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# NEW DEVELOPMENT IN METAL RECOVERY FROM SECONDARY RESOURCES

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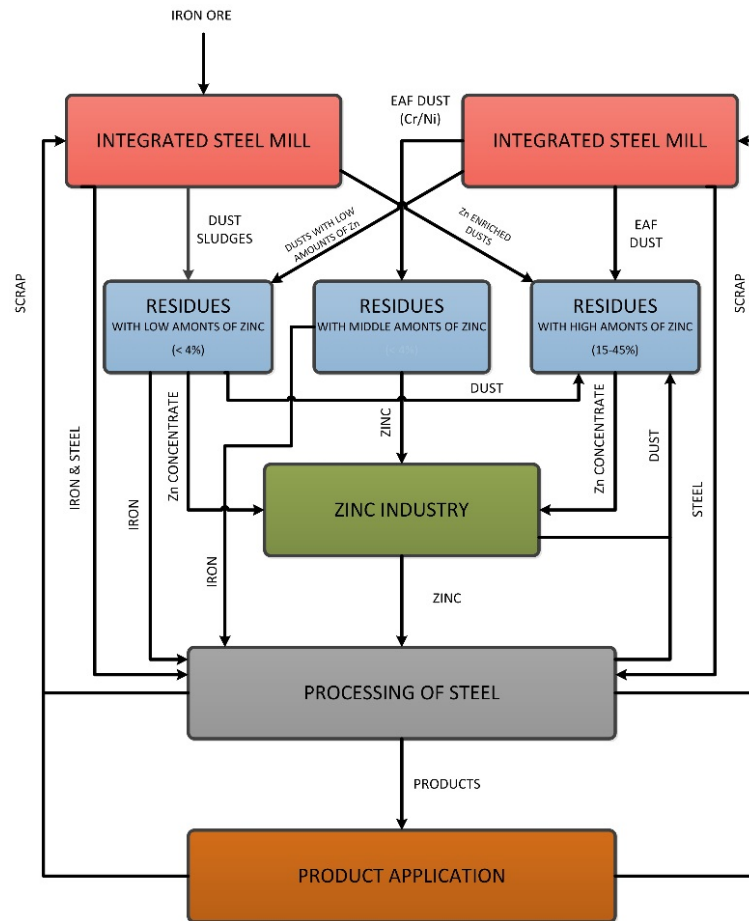
## Introduction

During the primary and secondary production of metals, different by-products accrue, which still contain amounts of valuable metals. Most of the so called process wastes go currently to landfill, only metals with a high market value like copper gets completely removed from various by-products except dusts from the copper recycling, because of their very complex structure. Possible problems by the dumping of metallurgical wastes in the future and the high level of raw material prices, led to developments of several recycling concepts. An example for this is the treatment of steel mill dusts. Especially during the smelting of steel-scrap in an electric arc furnace, high values of zinc can be found in the filter dust. Because of this high amount of the valuable metal zinc and the declaration of the electric arc furnace dust as hazard waste, recycling processes are still in operation. Over a couple of years, the waelz kiln got the most important process in this case<sup>1,2</sup> and is currently listed as the "Best Available Technique" in the European Union<sup>3</sup> or the "Best Demonstrated Available Technology" in the US<sup>4</sup>. This state of the art process has the disadvantage, that the generated product zinc oxide is contaminated with halides. Before it can be used in the primary production of zinc, a cleaning step must be done. Additionally, 700 kg of waelz slag remain at the end of the recycling, which go to landfill. The bad elution behaviour of this process waste prevents a usage as secondary resource. An alternative in this topic is the "2<sup>S</sup>DR" (Two Step Dust Recycling) process. The approach is a prevention of the currently accruing residues during the processing of steel mill dusts and an improving of the zinc oxide quality.

## Steel mill dust formation and their classification

Steel mill dust originates from an electric arc furnace, with an often high zinc content, as well as from integrated steel mills with generally lower amounts of zinc. Valuable metals in residues characterize the significance for a possible recycling. Due to this reason, the EAFD is more important than dusts from basic oxygen furnaces (BOF). Steelmaking processes with low values of zinc in their feeding materials are

developing recirculation systems to enrich their materials up to higher contents<sup>5</sup>. Based on this a classification of the different dusts can be seen in Figure 1.



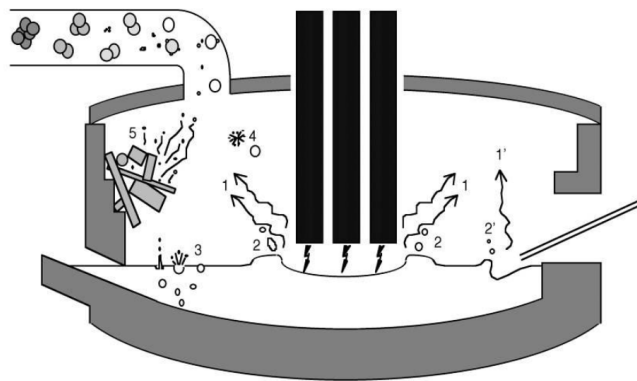
**Figure 1:** Network between the iron- and steel industry and zinc industry<sup>6</sup>

As shown in Figure 1, the procedure of dust utilization depends on the classification and can for this be different. For a classification the structure, the morphology and of course the chemical analysis must be known for the dust, to allow a decision concerning the most appropriate recycling strategy. For a better understanding of the dusts morphology and history the different process steps of the electric steel production can be divided in five steps<sup>7</sup>:

- furnace charging (input materials get charged with special buckets)
- melting (the three graphite electrodes produce an electric arc which melts the charging feed and leads to an iron bath and liquid slag)

- refining (removing of different elements, because of reactions between slag and metal bath and oxygen get injected to remove the dissolved carbon and carbon monoxide (CO) bubbles get produced)
- slag formation (CO bubbles lead the slag foaming)
- casting (if all demands on the product quality are reached, the tapping starts)

In dependence on the operation, different opportunities exist for dust formation. Figure 2 shows the link between process and the reasons for solid particles in the off-gas stream.



**Figure 2:** Dust formation EAF<sup>7</sup>

A volatilization of phases or elements takes place because of the high temperature in the arc zone (1) and through the oxygen jet (1'). In both areas, a projection of droplets (2, 2') takes place. Bursting CO bubbles are also responsible for fine droplets (3) at the boundary layer between gas area and liquid slag. Contact between a droplet and oxidizing atmosphere in the freeboard of the EAF can cause a bursting (4). Feeding material can also contain some powder materials, which directly enters the off-gas stream (5).<sup>7</sup> Investigations showed that the main part of dust in the off-gas occurs through the bursting of CO bubbles and the effect of volatilization. Fly-off particles are sometimes too big for leaving the reactor through the gas stream and fall back into the liquid bath.<sup>8</sup>

## The 2<sup>s</sup>DR process for steel mill dust recycling

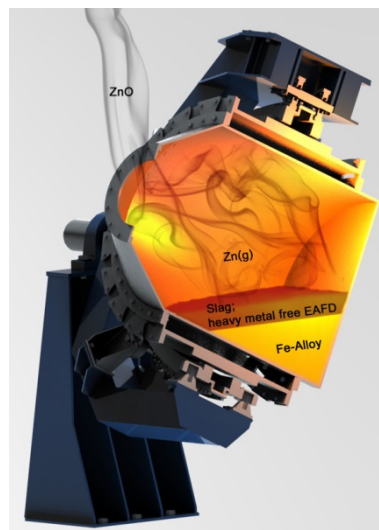
The quality and with it also the attainable price are bound to the purity of products. In case of the steel mill dusts the main impurities chlorine and fluorine are essential

seen, but a higher quality of the saleable product can be reached, therefore it should be accepted. The tapped remaining material gets mixed with a carbon carrier and maybe some additives, and is charged into the reduction process, where zinc and iron is recovered. An optimization would be the direct transfer between these two steps in hot state to save energy costs.

### Reduction of steel mill dust

At the beginning of a successful recycling concept development, the most useful process concept must be evaluated. Out of such an evaluation, the TBRC (Top Blown Rotary Converter) has been found as the best technology.

The material clinkered in the first step is now charged into the second one, which can be seen as the one where the valuable components are recovered. As a function of quantitative proportion from clinker to iron bath an additional value of reducing agent might be necessary. The carbon dissolved in the iron reduces the oxides of the charged material. Depending on the origin of steel mill dust, the melting points can differ, especially regarding to the basicity. Therefore, it can be necessary to supply additives to the process, to guarantee a treatment temperature of 1400-1450 °C. The reduced iron droplets settle down and get collected in the liquid metal bath. Under these conditions the metallic zinc evaporates and leaves the furnace via the gas phase. A reoxidation in the freeboard of the vessel is the best case, because of the energy recuperation. However, the requirements concerning the facility itself are much higher compared to an oxidation with excess air in the off-gas system. The general overview for an element distribution is given in Figure 4.



**Figure 4:** Principle of the second recycling step<sup>12,13</sup>

Additionally other metal oxides are also reduced and enter the metal bath. As product a filter dust as well as a ferrous alloy is the result. Slag, which is low in heavy metals and shows a volume-stability, can be used in further applications. The rotating speed of the vessel influences essentially the reaction rate, by which short process times of the discontinuous practice can be realized. Contrary to the first step the reduction process is done in liquid state.

## Flue dust generation during copper recycling

Depending on the used raw material, the secondary production of copper can be divided in a melting and reducing step followed by converting, pyrometallurgical and finally electrolytic refining. Figure 5 shows a typical flow sheet for modern copper recycling with an integrated lead-tin recovery process. It can be seen, that the different raw material grades are charged in various stages. The first two processes can be identified as main dust emitter, because they process the lowest grades.

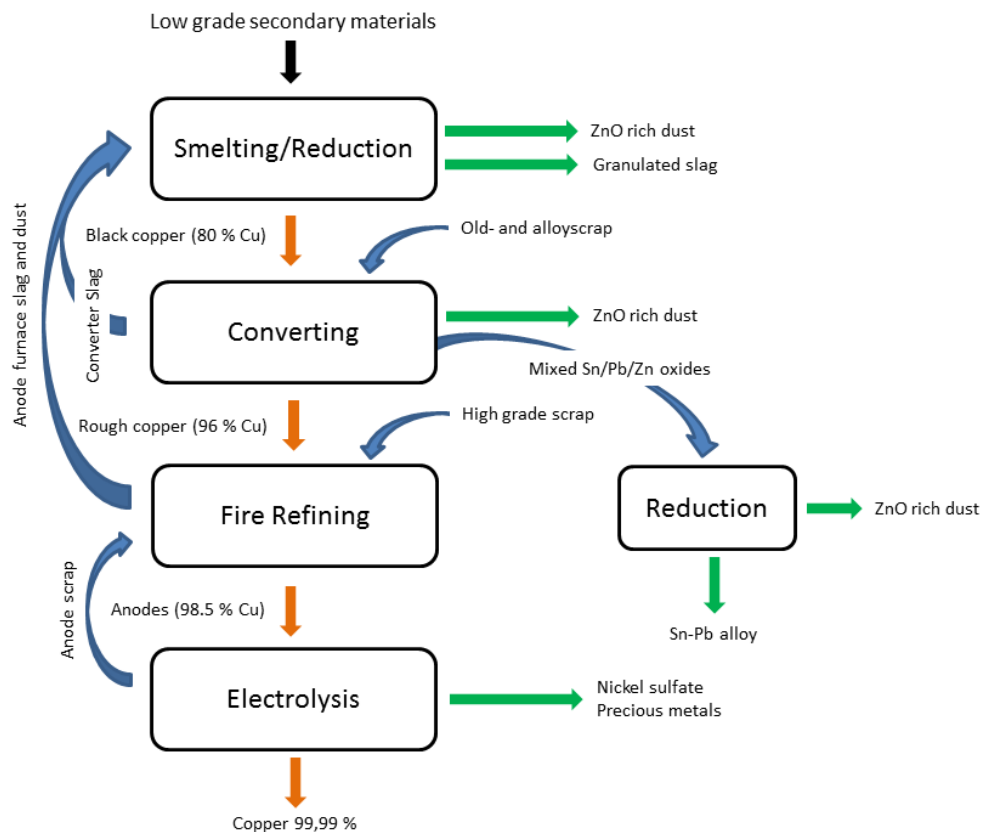


Figure 5: Principal flow scheme of the copper secondary production<sup>14,15</sup>

In general, two mechanisms, the vaporization and the transportation of particles with the off-gas stream, are responsible for the flue dust generation in pyrometallurgical processes. Based on these formation behaviors, the particulate matter in off-gas can be divided in chemical- or mechanical formed dust. Former is generated by vaporization and a subsequent condensation (respectively oxidation) after leaving the reactor. This effect is not undesirable at all, as impurities (especially zinc) can be removed from copper by using this method. On the other hand insufficient raw material preparation or unsuitable reactor design, respectively operation mode can result in mechanical formed dust, so called carry over. Such materials contain copper and process agents like slag etc., therefore, this effect should be minimized. Based on these facts, the quality as well as the quantity of the generated flue dust strongly depends on the feed material composition and the used process technology including the operation parameters.<sup>14-17</sup>

### **Smelting and reduction**

In the first step (see also Figure 5) of copper recycling, typical low grades like slags, dusts, sludges, electronic scraps etc. are processed. The aim is to reduce existing copper oxide from different residues and to generate so called black copper with a purity of approximately 80 % Cu. Based on the feed material the impurity-input and -diversity are very high. In general, they can be divided in metallic- (like zinc, lead, tin etc. from alloys), nonmetallic- (oxides and other metal-compounds from slag, sludges etc.) and organic-contaminants (plastics in scrap and especially electronic scrap). Finally, such materials as well as the used operating conditions lead to the presence and also formation of volatile phases.<sup>14,15,17-19</sup>

Zinc represents a typically volatile impurity in the copper recycling, which is also one of the most important ones. It originates from alloys (e.g. brass) and non-metallic materials, like the slag from the subsequent converting process. As a result of the reducing conditions during the smelting, zinc oxide is partly or completely transformed to zinc, dependent on the operation mode. At the used temperatures the vapor pressure of the produced metal is very high and therefore, a major amount is vaporized. In turn, the gaseous zinc is reoxidized and therefore condensed as zinc oxide in the off-gas system. Finally very high zinc-oxide concentrations are found in the flue dust of the smelting and reduction stage.<sup>14,15,17-19</sup>

Other dust-relevant impurities in this process are the metals lead and tin. Many copper alloys contain these materials and also a lot of solders are made out of them. Furthermore, non-metallic raw materials like drosses and especially refining slags are contaminated with lead and tin. For this they enter the smelting and reduction stage, where a reduction and a partial volatilization occur. Metallic tin shows a low vapour pressure at the used process temperatures, by what a transfer to the gaseous state is

prevented. In contrast, its sub-oxide or sulfide can be easily volatilized at the used temperatures. Lead is basically vaporized as oxide, although metallic lead shows a relatively high vapor pressure. Consequently, the strong reducing conditions in the smelting and reduction step minimize the lead and tin vaporization.<sup>14,15,17-19</sup>

Modern copper recycling facilities are also processing electronic scrap. Those materials lead to precious metal input, which can be recycled within the copper secondary route. But those materials contain also high amounts of plastics, whereby also copper scrap is contaminated with them, as a result of insufficient scrap pretreatment (e.g. cable coatings). Principally, the input of plastics is not unwanted at all, as they can substitute reduction agents, like coke. On the other hand, the input of these materials requires an off-gas treatment to destroy generated dioxins and furans. Furthermore, the plastics contain very often halogens, like chlorine, bromine and fluorine, which in turn lead to dust generation as a result of metal halide formation. Polyvinylchloride for example, one of the most important plastics, contain 57 % of chlorine. Another halogen source is given by electronic scrap, where bromine is used as flame retardant. If such a material enters the smelting and reduction step, it is decomposed and the resulting free halogens react with the metals and their compounds. Finally the produced metal halides show a high vapor pressure at the used temperature, which results in vaporization and therewith in a valuable metal loss.<sup>14,15,20</sup>

Beside the typical chemical formed flue dust, explained above, also mechanical formed dust is generated in the smelting and reduction step. This phenomenon strongly depends on the reactor design, the operation mode and the raw material constitution. Typically, this process stage shows a high quantity of carry over, as a result of the high amount and velocity of the gas-phase. Furthermore, the low grade raw material can contain fine particles, which enter directly the off-gas stream.<sup>16</sup>

## **Converting**

After the smelting and reduction step, the black copper has to be processed in an oxidizing step to remove further impurities remaining from the first step. These are mainly iron, lead, tin and copper. As it can be seen in Figure 5, old and alloy scrap is added during this process for cooling, which causes an additional impurity input. Based on the high temperatures, the bigger portion of zinc is vaporized and consequently oxidized in the off-gas system. Lead should be concentrated in the slag, but as a result of high vapor pressures of the metal and the oxide, a significant amount is volatilized. For the removal of tin two different strategies exist. On the one hand, the tin can be fixed in the slag together with lead in a second converter period (after slagging iron) or it can be concentrated in the flue dust by evaporating the sub-



oxide of tin (SnO). Whatever method is used, the lead and tin rich residue should be further treated to recover these two metals, as shown in Figure 5.<sup>14-17</sup>

High turbulence in the converting process allows a high removal effectiveness of the impurities and only small amounts of lead and tin remaining in the converter copper (96 % Cu). But these conditions lead also to mechanical formed dust, which can contain significant copper concentrations.<sup>14,15</sup>

### **Fire Refining**

The fire refining represents the last pyrometallurgical step in the copper recycling. Beside converter copper high grade scrap is added. During the fire refining a slight reduction and oxidation is carried out to achieve a further decrease of the impurity amount. Although some lead- and tin-oxide as well as some zinc are vaporized, the flue dust generation in this step is rather low compared to the former processes and the percentage of carry over in the dust is high. Therefore, this dust is directly returned to the smelting and reduction step.<sup>14,15,17</sup>

### **Potential Recycling Technologies for secondary copper dust**

Based on the high zinc content of dusts from the secondary copper industry, they represents a latent high grade material for the zinc production, especially as this industry allows the supplementary recovery of the additional included valuable metals like copper, lead and tin. However, these secondary sources cannot be processed directly in the zinc primary industry, due to their high halogen amount.<sup>21,22</sup> The primary zinc production, in particular the electro-winning process, is very sensitive against chlorine and fluorine, as hydrofluoric and hydrochloric acid is generated. These substances lead to the corrosion of the lead anode on the one hand and to the destruction of the aluminium oxide layer of the cathode on the other hand. Moreover, the chlorine in the solution causes chlorine gas formation at the anode, which implies safety risks. Therefore, the maximum halogen concentrations in the zinc electrolysis are limited to 100 mg/l Cl and 50 mg/l F. The effect of bromine in the electrolysis is not studied now, but theoretically it should also form bromine gas, which is much more poisonous than chlorine gas. Consequently, secondary copper dusts need separate processes for the valuable metal recovery.<sup>21</sup>

The recycling of secondary copper flue dusts allows hydrometallurgical as well as pyrometallurgical processes, which are discussed in the next sections.

## Hydrometallurgical recycling

The hydrometallurgical methods offer numerous options to recover the valuable metals. In principle they are leached completely or partly followed by a selective extraction. Very often a previous halogen removal is carried out, as they can influence the processes while moderate to low values can be achieved by simple water or soda leaching.

The conventional technology for the recycling of secondary copper dusts is dissolution of zinc and copper with sulfuric acid followed by cementation. Lead and tin are not soluble at the used conditions and can be separated by filtration. The lead and tin rich filter cake can be further processed in the lead industry. Afterwards copper is removed from the solution by cementation. Therefore, iron scrap or zinc represent potential cementation agents. Zinc offers the advantage that no iron enters the process. If iron is already present in the solution, it can be used as cementation agent, as it is cheaper than zinc and has to be removed in further stages anyway. Finally the zinc is recovered by crystallization of zinc-sulfate.<sup>23,24</sup>

Another, relatively similar approach is given by separating the zinc from the solution via solvent extraction followed by electrolysis to recover metallic zinc. This technology is known as Zincex process, but due to the risk of halogen and organic contamination of the electrolyte it is not widely applied yet.<sup>23-25</sup>

Beside the typical sulfuric acid based processes, also ammonia can be used to recover the valuable metals. The most common method using this medium is given by the so called EZINEX process. Thereby ammonia chloride is used to dissolve the heavy metal fraction (except iron) followed by solution purification via cementation with zinc. In the end the pure zinc is recovered by a novel electrolysis, which forms the basis of the EZINEX technology. Instead of the sulfate system, which is usually used in the zinc industry, a chloride based electrolysis is applied. The presence of  $\text{NH}_3$  eliminates harmful chlorine and the used graphite anode is resistant against hydrochloric acid. Furthermore the fluorine sensitiveness is also low, because of the  $\text{Ca}^{2+}$  existence (formation of  $\text{CaF}_2$ ) and the used titanium cathodes.<sup>23,24,26</sup>

The leaching of metal oxides in the  $\text{NH}_3\text{-(NH}_4)_2\text{CO}_3$  represents an alternative ammonium treatment, but due to the interference of chlorides, a halogen removal in advance is necessary. After solution purification by cementation zinc carbonate can be precipitated.<sup>23,24</sup>

A relatively new method is given by the so called FLUREC process. It leaches the heavy metal fraction with a hydrochloric acid containing solution. A subsequent cementation removes lead, copper etc. and enables a selective solvent extraction.

After re-extracting the zinc into a sulfuric acid solution, high purity zinc can be recovered by conventional electrolysis.<sup>24,27</sup>

Another opportunity is presented by leaching of copper secondary flue dust with caustic soda. This method enables a selective dissolution of lead and zinc, whereas the lead can be cemented by zinc to purify the solution in a subsequent step. Finally the pure zinc is recovered by electrolysis. Based on filtration problems, limited dissolution of zinc-ferrite and the necessary advanced halogen removal, this process is not really appropriate for treating secondary copper dusts.<sup>23,24,28</sup>

### **Pyrometallurgical recycling**

Pyrometallurgical processes are only rarely used for the copper dust recycling. The only common used process reduces the contained metal compounds and forms a metal bath. Soda is added to fix sulfur in the slag and to decrease the necessary process temperature. Zinc is vaporized and concentrated in the flue dust. Finally the liquid metal is cast into ingots and in the end sold as lead tin alloy for the solder industry. In fact only high tin and lead contents in combination with low halogen concentrations justify such a processing. Therefore, this process is not suitable for modern secondary copper dusts with high halogen concentrations.<sup>23,29</sup>

### **Summary**

Sustainability, high amounts of occurring residues and stricter environmental laws, require new strategies for recycling. In the case of steel mill dust treatment various concepts are available. However, different potentials of such residues are not realized yet. This especially refers to the two main problems of too high amounts of produced slag through the waelz kiln and the low zinc oxide product quality. In contrast a simultaneous metal recovery would show different benefits, like the production of an iron alloy, which generates a saleable product and reduces also the cost for landfilling, due to the resulting lower amounts of process waste. Such a process combined with a cleaning step of the charged dust will result in a higher product quality of the generated zinc oxide. The so called "2<sup>S</sup>DR" is a useful recycling concept to reach a Zero-Waste process. Through the two pyrometallurgical steps, clinkering and reduction, performed in a TBRC as main centerpiece, iron alloy, zinc oxide and a stabilized slag can be produced. The concept of this process is especially dedicated and according to the result feasible for small scale operations established within the steel mill where the dusts are generated. Furthermore, other secondary materials could also be treated with this method to enable simultaneous metal recycling and a useable residue. One example for this is the very complex dusts from the secondary copper industry.

## References

1. J. Rütten, "Various Concepts for the Recycling of EAFD and Dust from Integrated Steel Mills" in *Proceedings of 3rd Seminar Networking between Zinc and Steel*, Leoben, 77-90 (2011).
2. A. D. Zunkel, "EAF dust as an electrolytic zinc resource", in *Proceedings of Third International Symposium Recycling of Metals and Engineered Materials*, 579-587 (1995).
3. *Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, [http://eippcb.jrc.ec.europa.eu/reference/BREF/nfm\\_bref\\_1201.pdf](http://eippcb.jrc.ec.europa.eu/reference/BREF/nfm_bref_1201.pdf), requested 2001.
4. *Best Demonstrated Available Technology (BDAT) Background Document for K061*, U.S. Environmental Protection Agency, <http://www.epa.gov/nscep/index.html>, requested 15.05.2014.
5. K. Pilz, "Processing of zinc bearing by-products in an integrated steel mill, voestalpine Stahl GmbH, Linz". in *Proceedings of 61st Meeting of the GDMB Zinc Expert Committee*, Edited by GDMB, Leoben, Austria, 2013.
6. H. Bartusch, A. Fernández, M. Ana and M. Fröhling, "Erhöhung der Energie- und Ressourceneffizienz und Reduzierung der Treibhausgasemissionen in der Eisen-, Stahl- und Zinkindustrie (ERESTRE)", *Erhöhung der Energie- und Ressourceneffizienz und Reduzierung der Treibhausgasemissionen in der Eisen-, Stahl- und Zinkindustrie (ERESTRE)*, 2013.
7. A.-G. Guézennec, J.-C. Huber, F. Patisson, P. Sessiecq, J.-P. Birat and D. Ablitzer, "Dust formation in Electric Arc Furnace: Birth of the particles", *Powder Technology*, **157** (1-3) 2–11 (2005).
8. J. P. Birat, M. Schneider and B. Gros, "Recycling of steel and recycling of zinc: a steel producer's viewpoint", *Revue de Metallurgie-Cahiers d'Informations Techniques*, **95** (6) 721-730 (1998).
9. G. Ye, J. White and L.-Y. Wei, "Association of halogens in electric arc furnace dust and zinc oxide fume before and after leaching" in *Proceedings of Global Symposium on Recycling Waste Treatment and Clean Technology, REWAS'99*, 1503-1510, 1999.
10. S. R. Badger and W. K. Kneller, "The characterization and formation of electric arc furnace (EAF) dusts" in *Proceedings of 55th Electric furnace conference*, Chicago 95-97, 1998.
11. S. Steinlechner and J. Antrekowitsch "Options for Halogen Removal from Secondary Zinc Oxides" in *Proceedings of 3rd Seminar Networking between Zinc and Steel*, Leoben, 47-56, 2011.
12. C. Pichler and J. Antrekowitsch, "Alternative Verfahren zur Aufarbeitung von Stäuben aus der Stahlindustrie", *Mineralische Nebenprodukte und Abfälle*, (2014).
13. G. Rösler, C. Pichler, J. Antrekowitsch and S. Wegscheider, " "2sDR": Process Development of a Sustainable Way to Recycle Steel Mill Dusts in the 21st Century" *JOM*, **66** 1721-1729 (2014).
14. M. Ayhan, "Das neue HK-Verfahren für die Verarbeitung von Kupfer-Sekundärmaterialien", *Intensivierung metallurgischer Prozess: Heft 87 of Schriftenreihe GDMB*, 197-207 (2000).
15. M.E. Schlesinger et al, "Extractive Metallurgy of Copper 5th edition", Elsevier, 2011.
16. B. Björkman and C. Samuelsson, "Dust Forming Mechanisms in the Copper Converting Process", in *Proceedings of Second International Symposium on Extractions and Processing for the Treatment and Minimization of Wastes, TMS*, 105-114, 1996.
17. K. Hanusch and H. Bussmann, "Behavior and Removal of Associated Metals in the secondary Metallurgy of Copper", in *Proceedings of Third International Symposium Recycling of Metals and Engineered Materials*, TMS, 171-188, 1995.
18. L. Muchova, P. Eder and A. Villanueva, "End-of-waste Criteria for Copper and Copper Alloy Scrap", JRC, 2011.
19. A.R.F. Barroso, ENGR5187 "Solid Waste Processing and Recycling, Copper Recycling", Laurentian University, 2010.
20. E. Shibata et al, "Behaviors of antimony oxide, copper and silver during the thermal decomposition of brominated flame retardants", in *Symposium Recycling and Waste Management, Proceedings of Copper 2013*, Chile, 289-296, 2013.
21. J. Antrekowitsch and D. Offenthaler, „Die Halogenproblematik in der Aufarbeitung zinkhaltiger Reststoffe“, *BHM*, **155** 31-39 (2010).

22. J.E. Litz, "Flue Dusts: An Ideal Feed For Resource Recovery, Residues and Effluents - Processing and Environmental Considerations", in *Proceedings of TMS*, 223-239, 1991.
23. N.L. Piret, "Criteria for Optimization of Recycling Processes of Primary and Secondary Copper Smelter Dusts", in *Proceedings of Third International Symposium on Recycling of Metals and Engineered Materials*, Point Clear, Alabama, 189-214, 1995.
24. M.K. Jha, V. Kumar and R.J. Singh, "Review of hydrometallurgical recovery of zinc from industrial wastes", *Resources, Conservation and Recycling*, **33** 1-22 (2001).
25. D. Martin et al, "Extending zinc production possibilities through solvent extraction", *The Journal of The South African Institute of Mining and Metallurgy*, 463-467 (2002).
26. M. Olper and M. Maccagni, "From C.Z.O. to Zinc Cathode without any Preatreatment" In *Proceedings of The EZINEX Process, Lead and Zinc 2008*, Durban, South Africa, 85-98, 2008.
27. S. Schlumberger and J. Bühler, "Urban mining: Metal recovery from fly and filter ash in Waste to Energy plants", in *Proceedings of Ash Utilization 2012*, Stockholm, Sweden, 2012.
28. A. Stefanova and J. Aromaa, "Alkaline leaching of iron and steelmaking dust", *Aalto University publication series Science + Technology*, **1** (2012).
29. G. Fleischer, R. Kammel, U. Lembke, „Zur pyrometallurgischen Verarbeitung von zinn-, blei- und zinkhaltigen Flugstäuben“, *Recycling von Metallen*, 94-100 (1989).