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# Recovery of Zinc and Iron from Steel Mill Dusts by the use of a TBRC: A possible Mini-mill Solution?

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## Abstract

The search for an effective mini-mill solution to treat zinc containing residues from steel industry or also cupola furnaces has a long history but has not been very successful yet due to several reasons. Some of them are: Not available technologies, the not well known and not developed product market by the steel producers, still relatively low treatment charges for the landfilling and no effective solution for an additional iron recovery. The present paper describes a process where in two subsequent steps by the use of a Top Blown Rotary Converter technology a simultaneous recovery of zinc, iron and other valuable metals should be possible. Investigations which were done in an advanced technical scale gave satisfying results. These data allowed the calculation of a mass- and energy balance. First economic considerations underline that with such a concept a feasible mini-mill solution could be established for the mentioned residues.

## Introduction

During steel production dusts are generated in an amount of 15 to 23 kg /t of steel mainly including iron oxides, zinc oxide, typical slag compounds, lead and halogens. Worldwide two main steel production routes are operating whereof the electric arc furnace route (EAF) with approximately 30 % of the world production generates dusts with high zinc contents up to 40 %, due to the high amount of charged galvanized scrap. The alternative integrated route produces steel in a basic oxygen furnace (BOF) with a comparable low ratio of charged scrap resulting in a dust with low zinc contents normally below 10 %. In some cases the BOF-dust is re-circulated in the furnace and with this reaches zinc values up to 27 %. Thereof 40 to 45 % of the yearly generated electric arc furnace dusts are recycled to recover first of all zinc by different technologies where the waelz kiln is far the dominating concept. Due to various disadvantages like low yields, the recovery of only one metal and the generation of huge amounts of residues there is still the demand for alternatives. Table 1 gives typical compositions of the mentioned dusts. [1], [2]

Table 1: Typical compositions of investigated dusts during the last ten years (mainly Europe)

| % | Zn | Pb | $SiO_2$ | CaO | Na | K | F | Cl | Fe |
|---|---|---|---|---|---|---|---|---|---|
| EAF | 18-40 | 2-7 | 3-5 | 8-9 | 1.0-2.0 | 0.8-1.5 | 0.2-0.5 | 2.0-5.5 | 18-35 |
| BOF | 1-15 | 0-2 | 2-6 | 5-15 | 0-1.0 | 0.5-1.1 | 0-0.5 | 0-2.0 | 24-45 |

Further disadvantages regarding the present situation from the view of the steel mills are:

- the necessity to transport the dust to central recycling units often for several 100 km generating high transport costs
- the dependency on price politics of recycling companies
- the payment of treatment fees

Therefore since many years there is the idea to develop treatment concepts which could be installed directly at the steel mill allowing a recycling of the dust under economic conditions also with comparable small throughputs.

Most of the existing processes like the already mentioned waelz kiln as well as others like rotary hearth furnaces or the Primus processes do not offer such a so called mini-mill-solution.

During the investigations at the University of Leoben in the last years following points have to be found as mandatory to create such an efficient mini-mill-solution especially for the treatment of EAF-dusts:

- iron has to be recovered in form of an alloy and for this the necessity of a melting process
- halogens have to be separated successfully to increase the quality of the zinc oxide
- the remaining slag should be low in critical metals like lead and should have an optimum composition and behaviour, so that utilization in road construction or even in cement industry is possible

Also investigations on the treatment of BOF-dusts were done but as a fact of the generally low zinc content compared with the low value of the main component iron, it is not easy to reach an economical solution. This is only possible in the described case where the dust is re-circulated and with this the zinc content increased up to at least 15 % [1, 2].

## Investigated process

The investigated concept that should fulfill the above mentioned criteria is based on a two-step process, where the reduction is done by a carbon containing iron bath. Hereby the residues are charged with reducing agents on a liquid metal bath, the oxides become reduced and volatile compounds are evaporated. Also the iron bath contains an amount of 3 % carbon at the beginning of the procedure. Not volatile compounds are partly caught by the metal bath or remain in the slag. Figure 1 shows the process principle of the recycling procedure.

The desired results are as stated a marketable iron alloy, a stabilized slag, which can be used very likely in the cement industry or in road construction and a crude zinc oxide caught from the off-gas stream by a bag house.

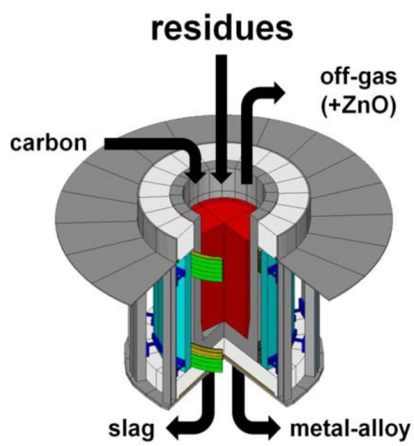



Figure 1. Basic schema of the Iron Bath Process

Nevertheless there are also some problems which have to be considered during the investigation of this process. The iron bath technology has the same disadvantage like all other pyrometallurgical recycling processes for steel mill dusts based on one process step. Unwanted impurities are fumed with the zinc and they are concentrated in the resulting crude zinc oxide. Especially when charging electric arc furnace dusts from carbon steel production directly, the content of lead, chlorine, fluorine, potassium and sodium in the resulting filter dust becomes very high. These contaminations, especially the halogens, are harmful for the possible utilization areas first of all the winning electrolysis where only very low amounts of these elements are allowed but also for others like the zinc sulfate production [3].
In Figure 2 a simple thermodynamic study shows the performance of an electric arc furnace dust under rising temperature with added reducing agents as it would be done on a reducing iron bath. The picture provides data for the behaviour of the dust above 1100 °C for the Zn, Fe and some of the chlorides. Nevertheless, it gives lead in its metalized form which is clear from the thermochemical point of view due to its noble character and therefore the easy reduction of the oxide. This definitely would not happen in the real process where lead oxide or chloride would be evaporated before its reduction, leaving the reaction zone with the off-gas.
This underlines that the zinc oxide product for sure would contain a high amount of impurities, mainly halides and lead oxide.

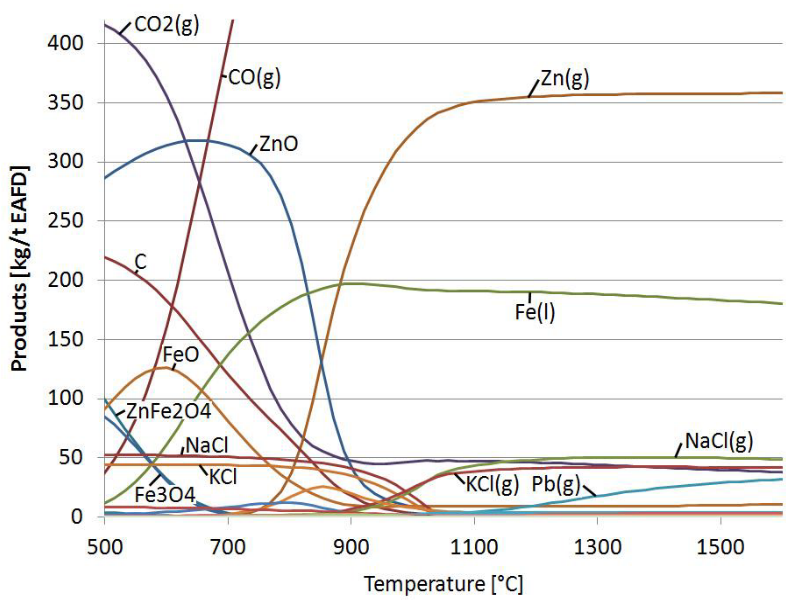



Figure 2. Equilibrium curves of a steel mill dust under reducing conditions

Due to that problem a further process step is taken into account. One option is an additional pyrometallurgical step before the iron bath process. During such a treatment under oxidizing conditions - clinkering - in the field of 1000 – 1200 °C impurities are removed and the cleaned material can be charged after this procedure on a liquid iron bath to reduce the oxides and fume the zinc and reach a high quality zinc oxide.
An important economical factor is the usage of the process energy from the first clinkering step by charging the hot material in the second stage on the liquid iron bath. Figure 3 shows the implementation of the clinkering step onto the iron bath process. A further important point would be to use the energy from the zinc re-oxidation in the off-gas stream in the previous processes.

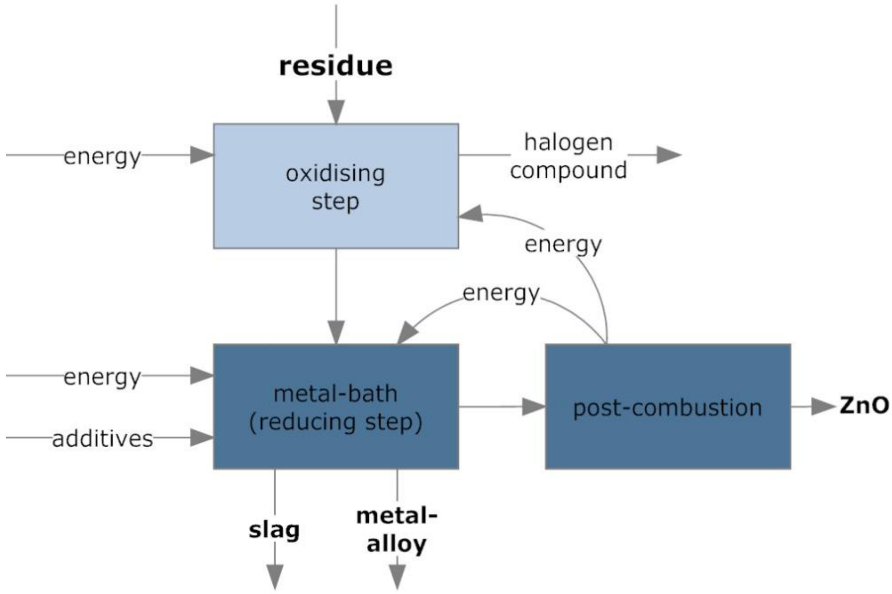



Figure 3: Implementation of a clinkering step in the iron bath process

If the quality of the filter dust is high enough the product can be directly sold to the primary zinc industry without any previous cleaning steps like soda-washing. Or it could probably break into other markets where higher revenues are possible, which would also justify a high energy demand. The “cash cow” of the process is first of all the zinc oxide. Therefore high amounts have to be produced which is easier to achieve by the use of higher zinc containing secondary materials like electric arc furnace dusts. While the waelz process is not only limited by too low zinc contents in the dust but also by too high zinc levels above 30 % for several reasons, such values are welcome for the described concept what is an important advantage.

## Investigations concerning slag optimization

In Figures 4 to 6, two developed scenarios for the treatment of steel mill dusts from electric arc furnaces (EAF) and basic oxygen furnaces (BOF) are shown. Because of the problem that under reducing conditions different oxidation stages of iron occur, the equilibrium has to be considered by setting a partial pressure of oxygen with 0.21, which overlays the ternary system and for this allows the formation of the different oxides in equilibrium. Furthermore, different phases aside from iron, calcium and silicon oxides have to be considered.

The optimization by e.g. additives is not a simple procedure which could only be derived from one system. The fact that during a reduction of steel mill dust on a reducing iron bath three different diagrams become relevant led to the challenge of a “cross linked” investigation, which is not easy to handle. To be able to cope with this, it is mandatory to have a computational thermochemical solution which enables to judge whether or not a parameter setting is a possible solution for all relevant ternary systems and how the individual ternary system would change with such a setting.

With this information, trials in the heating microscope were performed verifying the calculated results.

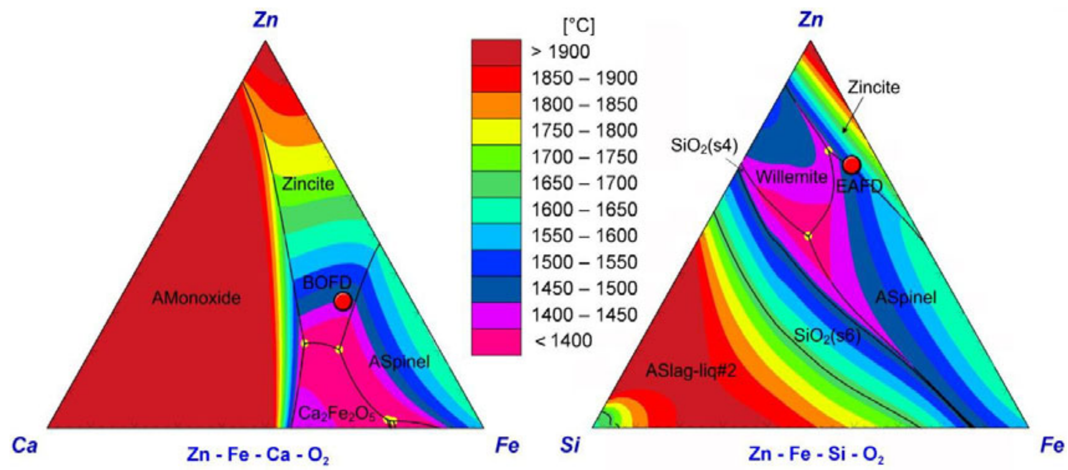



Figure 4: BOFD (left) and EAFD (right) during melting under atmospheric conditions

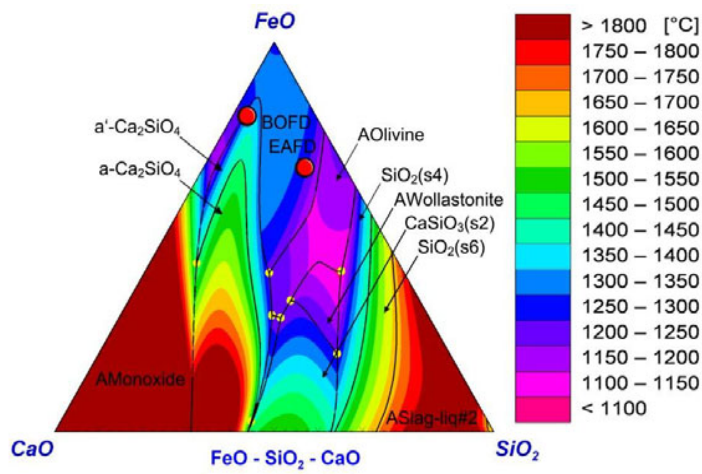



Figure 5: BOFD and EAFD under partial reducing conditions

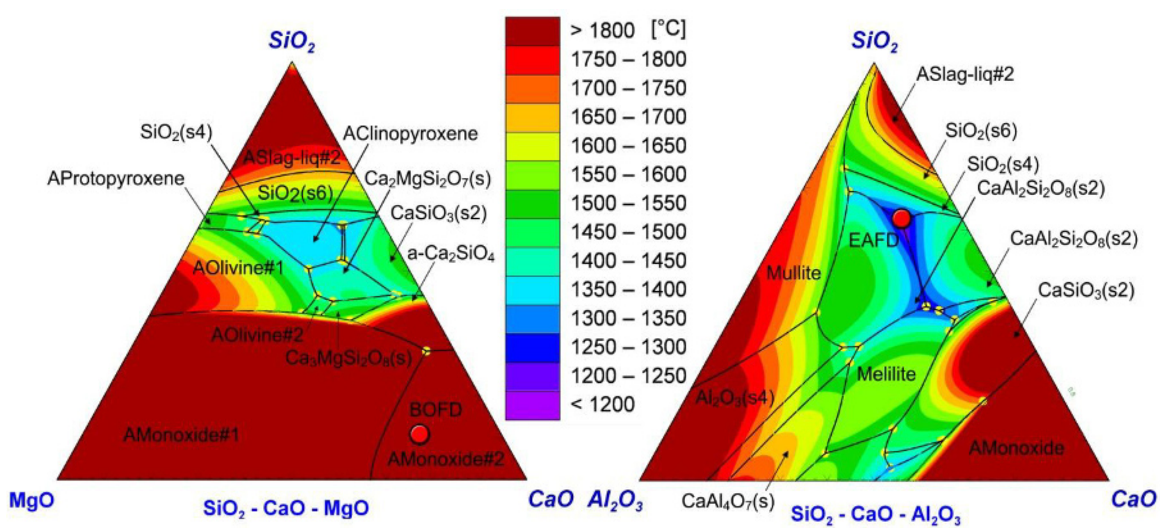



Figure 6: BOFD (right) and EAFD (left) at the end of the process (fully reduced)

The graphs in Figure 7 show the slag regime calculated and determined by the heating microscope for EAF dust and BOF dust as well as an alternative generated by additives (e.g. $SiO_2$).
From these investigations, it was found that special heating microscope analysis is a reliable tool for the evaluation of materials behaviour concerning melting, optimization trials and taking some boundary conditions into account, can also be applied for complex materials like e.g. electric arc furnace dusts. The graphs show that the discrepancy between calculated and measured (dotted lines) values is rather low. The only exceptions are formed by the BOF dust trial at the end of the process. The reason for this is simply due to a measurement limit caused by the maximum adjustable temperature of 1650 °C of the heating microscope.

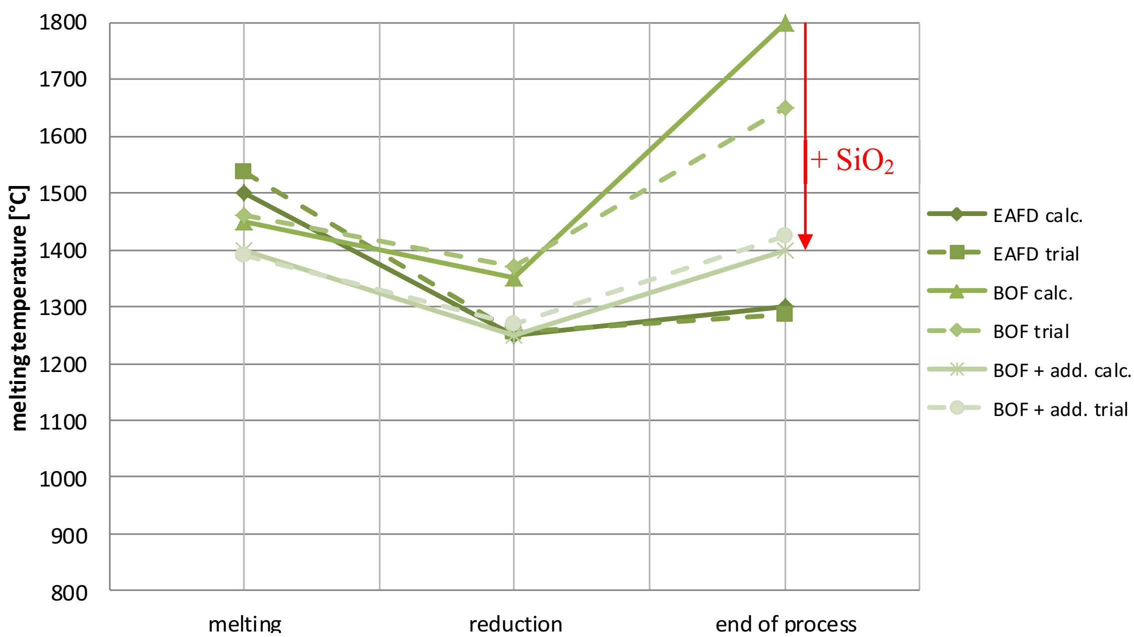



Figure 7: Evolution of melting points of slags during different process steps calculated by Factsage and determined as mean value of three measurements each

## Experimental setup

Both process steps were investigated at the University of Leoben. After some basic lab scale tests clinkering and melting trials were done in a TBRC (Top Blown Rotary Converter, Figure 8).
The burner is operated by methane and oxygen with a maximum capacity of 75 kW. The maximum achievable temperature, depending on the investigated process, lies at around 1600 °C. The volume of the combustion chamber is about 80 liters, which means a maximum material input of about 20 liters. The cooling of the off-gas is done by excess air.

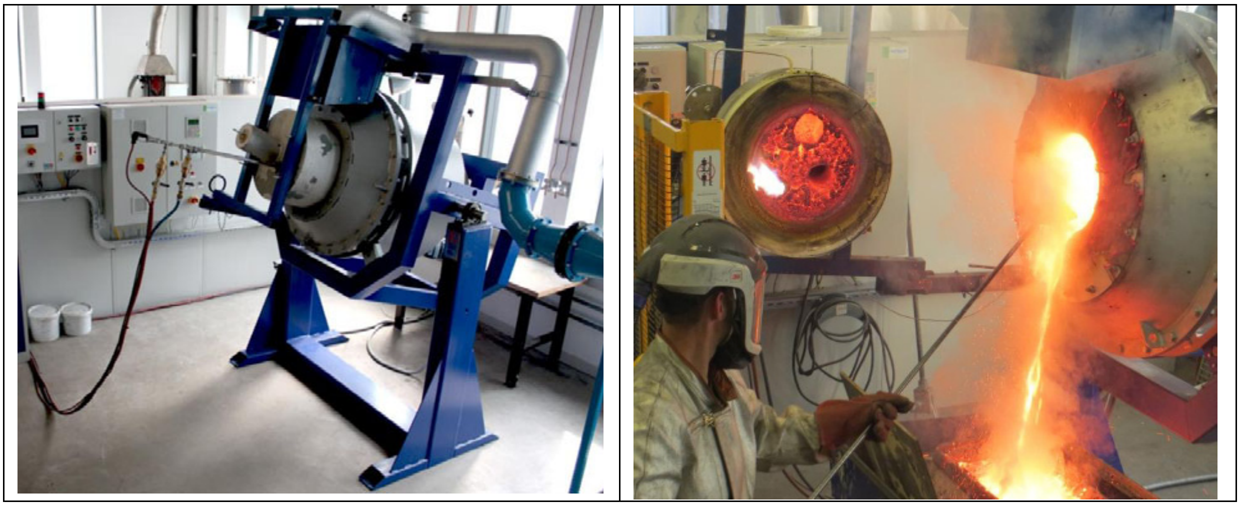


Figure 8: Top Blown Rotary Converter (TBRC)

## Results of investigations

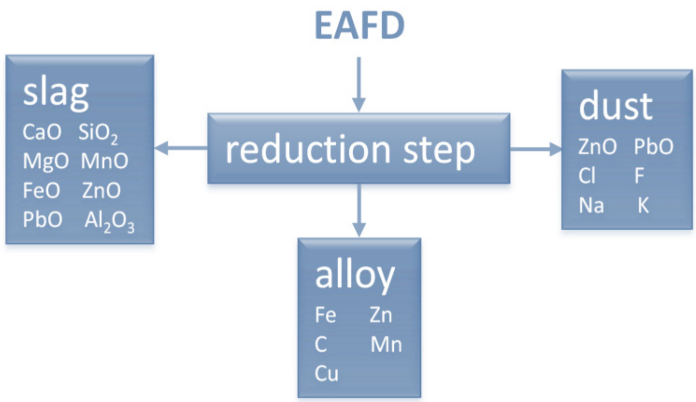
Trials in the TBRC for the first clinkering step were carried out with 30 kg of EAFD-pellets which were charged in the 1100 °C preheated furnace and treated for 30 to 60 minutes. The results showed a satisfying volatilization of fluorine, chlorine and lead especially after 60 minutes. Table 1 gives the extraction rates of lead, chlorine and fluorine under different treatment times.

Table 1: Clinkering trials in the TBRC (mean values of 3 trials each)

| yield [%] | Pb | Cl | F |
|---|---|---|---|
| EAF-dust (30 min) | 76.1 | 68.4 | 76.9 |
| EAF-dust (60 min) | 87.9 | 95.1 | 94.4 |

Due to some volatile zinc-compounds also some zinc losses resulted but were relatively low with an average amount of 3.5 % in the clinker. With this the zinc amount in the dust pellets increased from 32 % to roughly 35 %.

The clinkered material was then charged in hot stage (800 °C) into the second process step, the reduction. This was also carried out in the TBRC providing a carbonized iron bath at 1400 °C. The mass ratio of iron bath to clinkered pellets was 4:1.
Zinc and iron oxides were reduced and zinc evaporated. Remaining halides and lead oxide went into the off-gas with the zinc. Figure 9 gives a scheme of the elements distribution as well as the mean distribution values of three experiments.




| | slag | alloy | dust |
|---|---|---|---|
| Zn | 3.0 % | 1.5 % | 95.5 % |
| Pb | 1.0 % | 0.0 % | 99.0 % |
| Fe | 14.2 % | 85.2 % | 0.6 % |
| Cl | 1.0 % | 0.0 % | 99.0 % |

Figure 9: Elements distribution for the system EAFD-carbon-iron bath

The results of the treatment of EAFD on an iron bath gave relatively accurate and detailed information about element distribution and dependence on parameters like temperature, slag composition, etc. Nevertheless, an important field is iron reduction, which was found to be the one with the lowest speed and with this also the lowest yield. Here it is foreseen for the upcoming trials to study the kinetics of this reaction. This will be mainly influenced by the slag composition as well as the temperature and the reaction surface. Two types of slag will be investigated in detail in further trials. Both should lie in the area of 0.9 to 1.2 concerning their basicity to meet the requirements for slag utilization after reduction. The difference would be that one slag is completely based on calcium- and silicon-oxide, while the other one should include a certain amount of wustite. The reactive surface conditions will be changed by using a conductively heated furnace where the relative surface is low and a TBRC where the mixture of charged material, slag and iron bath is expected to be a maximum.
The most interesting product, the recovered zinc oxide, showed the following composition:

Table 3: Composition of the zinc oxide (average values from 3 trials)

| % | ZnO | $Fe_2O_3$ | Cl | Pb | F | others |
|---|---|---|---|---|---|---|
| dust | 96.8 | 1.1 | 0.25 | 0.3 | 0.15 | 1.4 |

The quality can be seen as similar to that one of a washed waelz oxide or even higher due to the low lead content and also low amounts of carry over. Nevertheless, there is a potential for improvement in further optimization trials.
Table 4 gives the average composition of the produced iron alloy:

Table 4: Composition of the iron alloy (average values from 3 trials)

| % | Fe | S | Cu | Pb | C | others |
|---|---|---|---|---|---|---|
| alloy | 95.7 | 0.5 | 0.7 | 0.1 | 2.4 | 0.6 |

Of course copper and sulphur are unwanted elements for utilization in the steel mill. Nevertheless, the use for the production of cast iron is one option but also for the steel production if an appropriate dilution could be realized.

Figure 10 gives a general overview of the two step process with the most important elements and compounds in the various products as well as a mass balance.

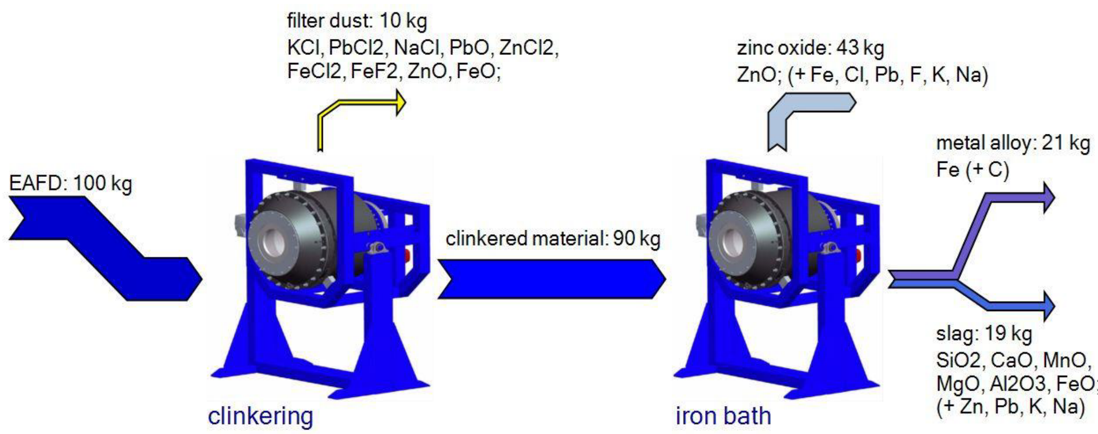



Figure 10: Results of first trials for the EAFD-treatment in the TBRC, off-gas is not considered

## Economic considerations

Economic calculations are always difficult to generalize and very dependent on regional business of the individual steel mill. Roughly the revenues from the products could be calculated assuming that the slag goes out for zero costs. The zinc oxide was calculated with 70 % of the LME zinc value, which is based on utilization in primary metallurgy applying the usual concentrate formula. For a LME-value of 1850 USD/t of zinc revenues of 615 USD per ton of charged EAF-dust could be realized. For the iron alloy a low steel scrap price of 300 USD/t was taken as basis for the calculation resulting in revenues generated by the iron alloy of 60 USD per ton of charged EAF-dust. Taking treatment charges into account which are normally paid by the steel mill to the recycler further 50 USD per ton of dust can be added. Summing up overall revenues of 725 USD per ton of EAF-dust should be possible. Based on CAPEX and OPEX calculations this amount should make an economic treatment easily possible down to yearly throughputs of roughly 10000 tons of dust.

With this, the mini-mill solution should be realizable with the additional advantage of an environment friendly concept that only produces very low amounts of newly generated residues.

## Conclusion

Recycling of steel mill dusts nowadays is a centralized business which shows various disadvantages for the dust producing steel mills. A compact mini mill solution for a single one or a certain number of small steel mills would be an interesting step forward in recycling of zinc and iron. Investigations at the Christian Doppler Laboratory/University of Leoben developed a two-step process based on a top blown rotary converter which should enable the treatment of comparable low dust amounts under economic conditions. Essential steps are the slag optimization, the pre-treatment in form of a clinkering-process and the reduction on a reducing iron bath. Results from experiments in a technical scale gave satisfying results which of course could be improved by further optimization trials. First economic considerations were also promising due to the flexibility of the chosen aggregate concerning its minimum throughput for economic operations.

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