

# Potential Measurements in a High Current Winning Electrolysis

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High current density electrolysis is defined as using a current density  $\geq 1000 \text{ A/m}^2$ . Currently, technical current densities of only approximately  $300 \text{ A/m}^2$  are indicating that a 300 % increase in productivity should be achievable using high current electrolysis. A series of experiments was performed to determine the current density throughout the cell under different conditions, using current density potential curves. These investigations indicated that unsatisfactory fluid flow in the lower region of the electrolyte occurred if no gas injected forced circulation was employed, and thereby, a lower achievable limiting current density was possible. In contrast, a 4-fold higher limited

current density was obtained in the lower region of the cathode if forced convection, using gas injection, was employed. To determine if high current electrolysis was feasible under standard and air agitation conditions, a high current electrolytic cell was designed and constructed. Using this cell it was possible to produce compact and smooth copper cathodes.

Keywords:

Copper – High current electrolysis – Current density potential curves – Gas agitation

## Potentialmessungen in einer Hochstromgewinnungselektrolyse

Von einer Hochstrom-Elektrolyse spricht man bei Stromdichten  $\geq 1000 \text{ A/m}^2$ . Zur Zeit werden technische Stromdichten von rd.  $300 \text{ A/m}^2$  realisiert, das bedeutet, dass eine Hochstrom-Elektrolyse eine Produktivitätssteigerung um mehr als 300 % mit sich bringt. Es wurden Grenzstromdichten mittels Stromdichtepotentialkurven ermittelt. Diese Untersuchungen konnten die Problematik der schlechten Beströmung des unteren Drittels der Kathode bei ausschließlich natürlicher Konvektion aufzeigen und den positiven Einfluss der gasblaseninduzierten Strömung nachweisen. Die Grenzstromdichte am unteren Ende der

Kathode bei Versuchen mit gasblaseninduzierter Rührung ist fast viermal so hoch wie bei Experimenten ohne Gasrührung. – Nach Auswertung dieser Ergebnisse wurde eine Hochstromelektrolyse im halbtechnischen Maßstab gebaut und betrieben. Die damit erzeugten Kathoden wiesen einen kompakten und glatten Kupfer-Niederschlag über die gesamte Höhe auf.

Schlüsselwörter:

Kupfer – Hochstromelektrolyse – Stromdichtepotentialkurven – Gasrührung

## Mesures potentielles dans une électrolyse à électricité élevée

## Medición de los potenciales en la electrolisis para la obtención de alta corriente

Previous analyses done by the Institute of Non Ferrous Metallurgy, University of Leoben, Austria, [1, 3, 4] and other laboratories [2, 7, 8] have shown that the structure of the metallic cathode precipitation varies over the cathode area. At the top, the cathodic precipitation is smooth and compact, in contrast to the bottom, where the formation of dendrites is more probable and the possibility of short circuits is greater. To operate at higher current densities and improve efficiency and quality of the cathode it is necessary to increase the limited current density and minimize the diffusion layer thickness. However, to obtain a thin diffusion layer, the convection in the cell must be increased to causing an increased copper ion movement. Thereby, a regular, smooth, and compact precipitation would also be possible at higher current densities.

Gas bubbles that originate from the anodes and differences in concentration of ions – electrolyte density differenc-

es – produce natural convection in this electrolysis system. At the bottom of the cell the electrolyte is nearly free of gas bubbles, therefore, the electrolyte flow in this area is low. This results in the electrical resistance also being lower at the bottom of the cell than at the top. Furthermore, in the bottom electrolyte, where the resistance is low, a higher current density is induced. The literature indicates that to increase the mass transport coefficient in the bottom area of the cathode and produce a smooth cathode precipitation, a forced convection by gas injection is required. In the following experimental series, the limited current density, which is influenced by gas injected convection, was measured. Furthermore, a high current density copper winning electrolysis was operated.

This work was an extension of previous analyses [1, 3, 4] that examined the influence of forced convection, by gas injection, on the diffusion layer thickness and indicated that

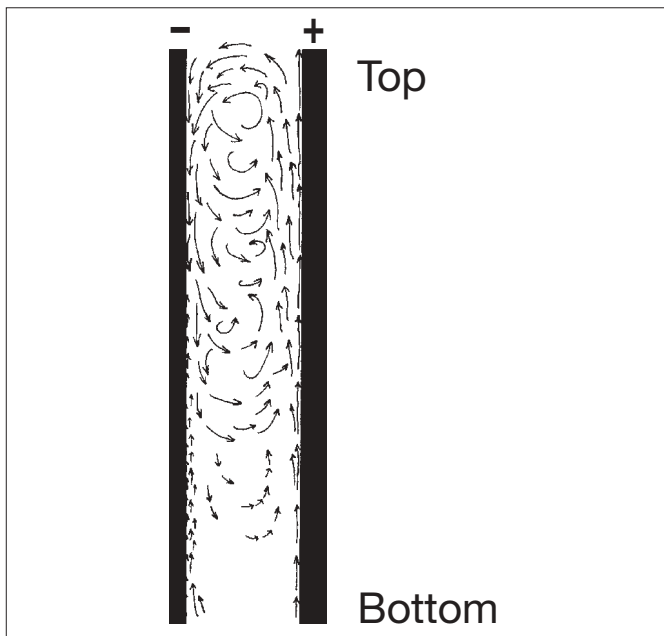


Fig. 1: Schematic drawing of the gas injected agitation at the winning electrolysis [3]

the cathodic limited current density should be further investigated. The typical working current density is far below the limited current density for the system. ROMBACH et al. [5] stated that the technical current density used in conventional electrolysis is approximately 25 to 30 % of the limiting current density. Operating at current densities closer to the limiting current density causes a rougher, not so compact precipitation with an increased probability of dendrite formation. Furthermore, by increasing the current density above the limiting current density a powdery precipitation at the cathode can occur.

In Figure 1 the convection conditions in a copper winning electrolytic cell are illustrated. In the top region, the presence of many naturally produced gas bubbles mix the electrolyte and the resulting increased turbulence causes a decrease in the hydrodynamic limiting thickness. Furthermore, in this area the electrolyte resistance will increase due to the higher gas bubble density. Thereby, the current density at the top part of the cathode will be lower than at the bottom and this will result in a compact and smooth precipitation at the top. However, below the top region is an area with a thick hydrodynamic limited layer. In this region there is no increased electrolyte flow due to gas bubble agitation.

This causes a decrease in the relative velocity between the electrolyte and the electrode. Furthermore, in this relatively thick hydrodynamic layer, the related limited current density is lower. Variations in the local current density along the electrode also cause the qualitatively poor copper precipitations, previously described.

## 1 Experimental setup for the electrochemical measurements

The following investigations illustrate the relationship between the current density and the electrode height, in a

high current electrolysis, with forced gas injection agitation [6]. Figure 2 depicts the setup for the current density potential measurement. The model cell was manufactured from transparent PVC (height  $\times$  length  $\times$  width = 1000  $\times$  100  $\times$  35 mm). The electrodes used were “prengaman” electrodes (lead-tin-calcium-alloy, height  $\times$  width  $\times$  thickness = 1000  $\times$  100  $\times$  10 mm). The synthetic electrolyte contained 165 g/l  $H_2SO_4$ , 50 g/l Cu, and no inhibitors. The distance between the electrodes was 35 mm and a constant electrolyte level of 950 mm maintained a fixed active cell area. The gas injection was performed using stainless steel pipes at the bottom of the cathode and direct at the cathode side with a stainless-steel pipe. The two single pipes, each with three equidistant holes of the same diameter, were installed at the front of the cell and the bottom edge of the cathode was streamed with air. The decrease in the hydrodynamic limited layer, using air turbulence to increase the convection should be shown. It was possible to operate the high current density copper winning electrolyses without any inhibitors.

The initial experiments involved determining the correlation between the nozzle diameter and the velocity and size of the bubbles produced. Details of the four different nozzles evaluated in Table 1. The bubble production, from the different nozzles, was recorded using a high speed video camera. Photographs of the ascending bubbles are presented in Figure 3.

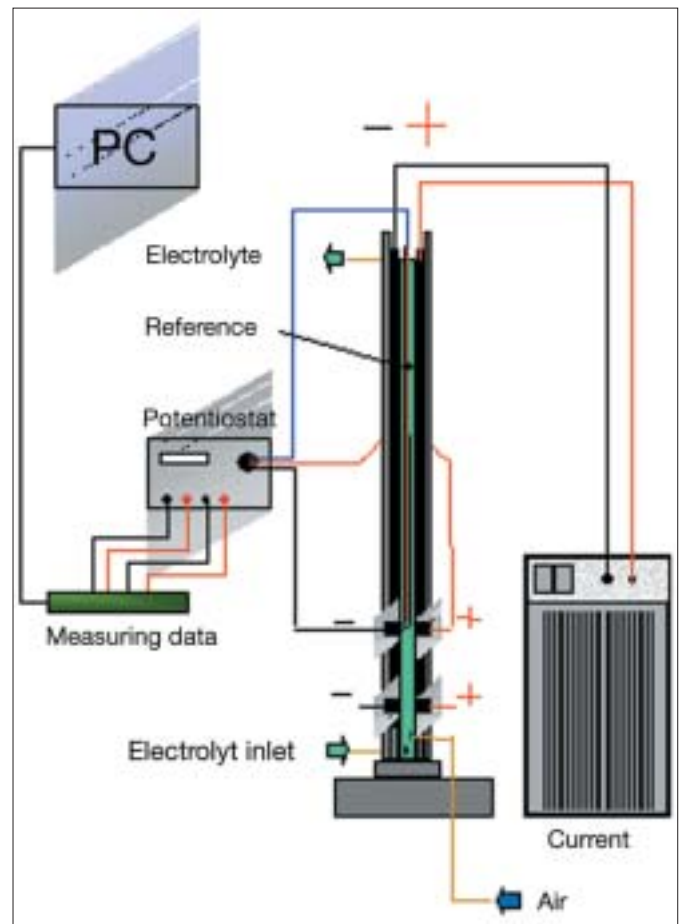


Fig. 2: Experimental setup for the current density potential measurements

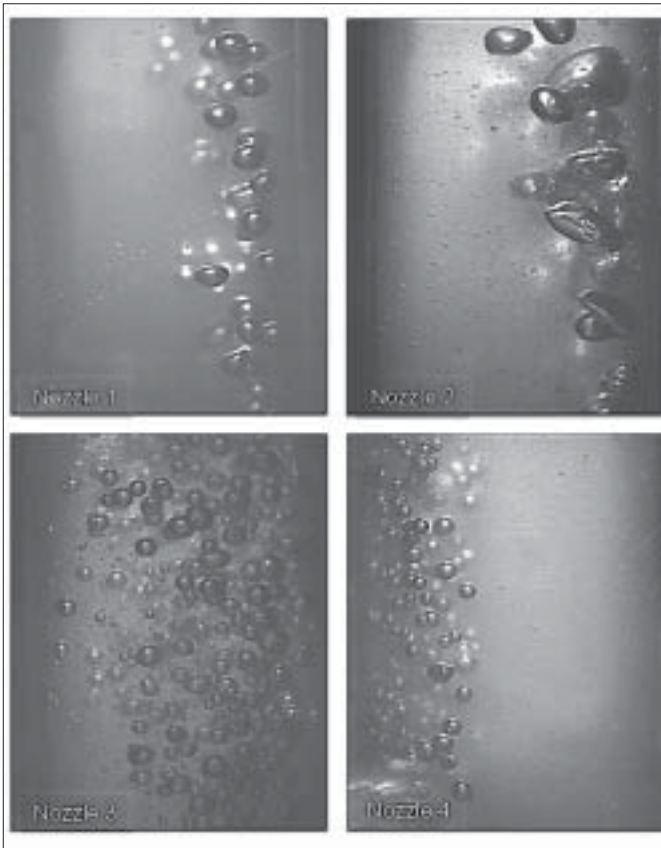


Fig. 3: Photographs of gas bubbles

Tab. 1: Diameters of the nozzles and of the gas bubbles produced

Nozzle	Nozzle diameter [mm]	Gas bubbles diameter [mm]
1	0.4	2.3
2	0.3	1.98
3	0.2	1.51
4	0.1	1.25

The average velocity of the gas bubbles was calculated as  $v_m = 0.4$  m/s. The synthetic electrolyte flowed through a stainless steel pipe located between the electrodes at the bottom electrode level. There were six holes in total, each with a diameter of 3 mm. The bath was exchanged three times an hour giving an incoming electrolyte velocity of  $v = 0.056$  m/s that corresponded to an average electrolyte velocity flow of  $v_m = 8 \times 10^{-4}$  m/s.

The primary aim was to produce a regular smooth dense precipitation over the entire height of the electrode. 1000 mm electrodes were selected for the analysis to produce flow conditions near the cathode similar to those in a technical electrolysis cell.

The experimental setup to measure the current density potential is illustrated in Figure 4. The current density potential measurement electrodes, manufactured from a lead-tin-calcium alloy (pregaman), had an active surface area of 1 cm<sup>2</sup>. These small electrodes were embedded in a polymer matrix. These electrodes could be precisely installed at a defined height (Table 2) on the main electrodes and the contact was provided on the back of the electrode using a M4×35 thread. This rapid removable system for the

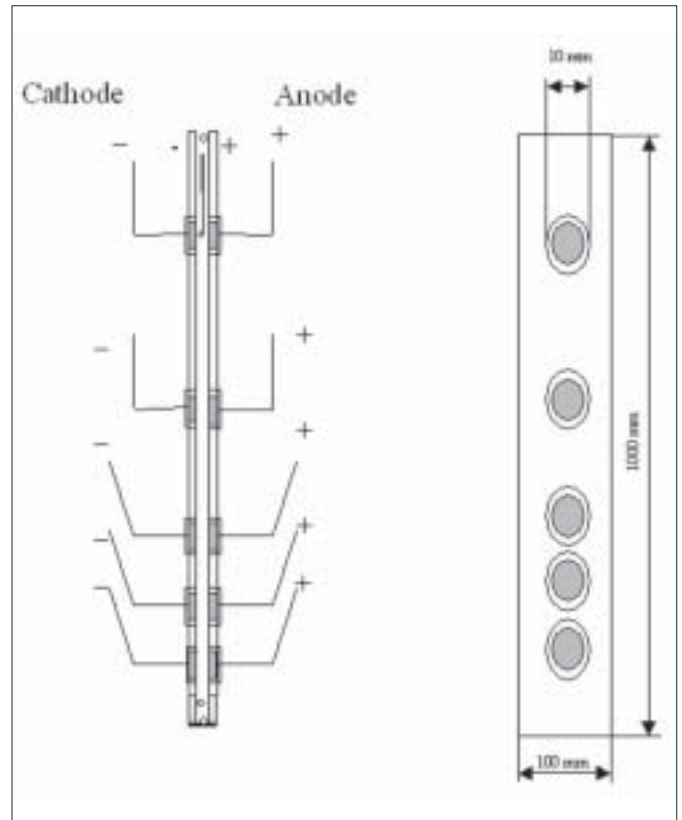


Fig. 4: Positioning of the current density potential measurement electrodes

Tab. 2: Height (1 = top, 5 = bottom) of the installed electrodes (Figure 4)

Height	1	2	3	4	5
[mm]	25	80	180	400	650

small electrodes was very important because, prior to the measurements being taken, each electrode had to be polished. Furthermore, using this system the installation at particular points was guaranteed. The reference electrode, a saturated mercury/mercury chloride electrode (Hg/Hg<sub>2</sub>Cl<sub>2</sub>, REF 601, Radiometer Copenhagen) could be optimally positioned using a glass rod with a “Luggin” capillary. The glass spike of the “Luggin” capillary was less than 1 mm from the working electrode. Problems were encountered during the investigation with electrolyte leaking into the reference electrode. Therefore, the capillary was filled with agar-agar solution. The current density potential measurements were performed using a Potentio-Galvano-Scan Wenking PGS 77.

## 2 Examination of the steady state potential

To guarantee identical experimental conditions, the potential time curve was measured at the beginning of the experimental series and during this calibration period the anode was formatted with a constant current of 100 mA (1000 A/m<sup>2</sup>). This polarizing procedure was necessary because of the non conducting PbSO<sub>4</sub>-layer present on the anode. If a lead or lead alloy anode is placed in the sulphuric acid containing electrolyte, used in these experiments, a non conducting layer immediately forms. To convert this

layer to chemically active PbO<sub>2</sub> it is necessary to polarize the anode.

Prior to use the cathodes, the surfaces were polished with wet polishing paper with a grain size distribution of 180, 320 and 800. After polishing, the cathodes were washed, dried and installed in the cell. The electrolyte used in the cell was synthetic. The measurement of the current density was performed under increasing voltage conditions. The data program “Dasy Lab” automatically recorded the results. To ensure relevant results the experimental parameters used in industrial operations were selected and are detailed in Table 3.

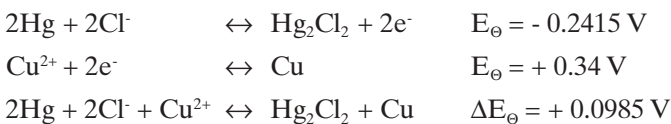
Tab. 3: Experimental parameters

Active electrode height	950 mm
Electrode width	100 mm
Electrode distance	35 mm
Bath exchange	3/h
Amount of air	84 l/h
Distance of drilling holes	15 mm
i	1000 A/m <sup>2</sup>
T	60 °C
c <sub>Cu</sub>	50 g/l
c <sub>H<sub>2</sub>SO<sub>4</sub></sub>	165 g/l
Prengaman electrode	PbSn1.4Ca0.12
Inhibitor	no

The anode and cathode were assembled as detailed in Figure 4. Further details relating to the measurement of the current density potential curves for the heights 1 and 3 are detailed in the following sections.

The steady state potential is calculated as follows:

Reference electrode:



Tab. 5: Standard electrode potential and equilibrium constant

Equations of reaction	E <sub>⊖</sub>	K <sub>⊖</sub>
Hg <sub>2</sub> <sup>2+</sup> + 2e <sup>-</sup> → 2Hg	0.7961	1.65779E-17
Hg <sub>2</sub> Cl <sub>2</sub> + 2e <sup>-</sup> → 2Hg + 2Cl <sup>-</sup>	0.2415	
Hg <sub>2</sub> <sup>2+</sup> + 2Cl <sup>-</sup> → Hg <sub>2</sub> Cl <sub>2</sub>	0.5546	
Hg <sub>2</sub> Cl <sub>2</sub> → Hg <sub>2</sub> <sup>2+</sup> + 2Cl <sup>-</sup>	-0.5546	

$$\Delta G_\ominus = -RT \ln K_\ominus = zF \Delta E_\ominus \quad (1)$$

$$\ln K_\ominus = \frac{z \cdot F \cdot \Delta E_\ominus}{R \cdot T} \quad (2)$$

$$K_\ominus = c^2(\text{Cl}^-) \cdot c(\text{Hg}_2^{2+}) \quad (3)$$

$$c(\text{Cl}^-) = 4.068 \cdot 10^{-9} \text{ mol/l}$$

$$\Delta E = \Delta E_\ominus - \frac{R \cdot T}{z \cdot F} \ln \frac{1}{[\text{Cu}^{2+}] \cdot [\text{Cl}^-]^2} \quad (4)$$

$$\Delta E = -0.45934 \text{ V}$$

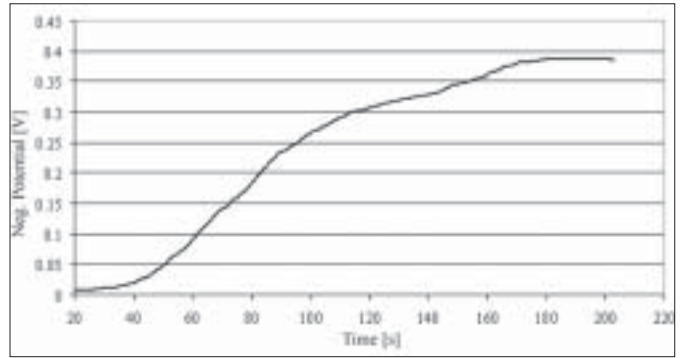


Fig. 5: Steady state potential

During the first experimental analysis investigations the “start steady state potential” was measured. This was performed without connecting the main electrodes but with the forced gas injection operational. Figure 5 details the steady state potential measurements obtained. Comparison of the calculated  $\Delta E_{\text{calculated}} = -0.45934 \text{ V}$  and the measured  $\Delta E_{\text{measured}} = -0.39 \text{ V}$  revealed a difference of 69 mV. However, it should be taken into consideration that the increased electrolyte turbulence was due to the gas injection. Therefore, the relatively high difference between the calculated and measured the steady state potential was principally due to the effect of the gas bubbles on the Luggin capillary.

### 3 Measurement and evaluation of the current density potential curves

In the first experimental analysis investigations the 1 cm<sup>2</sup> electrodes were connected and polarized. However, the main electrodes were not connected and the gas injection was not performed. The result of these initial investigations were current potential curves (CP-curves) in the absence of gas injection and without the main electrodes being connected. The limited current density was 1500 A/m<sup>2</sup>.

Industrial technical winning electrolyses would operate at current densities of approximately 350 A/m<sup>2</sup>, which is 25 % of the limiting current density [5]. Therefore, by calculation, in industry limiting current density is 1400 A/m<sup>2</sup>. During this experimental series limiting current density values of 1500 A/m<sup>2</sup> were recorded. Therefore, a strong concurrence was found between the experimentally determined values and industrial operating limiting current densities. During further analyses the main electrodes

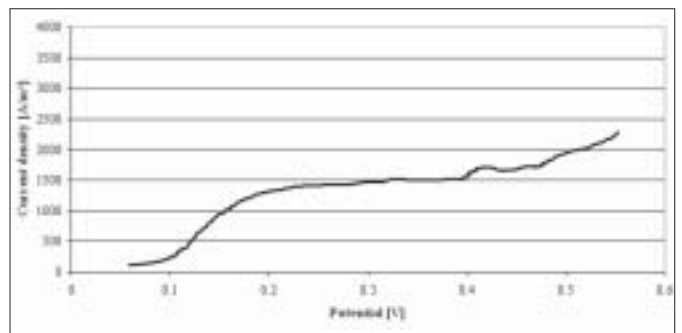


Fig. 6: CP-curves in the absence of gas injection and without the main electrodes connected

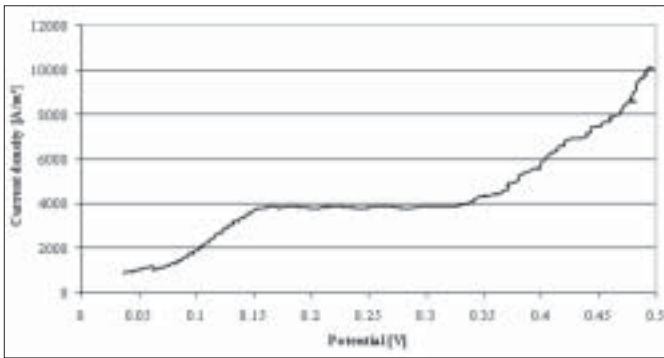


Fig. 7: CP-curves in the absence of gas injection, with the main electrodes connected and the current density potential measured at height 3

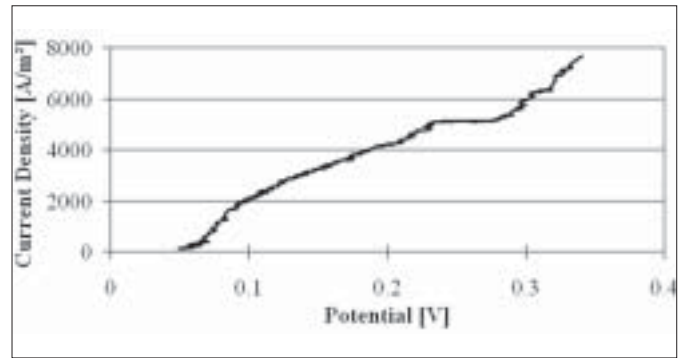


Fig. 9: CP-curve with air agitation, the main electrodes connected, and the current density potential measured at height 1

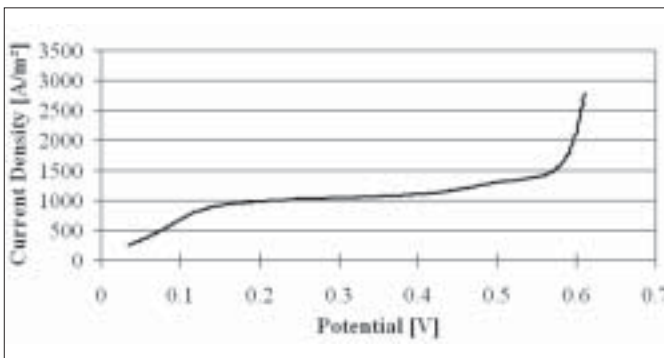


Fig. 8: CP-curve in the absence of gas agitation with the main electrodes connected, and the current density potential measured at height 1

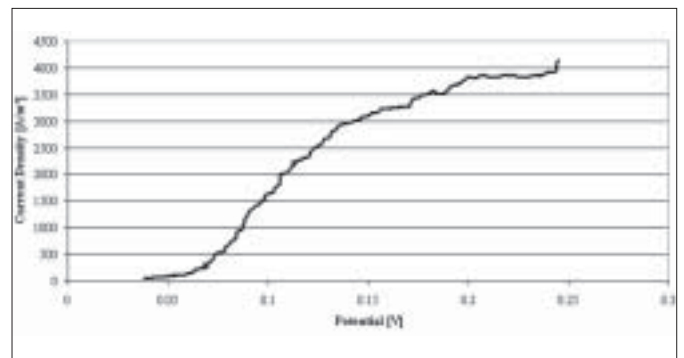


Fig. 10: CP-curve with air agitation, the main electrodes connected, and the current density potential measured at height 3

were connected and significant results of gas bubbles were produced. The significant number of gas bubbles produced caused a high level of turbulence. Figure 7 illustrates a CP-curve in the absence of gas injection with the main electrodes connected.

The current density potential measurement electrodes were at height 3 on the main electrodes. At this height the influence of the natural gas stirring was significant. The limiting current density was 4000 A/m<sup>2</sup> at height 3 and 1000 A/m<sup>2</sup> at height 1 (Figure 7 and 8). Comparing this current density at height 3 with the CP-curves from height 1, the following conclusions can be made:

- The gas bubble induced convection has no influence at the bottom (lower 20 mm) of the cathode.
- The influence of the natural convection on the hydrodynamic limited layer is minimized.
- A minimal current density results.

These issues were not only investigated in these experiments [1], but have also been previously described [6]. At height 1, no gas bubble induced convection influence was detected.

However, by activating the external gas injection (Figure 9 and 10), the hydrodynamic layer should be minimized in the lower regions of the cathode. Furthermore, by increasing the limiting current density, improved and better conditions for a smooth copper precipitation production, should be guaranteed.

After activating the forced convection, both natural and external gas bubble convections are combined. The limiting current densities recorded under the different condition are detailed in Table 6.

Tab. 6: Limiting current densities detected under the different conditions

	$I_{\text{limit}} - \text{H1}$ [A/m <sup>2</sup> ]	$I_{\text{limit}} - \text{H3}$ [A/m <sup>2</sup> ]
Without air agitation/without the main electrodes connected	1500	
Without air agitation/with the main electrodes connected	1200	4000
With air agitation/with the main electrodes connected	5000	3900

## 4 Conclusion

Table 6 illustrates that inducing a forced convection by air injection could solve the problem of a low limiting current density in the bottom region of the cathode. Furthermore, it was evident that the influence of this forced convection was principally in the lower cathode region (height 1). After this experimental series was concluded the air injection was used in a high current density copper winning system. This system worked effectively and without any problems. The results are presented in [6].

## Literature

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