The Lead Anode in Galvano Technique – A High Tech Operating Resource?

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The field of galvano technique covers various processes like hard chromium or zinc plating, stainless steel pickling, anodization, production of copper foils and metal extraction of zinc, copper, nickel, manganese, cobalt and cadmium. Lead anodes are used for galvano technique since decades. While in former times most of the production sites have produced the anodes on their own, now the market offers anodes designed by specialized manufacturers. This evolution was a must in the continuous development of the processes in surface treatment and also metal extraction. Both industries, the service industry for surface treatment and electrolysis for metal extraction, have optimized their processes under respect of efficiency, cost and energy. The specific challenge in electrolysis is processability of secondary materials and the reduction in working capital, because of the huge amount of anodes needed. All these developments place higher demands on the anode design and services, circumstances that cannot be met by in-house production. So the time for specialists in Lead-processing had come. Specific customer processes and needs, as well as individual service requirements need to be fulfilled by the anode design. This report will give a short impression of today‘s anode design for surface treatment and metal extraction. Lead anodes – an unspectacular product, which has to meet high demands in today’s time – a high tech operating resource.

Keywords:

Anode – Electro plating – Stainless steel pickling – Metal extraction –Recycling

Die Blei-Anode in der Galvanotechnik – ein High-Tech-Betriebsmittel?

Der Bereich der Galvanotechnik deckt verschiedene Prozesse ab, wie Hartverchromen oder Verzinken, Edelstahlbeizanlagen, Anodisieren, Herstellung von Kupferfolien und Metallgewinnung von z.B. Zink, Kupfer, Nickel, Mangan, Kobalt und Kadmium. Blei-Anoden werden in der Galvanotechnik seit Jahrzehnten genutzt. Während früher viele Produktionsstätten ihre eigenen Anoden hergestellt haben, bietet der Markt heute eine Vielzahl an spezialisierten Anodenherstellern. Diese Entwicklung war ein Muss in dem sich kontinuierlich weiterentwickelnden Prozess im Bereich der Oberflächenbehandlung sowie der Metallgewinnung. Beide Bereiche, sowohl die Service-Industrie für die Oberflächenbehandlung als auch die Elektrolysen zur Metallgewinnung, haben ihre Prozesse im Hinblick auf Effizienz, Kosten und Energie optimiert. Die besondere Herausforderung bei der Elektrolyse ist die Verarbeitbarkeit von Sekundärstoffen und die Reduzierung des Betriebskapitals aufgrund der hohen Anzahl von Anoden. All diese Entwicklungen stellen höhere Anforderungen an das Anodendesign und den Betrieb; diese Umstände konnten nicht durch eine Eigenproduktion gedeckt werden. Die Zeit der Spezialisten in der Bleiverarbeitung war gekommen. Kundenspezifische Prozesse und Wünsche sowie individuelle Dienstleistungsanfragen müssen mit dem Anodendesign abgedeckt werden. Dieser Bericht spiegelt in einer kurzen Darstellung das heutige Anodendesign für die Oberflächenbehandlung und Metallgewinnung wider. Blei-Anoden – ein unspektakuläres Produkt, das die hohen Anforderungen der heutigen Zeit zu erfüllen hat – ein High-Tech-Betriebsmittel.

Schlüsselwörter:

Anode – Galvanikanoden – Edelstahlbeizanoden – Metallgewinnung –Recycling

L’anode de plomb dans le domaine de la galvanoplastie - un moyen de production de haute technologie ?

El ánodo de plomo en la galvanotecnia – equipo de alta tecnología?

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1 Introduction

Galvano technique respectively electroplating is an industrial sector of worldwide importance for metal extraction and the surface treatment of workpieces in any geometrical shape. While this electrolytic process is used in metal extraction of primary and secondary materials for the production of

- zinc,
- copper,
- nickel,
- manganese,
- cobalt and
- cadmium

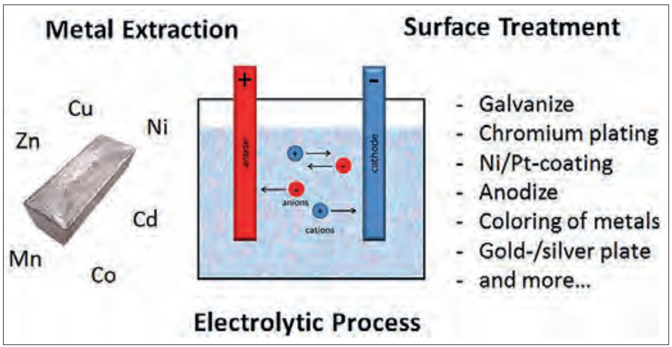

Fig. 1: Schematic illustration of the electrolysis process and examples of the application

and in the area of surface treatments for the

- finishing

of objects and workpieces of any geometrical shape. In this context, one talks about decorative electroplating. It is also used for

- corrosion protection,
- protecting against wear and tear,
- catalysis,
- improving electrical conductivity and
- reducing friction forces,

i.e. as functional electroplating (Figure 1).

The central elements in the electrolytic process are cathode and anode. This presentation will focus on the anode in the respective area of electroplating.

2 The anodes in surface treatment

The anodes in galvanic processes or in most other process are customized and optimized in co-operation with the end user. In some cases also the production could be optimized. Some examples are given below.

2.1 Anodes for hard chrome plating

In Figure 2, a chrome plating reactor designed by the company Topocrom is shown [1].

The challenge for hard chrome plating of long cylinders is to guarantee a uniform chrome thickness over the full length of the component to be chrome plated. Under normal circumstances the electric resistance becomes higher and higher over the length of the component to be chrome plated which means that the deposit of chrome becomes lower and lower. This is the so-called carrot effect. To ensure an entire smooth service and operation high efforts have to be undertaken in machining of the chrome plated

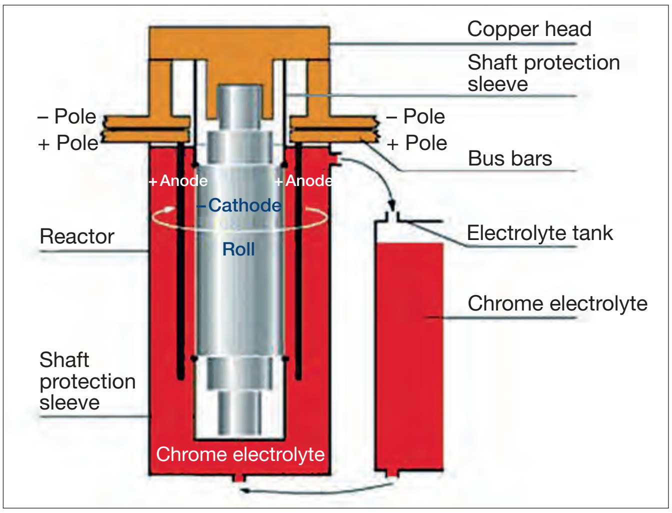

Fig. 2: Pretex® reactor for chrome plating [1]

parts. Due to excellent and homogeneous bondings between the lead tubes and the copper rods inside the chrome plating anodes an equal chrome thickness with narrow tolerances can be achieved over the whole length of the component to be chrome plated. An example for the latest state of the art of an anode design, developed by JL Goslar for hard chrome plating with a total length of 7612 mm is shown in Figure 3.

2.2 Anodes for stainless steel pickling

In Figure 4 the principal process flow of a stainless steel plant in Finland established by Outokumpu at Tornio is shown. The lead lined anodes are used in the electrolytic pickling section (red encircled) [2].

In such electrolytic pickling sections two important requirements have to be ensured:

- long operational life time of the anodes and
- an increase of the pickling capacity.

The biggest issue regarding the operational life time of lead anodes are the generation of H_2 and O_2 bubbles during the electrolytic pickling process. These bubbles are required for the pickling of the stainless steel band but cause an abrasion of the lead lining by cavitation when they are collapsing. A schematic illustration of the electrolytic pickling configuration (Figure 5) prepared by Nulifer Ipek and a corresponding picture (Figure 6) is given next [3].

The operational life time of these anodes can considerably be increased by:

- using hard lead (Pb92Sb8) for the lead lining of these anodes,

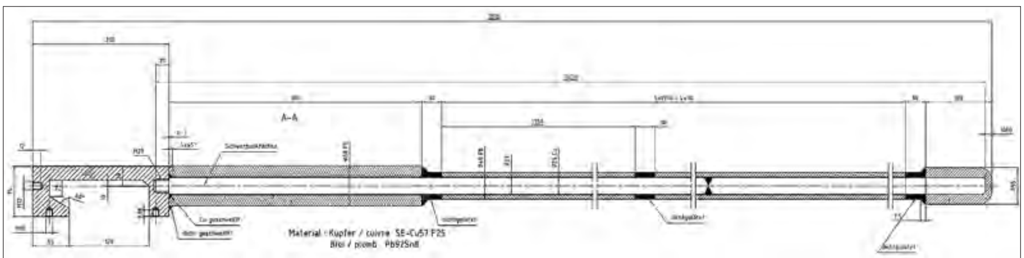

Fig. 3: Drawing of a lead anode for Pretex® reactor

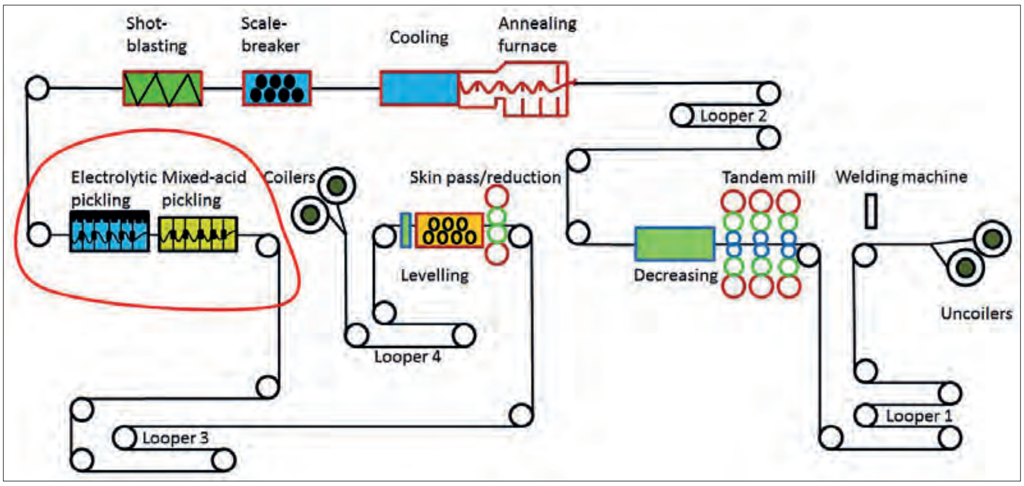

Fig. 4:
Outokumpu stainless steel plant at Tornio, Finland, with electrolytic pickling section [2]

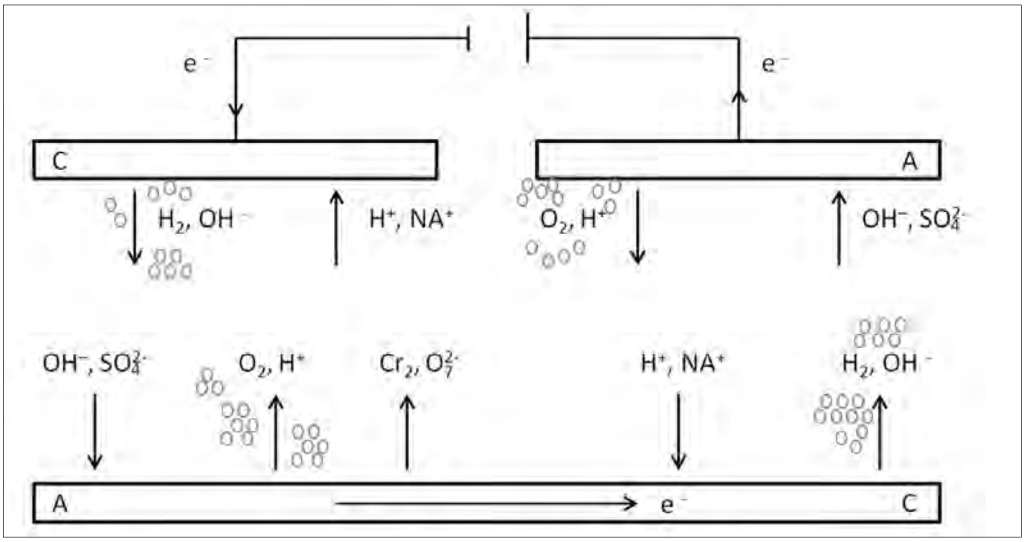

Fig. 5:
Schematic illustration of the electrolytic pickling configuration [3]

- increasing the lead lining thickness in those areas where the bubbles will collapse.

The other issue is the increase of the pickling capacity. The important factor for optimization of the pickling capacity is the electric current flow from the anode to the stainless steel band and from the steel band to the cathodes. In electrolytic pickling sections as shown in Figure 7 this cannot be assured absolutely because short circuits between the anodes (red) and the cathodes (blue) will occur from time to time due to the short distance between anodes and cathodes.

Fig. 6: Bottom view of anodes, showing oxygen bubbles [3]

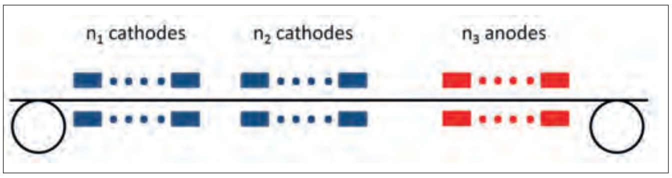

Fig. 7: Electrolytic pickling sections

These short circuits can be prevented if the distance between the anodes (red) and the cathodes (blue) is increased and the electric current is forced to flow into the stainless steel band. This allows a considerable increase of the pickling capacity.

Under normal circumstances there is a given and limited space in such pickling sections. Therefore we have – in co-operation with one of our clients – established a so called compact anode which allows increasing the distance between the anodes and cathodes (Figures 8, 9).

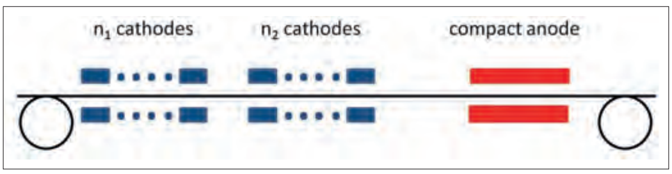

Fig. 8: Electrolytic pickling sections with compact anode

Fig. 9: Compact anode ready for transport at JL Goslar GmbH

3 The anode in metal extraction

Particularly in electrolysis operations in the zinc industry, it was customary in the past for companies to produce anodes themselves by a simple casting process. In this type of production the focus was certainly not to produce an efficient anode or to exploit every opportunity for recycling. This was, however, a circumstance that was also borne by the operating conditions of the time, as the availability of clean concentrates was given and the notion of wanting to use secondary materials, or even of have to use secondary materials, had not yet arisen.

Increasing energy costs were certainly 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, then led to the first recognition of anodes as a rolled product. Particularly for focal-point alloys, such as PbAg in the extraction of zinc or of PbSnCaAl in the copper removal of copper electrolysis, the effects of the anode characteristics from these alloys are demonstrated best.

In the case of PbAg alloys in particular, the change from the cast anode to the rolled anode plate was a significant step forward, as the positive effects, such as a higher effectiveness and an improved level of corrosion resistance, went along with a simultaneous lowering of the silver content. While silver contents of up to 1 % were normal when a cast anode plate was used, the silver content in today‘s anodes has been reduced to low values between 0.5 and 0.65 %.

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. A consequence of this was the fine granulation of the solidified structures. 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 a clear elongation of the grains and, at the same time, an enrichment of the silver at the grain boundaries. The Figures 10 and 11 show the clear differences in grain sizes and silver contents for a cast anode in comparison with a rolled anode [4].

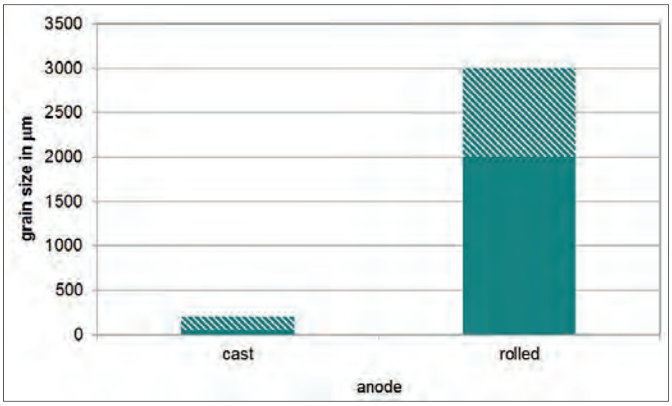

Fig. 10: Representation of the different grain sizes of cast and rolled anodes [4]

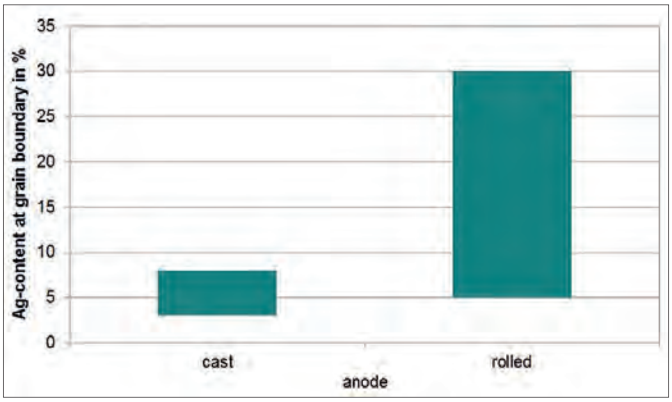

Fig. 11: Silver content at the grain boundaries of cast vs. rolled anode plates [4]

The formation of these elongated grains in combination with high silver contents at the grain boundaries improve and increase the effectiveness of the anode like an electric cable. The enrichment of silver at the grain boundaries also improves corrosion resistance and protection. Rolled anode plates clearly exhibit more favourable corrosion behaviour with a reduced silver content (Figure 12).

Additional surface treatments of the anodes will help the PbAg anodes in developing their full operational performance in the shortest possible time (Figure 13). Pb and Mn protective layers form quickly and homogenously as a result of this final treatment.

Additional points that will help to improve the effectiveness of the rolled anodes are

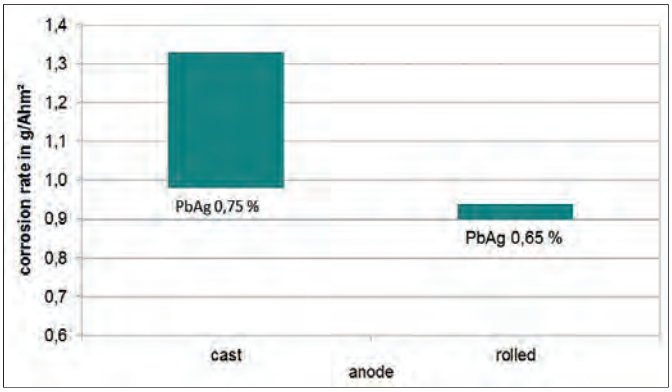

Fig. 12: Corrosion rates of cast vs. rolled anode plates [4]

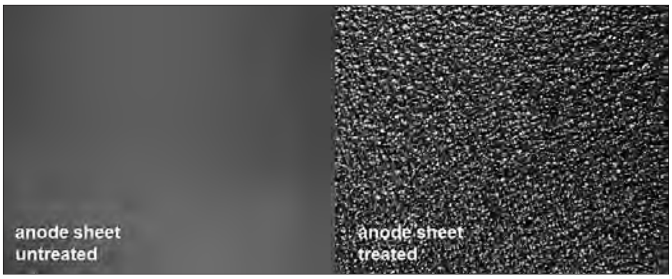

Fig. 13: Anode surfaces without vs. with post-treatment

- the complete and homogenous full-surface formation of inter-metallic phases that improve the bonding between the copper bar and the lead lining and
- an error-free welding seam by using an automated welding process.

To ensure optimum conditions in the formation of the intermetallic phases, the copper bar passes through a number of different chemical treatment baths before being finally immersed in the tin-plating bath. The time the copper bar is immersed is attuned to the full-surface interconnecting of the copper bar surface and the necessary heat up of the copper bar. The subsequent transfer into the head-casting machine with the casting of the lead alloy completes the production of the anode head. This process, when carried out with optimized operating parameters and a high level of automation, can deliver a constant and high level of quality and an excellent and strong surface bonding with adhesion rates equal or higher than 95 % (Figure 14).

Fig. 14: Automatically tinning plant and casting device at JL Goslar Anoden GmbH

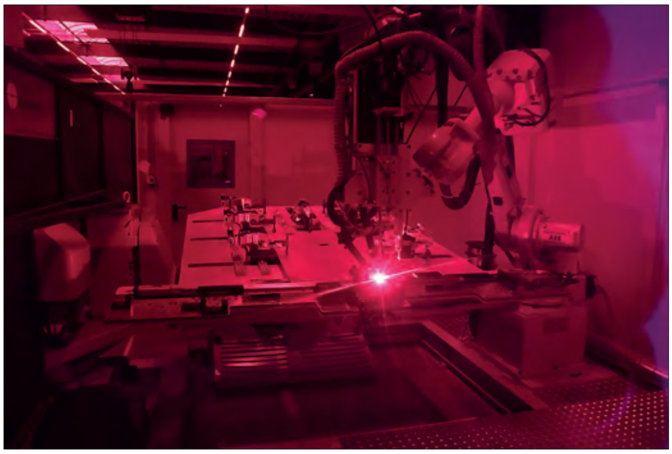

Fig. 15: Automated welding process in anode production at JL Goslar Anoden GmbH

The last process step in the anode producing is welding of the anode head and anode plate. There also exist all the opportunities given by automation. Using suitable manipulators, adapted welding power sources combined with laser seam-tracking sensors and online parameter-monitoring sensors ensure a high-quality welding seam with an excellent electrical conductivity and optimized current transfer (Figure 15).

A further step in optimising the anode production is recycling of used anodes that have reached the end of their service lives. Here, the recycling is not limited simply to recovering lead alloys, but extends to reusable copper bars and stainless steel hooks. Even the dross that arises in the re-melting process can undergo post-treatment to recover all of the metals elements that are recoverable (Figure 16).

Electrolysis operators are having every opportunity to optimize their process and to its performance limits, when making use of all the measures established in the manufacturing of lead anodes at a specialized manufacturing fa-

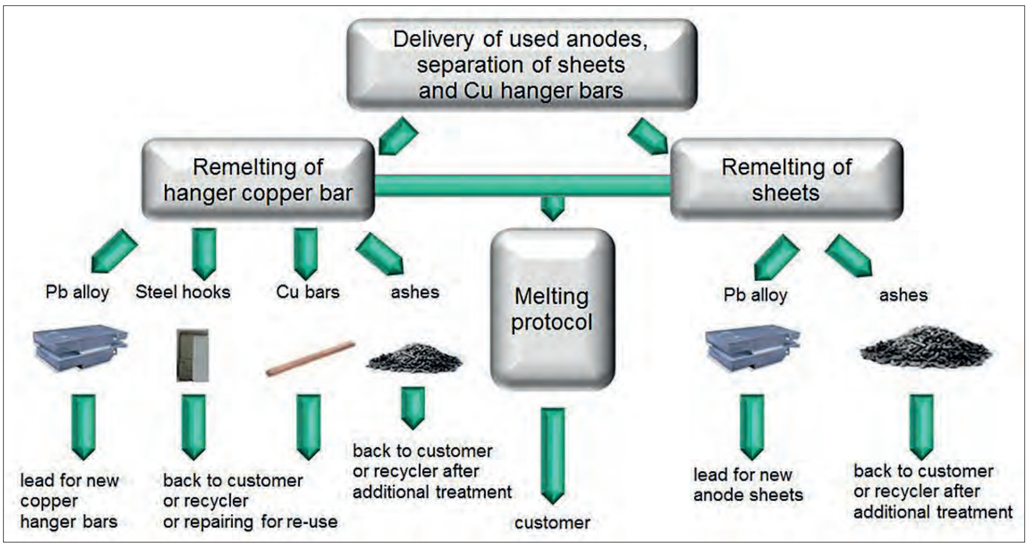

Fig. 16:
The recycling process of old anodes at JL Goslar GmbH

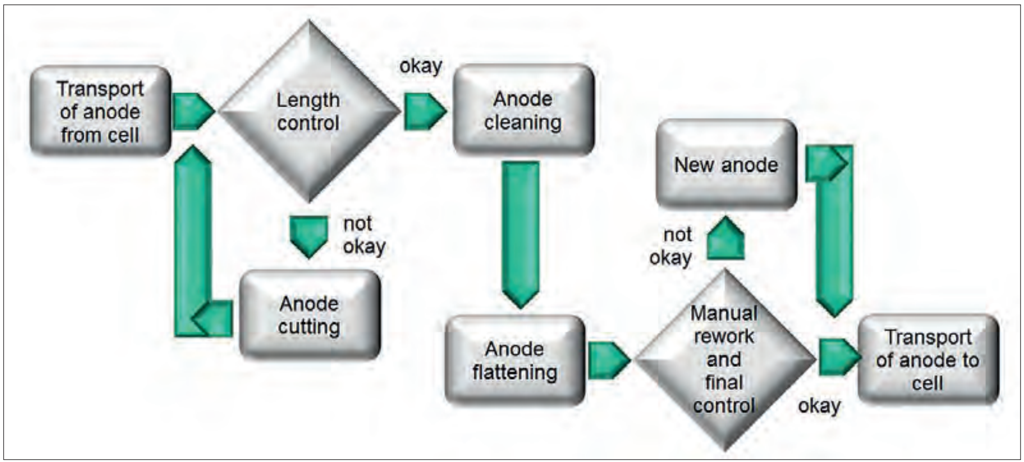

Fig. 17:
Flow chart of anode care

cility. Furthermore, the use of rolled anodes and the corresponding manufacturing process is also a good basis for the use of secondary materials. An anode cannot, however, be considered to be maintenance-free. Careful maintenance of the anode will retain the positive characteristics from the manufacturing process and plays its part in achieving a long service life. The following flow chart represents a possible procedure for preserving the function of an anode (Figure 17).

4 Conclusion

Only some major details in the field of modern galvano technique have been explained and shown in this article. Nevertheless it has been clearly demonstrated that productivity and efficiency in electrowinning and metal coating can be improved when using modern high quality lead anodes. Specialized lead anode manufacturers have gathered a deep and extensive know-how over the years when supplying tailor-made anodes to various end users and can help to develop new solutions.

Especially innovative and resource-saving solutions are developed with the long term experience in lead alloys. The negative image of this metal may not have helped in the past to support targeted application development. But even today lead is still an indispensable material in many industrial applications. Investments of lead-processing companies in new and more sophisticated equipment and manufacturing processes are the consequences from these facts.

Lead anodes – an unspectacular product, which has to meet high demands in today's time – a high tech operating resource.

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