface, which delivered the worst results regarding the distribution characteristics. If a more marginal feeding is preferred, instead of the central feeding achieved without using an interface, it is recommended to increase the inclination angle of the feeding tube to 60 ° and change the interface design to a type B one. The more uniform distribution achieved by this way can be seen from **Figure 52**.

Due to a statistical design and evaluation of the experiments the influence of inclination angle, coke grain size and interface design on the coke distribution can be classified as follows.

- A change of the interface design from type A to type B improves the distribution by 8 %.
- By increasing the inclination angle from 40 ° to 60 ° the distribution improves by 16 %.
- The influence of the coke grain size on the distribution behaviour is negligible since the difference between the smallest and largest grain size is just 3 %.

Figure 50: Coke distribution in the InduCarb reactor (60 °, no distributing interface used)

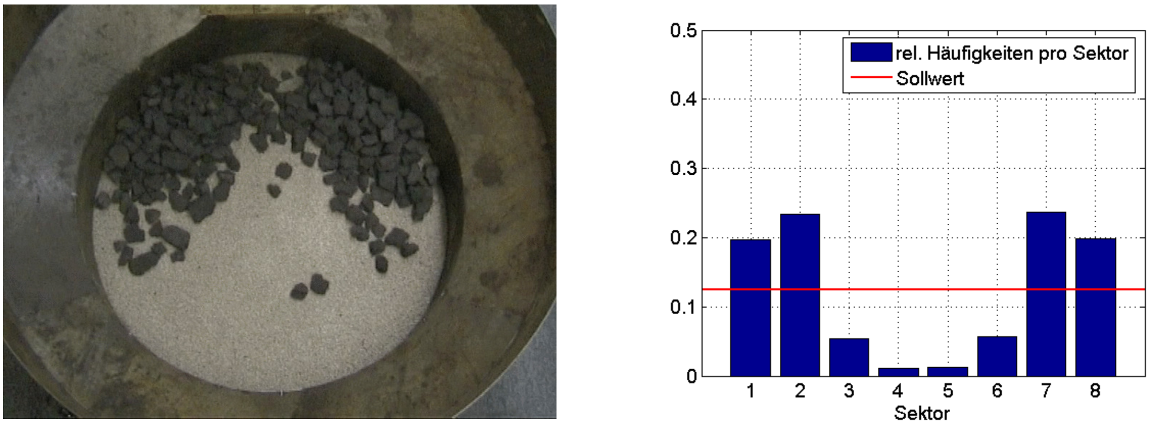


Figure 51: Coke distribution in the InduCarb reactor (40°, type A distributing interface)

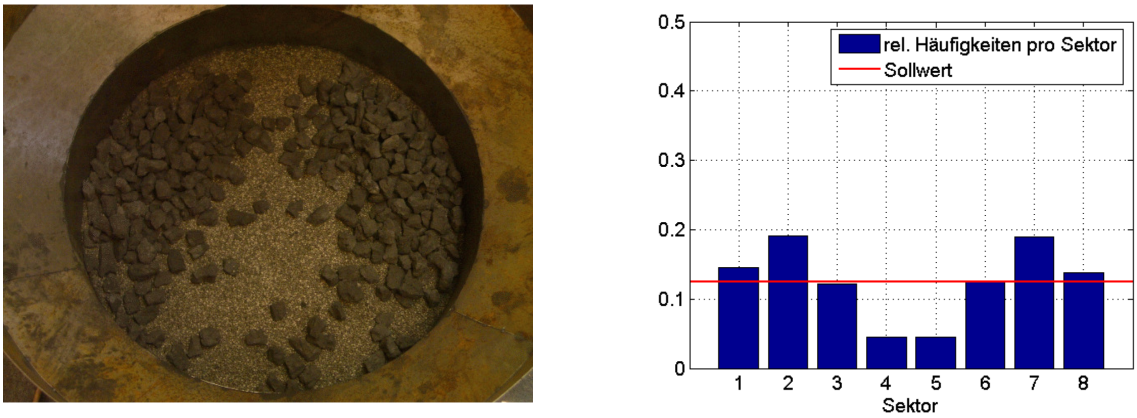


Figure 52: Coke distribution in the InduCarb reactor (60°, type B distributing interface)

While the distribution unit worked very well, the feeding tube caused some problems. The main problem was that the required pushing force of the coke pushing cylinder was very high (see **Figure 53**), sometimes even exceeding the maximum power of the pushing cylinder. Especially with increasing coke grain size also the power demand increased. An example, where the required power exceeded the maximum force of the cylinder shows **Figure 54**. Due to these problems the feeding unit was redesigned into a vertical feeder with a horizontally moving feeding plate as shown in **Figure 55**.

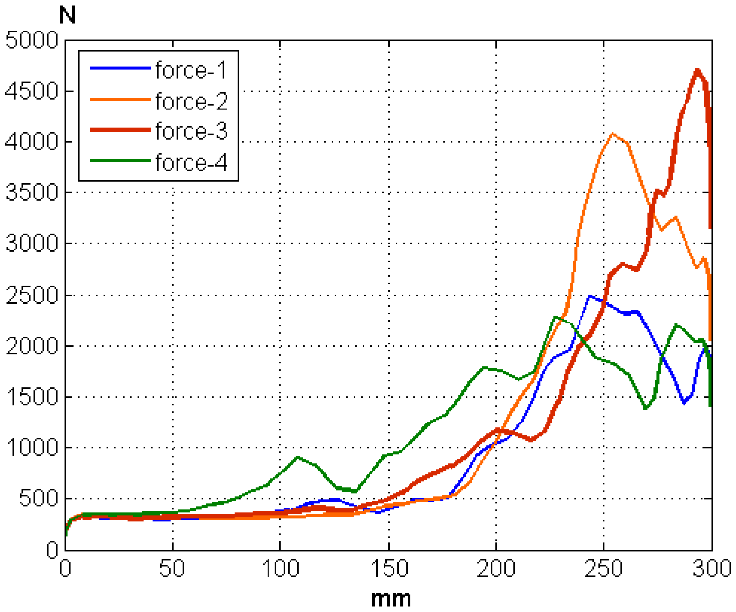


Figure 53: Power requirement of the coke pushing cylinder

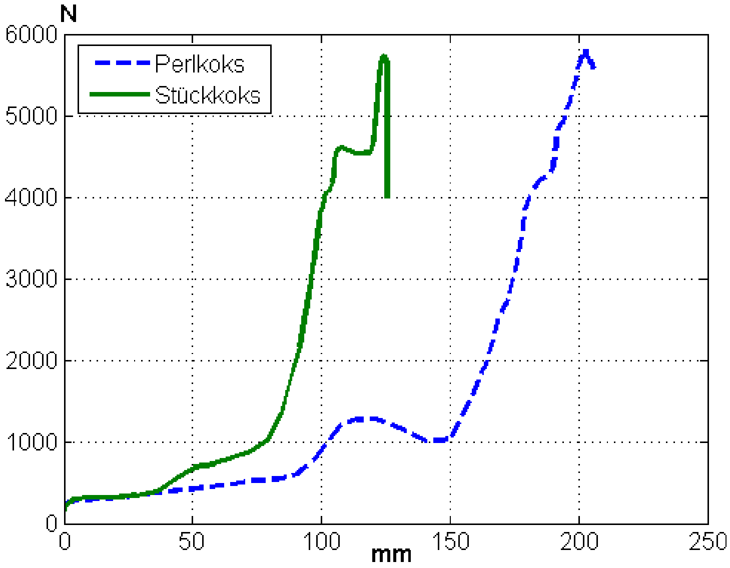


Figure 54: Pushing force of the coke pushing cylinder in a case where the required power exceeded the maximum cylinder force

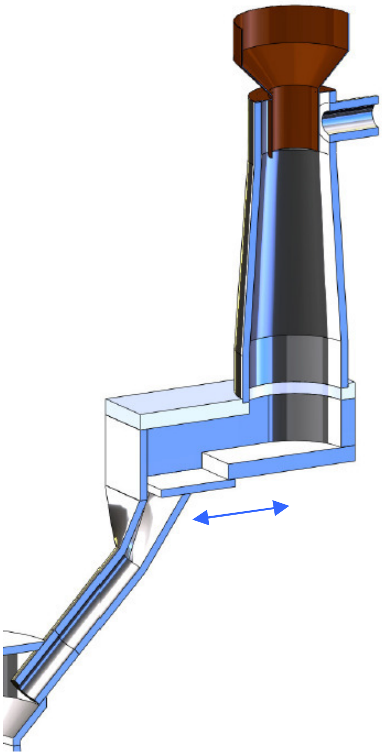


Figure 55: Modified, vertical coke feeding unit

Apart from the development and testing of the mechanical feeding unit also a thermal engineering of the pre-heater, which is shown in detail in **Figure 56**, was performed. The essential parameters and presettings for the thermal engineering were that the CO and Zn vapor containing off-gas enters the pre-heater with a temperature of 1600 °C and can only be cooled down to 906 °C – the boiling point of Zn – in order to avoid condensation of zinc on the coke in the pre-heater.

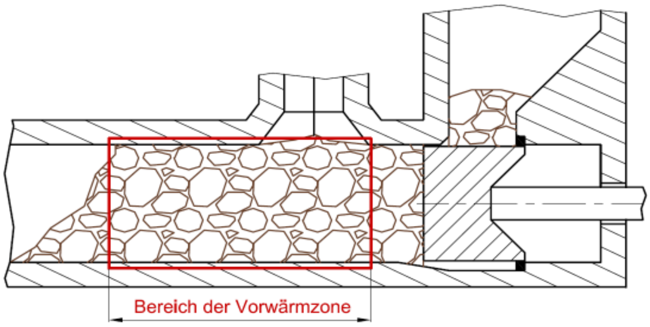


Figure 56: Schematic drawing of the coke pre-heating unit

As the off-gas- and coke temperature graphs in **Figure 57** and **Figure 58** show, the maximum length of the pre-heater under these specifications is around 0.5 m. If the pre-heating zone is longer, the off-gas cools below 900 °C and as a consequence major problems due to zinc condensation would arise. With a length of 0.5 m the off-gas would leave the pre-heating unit with a temperature between 937 °C and 1028 °C while the coke is heated up to a temperature between 982 °C and 1186 °C, depending on the coke consumption in the InduCarb reactor, which was assumed in the calculations with a medium feeding rate of 300 kg/h.

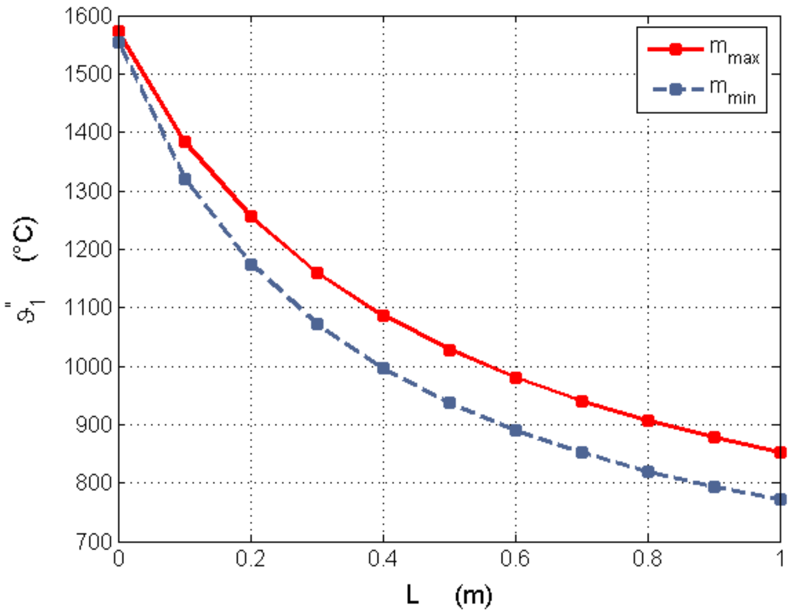


Figure 57: Off-gas temperature in dependence of pre-heater length

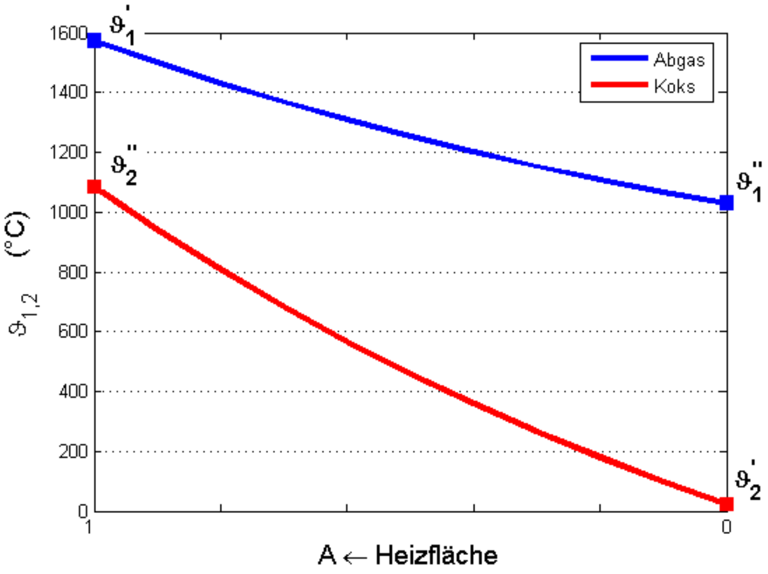


Figure 58: Development of off-gas and coke temperature for a pre-heater length of 0.5 m

3.3.2.7 InduCarb off gas treatment (Task 3.4)

The InduCarb off gas mainly consists of gaseous Zn and CO. As already mentioned, part of the sensible heat of the off gas should be used to preheat the coke for the InduCarb. However it is important, that during the coke preheating process the off gas does not cool below the condensation temperature of Zn (906 °). The gas leaving the coke preheater with a temperature of around 1000 °C has to be further processed to recover the zinc contained in it, which is the main task of this work package.

To recover the zinc there are essentially three options:

- condensation of liquid, metallic zinc
- production of ZnO by burning the off gas with oxygen or air
- production of ZnO by reforming the off gas with water

Although the liquid zinc condensers are a proven technology, they are reported to require a lot of maintenance and tend to dross formation, which negatively influences condenser efficiency. In addition to this research work in this area would not make much sense, since the technology is already fully developed. The burning of the off gas with oxygen or air to produce ZnO is a very exothermic process and just makes sense, if there is any use for the generated thermal energy.

The basic idea of the reforming concept is to inject water into the Zn-CO off gas so that – according to the following reaction equations – H_2 and ZnO are formed.

$$Zn + H_2O \Leftrightarrow ZnO + H_2 \qquad \Delta H_{1000\,°C} = -220\ kJ$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta H_{1000\,°C} = -32\ kJ$$

As the thermochemical calculation in **Figure 59** shows, the reforming reaction of Zn to ZnO starts at a temperature between 1050 °C and 1100 °C and is completed at a temperature of around 800 °C. An important finding from this calculation is that at temperatures above 1100 °C it is not possible from the thermochemical point of view to reform the off-gas, which means that it is not possible to oxidize the zinc with water vapour at these temperatures. So it makes sense to pre-cool the off gas by pre-heating the coke and then going into the reformer. Since the reforming reactions are exothermic, as the ΔH values to the reaction equations show, it is reasonable to inject water in excess to cool down the off gas by water vaporisation.

As can be seen from the diagram in Figure 59 and the reaction equation above, a side effect of the reforming reaction is, that apart from the Zn also a certain amount of the CO is oxidized to CO_2. However for each mole of CO oxidized to CO_2 one mole of H_2 is formed, so that the chemical energy of the off-gas is not significantly lowered, which is also confirmed by the relatively small ΔH of this reaction

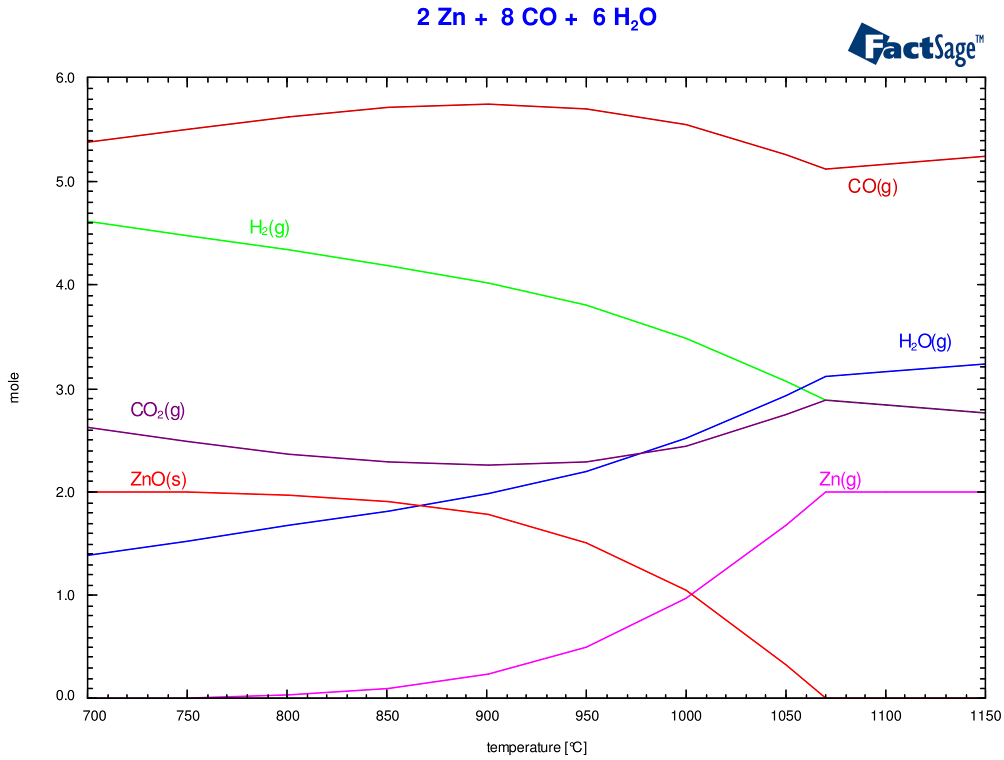


Figure 59: Products of the off-gas reforming reaction in dependence of temperature

With the findings from these thermochemical considerations a laboratory scale testing facility for the treatment of a Zn-CO containing off-gas, as evolving form the InduCarb reactor, was designed, constructed and put into operation. The experimental set-up in its final form, resulting from several modifications and redesigns, is schematically shown in **Figure 60**.

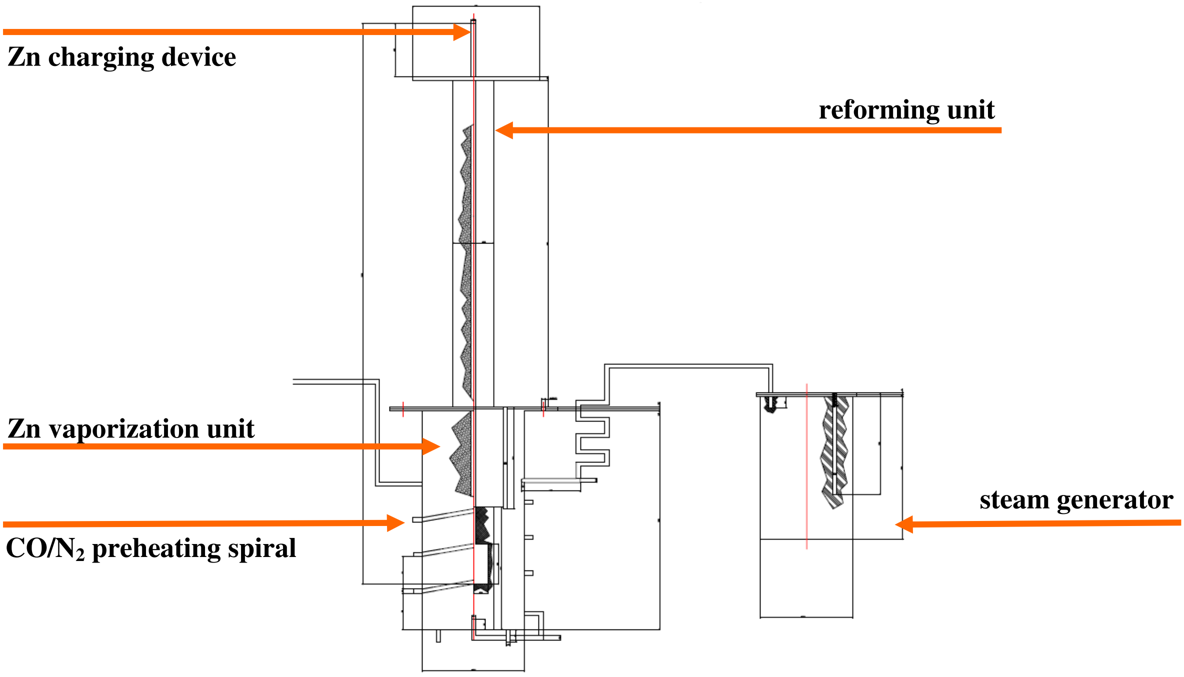


Figure 60: Schematic drawing of the experimental set-up for the reforming of Zn-CO containing gases with water vapour

The key units of this set-up are the steam generator, the vaporization unit, where the Zn-CO gas mixture is generated and the reformer, where the oxidation of Zn to ZnO takes place. A photo of the combined vaporization and reforming unit is shown in **Figure 61**. The lower part of the retort (= vaporization unit) is placed in a resistance heated furnace at a temperature of around 1050 °C. Inside the retort, the zinc – charged with a crucible through the reformer (photo on the right in Figure 61) – is vaporized and mixed with the preheated CO entering the retort from the bottom. The gas, now consisting of Zn and CO, is finally reformed with preheated water vapor, entering in the upper third of the retort. The Zn-CO-H_2O gas mixture now passes the reformer where, according to the following equations, the reforming reaction takes place.

$$Zn + H_2O \Leftrightarrow ZnO + H_2$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

In order to control the reforming reactions, the reformer is placed in a half-shell furnace which allows to vary the temperature between 700 °C and 1000 °C. To determine the degree of Zn to ZnO and CO to CO_2 oxidation by the water vapor, the gas leaving the reformer is analyzed for CO, CO_2 and H_2. The described set-up with the different furnaces, the gas analyzing unit and the steam generator is shown in the photography of **Figure 62**.

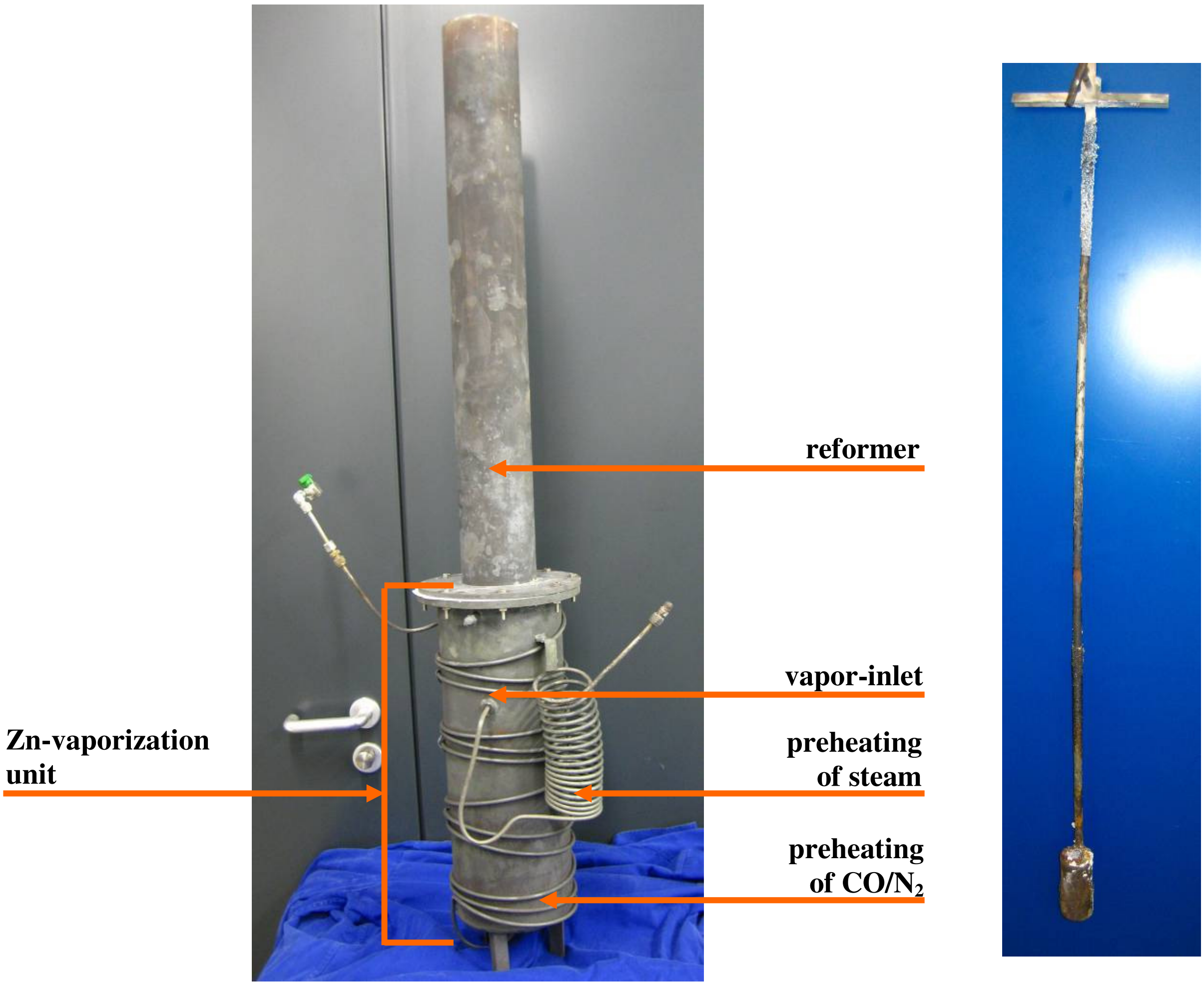


Figure 61: Photo of the vaporization & reforming unit (left) and the Zn charging device (right)

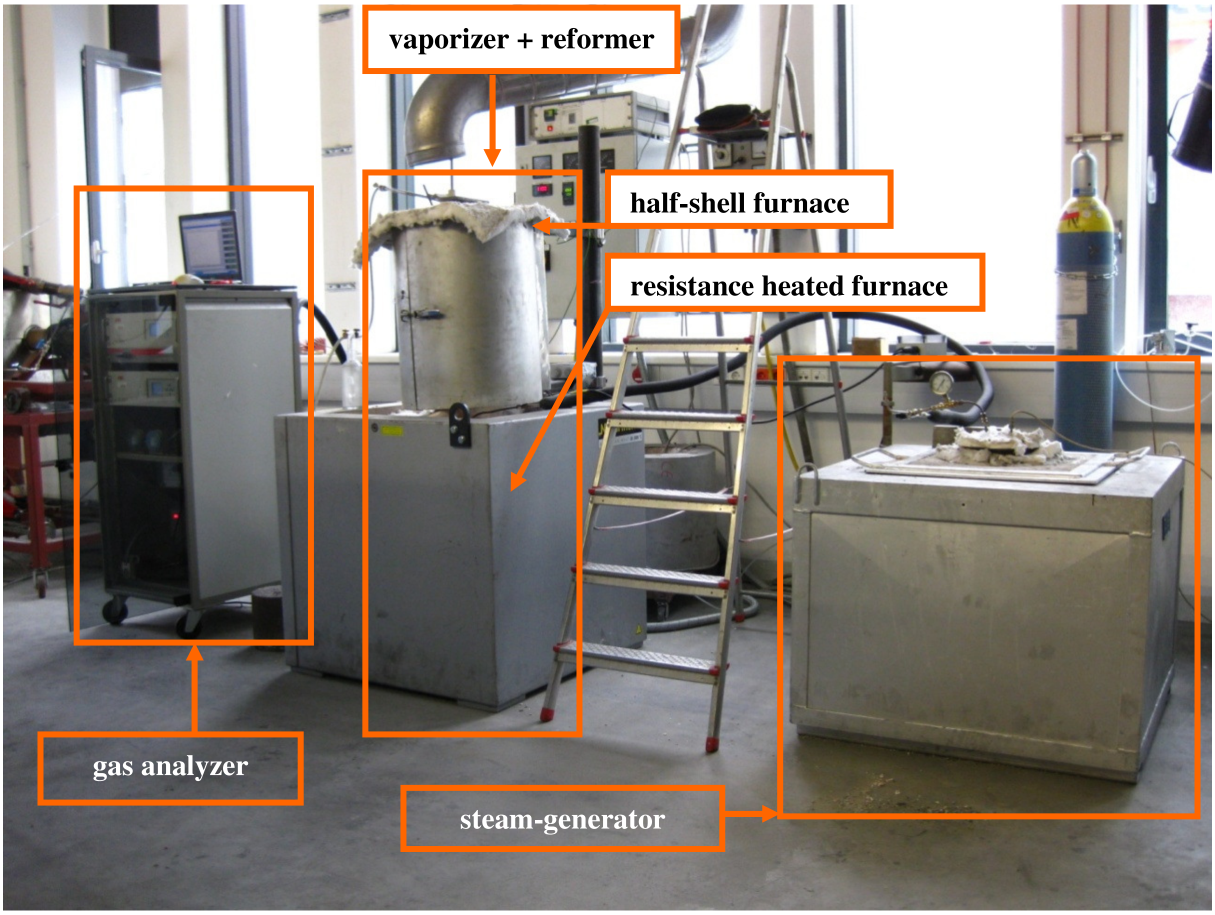


Figure 62: Photography of the experimental set-up

The aim of the tests performed with this experimental set-up was to determine the optimal reforming temperature in order to maximize the conversion degree of Zn to ZnO. Besides this it was also of interest to which degree the CO was transferred to CO_2 and whether the amount of water added has an influence on the experimental results. The range of parameters investigated covered reforming temperatures from 700 - 1000 °C, Zn-contents in the CO-Zn mixture of 10 - 20 % and steam in an amount of 3 - 9 times the stoichiometric amount of Zn contained in the off-gas. The development of the off-gas composition during the reforming shows **Figure 63**. At the start of the trial the retort is only fed with CO and steam which react to a mixture of 63.5 % CO, 20.5 % CO_2 and 16 % of H_2. Short after the Zn is charged and its vaporization starts, also the reforming of the Zn to ZnO initiates, which is indicated by the rise of the H_2-concentration in the off-gas according to the reaction:

$$Zn + H_2O \Leftrightarrow ZnO + H_2$$

When the Zn is fully vaporized after about 25 minutes the H_2-content falls again and the trial is finished. By knowing the gas composition, its volume and the amount of vaporized zinc it is possible to calculate the conversion degree of Zn to ZnO after the trial. The achieved conversion degree at different reforming temperatures is displayed in the diagram in **Figure 64**. It is obvious from the diagram that a reforming temperature of 800 °C delivers the best results and allows an almost full conversion of the Zn to ZnO. The continuous decrease in conversion efficiency with increasing temperatures can be primarily explained by thermodynamical reasons, as the comparison with the theoretical calculation in Figure 59 shows. Although the thermodynamical conditions for the reforming further improve with decreasing reforming temperatures, the conversion degrees decline again below 800 °C. The reason for this is, that the Zn vapor starts to condense at temperatures below 906 °C. Although the zinc still has a certain partial pressure at temperatures below 906 °C, which allows still good reforming conditions around 800 °C, this pressure rapidly falls with further decreasing temperature. Since the reaction mechanism then changes from a gas-gas reaction to a liquid-gas reaction, the reaction kinetics is significantly decelerated and as a consequence also the conversion degree falls. However with a medium conversion efficiency always higher than 90 % in the temperature range from 700 to 950 °C, there is a wide process window for the operation of the process in which good and satisfying results can be obtained.

As the experiments also turned out, the amount of water and the zinc content of the off-gas are of minor importance with respect to the achieved conversion degree. The same is for the amount of CO transferred into CO_2 which always varies between 16 and 18 % of the original CO volume.

The general conclusion from these experiments is, that the investigated reforming of the CO-Zn off-gas evolving from the InduCarb is a highly interesting alternative to liquid zinc condensing and also to the simple burning of the off-gas. Especially since the reforming simultaneously allows to generate a marketable ZnO product on the one hand and to conserve the chemical energy of the off-gas during the cooling process on the other hand it's a nearly perfect solution for the process chain Flash Reactor-InduCarb. While the ZnO can be sold as valuable raw material to hydrometallurgical zinc winning, the cold CO and H_2 rich gas from the reforming unit can be perfectly used as fuel in the Flash Reactor. Since the optimal reforming temperature lies around 800 °C also the link with the coke pre-heater, where the off-gas leaves with about 900 °C, is an ideal solution.

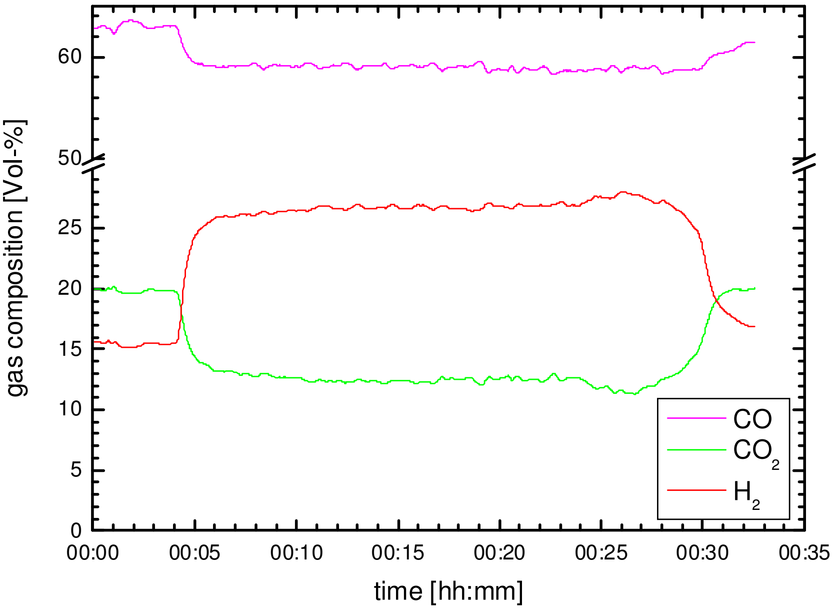


Figure 63: Development of the off-gas composition during a reforming trial with a CO-Zn gas mixture

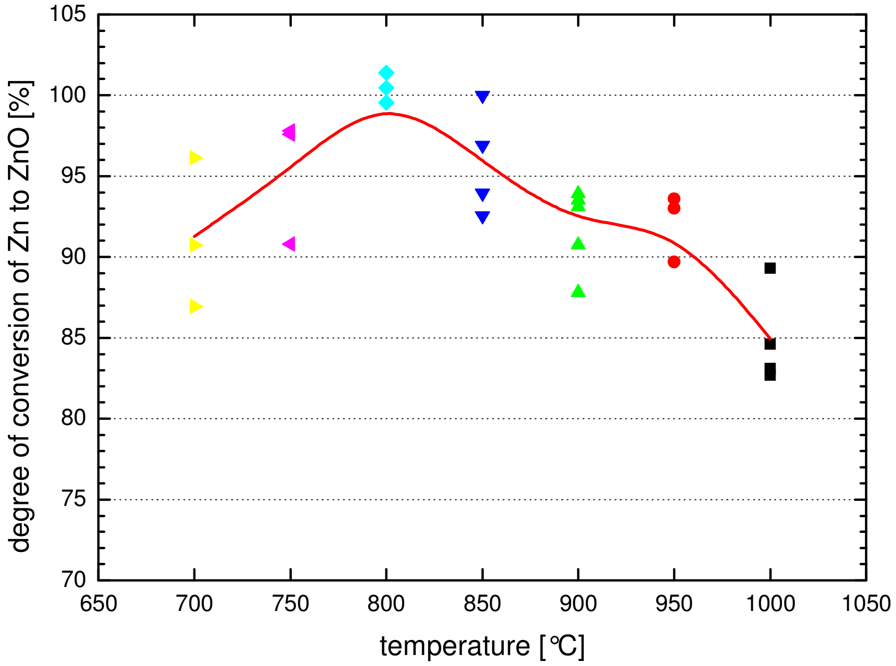


Figure 64: Conversion degree of Zn to ZnO in dependence of the reforming temperature

3.3.2.8 Development, Optimisation and validation of process model for carbothermic reduction of molten stainless steel waste in inductively heated coke bed (Task 4.1, 4.2)

An initial one stage process model for carbothermic reduction of molten stainless steel waste in inductive heated coke bed has been modelled by BFI by use of the Fact Sage Software. The model bases on the thermochemical equilibrium calculation in one single reaction volume. The reactor dimensions taken into account and the amount of the input and output materials are based on the results of Task 2.1.

The following parameters have been applied for the process model, the time basis is one hour:

- High-Cr stainless steel slag as input material to be processed in the coke bed reactor. Amount: 300 kg
- Amount of coke-bed-carbon: 135 kg
- Temperature of coke bed: 1600°C.

Two input temperatures of stainless steel waste have been taken into account: Room temperature of 20°C, which means addition of solid input material (e. g. dust) and 1400°C, which is equivalent to the temperature of a pre-molten slag e. g. from a cupola furnace.

The chemical composition of the stainless steel slag taken into account for the model calculations is presented in **Table 13**. This slag is the high-Cr EAF slag (see chapter 3.3.1.1) with an addition of 15 % SiO_2 for achieving a liquid slag.

Table 13: Chemical composition of the stainless steel slag taken into account for the model calculations

	CaO	**SiO_2**	**MgO**	**Al_2O_3**	**MnO**	**Cr_2O_3**	**FeO**
Mass fraction in wt.-%	38	31	5	4	2	22	1

The aim of thermochemical equilibrium calculations for processing of molten stainless steel slag in the coke bed reactor is the determination of the following parameters:

- Required temperature for the reduction of Cr_2O_3
- Coke consumption of the coke bed reactor
- Chemical composition of output phases
- Necessary heat supply for different of the input material (slag) temperatures (20°C and 1400°C)

The result concerning the chrome reduction and behaviour of carbon is reported as follows. **Figure 65** shows the amount of the main chrome and carbon containing compounds in dependence of temperature.

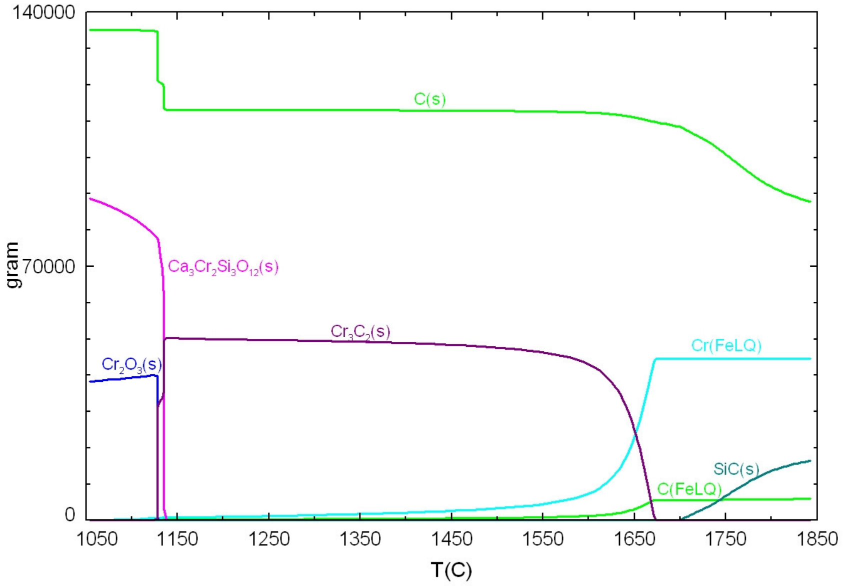


Figure 65: Amount of the main chrome and carbon containing compounds in dependance of temperature

According to the thermochemical calculations, beginning with a temperature of slightly lower than 1150°C, all chromium is stable as chromium carbide. Chromium reduction from the chromium carbide takes place within the temperature interval between 1550°C and 1675°C. Here metallic chromium is formed, which reports to the metal phase (FeLQ ->liquid steel). Above 1700°C further carbon is consumed for SiC formation.

Within the temperature interval of 1350°C to 1650°C, the calculated slag composition remains almost constant. With further increasing temperature, the basicity (CaO:SiO_2 ratio) rises. The alumina content increases and the MgO content decreases at the same time. The calculated chromium content of the metal phase rises up to 75 % at 1670°C, which makes it a valuable pre-alloy. For complete chromium reduction in the coke bed reactor for an input material temperature of 20°C a total heat supply of 275 kWh is estimated. The results of the coke bed reactor process model are summarised as follows:

- The reduction of Cr_2O_3 effectively begins at a temperature of 1575°C and is completed at 1670°C,
- The coke consumption is approximately 25 kg/h in the inductively heated coke bed,
- The heat supply per hour for 300 kg input slag is approximately 275 kWh for an input material temperature of 20°C and approximately 85 kWh for an input material temperature of 1400°C (e. g. premolten slag).

Based on the results of smelting technology trials of BEGMBH, the BFI has performed the optimisation and validation of the previously developed carbothermic reduction model. The initial model is a one stage reactor assuming a uniform temperature distribution in the coke bed by inductive heating. But results of inductive heating trials clearly showed that in the inductively heated coke bed a concentric heat distribution exists with the highest temperature (best inductive coupling) at the outer part near the induction coil and the lowest temperature (lowest inductive coupling) in the centre of the coke bed.. So, the concentric heat distribution in the coke bed reactor has been taken into account for the model optimisation.

Consequently, an optimised coke bed reactor model has been developed by use of FactSage and HSC software, which is divided into two main reaction units, representing different reaction temperatures. The temperature in the outer area is defined to 1600°C and in the inner area 1400°C. The input components of each reaction unit are “input slag”, “coke” and “false air”. Additionally, an energy feed (thermal energy -> induction heating) is added to the reaction units. The distribution of input components and phases between the reaction units is defined by the user. The output phases are “output slag”, “output metal” and “exhaust gas”, which contains the gas phase and dust components. For calculation of composition and temperature of each final output phase, mixer units have been integrated, which are charged by the corresponding phases from both reaction zones. All output phases finally enter the unit “Heat exchange Output”, in which a further overheating of the components (Energy feed) is performed and the output temperature of all phases is equalised. A schematic diagram of the optimised coke bed reactor model is presented in **Figure 66**.

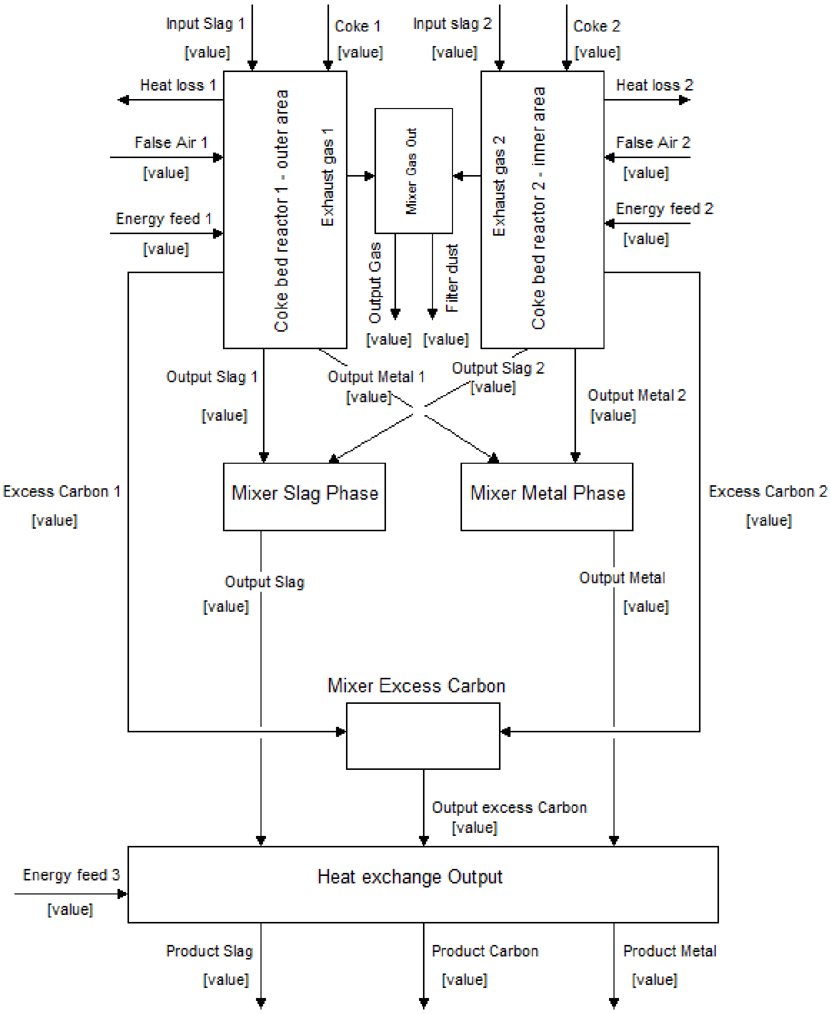


Figure 66: Schematic diagram of the optimised coke bed reactor model

In each of the process units mass and energy balancing is performed. The element distribution in the main reaction units “Coke bed reactor 1 – outer area” and “Coke bed reactor 2 – inner area” is calculated according to different element distribution models, which have been developed by thermochemical equilibrium calculations with reference residual materials by use of the FactSage Software. The resulting element distribution tables have been integrated in the HSC software for setting up an overall process model of the coke bed reactor. In **Table 14** and **Table 15** the element distribution model for the coke bed reactor at 1400°C respectively 1600°C is presented. These distribution tables have been calculated by chemical equilibrium calculations with the FactSage software. Reference input material for the calculations is a typical cupola furnace slag with addition of a spray roasting residue (15 % of metallic charge).

Table 14: Element distribution model for coke bed reactor at 1400°C

Phase	Al	Ar	C	Ca	Cr	Fe	H	Mg	Mn	Mo	N	Ni	O	S	Si	Zn
Gas phase	0,0	100	99,4	0	0	0	100	0	0,6	0	100	0	46,4	0	0	100
Slag incl. pure mineral species	100	0	0	100	0	0,8	0	100	99,16	96,7	0	0	53,6	100	51,8	0
Metal phase	0	0	0,6	0	100	99,2	0	0	0,24	3,3	0	100	0	0	48,2	0
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Table 15: Element distribution model for coke bed reactor at 1600°C

Phase	Al	Ar	C	Ca	Cr	Fe	H	Mg	Mn	Mo	N	Ni	O	S	Si	Zn
Gas phase	0	100	99,4	0	0	0,1	100	3	32,2	0	100	0	52,5	0,4	0,1	100
Slag incl. pure mineral species	100	0	0	100	0	0,1	0	97	42	82,2	0	0	47,5	99,6	40,7	0
Metal phase	0	0	0,6	0	100	99,8	0	0	25,8	17,8	0	100	0	0	59,2	0
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

The distribution of false air, input slag and coke between the reaction units has been defined to 67 % to the outer area of the coke bed reactor and 33 % to the inner area, assuming that the inner area has half the diameter of the outer area. Further input parameters of the model are the starting composition of the slag and the desired tapping temperature of the coke bed reactor.

3.3.2.9 Adaptation of cupola process model for Waste oxide melting (Task 4.3)

Based on initial calculations by the SimuSage software and on the existing BFI cupola furnace model, a new element and component distribution model including heat and material balances has been developed by use of the HSC software. This model is able to predict successfully the chemical composition and the amount of the products at given input materials for the cupola furnace process.

For normal operation of the cupola furnace, the following input streams have been applied: Coke, limestone, dolomite, FeSi, iron scrap, pig iron, hot blast (air, 500°C) and false air (5 vol.-% of hot blast). The chemical composition of the calculated input materials is based on operational data of the cupola furnace process. The output streams of the cupola furnace process are: Cast iron, slag, top gas dust and process gas. In **Table 16**, for these output streams the new calculated element distribution model is presented, which resulted in realistic amount and composition of the output materials streams. The calculated amount of the different materials streams (based on 1000 kg of cast iron) is shown in **Figure 67**.

Table 16: New developed element distribution model

	Al	**C**	**Ca**	**Cr**	**Fe**	**H**	**Mg**	**Mn**	**Mo**	**N**	**Ni**	**O**	**S**	**Si**
	Distribution in wt.-%													
Cast iron	0	23	0	50	99,9	0	0	94	0	0	100	0	66	74
Slag	97,5	0	99,4	50	0,1	0	98	6	100	0	0	7,98	30,5	24
Top gas dust	2,5	0,4	0,6	0	0,1	0	2	0	0	0	0	0,4	1,8	2
Process gas	0	76,6	0	0	0	100	0	0	0	100	0	91,6	1,8	0
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100

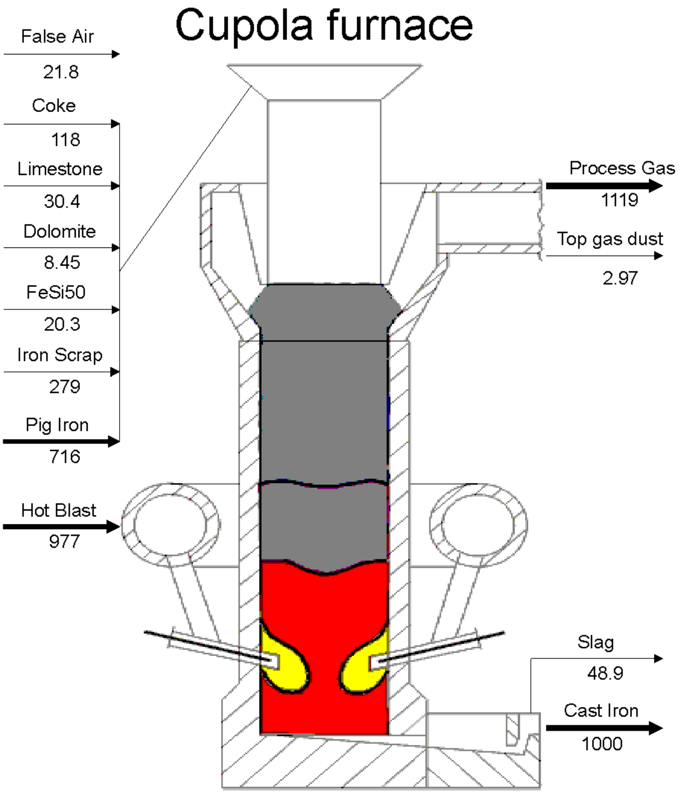


Figure 67: Amount of the different materials streams calculated by the cupola process model (in kg; based on 1000 kg of cast iron)

In **Table 17** to **Table 19** the calculated chemical composition of the output streams of the cupola process are presented.

Table 17: Calculated chemical composition of cast iron

Cast iron	Cast iron in wt.-%
Fe	93,3
C	3,4
Si	2,5
Mn	0,7
Cr	<< 0,1
S	0,1

Table 18: Calculated chemical composition of slag and top gas dust

Slag and dust	Slag in wt.-%	Top gas dust in wt.-%
C		20,1
Al_2O_3	8,9	3,8
SiO_2	43,8	47,8
CaO	39,3	3,9
Cr_2O_3	0,25	
MgO	3,3	1,1
MnO	1,2	
FeO	2,5	
Fe_2O_3	0,0	22,5
S	0,9	0,8

Table 19: Calculated chemical composition of the process gas

Process gas	Process gas in vol.-%
CO	16,7
CO_2	8,0
N_2	69,4
O_2	4,2
SO_2	0,002
H_2O	0,3
H_2	1,5

The results of the calculation are similar to operational cupola furnace process data. This proves the applicability of the new distribution model for the cupola furnace process. The adapted cupola furnace model will be the basis for the combination with the inductively heated coke bed model (Task 4.4).

3.3.2.10 Combining inductively heated coke bed model with adapted cupola process model (Task 4.4)

For combining the inductively heated coke bed reactor and the cupola furnace, the respective models (Tasks 4.1, 4.2, 4.3) have been linked together by the BFI. In **Figure 68** a schematic view of the combined process is presented.

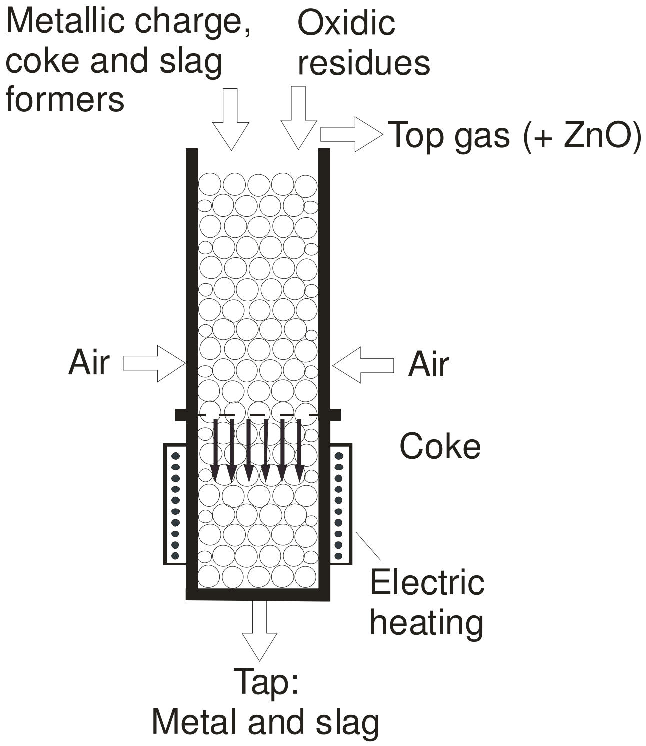


Figure 68: Schematic view of the combined cupola furnace, coke bed reactor process

The cupola furnace is used for premelting and prereduction of the residues. The oxidic residues are introduced in the cupola furnace in a quantity of 15 % of the metallic input. The product slag of the cupola furnace is fed to the coke bed reactor, where the final reduction of metal oxides takes place. The metal phase from the cupola furnace (Cast iron) does not react any more in the coke bed reactor, and consequently is introduced in the mixer unit for the metal phase within the coke bed reactor model. Here it is mixed with the metal output of the two coke bed reactor reaction units.

For comparison, two different residues with a high chromium content have been considered: A high-Cr EAF slag from stainless steelmaking and a spray roasting residue (chemical analysis, see chapter 3.3.1.1.). The main differences between both selected residues are the iron content, which is high for the spray roasting residue and low for the EAF slag, as well as the content of slag forming components, which is high for the EAF slag and negligible for the spray roasting residue. So, the process simulation using both types of residues gives a good overview on different possible operational modes of the combined cupola furnace / coke bed reactor process.

The material balance for processing 1000 kg of a **spray roasting residue** within the cupola furnace is presented in **Table 20**. The spray roasting residue amounts to 15 % of the metallic charge of the cupola furnace (FeSi, Iron Scrap, Pig iron). For these conditions, the slag output is 510 kg/t of residue and the Cast iron output is 7.150 kg/t of residue.

Table 20: Material balance for processing 1000 kg of a spray roasting residue within the cupola furnace

Input	kg	Output	kg
False air	144	Process gas	7503
Coke	771	Top gas dust	20
Limestone	196	Slag	510
Dolomite	52	Cast iron	7150
FeSi	131		
Iron Scrap	1824		
Pig Iron	4680		
Hot blast	6386		
Spray roasting residue	1000		
Total	15183	Total	15183

The material balance for processing the product slag of the cupola furnace within the coke bed reactor (reference: 1000 kg spray roasting residue) is presented in **Table 21**. The product slag amounts to 265 kg/t of spray roasting residue and the amount of the product metal to 148 kg/t of spray roasting residue.

Further, a low amount of unreacted excess carbon (14 kg/t) leaves the coke bed reactor.

Table 21: Material balance for processing the product slag of the cupola furnace within the coke bed reactor (reference: 1000 kg spray roasting residue)

Input	kg	Output	kg
False air	22	Process gas	175
Coke	71	Filter dust	7
Input slag	510	Product slag	265
Balance	5	Product metal	148
		Excess carbon	14
Total	608	Total	608

The overall amount of product metal from both parts of the coupled process is 7.298 kg/t of spray roasting residue.

The chemical composition of the final product slag (coke bed reactor) for processing of a spray roasting residue is presented in **Table 22**. The final slag is (nearly) free from chromium oxide and iron oxide and to a large extent only contains slag formers.

Table 22: Chemical composition of the final product slag (coke bed reactor) for processing of a spray roasting residue

Component	wt.-%
SiO_2	34,6
Al_2O_3	11,8
CaO	47,6
Cr_2O_3	0
MgO	4,0
MnO	0,85
FeO	0,009
Fe_2O_3	0
S	1,3

The chemical composition of the final product metal (after mixing of the product metals from Cupola furnace and coke bed reactor) for processing of a spray roasting residue is presented in **Table 23**. The product metal is a cast iron (C and Si: ca. 3 %) with elevated content of chromium (2,4 %) and Ni (1,1 %).

Table 23: Chemical composition of the final product metal (after mixing of the product metals from Cupola furnace and coke bed reactor) for processing of a spray roasting residue

Element	wt.-%
Fe(l)	89,9
C	3,1
Si(l)	2,9
Cr	2,4
Ni(l)	1,1
Mn(l)	0,6
Mo	0
S	0,08

The material balance for processing 1000 kg of a **high-Cr EAF slag** within the cupola furnace is presented in **Table 24**. The EAF slag input amounts to 15 % of the metallic charge of the cupola furnace (FeSi, Iron Scrap, Pig iron). For these conditions, the slag output is 1288 kg/t of residue and the cast iron output is 6.712 kg/t of residue.

Table 24: Material balance for processing 1000 kg of a high-Cr EAF slag within the cupola furnace

Input	kg	**Output**	kg
False air	144	Process gas	7157
Coke	771	Top gas dust	26
Limestone	196	Slag	1288
Dolomite	52	Cast iron	6712
FeSi	131		
Iron Scrap	1824		
Pig Iron	4680		
Hot blast	6386		
Spray roasting residue	1000		
Total	15183	Total	15183

The material balance for processing the product slag of the cupola furnace within the coke bed reactor (reference: 1000 kg high-Cr EAF slag) is presented in **Table 25**. The product slag amounts to 670 kg/t of EAF slag and the amount of the product metal to 373 kg/t of EAF slag.

Further, a low amount of unreacted excess carbon (34 kg/t) leaves the coke bed reactor.

Table 25: Material balance for processing the product slag of the cupola furnace within the coke bed reactor (reference: 1000 kg high-Cr EAF slag)

Input	kg	**Output**	kg
False air	56	Process gas	442
Coke	180	Filter dust	17
Input slag	1288	Product slag	670
Balance	13	Product metal	373
		Excess carbon	34
Total	1537	Total	1537

The overall amount of product metal from both parts of the coupled process is 7.068 kg/t of EAF slag.

The chemical composition of the final product slag (coke bed reactor) for processing of a high-Cr EAF slag is presented in **Table 26**. The final slag is (nearly) free from chromium oxide and iron oxide and to a large extent only contains slag formers.

Table 26: Chemical composition of the final product slag (coke bed reactor) for processing of a high-Cr EAF slag

Component	wt.-%
SiO_2	24,0
Al_2O_3	9,1
CaO	58,4
Cr_2O_3	0
MgO	7,7
MnO	0,3
FeO	0,002
Fe_2O_3	
S	0,42

The chemical composition of the final product metal (after mixing of the product metals from Cupola furnace and coke bed reactor) for processing of a high-Cr EAF slag is presented in **Table 27**. The product metal besides C (3,2 %) contains an elevated content of silicon (5,2 %) and chromium (2,5 %).

Table 27: Chemical composition of the final product metal (after mixing of the product metals from Cupola furnace and coke bed reactor) for processing of a high-Cr EAF slag

Element	wt.-%
Fe(l)	88,2
C	3,2
Si(l)	5,2
Cr	2,5
Ni(l)	0
Mn(l)	0,9
Mo	0
S	0,09

3.3.2.11 Process concepts and cost optimisation (Task 5.1)

BFI

As described in chapter 3.3.2.10, the BFI has modelled two different scenarios of operational conditions concerning processing of oxidic residues by a coupled process of cupola furnace and iductively heated coke bed reactor. The first scenario involves the processing of a spray roasting residue (high Fe, Cr, Ni; no slag formers), while in the second scenario the processing of a high-Cr EAF slag from stainless steelmaking is modelled. In contrast to the first residue, the high-Cr EAF slag contains a high amount of Cr and slag forming components and a very low amount of iron. By comparison of the required energy and consumables demand for processing of both types of residues, an economic assessment for the processing of these very contrary residues is performed. In **Table 28** the coke and electric energy demand for the coupled cupola furnace / coke bed reactor process is compared for processing of the two different residues. The reported data are based on an amount of 1000 kg of residue, a coke bed reactor tapping temperature of 1600°C and an inductive conversion efficiency of electric energy to thermal energy of 60 %.

Table 28: Comparison of coke and electric energy demand for the coupled cupola furnace / coke bed reactor process (processing of 1000 kg spray roasting residue resp.high-Cr EAF slag)

		Spray roasting residue	High-Cr EAF slag
Coke consumption (total) 1)	In kg	842	951
Coke consumption of coke bed reactor unit 1)	In kg	71	180
Thermal energy feed – coke bed reactor unit 1)	In kWh	981	1743
Electric energy consumption coke bed reactor unit 1), 2)	In kWh	1635	2905
Electric power (300 kg input slag/h) 1), 2), 3)	In kW	962	677

1) related to 1000 kg of residue; Tapping temperature of coke bed reactor 1600°C
2) inductive conversion efficiency electric energy -> thermal energy = 60 %
3) related to processing of 300 kg input slag per hour

Since the coke consumption of the cupola furnace unit is estimated to be equal for processing of both residues, the differences of coke and electric energy consumption are attributed only to the coke bed reactor unit. For processing of 1000 kg residue, the coke consumption of the coke bed reactor unit is 2,5x higher for the high-Cr EAF slag compared to the spray roasting residue. (180 kg resp. 71 kg). Also the thermal energy feed and the electric energy consumption is significantly higher for processing of the EAF slag compared to the spray roasting residue (factor: 1,8). Both, coke and energy consumption is significantly higher for the EAF slag, because the slag amount to be processed is much higher (265 kg product slag for 1 t of spray roasting residue, 670 kg slag for 1 t of high-Cr EAF slag). Generally, the electric energy consumption of the coupled process is high with 2905 kWh respectively 1635 kWh for processing 1 t of the EAF slag respectively the spray roasting residue.

In order to estimate the required electric power connection for the inductively heated coke bed reactor, the power demand has been related to 300 kg input slag per hour, which is the design value of the coke bed reactor model. In this case the power demand is higher for the spray roasting residue (962 kW) than for the high-Cr EAF slag (677 kW), because the spray roasting residue contains a higher amount of iron- and Ni-oxide and consequently the energy demand for the reduction of the oxides increases.

BEGMBH

One essential part for the evaluation of the coupled Flash reactor and InduCarb process for treating stainless steel residuals is a mass and energy balance of the whole process chain. The mass and energy balance presented in the following diagrams is mainly based on the results of the coupled trials as well as on a few theoretical and thermo chemical calculations. Since the treatment of the EAF dust is the main aim of the investigated process the displayed mass and energy balance is normalized to 1 ton of EAF dust.

Since the Flash Reactor only serves as an oxidizing smelting unit, no major changes on the smelted EAFD occur. This becomes obvious when looking at the mass balance of the Flash Reactor, displayed in **Figure 69**. According to it from 1000 kg of EAFD and 50 kg of fluxes (SiO_2) put into the Flash Reactor result around 960 kg of liquid slag and 83 kg of flue dust. The flue dust mainly consists of mechanical carry over, of vaporized chlorides and fluorides as well as of some ZnO. The loss of Zn during the oxidizing smelting can be explained as follows: Although the flame of the Flash Reactor is run at a lambda of > 1 there exist reducing parts in the flame (in the area where the CH_4 is mixed with the O_2). In these parts the ZnO of the dust is reduced to Zn, which then immediately vaporizes. Although the Zn-vapour is then reoxidized in the oxidizing Flash Reactor atmosphere these fine particles of ZnO don’t melt and go into the slag but are removed with the off-gas. The Zn losses through this phenomenon amount to roughly 15 % of the total Zn contained in the EAF dust – however to minimize these losses it is intended to reprocess the carry-over dust in the Flash Reactor by mixing it with the EAFD.

The mass balance also shows that the oxygen demand of the Flash Reactor is quite high, since the melting of 1 t of EAFD requires around 550 kg or 385 Nm^3 of pure oxygen, which represents an essential cost factor for the whole process. The CH_4 requirement amounts to 125 kg or 175 Nm^3 per ton of EAFD.

In the second step - the InduCarb reactor - the reduction of the liquid slag, coming from the Flash Reactor, occurs. Since the InduCarb reactor is a very powerful reduction unit and the liquid premelt contains a lot of reducable metal compounds the main part of the slag coming from the Flash Reactor is transferred into a valuable iron alloy. This means that after the reduction process only 185 kg of (an inert) slag remain while simultaneously 455 kg of metals in the form of an iron alloy are recovered. Additionally 171 kg of zinc vapour are formed, which leave the InduCarb reactor as a part of the 477 kg of off-gas, which is then treated according to the suggested gas reforming process.

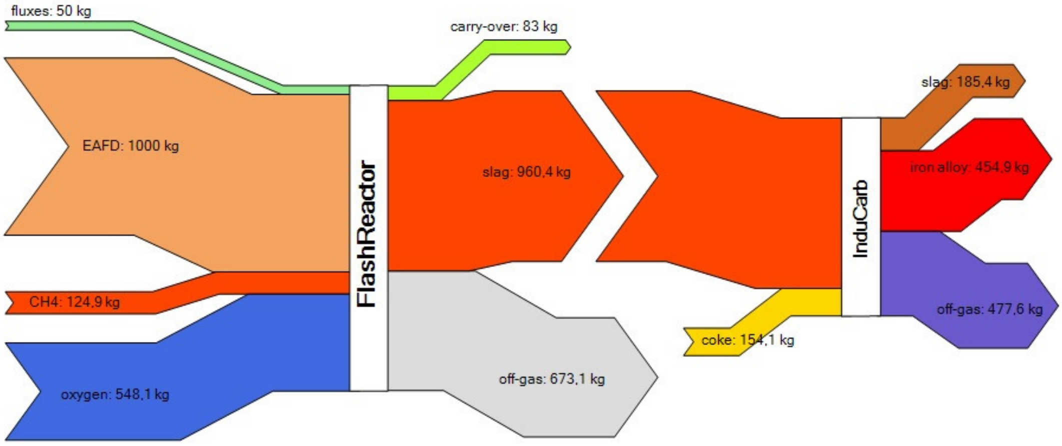


Figure 69: Mass balance for the treatment of 1 t of EAFD with the combined Flash Reactor – InduCarb process

A mass balance of this gas reforming process is shown in **Figure 70**. The off-gas itself is composed of 19.3 % of Zn vapour (171 kg, 58.7 Nm^3) and 80.7 % of CO (306 kg, 245.1 Nm^3) so it represents both an energy source (CO) as well as a zinc carrier. To recover the Zn as pure ZnO from the off-gas and to simultaneously use the chemical energy of the off the gas reforming process, described in WP 3.4, was developed. As the mass balance shows the off-gas is turned from CO and gaseous Zn into 213 kg of (pure) ZnO as well as into 203 Nm^3 of CO and 100 Nm^3 of H_2 (and 42 Nm^3 of CO_2) by the addition of 176 kg of water in the gas reforming step. So after a further cooling step, a filtering of the ZnO and a H_2O condensing step this gas can be used as fuel for the Flash Reactor and substitute there CH_4.

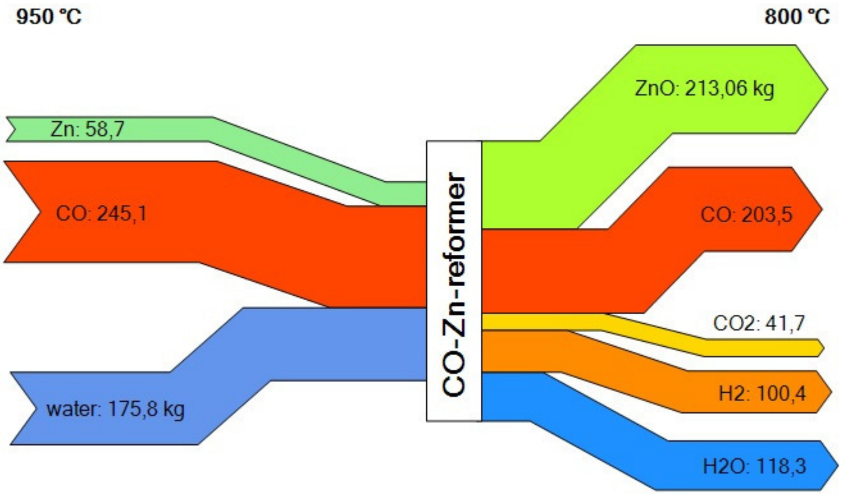


Figure 70: Mass balance of the gas reforming step for the InduCarb off-gas (unit: Nm^3 - if not displayed differently)

Since the slag is inert, doesn't contain any harmful heavy metals and shows stable elution behaviour it is not a waste product but a raw material for further applications (cement industry, road construction, etc.). The iron alloy represents a valuable raw material for stainless steel production (75 % Fe, 10 % Cr) and the off-gas is an energy source as well as a Zn carrier. In the end this means that the coupled Flash reactor – InduCarb process is able to turn the (as harmful waste classified) EAFD in to valuable products without generating any harmful side products. From the technical point of view this makes the process very attractive and advantageous for the treatment of EAFD.

However there is also an energetic aspect, which has to be discussed in order to classify the process. In this context **Figure 71** shows the energy balance of the whole process chain. In total the process requires an energy supply of 9215 MJ in order to treat 1 t of EAFD – thereof come 4477 MJ from the burning of CH_4 with O_2 and 4739 MJ or 1.31 MW are supplied in the form of electrical energy in the InduCarb reactor. This high energy consumption is mainly caused by the high temperatures recovered in both the Flash Reactor as well as in the InduCarb. In order to reduce the total energy consumption a coke preheating has been suggested (see task 3.3) and an (chemical) energy recovery from the InduCarb off-gas by the developed gas reforming process. In total these measurements allow to save roughly 2000 MJ, but nevertheless is the remaining energy demand (~7.000 MJ) still significantly high. Especially the heat losses with the off-gas in the Flash Reactor (2.455 MJ) and the losses caused by the conversion of the electrical energy to thermal energy in the InduCarb reactor (1.658 MJ) are critical in terms of energy consumption, but are difficult to minimize.

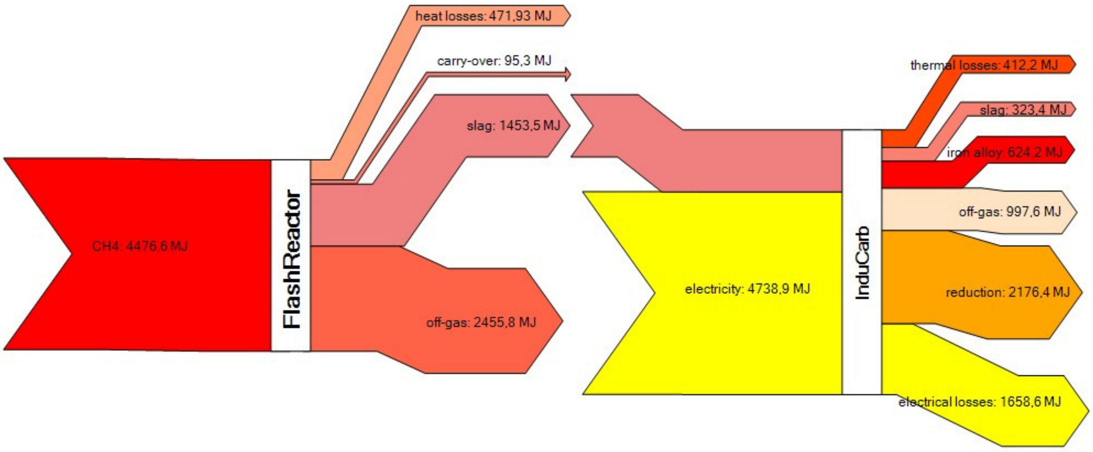


Figure 71: Energy balance for the treatment of 1 t of EAFD with the combined Flash Reactor – InduCarb process

In the simplified process flow-sheet, shown in **Figure 72**, the named energy saving measurements (coke preheating (23) & use of reformed gas as fuel in Flash Reactor (33)) are already included. In the suggested flow-sheet for the treatment of stainless steel residuals the first step is the Flash Reactor where the EAFD is molten with the help of a specially designed CH_4–O_2–dust burner (1-7). The off-gas from the Flash Reactor is first cooled (8-10), then dedusted by a cyclone (11-12) and finally filtered in a bag filter (13-14) before it is liberated into the atmosphere through the stack (15). The molten dust forms a liquid sump (16) at the bottom of the Flash Reactor from where it is continuously fed to the reduction unit – the InduCarb reactor (17-19). The gas formed during the reduction of the slag in the hot coke bed (80 % CO, 20 % Zn) leaves the InduCarb reactor in counter current flow to the remaining slag and iron alloy at the top of the reactor. The remaining slag as well as the iron alloy leave the reactor through a siphon system at the bottom of the reduction shaft. The sensible heat of the off-gas (1600 °C) is used to preheat the coke required in the InduCarb. In this step (21-23) the coke is preheated to a temperature between 982 °C and 1186 °C, depending on the coke consumption in the InduCarb reactor, while the off-gas is cooled to a temperature between 937 °C and 1028 °C. After the coke preheater the CO-Zn-gas mixture enters a dedusting unit (25-26) (removing of fine coke particles) and then enters the reforming unit (27-29), where it is transferred from a CO-Zn-gas to a mixture of CO, CO_2, H_2, H_2O and solid ZnO. After a further cooling step (30) the cooled off-gas enters a bag filter (31-35) in order to remove the pure ZnO. After this step the remaining gas can serve as additional fuel in the Flash Reactor.

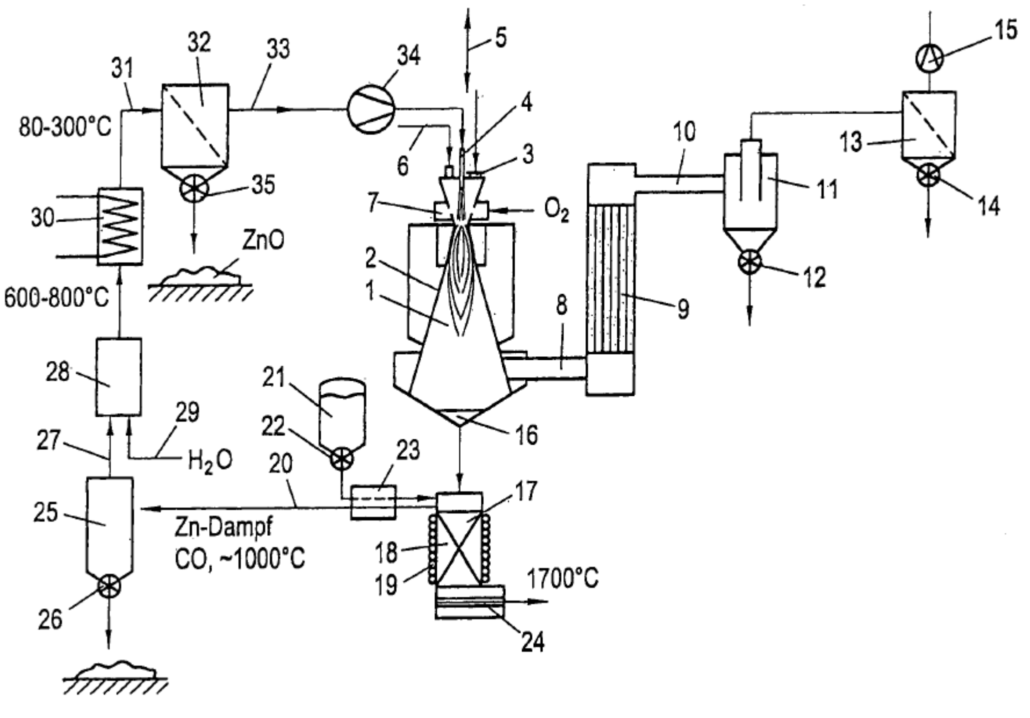


Figure 72: Simplified flow sheet of combined Flash Reactor and InduCarb process for treating stainless steel residuals

3.3.3 Briquetting with vegetable binders and briquette utilisation in EAF

3.3.3.1 Briquetting investigations (Task 2.3)

In order to identify principal operational parameters, preliminary briquettes have been produced by means of a laboratory apparatus. At first, it has been decided to analyse the binding behaviour, therefore in these tests no reducing agent has been added. In view of an industrial use, the most important characteristics of briquettes are: suitable density value (2.7 - 3.1 g/cm^3, so as to prevent floating on slags surface) and mechanical resistance to handling (without fragmentation or pulverisation).

The main steps for briquette preparation were:

- mixing of the solid components to facilitate the homogenization of the materials,

- water addition to activate the binding effect,
- charging of the mixture into the cylindrical shape mould, selected with specific dimensions (height and diameter),
- mechanical pressing,
- drying and storage of the obtained briquette.

A more detailed description of the procedure for briquette preparation is reported in **Annex 2**.

The minimum operative force, acting on the surface briquette, was 300 bar. This value has been demonstrated (see afterward figure 4) to be the minimum force in order to guarantee the compactness, to augment the density and the mechanical resistance to impacts, movements and all the different phases of management.

Mechanical pressing reinforced the bonds between the different materials. The supposed mechanism could be lied to the increasing of the surface contact among the units, made by gel surrounded particles, that reinforces mutual entangle of molecules.

In laboratory trials it has been proved that briquettes remain stable also when the storage takes place in not protected area. The high pressure value compacted briquette structure, reducing the ways for water entry. This means that the briquette remained protected by high humidity content of the environment.

The conducted experimentation has demonstrated the importance to use a suitable water percentage. In fact, three different percentages have been tested:

- 1% of water, the mixtures resulted too dry and the binding of the constituents was accomplished,
- 3% of water, the obtained briquettes were too much soft, not compact,
- 2% of water, the obtained briquettes were compact with un appropriate plasticity degree for not crushing during normal handling.

After pressing, the briquettes with a water content of 3% have been dried at 110°C. This procedure was done in order to verify if, eliminating water excess, briquettes could reach anyway a suitable compactness. Weight losses of briquettes at different drying time are shown in **Figure 73**.

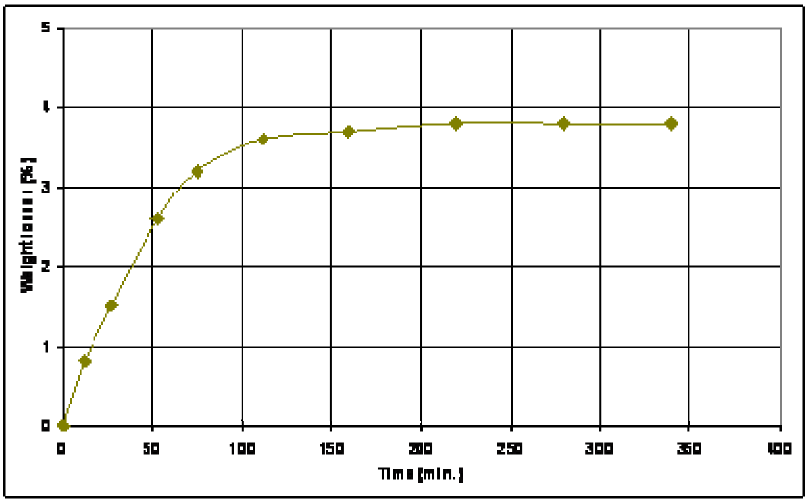


Figure 73: Weight loss versus time at 110°C

As it can see, weight losses (that is supposed to be only water) are higher than 3% due to the residual water content of the iron oxides. The most part of the water (>96%) is lost in 2 hours, so the drying can be considered complete. By drying, the viscosity of the gel structure is strongly increased (and the stability of the electrostatic bonds too). As a final result, a polymeric structure, glue that links together oxide particles, has been obtained and the briquette targets the desired mechanical resistance.

Dried briquettes are shown in **Figure 74**.

Figure 74: Dried briquettes

From an industrial point of view, in order to prevent floating on slags surface, it is important to reach, in the briquettes, a specific weight higher than 2.8 g/cm^3. The briquettes density has been measured: results showed that it is essential to apply a loading pressure higher than 300 bar to reach the desired density value (**Figure 75**).

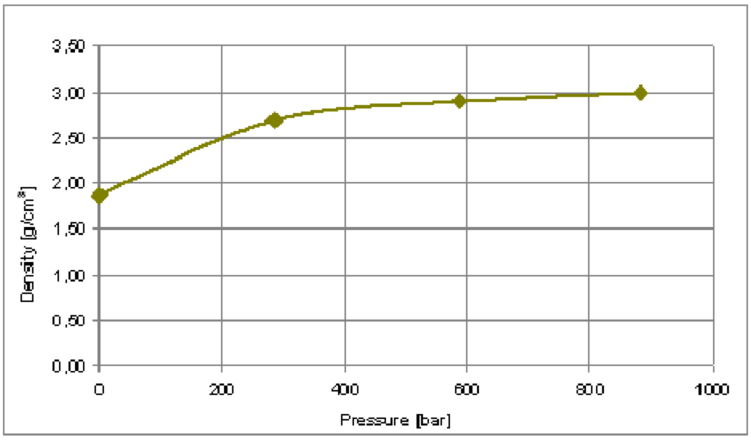


Figure 75: Density of the obtained briquettes versus loading pressure

In conclusion, a briquetting procedure has been defined and compact briquettes with suitable industrial mechanical characteristics and density value have been obtained.

The briquetting procedure has been tested with residual iron oxides. Three different types of iron residues have been utilised in order to have a suitable quantity of briquettes for pilot plant tests (about 15 for each type).

Their composition is reported in **Table 29** while the composition of corresponding briquettes, expressed as weight percentage, is reported in **Table 30**. In particular, the briquettes named A were made packing the “blast grinding” residual coming mainly from austenitic steel (size = 63 -250 µm); the B briquettes were packed using the “fine metals” residual and the C briquettes were build-up using very fine residual “blast grinding” coming mainly from ferritic stainless steel (size < 90 µm).

Both iron residuals, named A and B, have permitted to obtain compact and solid briquettes with a density value of 3.0 g/cm^3. Some of them (dried briquettes) have been utilised for a “fall test” over 1m in order to evaluate alteration due to the fall: no fracture could be observed after more than 10 falls.

Table 29: Composition of iron residual

Compound (%)	Iron residual A	Iron residual B	Iron residual C
Si	0,34	4,44	0,46
Al	0,08	0,53	0,12
Ca	0,11	5,71	0,14
Mg	0,14	0,48	0,19
Mn	0,69	0,32	0,76
Fe	79,1	67 + 11*	73,7
Ti	<0,05	<0,05	<0,05
Cr	5,5	1,37	13,3
Ni	2,25	0,07	0,59
V	0,03	-	0,08
O	11,71	9,08	10,61

* 11% represents the part of metal recovered/separated before the chemical analysis, it has been expressed as pure iron but more probably it is an alloy with Cr, Ni,…

Table 30: Composition of briquettes used in pilot plant tests

Compound	Briquettes A*	Briquettes B*	Briquettes C
Iron residual - %	79,4	83,3	81,2
Wheat flour - %	11,9	8,3	9,8
Fe-Si - %	7,6	7,5	5,7
Water - %	1,1	0,9	3,3

* after drying

In addition, analysis of the effects of temperature and humidity during briquettes storage has been carried out, with the aim to define the best industrial operative conditions. Briquettes preserve their characteristics for long time if stored in a dry environment. In **Figure 76** both type of briquettes after a storage of 3 months period are illustrated.

Figure 76: A (left) and B (right) briquettes after 3 months

On the contrary, iron residue named C, utilised in the same condition of the other types of residue, has a very bad briquetting characteristics: no one dried briquettes resulted sufficient compact and solid. It has been decided to not continue to use this type of briquettes.

In **Table 31** the geometric characteristics of the utilised briquettes are reported.

Table 31: Briquettes with different geometry

Briquettes:	*Small*	*Medium*	*Large*
Diameter (cm)	5,05	5,06	5,05
Height (cm)	1,58	2,66	3,14
Volume (cm^3)	31,6	53,5	62,8

3.3.3.2 Determination of optimised process parameter for industrial pre-treatment and recovery processes (Task 3.5)

Heat capacity and thermal diffusivity of the briquettes have been determined to evaluate the melting behavior and design properly the experimentation in pilot plant. The basic idea is to use an amount of briquettes enough to significantly modify the trace element concentration but, on the opposite side, to avoid the too rapidly decreasing of the furnace temperature caused by the briquettes charging. Moreover, it is important to ensure a rapid heating of the briquettes to promote the reactions of iron reduction and the consequent heat generation.

The heat capacity has been evaluated on the basis of an average chemical composition of the briquettes and considering the heat capacity of carbon for the wheat flour. The so calculated specific heat is 900 J/K/kg at 1600°C [1]. Thermal diffusivity has been measured by means of laser flash apparatus[3]: at 1350°C (temperature close to FeO melting) the measured thermal diffusivity is $2 \cdot 10^{-4}$ m/s^2.

An heating time (from room temperature to 1400°C) of 3 minutes per each briquettes has been estimated on the basis of the measured thermal diffusivity (this melting time should be even lower, because the briquettes size decreases during heating).

Considering both briquettes thermal diffusivity and heat capacity, a rapid start of their heating, and subsequent of the corresponding exothermic reactions of iron reduction, has been expected.

The determination of melting behaviour of the obtained briquettes has been performed during pilot plant tests. The behaviour at the melting of *A* and *B* briquettes have been tested in a VIM furnace (Vacuum Induction Melting, 10 litre crucible, see Annex 3) in argon atmosphere. A maximum pressure value of 350 mbar has been set up during the melting phase in order to hamper bubble formation in the metal bath. Melting temperatures have been measured by both pyrometer and thermocouple and the behaviour of briquette during the heating has been visually observed.

It has been decided to place both Fe ARMCO (used to simulate the EAF bath) and briquettes together in a graphite crucible and to heat the system until 1550°C. After Fe and briquettes complete melting, the system has been cooled in argon and solid samples have been collected for chemical analysis.

During the briquettes melting, temperature slowly decreased. This decrease (about 10°-15°C) was higher in case of *A* briquettes due to the longer melting time.

In the same inert atmosphere, briquettes *A* and *B* have shown a different melting behaviour, probably due to their different chemical composition. After the total Fe fusion, *A* briquettes melted in a period four time higher than *B* briquettes without fumes generation.

In case of *B* briquettes a dense black fume has been generated, suddenly at their melting starting, the observing porthole has been obscured for few minutes. At the end of the trial, carbon residues have been detected on the wall and a pungent odour has been smelt at the opening of the furnace (**Figure 77**).

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[3] In the flash technique, one surface of a sample with slab geometry is illuminated with a pulse of radiant energy, (laser) and the subsequent temperature transient is recorded at the opposite surface, by an infra-red sensor. The thermal diffusivity is evaluated from the temperature increasing.

These phenomena could be caused by the binder reaction in reducing atmosphere. *A* briquettes contained high concentration of metal oxides (in particular Fe and Cr) which oxygen has been used by the wheat flour carbon to produce CO/CO_2. B briquettes contain almost not oxidised metal forms and slag residues (the measured oxygen comes, mainly, from calcium silicate that is the major component of the slag, see Table 29). In this case the oxy-reduction reaction could not take place and the binder pyrolised/gasified.

The briquettes melting has been visually followed with a camera in both tests.

Figure 77: Carbon residue on the furnace wall after the melting test

Only in case of *A* briquettes, pure CaO has been added after the total metal melting. At the end of the test, the following samples have been collected: 2 samples of the metal part, at the top and at the bottom, and 1 sample of slag (**Figure 78**).

Figure 78: Metal part and slag after *A* (left) and *B* (right) briquettes tests

Chemical analysis have shown a high iron/alloy yield (Ni, Cr, Mn, Ti, yield > 96 %), as reported in **Table 32** - **Table 33**. The high carbon value measured in the metal is due to the partial dissolution of the crucible.

Table 32: Chemical analysis of metal phase (test with *A* briquettes)

Parameter	at the top	on the bottom	*Average value*
Si %	0,73	0,74	*0,735*
Al %	<0,01	<0,01	*<0,01*
Mn %	0,177	0,18	*0,179*
Ti %	<0,01	<0,01	*<0,01*
Cr %	0,68	0,69	*0,685*
Ni %	0,35	0,35	*0,35*
V %	<0,01	<0,01	*<0,01*
C %	6,39	6,41	*6,4*
P %	0,12	0,14	*0,13*

Table 33: Chemical analysis of metal phase (test with *B* briquettes)

Parameter	Metal part			Slag
	at the top	on the bottom	*Average value*	
Si %	0,6	0,63	*0,61*	13,5
Al %	<0,01	<0,01	*<0,01*	2,61
Mn %	0,246	0,243	*0,245*	-
Ti %	0,02	0,02	*0,02*	-
Cr %	2,50	2,54	*2,52*	0,22
Ni %	0,8	0,81	*0,8*	<0,01
V %	0,03	0,02	*0,025*	<0,01
C %	5,0	5,1	*5,05*	0,28
P %	0,15	0,18	*0,165*	0,01
Ca %	-	-	-	30,9
Mg %	-	-	-	3,18
S %	0,0005	0,0005	0,0005	0,16

Following the obtained data with *B* briquettes, new melting test has been performed in air atmosphere so as to better simulate the EAF conditions. For this test a muffle furnace and an alumina crucible have been used. The temperature has been increased until 1530°C, following permanence at 1370°C for five minutes that stabilised furnace temperature. After cooling, two phases have been identified, as already observed during pilot plant tests: a metal part and a glassy slag (**Figure 79**). This confirms the briquettes capacity to produce metal with high yield (> 90 %, confirmed also by the chemical analysis).

Figure 79: Metal and slag after B briquettes melting in oxidising atmosphere

The briquettes capability to remain at the interface slag/steel has been visually verified. At the end of the test, two samples of the metal part have been collected at the top and at the bottom. Chemical analysis have shown a high iron/alloy yield (Ni, Cr, Mn, Ti, yield > 96 %), as reported in **Table 34**.

Table 34: Chemical analysis of metal phase (test with *B* briquettes)

Table 11: Chemical analysis of metal phase

Briquettes:	*Small*	*Medium*	*Large*
Parameter	Average value	Average value	Average value
Si %	0,45	0,66	0,74
Al %	<0,01	<0,01	<0,01
Mn %	0,11	0,14	0,18
Ti %	<0,01	<0,01	<0,01
Cr %	0,53	0,61	0,68
Ni %	0,19	0,29	0,35
V %	<0,01	<0,01	<0,01
C %	6,2	6,6	6,4
P %	0,05	0,09	0,13

The high carbon value measured in the metal is due to the partial dissolution of the crucible.

Same procedure has been followed and same tests have been performed in case of briquettes of different geometry (see Table 31). Results confirms both the high iron/alloy yield and the briquettes capability to remain at the interface slag/steel.

3.3.3.3 Process concepts and cost optimisation (Task 5.1)

Preparation of a suitable quantity of briquettes for a pre-industrial experimentation, has been carried out. Wheat flour and water content quantity have been optimised.

Operative sequence of briquetting

A demonstrative plant for briquettes preparation has been used during CSM experimentation. Main characteristics are described in **Table 35** (see also Figure 79).

Table 35: Characteristics of briquettes machine

	Diameter (cm)	Surface (cm^2)	Pressure (bar)	Force (kgf/cm^2)
Cylinder	35	962	300	288488
Briquettes	10	79	3675	-

In **Figure 80** the operative sequence of the briquetting for the preparation of a suitable amount for pre-industrial trial is shown.

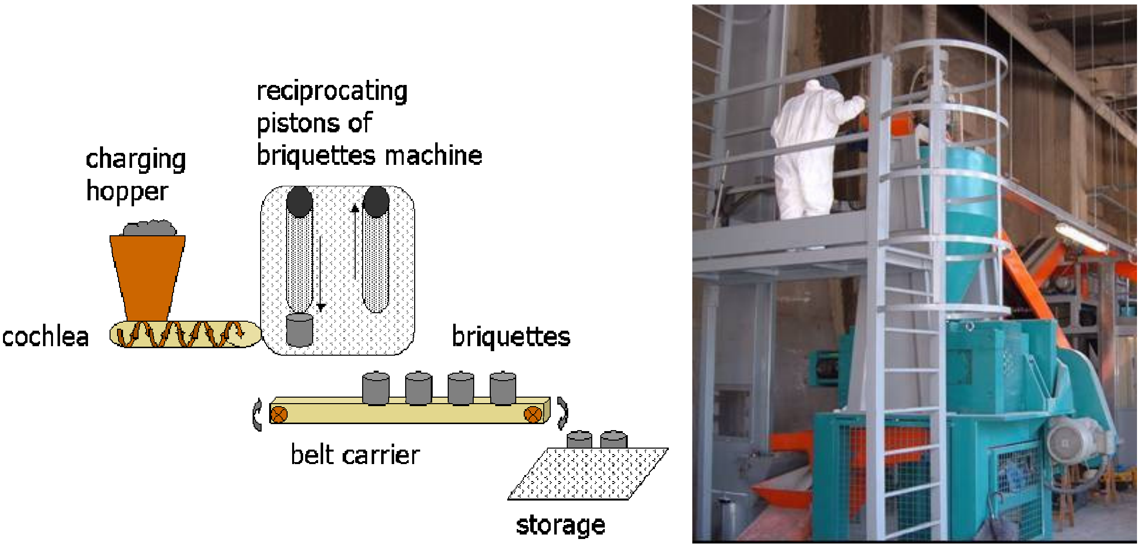

Figure 80: Scheme and photo of the briquetting system

The briquetting system functions as described in the following:

- material (additives and iron residual) are charged in the hopper and pushed in the briquetting machine by a cochlea, which movement is coordinated with the pistons movements,
- the material is pressed at about 3700 bar by reciprocating pistons,
- the formed briquettes are pushed out of the machine on a belt carrier and stored in a box.

The sequence of the operations is totally controlled by a PLC. Obtained briquettes are height 15cm.

<u>Encountered problems during the preparation of a suitable quantity of briquettes for the pre-industrial trial</u>

At first, briquette composition **A**, described in **Table 36** and utilised in melting tests in a VIM furnace, has been selected for the preparation of briquettes.

Table 36: Composition of briquettes

Compound	Briquettes **A**	Briquettes **A1**	Briquettes **A2**
Iron residual - %	79,4	79,4	82,3
Wheat flour - %	11,9	13,0	10,4
Fe-Si - %	7,6	7,6	7,3
External Water - %	1,1	0	0

During the preparation of briquettes, the machine showed operative difficulty. The performed maintenance procedure on the briquettes machine showed presence of a plastic water-flour-iron residual mixture that blocked part of the machine. Moreover, obtained briquettes were weak, wet and with a high tendency of crumbling (**Figure 81**).

Figure 81: Briquettes type A (weak and wet)

The reason has been identified in the too high water content of the utilised iron residual. A drying test performed on a sample of the utilised iron residuals, stored in open air and covered by a waterproof material, determined a water content of about 4%, higher than the expected one (**Figure 82**).

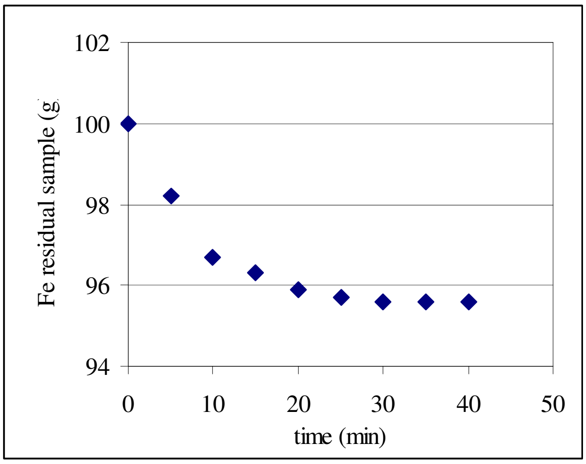

Figure 82: Weight loss of a iron residual sample during drying at 110°C

In order to adsorb water in excess and to prepare a new set of briquettes, the starting composition has been changed (Table 35, briquettes A1): additional water has been eliminated and higher quantity of wheat flour has been utilised. Briquettes, having this new composition, seamed more compact but, during normal operations of transport, they crumbled (**Figure 83**). Although water has been reduced, wheat flour content was too high (**Table 37**).

Figure 83: A1 briquettes

Table 37: Water and wheat flour percentage in the different briquettes

	Briquettes **A**	Briquettes **A1**	Briquettes **A2**
Water content of iron residual (%)	theor.: 0 real: 4,0	4,0	2,5
Wheat flour respect iron residual (%)	theor.: 15,0 real: 15,6	17,0	12,9
Water respect wheat flour (%)	theor.: 9,2 real: 35,9	24,4	19,8

In order to produce compact and resistant briquettes (as the obtained one in laboratory scale), a sample of iron residual has been dried and a final water content of 2,5 % has been obtained mixing dried and not dried iron residual. A new set of briquettes has been produced, named A2 (Table 35 - Table 36, **Figure 84**).

Figure 84: A2 briquettes

3.3.3.4 Productivity analysis of EAF briquette utilisation and comparison of the different technologies of briquette utilisation in EAF (Task 5.2, 5.3)

CSM has tested the behaviour at the melting of stainless steel briquettes during pre-industrial trials in a 1 ton capacity furnace (**Figure 85**).

Main characteristics of the CSM pilot DC electric arc furnace are:

- Transformer Power: 1.9 MVA
- Maximum current intensity: 6 kA
- Maximum active power: 1.5 MW
- Inner working shell diameter: 900 mm
- Electrode diameter: 350 mm

Feature and devices

- Sealing system for air leaching stop (tight furnace)
- Feeding systems for continuous addition
- Hollow electrode for gas and liquid injection into the plasma
- Dry de-dusting system
- Gas analysis both at the exhauster and at the stack
- Post combustion chamber
- Camera for internal observation and phenomena registration

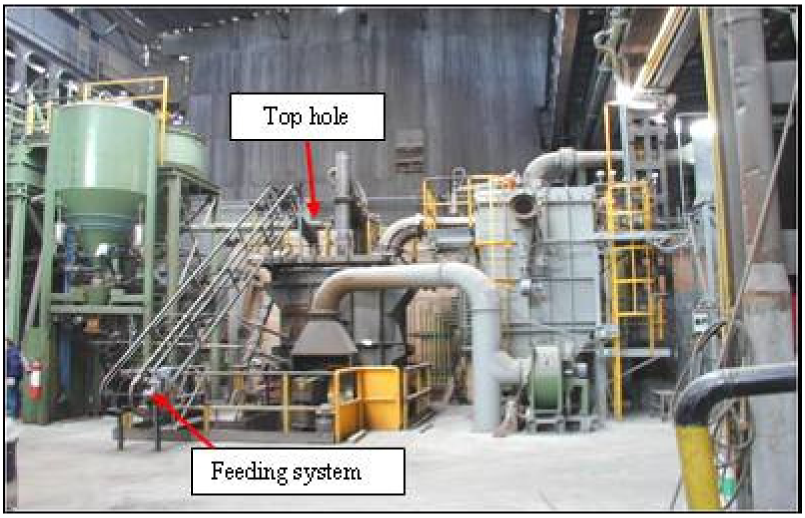

Figure 85: CSM pilot DC electric arc furnace

CSM has conducted two different trials in the DC electric arc furnace, in order to test the modality of briquettes charging in the EAF.

In order to ensure a small perturbation of bath temperature during briquettes charging/melting into the furnace, considering a metallic bath of 800 kg into the pilot furnace, it has been estimated, on the basis of both thermal diffusivity and heat capacity, a briquettes quantity to be used for tests in the range of 70-75 kg.

The *first test* has been carried out charging briquettes in a preformed bath (using scrap) in continuous charge. Metal bath samples have been collected at different time and chemically characterized, in order to define the yield of the process.

The preformed bath had the following characteristics:

- 800 kg of scrap
- 55 kg of synthetic slag (CaO – 35 kg, MgO – 6 kg, SiO_2 – 11 kg, Al_2O_3 – 3 kg)
- 45 kg of carbon steel scale

After the bath melting (1550 °C), a sample of metal was collected and, after that, 12 kg of Ni (99,9% of purity) was added as tracing for the process yield evaluation. Once Ni melted, a second metal sample has been collected. Then 70 kg of briquettes (A2 composition in table 12) have been added and a final metal sample has been collected after their complete melting. The briquettes were charged by means of a cup chain through a special top hole on the roof.

The dilution of Ni in the samples collected, demonstrated that the Fe yield are more than 90%, as shown in **Table 38**.

Table 38: Nickel concentration in the collected samples (trial 1)

	1 sample	2 sample	3 sample	yield
Ni	<0.5 mg/kg	1.33±0.05 %	1.21±0.05 %	90.97 %

Fume analysis conducted during the experimentation are reported in **Figure 86** (in particular, have been detected CO, NO_2 and O_2 - SO_2 was almost all the time under detection limit). As it can see, there is a decrease of O_2 each time that the furnace has operated having closed the top hole; there are some picks of CO due to the partial oxidation of the carbonious part of briquettes.

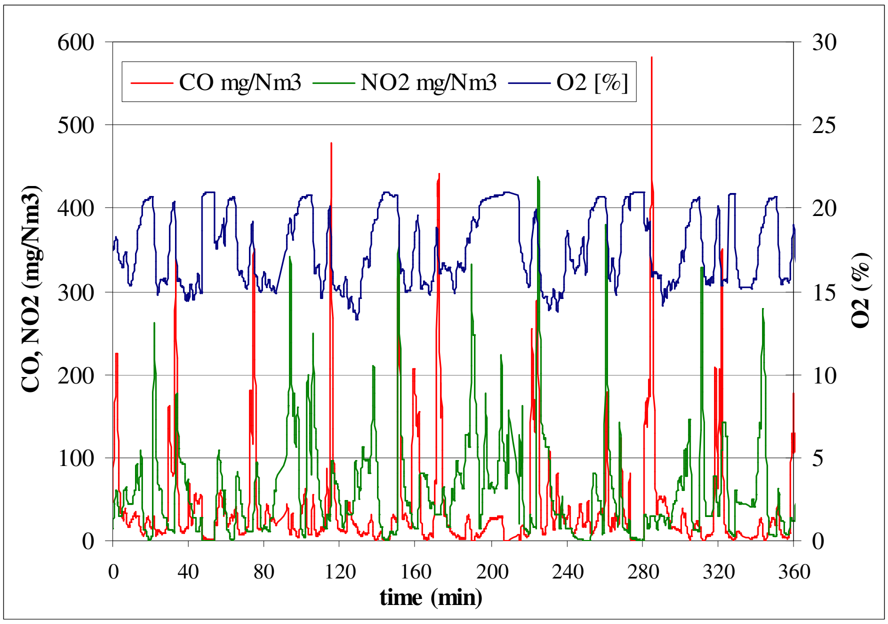

Figure 86: Fume analysis at the exit of the furnace (trial 1)

Analysis of slag composition and leaching are reported in **Table 39** - **Table 40**: all values are lower than the corresponding Italian Law limits for inert wastes (DM 3/8/2005, Tab.2).

Table 39: Composition of slags (trial 1 and 2)

	Trial 1	Trial 2
CaO %	60,74	63,98
MgO %	10,33	9,37
SiO_2 %	22,68	21,15
Al_2O_3 %	5,32	4,35
Cr_2O_3 %	0,18	0,21
NiO_2 %	<0,01	<0,01
V_2O_5 %	<0,01	<0,01
C %	0,66	0,86
P %	<0,01	<0,01
S %	0,02	0,03

Table 40: Leaching of produced slags (trial 1)

Parameter	Law limit Inert waste - µg/l	**Slags** µg/l	**Parameter**	Law limit Inert waste - µg/l	**Slags** µg/l
Cu	200	<0,05	**Sb**	6	n.d.
Zn	400	2,8	**Be**	-	<0,05
Ni	40	<0,05	**V**	-	<0,05
As	50	<0,05	**Co**	-	<0,05
Cd	4	0,06	**Mo**	50	n.d.
Cr_{tot}	50	<0,05	**DOC (mg/kg)**	50	n.d.
Pb	50	<0,05	**Cl^- (mg/kg)**	80	0,28
Ba	2000	<0,05	**F^- (mg/kg)**	1	0,32
Se	10	<0,05	**SO_4^{--} (mg/kg)**	100	1,06
Hg	1	<0,05	**NO_3^- (mg/kg)**		10,37

The performed test has shown that iron recovery reached value higher than 90%. Leaching of produced slags respected limits for inert materials.

The *second* has been carried out charging in batch a suitable quantity of briquettes together with scrap. Metal bath samples have been collected at different time and chemically characterized, in order to define the yield of the process.

The metallic bath had the following characteristics:

- 800 kg of scrap
- 75 kg of briquettes (same composition utilised in the first test)
- 10 kg of Ni (99,9% of purity, as tracing element)
- 55 kg of synthetic slag (CaO – 37 kg, MgO – 5.5 kg, SiO_2 – 10 kg, Al_2O_3 – 2.5 kg)
- 45 kg of carbon steel scale

After the bath melting (1550 °C), a sample of metal was collected. The melting time in this case has been more longer than the first test and the top hole of the furnace has been few time opened to control the accomplishment of the melting. Chemical analysis of the melted bath showed that the Fe yield is more than 90%, as shown in **Table 41**.

Table 41: Nickel concentration in the collected samples (trial 2)

	In the scrap	1 collected sample	yield
Ni	<0.5 mg/kg	1.09±0.05 %	90.32 %

Fume analysis conducted during the experimentation are reported in **Figure 87** (in particular, have been detected CO, NO_2 and O_2 – SO_2 was almost all the time under detection limit). Gases trend has similar to the observed one during the first test.

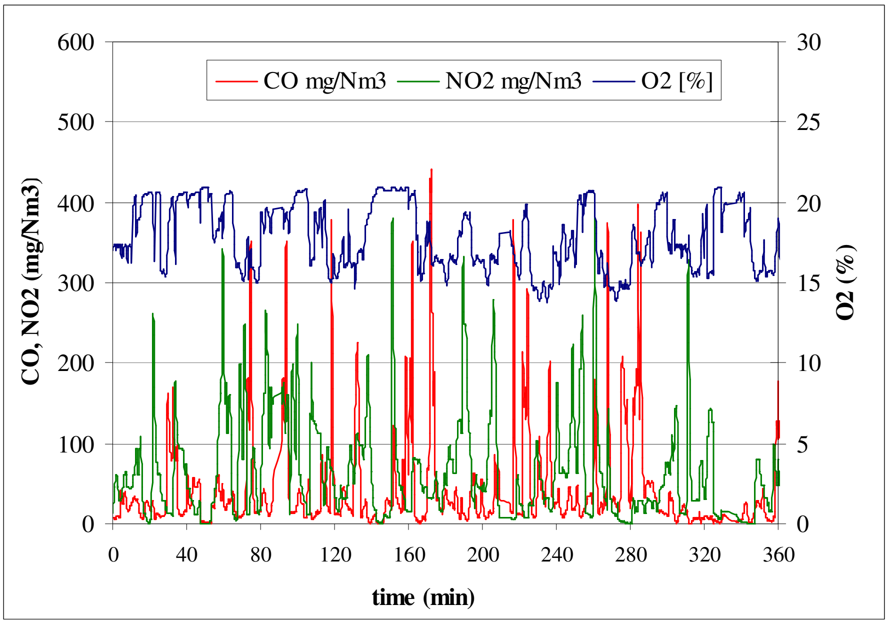

Figure 87: Fume analysis at the exit of the furnace (trial 2)

Analysis of slag composition and leaching are reported in Table 39 and **Table 42**: all values are lower than the corresponding Italian Law limits for inert wastes (DM 3/8/2005, Tab.2).

Table 42: Leaching of produced slags (trial 2)

Parameter	Law limit Inert waste - µg/l	**Slags** µg/l	**Parameter**	Law limit Inert waste - µg/l	**Slags** µg/l
Cu	200	<0,05	**Sb**	6	n.d.
Zn	400	1,7	**Be**	-	<0,05
Ni	40	<0,05	**V**	-	<0,05
As	50	<0,05	**Co**	-	<0,05
Cd	4	<0,05	**Mo**	50	n.d.
Cr_{tot}	50	<0,05	**DOC (mg/kg)**	50	n.d.
Pb	50	<0,05	**Cl^- (mg/kg)**	80	0,34
Ba	2000	<0,05	**F^- (mg/kg)**	1	0,46
Se	10	<0,05	**SO_4^{--} (mg/kg)**	100	2,15
Hg	1	<0,05	**NO_3^- (mg/kg)**		11,6

Preliminary economical evaluation of the developed process

A preliminary economical evaluation of the developed process has been done in order to estimate the advantages in the internal reuse of iron residue by means of briquettes preparation and utilisation.

Considered costs of briquettes components and recovered steel value are reported in **Table 43**.

Table 43: Considered costs for the economical evaluation

Parameter	Cost (€/t)
Binder (flour)	350
Ferrosilicon 75%	930
Recovered steel	300
Iron residues disposal cost (actual average)	3

It is supposed to recover 1 ton of iron residues by means of briquettes melting in the EAF furnace. The economical evaluation, considering only the briquettes production, seams to be favourable (about +130€ each ton of used iron residues, **Table 44**). Nevertheless, it is important to define costs lied to additional energy consumption and slag disposal (and eventual lime use[4]).

Table 44: Estimated costs/recovery

Parameters		self reducing	
	unit	weight	value (€)
Iron residues (disposal)	t	1	3
Briquette	t	1,22	
Binder	kg	126,37	-44,23
Ferrosilicon 75%	kg	88,70	-82,49
Production recovery	kg	850,01	255,00
Total			***131,28***

---

[4] Silicon requires additional lime to neutralise the acid effect on the slag due to the silicaformation

3.4 Conclusions – Overall evaluation, Process comparison (Task 5.4)

Inductively heated coke bed reactor process (BFI, BEGMBH)

As a first step of the investigations for development of the inductively heated coke bed reactor process, for selection of suitable residues data have been collected on physical properties and chemical composition of the residues. Suitable slag forming additives (mainly SiO_2) have been selected for providing a sufficiently liquid slag at the operating temperature (1600°C) of the coke bed reactor.
A basic design of the inductively heated coke bed reactor - including geometry, coke size and inductor power - has been worked out by BFI and BEGMBH. For definition of the coke bed reactor geometry the BFI has performed flow investigations at an original size cold model and laboratory trials concerning carbothermic chromium reduction kinetics. BEGMBH has performed inductive heating trials at a coke bed reactor test rig.
The diameter of the coke bed reactor was determined to 600 mm, the height to 800 to 1200 mm. A coke bed reactor of this size is able to process 300 l/h (approx. 900 kg/h) of liquid charged input slag. The optimum induction frequency determined between 75 and 105 kHz. The conversion efficiency (electric energy -> thermal energy) of the inductive heating resulted to 60 %.
Further, a concept and design of the peripheral equipment of the inductively heated coke bed reactor has been developed by BEGMBH. For coke feeding and preheating a unit with a pushing cyclinder and a vertical feeder have been investigated. Since the required pushing force of the coke pushing cylinder some cases exceeded the available hydraulic power, finally a vertical feeder concept has been selected for coke feeding and preheating.
For off gas treatment of the inductively heated coke bed reactor, a steam reforming process has been investigated by thermochemical calculations and finally tested by technical scale trials. The zinc and CO-containing off gas by use of water steam is converted into a ZnO product and a hydrogen and CO-rich off gas, which may be used as fuel in the Flash Reactor. The optimum temperature for treatment of the off gas is 800°C, at which the conversion degree of Zn to ZnO with nearly 100 % reached its maximum.
BEGMBH has developed a concept for coupling the flash reactor and the inductively heated coke bed reactor. At first, a suitable tapping concept for the flash reactor has been developed by comparison of different alternative concepts. The favoured flash reactor tapping concept resulted to be a spray feeding system, which uses a tundish where the melt is atomized with either a reactive (O_2, CH_4) or an inert gas (N_2) through the bottom tuyere directly on the coke bed. This concept allows a very uniform melt distribution over the cross-section of the coke bed. By technical scale trials, the coupling of both processes was tested. The composition of product slag and product metal phase have been analysed and the element distribution respectively the metal yield have been calculated: For the three valuable metals Cr, Fe and Ni a very high yield of 92 % to 96 % was achieved. Finally, mass and energy balances for the coupled process have been calculated for economic assessment and a process flow sheet for the final concept was proposed. The total energy input of the coupled flash reactor/coke bed reactor process was calculated to 2560 kWh/t of processed residue (not included: Credits due to coke preheating and gas reforming) of which 1316 kWh/t is the electric energy consumption of the inductively heated coke bed reactor.
BFI has developed a software based process model for the inductively heated coke bed reactor and a coupled process of a cupola furnace for premelting and pre-reduction of the residues and a coke bed reactor for final reduction. By use of the model, heat and material balances for two reference residues have been predicted as well as the chemical composition of the products slag and metal. Independently from the residue, the slag is free of valuable metals and the product metal is a cast iron (high Cr and Si) with elevated content of Cr (and Ni, depending on residue). As a base for economic assessment of the coupled cupola furnace/coke bed reactor process, the electric energy consumption and the coke consumption have been determined. Depending on the type of residue the coke consumption of the coke bed reactor unit lies between 71 and 180 kg per tonne of processed residue and the electric energy consumption of the coupled process is in the range of 1635 - 2905 kWh/t.

Briquetting with vegetable binders and briquette utilisation in EAF (CSM)

During this project CSM has been developed a technology for briquetting in order to reuse iron oxides residual from stainless steelmaking to be operated by the steelworks itself.

CSM has selected both iron oxides residuals and vegetable binders to produce suitable briquettes for pilot plant scale tests. In particular, concerning vegetable binders, wheat flour has been chosen due to its easy availability and lower cost (especially in case of expired flour). Main briquetting process parameters, as forming pressure and humidity content, have been set up and correlate with the briquettes density. Conclusion on the briquettes preparation are:

- water content higher than 3 % causes weak and crumble briquettes,
- a content of wheat flour higher than 13 %, although has the function to absorb excess of iron residual water, results in a lack of mechanical resistance of the briquettes,
- briquettes, at the exit of the machine, need a storage in aerated and dry location, so as to favour the drying of the binding agent and the obtainment of a material more resistant to traction and flexion.

Different briquettes, in terms of forms, dimensions and type of steelwork residual, have been prepared in order to analyse their behaviour at the melting. Tests were carried out both in a VIM furnace and in a 1 ton capacity electric furnace. Results of melting test in VIM furnace have shown:

- preservation of briquettes characteristics for long time (>3 months) if stored in a dry environment,
- briquettes capability to remain in the interface slag/steel,
- high iron/alloy yield (> 90 %),
- generation of fumes (from the vegetable binder) in case of low oxygen concentration to be used for generating CO/CO_2,
- relation between melting time and chemical composition of iron residues.

Comparison of the different briquette technologies utilisation in the pre-industrial test, *from a chemical point of view*, has not shown significant differences between the continuous injection or the charging in batch of briquettes. In fact, in both cases:

- gases compositions, temperature values and dioxins concentration have similar value,
- leaching of produced slag respected Italian Law limits for inert materials,
- iron recovery reached value higher than 90 %.

Also energy consumption, compared with the melting of a standard bath done by CSM during previous tests, has not shown a significant increase.

From a process management point of view, in order to optimise iron recovery, it is suggested to introduce briquettes together with the second (or/and third) bucket so to have the better melting conditions. Briquettes are more heavy than the slag so, during the charge of the second bucket, they go directly in the melted bath that, in this case, is higher respect to the starting conditions (melted bath after the heat of the previous heat). In addition, being the second bucket added to melted bath at ambient temperature, this procedure avoid dioxins formation during the pre-heating, normally performed with the first bucket.

A preliminary economical evaluation of the developed process has been done in order to estimate the advantages in the internal reuse of iron residue by means of briquettes preparation and utilisation. The economical evaluation, considering only the briquettes production, seams to be favourable (about +130€ for each ton of used iron residues). Nevertheless, it is important to define costs lied to additional energy consumption and slag disposal.

3.5 Exploitation and impact of the research results

Inductively heated coke bed reactor process (BEGMBH, BFI)

As a result of the investigations concerning the inductively heated coke bed reactor process, the industrial applicability of a coupled process (flash reactor/coke bed reactor) is proven by lab scale and technical scale trials. Further, the basic design of the inductively heated coke bed reactor including coke feeding system and off-gas treatment is available. Thus, a following step for dissemination of the new developed inductively heated coke bed reactor process would be the industrial implementation of a pilot or demonstration plant concerning a coupled process of flash reactor and inductively heated coke bed reactor. For the combined process of coke bed reactor and cupola furnace a software based process model is available, which will be used as a tool for supporting industrial implementation of the new recycling process.

The coupled process of flash reactor and inductively heated coke bed reactor is a suitable process for on-site recovery of EAF dusts from stainless steelmaking. Potential customers for application of the new process are all stainless steel producers. In contrast to this, the combined process of coke bed reactor and cupola furnace is a potential application for foundries or smelters operating a cupola furnace. In the course of process alterations, an inductively heated coke bed reactor may be integrated in the cupola furnace. For industrial implementation of this concept, further engineering work is required.

New briquetting technology using vegetable binders and direct recycling in the EAF (CSM)

Experiments, concerning the analysis of the briquettes melting behaviour, conducted during this project, both in VIM furnace and in pilot plant scale, have shown an iron recovery higher than 90 %. This appears as a very encouraging result, specially considering that, from a chemical point of view, no significant difference have been detected.

Results of the analysed process, however, need to be confirmed and validated with industrial tests in a EAF, possibly utilising briquettes prepared with different iron residues. In particular, during real scale trials, it is important to analyse energy consumption, quality of slag (also by means of leaching test) and dioxins production along the fume duct.

In following industrial trials, a more detailed economical evaluation of the whole process (from the briquettes production until their complete melting in EAF) could be done so as to verify the convenience of internal iron residues recycling by means the briquettes utilisation.

Patents/Publications

In the course of the project, no patents have been filed and no publications or conference presentations resulted from the project.

List of Tables

List of Figures

List of References

[1] I. Barin, O. Knacke, O. Kubaschewski, "*Thermochemical Properties of Inorganic Substances: Supplement*", Springer-Verlag, Berlin (1977)

Technical Annex I

EUROPEAN COMMISSION
RESEARCH DIRECTORATE-GENERAL

22. X. 2009

RTD.K4/RL/MA/aa D(2009)561957

VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH
Dipl.-Ing. Gerald STUBBE
SOHNSTRASSE 65
DE-40237 DUESSELDORF
Germany

REGISTERED LETTER

AMENDMENT No (2)
TO CONTRACT No (RFSR-CT-2007-00010)

HAVING REGARD TO contract No (RFSR-CT-2007-00010) signed on 26/06/2007
and amendment n°1
(hereinafter called the "Contract").

WHEREAS the Contractor BOHLER EDELSTAHL GMBH & CO KG "BEGMBH" asked the Commission , by letter of 20/11/2008 for:

- A Change of denomination of the following Contractor ("BEG")
- An amendment of the Contractor's banking details

IT HAS BEEN AGREED as follows:

Article 1.-

Change of denomination of activity of one contractor

The denomination of the following Contractor has changed:

Old denomination	New denomination	With effect from date
BEG (BOHLER EDELSTAHL GMBH")	BEGMBH (BOHLER EDELSTAHL GMBH & CO KG)	16/01/2008

Change of banking details

The Contractor's banking details indicated in Article 8 of the contract are amended as follows:

New Banking Details of "BEGMBH"	
Name of Bank:	DEUTSCHE BANK AKTIENGESELLSCHAFT FILIALE WIEN (VIENNA BRANCH
Address of branch:	4, HOHENSTAUFENGASSE VIENNA Austria
Precise denomination of legal entity:	BOHLER EDELSTAHL GMBH & CO KG
Full account number (including bank codes):	IBAN_ONLY

IBAN account code:	AT081910000031484000
Bank Account Holder:	BOHLER EDELSTAHL GMBH & CO KG

Article 2.-

All the other provisions of the Contract remain unchanged and shall continue to have full force and effect.

Article 3.-

This amendment, forming an integral part of the Contract, enters into force at the date of dispatch of the registered letter.

I request you to notify all the contractors of the content of the present amendment.

Yours faithfully.

On behalf of the Commission:

Name: Raffaele LIBERALI

Function: Director Directorate K

Signature:

(seal of the organisation)

Date: 28/11/08

AMENDMENT No (1)

TO CONTRACT No (RFSR-CT-2007-00010)

(the "Community"), represented by the Commission of the European Communities (the "Commission"), itself represented for the signature of this contract by Mr Raffaele LIBERALI, Director DIRECTORATE K of EUROPEAN COMMISSION DIRECTORATE GENERAL RESEARCH or his duly authorised representative,

of the one part,

and

VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH "BFI" (the "coordinator"), established in SOHNSTRASSE 65, 40237 DUESSELDORF-GERMANY, represented by its legal/statutory/authorised representative, Mr WUPPERMANN, Managing Director,

and

cor

BOHLER EDELSTAHL GMBH & Co KG "BEG" , established in MARIAZELLERSTRASSE 25,8605 KAPFENBERG-AUSTRIA, represented by its legal/statutory/authorised representative, Mr BAUER, Chief Executive,

CENTRO SVILUPPO MATERIALI SPA "CSM" , established in Via di Castel Romano 100/102,00128 ROMA-ITALY, represented by its legal/statutory/authorised representative, Mr BRUNO, Chief Executive Officer,

TRIBOVENT VERFAHRENSENTWICKLUNG GMBH "TRIBOV" , established in Brunnenfelderstrasse 59,6700 BLUDENZ/BUERS-AUSTRIA, represented by its legal/statutory/authorised representative, Mr HEPBERGER, General Manager,

(collectively the "contractors"),

of the other part,

(collectively the "contracting parties")

HAVING REGARD TO contract No (RFSR-CT-2007-00010) signed on 26/06/2007 (hereinafter called the "Contract").

WHEREAS the Coordinator VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH "BFI" asked the Commission , by letter of 16/07/2008 for:

- The modification of the Coordinator's Scientific Officer
- Replacement of one or more participants
- Change of denomination of one Participant: BETRIEBSFORSCHUNGSINSTITUT VDEH - INSTITUT FUER ANGEWANDTE FORSCHUNG GMBH* "BFI"
- An amendment of the Contractor's banking details
- A modification of the Community contribution
- A modification of the Description of work (Annex I)
- A modification of the table of breakdown of the costs
- A modification of total estimated eligible costs

4 17/9/8

IT HAS BEEN AGREED as follows:

Article 1.-

Modification of the Coordinator's Scientific Officer

Gerald STUBBE will assume the role of Scientific Officer of VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH "BFI" (the Coordinator).

Replacement of one or more participants

Date of effective replacement: 16/07/2008

TRIBOVENT VERFAHRENSENTWICKLUNG GMBH ("TRIBOV") will no longer participate in the Project as a partner.

TRIBOVENT VERFAHRENSENTWICKLUNG GMBH ("TRIBOV") remains bound by the obligations of the contract as regards the part of the Project that it has carried out.

Notwithstanding the termination of the participation of TRIBOVENT VERFAHRENSENTWICKLUNG GMBH ("TRIBOV") the provisions set out in Article 2.2 of the contract shall continue to apply to it.

BOHLER EDELSTAHL GMBH & Co KG* ("BEG") assumes for its account the part of the Project assumed hitherto by TRIBOVENT VERFAHRENSENTWICKLUNG GMBH ("TRIBOV") in accordance with the technical annex.

Change of denomination

The denomination of the following Contractor has changed from the date as specified in the following table:

Old denomination (acronym)	New denomination (acronym)	With effect from date
BETRIEBSFORSCHUNGSINSTITUT VDEH - INSTITUT FUER ANGEWANDTE FORSCHUNG GMBH* (BFI)	VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH (BFI)	01/01/2008

Change of banking details

The Contractor's banking details indicated in Article 8 of the contract are amended as follows:

New Banking Details of "BFI"	
Name of Bank:	COMMERZBANK AG
Address of branch:	25, BREITE STRASSE DUESSELDORF Germany
Precise denomination of the account holder:	VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH
Full account number (including bank codes):	IBAN_ONLY
IBAN account code:	DE76300400000123181000
Bank Account Holder:	VDEH-BETRIEBSFORSCHUNGSINSTITUT GMBH

17/9/18

Change of the Community contribution

The total maximum Community financial contribution allocated to the Project specified in Article 3.2. of the contract is modified as follows:

Previous contribution(EURO)	New financial contribution(EURO)
973601.00	938099.00

Modification of the description of work

The annex I (technical annex) is modified as attached to this amendment.

Amendment of table I of the estimated breakdown of the total estimated allowable costs

The table of estimated breakdown of estimated allowable costs between contractors is modified as attached to this amendment.

Change of the total estimated eligible costs

The **total estimated allowable costs** of the Project specified in Article 3.1. of the contract is modified as follows:

Previous total allowable costs(EURO)	New total allowable costs(EURO)
1622667.00	1563498.00

Article 2.-

All the other provisions of the Contract remain unchanged and shall continue to have full force and effect.

Article 3.-

This amendment, forming an integral part of the Contract enters into force as from its signature by all the contracting parties .

Done at Brussels, in 5 copies in English.

17/9/15

For VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH("BFI"):

Name: Mr Carl-Dieter WUPPERMANN

Function: Managing Director

Signature:

Wuppermann

(stamp of the organisation)

VDEh-Betriebsforschungsinstitut GmbH
Postfach 10 51 45 40042 Düsseldorf
[illegible] 40237 Düsseldorf

& Co KG co:

For BOHLER EDELSTAHL GMBH*("BEG"):

Name: Mr Robert BAUER

Function: Chief Executive

Signature:

(stamp of the organisation)

BÖHLER Edelstahl GmbH & Co K(
Mariazeller Straße 25
8605 Kapfenberg

For CENTRO SVILUPPO MATERIALI SPA("CSM"):

Name: Mr Roberto BRUNO

Function: Chief Executive Officer

Signature:

(stamp of the organisation)

CENTRO SVILUPPO MATERIALI S.p.A.
CHIEF EXECUTIVE OFFICER
DR. ROBERTO BRUNO

For TRIBOVENT VERFAHRENSENTWICKLUNG GMBH("TRIBOV"):

Name: Mr Ronald HEPBERGER

Function: General Manager

Signature:

TRIBOVENT
Verfahrensentwicklung GmbH
Brunnenfelderstraße 59
A-6700 Bludenz

(stamp of the organisation)

For the Commission:

Name: Raffaele LIBERALI

Function: Director Directorate K

Signature: - (stamp of the organisation)

Date: 2/12/08

17/9/8

17/5/8

Estimated breakdown of the total estimated *allowable costs* and *pre-financing*

Contract No RFSR-CT-2007-00010

NAME	TOTAL ESTIMATED ALLOWABLE COST (euro)	MAXIMUM CONTRIBUTION (euro)	FIRST PRE-FINANCING (euro)	FIRST FINANCIAL GUARANTEE (euro)	SECOND PRE-FINANCING (euro)	AGGREGATED FINANCIAL GUARANTEE (euro)
Coordinator VDEH - BETRIEBSFORSCHUNGSINSTITUT GMBH (BFI)	416,083.00	249,650.00	99,000.00	0.00	99,000.00	0.00
Principal Contractor BOHLER EDELSTAHL GMBH & Co KG (BEG) Cor	719,415.00	431,649.00	84,000.00	0.00	261,000.00	0.00
Principal Contractor CENTRO SVILUPPO MATERIALI SPA (CSM)	428,000.00	256,800.00	102,000.00	0.00	102,000.00	0.00
Principal Contractor TRIBOVENT VERFAHRENSENTWICKLUNG GMBH (TRIBOV)	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	1,563,498.00	938,099.00	285,000.00	0.00	462,000.00	0.00

EUROPEAN COMMISSION
RESEARCH DIRECTORATE-GENERAL

Directorate G – Industrial Technologies
Research Fund for Coal and Steel

ANNEX I
Form 1-1
OBLIGATORY AT THE SUBMISSION STAGE

[illegible] TECHNICAL ANNEX

Project acronym: URIOM

Proposal No[2]: RFS-PR-06109

Contract No: RFSR-CT-2007-00010

TITLE: Upgrading and Utilisation of Residual Iron Oxide Materials for hot metal production

---

1. OBJECTIVES

The main aim of URIOM is to develop new technologies for reuse of residual iron oxides especially from stainless steelmaking within European steel industry to be operated by the steelworks itself. That will be addressed through the following objectives:

- To undertake physicochemical analysis especially of residual iron oxide materials from stainless steel making (EAF-, and AOD off gas cleaning)
- Development of a technology for briquetting of stainless steel residuals with vegetable based binder and direct recycling into the EAF
- Development of the innovative inductively heated coke bed technology as a key process for recycling stainless steel residuals with a complete recovery of alloying elements for steelmaking, zinc for non ferrous metals use and slag usable for building applications
- Development of an process model for carbothermic reduction of oxidic stainless steel residuals for fixing regulations for the development of an inductively heated cupola furnace process
- Overall evaluation and comparison of the different technologies proposed for reuse of stainless steelmaking residuals

2. *Work Programme and distribution of tasks*

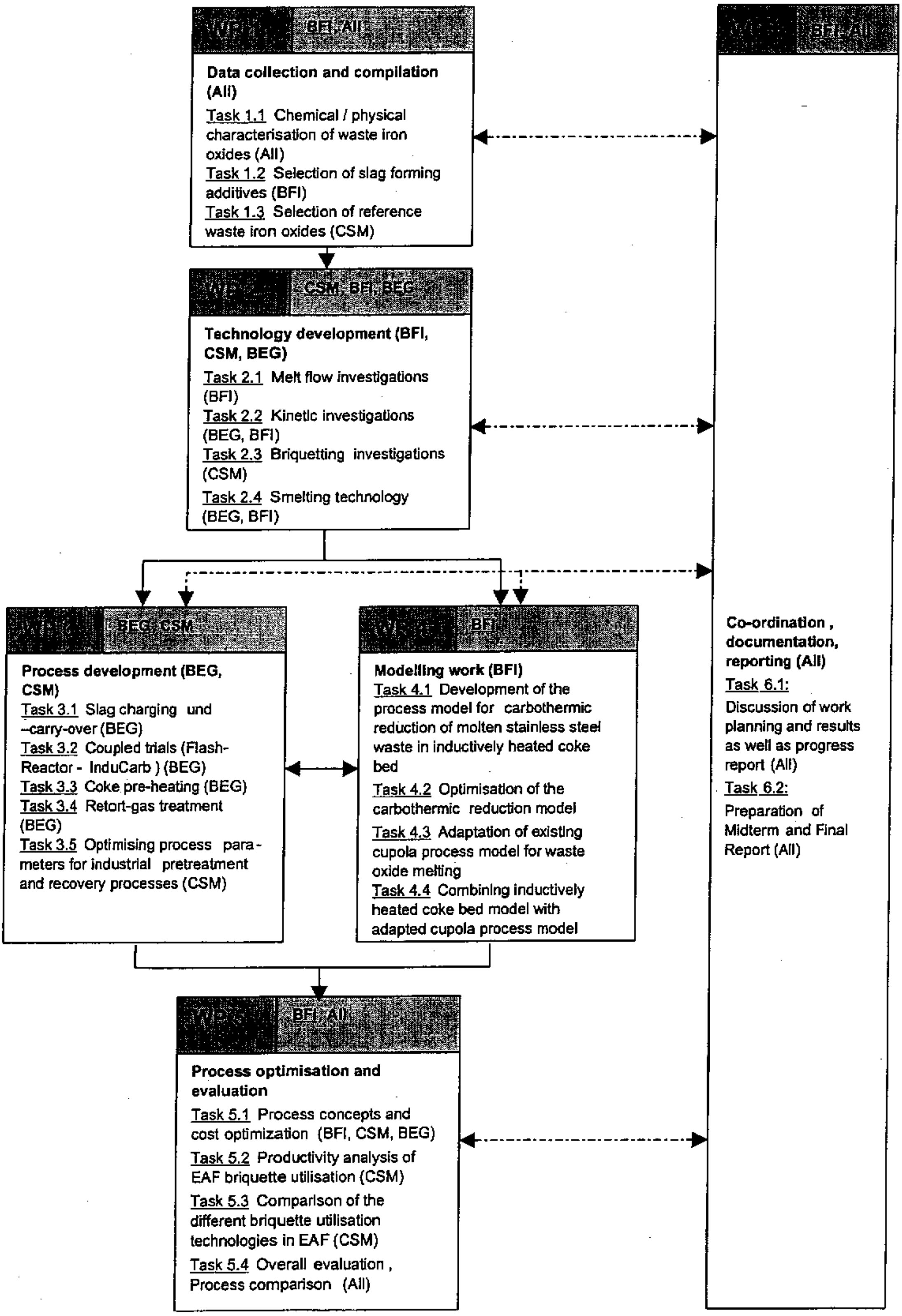

Figure 1: Work programme and distribution of tasks

ANNEX IV
Form 1-2
OBLIGATORY AT THE SUBMISSION STAGE

WORK PACKAGE DESCRIPTION	**WP No**	**1**

Work package Title	**Data collection and compilation**	**Number of man hours**[29]
WP Leader	BFI	400
Contractor (s)	BEG	300
	CSM	400
Total		1100

1 – Objectives

The objective of WP1 is to get representative data about composition and physical properties of the residual iron oxides especially from stainless steelmaking as the necessary database for the for the process development. The process development covers three different routes:

- briquetting stainless steelmaking residuals with vegetable based binders
- charging of self-reducing residual briquettes into the EAF
- two staged flashmelting of residual dusts and carbothermic reduction of the melt in inductively heated coke bed
- extending Oxicup process by application of the inductively heated coke bed technology for the cupola hearth

As for the carbothermic reduction a liquid metal as well as slag phase is necessary the addition of slag forming components has to be taken into account, especially to avoid unwanted reducing of silicon oxide leading to a raised energy and coke consumption.

For briquetting of the residuals it is necessary to define the binder materials as well briquetting mixtures taking into account to achieve a minimised void fraction by the resulting size distribution.

2 - Work programme and distribution of tasks with indication of participating contractors

Task 1.1 Chemical / physical characterisation of waste iron oxides (All)

Mill scales as well as zinc and lead containing residuals especially from stainless steel production, will be characterised in terms of chemical composition and present phases, moisture and oil content, density, grain size distribution, and melting temperature. **The characterisation of the stainless steel residues will be carried out on the base of production data (chemical composition) of a period of 6 month, completed by additional analysis of moisture, grain size distribution, density and melting temperature.**

Task 1.2 Selection of slag forming additives (BFI)

Concerning the carbothermic reduction of chromium oxide containing residual materials the addition of slag forming agents will be necessary to ensure liquid slag and metal phases during reduction. That selection shall be done based on thermochemical calculations using FactSage thermochemical software. **Potential additional slag formers, which will be taken into consideration, are Al_2O_3, MgO, CaO and SiO_2.**

Task 1.3 Selection of reference residual iron oxides (CSM)

In this phase of the research mixtures of residual iron oxides and vegetable binders (pin resin, saw dust, starch) at different percentage will be defined.

After the definition of the mixtures for briquette production, the amount of exothermal reducing agents like FeSi dust or Al drosses to be added to the mixtures will be defined.

3 - Interrelation with other work packages (please give WP No)

WP 2

4 - Deliverables and milestones

D1.1 Residual iron oxides chemical / physical characteristics

D1.2 Type and amount of slag forming additives for carbothermic reduction process

D1.3 Reference waste iron oxides mixture for briquetting investigations

ANNEX IV
Form 1-2
OBLIGATORY AT THE SUBMISSION STAGE

WORK PACKAGE DESCRIPTION	WP No	2

Work package Title	**Technology development**	**Number of man hours[29]**
WP Leader	CSM	1200
Contractor (s)	BFI	1200
	BEG	190
Total		2780

1 – Objectives

The objective of this work package is the providing of basic data necessary for the development of the different proposed technologies for reuse of oxidic stainless steel waste. This includes mainly investigations in laboratory scale in order to determine limitations by the flow characteristics of liquids through bulk good and kinetic investigations regarding to reduction reaction. Further on, briquetting tests will be carried out in order to determine the optimum compression parameters for briquette-use in the EAF.

2 - Work programme and distribution of tasks with indication of participating contractors

Task 2.1 Melt flow investigations (BFI)

BFI shall characterise the melt flow in the coke bed via measuring residence time distribution (RTD) of the model melt in a cold transparent model with packed bed considering the physical similarity via Reynolds and Schmidt number with even liquid load over the cross section of the packed bed. The measured RTD shall be adapted via combination of different reactor model RTDs taking into account the flow behaviour. A second important aspect is the determination of the flooding limitation of the packed bed and the permeability of the packed bed for gas and liquid phase.

Task 2.2 Kinetic investigations (BFI, BEG)

For carrying out the kinetic investigations for carbothermic chromium oxide reduction the BFI high temperature furnace shall be maintained and prepared with an available inert gas purging unit as well as an also available rotating sample unit. The investigations itself shall be carried out in the temperature range between 1600 and 1800°C using a defined rotating carbon cylinder by systematically variation of temperature and rotational speed as well as melt composition (e.g. chromium content, slag basicity, and alumina content). **The reduction kintetic will be measured by the chemical analysis of the main components of the slag - especially Cr_2O_3- and the metal in dependence on reaction time. The resulting quantities of slag and metal phase in dependence on slag composition, reaction time and temperature will be determined by microscopic analysis of representative microsections. (BFI)**

The kinetic investigations of carbothermic zinc oxide reduction will be carried out by trials on an inductively heated coke bed in laboratory scale. To vary important parameters which affect the kinetic of the zinc reduction (e. g. coke size, temperature, slag composition) a suitable design of the equipment will be necessary. The inductively heated coke bed reactor will be developed, built and operated by TRIBOVENT (TVT) as assistance for BEG (Assistance from third parties).

Depending on the results, the number of trials is estimated to 10-30. Evaluation of the trials will be carried out by chemical analysis of input (oxidic residues) and output materials (slag, metal and gas phase) (BEG).

Task 2.3 Briquetting investigations (CSM)

The cold high pressure briquetting of the mixtures defined at the previous work package, will be carried out with an apparatus that will be properly modified for this purpose.

Variables of the briquetting investigations are:

- **densification pressure**
- **binder/binder mixture content**

The high density briquettes produced, will be characterised in terms of density that has to result higher than slag density. Moreover the test on mechanical resistance of the briquettes will be carried out.

Task 2.4 Smelting technology (BFI, BEG)

A slag melt reduction technology concept for the inductively heated coke bed shall be defined based on the results of task 2.1 and 2.2. That concept covers the

- geometry for the inductively heated coke bed vessel (diameter, height),
- suitable coke size to achieve sufficient bed permeability for the liquid and gaseous phases,
- sufficient reactive coke surface for the reduction reaction,
- necessary inductor power to meet the energy demand for the endothermic reduction process.

A major part of the technology concept for the inductively heated coke bed reactor (InduCarb) will be worked out by TVT as assistance for BEG (Assistance from third parties).

3 - Interrelation with other work packages (please give WP No)

WP 3, 4.

4 - Deliverables and milestones

D2.1 Melt flow characterised by residence time distribution, flooding limit for the packed bed, slag distribution – tundish concept
D2.2 Kinetic data for carbothermic reduction of molten residuals from stainless steelmaking
D2.3 Reference briquettes made of the selected waste, produced with different mixture techniques
D2.4 Basic lay-out for inductively heated coke bed reduction technology

ANNEX IV
Form 1-2
OBLIGATORY AT THE SUBMISSION STAGE

WORK PACKAGE DESCRIPTION	WP No	3

Work package Title	Process development	Number of man hours[29]
WP Leader	BEG	3430
Contractor (s)	CSM	2100
Total		5530

1 – Objectives

Objectives of this work package are the design and construction of the interface between Flash-Reactor for slag melting and InduCarb-Reactor for reduction of the valuable constituents of the oxidic waste from stainless steel production. In this context constructional problems of feeding of the hot liquid slag and the pre-heated coke into the InduCarb-Reactor are to solve. Further on a suitable off-gas treatment shall be developed that enables the recovery of volatile Zinc from the off-gas before using it as an additional heat source for the Flash-Reactor.

2 - Work programme and distribution of tasks with indication of participating contractors

Task 3.1 Construction of the interface for melt charging and –carry-over into the inductively heated coke bed reactor (InduCarb) (BEG)

An oxy-fuel heated high temperature flash smelter shall be used for melting the residual stainless steel oxides separating zinc, iron, nickel and chromium oxide from the volatile oxides and chlorides. That melt shall be charged into the inductively heated coke bed reactor. Therefore it is necessary to develop, construct and build an interface between the flash smelter and the inductively heated coke bed reactor. Main details are:

- Tapping concept flash smelter, tuyére/nozzle concept
- Strategy and devices to prevent slag freezing
- Evaluate optimum slag melt distribution (pilot scale)

BEG will be assisted by TVT in development of a feeding concept regarding liquid material supply to the inductively heated coke bed from the flash smelter (Assistance from third parties).

Task 3.2 Coupled trials (Flash-Reactor - InduCarb) (BEG)

After build up of the slag charging interface as well as the InduCarb reactor and the commissioning of the new equipment reduction trials shall be carried out with residuals from stainless steel making at BEG. Those trials shall give information about the slag flow properties and reduction degree depending on temperature, composition, coke size, height of coke bed and the volume flow of the melt. **Depending on the results and the grade of influence of the single parameters, the number of trials is estimated to 10-30.** The evaluation of the trials will be done by mass and energy balancing and by chemical analyses of the slag for determining reduction degree. BEG will consult TVT in planning and performance of the coupled trials (Assistance from third parties).

Task 3.3 Coke feeding and pre-heating (BEG)

For coke feeding and preheating the following concepts shall be evaluated:

- forced feeding,
- feeding by gravity,
- direct preheating via combustion,
- indirect preheating via external heat exchanger.

Within this investigations, the coke channel design is of main importance. Cold model assisted bulk mechanical investigations shall be carried out in order to determine the optimum constructive solution for the coke channel with respect to conveying characteristic. The dimensions of the coke preheating stage shall be defined by heat transfer calculations. The results of the calculations shall be experimentally verified at a hot preheating facility which is constructed and build up for that purpose.

Task 3.4 InduCarb off gas treatment (BEG)

Based on thermodynamical gas equilibrium calculations and laboratory investigations a basic concept and design of a gas reforming unit shall be worked out taking into account to oxidise the zinc vapour in the off gas of the InduCarb reactor by introducing water vapour producing an equivalent amount of hydrogen and solid zinc oxide. This innovative gas reforming technique is necessary to use the gas after separation of the solid zinc oxide as fuel for the flash smelter. The gas reforming unit shall be tested with rented facilities (e.g. gas cleaning, post combustion) at the pilot-plant site.

Due to the operation with dangerous components like CO and H_2 a suitable safety concept must be worked out and applied for the experimental work as well as for a later pilot or industrial installation.

Task 3.5 Determination of optimised process parameter for industrial pre-treatment and recovery processes (CSM)

Determination of thermal capacity and thermal diffusivity will be performed on the optimised mix. The behaviour at the melting of briquette for various compositions will be tested in a VIM furnace (10 litre crucible) in Ar atmosphere. Melting temperature will be measured by both pyrometer and thermocouple and a camera will be installed in order to follow the behaviour of briquette during the heating.

3 - Interrelation with other work packages (please give WP No)

WP 2, 4, 5.

4 - Deliverables and milestones

D3.1 Interface solution, hot tested

D3.2 Documented results and interpretation of the trials, Dimensioning data for inductively heated coke bed process

D3.3 Dimensioning data for coke feeding and preheating unit

D3.4 Reformer Unit, safety concept

D3.5 Process parameter for optimised industrial pre-treatment and recovery process

ANNEX IV
Form 1-2
OBLIGATORY AT THE SUBMISSION STAGE

WORK PACKAGE DESCRIPTION	WP No	4

Work package Title	Modelling work	**Number of man hours**[29]
WP Leader	BFI	1700
Contractor (s)		
Total		1700

1 – Objectives

The objective of the WP 4 is the development of suitable process model for the carbothermic treatment of oxidic residues from stainless steelmaking which models both smelting and carbothermic reduction step. As the general idea is the upgrading of the conventional cupola furnace process by an additional, inductively heated hearth for reduction step, this shall be modelled by a new developed carbothermic reduction model, which will be integrated in an adapted BFI-cupola furnace model. Thus, an evaluation of the proposed technology for the recycling of oxidic stainless steel residues with regard to industrial practicability and achievable benefit can be carried out and parameters for dimensioning of a future steel works-integrated carbothermic reduction plant can be predicted.

2 - Work programme and distribution of tasks with indication of participating contractors

Task 4.1 Development of the process model for carbothermic reduction of molten stainless steel waste in inductively heated coke bed

Base of the model for the carbothermic reduction are multi-phase multi-component thermochemical equilibrium calculations assisted by Gibbs energy minimisation carried out by the soft ware FactSage. The proposed carbothermic reduction process of stainless steel residues shall be modelled as an counter flow reactor, which mainly consists in a coke bed, an slag/metal melt-down stream and a off-gas up stream. This will be carried out assisted by the SimuSage soft ware. The model will be divided into a number of reaction volumes for modelling 2-dimensional temperature fields, taking into account also heat losses by the reactor walls and external heat supply by the inductive heating. Input parameters of the model shall be the starting composition of the slag and the desired tapping temperature after reduction. Results of the calculation assisted by the newly developed carbothermic reduction model will be the necessary input temperature at the reactor entrance, the coke consumption, the final composition of tapped slag and metal, and the necessary heat supply by the inductive heating.

Task 4.2 Optimisation and validation of the carbothermic reduction model

After virtual construction of the carbothermic reduction model, the optimisation and validation of the carbothermic reduction model shall be done by using the experimental results from InduCarb-Reactor trials in WP3 and WP 5. Main aspects of the optimising work are heat and mass balance and the correct prediction of slag/metal tapping composition and coke consumption.

Task 4.3 Adaptation of existing cupola process model for waste oxide melting

Aim of this task is to model correctly the properties of the stainless steelmaking residues when fed to the carbothermic reduction reactor. Since the future planning is to integrate the carbothermic reduction module into a briquette charged cupola furnace process, this upstream process influences strongly the properties of the material input of the following carbothermic reduction reactor. Thus, the upstream process has to be taken into account for modelling the cutting site to the carbothermic reduction reactor. This shall be carried out by adaptation of an existing BFI-cupola furnace model. The adaptation includes mainly an extended repertory of oxidic substances for material input, because oxides of the alloying elements, especially chromium oxide, are to consider in contrast to the conventional cupola furnace process. The result of the adaptation will be a "pre-melt" (oxidic/metallic) consisting in an input parameter set of temperature, oxidation stage and composition, which is typical for the cupola furnace process.

Task 4.4 Combining inductively heated coke bed model with adapted cupola process model

By combination of the adapted BFI-cupola furnace model and the carbothermic reduction model the complete process of carbothermic reduction of stainless steelmaking residues will be represented in one model. Further work shall be done for optimisation and validation of the model by comparing with experimental results from WP 5 in order to predict heat and material balances and the chemical composition of the tapping material with a sufficient accuracy.

3 - Interrelation with other work packages (please give WP No)

WP 3, 5.

4 - Deliverables and milestones

D4.1 carbothermic reduction model

D4.2 optimised carbothermic reduction model

D4.3 adapted cupola furnace-model for calculation of stainless steelmaking residuals processing, taking into account the specific influence of briquetted stainless steelmaking residuals melting in a cupola process

D4.4 adjusted process model for carbothermic reduction treatment of oxidic stainless steel waste, consisting in a smelting-module (adapted BFI-cupola furnace model) and a carbothermic reduction module

ANNEX IV
Form 1-2
OBLIGATORY AT THE SUBMISSION STAGE

WORKPACKAGE DESCRIPTION	WP No	5

Work package Title	**Process optimisation and evaluation**	**Number of man hours[29]**
WP Leader	BFI	500
Contractor (s)	BEG	440
	CSM	1800
Total		2740

1 – Objectives

The objective of the WP is the process optimisation and the development of general process concepts for the proposed technologies for carbothermic reduction or briquetting of oxidic stainless steel waste.

2 - Work programme and distribution of tasks with indication of participating contractors

Task 5.1 Process concepts and cost optimisation (BFI, CSM, BEG)

Basis for the CSM process concept are the results of tests in a 1 t DC electric arc furnace, which will be carried out introducing briquettes above a pre-formed bath (using scrap) in continuous charge. During this experimentation analysis of exhaust gas (CO, SO_2, NO_x, O_2) will be monitored at the stack and samples of gas will be taken at furnace hood. **These trials shall be carried out during selected heats of the alloy fixed in WP1 in a production period of 12 month.** (CSM).

The BFI shall work out a process concept based on a cupola process with inductive heated hearth and determine the specific costs and benefits. By modelling of various scenarios of operational conditions assisted by the process model developed in WP 4, the most economic operation mode shall be determined taking into account operational costs (energy, consumables, etc.) and yield from the recycled residual material.

BEG shall work out a process concept based on two staged flash melter/InduCarb process for stainless steel residues processing economic feasibility and environmental aspects. **Analysis of the slag properties with regard to the later use as a buliding material, leaching behaviour and content of free carbon will be determined on an representative number of product-slag samples(ca. 30 samples).**

Task 5.2 Productivity analysis of EAF briquette utilisation (CSM)

The productivity analysis will be performed in comparison with the melting time and the temperature measurement (target 1600°C) at the end of the heat in respect to the reference heats. In this field it is very important to maintain at constant value of the power during the experimental heat. **Slag and metal chemical analyses will provide data necessary for the masse balance and evaluation of the degree of metal recovery from the briquetts. Investigation of the leaching behaviour (esp. Cr-oxide) of the resulting slag will give informations for the utilisation of the slag as building material. These trials shall be carried out during selected heats of the alloy fixed in WP1 in a production period of 12 month.**

Task 5.3 Comparison of the different technologies briquette utilisation in EAF (CSM)

The comparison of different technology (continuous charge and batch charge) will be carried out as consequence of the experimental test.

Task 5.4 Overall evaluation, Process comparison (All)

Determination of pros and cons of the different processes

3 - Interrelation with other work packages (please give WP No)

WP 2, 3 and 6. The knowledge gained from the development of process concepts with regard to cost and productivity optimisation in WP 5 will flow back to the technology development (WP 2) and process development (WP3) work by supplying economic limitations of process parameters. That can possibly lead to the choice of physico-chemical parameters of the input material (melt or briquette) slightly away from the ideal parameters based on pure equilibrium conditions or reaction kinetics, what has to be considered in WP2. In the same way adjustment of the thermochemical process model in WP4 will be carried out according the economical aspects and limitations gained in WP5.

4 - Deliverables and milestones

D5.1 Process concepts for processing of stainless steel residuals
D5.2 Productivity data for briquette operation
D5.3 Suitable briquetting technology
D5.4 Process comparison and recommendation

ANNEX IV
Form 1-2
OBLIGATORY AT THE SUBMISSION STAGE

WORK PACKAGE DESCRIPTION	WP No	6

Work package Title	Coordination , documentation, reporting	**Number of man hours**[29]
WP Leader	BFI	600
Contractor (s)	BEG	200
	CSM	200
Total		1000

1 – Objectives

Objective of this work package is the coordination of the partners work, its documentation and the reports of the achieved research results

2 - Work programme and distribution of tasks with indication of participating contractors

Task 6.1 Discussion of work planning and results as well as progress report (All)

The project steering committee, consisting of members of each project partner, will plan the project work, review the technical and financial performances, and ensure the completion and deliverables of the work programme. It will meet at the beginning of the project and at six-monthly intervals thereafter at different partners sites. At those meetings the work planning as well as the achieved results shall be discussed for preparation of the progress reports as well as the contents of the Midterm and Draught Final Report .

Task 6.2 Preparation of Midterm and Final Report (BFI, All)

For preparation of the Midterm as well as the Draught Final Report all project partners prepare their reporting parts and deliver them to the coordinator who shall generate the corresponding written report as well as the necessary presentation of the work and results at the meeting of the TGS expert group for adjustment with all partners. The coordinator has to secure the in time delivery of the reports to the Commission as well as the corresponding TGS expert group and is responsible for the oral results presentation as well as the information of the project steering committee about the discussion results of the expert group.

3 - Interrelation with other work packages (please give WP No)

WP 1 - 5

4 - Deliverables and milestones

D6.1 Progress reports
D6.2 Midterm Report, Final Report

ANNEX IV
Form 1-3
OBLIGATORY AT THE SUBMISSION STAGE

PROGRAMME BAR CHART (TASK, PARTNER, DELIVERABLES, MILESTONES)

Work packages	*Work packages' title*	*Deliverables*	**Hours on project/ Contractor(s)**				**1st year**				**2nd year**				**3rd year**				**4th year**			
			BFI	BEG	CSM		I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II		
WP 1	**Data collection and compilation**		**400**	**300**	**400**																	
Task 1.1	Chemical / physical characterisation of waste iron oxides	D1.1	200	300	200		■	■														
Task 1.2	Selection of slag forming additives	D1.2	200				■	■														
Task 1.3	Selection of reference residual iron oxides	D1.3			200		■	■														
WP 2	**Technology development**		**1200**	**190**	**1200**																	
Task 2.1	Melt flow investigations	D2.1	500					■	■	■	■											
Task 2.2	Kinetic investigations	D2.2	550	90				■	■	■	■	■										
Task 2.3	Briquetting investigations	D2.3			1200			■	■	■	■	■										
Task 2.4	Smelting technology	D2.4	150	100							■	■										
WP 3	**Process development**			**3430**	**2100**																	
Task 3.1	Construction of the interface for melt charging und –carry-over into the inductively heated coke bed reactor	D3.1		1230						■	■	■	■									
Task 3.2	Coupled trials (Flash-Reactor - InduCarb)	D3.2		100									■	■	■	■						
Task 3.3	Coke feeding and pre-heating	D3.3		1500					■	■	■	■	■									
Task 3.4	InduCarb off gas treatment	D3.4		600						■	■	■	■									
Task 3.5	Determination of optimised process parameter for industrial pre-treatment and recovery processes	D3.5			2100					■	■	■	■	■	■							
WP 4	**Modelling work**		**1700**																			
Task 4.1	Development of the process model for carbothermic reduction of molten stainless steel waste in inductively heated coke bed	D4.1	500						■	■	■	■										
Task 4.2	Optimisation of the carbothermic reduction model	D4.2	400									■	■	■	■	■						
Task 4.3	Adaptation of existing cupola process model for waste oxide melting	D4.3	300									■	■	■								
Task 4.4	Combining inductively heated coke bed model with adapted cupola process model	D4.4	500												■	■	■	■				
WP 5	**Process optimisation and evaluation**		**500**	**440**	**1800**																	
Task 5.1	Process concepts for processing of stainless steel residuals	D5.1	350	140	150										■	■	■	■				
Task 5.2	Productivity analysis of EAF briquette utilisation	D5.2			700										■	■	■	■				

Task **5.3**	Comparison of the different technologies briquette utilisation in EAF	D5.3			650										■	■	■	■				
Task **5.4**	Overall evaluation, Process comparison	D5.5	150	300	300													■	■	■		
WP 6	**Coordination , documentation, reporting**		**600**	**200**	**200**																	
Task **6.1**	Discussion of work planning and results as well as progress report	D6.1	100	100	100					■	■	■	■	■	■	■	■	■	■	■		
Task **6.2**	Preparation of Midterm and Final Report	D6.2	500	100	100						■	■	■					■	■	■		
Total Hours on project			**4400**	**4560**	**5700**																	

EUROPEAN COMMISSION
RESEARCH DIRECTORATE-GENERAL

Directorate G – Industrial Technologies
Research Fund for Coal and Steel

Appendices

ANNEX 1: Gelatinisation of starch and gluten formation

Gelatinisation of starch

Chemically, starches are polysaccharides that consist of repeating glucose units. Starch molecules have one of two molecular structures: a linear structure, known as amylose; and a branched structure, known as amylopectin. Amylose and amylopectin associate through hydrogen bonding and arrange themselves radially in layers to form granules.

Starch granules come in a wide variety of sizes ranging from 3 microns to over 100 microns. With some starches the granule size is polymodal, meaning the granules can be grouped into more than one size range. Granule shape also can be diverse. Granule shapes include symmetrical spheres, asymmetrical spheres, symmetrical disks and asymmetrical disks. Some granules exhibit their shape smoothly, while others are polyhedrons with a faceted surface.

Wheat starch has an amylose content of around 25% (and 75% of amylopectin). Its granules are relatively thick at 5 to 15 microns with a smooth, round shape ranging from 22 to 36 microns in diameter. Wheat starch is bimodal in that it also has a group of starch granules of a different size. In this case, these other granules are very small, with diameters of only 2 to 3 microns.

When starch is dispersed into water and heated, the water penetrates into the starch granule from the outside inward until the granule is fully hydrated. Once hydrated, the hydrogen bonding between the amylose and the amylopectin maintains the integrity of the granule and it begins to swell from the hilum (center). Therefore, starch undergoes a transition process, during which the granules break down into a mixture of polymers-in-solution, known as gelatinization (**Figure 1**).

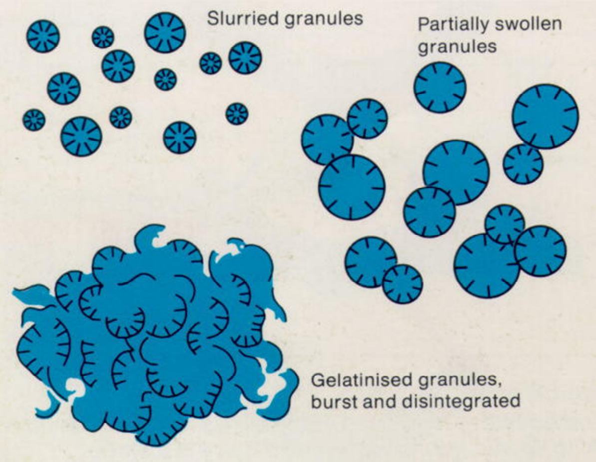

Figure 1: Gelatinisation process

Once gelatinized, the swollen granules may increase the viscosity of the dispersion, and/or associate to form gels and films. The polysaccharide chains are linked together by electrostatic forces like hydrogen or Van der Waals bonds inside gel (**Figure 2**).

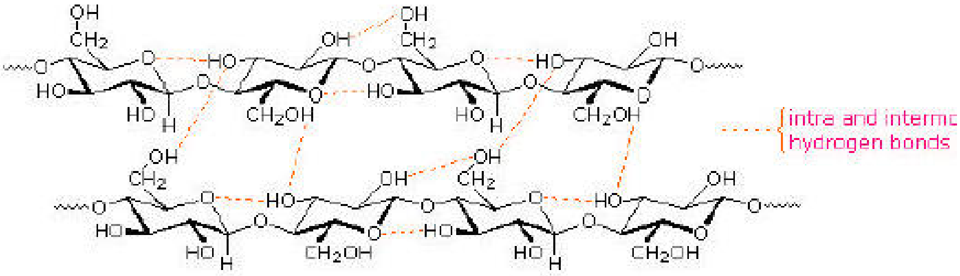

Figure 2: Glucose units linked by electrostatic bonds like hydrogen bond

The polysaccharide composition and structure affects the gel activation temperature. The amylose gives the gel strength and the amylopectin gives high viscosity. Generally, the higher the amylose, the higher is the gelatinization temperature. In fact, amylose molecules, because of their linearity, line up more readily and have more extensive hydrogen bonding, consequently, it requires more energy to break these bonds and gelatinize the starch. Wheat starch has the lower temperature of gelatinization respect to other type of starch (**Table 1**).

Table 1: Gelatinization temperatures of different starches

Starches	*Gelatinization temperatures (°C)*
Maize	70-75
Sorghum	70-75
Rice	68-75
Wheat	52-54
Barley	61-62
Potato	56-69

Gluten formation

Protein content in flour varies from 6% to 14.5% depending on the types of wheat. Wheat proteins contain albumins, globulins, gliadins and glutenins, four basic proteins identified on the base of their solubility in different solvents.

In particular, gliadins and glutenins are insoluble proteins in water. Gliadins have intra-molecular disulfide linkage while glutenins have both inter- and intra-molecular disulfide linkages: this fact explains because gliadins are compact and in the globular shape and the glutenins are linear and have relatively higher molecular weight 50,000-millions compare with the molecular weight of gliadins 20,000-50,000 (**Figure 3**).

In the presence of moisture such as water, glutenin and gliadin relax from their tangled state. Pressure exerted through mixing helps these relaxed strands of proteins to line up and form a strong, cohesive network. In fact, water molecules form hydrogen bond with the protein chain favouring their deployment and stretch during the amalgamation: cross-links are formed that stabilise the new structure, the gluten. Gluten is basically a network of proteins that is both elastic and plastic. It has the ability to stretch into a very thin film without tearing, and spring back into its original form.

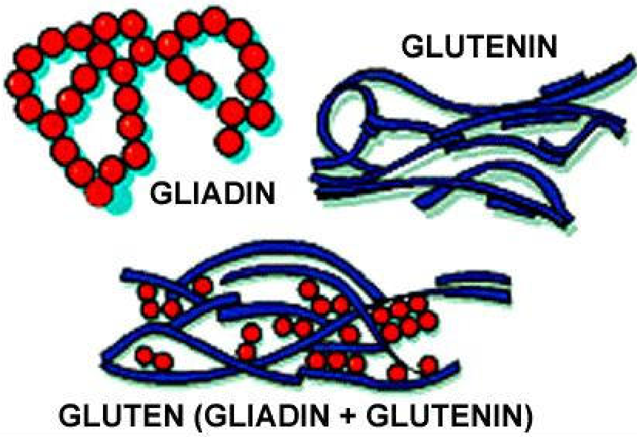

Figure 3: Structure of gliadin, glutenin and gluten

References

1. Ratnayake WS, Jackson DS "*Starch gelatinization*", Adv. Food Nutr. Res. 2009, 55, pag. 221-68
2. Lund D. "*Influence of time, temperature, moisture, ingredients, and processing conditions on starch gelatinization*", Crit. Rev. Food Sci. Nutr. 1984, 20(4), pag.249-73
3. "*Starch*", http://www.lsbu.ac.uk/water/hysta.html
4. Tibor Abonyi et al., "Synthesis of Gluten-Forming Polypeptides. 1. Biosynthesis of Gliadins and Glutenin Subunits", Journal of Agricultural and Food Chemistry 2007 55 (9), 3655-3660

ANNEX 2: Procedure for briquette preparing

The main steps for briquettes preparation were:
- mixing of the solid components to facilitate the homogenization of the materials,
- water addition to activate the binding effect,
- charging of the mixture into the cylindrical shape mould, selected with specific dimensions (height and diameter),
- mechanical pressing,
- drying and storage of the obtained briquette.

After mixing, the material is charged into the chamber of the mould. Into the chamber is then introduced the piston (**Figure 1**).

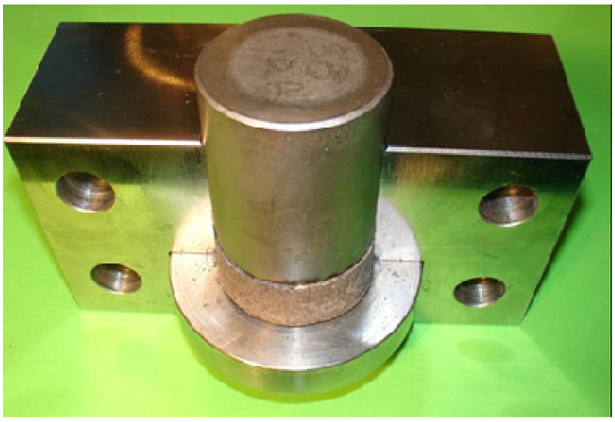

Figure 1: Material on a plate is charged by the piston into the mould

The mould is placed on the press to be loaded (**Figure 2**).

Figure 2: Charged mould and piston are loaded by press

After the loading, the mould is open and the briquette (classified) can be removed and it is ready to next step (**Figure 3**). The briquettes obtained have a density of about 3,00 g/cm^3, are defect and cracks free and completely dried.

The work carried out in laboratory has been also dedicated to define the water content of the mixtures and the loading pressure to mould them. The water, to be added to the mixtures, firstly depends on the amount of vegetable binders. To set the correct amount of the water, it is then necessary to exactly determine the water content in the waste material to be used.

The loading pressure to charge the mixtures has to settle and to compact the constituents, reducing as well as possible the voids and porosity, and to attain the need density.
After the first laboratory trials the following briquetting parameters have been set-up:
- overall amount of water in the mixtures: 1,0 ÷ 2,0%;
- loading pressure: 400 bar;

Charging the mould with 150÷200 grams of mixtures, briquettes of 2,5÷3,5 cm can be obtained.
Figure 4 shows the final briquette.

Figure 3: After press, mould is open and briquette is ready

Figure 4: Briquette (top and lateral view)

ANNEX 3: Vacuum induction melting and casting plant

The Vacuum Induction Melting furnace VIM is a laboratory plant for inductive melting, treating, casting and solidifying of special steels, Nickel based alloys, Cobalt based alloys, copper, aluminium alloys under controlled conditions.

The melting and casting process can be executed under vacuum, inert gas or ambient (air) pressure.

Charging, measuring of temperature and sampling are possible during the process via a vacuum lock valve.

Charging materials can be only raw materials, dry and grease or oil free. Final product can be ingots, bars and complex shape components

Figure 1: CSM VIM furnace

Process data are described in the following:

Melting:	1300 – 1600 °C (depending on alloy grade)
Atmosphere:	Vacuum, Inert gas or air (closed chamber)
Process pressure	5×10^{-5} – 300 mbar
Overheating temperature:	1750 °C
Temperature measurement	750 – 1800°C (thermocouple, optical pyrometer)
Sampling of liquid metals	Quarz mold
Casting mode:	Top pouring into Molds or Ceramic shells (investment casting)
Melting/Casting capacities	1- 11 dm^3

Figure 2: Picture of crucible during melting trials