FAQS WITH REGARDS TO OPERATING A COPPER TANKHOUSE ABOVE 400 A/m² USING METTOP-BRX TECHNOLOGY

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ABSTRACT

Since 2011, Xiangguang Copper Co., Ltd. operates one of their two 720 cells copper refining tankhouses with a current density of 420 A/m² and current efficiencies above 98 % in average. This was achieved by introducing the fresh electrolyte with the active inhibitors at higher flow rates parallel to the electrodes using the Mettop-BRX Technology.

Although for many years a total of two industrial applications are in operation worldwide, the successful implementation of this technology, that result in significant operational and economic advantages, has not been fully accepted within the industry due to misunderstandings, incorrect interpretations and lack of awareness.

This paper describes the technology in general and answers a lot of FAQs. Detailed figures and economic facts given from both industrial applications – the electro refinery at Xiangguang, China, as well as from Montanwerke Brixlegg AG, Austria – will help understanding the outstanding benefits from METTOP-BRX Technology.
INTRODUCTION

Whenever thinking about increasing tankhouse performance two major aspects have to be considered, the technological feasibility as well as the economic impact. For an optimized tankhouse performance, not only in copper industry but also for zinc electrolysis, the following points are of interest:

- High tankhouse capacity
- High current efficiency
- High chemical cathode quality
- Low operating cost
- Lower footprint
- Low bound capital

Increasing tankhouse capacity can generally be done in two ways: Either by increasing the cathodic deposition area (i.e., adding more cells or increasing the number of electrodes in the cell) or by increasing the current density. The former possibility is relatively cost-intensive, as new buildings and infrastructure are required, and sometimes it is not possible due to limited space and/or other restrictions. Increasing the current density is generally a matter of the actual electrical system but it is also limited as current efficiency and cathode quality tend to decrease with increasing current density, due to problems with both cathodic deposition and anodic dissolution. Consequently, the current densities that are used in electrorefining are far below the theoretical limiting current density.

According to physical and chemical laws, the only way to increase the current density in a way that ensures that the electrodeposition is still pure and that the metal sheets are smooth and of a high quality, is to minimize the diffusion boundary layer and/or to influence the electrocrystallization by an optimized inhibitor distribution. This can be achieved by increasing the flow directly at the cathode, for example by using a manifold inlet to achieve a parallel electrolyte flow and introduce the fresh electrolyte with the active inhibitors directly at the cathodes.

For meeting all those requirements, Mettop has developed together with Montanwerke Brixlegg AG, Austria a new type of manifold inlet: the METTOP-BRX Technology [1-3]. Described simply, the METTOP-BRX Technology increases the productivity of a conventional electrorefining cell by allowing the operator to increase the current density up to 400 – 420 A/m². This is accomplished by increasing the electrolyte flow rate and introducing it into the cell parallel to the electrode surfaces. Introduction of the electrolyte in this way, in contrast to introducing it at the end wall of the cell, aids the transfer of Cu²⁺ from anode to cathode by enhancing the natural convection of electrolyte between the two opposing electrodes, minimizing the diffusion boundary layer at the cathode surface, and improving the homogeneity of the electrolyte temperature and chemistry within the cell.

The parallel electrolyte flow can be realized by either using a Parallel Flow Device (PFD), namely a separate device that is installed in the cell, or a Parallel Flow Plate (PFP), namely an integrated system in the polymer concrete cell.

For providing a better understanding about the process and the economic output of installing the METTOP-BRX Technology the most frequently asked questions will be answered within the subsequent sections:

- Why does it work? – Theoretical background
- How does it work? – Hardware of the installation
- Can every existing tankhouse be equipped with PFD right away?
- Is METTOP-BRX Technology a well proven technology? - References
- What does it cost? CAPEX, OPEX and Revenue
WHY DOES IT WORK? – THE THEROETICAL BACKGROUND

To increase current density in a copper refining electrolysis the limiting current density has to be increased. The only physical quantity which can be influenced in a wider range is the diffusion boundary layer \( \delta_N \) as shown in equation 1. The concentration in the bulk electrolyte is limited to 45 to 50 g/l because above 50 g/l the movement of the Cu ions will be negatively affected. The diffusion coefficient could be influenced via the temperature but the temperature is limited to 65 °C.

\[
i_{lim} = n \cdot F \cdot D \cdot \frac{c^0}{\delta_N}
\]

Equation 1

Decreasing the diffusion boundary layer means increasing the relative movement of electrolyte in front of the cathode surface. The limiting current density is theoretically the highest current density which can be used in a given system. At the limiting current density the copper ions concentration in front of the cathodes is zero.

However, the current density used in industrial practice amounts only 30 to 35 % of the theoretical limiting current density. That ratio can be increased by an excellent operation practise. A perfect electrode lining, homogeneous copper concentration and electrolyte temperature distribution as well as a perfect inhibitor distribution (directly in front of the cathode!) are of importance.

To increase the limiting current density and the industrial used current density the following has to be done:

- Decreasing the diffusion boundary layer by increasing the relative electrolyte velocity between electrolyte and cathode surface.
- Distribution of all inhibitors directly in front of the cathodes

The electrolyte flow within an electrolysis cell can be divided in a forced convection and a natural convection. The forced electrolyte flow in a conventional electrowinning cell is shown in Figure 1. The electrolyte enters the cell at the bottom of the front and leaves it at the upper opposite end. One major disadvantage of this conventional arrangement of inlet and outlet is that the fresh electrolyte, and hence also the additives like inhibitors, is not inserted directly in front of the active cathode surface, where it is needed, and a part of it also leaves the cell by bypassing the electrodes on the sides. By using a conventional forced convection the relative movement between electrolyte and cathode is hardly influenced by the forced convection. The diffusion boundary layer is mainly influenced by the natural convection.

Figure 2 shows the natural convection in the cell, which occurs during electrowinning due to differences in electrolyte density near the electrodes. Close to the anode, the density of the electrolyte increases due to anodic dissolution and hence higher concentration of metal ions, whereas near the cathode a local decrease of density occurs due to electrodeposition. This natural convection was proven and determined quantitatively by measurements of fluid flow velocity between anode and cathode, as shown in Figure 3.
Again, to increase the limiting current density the diffusion boundary layer has to be decreased and therefore the relative movement (velocity) between electrolyte and cathodes surface has to be increased. This means higher electrolyte velocities enable higher limiting current densities in electrefining. These higher velocities can be realized by implementing a parallel electrolyte flow between the electrodes. The development of the Parallel Flow Device (PFD) enables this conditions. However, the position of the electrolyte inlet has to be chosen accurately, as a high electrolyte velocity at the anode can also cause problems with the anode.
slime, which may be detached from the anode surface, transferred to the cathode, and cause dendrites and buds there.

The flow profile of a parallel flow cell is shown in Figure 4.

![Figure 4 – Flow profile of a parallel flow cell](image)

Due to a higher electrolyte flow (up to three times higher than the standard flow) the velocity in front of the cathode is much higher and therefore the diffusion boundary layer is decreased. Which means a higher limiting current density and therefore a higher industrial used current density is achieved using the parallel flow concept.

**Inhibitor distribution**

To produce a very smooth copper cathode and to operate the tankhouse on a high current efficiency following inhibitors have to be added:

- **Glue:** 50 – 100 g/t copper
- **Thiourea:** 50 – 100 g/t copper
- **HCl:** 30 – 70 mg/l

The inhibitors are added to the electrolyte before the fresh electrolyte is entering the cell. In a conventional cell the inhibitors are not in front of the cathode (where they have to be; see Figure 1).

Using a parallel flow concept the inhibitors are introduced directly in front of the cathodes and therefore smooth copper cathodes are produced even at very high current densities (up to 450 A/m²). The inlet of the fresh electrolyte has to be close to the bottom of the cell (see Figure 5 left). By doing so, the upwards flow of the natural convection can be used and the fresh electrolyte (and all inhibitors) are directly in front of the cathode surface. The density of the fresh electrolyte is lower as the used electrolyte and this leads also to an upwardly flow.

Using the METTOP-BRX Technology a current density of up to 450 A/m² at a current efficiency of above 98 % can be achieved.
Overall, the impact of introducing a parallel flow can be summarized [4-6]:

- Due to a higher electrolyte flow rate (up to three times higher than a standard flow rate) and a flow directly in front of the cathode leads to a decreased hydrodynamic and diffusion boundary layer. A direct introduction of the inhibitors near the active cathode surface lead to a more homogeneous distribution of inhibitors on the cathode surface and furthermore increase the product quality in terms of surface quality.
- A simultaneous introduction of the inhibitor glue guarantees the same glue activity all over the cell lengths.
- Since the distance between the anode and cathode is precisely fixed, the current density distributions is more homogenous.
- The direct electrolyte introduction leads furthermore to a more homogenous electrolyte temperature distribution.

**HOW DOES IT WORK? – METTOP-BRX TECHNOLOGY HARDWARE**

There are two different approaches for optimization of the tankhouse performance, either when installing a perfectly new tankhouse (greenfield approach) or an upgrading of an existing tankhouse (brownfield approach).

**Brownfield Approach - Parallel Flow Device (PFD) for upgrading existing tankhouses**

The core of the METTOP-BRX Technology is a Parallel Flow Device (PFD; Figure 6 left side), which introduces the fresh electrolyte between each pair of electrodes within the tankhouse. Special positioning devices – so-called cathode spacers as shown in Figure 6 – provide an accurate electrode positioning, as well as a defined relative position of cathode and nozzles. The nozzles, which are designed for each individual tankhouse, direct the fresh electrolyte in an upwards flow in front of the cathode surface, which only enhances the already existing flow resulting from natural convection. The PFDs are customer-tailored to guarantee optimum results for each specific tankhouse.
Greenfield Approach – Parallel Flow Plate for optimized tankhouse performance

The Parallel Flow Plate (PFP) is a combination of PFD and the cell itself: In new tankhouses – or when replacing cells in an existing tankhouse – the METTOP-BRX Technology can be integrated in the polymer concrete cells as shown in Figure 7. The main idea is to cast the cell in a way that the volume for the electrolyte distribution system is already included. Therefore, only a stainless steel front plate with nozzles and cathode spacers – the Parallel Flow Plate – is attached to the cell. Implementing PFPs minimizes the installation effort, as only the front plate has to be mounted. Furthermore, these systems can be preassembled at the cell supplier and the customer can install the complete cells just like normal cells.
In both application cases the, the basic equipment can be summarized:

- A welded stainless steel construction (PFD) or a combination of the polymer concrete cell and a stainless steel plate (PFP) for distributing the fresh electrolyte evenly along the entire cell
- Stainless steel nozzles for introduction the fresh electrolyte precisely in between the anodes and cathodes
- Cathode positioning systems for ensuring the accurate spacing within the entire cell

Due to the fact that a higher electrolyte flow rate is required (the outlet velocity of the electrolyte per nozzle has to be calculated individually for each tankhouse) the overall tankhouse design has to be adapted and again can be divided between greenfield and brownfield projects.

**CAN EVERY EXISTING TANKHOUSE BE EQUIPPED WITH PFD EASILY?**

The use of high current density and the METTOP-BRX Technology requires an adequate tankhouse design. Optimum performance can only be achieved with a comprehensive design of the overall process and complete tankhouse equipment, comprising electrical and electrolyte system, as well as the mechanical components.

For installation of the METTOP-BRX Technology the following requirements have to be taken into account:

- Electrolyte system for high flow: Adequate piping diameters, as well as direct pumping instead of overhead tanks
- Electrical system for high current density: Suitable rectifier, transformer, and bus bars
- A good electrode quality/geometry is essential for exact positioning
- Polymer concrete cells – for smooth walls (PFD installation) and system integration (PFP)
- Crane positioning system to guarantee exact electrode positioning
- Stainless cathodes or smooth copper mother sheets

For a greenfield project the adequate design can be easily done. The correct pipe dimensions as well as the right pumps have to be calculated for a direct pumping system. There are no specific requirements for the inhibitor dosage system or filtering system.

For a brownfield project especially regarding the increased flow and circulation rate compared to the conventional system, the capacity of the piping and pumping systems will be the limiting factors, since the flow rate is increased by the factor of three. To overcome these problems individual solutions are offered.

Solutions like:

- Creating internal loops for two third of the electrolyte flow and using the existing piping for one third
- Increasing the current density by taking out anodes and cathodes and creating the higher flow using pumps installed into the calls
- Replacing partly the existing pipes and change to a direct pumping system
Figure 8 - Process flow sheet of a greenfield approach as realized in Xiangguang Copper Tankhouse No.2
IS METTOP-BRX TECHNOLOGY A PROVEN TECHNOLOGY? – REFERENCES

In both cases, brownfield and greenfield application, Mettop has industrial scale references for proving the applicability of the METTOP-BRX Technology. In the following sections a basic description of the installed system as well as the major benefits will be given.

Montanwerke Brixlegg AG, Austria – Upscaling an Existing Tankhouse [3,7,8]

The longest-standing METTOP-BRX Technology application is found at Montanwerke Brixlegg AG, a secondary copper producer in Austria, where after years of developments and high current density tests – 52 cells of the new tankhouse were equipped with PFDs in 2007. Due to the excellent results regarding cathode quality and current efficiency, the use of the METTOP-BRX Technology was extended by another 104 cells in 2011, using both PFDs and PFPs. Since autumn 2011, the new rectifier has been in operation, enabling a current density of more than 420 A/m², and half of the entire tankhouse has been operating at high current density.

Montanwerke Brixlegg AG has made the following observations and conclusions since the introduction of the METTOP-BRX Technology:

- The technology allows using higher current density and therefore increasing production.
- With additive adjustments the current efficiency can be increased by two to three percent.
- In case of bad anode quality, current efficiency can be kept the same as when using good anode quality – or can even be higher by using the METTOP-BRX Technology.
- A better cathode quality due to more homogeneous additive distribution can be achieved.
- Using the technology results in shorter down times when filling the groups due to higher flow and consequently faster filling. Furthermore, the higher flow enables a faster heating-up of the anodes (for new anodes) in the cold season.
- Fewer shorts occur due to accurate cathode positioning/guiding system.

Figure 9 – Installation of the PFD on site at Montanwerke Brixlegg AG and electrolyte flow after installation
Xiangguang Copper, China – Installation of a new Tankhouse

The first application of the METTOP-BRX Technology in an entire new tankhouse (720 cells) is Xiangguang Copper, a primary copper producer in China. The tankhouse engineering for their second tankhouse, which had been started up in May 2011, was done by Mettop. This tankhouse was constructed in the same way as the existing tankhouse, but now 300,000 t/a cathode copper, compared to the existing tankhouse with 200,000 t/a production capacity, can be produced by using the METTOP-BRX Technology. This increase in production rate of 50% is caused by the much higher current density, namely an increase from 280 A/m² in the old tankhouse up to 420 A/m².

As Xiangguang Copper decided from the very start that the new tankhouse will be equipped with the METTOP-BRX Technology and the high current density technology, Mettop designed the whole tankhouse accordingly. The tankhouse design included:

- Latest generation of PFDs (pyramid cathode spacers, hanging system, cleaning openings, handling hooks)
- Pumps for direct pumping (i.e., no overhead tanks) for approximately 100 l/min per cell
- Design of electrical system for 420 A/m² (2 electric circuits)
- Design of heat exchangers
- Good coordination of electrical and electrolyte circuits under consideration of potential differences
- Continuous addition of inhibitors

This first greenfield METTOP-BRX tankhouse started up in summer 2011. In December 2011, the average current density of the new tankhouse was higher than 98% (98.51%) at current density of 410 A/m², and the quality of the produced cathodes was excellent as shown in Figure 10. In 2012 Xiangguang Copper used 420 A/m² and achieved an average current efficiency of 98.3%. Today Xiangguang Copper reports current efficiency of > 99% at 420 A/m² [9].

Figure 10 – Tankhouse with METTOP-BRX Technology at Xiangguang Copper (left) and excellent surface quality of the cathodes
WHAT DOES IT MEAN ECONOMICALLY?

For the two industrial scale applications, either brownfield application as well as greenfield application, detailed economical calculations regarding operational expenditures, capital expenditures, savings and revenues have been conducted. Due to different power costs as well as different interest rate levels an economical calculation or evaluation has to be done for each customer individually. Just for an overview only a few points which are significant are given for a production of 400,000 t copper cathodes per year.

For a new tankhouse following CAPEX decrease can be achieve using 420 A/m² (by using the METTOP-BRX Technology) compared to a standard technology (310 A/m²).

- Lower overall tankhouse footprint (~ 20 %)
- Less cells (26 %)
- Less cathode plates (26 %)
- Less electrolyte and edge strips
- Less anodes in the tankhouse (25-30 Mio US$ bound capital reduction)!!

The costs for machines like anode preparation machine, stripping machine, etc. and for the electrical installation in terms of generator, rectifier, bus bar, etc. will stay the same assumed the same production for both systems.

For the OPEX calculation the two following parameters are of importance:

- Interest savings due to a much lower CAPEX costs
- Increase in power consumption due to a higher current density

Both industrial sites, where the METTOP-BRX Technology is used, report that the overall OPEX are decreased [9-11] and all economic calculations are supporting these statements even in countries with high power costs.

SUMMARY AND CONCLUSION

Today’s most advanced tankhouse technology – the METTOP-BRX Technology – allows increasing the current density and productivity, respectively, by up to 50 % compared to conventional copper electrorefining tankhouses. This technology can either be installed in existing facilities – in order to increase production – or considered in new plants – in order to reduce the footprint of the entire tankhouse.

The present paper illustrates the potential economic benefit of equipping copper electrorefining facilities with the METTOP-BRX Technology. Both for a greenfield project as well as for a brownfield upgrade, the economic value is shown by industrial inspired examples.

Right now the benchmark for a copper refinery is Xiangguang Copper, China, running their tankhouse no. 2 at 420 A/m² at a current efficiency > 99 % using the METTOP-BRX Technology.
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