



# Effect of As, Sb, Bi and Oxygen in Copper Anodes During Electrorefining

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## Abstract

This article presents the results of a three year research project funded by the “Sponsor Group Copper Electrorefining”. Investigated were passivation behaviour, anode dissolution, anode sludge formation and distribution coefficients of impure copper anodes with linear independent target contents of Sb, As, Bi and O processed at three current densities. The experimental setup is shown as well as the obtained results. Mathematical modelling of the results was done, analysing the influence of these factors and their interdependencies on the electrolysis process. All significant effects are displayed using scaled and centred coefficient plots describing the influence of the critical elements.

## 1 Introduction

Copper refining electrolysis is the essential process step to produce high-purity copper and precious metals. The anode copper used in the electrolysis process contains impurities, most frequently Ag, As, Au, Bi, Fe, Ni, O<sub>2</sub>, Pt, S, Sb, Se, Te, and Zn. Their content depends on the raw materials used (ores or scraps) and process conditions. During electrolysis impurities, ignoble to Cu, are dissolved into the electrolyte and the insoluble residue based on noble and insoluble components is collected as anode sludge. The accompanying elements cause different, mainly negative effects during the electrolysis process by reacting with each other or with the electrolyte components. These effects range from anode polarisation, copper losses in precipitation products up to cathode inclusions. Normally the content of certain impurities in industrial copper anodes is correlated as they derive jointly from complex resources. Such it is hard to separate the effects of the impurities on electrolysis parameters.



The target of the present study is the systematic investigation of impurity interactions in copper anodes in respect to their dissolution/passivation behaviour, anodic current efficiencies and distribution coefficients. Lab-scale produced anodes with various impurity combinations of the Cu-Ag-Ni-As-Sb-Bi-O-system are tested, with linear independent target contents of Bi, As, Sb and O. The use of synthetic anodes allows for separation of the effects of the different elements by using multivariate statistical methods. Trials have been carried out in series, each of 6 different anodes at identical conditions and were conducted at constant temperature.

This publication presents the results of a 3 years research project funded by the “Sponsor Group Copper Electrorefining”, showing the experimental setup as well as the effect of anode composition and anode current density on the electrolysis process.

## 2 Experimental setup

In order to investigate the “interaction of anode impurities”, 87 anodes are cast with linear independent compositions (Figure 1). Among the seven potential alloying elements only the content of Bi, Sb, As and oxygen are altered. Target contents are in the case of oxygen 1000 ppm, 2000 ppm and 4000 ppm, for Bi 0, 250 and 500 ppm, for Sb 0, 500 and 1000 ppm and for As 0, 1500 and 3000 ppm. The silver concentration is kept constant at 1000 ppm for all trials, the same applies for nickel with 2000 ppm. The combinations are illustrated in Figure 2.



Figure 1: Casting of anodes (left) and finished anode (right)

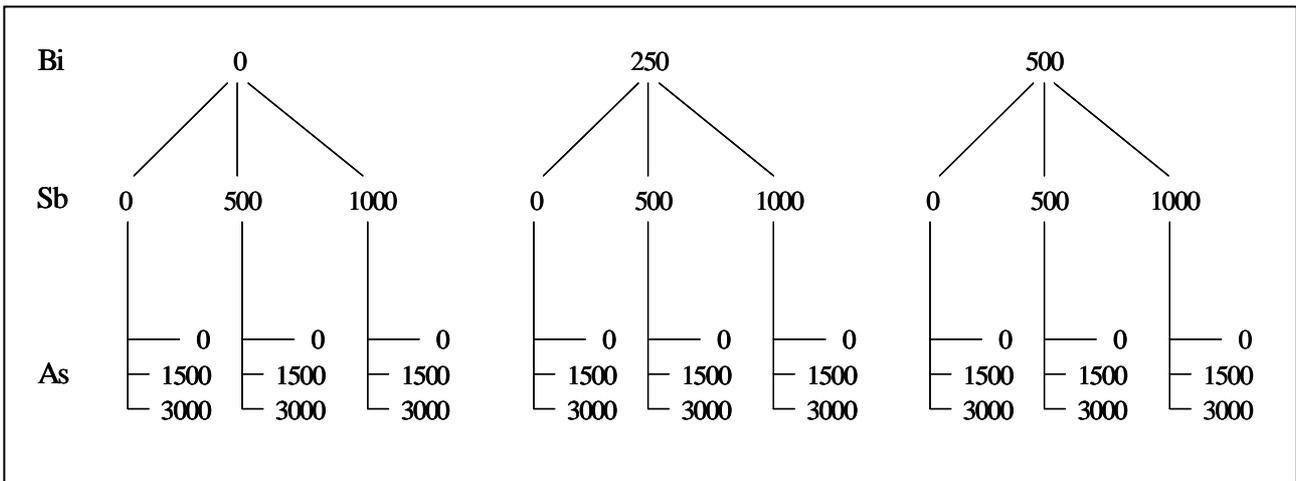


Figure 2: Planned chemical compositions (ppm levels) of the casted anodes (each anode was cast with 1000 ppm, 2000 ppm and 4000 ppm oxygen)

Each anode is run in three trials at current densities of 191 A/m<sup>2</sup>, 300 A/m<sup>2</sup> and 409 A/m<sup>2</sup>. All together 261 electrolysis tests have been conducted (partly with anodes of the same composition) and 26 parameters (e. g. anode polarisation, different elemental concentrations, different weights ...) have been recorded in each test. The initial composition of the synthetic electrolyte is kept constant for all trials with concentrations shown in Table 1. As inhibitors a combination of glue and thiourea is added to the initial electrolyte as well as continuously to the process during electrolysis.

The complete electrolysis test rig consists of six electrolysis cells each with one anode (430\*100\*25) and two cathodes (active surface 405\*110) connected to a holder shown in Figure 3. The distance between anode and cathodes was chosen to be 20 mm, thus assuring a regular natural convection between the electrodes. An inert gas airlift system is placed inside each cell to ensure electrolyte homogeneity during electrolysis trials replacing the typically used maintenance intensive and interference-prone mechanical pump systems.

Table 1: Starting composition of the electrolyte

Element	Content (g/l)	Added as compound
Cu	45	CuSO <sub>4</sub> ·5H <sub>2</sub> O
Ni	10	NiSO <sub>4</sub> ·6H <sub>2</sub> O
Sb	0.5	Sb <sub>2</sub> O <sub>3</sub>
As ( <sup>3+</sup> / <sup>5+</sup> )	10 (1:9)	As <sub>2</sub> O <sub>3</sub>
Bi	0.2	Bi <sub>2</sub> O <sub>3</sub>
H <sub>2</sub> SO <sub>4</sub>	170	H <sub>2</sub> SO <sub>4</sub>
Cl	0.05	HCl

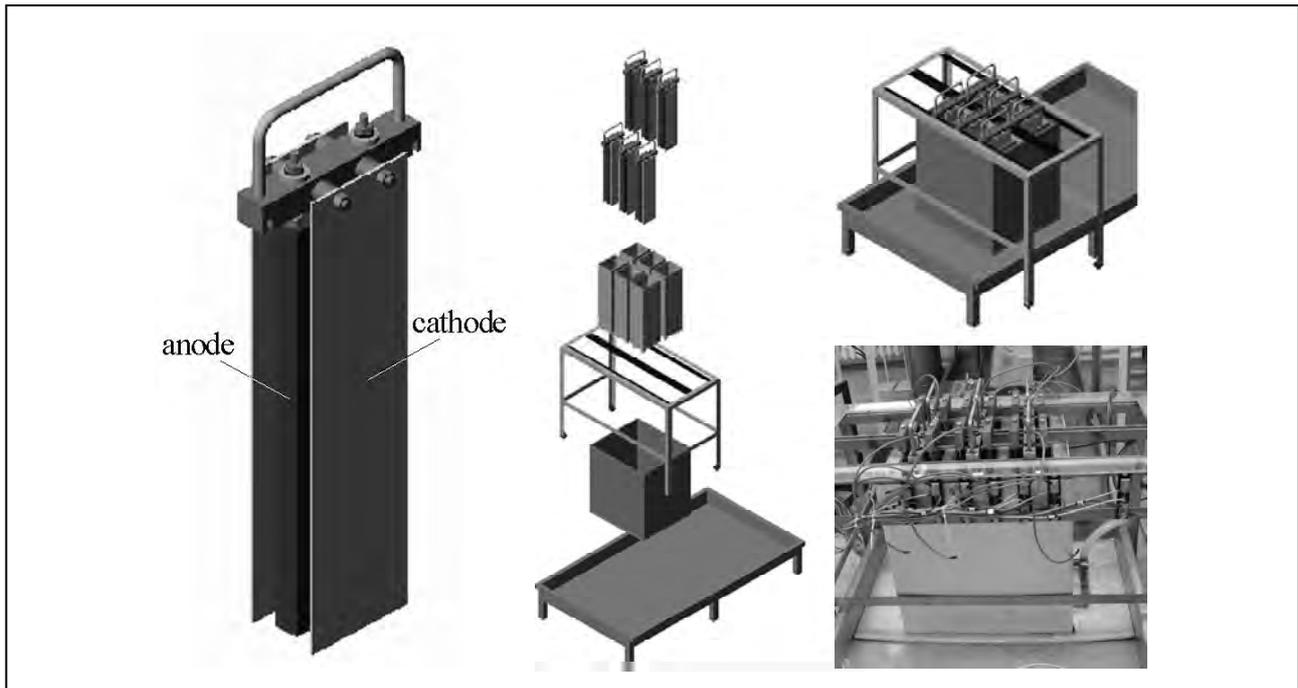


Figure 3: Anode and cathode holder (left), cell assembly (middle, right)

### 3 Electrolysis Procedure

After 2-3 days of preparation time the electrolyte with a temperature of 65 °C was pumped into the cell to the level of 405 mm active cathode height. Depending on the current densities used in the tests, different amounts of inhibitor concentrations have been added to the electrolyte and subsequently fed continuously to each cell during the trials. When all cells were prepared, the process was started with the required currents equally distributed between the two cathodes. For ensuring the required current densities, the shrunk dimensions of the anodes after each trial were taken into account for current settings (Table 2).

Table 2: Electrolysis process parameters of the three test series for each anode

$i_{\text{anode}}$ in A/m <sup>2</sup>	<b>300</b>	<b>191</b>	<b>409</b>
$A_{\text{anode}}$ in m <sup>2</sup>	0.098	0.089	0.077
I in A	29.4	19.9	31.6
$A_{\text{cathode}}$ in m <sup>2</sup>	0.089	0.089	0.089
$i_{\text{cathode}}$ in A/m <sup>2</sup>	330	190	355

During the trials the values of cell and electrode currents, polarization of each anode via a simple copper wire “reference electrode” and all cell voltages were measured. Deionised hot water has to be added to each cell every 12 hours due to vaporization. All cells are switched off after 1700 Ah, since this value is suitable for obtaining considerable amounts of copper at the cathodes and anode sludge at all three current densities and to ensure a reasonable final anode surface area. After every trial each cell is dismantled and the electrodes are removed (cathodes first), washed with hot de-



ionised water and brushed, to remove remaining anode sludge from the surface of the anodes. In the next step, the electrolyte from each cell is filtered and the collected anode sludge is immediately washed and dried. After that it is weighted and analysed by ICP as well as the electrolyte after stabilisation with acid.

## 4 Effect of anode impurities on the electrolysis process

All trials were assessed regarding passivation behaviour, anode dissolution/current efficiency, anode sludge formation and As, Sb and Bi distribution. As a criterion for a beginning passivation an increase in cell voltage of 40 mV during an eight hour period was defined. An example for passivating anodes is shown in Figure 4. During the entire series 26 out of 261 trials showed passivation with one anode passivating at 191 A/m<sup>2</sup>, nine anodes at 300 A/m<sup>2</sup> and 16 anodes at 409 A/m<sup>2</sup>. For mathematical modelling all non passivating anodes received a fictive passivation probability of 0 and the passivating ones that of 100 %.

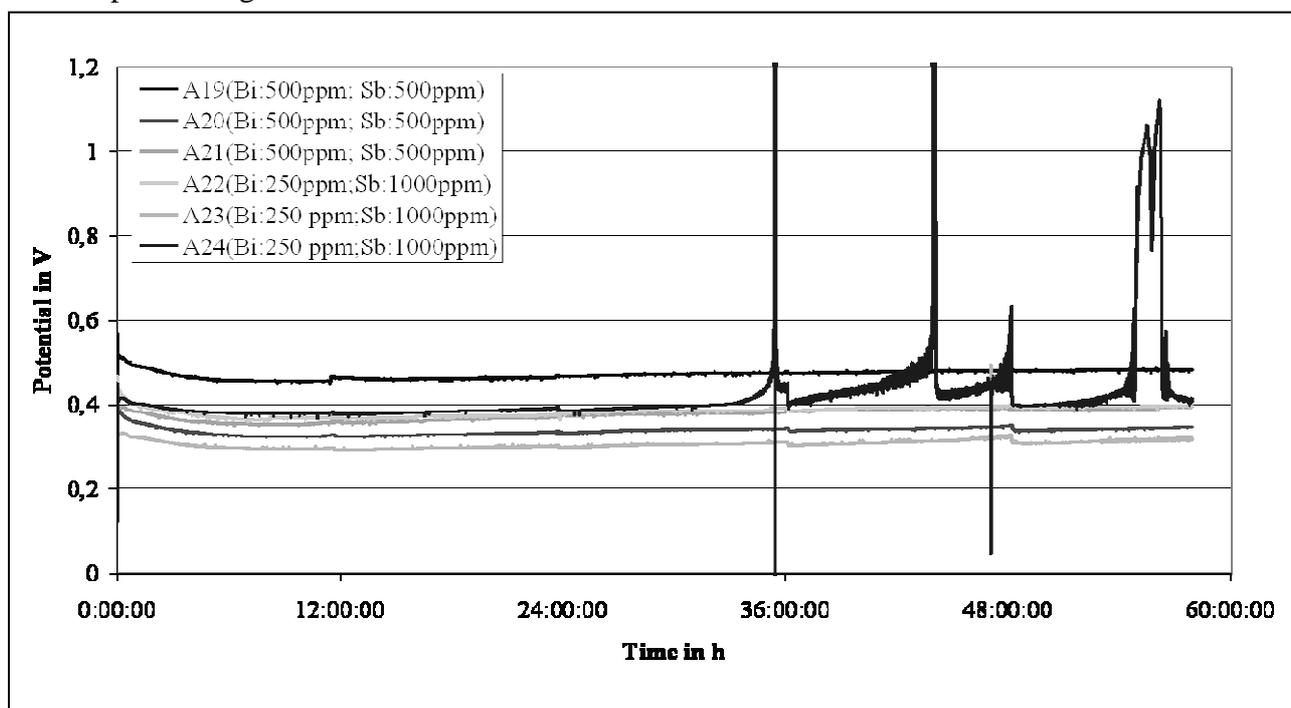


Figure 4: Anode potentials during electrolysis with passivation effects at 300 A/m<sup>2</sup>

To analyse the anodic dissolution behaviour the dissolved mass per Ah was ascertained for all trials. All results are higher than the theoretical dissolved copper mass per Ah calculated from Faraday's law, due to chemical dissolution of anode impurities, e. g. Cu<sub>2</sub>O. This results in current efficiencies between 100.4 % and 103.7 %. The amounts of anode sludge generated vary between 1.1 and 12.8 g/kg dissolved anode. For the analysis of the distribution coefficients to anode sludge of As, Sb and Bi only the anodes containing these elements were taken into account and the distribution coefficients were calculated for each anode according to the following equation:



$$\Pi_{AS}^i = \frac{m_{AS}^i}{m_{solA}^i} \quad (1)$$

$\Pi_{AS}^i$ : distribution coefficient of component i to anode sludge,  $m_{AS}^i$ : mass of component i in anode sludge,  $m_{solA}^i$ : mass of component i dissolved from anode

For arsenic distribution coefficients between 2.3 % and 34.1 % were obtained, for antimony this value shifted to 23 % and 100 % and for bismuth the distribution coefficients vary between 10.8 % and 100 %. The results indicate that there are large variations in the percentage of As, Bi and Sb reporting to the slime for different anode compositions.

## 5 Results of the mathematical modelling

All trials were mathematical analysed regarding their passivation behaviour, anode dissolution, anode sludge generation and elemental distribution using the Umetrics software Modde 5.0, a MS-Windows<sup>®</sup>-based software, providing design of experiments, analysis and optimisation. The programme processes measurable and metrical data respectively and is aiming at an optimal explanation of experimental results by means of linear and interaction regression models. For the present study it was used to mathematical display the results of the experiments in order to determine the effects of several factors and factor combinations on the electrolysis process. To visualize these effects scaled and centred coefficient plots of the significant effects are displayed in Figure 5 to Figure 7.

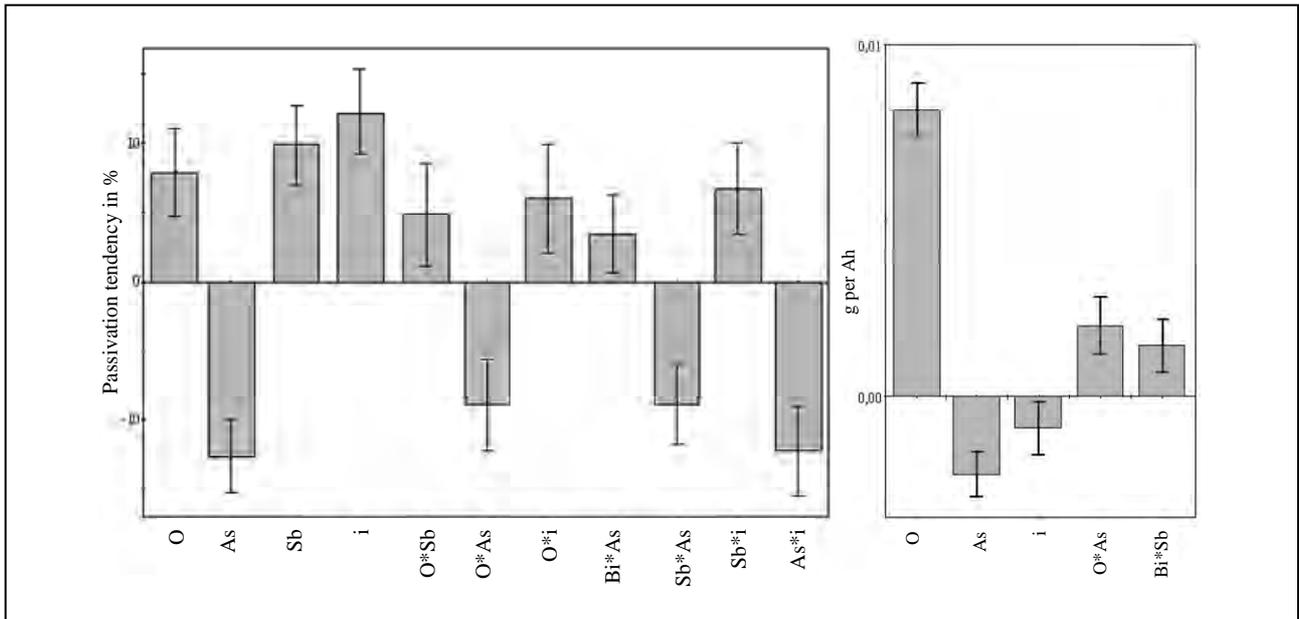


Figure 5: Scaled and centred coefficients for anode passivation tendency (left) and anode dissolution (right)

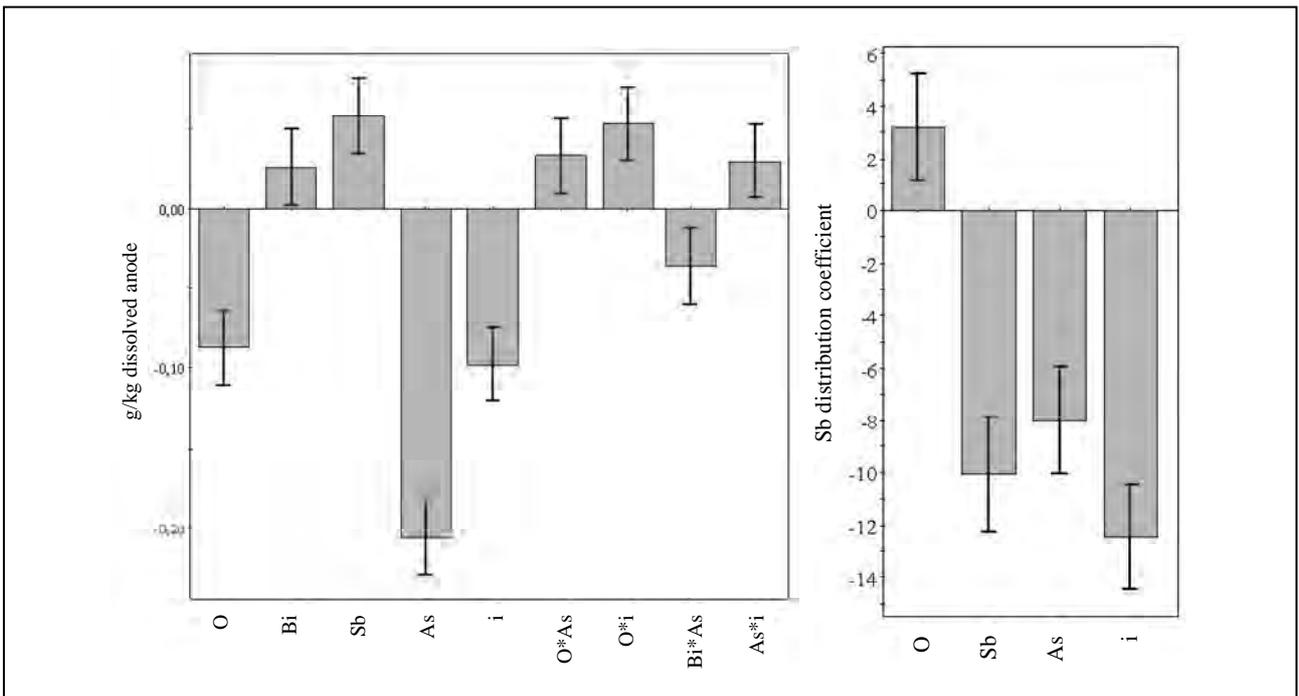


Figure 6: Scaled and centred coefficients for anode sludge generation (left) and Sb distribution to anode sludge (right)

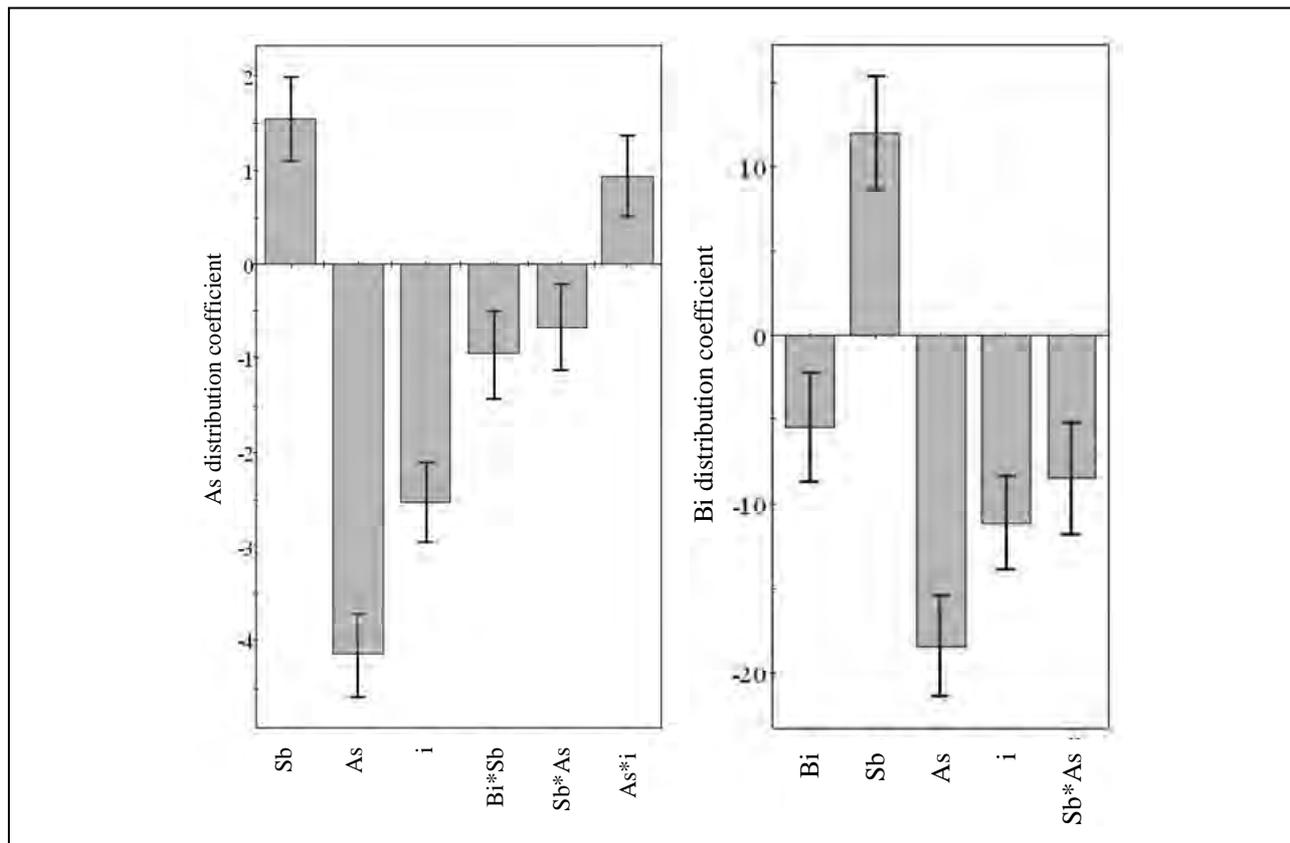


Figure 7: Scaled and centred coefficients for As distribution (left) and Bi distribution to anode sludge (right)

Depending on their electrochemical potential and bonding type within the anodes, the accompanying elements are becoming either dissolved into the electrolyte together with copper or they are transferred to the anode sludge by precipitation or non-dissolution. The results of this analysis are also shown in Figure 5 (right hand).

In case of the elements which report to the anode slimes it can be expected that with increasing concentration the amount of anode sludge will also rise. Considering the complex nature of the slimes themselves, the particular compounds which are present and their physical nature, the convective effects in the electrolyte and the quality of the cathode surface, it is a challenge to establish a quantitative relationships between anode composition and amount of anode sludge produced. The same problems account for the distribution of As, Sb and Bi to anode sludge. The results of the modelling obtained for this parameters and especially the kind of their interdependencies is shown in Figure 6 and Figure 7.

Based on the presented results it is possible to determine the effect of certain impurities and impurity combinations on the analysed process parameters. These effects are described in the following chapters and as far as already known an explanation for them is given.



## 6 Effect of arsenic

Arsenic has a huge influence lowering the passivation tendency (Figure 5) and except for the combination factor Bi\*As, which seems to have a small contrary effect, all other factor combinations containing As also have a strong trend to lower the passivation tendency, partly annulling the heightening effect of these single components. This explains why no anodes containing arsenic passivated during our investigation, independent of their chemical composition. Reason for that is that the oxidation of  $\text{As}^{3+}$  is reported to be more preferable and faster than that of  $\text{Sb}^{3+}$ . Therefore, the oxidation of  $\text{Sb}^{3+}$  to  $\text{Sb}^{5+}$ , which causes an exceeding of the much lower  $\text{Sb}^{5+}$  saturation limit in front of the anode, will not preferentially occur as long as sufficient amount of  $\text{As}^{3+}$  is dissolved in the electrolyte [1]. The second reason for the lowered passivation tendency of anodes containing arsenic is the precipitation of antimony and bismuth as hardly soluble compounds in the anode sludge [2]. This formation does not cause passivation because with rising As concentration at the phase boundary metal/electrolyte the pH value in front of the anode decreases leading to an increased solubility of the components in front of the anode and their precipitation happens mainly inside the electrolyte [3]. Furthermore the sludge adhesion gets lower during this process [4].

Arsenic has also the characteristic to decrease the dissolved specific anode mass (Figure 5). It is partly dissolved in the anode copper matrix (20-30 % according to [5, 6]) and gets electrochemically dissolved even before copper due to its ignoble character. Unlike copper it is forming trivalent ions whilst consuming more electrons and therefore the dissolved mass per Ah is declining. The contrary effect of As\*O is due to the formation of  $\text{As}_2\text{O}_3$  which forms at the grain boundaries and dissolves chemically into the electrolyte.

Figure 6 reveals that the amount of anode sludge is dependent on a lot of factors and the strongest influence can be determined as that of As, having the effect to lower the amount of anode sludge produced. The factor combinations As\*O and As\*i slightly increase the amount of anode sludge, but this is negligible compared to the single effects which do the contrary. Mechanisms accounting for this result are the same as for the prevention of passivation.

All distribution coefficients analysed (Figure 6, Figure 7) are influenced by the As content in the anode for the same reasons as it is lowering their precipitation to anode sludge. It is the main factor influencing the As and Bi distribution to sludge and is also a strong factor in the Sb distribution. Furthermore the factor combination Sb\*As is lowering the As and the Sb distribution to anode sludge and As\*i slightly increases the distribution of As. The reasons for the lower Sb distribution have already been explained. Regarding the distribution of As it is assumed that, for a fixed amount of impurities, in particular lead and antimony, a fixed amount of As is bound as insoluble complex oxides, leading to decreasing percentages of arsenic reporting to the anode slimes at increasing arsenic concentrations in the anode (if all other components stay the same) [7]. No satisfying explanation was found for the effect of As on the Bi distribution.



## 7 Effect of antimony

The anode antimony concentration is a strong factor influencing anode passivation (Figure 5). It shows interdependencies with the anodic arsenic and oxygen concentration as well as the current density, whereas the first factor combination leads to a decrease in the passivation probability (as explained before) and the other factor combinations to an increase. It was already examined by various authors [8] that antimony primary dissolves into the electrolyte in the trivalent form and gets then oxidised to  $Sb^{5+}$  in the presence of oxygen. By exceeding the much lower  $Sb^{5+}$  saturation limit in front of the anode passivation occurs. Figure 5 also shows that Sb itself has no significant influence on the anode dissolution degree in the analysed range.

The effect of Sb on the amount of anode sludge is quite forward (Figure 6). Antimony mainly reports to the anode sludge in form of various oxide components [12], so the higher the concentration of Sb in the anode the more anode sludge is produced.

All distribution coefficients analysed are influenced by Sb (Figure 6 and Figure 7). The antimony distribution to anode sludge (Figure 6) is decreasing with increasing anode Sb concentration and it is assumed that the same mechanism accounts as for As. In case of the other distribution coefficients (Figure 7) an increase in the anode Sb concentration results in an increase of the Bi and As distribution to anode sludge, due to the formation of insoluble Bi-Sb, As-Sb containing compounds. In combination with As resp. Bi this effect is reduced by interactions. The following figure shows the transfer mechanisms and interactions for As, Sb and Bi to electrolyte/anode slime.

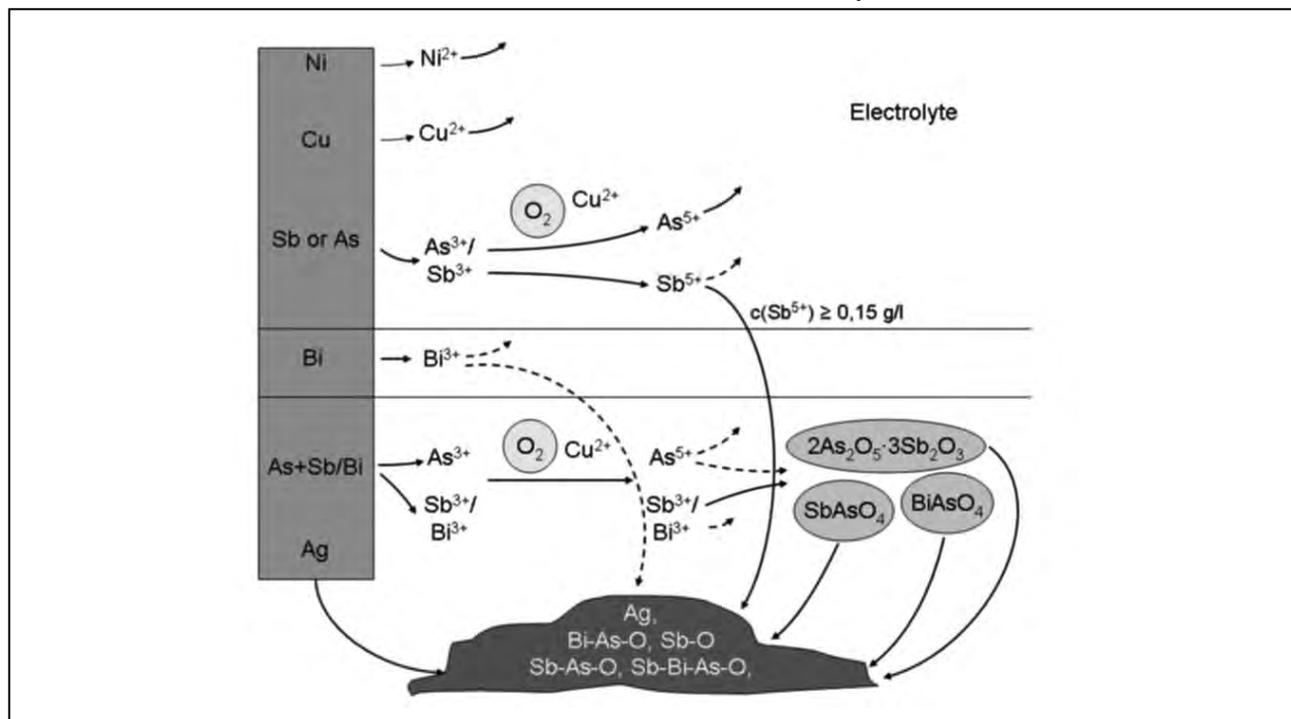


Figure 8: Transfer mechanisms for As, Sb and Bi to electrolyte/anode slime in copper refining electrolysis [13]



## 8 Effect of bismuth

The bismuth concentration of the anode has no significant effect on the anode passivation probability, the anode dissolution degree as well as the Sb and As distribution coefficients within the analysed parameter range (Figure 5 to Figure 7). Bi is only slightly influencing these parameters in combination with other anode impurities as already mentioned. Figure 6 shows that Bi has a slight increasing effect on the amount of anode sludge formed, which is, like for Sb, due to the formation of various oxide components [12]. Compared to the other factors Bi has only a minor influence on its own distribution coefficient (Figure 7) based on the same mechanisms as for arsenic on the As distribution coefficient. A fixed amount of Bi is bound as insoluble and complex oxides, leading to decreasing percentages of Bi reporting to the anode sludge at higher anode bismuth concentrations.

## 9 Effect of oxygen

Oxygen in the anode is mainly present in form of various oxides (Cu-, Ni-, As-, Sb-, Bi-) depending on the amount/type of impurities in the anode. The anode oxygen concentration significantly influences the passivation behaviour, the anode dissolution degree, the anode sludge generation as well as the metal distribution coefficients, especially Sb. As can be seen from Figure 5 oxygen is promoting passivation, as it impacts the anode slime structure and porosity. The higher the anode oxygen content the lower is the slime settling rate [7], thereby increasing the anode passivation tendency. This effect is further intensified by increasing current densities. The effect of As\*O and Sb\*O has already been explained and is due to their increased oxidation potential.

Figure 5 also shows high oxygen contents lead to an improved anode dissolution degree, as oxygen is forming oxide phases with the metal impurities, which extensively dissolve chemically or go to the anode sludge un-dissolved. No electrical current is needed for their removal and such the dissolved anode mass per Ah is rising. Components dissolved into the electrolyte lower the amount of anode sludge produced at the same time which can be seen in Figure 6. Combinations of oxygen with As and/or the current density reduce this effect slightly.

A rising oxygen concentration in the anode leads to an increased antimony distribution to anode sludge (via oxidation of  $\text{Sb}^{3+}$  to  $\text{Sb}^{5+}$  see Figure 8.) and is the only possibility to increase the Sb distribution coefficient (Figure 6). An increasing current density has only negative effects which can be partly compensated by combination with certain impurities.

## 10 Prediction of electrolysis parameters

Using all the data acquired during the electrolysis test trials and based on the mathematical modelling done it is possible to forecast process parameters. As an example the prediction of the As dis-



tribution to anode sludge for anodes with 2000 ppm O and 175 ppm Bi (1000 ppm Ag and 2000 ppm Ni) processed at 300 A/m<sup>2</sup> is shown in Figure 9. The accuracy of the model taken as a basis for this prediction was calculated to 83 %. The prediction chart presents the distribution coefficient of As in dependence of the As and Sb content of the anode. For instance the As distribution for 750 ppm Sb and 2000 ppm As is 15.2 %, according to the performed experimental investigation.

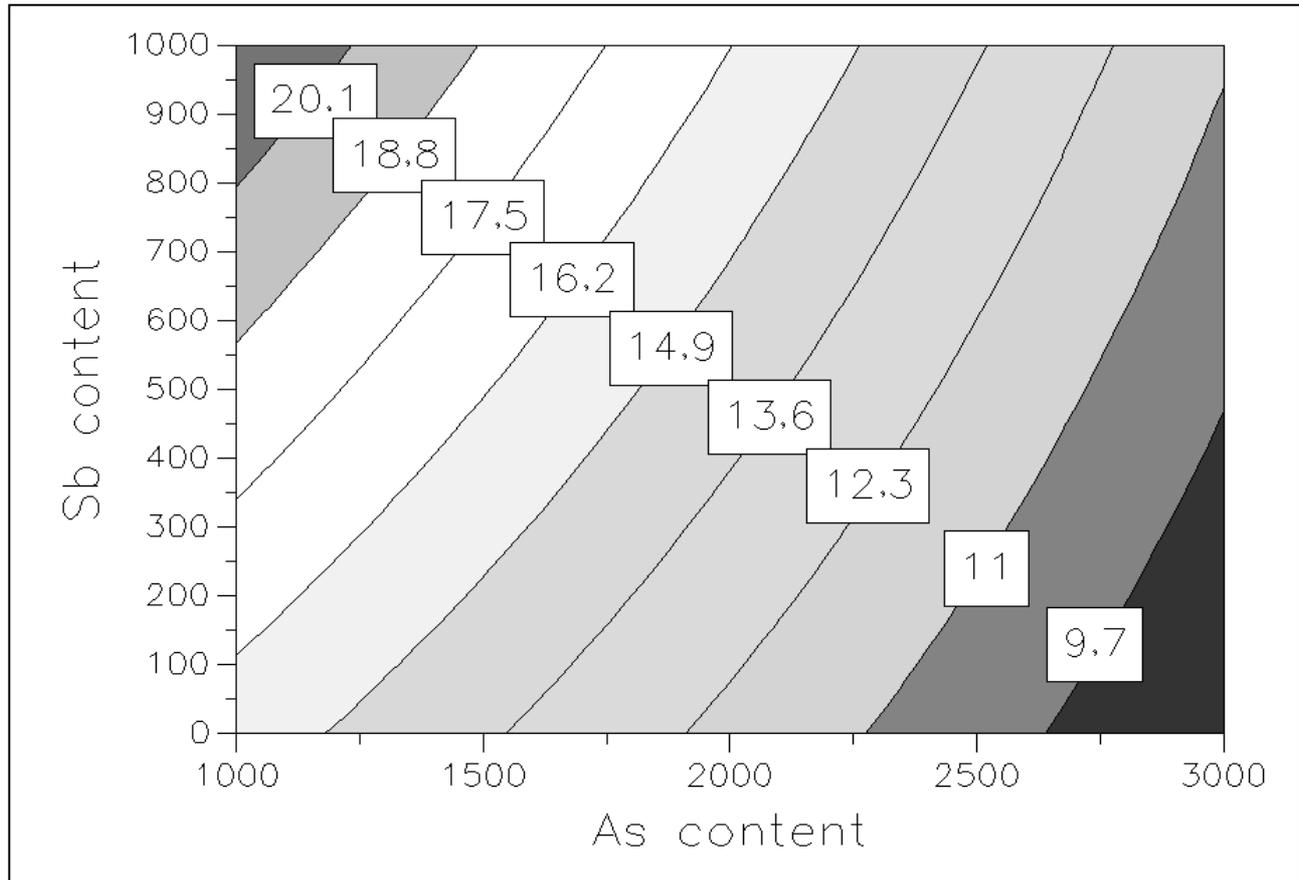


Figure 9: Prediction of the As distribution coefficient to anode sludge for anodes with 2000 ppm O and 175 ppm Bi (1000 ppm Ag, 2000 ppm Ni) processed at 300 A/m<sup>2</sup>

Another example is shown in Figure 10 displaying the prediction of anode dissolution for anodes processed at 300 A/m<sup>2</sup> with 500 ppm Sb and 150 ppm Bi (1000 ppm Ag and 2000 ppm Ni). The accuracy of the model taken as a basis for this prediction was calculated to 75 %. Generally the dissolution is between 1.193 g/Ah and 1.217 g/Ah for all anodes in the analysed range. For anodes with industrial typical oxygen concentrations of 2000 ppm the maximum dissolution seems to be 1.209 g/Ah. That means for an anode cycle of 7 days at 300 A/m<sup>2</sup> the dissolved anode mass is 108 - 110 kg for anodes with 1.8 m<sup>2</sup> surface and As contents up to 3000 ppm, Bi concentrations up to 350 ppm and Sb concentrations up to 1000 ppm.

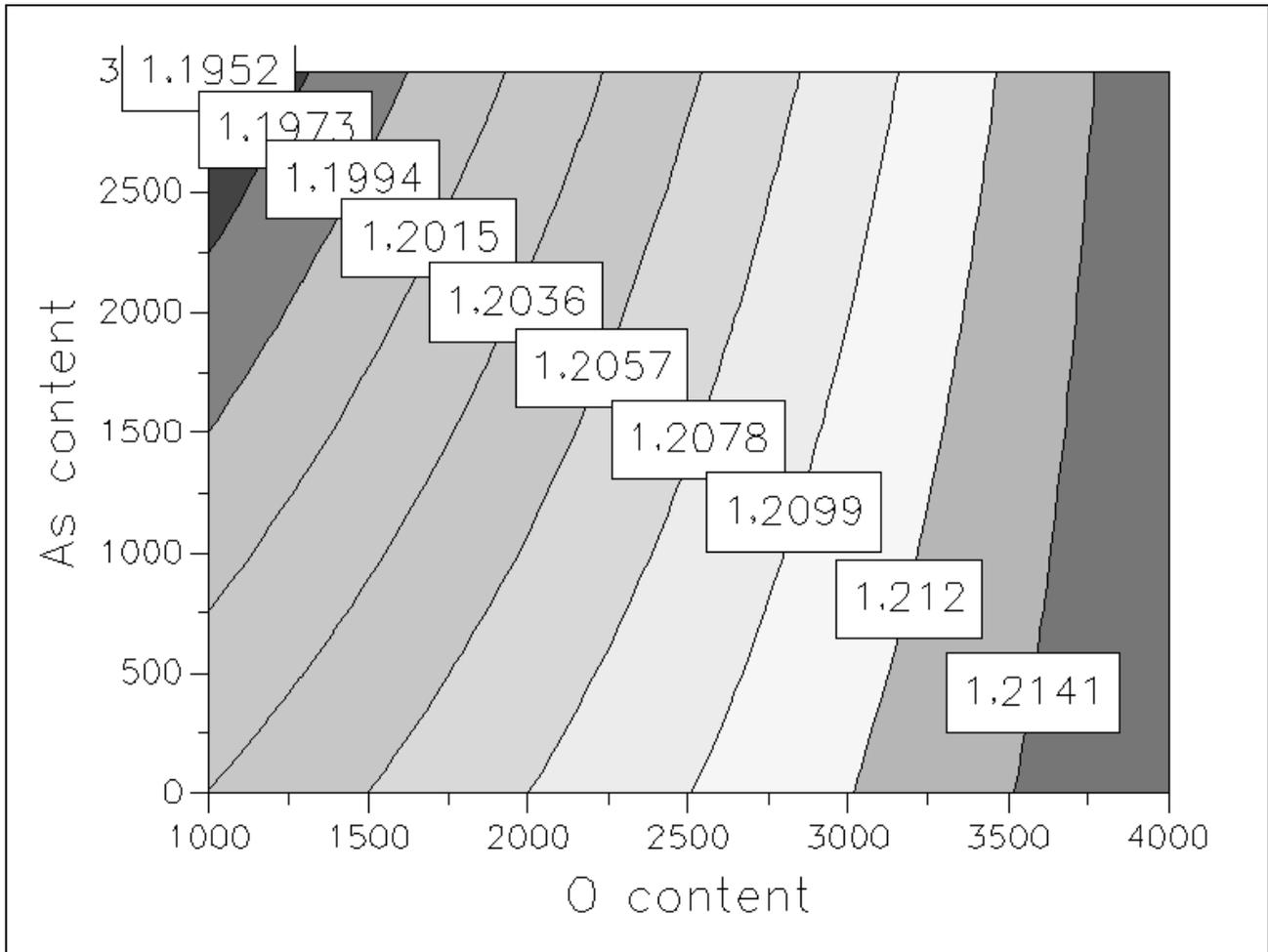


Figure 10: Prediction of the anode dissolution for anodes with 500 ppm Sb and 150 ppm Bi (1000 ppm Ag, 2000 ppm Ni) processed at 300 A/m<sup>2</sup>

The described investigation allows for designing prediction charts for all investigated effects and anode compositions, within the analysed range. Such it serves the possibility to directly calculate the effects of changing O, Sb, As and Bi concentrations in the copper anode at changing anode current densities.

## 11 Summary

In this research project the passivation behaviour, anode dissolution, anode sludge formation and distribution coefficients of impure copper anodes were experimentally investigated in lab-scale. Synthetically produced anodes with linear independent target contents of Sb, As, Bi and O were processed at three current densities. Mathematical modelling of the results was done, analysing the influence of these factors and their interdependencies on the electrolysis process. Significant effects can now be displayed using scaled and centred coefficient plots describing the influence of the critical elements. The results of this investigation can be summarized as follows:



**As** is

- Preventing anode passivation (and additionally partly inhibiting the effect of Sb, O and current density)
- Slightly decreasing the anode dissolution/anode current efficiency
- Decreasing the amount of anode sludge produced
- Decreasing the Sb and Bi distribution to anode sludge

The reduced anode passivation tendency is attended by higher concentrations of As, Sb and Bi in the electrolyte respectively in the cathode (in equilibrium).

**Sb** is

- Causing passivation (if not accompanied by As)
- Only significantly influencing the anode dissolution/anode current efficiency if accompanied by Bi
- Increasing the amount of anode sludge produced
- Increasing the As and Bi distribution coefficient

**Bi** is

- Not significantly influencing passivation
- Only slightly influencing anode dissolution/anode current efficiency if accompanied by Sb
- Slightly increasing the amount of anode sludge produced
- Not significantly influencing Sb distribution
- Only lowering the As distribution to anode sludge if accompanied by Sb

**O** is

- Increasing the anode passivation tendency as single component and in all factor combinations except if accompanied by As
- Increasing anode dissolution/current efficiency
- Increasing the amount of anode sludge generated, combined with As or high current densities this effect is less significant
- Slightly increasing the Sb distribution to anode sludge
- Not influencing As and Bi distribution

An increasing current density has only negative effects with respect to passivation tendency which can be partly compensated by combination of certain elements in the anode. The received results confirm some conclusions previously published and extend this knowledge with respect to interactions between these impurities. Moreover the statistical analysis quantifies these effects, making it now possible to calculate the strength of their influence in comparison to each other. The developed model can be used to predict the effect of impure anodes in the analysed range and therefore offer the production engineers a practical tool for improved control of the copper electrolysis process.



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