

Influence of As, Sb, Bi and O on Copper Anode Behaviour – Part 3: Elemental Distribution

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This article is the last of a three articles series of results from a three year's research project funded by the "Sponsor Group Copper Electrowinning". Investigated were dissolution/passivation behaviour, anodic current efficiencies, anode sludge formation and distribution coefficients of impure anodes with varying Sb, As, Bi and O contents processed at three current densities. Main focus of this article is the influence of As, Sb, Bi, O and the current density on the elemental distribution of As, Sb and Bi between electrolyte and anode sludge. Arsenic distribution was found to be mainly dependent on the arsenic concentration and to some extent on the antimony concentration of the anode as well as the anodic current density. The bismuth distribution is

mainly dependent on the arsenic and antimony concentration of the anode and also slightly on the anodic current density and the bismuth concentration of the anode. Finally the antimony distribution was found to be dependent on the current density, the arsenic and antimony concentration and to some extent on the oxygen concentration of the anode. Several prediction charts were built forecasting the elemental distribution for anodes within the parameter set.

Keywords:

Copper refining electrolysis – Impure anodes – Mathematical modelling – Anode behaviour – Anode sludge – Elemental distribution – Distribution coefficient

Einfluss von As, Sb, Bi und O auf das Verhalten von Kupferanoden – Teil 3: Elementverteilung

Dies ist der letzte von drei Artikeln über die Ergebnisse eines dreijährigen Projekts, finanziert von der „Sponsor Group Copper Electrowinning“. Untersucht wurden das Auflösungs-/Passivierungsverhalten, die anodische Stromausbeute, die Anodenschlammbildung und die Verteilungskoeffizienten von verunreinigten Anoden mit verschiedenen Sb-, As-, Bi- und O-Konzentrationen bei drei unterschiedlichen anodischen Stromdichten. Den Schwerpunkt dieses Artikels bildet der Einfluss von As, Sb, Bi, O und der Stromdichte auf die Elementverteilung von As, Sb und Bi zwischen Elektrolyt und Anodenschlamm. Dabei ist die Arsenverteilung hauptsächlich von der Arsenkonzentration und zum Teil von der Antimonkonzentration der Anoden abhängig sowie in geringem Maße von der anodischen Stromdichte. Die Bismutverteilung ist größtenteils

abhängig von der Arsen- und Antimonkonzentration der Anoden und darüber hinaus in geringem Maße von der anodischen Stromdichte und der Bismutkonzentration. Zum Schluss wurde der Antimonverteilungskoeffizient untersucht, welcher von der anodischen Stromdichte, der Arsen- und Antimonkonzentration und geringfügig von der Sauerstoffkonzentration der Anode abhängig ist. Mehrere Vorhersagediagramme wurden konstruiert, die die Elementverteilung für verschiedene Anoden innerhalb des Parametersatzes darstellen.

Schlüsselwörter:

Kupferraffinationselektrolyse – Verunreinigte Anoden – Elementverteilung – Anodenschlamm – Mathematische Modellierung – Verhalten von Anoden – Verteilungskoeffizient

L'influence de As, Sb, Bi et O sur le comportement des anodes en cuivre – section 3: La répartition des éléments La influencia de As, Sb, Bi y O sobre el comportamiento de ánodos de cobre – Parte 3: Distribución de elementos

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, O₂, Pt, S, Sb, Se, Te, and Zn. Their content depends on the raw material used (ores or scraps) and process conditions. During the electrolysis, the impurities, which are more ignoble than Cu, are dissolved into the electrolyte and the insoluble rest

based on more noble or 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. 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 from the same starting material. Therefore it is hard to separate the effects of the impurities on current efficiency, polarisation etc.

The target of the present study is the systematic investigation of selected impurity interactions in the copper anode 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 to separate the effects of the different elements by using multivariate statistical methods. The trials have been carried out parallel in six electrolysis cells with three different anode current densities.

This publication is the third and last part presenting the results of a three years research project funded by the “Sponsor Group Copper Electrorefining”. It focuses on the interdependencies between impurity content in the anode and the elemental distribution.

In a first paper [1] the design of a copper electrolysis experimental setup was shown as well as the casting of anodes. All experiments were analyzed regarding their passivation behaviour and as a result it was stated that higher Sb and/or O content and higher current densities significantly raise the passivation tendency, whereas a higher As content significantly lowers the passivation tendency. Bismuth turned out to have only a slight propensity to lower the passivation tendency. Using partial least square regression it was possible to predict passivation by assigning passivation probabilities to each anode in respect to their chemical composition and the anodic current density. The results confirmed mainly the information known from the literature. The statistical analysis however quantified the known effects and makes it possible to forecast the passivation behaviour of anodes within the analysed range of parameters.

The second paper [2] focused on the influence of As, Sb, Bi, O and the current density on the dissolved anode mass and especially on the anode current efficiency. For a better understanding of this dissolution process literature about the mineralogical structure of anodes depending on their chemical composition was reviewed and the significant aspects related to the tested anodes were summarized. Several prediction charts could be designed forecasting the dissolution of anodes within the analysed parameters. Also part of this work was the investigation of anode sludge generation depending on the chemical composition of the anode and the anodic current density. EDS analysis showed that the obtained sludges were extremely complex and inhomogeneous; SEM micrographs indicated that the grain size of the sludge is strongly influenced by the amount of Sb and Bi in the anode whereas oxygen seemed to have no impact. Investigating the parameters affecting the amount of anode sludge revealed that it is influenced strongly by As and also significant by O as well as the current density.

2 Experimental methodology

In order to investigate the “interaction of anode impurities”, 87 anodes are cast with linear independent compositions. Among the seven alloying elements, which can exist in each anode, the contents of Bi, Sb, As and oxygen are

altered. Target oxygen contents are 1000 ppm, 2000 ppm and 4000 ppm, Bi contents are 0, 250 and 500 ppm, Sb contents are 0, 500 and 1000 ppm and As contents are 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 total anode set (variation of parameters) is illustrated in the first article of this series [1]. Each anode is run in three trials at current densities varying between 191 A/m², 300 A/m² and 409 A/m². All together 261 individual electrolysis tests have been conducted. The initial composition of the synthetic electrolyte is kept constant for all trials with the concentrations already published. As inhibitors a combination of lime and thiourea is used, which is added to the initial electrolyte as well as continuously to the process during electrolysis.

Before starting the electrolysis, copper electrolyte was prepared individually and analysed for each test series with a volume of 36 l. Especially the As³⁺/As⁵⁺-ratio required special know how [1]. After two to three days of preparation time the electrolyte with a temperature of 65 °C was pumped into the cell to a 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 started with the required currents securing an equal current distribution between the two cathodes in each cell. As the currents have to be adjusted regarding the required anodic current densities of 191, 300 and 409 A/m², the shrunk dimension (respectively the reduced surface area) of the anodes after each trial is taken into account. This led to the process parameters summarized in Table 1.

Table 1: Electrolysis process parameters of the three test series for each anode

i_{anode} [A/m ²]	300	191	409
A_{anode} [m ²]	0.098	0.089	0.077
I [A]	29.4	19.9	31.6
A_{cathode} [m ²]	0.089	0.089	0.089
i_{cathode} [A/m ²]	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 had to be added to each cell every 12 hours due to vaporization. All cells were 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 size of the anode surface at all time. This led to electrolysis durations of 100 h 32 min, 57 h 49 min and 53 h 48 min. After every trial each cell was dismantled and the electrodes were removed, washed with hot deionised water and brushed, to remove remaining anode sludge from the surface of the anodes. In the next step, the electrolyte from each cell was filtered and the collected anode sludge was immediately washed and dried (Figure 1). After that it was weighed and analysed by ICP as well as the electrolyte.



Fig. 1: Removing of electrodes, filtering of electrolyte and remaining anode sludge after electrolysis

3 Elemental distribution between anode sludge and electrolyte

As the main target of the entire project was the investigation of the interactions of impurities on the dissolution behaviour, dimensionless distribution coefficients are introduced. For the individual anode impurities of each anode they were calculated according to the following equation:

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

Π_{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

The results indicated that there are large variations in the percentages of As, Bi and Sb reporting to the slime for different anode compositions. Special challenges for the determination of the distribution coefficients occurred due to the inhomogeneous composition of the anode sludge and therefore insecurities about the accuracy of the chemical analysis, also some problems occurred determining the exact amount of anode sludge produced. As a result mass balances were made balancing the whole electrolysis cell for each trial. All trials exceeding a balance of $\pm 20\%$ were not taken into account for the analysis. That way 214 experiments serve as data basis to investigate the elemental distribution. For the detailed analysis of the individual distribution coefficients only anodes containing these individual elements were taken into account, again reducing the amount of data for each analysis. The mathematical analysis of the obtained distribution coefficients was done using the Umetrics software Modde 5.0, a MS-Windows®-based software, providing design of experiments, analysis

and optimisation. The program 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 assess and display the results of the experiments in order to detect the effects of several factors and factor combinations on the distribution coefficients.

3.1 Distribution coefficient of arsenic

The distribution of arsenic between anode slime and electrolyte was published as being influenced primarily by the As content in the anode, and secondly to a large extent by other impurities, particularly Sb, Pb and O₂. It was assumed that, for a fixed amount of impurities, in particular lead and antimony, a corresponding amount of As is bound as insoluble complex oxides. This effect leads to decreasing shares of arsenic reporting to the anode slime at increasing arsenic concentrations in the anode, if all other components are kept constant [3]. Antimony raises the arsenic distribution to anode sludge mainly due to the formation of insoluble antimonates and arsenides [3, 4].

Increasing oxygen contents were found to decrease the arsenic distribution coefficient for anodes containing Pb (3000 ppm), As (1050 ppm), Sb (600 ppm), high concentrations of Ag, Se, Te and oxygen concentrations between 1800 ppm and 3300 ppm [3]. Contrary to that, it was also reported that the arsenic distribution value is independent of the oxygen content in the anode (anodes analysed only contained As > 1000 ppm and oxygen 300 ppm to 3000 ppm) [5].

Results obtained by different authors indicate that for anodes containing less than 0.01 % As, more than 70 % of this element reports to the slime. This value drops to less than 30 % if the As value in the anode exceeds 0.1 % (Figure 2) [6]. The same non-linear relationship was found by DEMAEREL [3] with a distribution of less than 15 % for 3000 ppm As in the anode (Pb < 4500 ppm, Sb < 2300 ppm). Further investigations identified a distribution coefficient of arsenic to the anode slime of 25 % at 1000 ppm As in the anode [7] and CORNELIUS even found distribution coefficients of in average around 10 % for anodes only containing As > 1000 ppm and oxygen (300 ppm to 3000 ppm) [5].

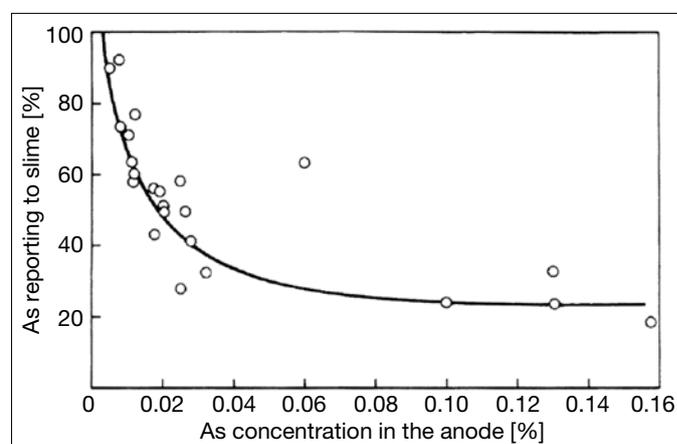


Fig. 2: The effect of As concentration in the anode on the percentage of As reporting to slime [6]

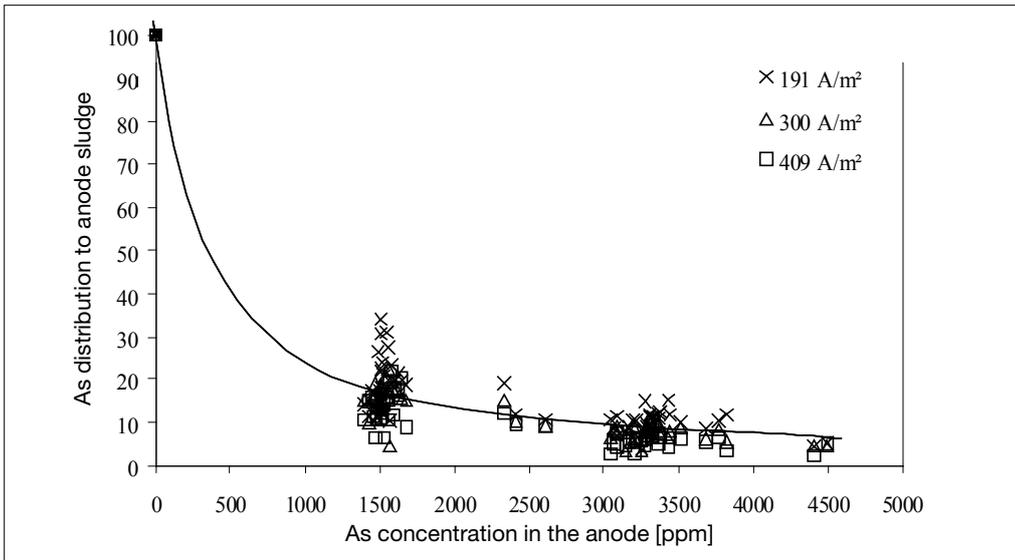


Fig. 3: Effect of As concentration in the processed anodes on the As-fraction reporting to slime (own investigation for anodes containing 0 to 1000 ppm Sb at three different anode current densities)

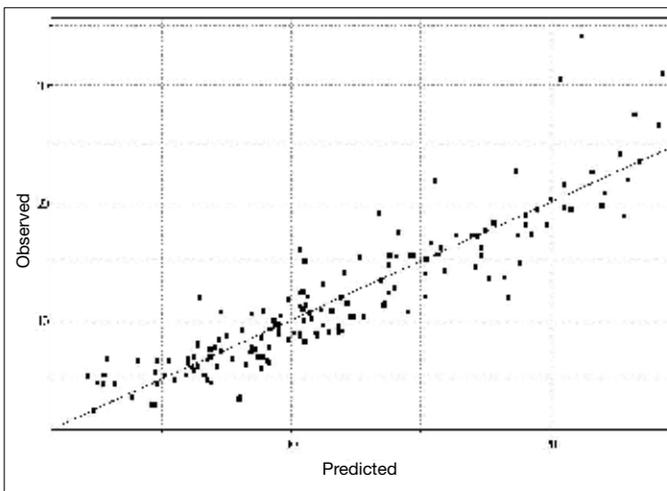


Fig. 4: Observed vs. predicted arsenic distribution to anode sludge

The present investigation reported in this article analyses anodes with As concentrations above 1400 ppm and lower lead concentrations than the cited articles, so the distribution coefficients are expected to be below 25 % for arsenic

in the anode sludge, which could be proved for all experiments except five tests (Figure 3). The obtained best-fit line confirms the results of DEMAEREL [3] and CLAESSENS [6]. Compared with Figure 2 it is quite obvious from the dot concentration that for the processed anodes the arsenic distribution is more sensitive to other impurities present in the anode. It is also obvious from this figure that the As distribution to the anode sludge is decreasing with increasing current density.

The distribution coefficient of arsenic to anode sludge obtained during the experiments varied from 2.3 % to 34.1 %. A further and more detailed mathematical modelling of the arsenic distribution took 157 trials into account, all containing between 1400 ppm and 4500 ppm arsenic with various concentrations of Bi, Sb and oxygen, processed at three anodic current densities. The quality of the designed model is displayed in Figure 4, showing the observed versus the predicted values. Except three experiments all points are close to the regression line indicating an acceptable fit. The predictive accuracy for the subsequent deduced diagrams is with a fit of 83 % quite good.

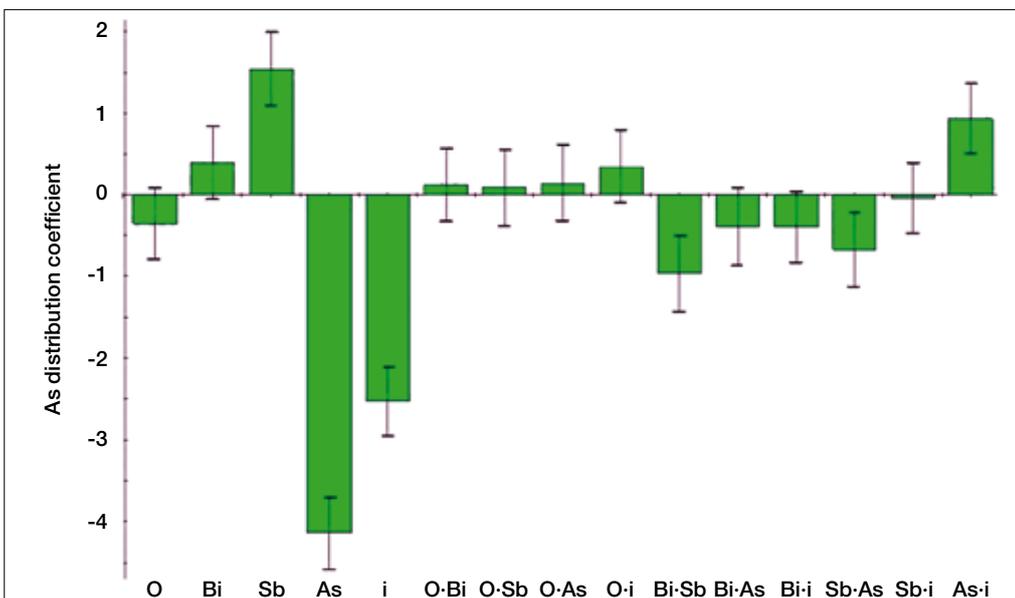


Fig. 5: Effects of process variables on arsenic distribution to anode sludge: Scaled and centred coefficients

Figure 5 displays the effect of all investigated factors and factor combinations on the distribution coefficient of arsenic to the anode sludge. Positive numbers stand for an increasing distribution coefficient (higher percentage of As in the sludge) by rising these factor/factor combination and negative numbers represent a reduction of the distribution coefficient while increasing these factor/factor combination. The black bars show the confidence interval. If they cross the zero line, the effect has to be defined as not significant. The smaller they are in comparison to the effect, the more accurate is the significance of the value.

The coefficient plot shows that the distribution coefficient of arsenic is mainly dependent on the As and Sb concentration in the anode as well as on the current density. An increasing arsenic concentration in the anode or a higher current density leads to stronger dissolution and a higher antimony concentration in the anode forces arsenic to enter the anode sludge. Except for the current density this result is in good agreement with previous investigations by other authors [3-7]. An influence of the anode oxygen content could not be securely detected, which was also found by CORNELIUS [5]. The influence of the current density might be due to some arsenic deposition or some inclusion of formed arsenides at/in the cathode.

In addition to that, the plot shows that not only single factors influence the distribution, but also their interactions. For example increased Sb concentrations raise the distribution coefficient of arsenic, but if Bi is also present in the anode or if the Bi concentration is raised parallel (Bi-Sb product) the distribution coefficient is influenced in the opposite direction. This is maybe the case, as Bi can substitute As to some extent during the precipitation of Sb. The same effect can be seen with the As-i factor, whereas the Sb-As factor is slightly intensifying the influence of As. The effect of the As/Sb ratio on the distribution coefficient of As was already reported previously with almost similar results [3, 4]. Based on the effects presented in Figure 5 the model allows to predict the distribution coefficient in the range of 1400 ppm to 3500 ppm As in the anode (example for fixed values of 2000 ppm oxygen and 150 ppm Bi). The results are displayed in the response prediction plot of Figure 6.

At 300 A/m² the arsenic distribution coefficient is between 13.8 % for Sb-free anodes containing 1400 ppm and 6.5 % for anodes containing 3500 ppm As. These values rise

up to 19.2 % resp. 8.9 % at antimony concentrations of 1000 ppm. At 409 A/m² anodic current density these values get as low as 4.5 % for anodes containing 3500 ppm As and no antimony resp. 14.6 % for anodes containing 1400 ppm As and 1000 ppm Sb.

3.2 Distribution coefficient of bismuth

Not much information was found by literature research about the distribution coefficient of bismuth in copper refining electrolysis. According to the investigation of CLAESSENS and BALTAZAR the only significant factor affecting the bismuth distribution is the concentration of lead in the anode. The detected dependence indicated that the amount of bismuth reporting to the slime increases rapidly with increasing lead concentration [6]. Other authors found the Bi distribution to be strongly influenced by the arsenic concentration of the anode. According to them the majority of the dissolved bismuth reacts with arsenic compounds of the electrolyte to form BiAsO₄ [8] and high As concentrations in the electrolyte also lead to an increase of bismuth in the cathode copper [9] due to a decrease of the cathodic polarisation [4].

During our test series only 127 of the relevant 214 trials contained bismuth in the anode and the distribution of bismuth to the anode sludge was varying extremely between the experiments. In 26 trials the amount of Bi in the anode slime exceeded the amount of Bi present in the anode up to a ratio of 370 %. Those values were artificially set to 100 % for the assessment. The lowest bismuth distribution detected was 10.8 %. For a full factor interaction model some values are missing, so unfortunately the interaction of all factors analysed (Sb, As, Bi, O and current density) could not be securely modelled. The missing values are displayed in Figure 7 and as can be seen most of them are found at low arsenic concentrations. Therefore the designed model might not be as accurate for low arsenic containing anodes (0 to 1500 ppm) as for anodes in the range of 1500 to 3000 ppm As.

In total the designed model shows an accuracy of 78 % displayed in Figure 8. As can be seen the model also predicts distribution coefficients above 100 % for some of the values.

Figure 9 displays the effect of all investigated factors and factor combinations on the distribution coefficient of bis-

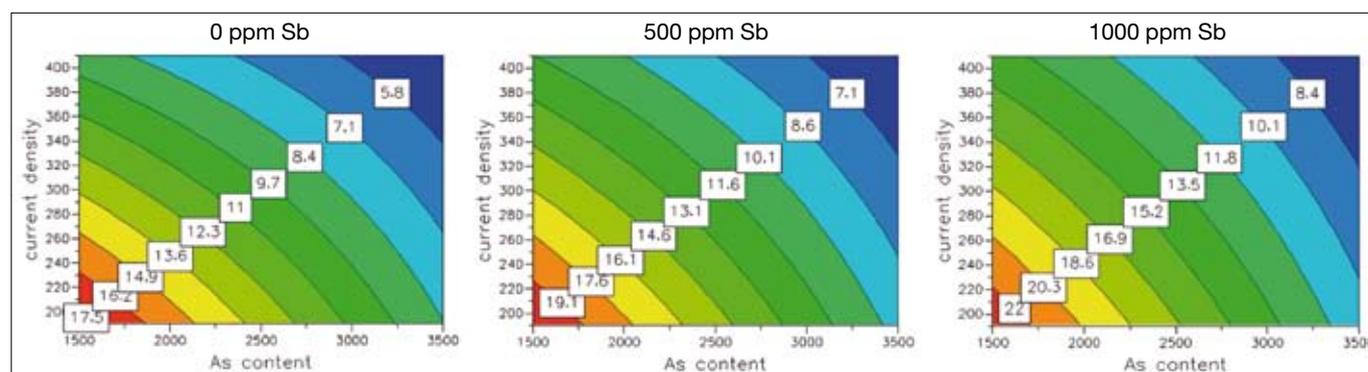


Fig. 6: Response Prediction Plot arsenic distribution to anode sludge, valid for 2000 ppm O and 150 ppm Bi

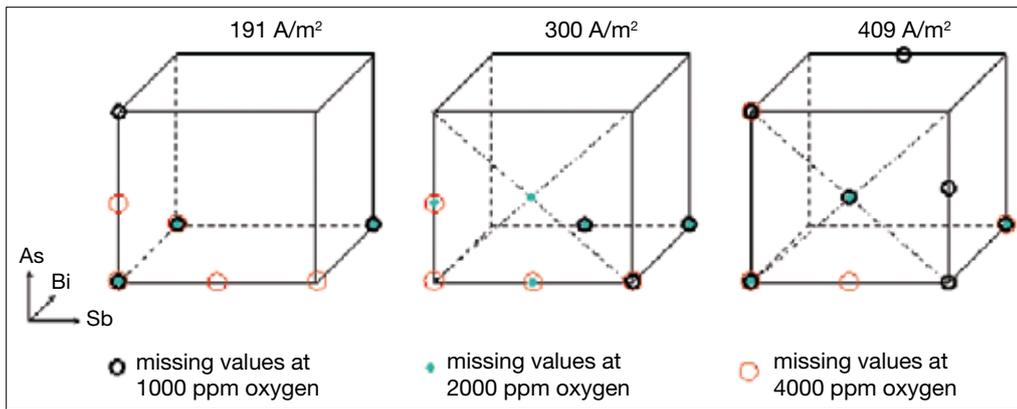


Fig. 7: Design region of the full factor interaction model with missing values for the bismuth distribution coefficient

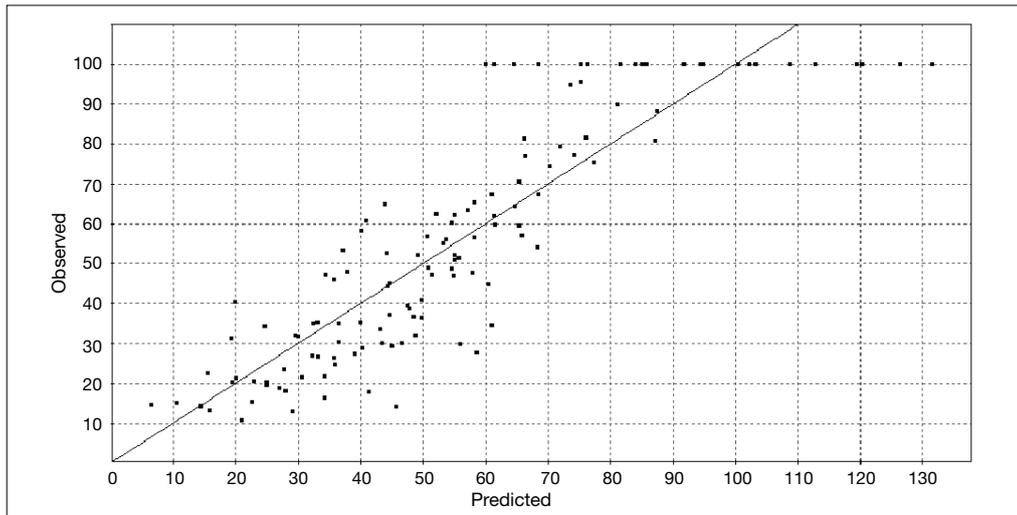


Fig. 8: Observed vs. predicted bismuth distribution to anode sludge

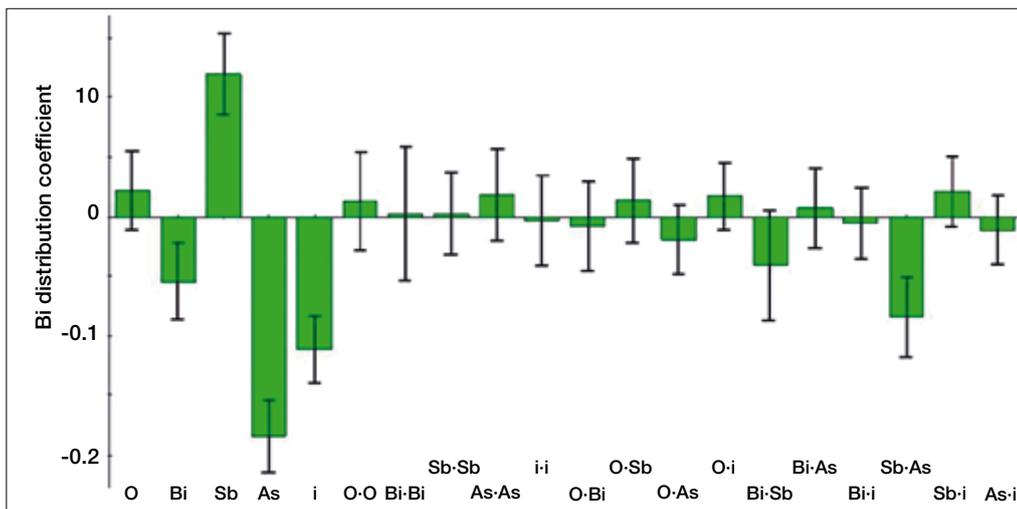


Fig. 9: Effects on bismuth distribution to anode sludge: Scaled and centred coefficients

mium to the anode sludge. For a more detailed view also quadratic and even cubic factors were taken into account, but they do not show any significant effect.

Generally the coefficient plot shows that only a few factors influence the distribution of bismuth to the anode sludge significantly. Increasing arsenic or bismuth concentrations in the anode or a higher current density lowers the distribution coefficient and at higher antimony concentration in the anode an increased amount of bismuth enters the anode sludge. Except for the influence of bismuth itself these are the same effects already obtained at the distribution of

arsenic, whereas the influence of the Sb concentration on the bismuth distribution is higher. We assume that similar to arsenic a fixed amount of Bi is bound as insoluble complex oxides, leading to decreasing percentage of bismuth reporting to the anode slime at higher bismuth concentrations in the anode (for a constant amount of impurities, in particular lead [6] and antimony).

As already discussed in [2] Bi in the anode sludge is always accompanied by Sb and it influences the distribution of Bi either by directly forming insoluble compounds at the anode surface or by reacting in the electrolyte. Therefore

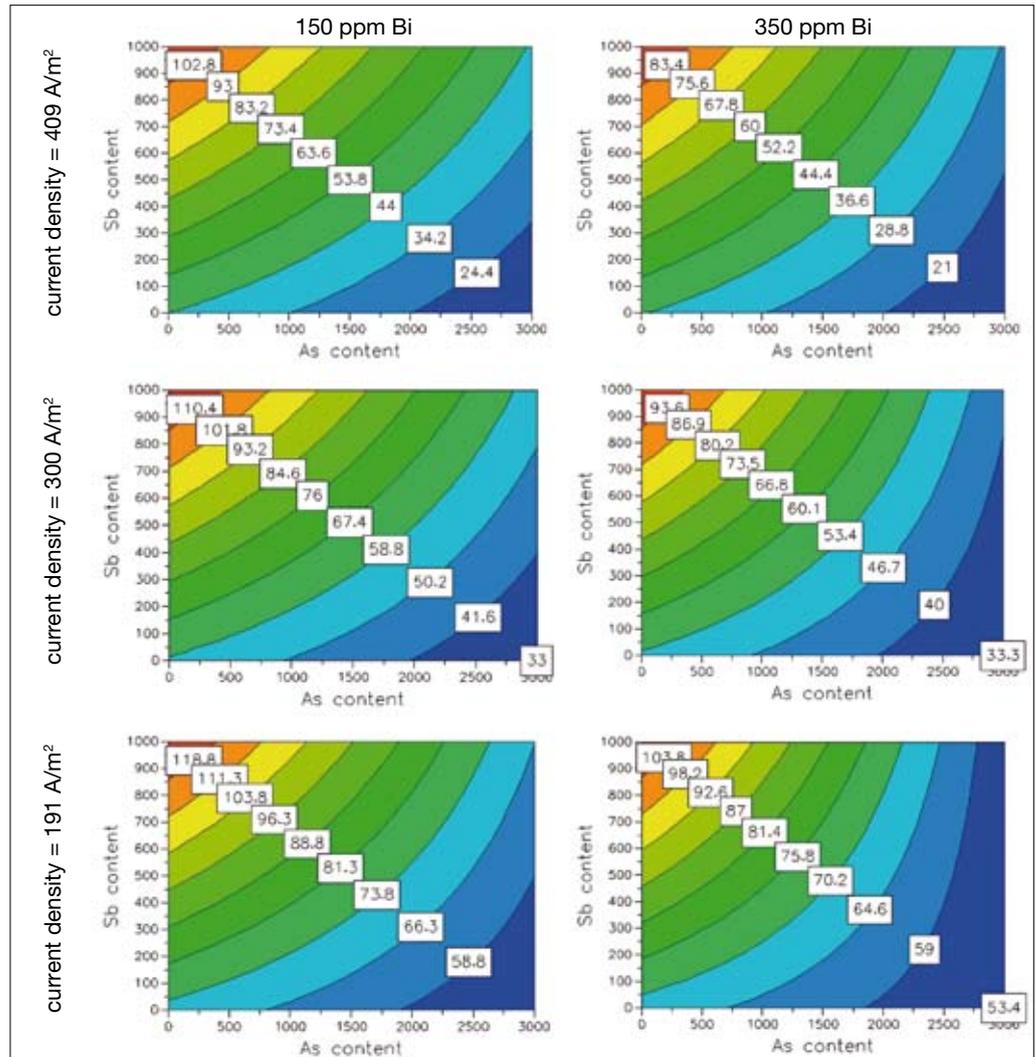


Fig. 10: Response Prediction Plot bismuth distribution to anode sludge, calculated for 2000 ppm O in the anode

higher Sb concentrations in the electrolysis system lead to increased Bi distribution to the sludge. According to literature [4, 9] the effect of arsenic and the current density on the bismuth distribution can be explained by higher bismuth deposition in the cathode and maybe by a shift in the solubility of As-Bi-Sb in the electrolyte. If the Sb concentration in the anode is raised in anodes also containing arsenic (As·Sb factor) the single effect of antimony is weakened. An increase of this factor leads to a decrease of the distribution coefficient of bismuth to the anode sludge, probably because Sb-As bearing compounds are formed preferable to those of Bi-Sb or Bi-As.

Based on the effects presented in Figure 9 the distribution coefficient of Bi to the anode sludge can be predicted for anodes with 150 ppm to 350 ppm Bi containing also 2000 ppm oxygen. The results are displayed in the response prediction plot in Figure 10. At 300 A/m² the bismuth distribution coefficient for anodes containing 250 ppm Bi varies from 55 % for anodes containing 0 ppm to 34 % for anodes containing 3000 ppm As and no antimony. These values rise to 100 % for anodes containing 0 ppm and to 48 % for anodes containing 3000 ppm As at antimony concentrations of 1000 ppm. At 409 A/m² these values get as low as 16 % for anodes containing 3000 ppm As and no antimony and 98 % for anodes containing 0 ppm As and

1000 ppm Sb. Values for other anode compositions can be taken from Figure 10.

3.3 Distribution coefficient of antimony

Antimony distribution is found to be mainly dependent on the concentration of As, Sb, Bi, Pb and Ni in the anode. Moreover, physico-chemical properties of the electrolyte such as T, H₂SO₄, dissolved oxygen and Cu²⁺ concentration determine the solubility of antimony in the electrolyte, the progress of secondary reactions and the precipitation of insoluble antimony bearing compounds. As the copper anode dissolves during electrorefining As, Sb, Bi, Pb and Ni in the copper matrix also dissolve [10]. According to the equations from CLAESSENS and BALTAZAR [6] the antimony concentration of the electrolyte is increasing with increasing arsenic concentration in the anode (as already discussed in the first two articles [1, 2]) and is decreasing with increasing Sb+Bi content. The oxidation of arsenic is much faster than that of antimony and occurs therefore preferentially. When an anode fails to supply enough arsenic ions to the electrolyte the oxidation of Sb³⁺ to Sb⁵⁺ occurs rather rapidly [11]. So for anodes containing As an increasing current density leads to a decreasing Sb distribution to the anode sludge. An increasing current density leads also to an increased deposition of antimony at the cathode, which

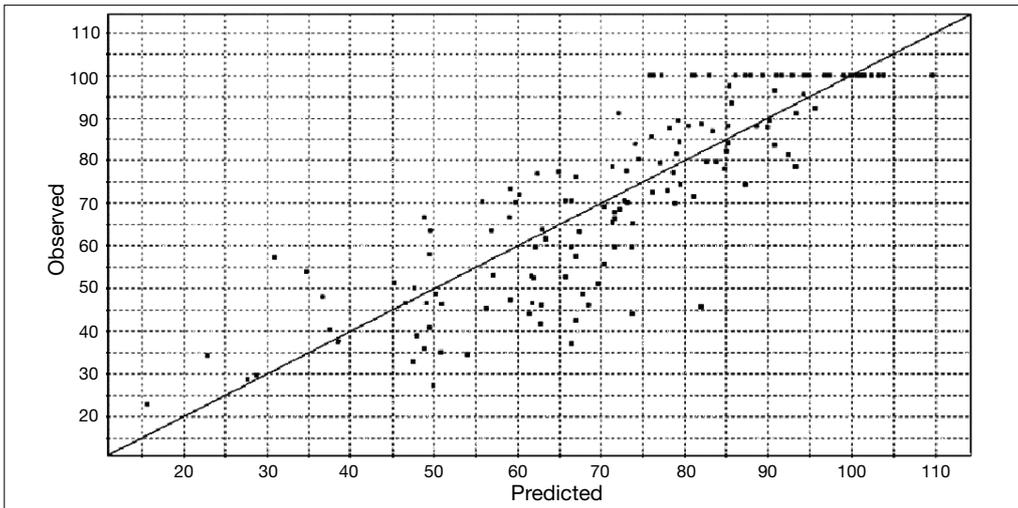


Fig. 11: Observed vs. predicted antimony distribution to anode sludge

is of cause dependent on the antimony concentration in the electrolyte [12]. Antimony distribution coefficients to anode sludge reported in literature range from 60 % for anodes containing 0.1 % Sb, As, Bi and Pb each [7] to 10.6 % to 100 % (159.3 %) for anodes with varying As, Sb, Bi and Pb contents [6].

During our test series 143 evaluated anodes contained antimony and the distribution of antimony to the anode sludge was varying extremely between these experiments. In 33 trials the amount of Sb in the anode slime exceeded the amount of dissolved Sb up to 304 %. This values were set by own definition to 100 % for the assessment. The lowest antimony distribution on the other hand was 23 %. Mathematical modelling of the Sb distribution to anode sludge leads to an accuracy of 73 % displayed in Figure 11. As can be seen the model designed, again predicts distribution coefficients above 100 %. In general the fit is not as good as already shown for As and Bi. Reason for that is, that the model is designed for constant physico-chemical properties (which strongly influence the Sb distribution [10]), but some of these properties varied from test to test, especially the final H_2SO_4 concentration of the electrolyte (135 g/l to 182 g/l H_2SO_4).

Figure 12 displays the effect of all investigated factors and factor combinations on the distribution coefficient of

antimony to the anode sludge. It shows that it is mainly dependent on the As, Sb concentration in the anode and the current density, an increase of each of these factors lowers the Sb distribution to the anode sludge. This result is in good agreement with investigations of other authors as described in the previous paragraph and a good foundation for the subsequent modelling of the antimony distribution coefficient. No influence of the anode bismuth content could be securely detected, maybe because of the low concentration of this element compared to the other anode impurities. As oxygen is needed for the oxidation (and subsequently precipitation) of Sb^{3+} to Sb^{5+} increasing anode oxygen contents lead to increased antimony movement to the anode sludge and this parameter is the only possibility to increase the Sb distribution coefficient. None of the multidimensional factors (O·Sb, O·i, As·i, ...) is significant compared to the influence of the single factors.

Based on the effects presented in Figure 12 the distribution coefficient of Sb to the anode sludge is predicted in the range of 500 ppm to 1000 ppm Sb in the anode for anodes containing 150 ppm bismuth. The results are displayed in Figure 13.

At 300 A/m² the antimony distribution coefficient for As-free anodes with oxygen concentrations of 2000 ppm and 150 ppm Bi varies from 89 % for anodes containing

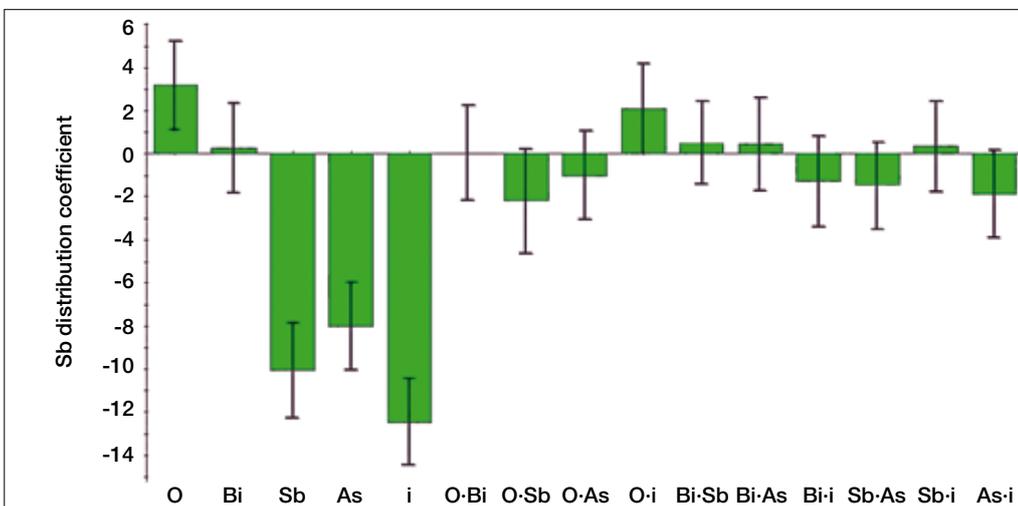


Fig. 12: Effects on antimony distribution to anode sludge: Scaled and centred coefficients

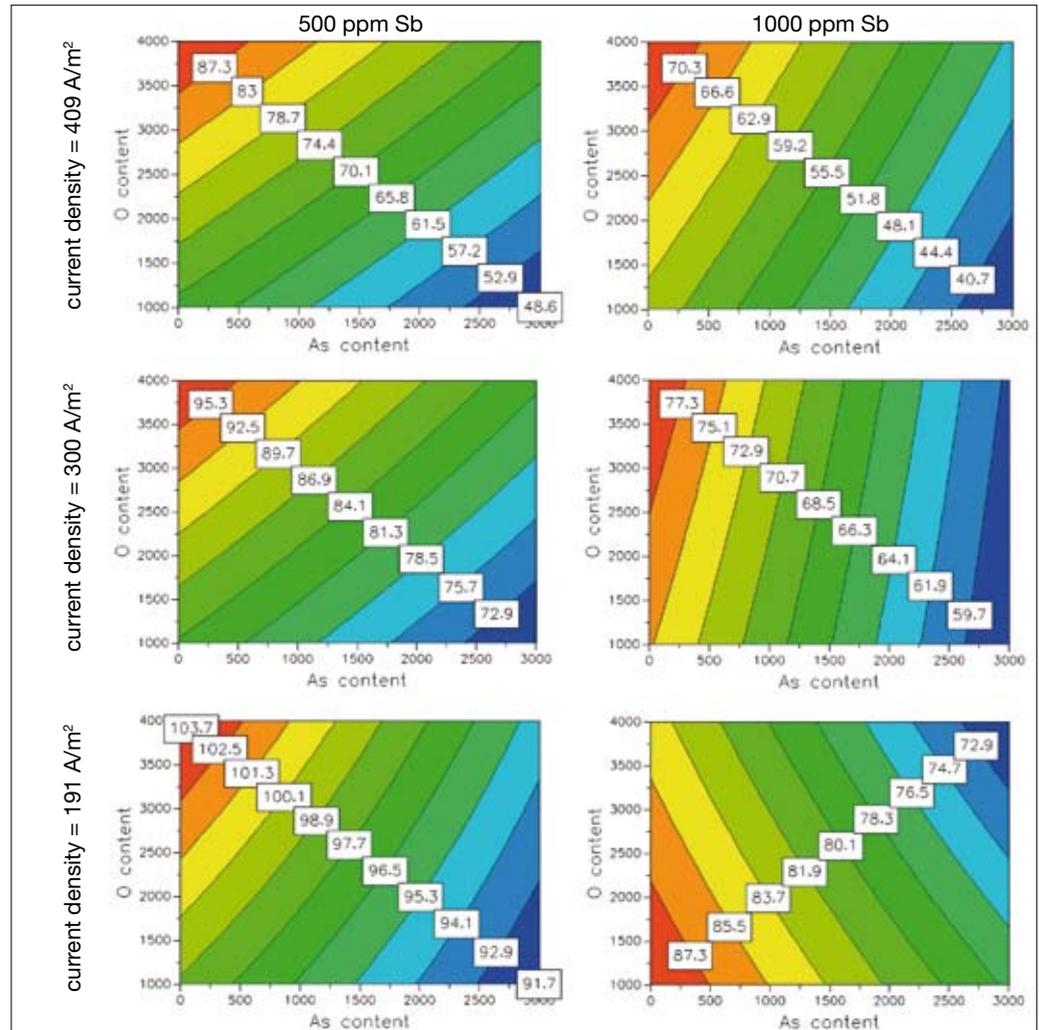


Fig. 13: Response Prediction Plot antimony distribution to anode sludge, calculated for 150 ppm Bi in the anode

500 ppm to 74 % for those containing 1000 ppm Sb. This values decrease at arsenic concentrations of 3000 ppm to 78 % respectively 58 %. At 409 A/m² these values get further 13 percent points lower for anodes containing no arsenic and 18 percent points lower for anodes containing 3000 ppm arsenic. Values for other anode compositions can be taken from Figure 13.

4 Summary

In this work the distribution coefficients of As, Sb and Bi “from anode to anode sludge” of lab-scale produced copper anodes was investigated. For the experiments 81 combinations of Cu-Ag1000-Ni1000-As-Sb-Bi-O anodes were synthesized. Avoiding the use of industrial anodes the resulted linear independent target compositions of the anodes made it possible to separate the individual effects of the elements using statistical methods. Main focus was the influence of As, Sb, Bi, O and the current density on the distribution of As, Bi and Sb. Using a full factor interaction model it was possible to ascertain significant factors influencing the distribution and with multiple linear regression it was possible to develop prediction models for the distribution coefficients of As, Bi and Sb to the anode sludge.

The distribution of **arsenic** is mainly dependent on its own (almost linear) and to some extent on the antimony concentration of the anode and the anodic current density. It can

be assumed that a fixed amount of As is bound as insoluble complex oxides with other impurities, in particular lead and antimony. The impact is a decreasing proportion of arsenic reporting to the anode slime with increasing arsenic concentration in the anode (if all other contents are kept constant). Antimony promotes the arsenic distribution to anode sludge mainly due to the formation of insoluble antimonates and arsenides precipitated jointly from the electrolyte. For anodes containing 2000 ppm O and 150 ppm Bi the distribution coefficient is predicted at 300 A/m² to 13.8/19.2 % for anodes containing 1400 ppm As and to 6.5/8.9 % for anodes containing 3500 ppm As and 0/1000 ppm Sb. At 409 A/m² these values get as low as 4.5 % for anodes containing 3500 ppm As (no antimony present in the anode) respectively 14.6 % for anodes containing 1400 ppm As and 1000 ppm Sb.

The **bismuth** distribution is strongly dependent on the arsenic and antimony concentration of the anode. A minor effect shows the anodic current density and its own concentration. Similar to arsenic a fixed amount of Bi is bound as insoluble complex oxides reporting to the anode slime. Bi in the anode sludge is always accompanied by Sb, therefore higher anodic Sb concentrations lead to increased Bi proportions in the slime. Arsenic and the current density on the other hand control the bismuth concentration in the cathode. For anodes containing 2000 ppm O, 250 ppm Bi and 0/1000 ppm Sb the distribution coefficients at 300 A/m²

are predicted to vary between 55/109 % for anodes containing 0 ppm As and 34/48 % for anodes containing 3000 ppm As. At 409 A/m² these values get as low as 16 % for anodes containing 3000 ppm As (no antimony) and reach 98 % for anodes containing 0 ppm As and 1000 ppm Sb.

The distribution of **antimony** is controlled by the current density, the arsenic and antimony concentration and to some extent by the oxygen concentration of the anode. Oxygen is needed for the oxidation of Sb³⁺ to Sb⁵⁺, so an increased anode oxygen content leads to an increased Sb distribution to the anode sludge. As on the contrary has the opposite effect, because the oxidation of arsenic is much faster than that of antimony and occurs therefore preferentially. An increasing current density leads to an increased deposition of antimony at the cathode and similar to arsenic a fixed amount of Sb is bound as insoluble complex oxides reporting to the anode slime. So an increased amount of Sb leads to a decreasing Sb distribution coefficient. At 300 A/m² the antimony distribution coefficient for As-free anodes with oxygen concentrations of 2000 ppm and 150 ppm Bi varies from 89 % for anodes containing 500 ppm to 74 % for those containing 1000 ppm Sb. These values decrease at arsenic concentrations of 3000 ppm to 78 % respectively 58 %. At 409 A/m² these values get further 13 percent points lower for anodes containing no arsenic and 18 percent points lower for anodes containing 3000 ppm arsenic.

The received results for the As, Sb and Bi distribution coefficient to anode sludge confirmed mainly results already identified by other authors and extended the knowledge with respect to interactions/dependencies. Based on the results summarized in this chapter, Figure 14 is constructed comparing the As, Sb and Bi distribution coefficients at certain anode compositions and current densities. Using the prediction charts shown in the earlier chapters this comparison can be also done for all other anode compositions within the analysed range.

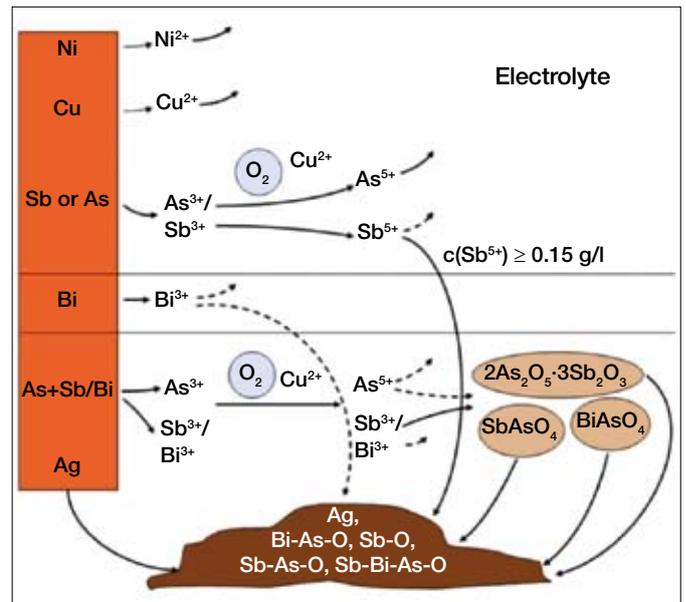


Fig. 15: Transfer mechanisms for As, Sb and Bi to electrolyte/anode slime in copper refining electrolysis

The transfer mechanisms for As, Sb and Bi to electrolyte/anode slime are visualized in Figure 15. Overall the results of this investigation offer the production engineers a practical tool for understanding and probably improved control of the copper electrolysis process, especially with respect to the anode composition.

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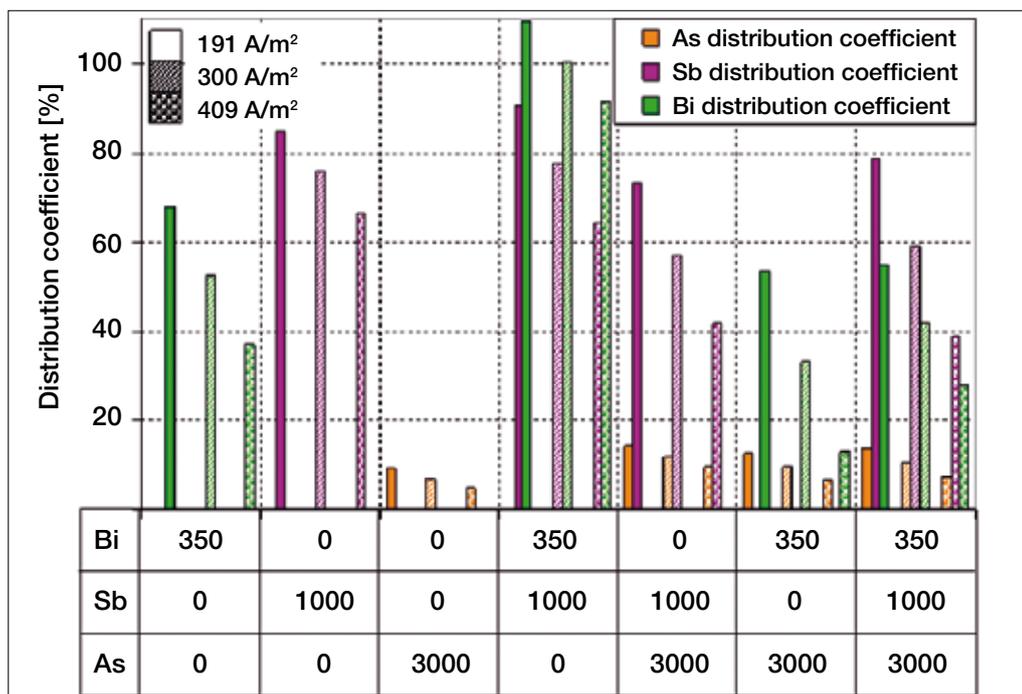


Fig. 14: Distribution of arsenic, antimony and bismuth during copper electrolysis at three current densities, 2000 ppm oxygen and different concentration levels of Bi, Sb and As in synthetic anodes

publish the results in this series. Special thanks are given also to M.Sc. S. Akbari for her voluntary assistance in the challenging first year of this extensive experimental research programme.

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