# From Cast Anodes to High Efficient Rolled Anodes in an Electrolytic Zinc Plant – A Field Report

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**Keywords:** Electrolysis, rolled anodes, efficiency

## Abstract

For zinc electrowinning, lifetime and electrochemical behaviour of anodes are of great importance. Especially, in case of an electrolyte contains high halogens concentrations deriving from a very high portion of treated secondary material.

However, with a well-equipped anode, good care, maintenance and attention to the flatness of the anode, consumption figures near to the layout figures can be achieved.

## 1 Introduction

In daily production, anodes for metal winning in an electrolysis plant are exposed to different kinds of stress. To fulfil the metallurgical and economical requirements, every plant operator has the ambition to use anodes which are best suited by

- chemical composition
- grain structure

to resist the operating conditions such as

- the adjusted power density
- the composition
- the temperature of the electrolyte

with a long lifetime as a result.

For this reflection, the practical example of a zinc electrolysis was chosen.

The literature describes two kinds of alloys for anodes for electrolytic zinc winning:

- PbAg-alloy
- PbAgCa-alloy.

The practice shows that mostly anodes made of PbAg-alloy are in use with a silver content of approx. 0.65 %.

# 2 Basics

Extensive investigations done by JL Goslar together with notable institutes generate a lot of technical expertises and complete the knowledge of the literature.

First of all, some common basics:

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 1). According to the investigation of Umetsu et al., an Ag-content of 0.65 % seems to be the optimum between electrochemical need and economical tenability [1].

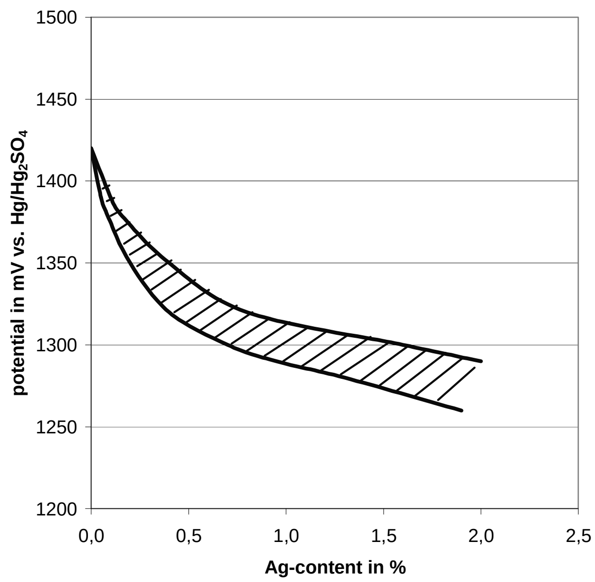



Figure 1: Correlation between Ag-content and potential

To give the Ag-content a high efficiency the grain structure plays an important role. The combination of the Ag-content and the right grain structure influence the corrosion rate and the oxygen over potential of an anode. These are two facts which have an influence to the economical behaviour of an anode regarding to the possible lifetime and the specific power consumption.

Also the chemical composition of the electrolyte has a major influence on the corrosion rate of an anode. One notable is the chlorine. Investigations show also here a linear correlation between chlorine content and corrosion rate (Figure 2) [2].

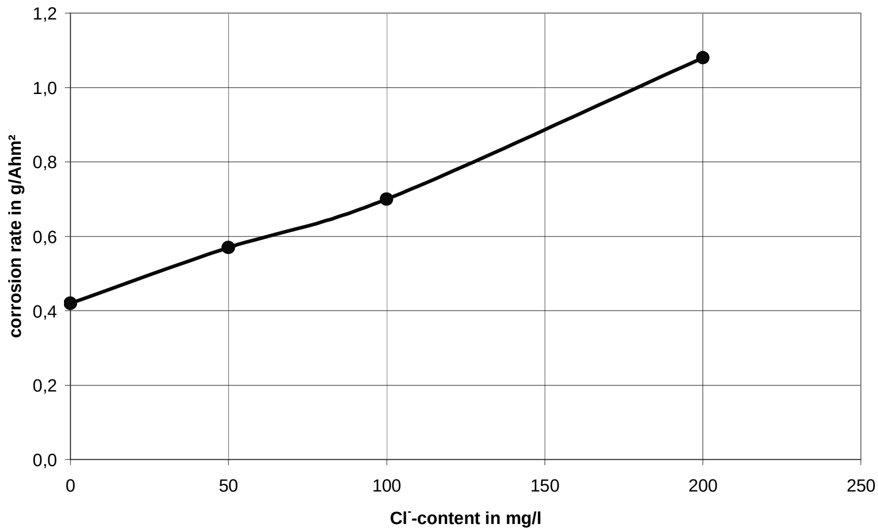



Figure 2: Correlation of chlorine content and corrosion rate

The investigated range up to 200 mg Cl/l is far away for most electrolyses because of today's higher input of secondary material compared to the past.

Figure 3 shows the influence of the electrolyte temperature on the corrosion rate and consider the normal range of operation. Critical high temperatures in hot summer times, given by insufficient cooling capacity, could increase the corrosion rate significantly [2].

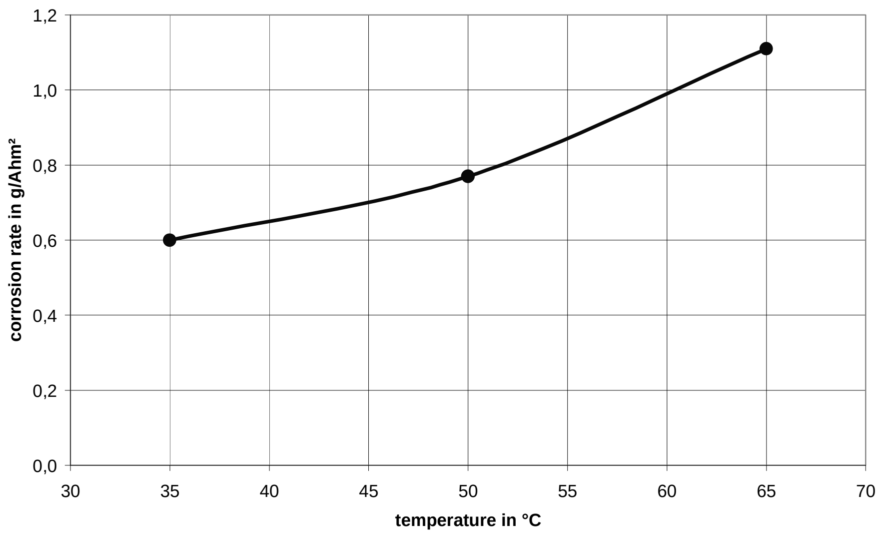
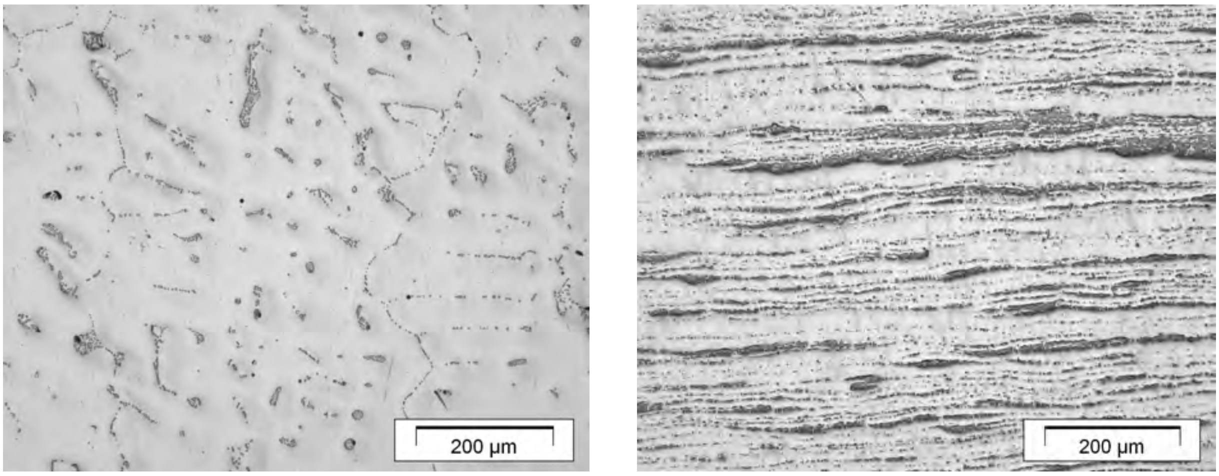



Figure 3: Influence of electrolyte temperature on corrosion rate

All these factors mentioned apply to cast and rolled anode, too. But the influence to a cast anode usually is higher than to a rolled anode in term of lifetime and the quality aspects mentioned in chapter 3 “Operator experience”.

In the past mainly cast anodes were used – mostly self produced by the plant operator. Only in the last approximately ten years rolled anodes became successful. JL Goslar produces these rolled anodes with great know how and a specific rolling process.

Microstructure investigations on cast and rolled anodes show grains of very different structure and size (Figure 4).




Cast anode | Rolled anode

Figure 4: Grain structures of cast and rolled anodes

While the cast grain size has a range from 50 to 200 µm, the coarse-grained microstructure after the rolling process is between 2000 and 3000 µm (Figure 5).

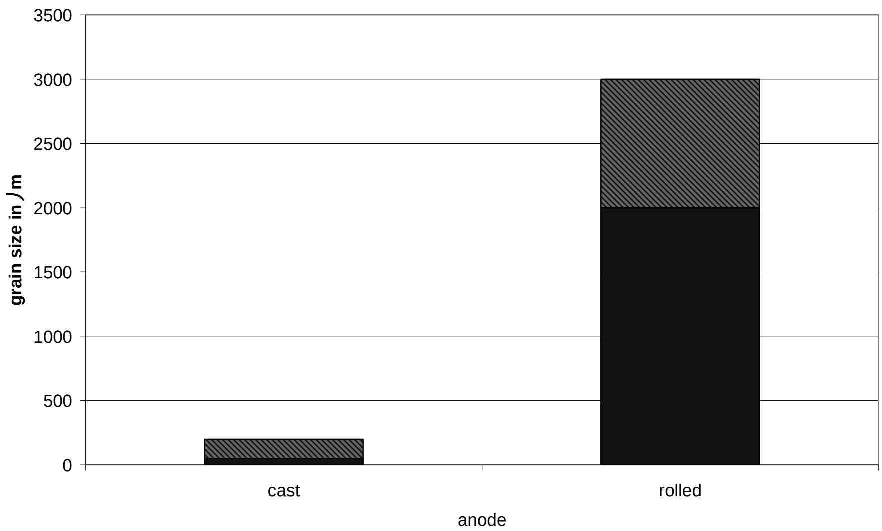



Figure 5: Comparison of grain size

The larger and elongated grains of a rolled anode optimize the Ag-distribution by concentration of silver on the grain boundaries. With cast anodes, a silver content at the grain boundaries of max. 8 % can be detected, while rolled anodes have a silver content up to 30 % (Figure 6).

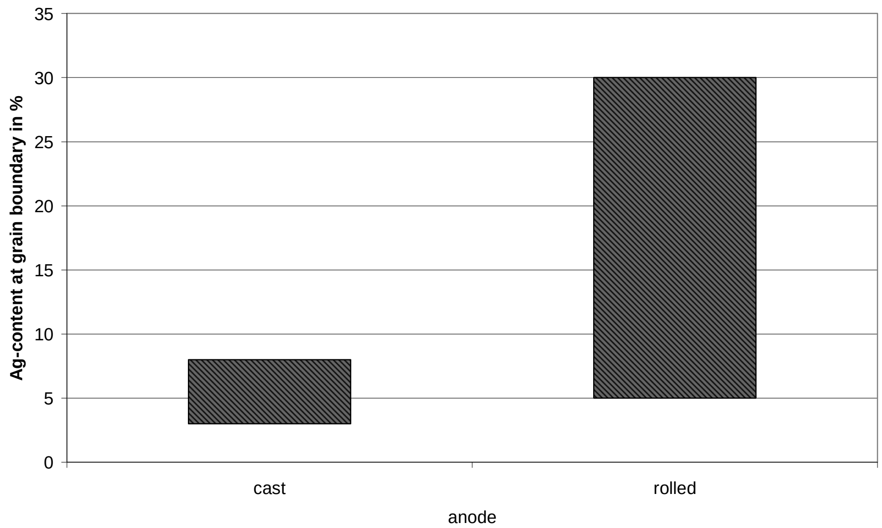



Figure 6: Silver content at grain boundary

The high silver concentration at the grain boundaries reduces the corrosion rate of the anode measured at a lab scale test (Figure 7). This is an additional positive factor.

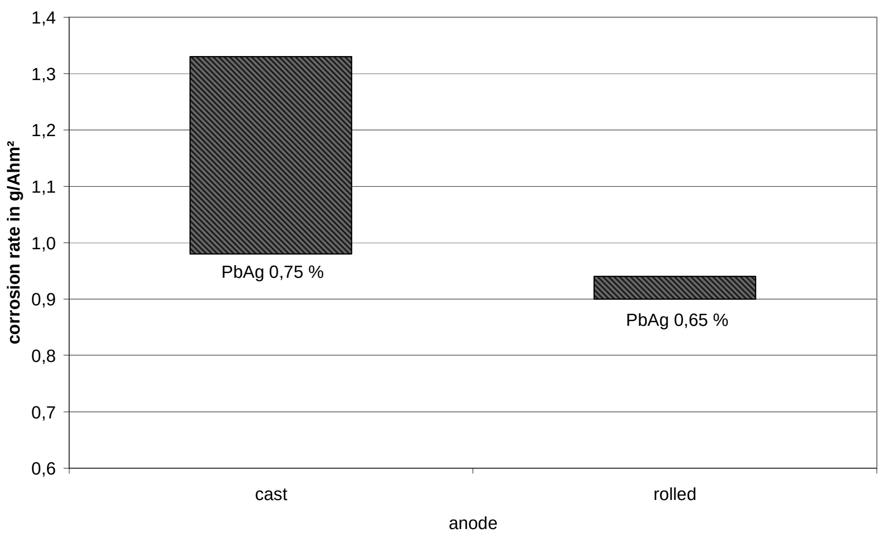



Figure 7: Comparison of corrosion rate

By these facts the better electrochemical behaviour and the improved conductivity of a rolled anode can be derived.

Also the formation of the $PbO_2$-layer has an influence of the corrosion rate. The fast formation of a firm and stable layer gives the anode it´s full capacity. Investigated layers of rolled anodes were firm and thin, the layer mass lower than with cast anodes (Figure 8). Also, this formation of the layer has an influence of the corrosion rate (Figure 9).

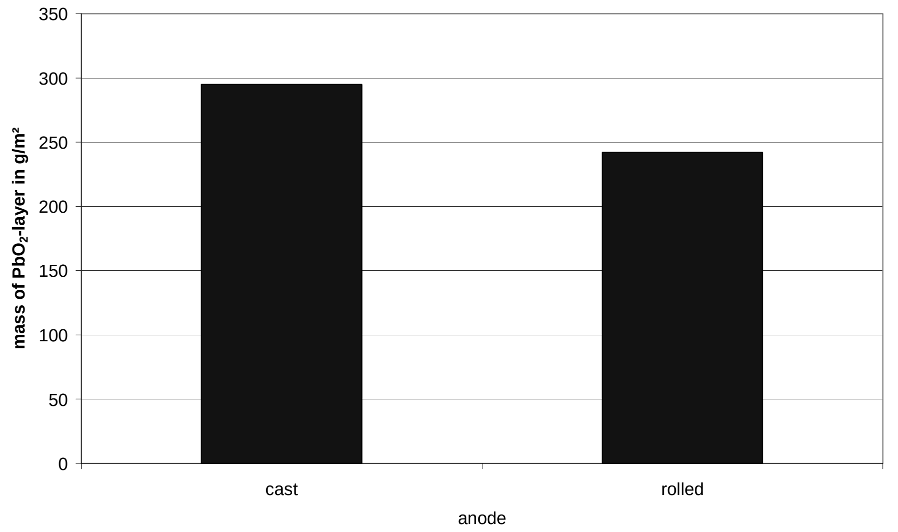



Figure 8: $PbO_2$-layer mass on cast and rolled anodes

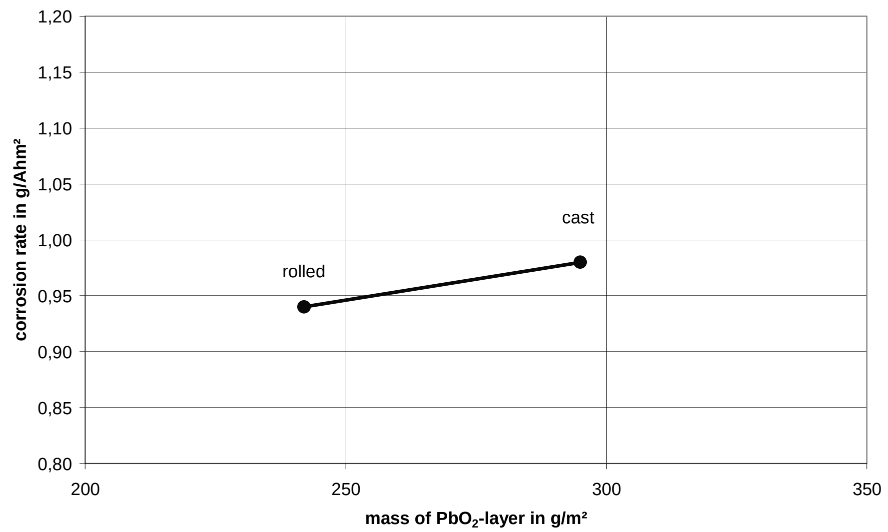



Figure 9: Correlation of $PbO_2$-layer mass and corrosion rate

All these advantages of a rolled anode give each operator of an electrolysis the opportunity to achieve a long lifetime with rolled anodes and to increase the input of secondaries because of the higher resistance against chlorine than found with cast anodes. Both are economical advantages to produce zinc in countries with high energy and labour costs.

After this short excursion about the behaviour of anodes in common and rolled anodes in particular, now the experiences in practice.

# 3 Operator experience [3]

First of all, some introducing technical information concerning this particular Zinc electrowinning plant.

The plant was a German Zinc electrolysis operating from 1968 to 2008. The theoretical capacity of the plant was in the order of 150,000 tpy cathodic zinc. The cathodic zinc production obtained in 2008 was 140,000 tpy. With this capacity the smelter was one of the smaller sized zinc electrowinning plants in the western hemisphere.

The cell house consisted of two rows of 53 cells each (Figure 10).

Figure 10: Cell house with two rows of 53 cells each

Each cell was equipped with 84 jumbo-cathodes with 3.5 m² surfaces and 85 anodes of corresponding size (Figure 11).

Figure 11: 3.5 m² Jumbo cathode

# 4 Secondary treatment

Although the smelter was small to medium-sized, it was well known to treat a very high, if not the highest amount of secondary material amongst Zinc electrowinning plants. The secondary material throughput could be increased year by year. In 2008, 36 % of the zinc produced was based on secondary material (Figure 12).

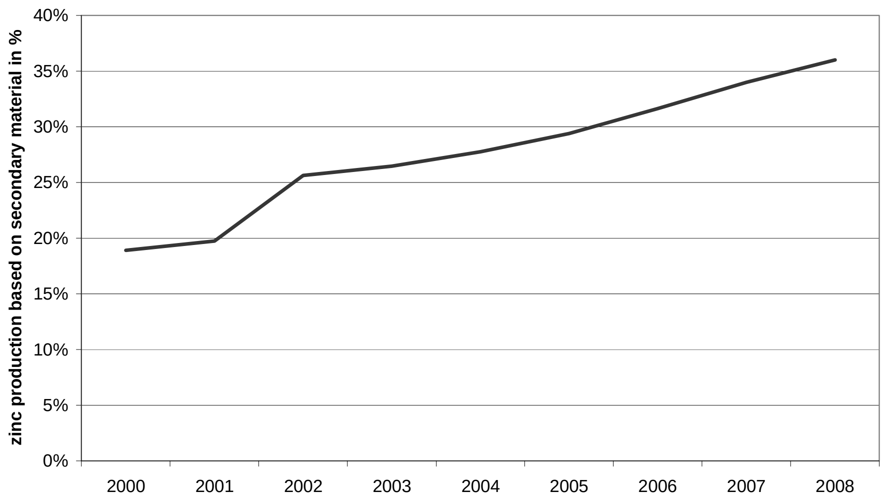



Figure 12: Development of zinc production based on secondary material

This high secondary input resulted in a very special composition of the electrolyte as shown in table 1.

Table 1: Composition of electrolyte in 2008 (average)

| Composition of electrolyte | | | | | |
|---|---|---|---|---|---|
| MgO | Na | Zn | Cl | F | Sr |
| [g/l] | [g/l] | [g/l] | [mg/l] | [mg/l] | [mg/l] |
| 21.5 | 8.1 | 52.7 | 650 | 58 | 10.2 |
| (18.8 to 24.6) | (7.2 to 9.0) | (51.8 to 54.0) | (481 to 876) | (49 to 72) | (4.7 to 20.2) |

The figures or rather the table show average values of the year 2008 with the operating ranges in brackets. The very high content of chlorine and fluorine is of significant importance. Corresponding to the increased throughput of secondaries the halogens rose and the smelter had to learn to manage and operate this with this electrolyte composition.

# 5 From cast to flat rolled anodes and dedicated services by JL Goslar

The cell house consisted of 106 cells with a total of 8904 cathodes and 9010 anodes. The cathodes were manufactured from typically used aluminium, while the anodes were made from lead-silver-alloy with 0.65 % Ag.

The cell house originally designed for cast anodes was changed over to flat rolled anodes with the beginning of the century making use of some advantages of this type of anode:

- The composition of the anode is homogenous all over the surface
- The surface is as flat as possible to avoid hot spots
- Long lifetime
- No cavities or shrinking holes as seen in cast anodes
- Good partnership with an anode producing company acting as a system partner.

JL Goslar offered to equip the smelter step by step with new flat rolled anodes and to establish a system from rolling, assembling, recycling and make up of the alloy on behalf of the smelter (Figure 13).

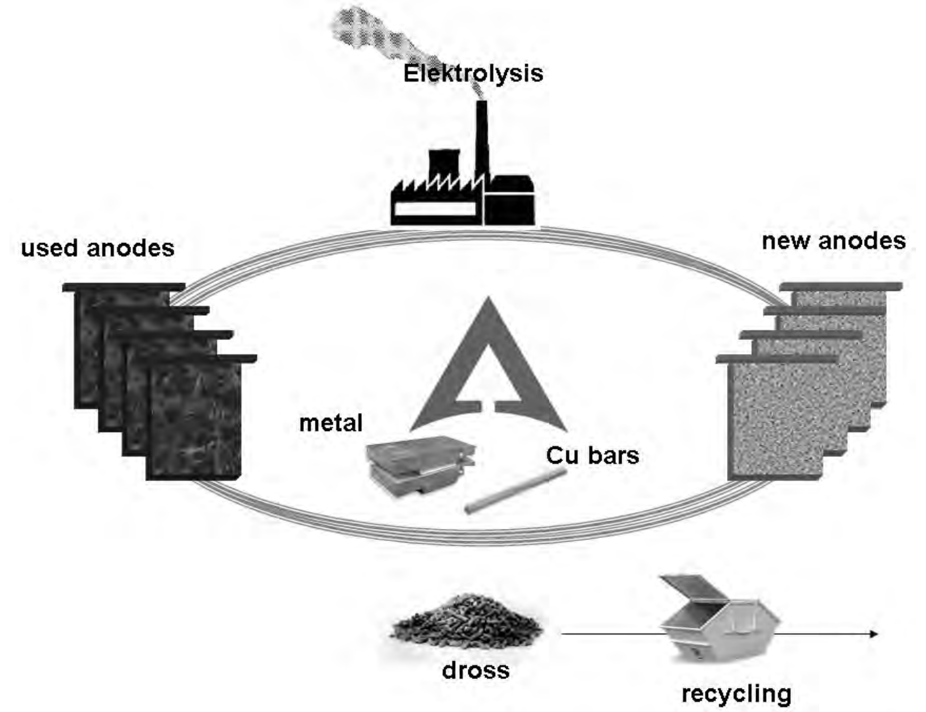



Figure 13: Recycling circuit of used anodes

JL Goslar produced the anode sheets by rolling and blasting, assembled the complete anode and delivered sets of anodes on demand to the smelter. To close the established loop used anodes are taken back to JL Goslar where the anodes sheet was separated from the supporting hanger bar for melting. After melting of the returned anodes scrap, the dross was removed and metal and dross were sampled and balanced. The required amount of new alloy was added to produce the same number of anodes as delivered as anodes scrap. New lead, as well as silver as the only alloying element was taken from consignment stocks at JL Goslar. The dross was treated on a tolling fee in a lead smelter. The amount of alloy, silver and/or drosses in the consignment stocks were cross accounted for once per month.

This cooperation was fruitful over many years, satisfying both sides.

# 6 Results

The following metallurgical results could be achieved with the implementation of flat rolled anodes and as shown in Figure 14:

- The specific power consumption per tonne of cathodic zinc was decreased from 3300 kWh in 2003 to 3074 kWh in 2008.
- The power efficiency was increased from 87.2 % in 2003 to 93.3 % in 2008.

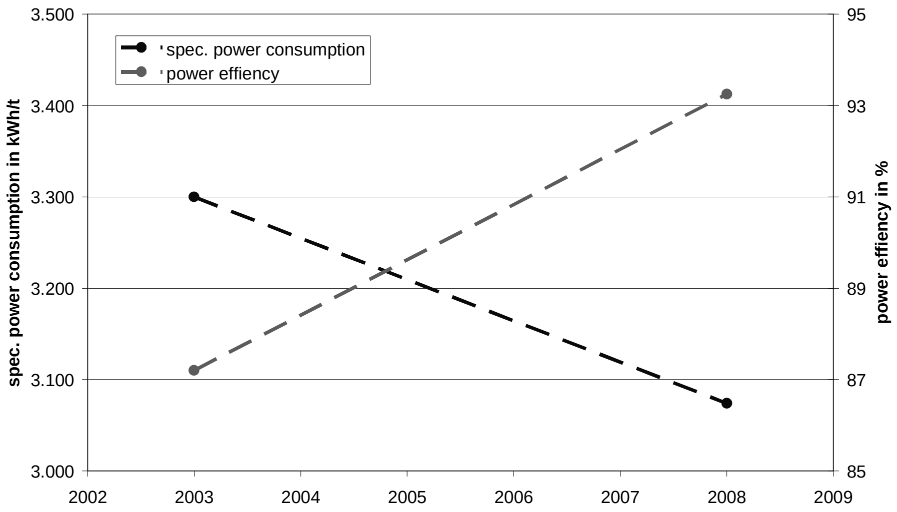



Figure 14: Development of specific power consumption and power efficiency

To make this all happen, a clear strategy for care and maintenance was necessary. After previously searching for a different system to detect hot spots resulting in higher lead in zinc concentrations, which all more or less failed, the smelter decided to go the other way round. This meant to take care of the flatness of the anodes.

This starts with the transportation of the anodes. For anodes of that size – jumbo anodes – it is more or less impossible to lift the anodes from pallets without bending most of them. Even the heavy weight of more than 250 kg could not avoid such bending. To solve the problem a steel frame was developed in close cooperation with JL Goslar in order to vertically transport the anodes (Figure 15).

Figure 15: Steel frame for vertical transport of anodes

This system minimizes any bending of the anodes during loading, unloading and transportation. The system is quite successful and is also in use at other smelters nowadays.

To maintain a defined anode surface it was necessary to frequently clean the anode during their lifetime removing the surplus of $MnO_2$. In order to achieve this, an anode cleaning machine was established, operating on a semi automatic mode. The flow chart of the operations can be seen in Figure 16.

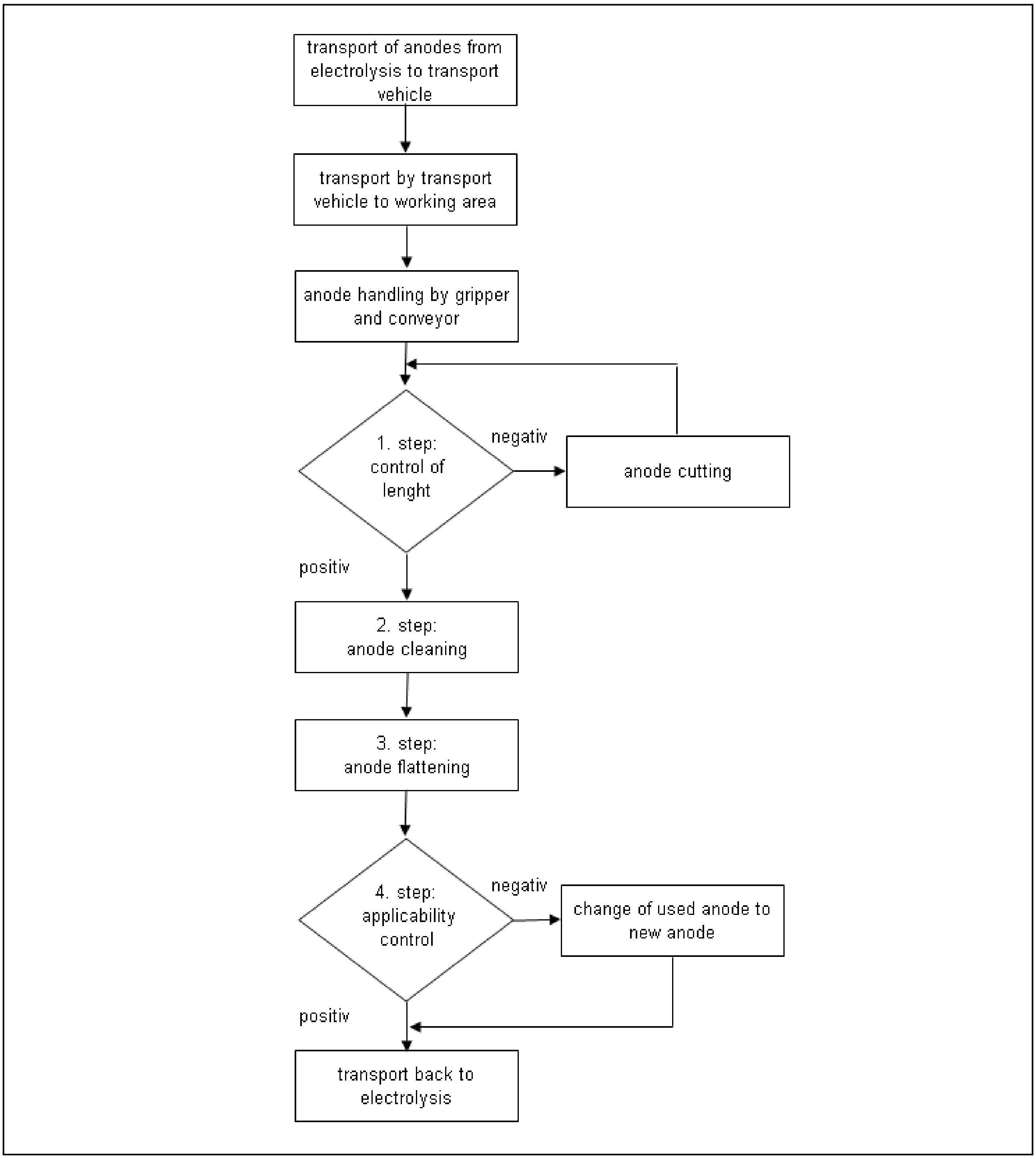



Figure 16: Flow chart of anode cleaning

After cleaning the anode with water at high pressure to remove only the surplus of $MnO_2$ without creating a blank metal surface, the anodes were pressed in a hydraulic press and trimmed afterwards to remove surplus lead and to keep the anodes at the right size. This anode cleaning was done at least every 20 days, at best below that figure. Altogether this leads to a prolonged lifetime of the anodes even in a system where the halogens content was extraordinary high. The overall lifetime of the anodes was increased from an average 3½ years in 2003 as in 2008 nearly 5 years (Figure 17).

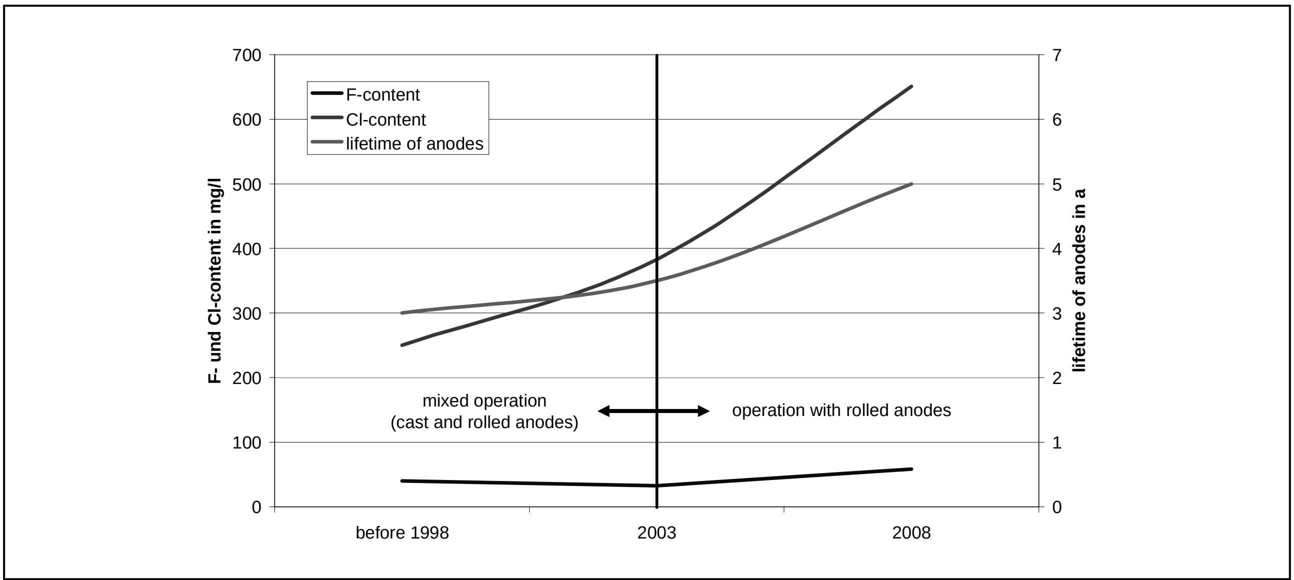



Figure 17: Lifetime of anodes

During the same time period the dross generation in the remelting process of the used anodes was reduced from 41 % in 2003 to approximately 30 % in 2008. In general, the dross formation is a loss of money, especially with regard to the high price for silver.

Better service of the anodes and less hot spots in the system could be seen in the Lead in Zinc content, and indirectly the Strontium consumption. To avoid a higher Lead content in Zinc, the addition of Strontium is common practice. Reduced Strontium consumption in combination with reduced Lead in Zinc figures show a reduction of hot spots during operations (Figure 18).

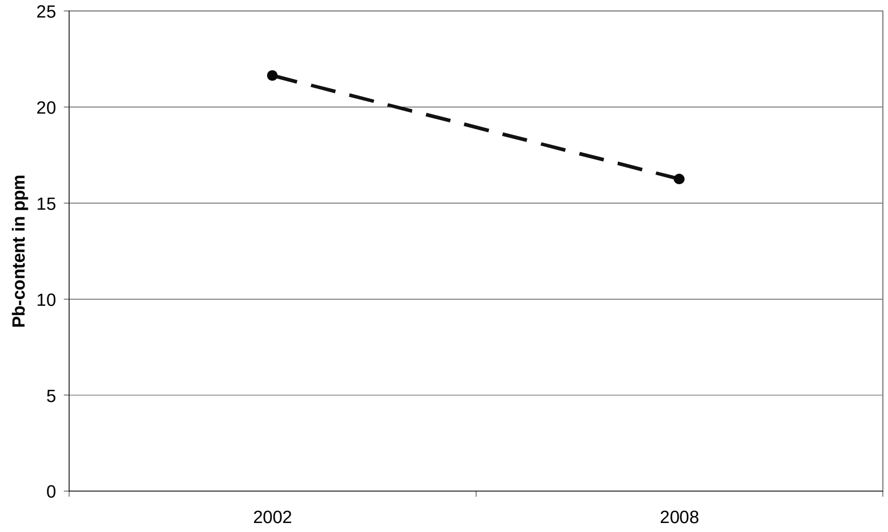



Figure 18: Development of Pb-content in cathodic zinc

# 7 Conclusion

Even in a difficult environment JL-Goslar´s flat rolled anodes made from lead-silver-alloy showed excellent metallurgical results. Besides the well known advantages like homogenous microstructure and silver distribution the integrity and stiffness of the anode becomes more and more important especially when using jumbo-cathodes and -anodes. In addition, it is necessary to sustain a strict care and maintenance strategy for the anodes.

# References

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