Zinc Recycling, a Necessity for Mature Societies and a Challenge for Developing Societies

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Abstract

The winning of non-ferrous metals often takes place at reworking plants. The input materials (in the past exclusively concentrates), i.e. primary materials, are purchased from all over the world and made into a blend at the plant. This blend was the guarantee of a manageable process; the process variables were at textbook levels. How-ever, increases in wage, energy and raw material costs in recent decades have forced the operators of these plants to continually seek new ways to reduce their costs. This report will look into the possibilities for cost reduction through changing the raw material basis. The areas of wages and energy will not be explicitly dealt with, but the positive effects of a different raw material basis and altered processes will be highlighted.

The use of secondary materials is very closely linked to the issue of finding alternative raw materials. These secondary materials are generally waste products from metallurgic processes. The use of these materials and their re-exploitation fall under the term "recycling". These secondary materials are available in different concentrations of exploitable valuable metals, sometimes in large quantities. Alongside treated secondary materials, the valuable metal content of which is at a concentrate level, treatment techniques that combine metal-containing secondary materials with secondary fuels - thus intensifying the recycling and having additional positive effects on cost reduction - have now also been tested.

However, in order to be able to make a high level of secondary input possible, changes in the relevant process management, or even new processes, are necessary. This includes the adaptation of the plant technology, particularly in terms of wear and effectiveness, which can be achieved through the correct choice of materials and extensive process monitoring, among other things.

The possibilities of secondary material input for winning non-ferrous metal will be highlighted using the example of two processes for generating zinc.

1 Zinc Circuit and Zinc Recycling

If you step today into a business it should be environmentally friendly. If you look on zinc for instance, only if recycling is possible galvanizing of automotive sheets will be realized in combination with a positive image and will be a business for the future. Therefor zinc recycling is nowadays state of the art in mature societies and will get more and more in the focus of developing countries. Zinc usage starts usually with galvanizing of steel. It takes several years before this galvanized steel shows up as scrap in an EAF producing EAF-Dust, which will be recycled for zinc winning. And like all non-ferrous metals zinc is ideal for recycling, because at the end of the recycling loop the quality and the composition of the metal shows no different to the one produced from primary materials.

2 The Imperial Smelting Technology

2.1 The ISF Process and its Possibilities

The first steps into zinc recycling were made in the pyrometallurgical zinc production. Here the Imperial Smelting technology is by far the leading one. The unique layout of such a plant gives the possibilities of multiple input of secondary material into the process:

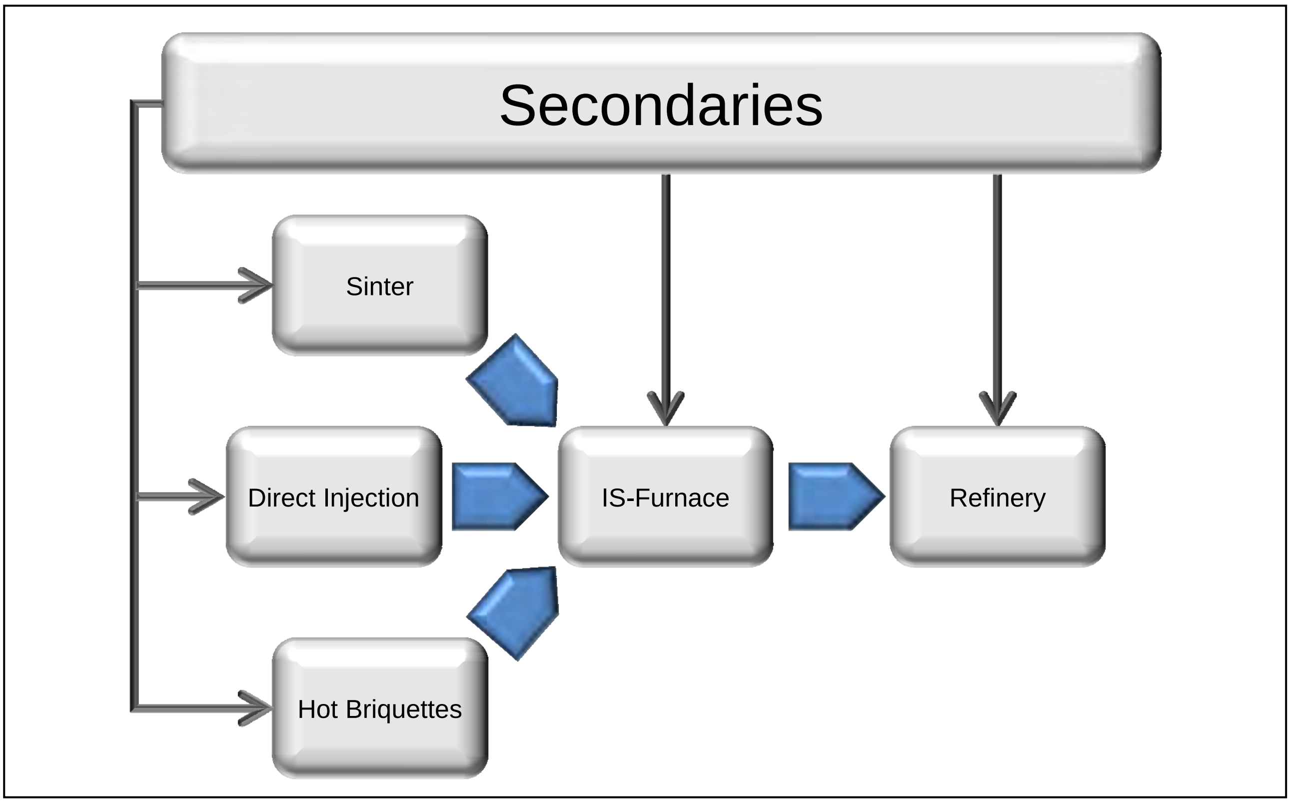


Figure 1: ISF-Process designed to treat recycling materials and concentrates [1]

This pyrometallurgical process can treat the following materials without any problem with Zinc contents from approx. 25 % for EAF-dust and batteries up to more than 95 % for top drosses.

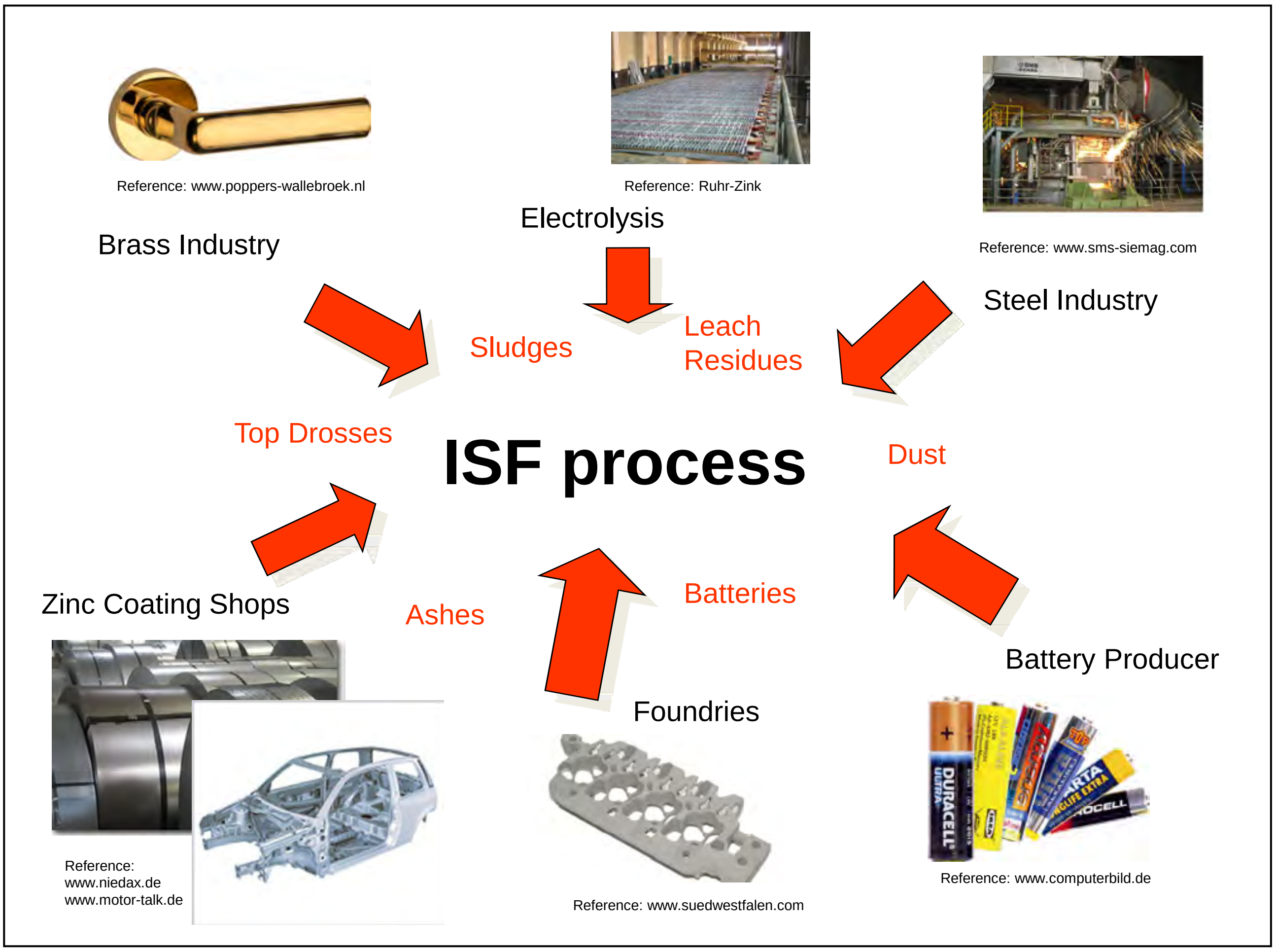


Figure 2: Wide range of secondaries to be treated in the various process steps of an ISF

3 Incorporation of Secondaries in the Feed Mix

The following tables give an overlock on different materials that can be handled in a pyrometallurgical plant:

Sinter plant:

- Neutral leach residue, galvanizing ashes, electro galvanizing residues, metal containing slags

Hot briquetting:

- Waelz oxides, galvanizing ashes, EAF dust

IS-Furnace:

- Top drosses, portable batteries, hard zinc
- Direct Injection: EAF-Dust, cupola furnaces residues
- Metallurgical Stones: EAF dust, waelz oxides

Refinery:

- Top dross, bottom dross, alloys

Typical analysis of these secondaries are shown in the following table.

Table 1: Analysis of secondaries

Sinter Plant							
Material		EAF-dust	Zn sludge	Leach residue	Zn hydro-sludge	Copula furnace residues	Lead slag
Moisture	%	1 – 10	20 – 60	25 – 70	50 – 82	1 – 34	1 – 2
Zn	%	20 – 35	34 – 72	18 – 56	22 – 46	25 – 40	4 – 6
Pb	%	1 – 5	0 - 3	0 - 7	0	0 - 1	50 – 55

Hotbriquetting Plant							
Material		Oven break	Zn ashes	Waelz oxid	Zn oxid		
Moisture	%	1 – 2	0 – 3	0	0 – 20		
Zn	%	60 – 75	50 – 76	55 – 65	30 – 56		
Pb	%	2	1 – 6	4 – 6	2 – 16		

IS-Furnace							
Material		Batteries	Zn scrap	Pb scrap	Hard Zn	Metallurgi-cal stones	
Moisture	%	3	0	0	0	< 15	
Zn	%	28	>95	0	92	> 25	
Pb	%	0	0	>95	0	> 1	

IS-Furnace – Direct Injection							
Material		EAF-dust	Copula furnace residues	Waelz oxid			
Moisture	%	0	0	0			
Zn	%	25 – 37	37 – 46	60 – 65			
Pb	%	3 – 4	<1	4 – 7			

Refinery							
Material		Top dross	Bottom dross	Alloys			
Moisture	%	0	0	0			
Zn	%	>95	>92	>90			
Pb	%	0	0	0			

4 Mixing Bed Technology for Maximizing Secondaries Input

Bulk concentrates are usually delivered in big lots of several thousand tons, but secondary materials are traded in much smaller lots of sometimes only 10 to 20 tons. To treat secondary materials in major amounts mixing and homogenization of the feed becomes more and more important. The mixing bed technology used over years in the iron producing industry is the chosen technology for nonferrous smelter, too. Only this technology guarantees homogenous feed to the process. To meet the target composition is not necessary, because a final make-up of the feed will be made within the relevant plant.

The mixing bed technology homogenized the feed and is the base of maximum secondary material input. The mixing beds are planned und build up in the way to fulfill the specification of the product. Only the target analysis of the aggregate content is free in this plan, because of adjustment by dosing bins in the plant. The calculation of the mixing beds needs to ensure not to overdose the target analysis.

Each change of a mixing bed means a disturbance for the process, in this case a certain quantity of each mixing bed must be given. The change of a mixing bed needs a stepwise program with a temporary overlap of both beds.

This technology can be used for every process, which needs a homogenous feed of different raw materials.

4.1 Future of ISF-Technology

Looking to all this materials the ISF seems to be the ideal recycling process, offering even the possibility to run the process on 100 % secondary feed, which has been shown by different ISF smelters already.

But due to high operating cost and environmental problems this technology disappears from Europe (except Poland) and is nowadays only present in Asia with a focus on China.

The ISF was leaving the business in Europe, but the residues are still produced and need to be recycled. Therefor the pressure on electro winning plants, the remaining zinc producing technology, has been increased to treat secondary material in an order of magnitude, which seems to be impossible in former times.

5 Zinc Electrowinning and its Possibilities

Electrowinning was 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. But with treating secondary materials new impurities, not known before in this order of magnitude, show up, especially Chlorine and Fluorine. Their concentration in the electrolyte should be more or less at zero by definition, otherwise electrowinning will be more or less impossible was the common understanding.

6 Necessary Developments for Electrowinning

To make zinc recycling in an electrolytic zinc plant happen you have to convince your employees from that nasty idea and finally you have to overcome several technical problems.

The classical roasting-electrowinning zinc plant offers you two points in the flow sheet, where secondary material could be added: roasting and / or leaching.

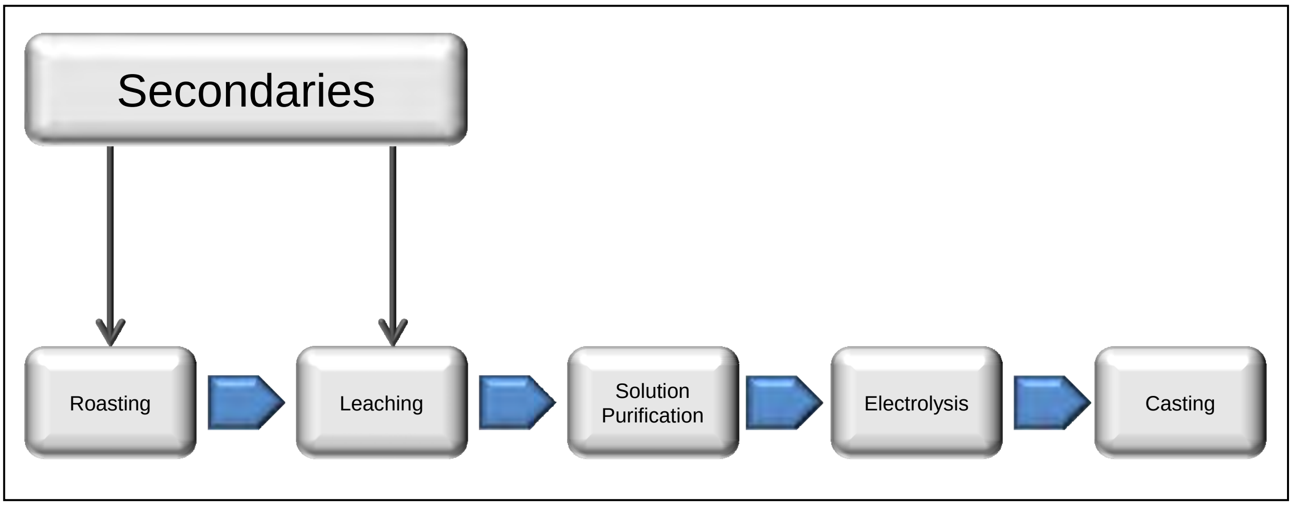


Figure 3: Block diagram Zinc producing by roasting/electrowinning route

Limited throughput of secondary materials :

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.

The leaching plant on the other hand has a limited throughput because of elements like Copper, Cobalt, Nickel and so on.

7 Behavior of Cathodes and Anodes

But whatever you do, the treatment of secondaries even in the roasting plant, is more or less leading to increased Figures of Cl and F in the electrolyte. Here the real bottleneck of the secondary material input is evident showing difficulties in cathode and anode behavior.

Table 2: Typical electrolyte with higher amounts of halogens:

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

Electrowinning takes place in cells fitted with anodes and cathodes.

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

Anodes, usually lasting for “ever” - meaning up to 8 years - show with increasing input of secondary materials a change in behavior. What was good over years has now to be investigated and is in the focus of new developments.

Fortunately zinc smelters have strong partners within the supporting industry. Confronted with new day to day problems in the electrowinning, these companies start in cooperation with the smelter research and development projects. Questions like what influence a higher halogen contend may have on Pb-Ag-anodes have to be investigated, what is the influence on the protective layer on the anodes have to answered. What crystal structure is necessary in the anodes and can this being transferred into an industrial production? What is the minimal Ag content? Show new alloys a better behavior?

What was the outcome of this research work?

8 Improvements by Flat Rolled Anodes

The first result was the development of flat rolled anodes instead of cast anodes, used for years in the industry. At first the corrosion rate has to be measured.

In the past, cast anodes were fabricated mostly with a silver content of 1 %. This content was necessary to avoid high corrosion rate. Investigations (Umetsu et al, [2]) led to the result, that the corrosion rate und the hardness of a lead-silver-alloy correlate more or less linear about a wide range of silver content and leaves this linear correlation from silver contents lower than 0,6 % (Figure 4). An Ag-content of 0,65 % seems to be the optimum between electrochemical need and economical tenability. Rolled anodes actually were fabricated with Ag-contents from 0,5 up to 0,65 %, but customers may ask for anodes with different Ag content.

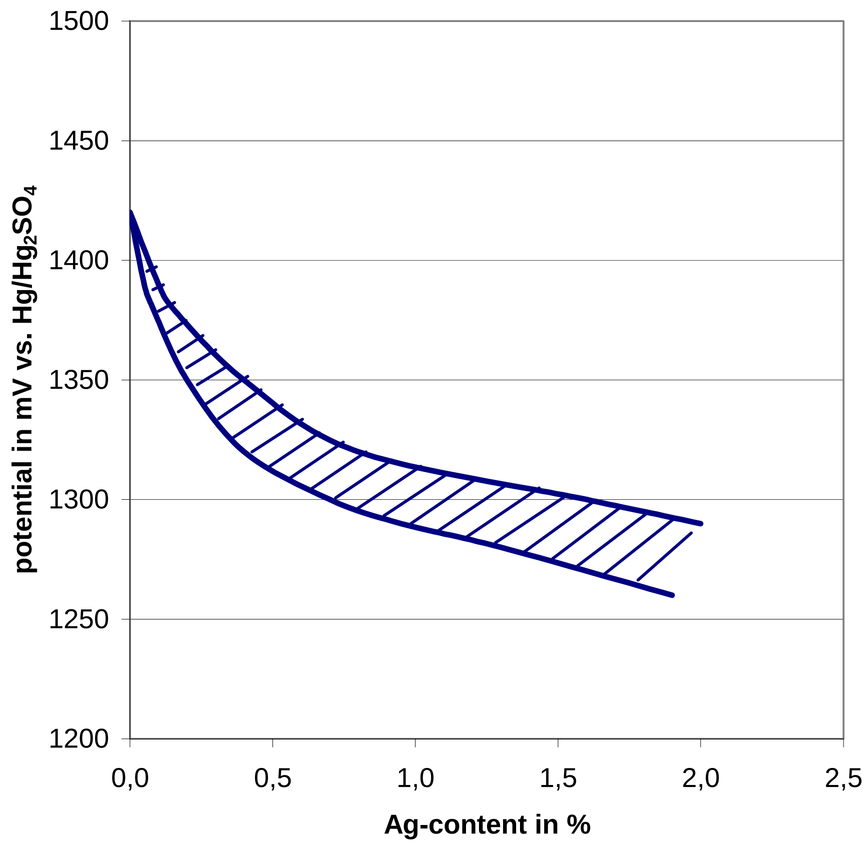
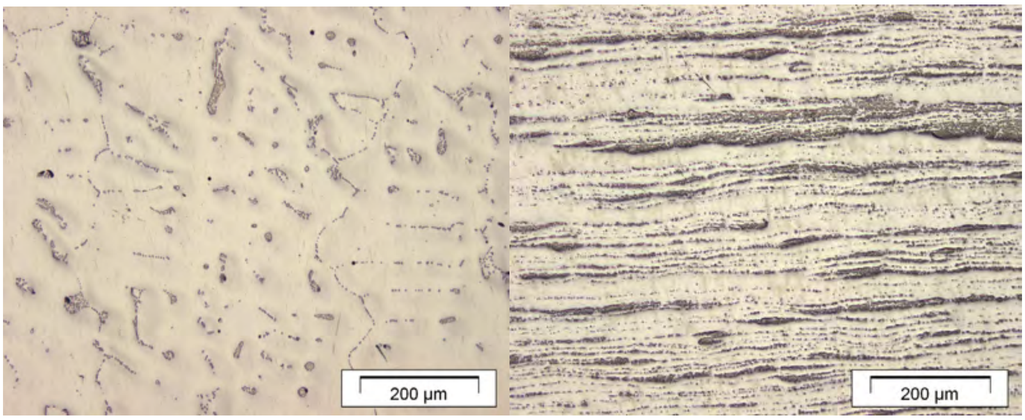


Figure 4: Correlation between Ag-content and potential

The grain structure plays an important role, to give the Ag-content a high efficiency even in electrolytes with unusual high halogen content. The combination of the Ag-content and the right grain structure influence the corrosion rate and the oxygen over potential of an anode. These two facts have an influence to the economical behaviour of an anode regarding to the possible lifetime and the specific power consumption [3].

Having a look to the microstructure on cast and rolled anodes, grains show a complete different structure and size (Figure 5).



Cast anode Rolled anode

Figure 5: Grain structures of cast and rolled anodes

The coarse-grained microstructure after the rolling process creates grain enforcement between 2000 and 3000 µm (Figure 6), while the cast grain size has a range from 50 to 200 µm.

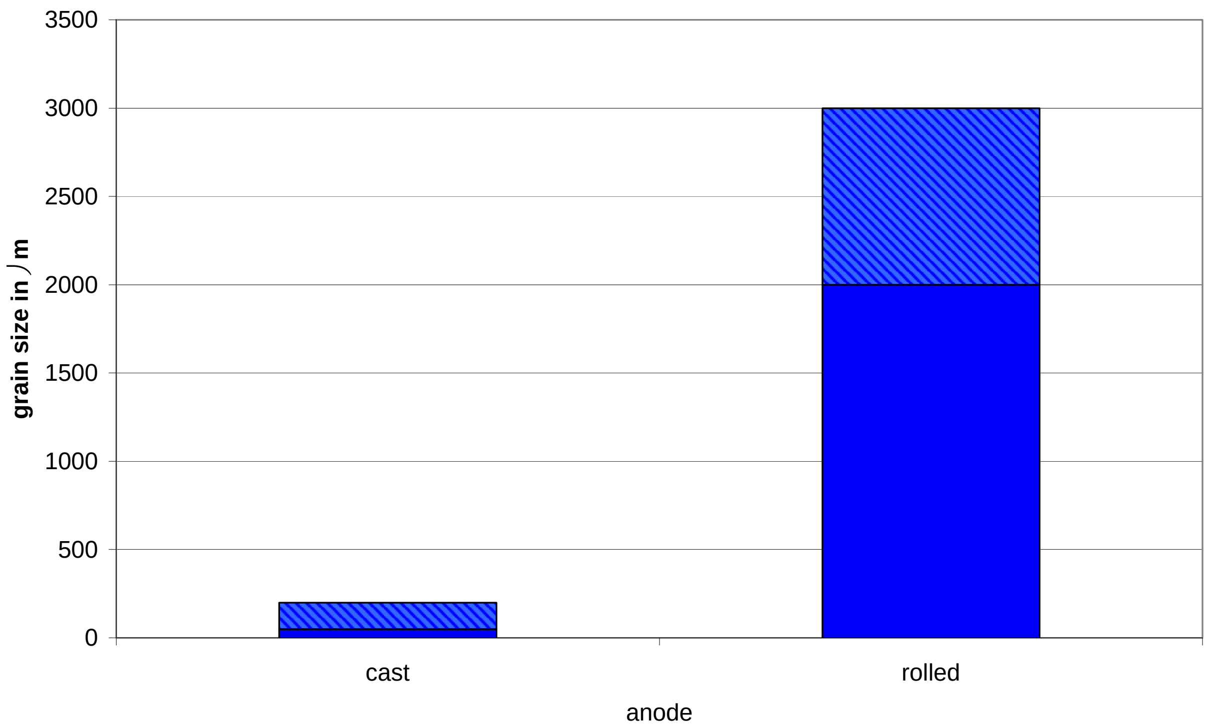


Figure 6: Comparison of grain size

The Ag-distribution by concentration of silver on the grain boundaries will be optimized by the larger and elongated grains of a rolled anode. While rolled anodes have here a silver content up to 30 %, with cast anodes, a silver content at the grain boundaries of max. 8 % can be detected (Figure 7).

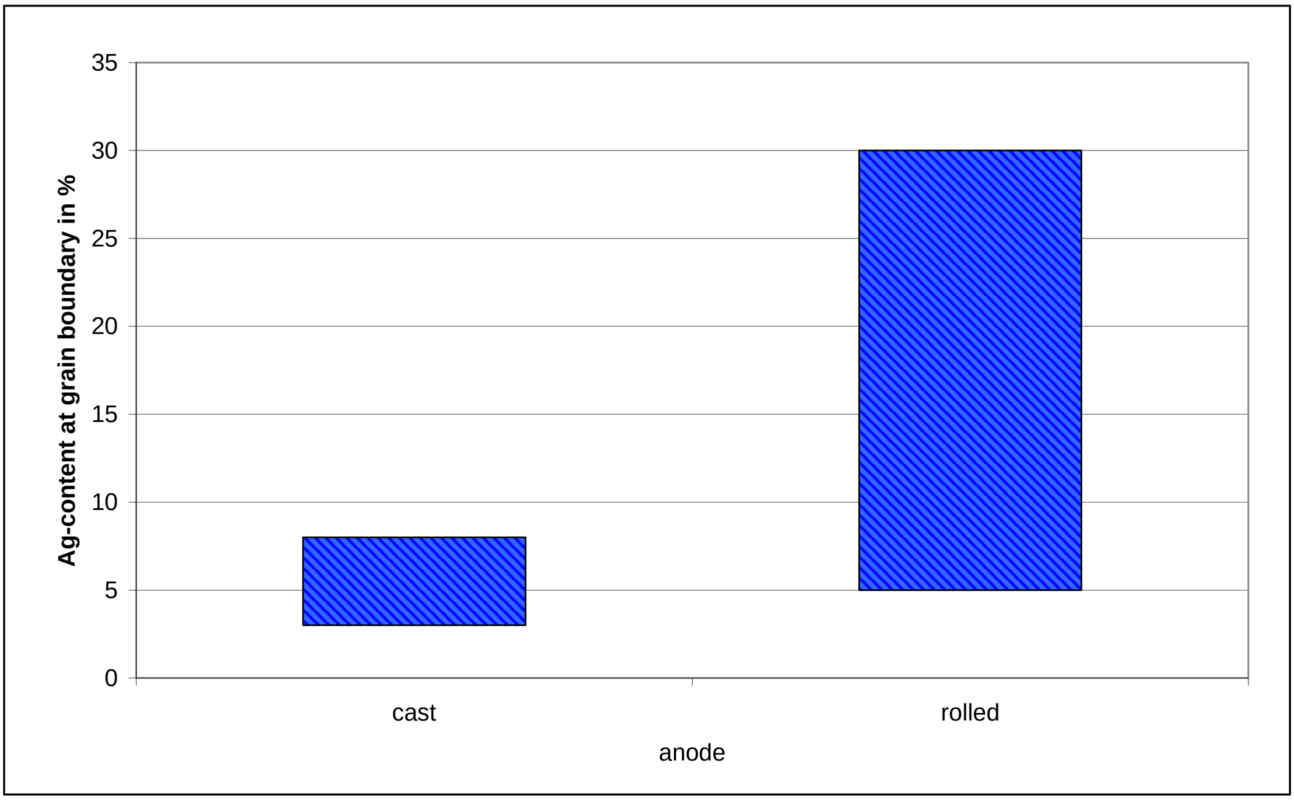


Figure 7: Silver content at grain boundary

The high silver concentration at the grain boundaries reduces the corrosion rate of the anode.

Also the chemical composition of the electrolyte has a major influence on the corrosion rate of an anode. One notable is the chlorine. Former investigations have shown a linear correlation between chlorine and corrosion rate. But the range of the chlorine concentration of these investigations considered only contents up to 200 mg/l. Such kind of chlorine content is in most of the electrolyses out of practice. The chlorine content today is much higher.

Therefore new lab tests were necessary performed with substances coming out of the industry. Different results could be seen as shown in Figure 8 [4]. The increase of corrosion at higher chlorine levels is less dramatically. But also here flat rolled anodes show lower corrosion than cast anodes.

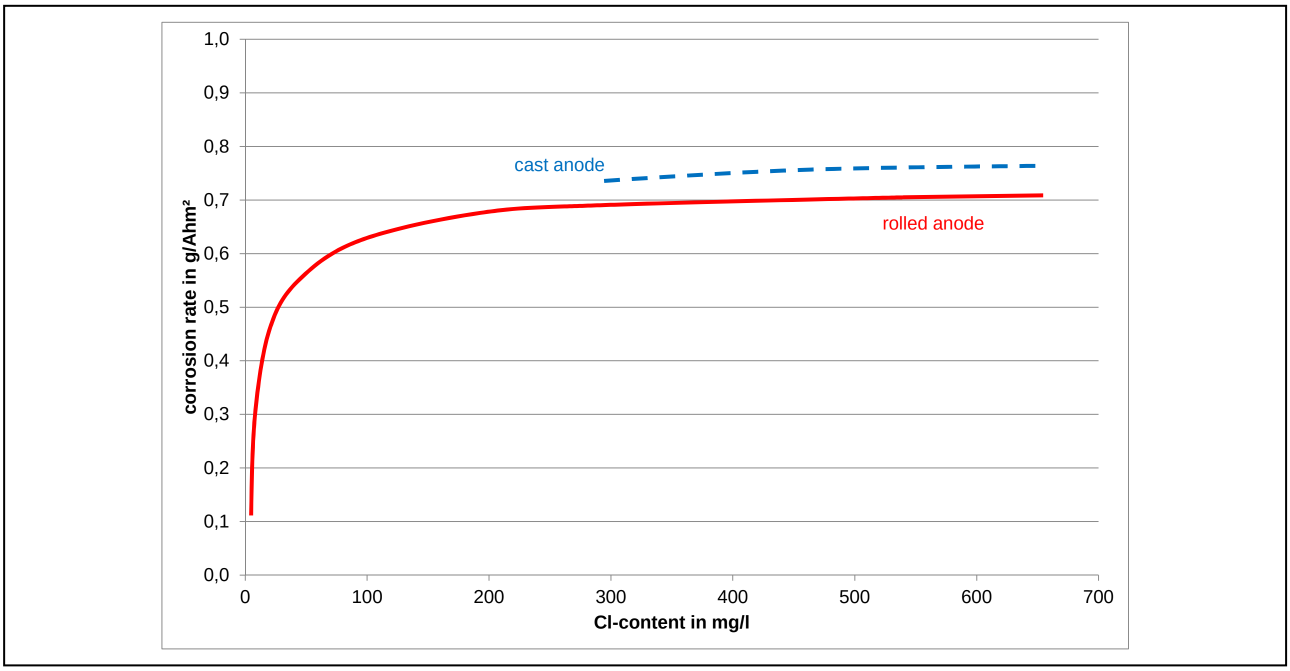


Figure 8: Correlation of chlorine content and corrosion rate

Flat rolled anodes show a well-defined surface, which is guaranteeing a more or less constant reactivity over the whole surface of the anode.

9 Cooperation of Smelter and Anode Manufacturer

Each electrolysis operates with a customized anode, development over decades of metal production. The range of anode design is varied (Figure 9).

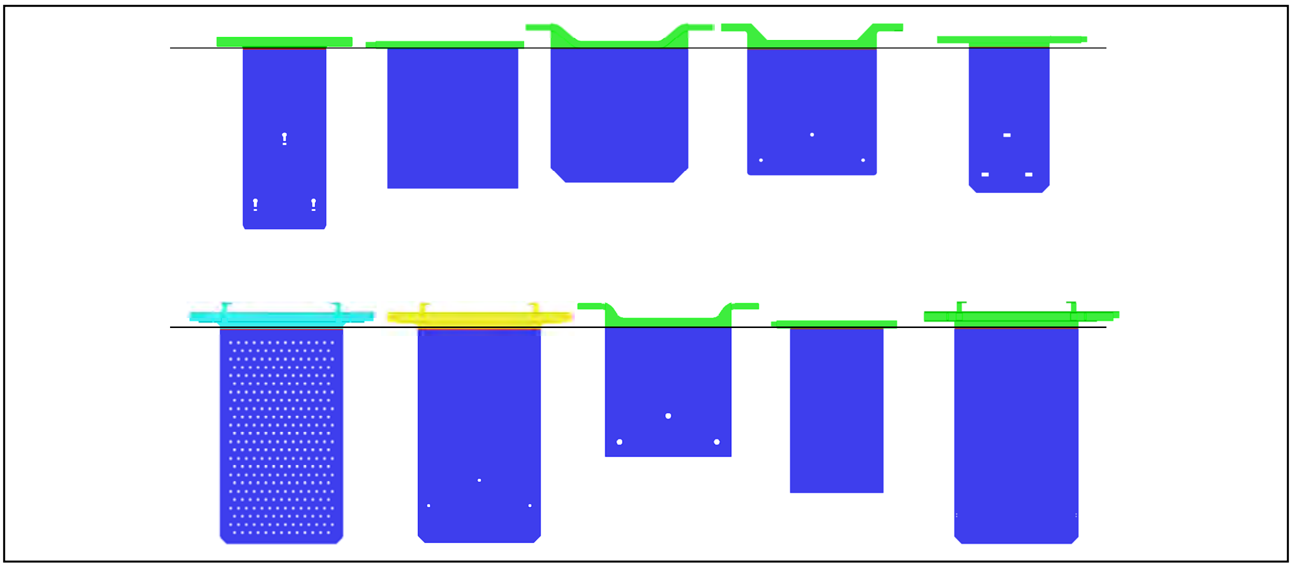


Figure 9: Different anode designs

A special physical treatment of the anode sheet surface supports the rapid formation of Lead and Manganese oxid layers (Figure 10).

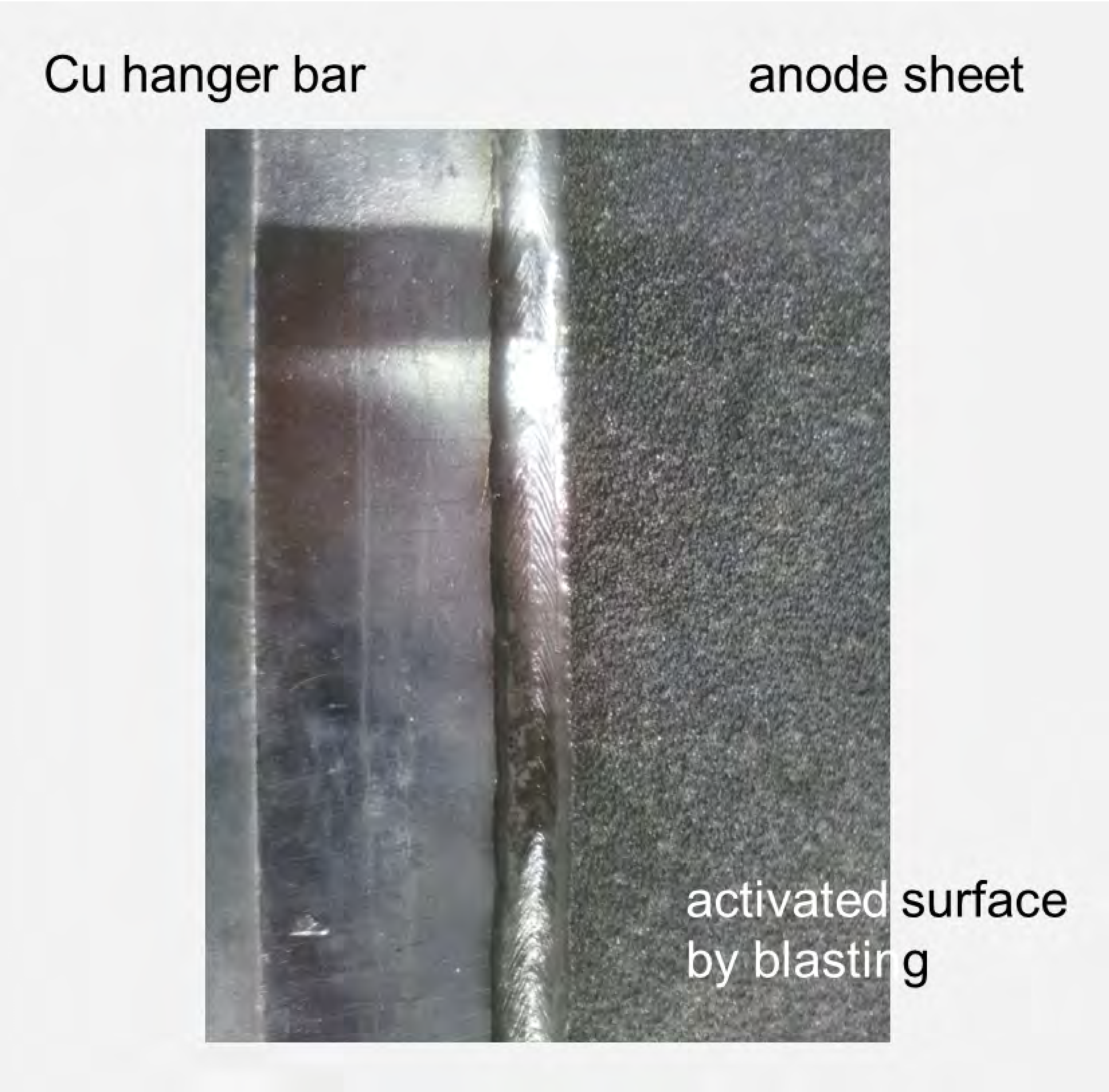


Figure 10: Surface treatment of anode sheet

In the past transport of anodes mainly happens by pallets. But today anodes, finally assembled for operation, will be transported in special steel frames (Figure 11). This steel frame makes unloading of anodes easy and free of any bending, so that the anode can be used in the cell house as flat as possible.

Figure 11: Pallet transport and steel frame transport with anodes ready for operation

The next development should be not only the production of tailor made anodes with respect to size and layout, but also with lower silver content.

A friutful cooperation between Zinc smelting industry and the anode producing company may lead to the production of anodes made from new alloys, lower in silver content by addition of for instance Ca as a logically next step. This type of alloy is increasing the hardness of the anode sheet, which will become more and more important factor in the future.

10 Service

Zinc producing industry is – like all industries – always looking for possibilities to increase the production. One possible solution of the problem could be the reduction of the free space between anode and cathode. To make this happen it is definitely necessary to have flat anodes, not only when delivering the anodes but also over the whole life cycle.

Every anode handling consists usually of several steps, as shown in Figure 12, starting with length control and cleaning with water at high pressures. To keep the flatness of the anodes it is important to do the following steps with every anode taken out of the bath.

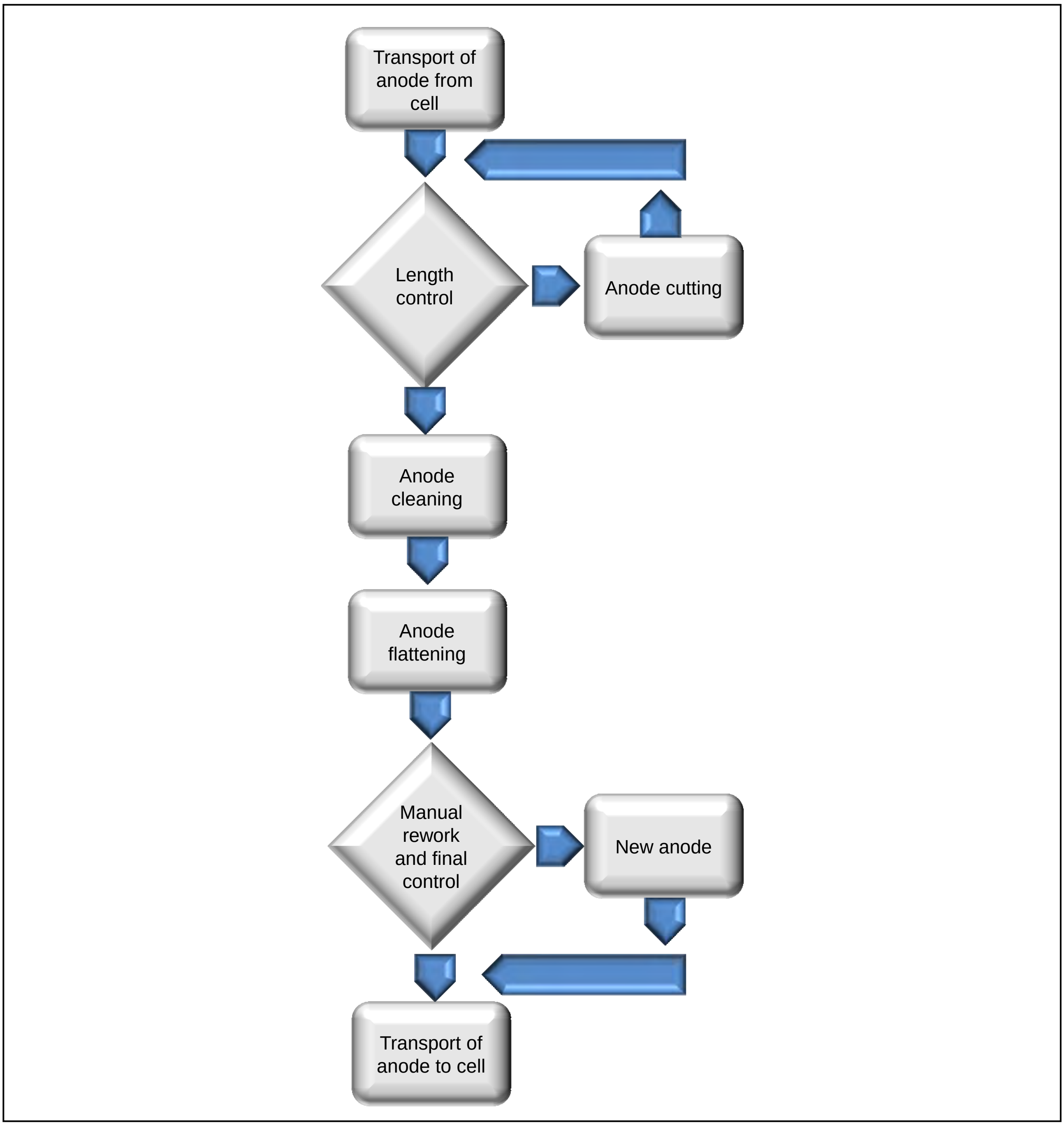


Figure 12: Anode care

Figure 13 shows a vertical press used as anode press within a zinc smelter. With a 80 - 120 kp/m² full load pressure this equipment is guaranteeing that at the end of the procedure the anode is without any change in adjustment. Only this adjustment gives the confidence to run the electrowinning step without disfunction. The mechanical engineering industry in cooperation with the anode manufacturer can provide adequate support.

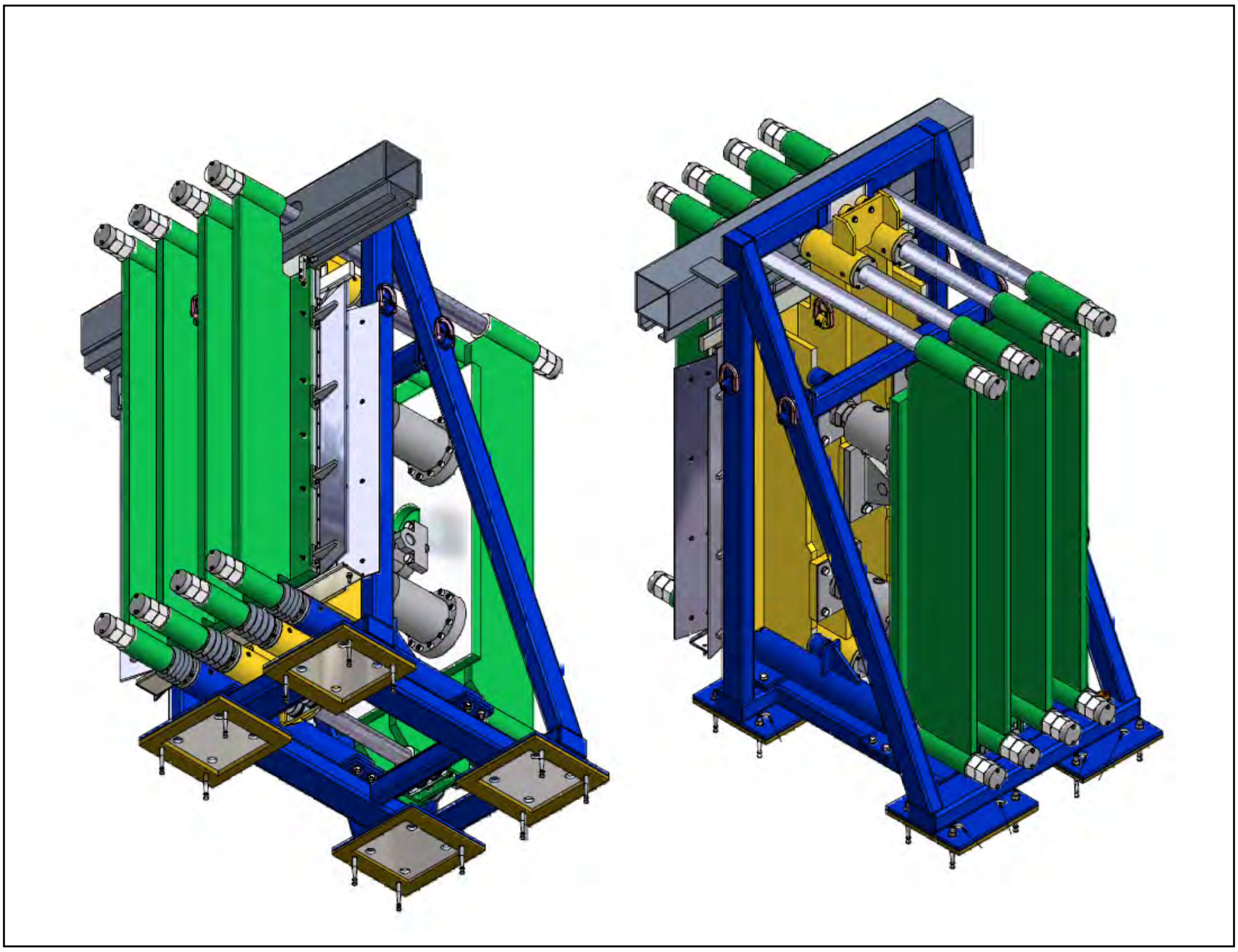


Figure 13: Anode press machine (product Hötten Industrie & Services, Germany [5])

Even best developed anodes don´t have an endless lifetime and have to be taken out of the cell to be replaced. Here the anode producing industry again is supporting the zinc smelting industry. They take care of the old anodes, clean and remelt them, take care of adjusting the right composition and deliver a brand new anode made from approx. 70 % of the old anode (consideration of mass loss during use), showing the best possible performance (Figure 14).

The recycling process treats each anode in its entirety. The processing of components like Cu bars and steel hooks follow the same carefully and documented way as the recovered metal. The reusability is the main focus, to lower the costs for a new anode. This means that the recycling is not restricted in metal recovery but also in re-work of all the other components which makes an anode.

A typical balance is given in the following Figure.

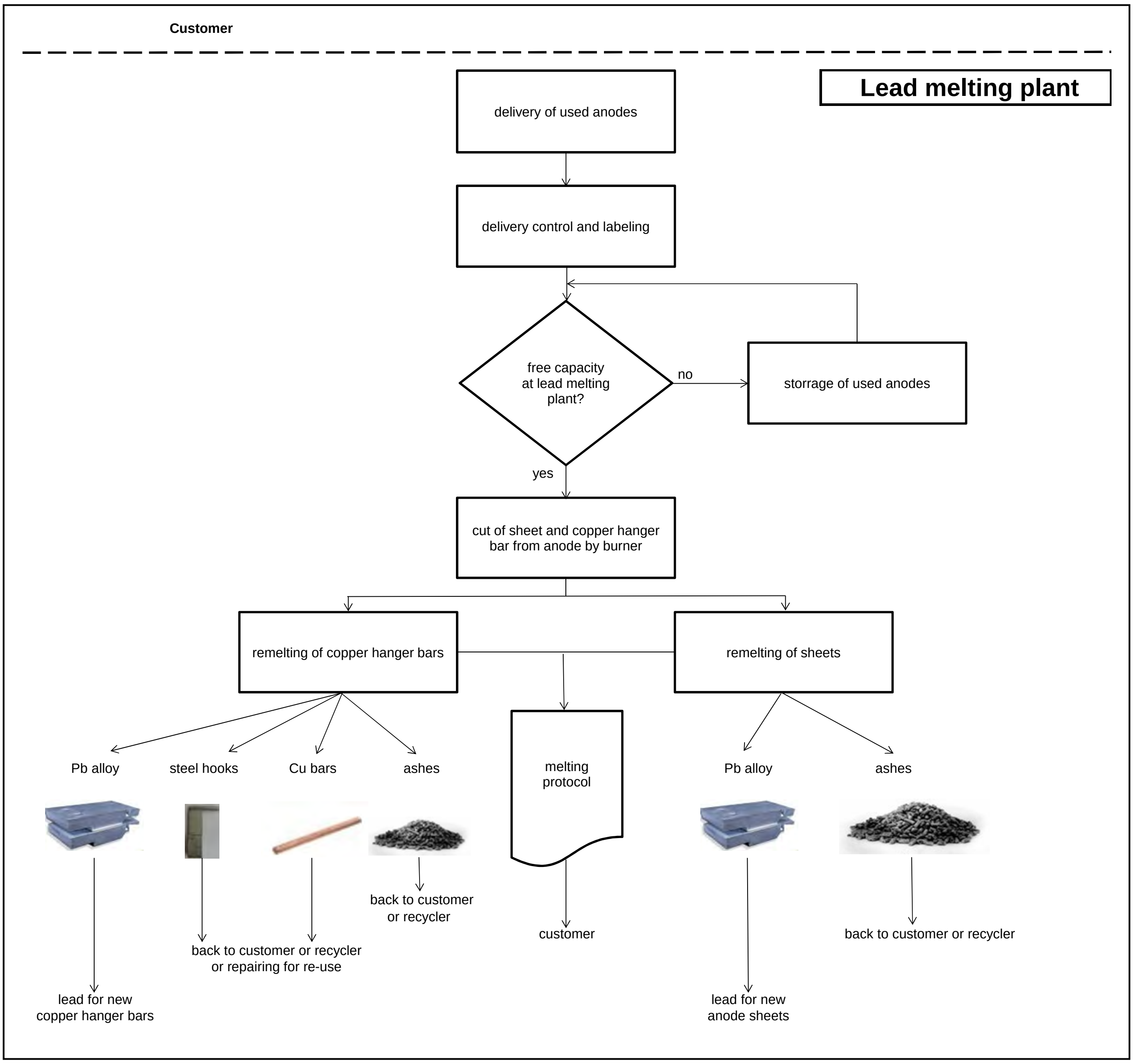


Figure 14: Recycling process JL Goslar GmbH of used anodes and its balance

11 Conclusion

Zinc recycling is a necessity for developed countries being a follow up other recycling operations like for instance steel scrap recycling. The technologies developed up to now will be transferred to developing countries and applied there. After closing pyrometallurgical zinc plants zinc winning by hydrometallurgical based more and more secondary material will be the future. The industry is nowadays prepared for treating this material and will see this as a challenge.

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