Bernd Böttcher (JL Goslar Anoden GmbH, Germany, b.boettcher@jlgoslar-anoden.de)
Dr. Franz Martin Knoop (JL Goslar GmbH, Germany, fm.knoop@jlgoslar.de)
Guido Hellmann (JL Goslar Anoden GmbH, Germany, g.hellmann@jlgoslar-anoden.de)

POTENTIAL FOR AN INCREASED USE OF SECONDARIES IN A ZINC ELECTROLYSIS - THE ROLLED PbAg-ANODE

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In the past, primary materials have mainly been used for Zinc production. In recent times, the production situation has changed. Natural resources are deteriorating, energy costs and consumption is an issue and environmental protection has initiated strong demands to production plants. In order to respect these items, alternatives for a cost effective Zinc production have to be found. An increased consumption of Zinc in consumable devices and industrial applications such as corrosion resistant layers on steel components leads to an increase of valuable residues, respectively an increased availability of secondary materials.

The Imperial Smelting Furnace is perfectly designed for the use of these secondaries. Unfortunately, due to production costs and environmental restrictions, there has been a development from pyrometallurgical to hydrometallurgical processes at much lower temperatures.

The continuous use of recycling Zinc products in an electrolysis is going along with an increased presence of halogens such as Chlorine and Fluorine. Corrosion of lead anodes as operating resources for Zinc winning and a decreased performance and lifetime will be the result. A solution to this problem is rolled high performance lead silver anodes. Rolled anodes have the advantage of a remarkable higher corrosion resistance in comparison to cast anodes. The reason is the silver enrichment on the elongated grains due to a controlled rolling process.

In the framework of meeting environmental requirements and in order to decrease costs by using less expensive secondaries, rolled lead silver anodes are offering a perfect contribution to both issues. Lead anodes are nearly 100 percent recyclable, means anode parts such as copper bar, stainless steel hooks, head and sheet lead can be separated and directly reused for the production of new anodes. Therefore, rolled lead silver anodes are matching perfectly into the actual environmental friendly demand for a higher rate of recycling and become therefore a product of the recycling.

Usage of seconaries for Zinc winning

Zinc is a metal that has become important over the last decades for many different industrial applications. Typical applications are:

- Galvanizing: e.g. galvanized or electrochemical deposition, sacrificial anode
- Zinc alloying: e.g. finished technical/industrial parts, die casting
- Brass and Bronze: e.g. household appliances, press plates
- Zinc Semi-Manufactures: e.g. strip (rolled Zinc on coils)
- Chemical solution: e.g. Zinc dust paint
- Miscellaneous

The different application share ratios of these industrial applications are shown in figure 1 [1].

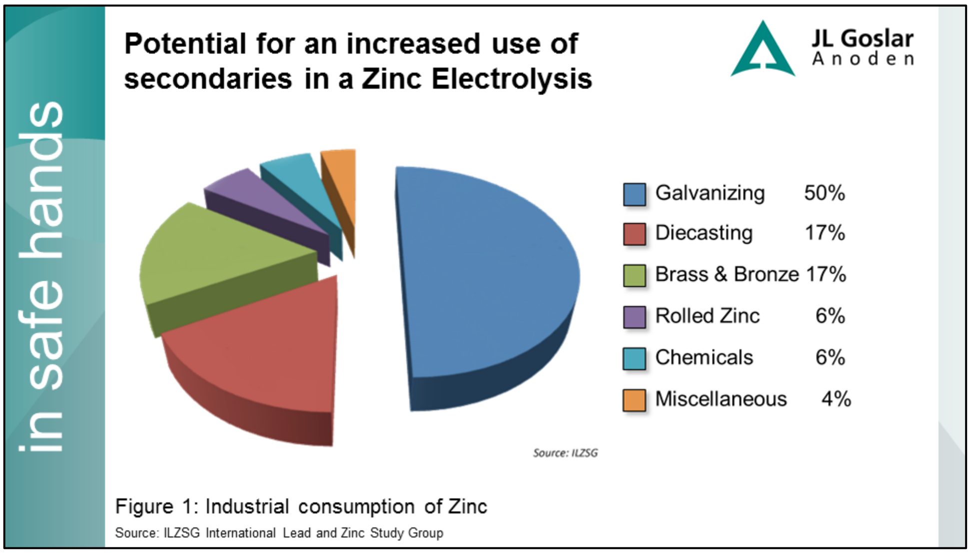

Figure 1: Industrial consumption of Zinc
Source: ILZSG International Lead and Zinc Study Group

In the beginning of the industrial production of Zinc, the primary source were sulphuric concentrates of zinc from ore as a mining product. Since all natural resources are not endless, also the availability of Zinc ore is limited, respectively has already shown deterioration.

In parallel Zinc has been more and more used in industrial applications and for industrial products. With an increased age, worn out industrial Zinc containing parts are increasingly appearing and are offering a high potential as secondary material for new Zinc production.

Nowadays, Societies and companies are showing more and more environmental responsibility and recycling has become an important issue. On one hand nature has to be protected against pollution but also an answer to the question, what to do with the increasing residues had to be found. Therefore, as in all other industrial segments, Zinc recycling has become an issue.

In order to industrialize Zinc recycling, pyrometallurgical procedures have been developed and used and especially the Imperial Smelting technology has been proofed by far as the leading one. The production flow of this technology is displayed in figure 2.

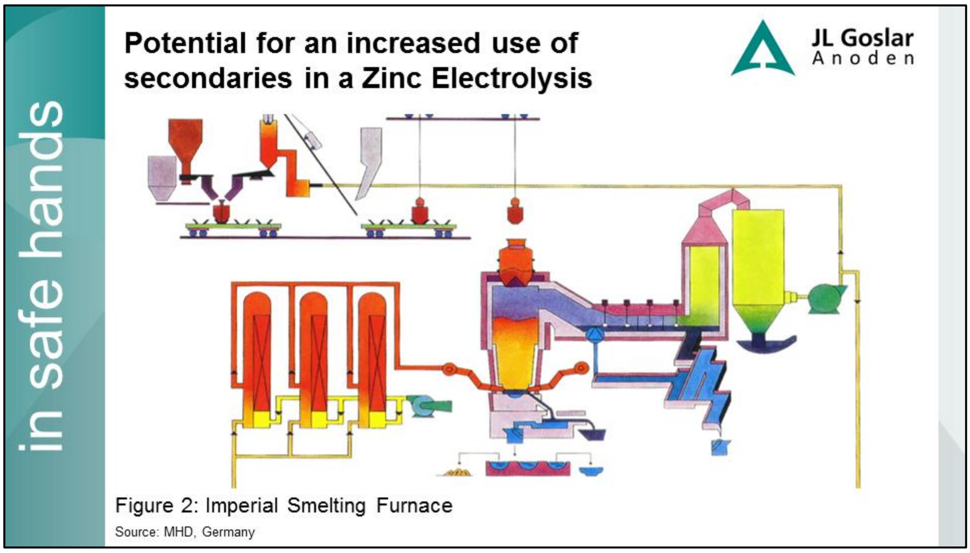

Figure 2: Imperial Smelting Furnace
Source: MHD, Germany

The unique layout of such an Imperial Smelting Plant offered the possibilities of multiple input of secondary material into the process. These can happen directly into the IS furnace or into the following refinery process as to be seen in the following figure 3.

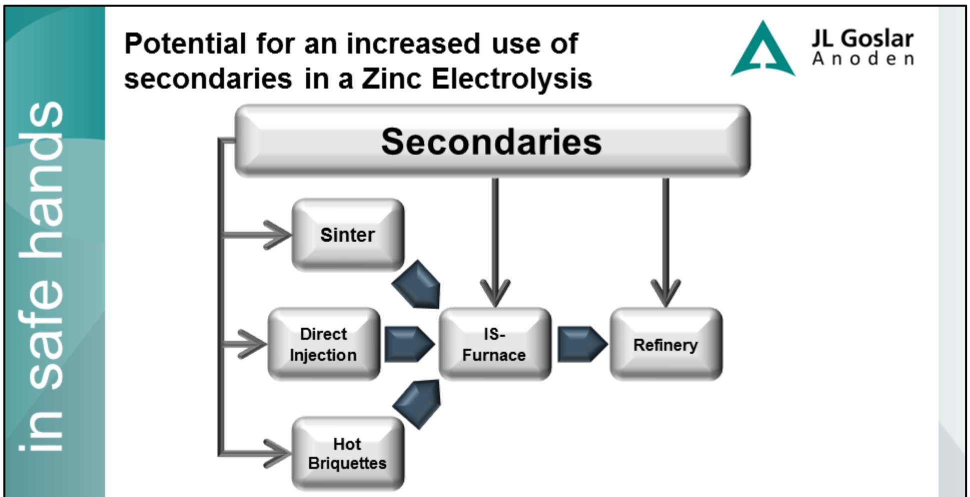

Figure 3: ISF-Process designed to treat recycling materials and concentrates
Source: Chart by JL Goslar GmbH

The following figure 4 shows the various sorts of Zinc containing material that can be used practically in an Imperial Smelting furnace. The range of Zinc content can be from approx. 25 % in EAF-dust and batteries up to more than 95 % in top dross.

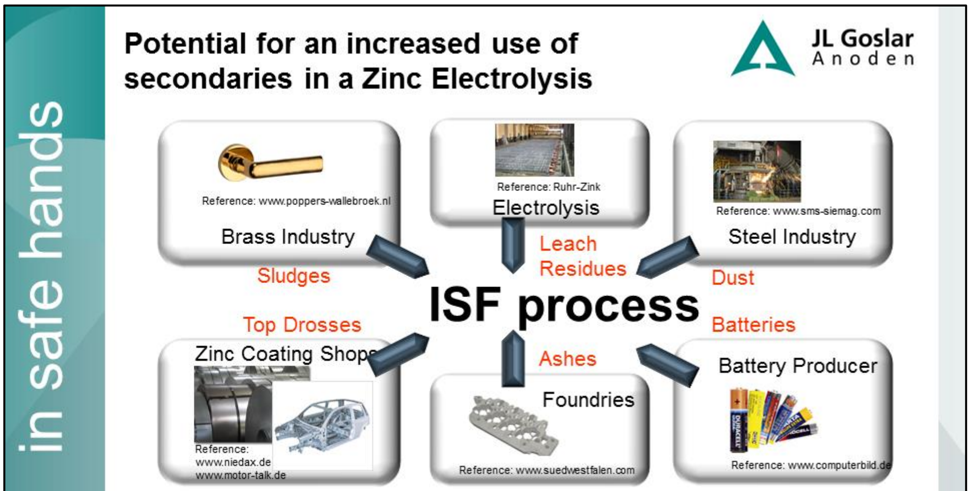

Figure 4: Wide range of secondaries to be treated in the various process steps of ISF
Source: Chart by JL Goslar GmbH

Future of ISF-technology

The imperial Smelting furnace has shown evidence that it is the ideal solution for the recovery of Zinc out of various secondary materials. The technology can be run at 100 % secondary feed and has been used by many Zinc smelters such as e.g. MHD (Germany), Portovesme (Italy), BZL (England) and Copsa Mica (Romania).

Unfortunately, high operation costs are involved in the process and it has become more and more difficult to meet environmental restrictions and finally all Imperial Smelting Furnaces in Europe have been closed. The only still existing one is in operation at Miasteczko Slaskie, Poland. The map in figure 5 shows the different previous locations of ISF plants and the only one remaining. There are also plants remaining in operation in Asia and especially in China.

The ISF as a pyrometallurgical possibility to extract Zinc from secondaries has been mostly vanished but the availability of Zinc residues is still given and increasing, respectively an alternative must be found and the change to the hydrometallurgical field of electrolytical metal extraction has been initiated, which seemed to be impossible in the past.

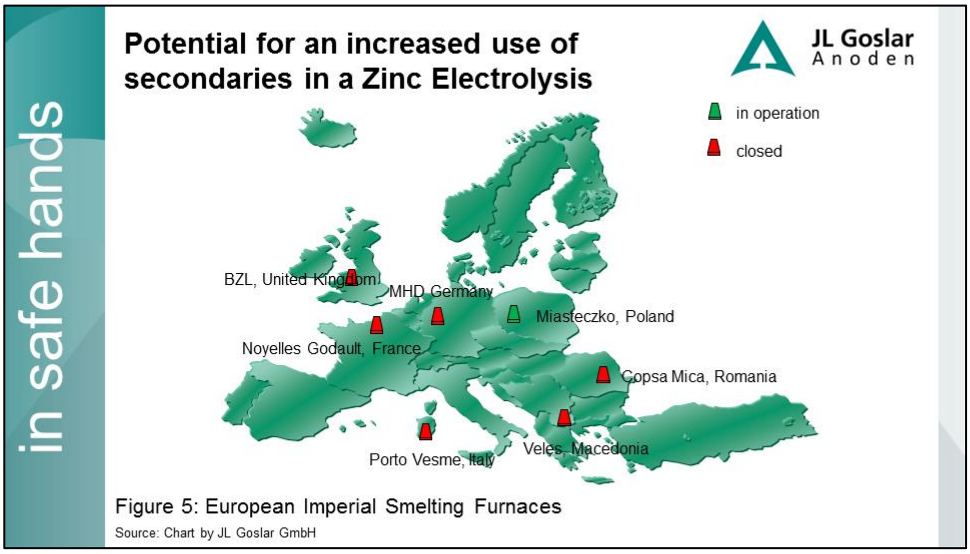

Figure 5: European Imperial Smelting Furnaces
Source: Chart by JL Goslar GmbH

Potential of rolled PbAg-anodes for Zinc electrowinning

Electrowinning was originally established as a process for treating only sulfide concentrates with well-known composition and a well-defined amount of impurities. All this was leading to comparable low cost production of SHG-zinc (Zn99.995).

In general, the classical roasting-electrowinning zinc plant offers you two points in the flow sheet, where secondary material could be added, roasting and / or leaching (figure 6).

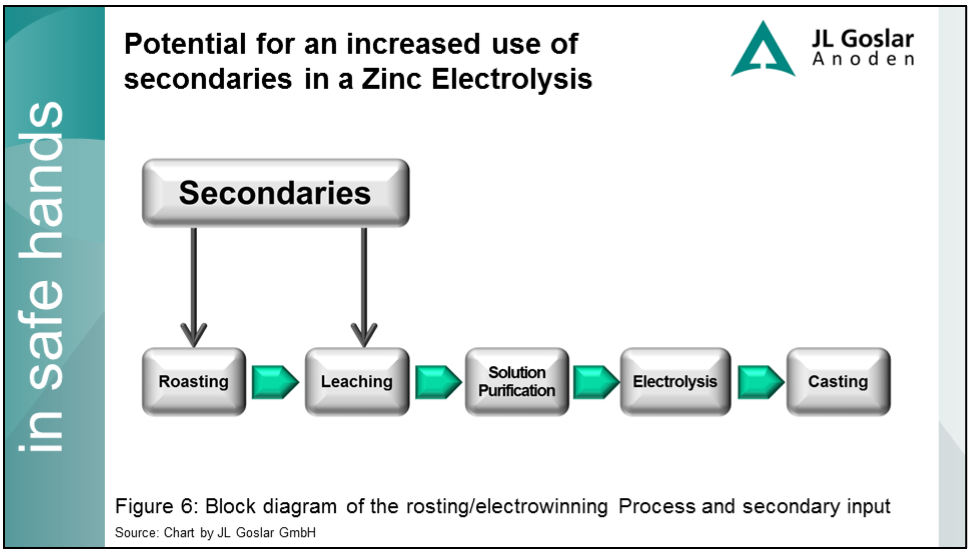

Figure 6: Block diagram of the rosting/electrowinning Process and secondary input
Source: Chart by JL Goslar GmbH

Nevertheless there are limitations in throughput and new impurities arising with the treatment of secondary material.

Firstly, the treatment of secondary mainly oxidic material in a fluid bed roaster is limited by the heat balance and by the addition of elements for lowering the melting point of the feed mix.

Secondly, the leaching plant has a limited throughput because of the new presence of elements such as e.g. Copper, Cobalt and Nickel.

But the major problem with the usage of secondaries are new impurities, in form of Chlorine and Fluorine at a magnitude that hasn't been experienced before (see table 1 below). Their concentration in the electrolyte should be more or less at zero by definition, otherwise electrowinning will be more or less impossible due to the following issues.

Potential for an increased use of secondaries in a Zinc Electrolysis

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in safe hands

Halogen		
F	mg/l	up to 75
Cl	mg/l	up to 850

Table 1: Typical electrolyte with higher amounts of halogens
Source: Chart by JL Goslar GmbH

An electrolysis consists out of a set of anodes and cathodes in a cell, surrounded by electrolyte, mainly sulphouric acid and Zinc sulfate. An increased presence of Chlorine and Fluorine has a strong impact on the anode and cathode as operating resources for metal extraction.

Fluorine is mainly influencing the cathode behavior showing a reduced lifetime and the necessity to brush the cathodes after each cycle. Only this brushing assures a fresh surface of the cathode and allows Zinc stripping even at higher Fluorine contents.

An increased presence of chlorine leads to a higher rate of corrosion on the anode sheets. The following figure 7 [2] demonstrates the corrosion development depending on the chlorine content. It has to be taken into account that today's values of chlorine content in Zinc electrolysis can go up to 850 mg/l as mentioned above.

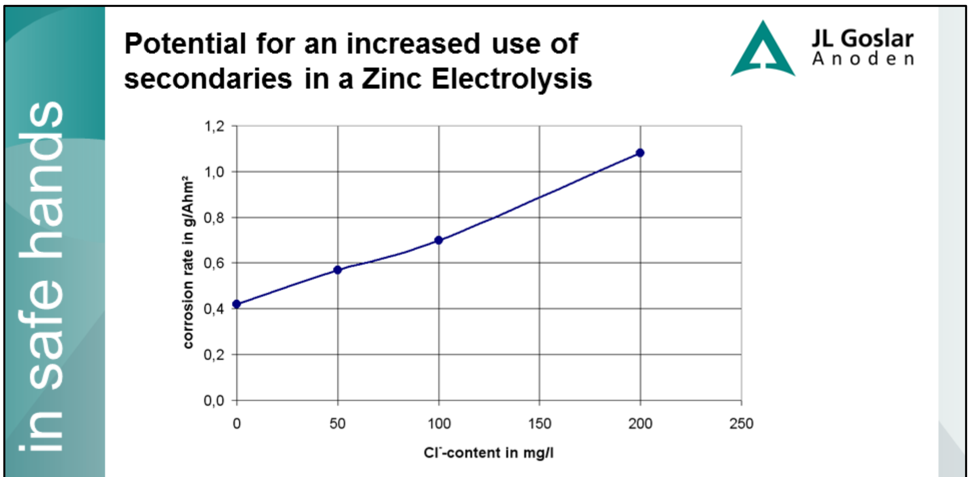

Figure 7: Correlation between chlorine content and corrosion rate [2]

Source: [2] M. Stelter, H. Bombach, P. Saltykov, Institute for Nonferrous Metallurgy and Purest Materials, Optimisation of lead anodes for zinc electrowinning, Zinkfachausschuss, 27. - 29.10.2004 San Juan (Spain)

As a second parameter for the ratio of corrosion on the anode sheet, beside the current density applied by the plant, is the temperature and the correlation can be seen in the following figure 8 [2].

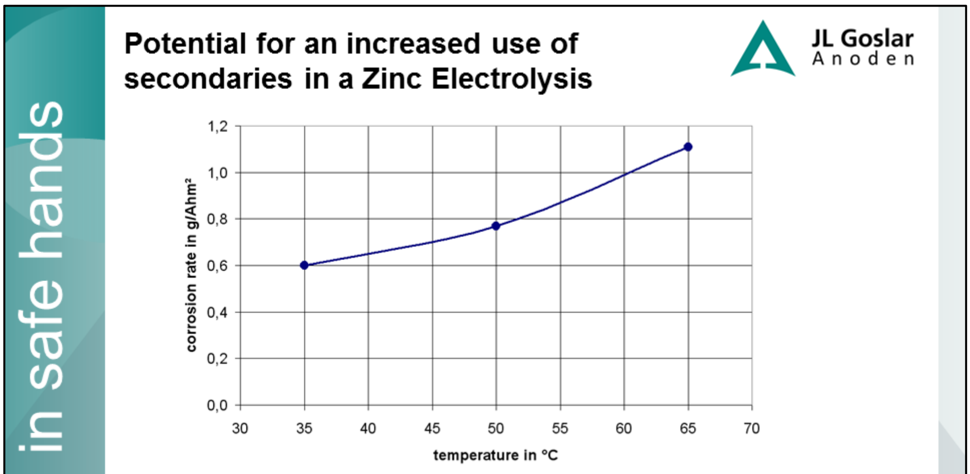

Figure 8: Correlation between temperature and corrosion rate

Source: [2] M. Stelter, H. Bombach, P. Saltykov, Institute for Nonferrous Metallurgy and Purest Materials, Optimisation of lead anodes for zinc electrowinning, Zinkfachausschuss, 27. - 29.10.2004 San Juan (Spain)

In order to manage this changed situation, an alternative to the existing anode had to be found.

The Anode in Metal Extraction

Lead silver anodes have been produced in-house in the electrolysis plant as a cast product. This was a simple and easy way to produce anodes according to the demand of this operating resource in process and satisfied the requirements with the treatment of clean primary sulphuric concentrates.

Since now the environment has changes with the continuous input of secondaries, the requirement on anodes has changed and a development was necessary to manage the high content of impurities and to achieve an acceptable lifetime of an anode.

In addition, increasing energy cost was also one of the main reasons to think about the efficiency of the anode – cathode system. Investigations carried out by the anode manufacturers, who had established themselves over the years as suppliers to the electrolysis companies, and who had also initially produced these anodes in the casting process, have started to develop anodes with rolled anode sheets for applications like copper extraction (PbSnCaAl-anodes) and Zinc extraction (PbAg-anodes).

Especially the development from cast anodes to the rolled anode sheets was a significant step forward for PbAg-anodes. The rolling process lead to a higher effectiveness and an improved level of corrosion resistance, with the positive side effect that in parallel, the silver content could be reduced. Silver as an alloying element in lead is responsible for corrosion resistance. The silver content in cast anodes at 1 % has been judged as sufficient but with the rolling process, the very high silver content can be reduced and nowadays, the usual content of 0,40 – 0,65 % has been evaluated as sufficient for corrosion protection and will grant an acceptable lifetime at an average of 4-5 years, of course always dependant on the process conditions and the careful treatment of the anodes. As a positive side effect, less silver has to be used from a natural resource point of view and the working capital can also be reduced.

An elongated lifetime of anodes in use is economical but extends also an early necessity of recycling. Therefore every electrolysis operator has the opportunity to optimize their process with a careful treatment and maintenance of the anodes during the production cycle. An anode cannot, however, be considered to be maintenance-free.

The following flow chart represents a possible procedure for maintaining and extending the function of an anode (figure 9).

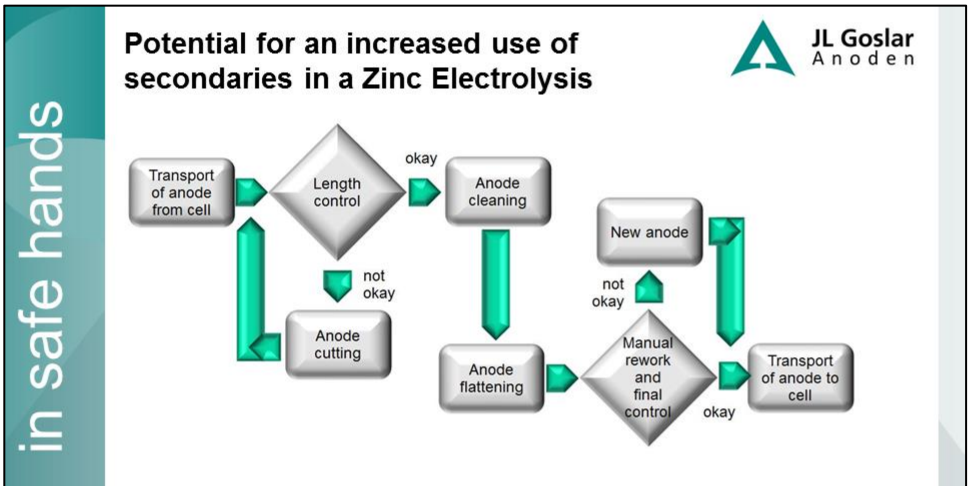

Figure 9: Flow chart of recommended anode treatment
Source: Chart by JL Goslar GmbH

What is now the major impact of the rolling process to the casting? The reason is the microstructure of the lead silver sheet.

Cast anodes were made in specialized casting moulds in which the copper bar was placed. The casting process was optimized by the casting temperature of the lead alloy and the pre-heating and/or the cooling of the casting mould. The result was a fine granulation of the solidified microstructure. The manufacturing of the slab in the production of rolled anode plates is also subject to defined parameters, within a defined temperature range. This forming process leads to an obvious elongation of the grains and the difference can be seen in the pictures of the different microstructures in figure 10 [2].

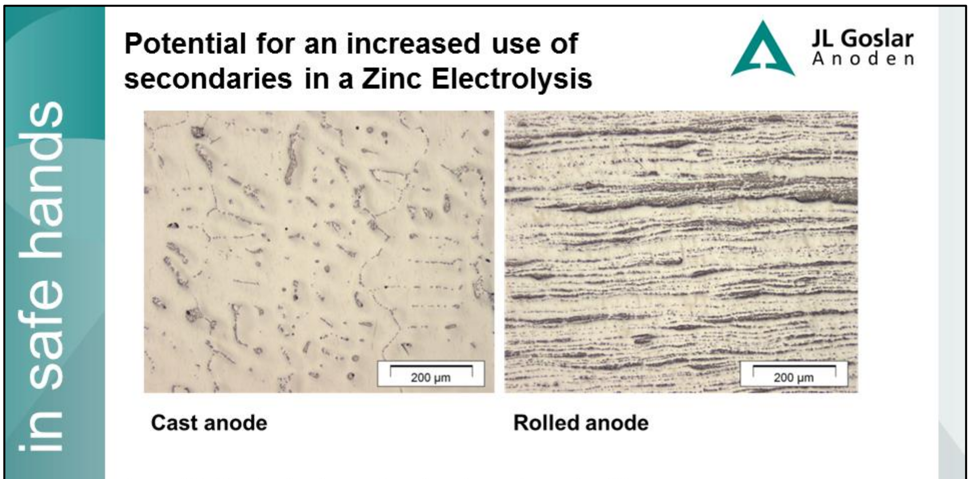

Figure 10: Grain structure of cast and rolled anodes [2]
Source: [2] M. Stelter, H. Bombach, P. Saltykov, Institute for Nonferrous Metallurgy and Purest Materials, Optimisation of lead anodes for zinc electrowinning, Zinkfachausschuss, 27. - 29.10.2004 San Juan (Spain)

Qualitatively, the grains are elongated drastically from up to 200 microns in cast anode sheets to 3.000 microns in rolled anodes sheets as you can see in figure 11 [3].

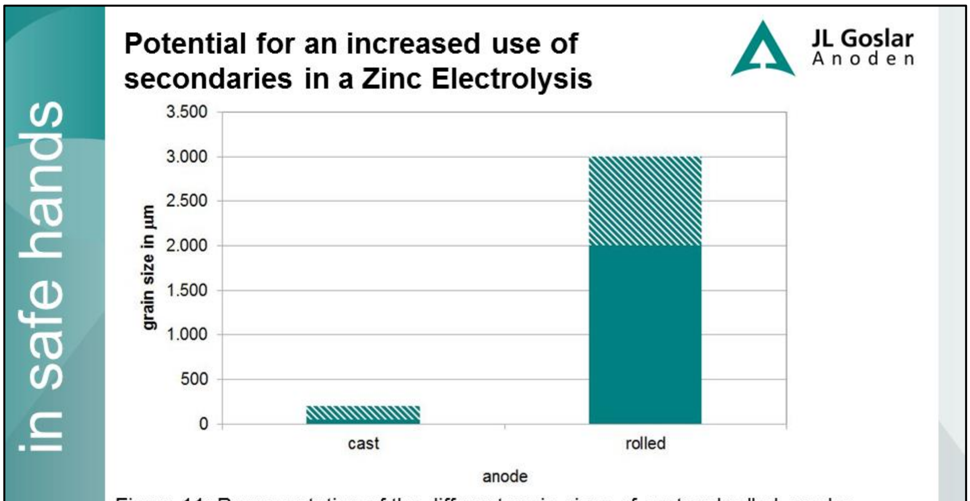

Figure 11: Representation of the different grain sizes of cast and rolled anodes
Source: Chart by JL Goslar GmbH

The elongated grains and the increased grain surface offers the possibility of a silver precipitation on those grain boundaries, which leads to much more active silver involved as a protection against corrosion [2]. Figure 12 shows that the Ag precipitation on the grain boundaries will be approximately 30% higher on the rolled anode sheets than on the cast anode [3].

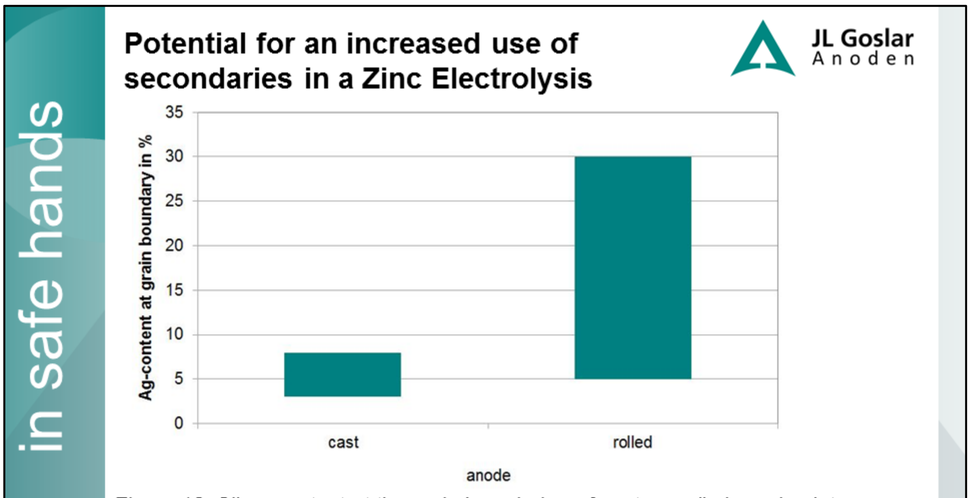

Figure 12: Silver content at the grain boundaries of cast vs. rolled anode plates

Source: Chart by JL Goslar GmbH

Figure 13 shows further on that even a rolled anode sheet at a lower silver content shows a lower corrosion rate than a higher alloyed cast sheet. Consequently in practice, the silver content can be reduced under the same electrolysis parameters [3].

The formation of these elongated grains in combination with high silver contents at the grain boundaries improves and increases also the effectiveness of the anode with an increased electrical conductivity, like an electric cable and less resistivity leading to an improved appliance of current density.

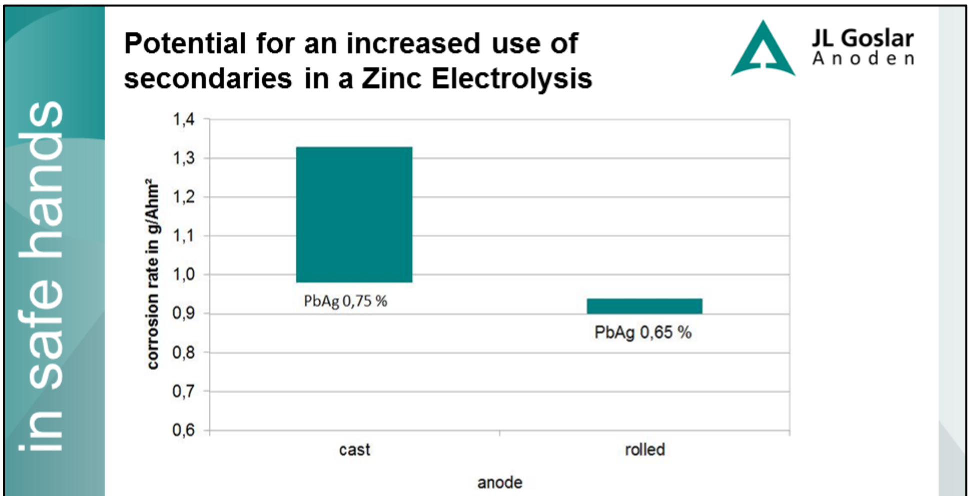

Figure 13: Corrosion rates of cast vs. rolled anode plates

Source: Chart by JL Goslar GmbH

Metal ball blasting of lead silver anode sheets, according to special JL Goslar procedure, will further support the formation of homogenous PbO_2 and MnO_2 layers on the anode sheet surface to achieve their full operational performance in the shortest possible time (figure 14).

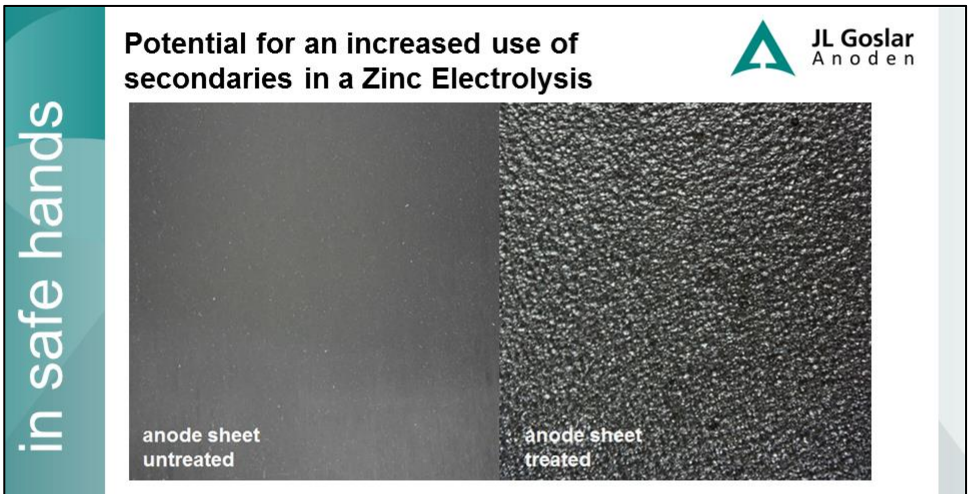

Figure 14: Anode surfaces without vs. with post-treatment
Source: Chart by JL Goslar GmbH

The rolled anode sheet is showing a lower rate of oxide adhesion, as displayed in figure 15 [3], in comparison to the cast anode which leads to less yield of oxide residues on the anode sheet surface as well as anode sludge inside the cells. Consequently, a reduced oxide residues has to be removed and recycled.

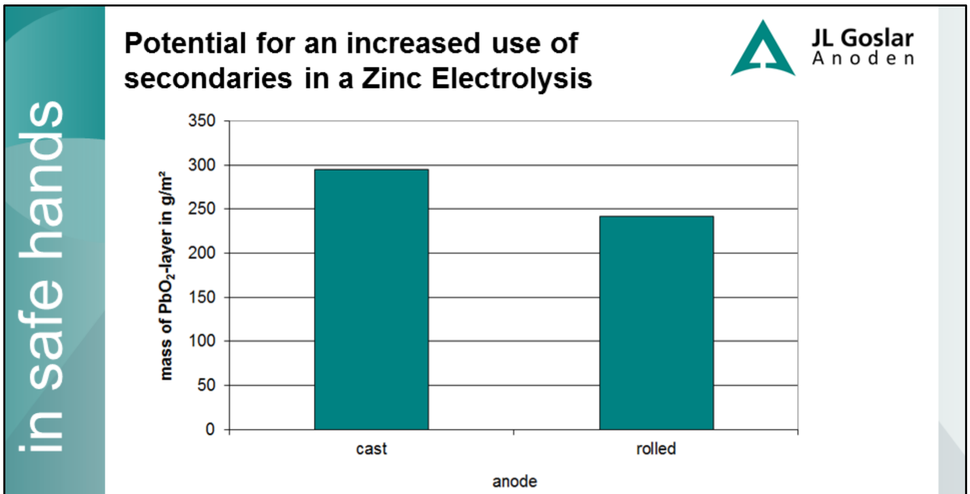

Figure 15: Oxide layer on cast and rolled anode sheets
Source: Chart by JL Goslar GmbH

Furthermore figure 16 shows that the rolled anode achieves a lower corrosion rate, respectively corrosion protection at a lower mass of oxide layer against the cast anode [3].

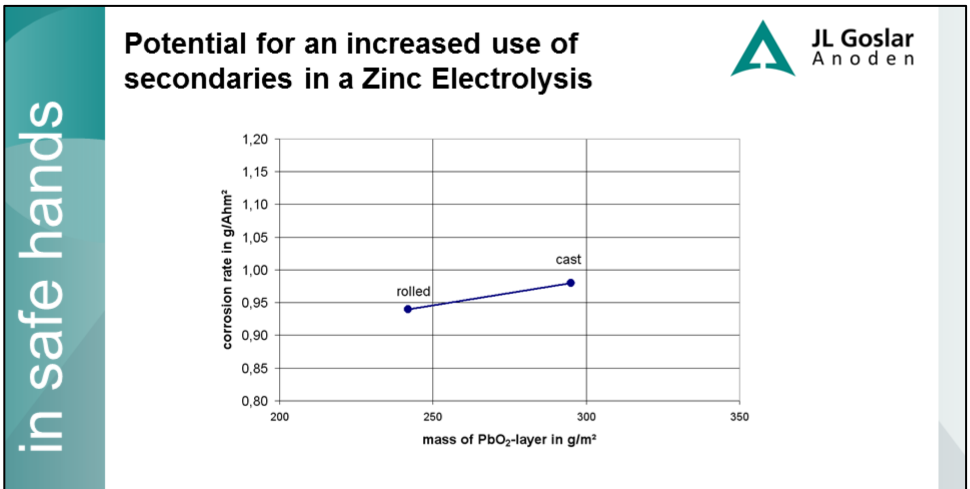

Figure 16: Correlation of PbO_2-layer mass and corrosion rate

Source: Chart by JL Goslar GmbH

The rolled anode has offered the usage of secondary materials, respectively the increased recycling of zinc containing residues. Nevertheless also the anode itself will reach only a certain lifetime and the question is how to deal with this sort of scrap.

The anode consists out of different component that can individually be evaluated, scrapped and recycled. As a first step, the worn out used anode should be sent back to the anode manufacturer. After the arrival, the anode head must be separated from the anode sheet. The reason lies in the possible different lead alloys of the head and the sheet but furthermore in Tin content in the head lead. This Tin is necessary to create a perfect bonding between the copper bar and the head lead but has a negative effect inside a Zinc electrolysis, respectively a Tin contamination of the sheet lead, being used for new anodes, must be avoided.

In general a smelting loss plus a mechanical loss can be expected but the remaining head and sheet lead will be reused for new anodes.

The copper bars and stainless steel hooks will be evaluated after the remelting of the head lead in order to see if they can be reused for the production of new anodes. In case of a heavy damage or strong corrosion, these components will be recycled, respectively transformed into new copper and stainless steel.

A schematic flow of the recycling process of used anodes can be seen in the following figure 17.

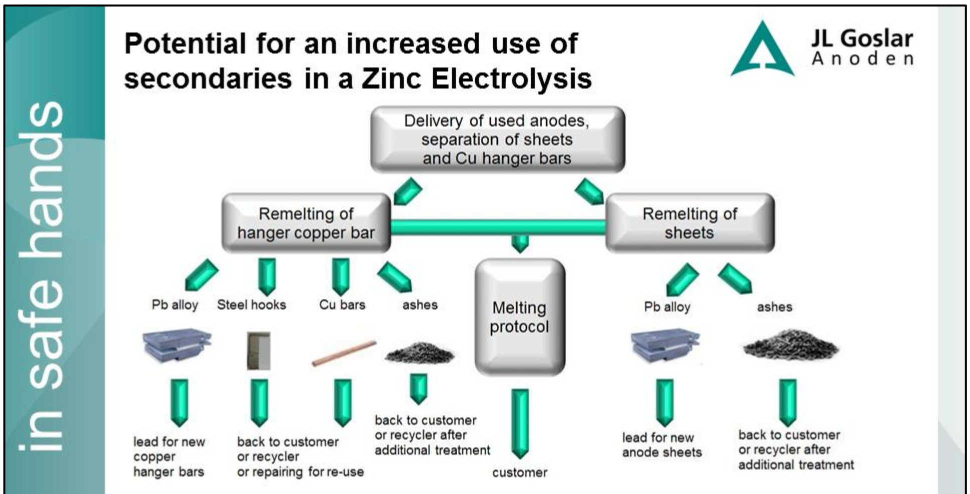

Figure 17: The recycling process of used anodes at JL Goslar GmbH, Germany

Source: Chart by JL Goslar GmbH

At last, there is a certain amount of ash and dross remaining. This can't be reused for the production of new anodes. Nevertheless it still contains a high amount of metal. In order to show responsibility to environmental issues as well an economical point of view, JL Goslar operates a further possibility of extraction of remaining metal inside the ash/dross in a second step after the regular remelting. Figure 18 is showing a so called MZR furnace as a process for ash after treatment.

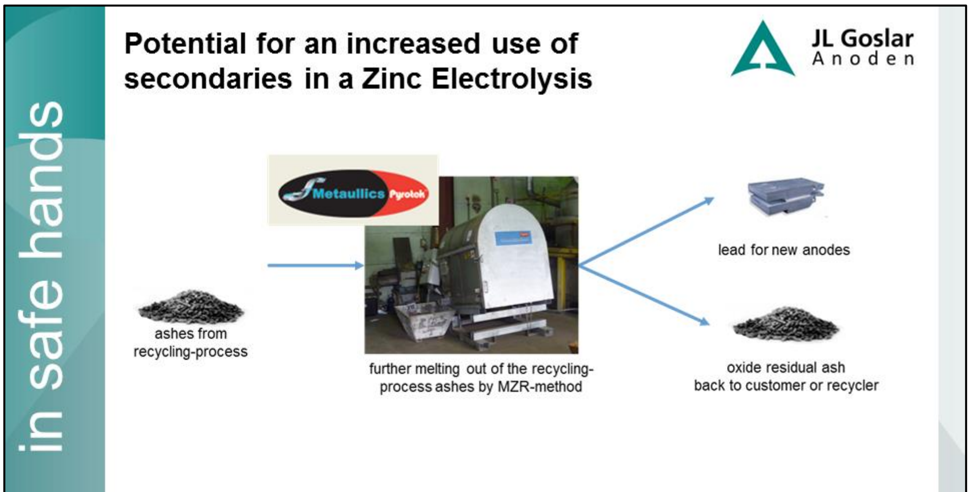

Figure 18: MZR furnace for the after treatment of ash

Source: Photos by JL Goslar GmbH

Conclusion

As a consequence of

- a deterioration of primary resources for Zinc extraction
- the availability of increasing volumes of secondaries and the need to deal with them
- and the advantage of higher Zinc content in refined secondaries (WOX) than in primary resources

a suitable production process to handle secondary materials had to be found. The Imperial Smelting furnace is the perfect choice to manage successfully this development. Nevertheless it is expensive and doesn't match with environmental restriction.

In the framework of the transformation from pyrometallurgical production routes to hydrometallurgical processes, the rolled lead silver anode offered the possibility for an increased use of secondaries in electrolytical Zinc winning and to perform with the corresponding increase of halogen contents such as chlorine. This realizes an efficient and economical way of recycling of Zinc containing residues.

A rolled anode has a sufficient lifetime, always depending on a careful treatment but has finally also to be scrapped. Lead anodes are consisting of different metallic parts that can individually be reused or recycled. Therefore, rolled lead silver anodes are matching perfectly into the actual environmental friendly demand for a higher rate of recycling and become therefore a product of the recycling.

References

[1] ILZSG International Lead and Zinc Study Group

[2] M. Stelter, H. Bombach, P. Saltykov, Institute for Nonferrous Metallurgy and Purest Materials, Optimisation of lead anodes for Zinc elelectrowinning, Zincfachausschuss, 27.-29.10.2004 San Juan, Spain

[3] B. Böttcher, Dr. Schwab, H. Walk, From cast to high efficient rolled anodes in an electrolytic zinc plant – a field report