Influence of As, Sb, Bi and O on Copper Anode Behaviour – Part 2: Anode Dissolution Behaviour and Anode Sludge Generation

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This article is the second of a three articles series of results from a three year research project funded by the "Sponsor Group Copper Electrorefining". 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 dissolved anode mass respectively the anode current efficiency and the generated amount of anode sludge. For a better assessment of the experimental results 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. The anode current efficiencies varied between 100.4 % and 103.7 % dependent on the anode composition. The factor with the highest impact is oxygen, which influence is approximately four times higher than the influence of As respectively As · O. Investigating the factors influencing the amount of anode sludge revealed that it is influenced by a lot of factors, but mainly by As and partly by O and the current density. Several prediction charts were designed forecasting the dissolution of anodes and the amount of anode sludge produced within the parameter set.

Keywords:

Copper refining electrolysis – Anode dissolution – Impure anodes – Mathematical modelling – Anode behaviour – Anode sludge

Einfluss von As, Sb, Bi und O auf das Verhalten von Kupferanoden – Teil 2: Anodenauflösung und Anodenschlamm-Entstehung

Dies ist der zweite von drei Artikeln über die Ergebnisse eines dreijährigen Projekts, finanziert von der „Sponsor Group Copper Electrorefining". 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 das Auflösungsverhalten von Anoden bzw. auf die anodische Stromdichte und die entstehende Menge Anodenschlamm. Zur besseren Bewertung der Ergebnisse wurden Literatur über die mineralogische Struktur von Anoden in Abhängigkeit von ihrer chemischen Zusammensetzung analysiert und die wichtigsten Aspekte zusammengefasst. Die aus den Versuchen resultierende anodische Stromausbeute variierte zwischen 100,4 % und 103,7 %, wobei der Faktor mit dem größten Einfluss Sauerstoff ist – mit einem etwa viermal höheren Einfluss als As bzw. As · O. Untersuchungen der entstehenden Menge Anodenschlamm zeigten, dass diese von vielen Faktoren beeinflusst wird, hauptsächlich von As und z.T. von O und der Stromdichte. Mehrere Vorhersagediagramme wurden konstruiert, die die Auflösung von Anoden und die Menge des gebildeten Anodenschlamms innerhalb des Parameter-Satzes darstellen.

Schlüsselwörter:

Kupferraffinationselektrolyse – Verunreinigte Anoden – Anodische Auflösung – Anodenschlamm – Mathematische Modellierung – Verhalten von Anoden

L'influence de As, Sb, Bi et O sur le comportement des anodes en cuivre – section 2: Dissolutíon des anodes et formatíon de la boue anodique

La influencia de As, Sb, Bi y O sobre el comportamiento de ánodos de cobre – Parte 2: Desintegración de ánodos y la formación de barros anódicos

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, 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, dissolve 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 Ni-containing 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 separating 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 second part presenting the results from 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 copper anode dissolution behaviour as well as the generation of anode sludge.

In the first paper of this series [1] the design of the copper electrolysis experimental setup was described in detail as well as the preparation method of the anodes. All experiments were analyzed regarding their passivation behaviour and as a result it could be stated that higher Sb and/or O contents 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 literature. The statistical analysis however quantified the known effects and made it possible to forecast the passivation behaviour of anodes within the analysed range of parameters.

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 ratio of the As^{3+}/As^{5+}-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 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 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 shrinked 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/m²]	300	191	409
A_{anode}	[m²]	0.098	0.089	0.077
I	[A]	29.4	19.9	31.6
$A_{cathode}$	[m²]	0.089	0.089	0.089
$i_{cathode}$	[A/m²]	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 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 leads to electrolysis durations of 100 h 32 min, 57 h 49 min and 53 h 48 min. After every trial each cell is dismantled and the electrodes are removed (cathodes first), 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 is filtered and the collected anode sludge is immediately washed and dried. After that it is weighed and analysed by ICP as well as the electrolyte.

3   Anode dissolution

It is common knowledge that during electrorefining some of the anode impurities dissolve together with copper, either electrochemically if they are more ignoble than copper or just chemically. In all cases these elements concentrate in the electrolyte. The other anode compounds are insoluble and accumulate in the anode slimes and anode

dissolution as well as elemental distribution is dependent on the mineralogical structure of the anode.

3.1 Anode structure

Previous investigations were made by various research groups analyzing the mineralogical structure of accompanying elements in the anode. The results published can be summarized to:

- Anodes as used in the present investigation with less than 3000 ppm Ni allow the assumption, that no Ni is oxidized.

- Taking into account, that arsenic has a binary solubility in Cu up to 7.75 wt%, it should be present only in solid solution. But due to non equilibrium solidification processes there is a strong enrichment of As at the grain boundaries and according to [2] the formation of Cu_3As might be possible. This was proven by the fact that this phase was found even at anodes with As concentrations of 7000 ppm.

- If As is accompanied by oxygen, As can also be found as oxide shells at the surface of Cu_2O noodles [3]. After addition of Pb and/or Sb As can form complex oxide phases with a wide range of compositions [4,5]. Together with Bi the dominant oxide phase is Cu-Pb-As-Sb-Bi-oxide which gets dissolved during electrolysis forming solid $PbSO_4$ and the other components partly precipitate as $SbAsO_4$, Sb-As-Bi-oxide or Pb-Sb-oxide [6].

- The Bi solubility in Cu is 0.01 % and a lot lower than that of As, so only a minor fraction is likely present in solid solution [7, 2]. If the Bi content exceeds the solubility it is present as thin films at the grain boundaries causing cementation reactions of Cu on Bi [8, 2]. Own SEM analysis showed that Bi mainly forms Cu-Bi-oxides at the grain boundaries and after addition of Sb Cu-Sb-Bi-oxides, this is in good agreement with the structures observed by BEAUCHEMIN [7].

- The solubility of Sb in Cu is higher than that of Bi. CHEN [6] reported that about one third of the Sb is present in solid solution. On the contrary BEAUCHEMIN found that approximately 1/5 of the total Sb is in solid solution [7] whereas NOGUCHI [9] published that Sb is forming solid solutions with copper up to 2750 ppm in oxygen containing anodes and Sb_2O_3 is forming at the grain boundaries above this concentration.

- It is very unlikely that insoluble "Kupferglimmer" is formed, at Sb concentrations below 1000 ppm.

These statements can be summarized that during electrorefining As, Sb and Bi in solid solution dissolve completely and the oxide inclusions dissolve extensively. Most of the dissolved Sb and Bi precipitates as $SbAsO_4$ or Sb-Bi-As-O phases [2, 3]

3.2 Mathematical analysis of the anode dissolution behaviour

255 trials were conducted using anode compositions according to the first article. But only 213 were taken into account to analyse the dissolution behaviour of anodes

Fig. 1:   Left: regularly dissolved anode at 409 A/m²; right: strongly dissolved anode at 409 A/cm²

regarding their chemical composition, 41 anodes had to be excluded because they reached passivation (26) or due to extremely low or strong/inhomogeneous dissolution behaviour. Figure 1 shows an example where the final anode shape caused such unwanted conditions (current density, potential …). Remarkable is that all six anodes showing an extremely strong dissolution appeared during the same trial, so it has to be assumed that the effect was not related to the anode composition but to the electrolysis setup itself. Due to the low dissolution nine anodes were excluded, too. If the dissolved mass per Ah for anodes was lower than 25 % compared to the mean value of all tests with this composition, these trials were excluded as well, assuming that the dissolution was hindered may be due to the formation of a layer.

Of the remaining 213 anodes 12 anodes were run with 2000 Ah, 6 anodes were processed with 1675 Ah and the rest fluctuated between 1700 Ah and 1706 Ah. In order to compare the results of all trials the dissolved mass per Ah was ascertained. The calculated data can be seen in Figure 2. All results are higher than the theoretical dissolved copper mass per Ah calculated from Faraday's law, which is 1.1855 g/Ah at 100 % current efficiency. This is mainly due to the fact that oxides dissolve chemically into the electrolyte. As can be seen from Figure 2 the current density has no significant effect on the dissolution behaviour. There seems to be a slight increase of the dissolved anode mass with ascending impurity content but this is not a proven effect. The nature of these impurities and their combination among each other is important and needs further investigation using statistical analysis tools.

Statistical analysis of the passivation behaviour was done using the Umetrics software Modde 5.0, a MS-Windows®-based software, providing design of experiments, analysis and op-
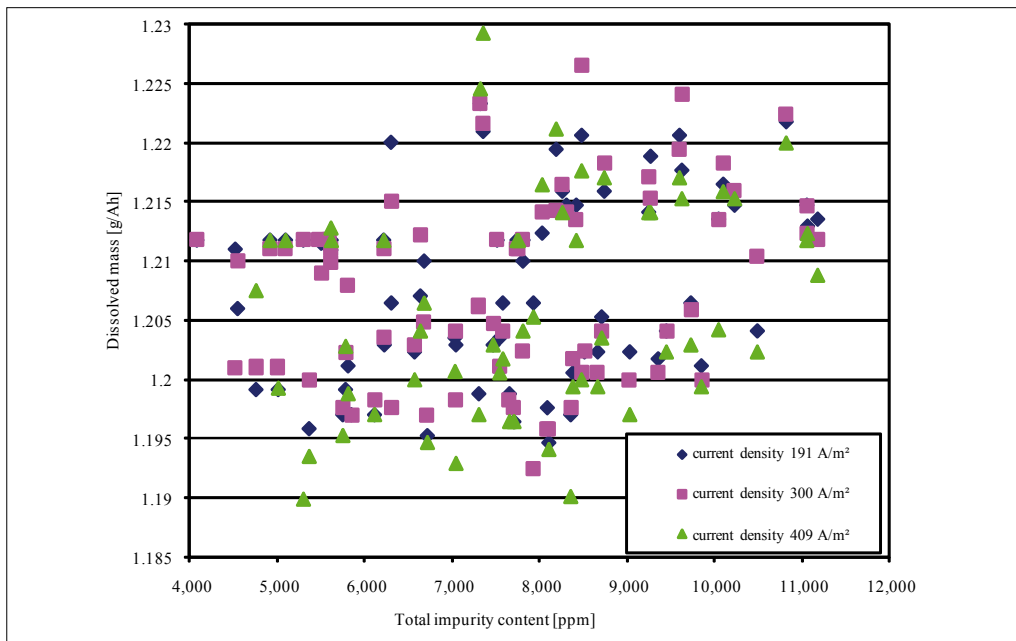
Fig. 2:
Dissolution behaviour of anodes vs. the total impurity content (Faraday value for copper is 1.1855 g/Ah)
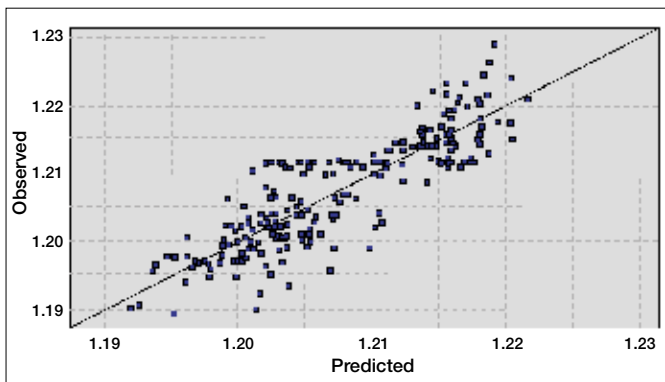

Fig. 3:   Observed vs. predicted anode dissolution, proving the general fit of the model

timisation. 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 probable effects of individual factors and factor combinations on the dissolution behaviour. All fits were done using multiple linear regression which leads to better fits than partial least square regression, resulting in a fit of 75 % to the regression model which is visualized in Figure 3. For a better fit more trials at high current density and high Sb contents are needed, because most of these trials had to be excluded unfortunately due to passivation [1].

Figure 4 displays the effect of the current density, the contents of O, Bi, Sb, As as well as selected parameter (factor) combinations on the dissolution tendency taking into account the 213 above described processed anodes. Positive effects stand for heightening and negative effects for lowering the current specific dissolution degree (weight loss in g/Ah). The black bars show the confidence interval. If they cross the zero line, the effect has to be defined as not significant, the smaller the black bars are in comparison to the effect, the more accurate is the significance value.

As can be seen from Figure 4 the oxygen content has the strongest and nearly the only effect on the dissolution behaviour, only As, As·O and the Bi·Sb concentration have a small significant effect as well. The influence of oxygen is straight forward and can be explained easily. Oxygen is forming oxide phases with the metals of the anode, which extensively dissolve chemically or accumulate in the anode
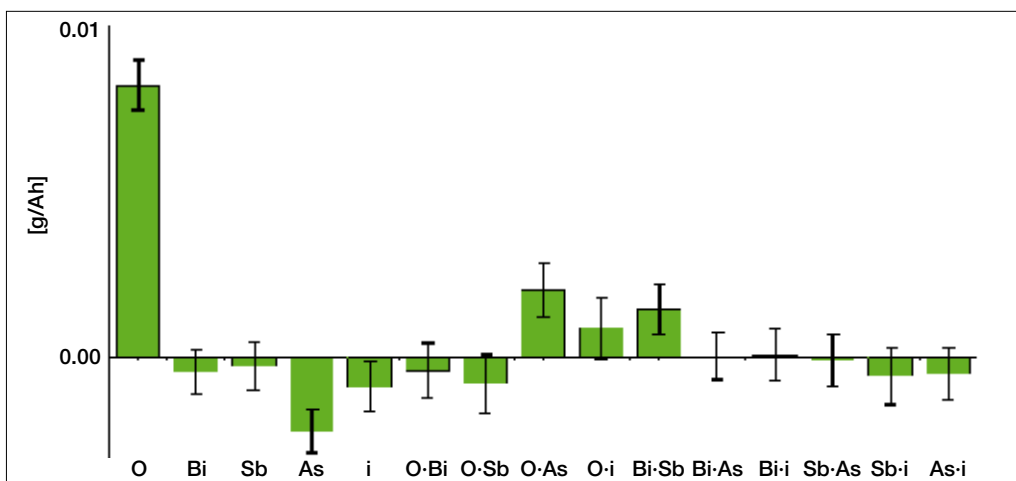

Fig. 4:
Coefficient plot anode dissolution

sludge undissolved. There is no electrical current needed for their removal and such the dissolved mass per Ah is rising.

Arsenic has the characteristic to decrease the dissolved specific anode mass. It is partly dissolved in the anode copper matrix (one fifth to one third [6, 10]) 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 same mechanism accounts for Bi and Sb, which exist as solid solutions in the anodes as well. Such a rising Bi and Sb content should also have a small decreasing effect on the dissolved anode mass but according to Figure 3 this effect could not be determined as significant. This is probably due to the smaller amounts of Sb and Bi within this investigation and their lower solubility in Cu (2750 ppm for Sb and 100 ppm for Bi [7, 9]). Therefore only approximately one fifth of Sb can be assumed to be in solid solution and for Bi this value is even less [7]. The contrary effect of As·O is due to the formation of As_2O_3 which forms at the grain boundaries and dissolves chemically into the electrolyte. If Bi and Sb are present (Bi·Sb) in the anode these elements prefer to form Cu-Sb-Bi-oxides at the grain boundaries, which also get chemically dissolved and mostly precipitates directly into the anode sludge.

According to the investigation with Modde the current density might have a small decreasing effect as well, but this is not certain. Of cause the absolute amount of anode mass dissolved is increasing with increased current density. But this dependence is not linear according to polarisation phenomenons, so the specific mass dissolution per Ah is decreasing. All other factors or factor combinations have no significant effect on the dissolution behaviour of the anodes or as the case may be for Sb and Bi their effect can not be determined definitely with the present results from this investigation.

3.3 Prediction of the anode dissolution behaviour

The fitted model can now be used to make predictions about the dissolution behaviour of anodes. Since oxygen seems to have an extremely large influence a response prediction plot was made depending on the oxygen content (Figure 5). This plot displays a curve representing the variation of the dissolved anode mass per Ah when the O content varies from 1000 ppm to 4000 ppm. All other factors are constant on their averages and the 95 % confidence
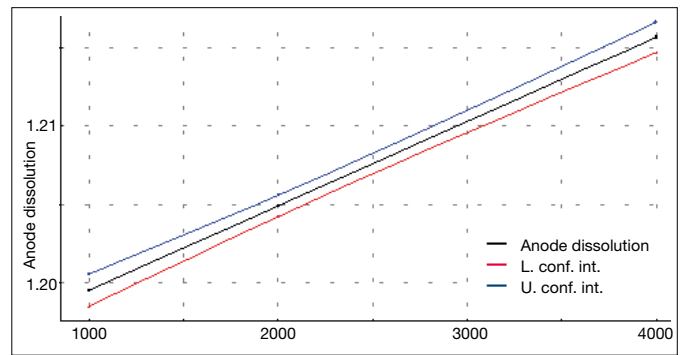

Fig. 5: Anode dissolution prediction plot depending on the oxygen content in g/Ah including lower and upper interval levels for 95 % confidence

interval is displayed in the plot as well.

To visualize even the small effects of all other significant factors 4D contour plots are made (Figure 6) predicting the dissolution of anodes in respect to the O and As content as well as the current density. 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 journey of seven days at 300 A/m² the dissolved anode mass is 108 to 110 kg for anodes with 1.8 m² surface and As contents up to 3000 ppm, Bi concentrations up to 350 ppm and Sb concentrations up to 1000 ppm.

The anodic current efficiency (equation 1) runs parallel to the dissolved anode mass and is for all anodes above 100 % due to the mentioned chemical dissolution effects. It is calculated with the dissolved mass/Ah observed/predicted and the theoretical copper mass of 1.1855 g/Ah calculated earlier. The current efficiency for the performed trials is varying between 100.4 % and 103.7 %.

$$\eta = \frac{m_{act.}}{m_{theo.}} \qquad (1)$$

η: current efficiency, m_{act}: actual dissolved anode mass, $m_{theo.}$: theoretical dissolved anode mass (1.1855 g/Ah)

4 Generation of anode sludge

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
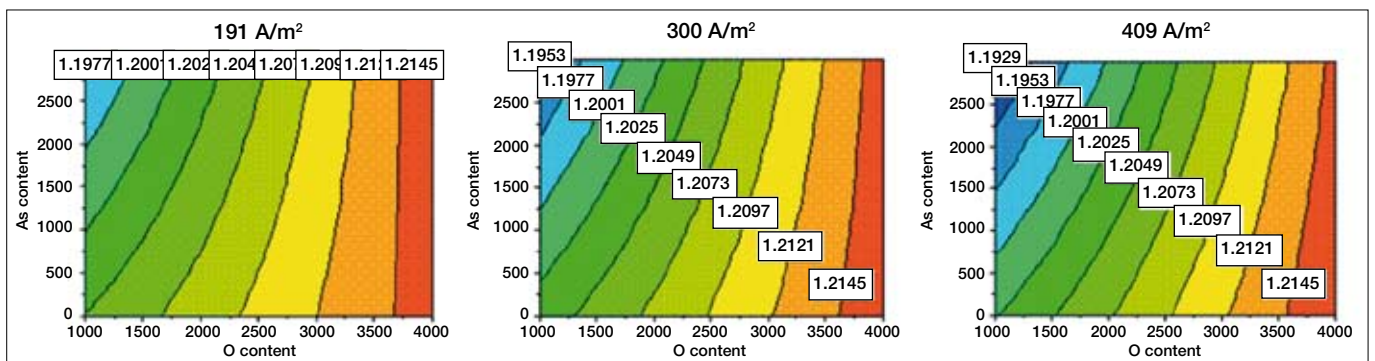

Fig. 6: Response prediction plot anode dissolution, calculated for anodes containing 500 ppm Sb and 150 ppm Bi

precipitation or non-dissolution. So the amount of anode sludge is strongly depending on the chemical composition of the anodes. In case of elements which report to the anode slimes it would appear 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.

4.1 Anode sludge homogeneity

The anode sludge was collected by immediately removing the electrodes after each trial, washing them with hot deionised water and finally brushing them in order to remove remaining anode sludge from their surfaces. Parallel the electrolyte from each cell was hot filtered and the collected anode sludge was immediately washed. After that both slimes were merged, dried, weighed and analysed by ICP for the As, Sb, Bi, Ag, Ni, Cu and S content. To investigate the homogeneity of the anode sludge, nine samples were analysed by EDS at five different spots and the results were compared with the ICP results of the whole sample. The EDS analysis varied in large ranges as shown for three samples in Table 2. Compared to the value obtained from ICP analysis, none of the average EDS-data is even close, so it is clear that EDS results can not be taken as absolute numbers. But they show qualitatively, that the anode sludge is extremely inhomogeneous. For silver they vary between -54.8 to +80.3 % compared to the ICP result and -55 to +67.4 % for copper. As a result it was taken special care to obtain homogenous samples for all slime analysis by means of automatic sub-sampling.

4.2 Morphology

Additionally to the occurrence of elements present in the slime phases the morphological structure was investigated

Table 2: EDS analysis of anode sludge samples, compared with ICP-data (all values in %)

Element	Sample	EDS average	ICP	Deviation EDS to ICP
Ag	A4	52.9	31.9	40.1 - 79.6
	A16	53.3	44.7	-4.0 - 36.2
	A22	12.4	17.9	-54.8 - 5.6
Cu	A4	22.0	38.0	-55.0 - (-20.5)
	A16	7.6	12.9	-48.8 - (-26.4)
	A22	6.5	4.3	30.2 - 67.4
Sb	A4	10.9	7.3	30.1 - 98.6
	A16	16.7	14.4	-11.8 - 60.4
	A22	40.3	30.4	20.4 - 40.8
As	A4	11.2	2.9	196.6 - 400.0
	A16	9.5	3.2	131.3 - 300.0
	A22	20.6	8.5	110.6 - 187.1
Bi	A4	Not detected	1.8	-
	A16	9.3	5.4	50.0 - 98.2
	A22	18.9	11.0	59.1 - 80.0

by SEM and EDS for 24 samples processed at 300 A/m² anodic current density. The corresponding chemical analysis of ten of these anodes is given in Table 3. Also the amount of anode sludge and detected phases are indicated. Lines marked in lighter blue indicate passivating anodes. As can be seen from Table 3 the single anode sludge phases are quite complex. All anode sludges contain arsenic and antimony even if there was no arsenic respectively antimony present in the anodes. It also shows that Bi is not present in anode sludges from anodes only containing low amounts of bismuth (~ 150 ppm) and no As and/or Sb, but it is present in anode sludges from anodes not containing Bi but Sb. Anode slime phases containing Bi always contain also Sb, but not necessarily As. The formation of these slime phases seems to be independent of the oxygen content of the anode.

For a detailed morphological analysis, X-ray diffraction analysis would have been necessary to example assess

Anode	O conc. [ppm]	Bi conc. [ppm]	Sb conc. [ppm]	Mass of anode sludge [g]	EDS detected elements in apparent anode slime phases
A3	3721	0	0	7.3	Cu-O, Cu-S-O, Ag, Sb-As-Ag-S-Cu-O
A4	1317	150	0	7.2	Cu-S-O, Sb-Ni-Fe-O-S-Cu, Cu-O-Ag, Sb-As-Ag-S-Cu-O, Sb-As-Ag-Cu-O, Sb-Cu-As-O
A5	2402	150	0	7.2	S-Cu-As-O-Ag-Sb
A6	4825	140	0	6.8	Cu-S-O-Ag-As-Sb-Ni, Cu-Ag-As-Sb-S-O
A9	4413	310	0	5.2	Ag-Sb-Cu-Ni-Fe-As-Bi-O, Ag, Ag-Sb-As-Ni-O-Cu-Bi, As-Bi-Ag-Sb-O, Ag-Ni-Cu-As-Sb, Bi-As-Sb-O, As-Sb-Bi-Cu-Ni-O
A10	1524	0	440	7.2	Sb-Ag-As-O-Bi-Cu, Sb-As-O-Ag, Sb-As-Ag-O-Cu, Ag-Cu-O-Sb-As-Ni, Ag, Cu-Ni-Sb-As-Ag-Bi-O
A15	4241	0	970	4.0	Ag-Cu-Sb-As-O, Ag-Cu-Ni-Bi-Sb-As-O, Ag-Cu-S-O-Sb-As-Ni, Bi-Ag-Sb-As-O-Cu-Fe
A17	2408	140	440	6.7	Ag-Sb-As-Cu-Ni-O, Ag-Sb-As-Cu-S-Ni-O, Bi-Sb-As-Cu-S-Ni-O, Bi-Sb-Cu-Ni-As-Ag-O
A20	2251	320	467	11.1	Ag-Sb-Bi-Cu-Ni-As-O, Sb-Bi-As-Cu-Ag-O, Bi-Sb-Fe-Ni-Cu-As-Ag-O
A22	925	170	920	10.2	Ag-Sb-As-Bi-Cu-Ni-O, Sb-As-Cu-O, Sb-Ag-Cu-Bi-O-As

Table 3: Chemical composition of anodes processed at 300 A/m² anodic current density and detected phases in the corresponding anode sludge
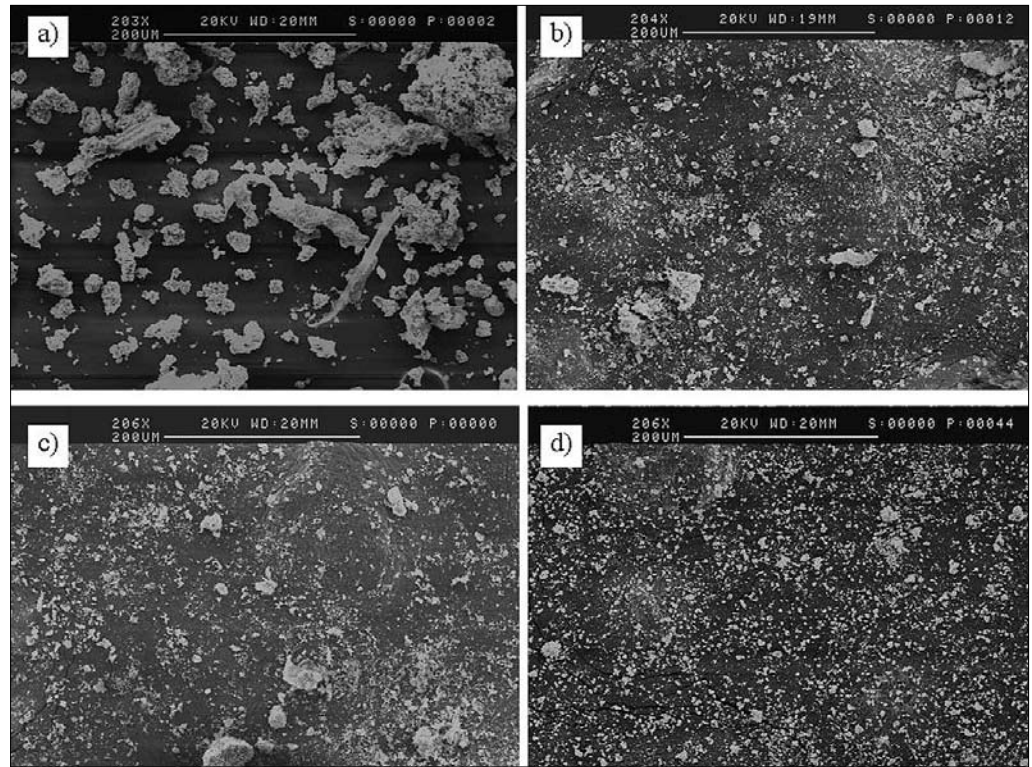
Fig. 7:
Morphology of different anode sludge samples (SEM) at a magnification of 200, all anodes contained ~ 2000 ppm oxygen;
a: no Sb/no Bi
b: 300 ppm Bi/0 ppm Sb
c: 480 ppm Sb/0 ppm Bi
d: 140 ppm Bi + 440 ppm Sb

whether silver is present predominantly in metallic form. Unfortunately these were not funded within the project.

No obvious effect on the anode sludge grain size could be detected at varying oxygen contents (1000 ppm to 4000 ppm). Figure 7 shows EDS micrographs of four selected slime samples, the corresponding anodes contained 2000 ppm oxygen and varying concentrations of bismuth and antimony. Comparing the results it becomes obvious that bismuth and antimony in the anode have a significant effect on the grain size of the anode sludge. Anode sludge a) is obtained from an anode only containing Cu, Ni, Ag and O showing a bigger grain size than the anodes additionally containing Sb and/or Bi. If only Bi or Sb is present, still some large particles can be found, but no longer in anode sludges from anodes contain-

ing both Sb and Bi. Summarizing it can be stated that Sb and Bi in an copper anode lead to finer grain sized anode sludges whereas the combined influence of both elements seems to be stronger than the influence of the single components.

4.3 Mathematical analysis of the generation of anode slime

The amounts of anode sludge produced during all 255 analysed experiments varied between 2.3 g and 24.2 g with average values of 4.0 g/kg dissolved anode at 191 A/m², 3.2 g/kg dissolved anode at 300 A/m² and 3.1 g/kg dissolved anode at 409 A/m². All obtained amounts of anode sludge per kg dissolved anode are displayed in dependence of the total impurity content of the anodes (without Ni) in Figure 8.
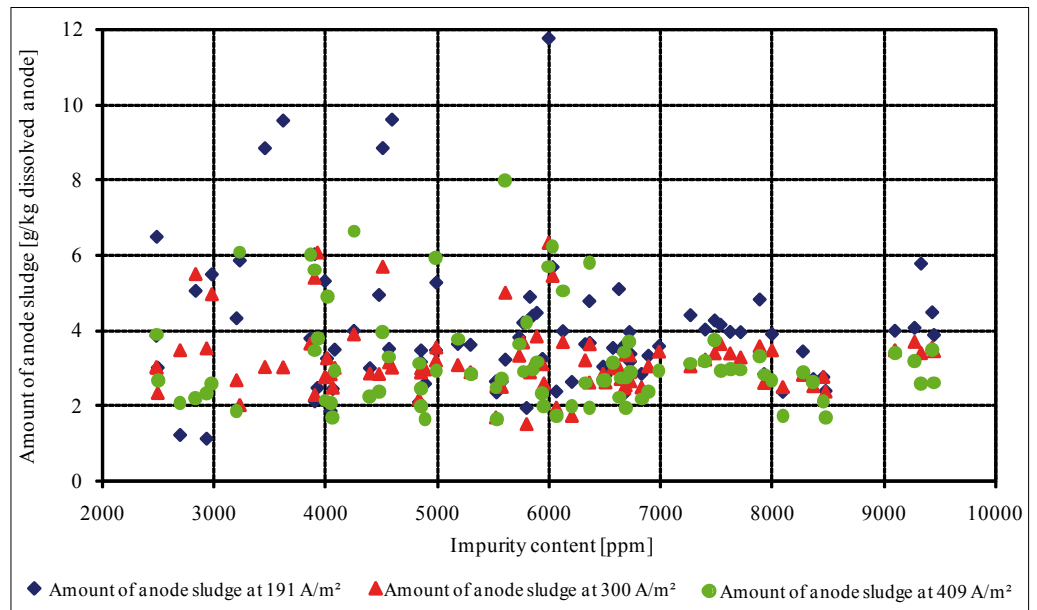

Fig. 8:
Amount of anode sludge/kg dissolved anode vs. the total impurity content (without Ni)

But it is not possible to detect any correlation according to this chart, it is only noticeable that the data of anode sludge mass becomes more stable and in average slightly lower for impurity contents > 6500 ppm.

The attempt to model the generated amount of anode sludge against the anode composition was not successful due to different dissolution behaviours of the anodes. The fit resulting from that kind of model was only 26 %, even if the trials run at 2000 Ah were excluded. A second approach to model the mass ratio of anode sludge to the dissolved anode was also not successful leading to a fit of only 27 %. Reasons for this were problems to determine the exact amount of anode sludge and the accuracy of the chemical analysis due to the discussed inhomogeneity of the anode sludge. Therefore mass balances were made balancing the whole electrolysis cell for each trial. All trials showing an input/output balance less than 80 % were excluded from the following analysis. That way 214 trials (partly different to those selected in chapter 3.2) could be used to model the generated amount of anode sludge which led to a fit of 50 %. This still insufficient fit is predominantly caused by extremely changing amounts of copper in the anode sludge varying from 0.1 g to 14.1 g respectively 3.1 % to 61.5 % mainly due to the inclusion of metallic copper from disproportion reactions and cathode deposit debondings. In a next step of optimizing the model, the amount of anode sludge was reduced about the copper content and correlating this number with the dissolved anode mass resulted in a fit of 73 %. According to this procedure Figure 9 displays the influence of various impurities and impurity correlations on the amount of anode sludge generated per kg dissolved anode mass.

The coefficients plot shows the changes in the amount of anode sludge in g/kg dissolved anode caused by an increase of different process parameters. It reveals that the amount of anode sludge is dependent on a lot of factors where the strongest influence can be determined as As, O and the current density. All three factors, when being increased, have the effect to lower the amount of anode sludge produced. Sb- and slightly also Bi-contents in the anode increase the amount of anode sludge. Surprisingly the factor combinations As·O, O·i and As·i appear to increase the amount of anode sludge, although the single effects do the contrary.

The impact of Bi and Sb is quite forward, Bi and Sb mainly report to the anode sludge in form of various oxide components [11], so the higher the concentration of Bi and Sb in the anode, the more anode sludge will be produced. It has already been reported that the As content of the anodes controls the Sb content of the electrolyte [8]. Arsenic dissolves as a three valent ion into the electrolyte and is further oxidized to As^{5+} in the presence of oxygen (ions) catalysed by cuprous ions. The oxidation of Sb^{3+} to Sb^{5+} will not occur as long as As^{3+} is dissolved into the electrolyte [12, 13] and given that the saturation limit of Sb^{5+} is a lot lower than that of Sb^{3+} [12], less antimony will precipitate to the anode sludge. The amount of anode sludge will decrease. In the reported investigation Sb was always present in the electrolyte as well as oxygen in the anode, so it is not possible to assess the effect of arsenic without antimony being present in the system.

It is common knowledge that higher current densities (anode potentials) lead to an increased dissolution of nobler elements than Cu like Ag or stable intermetallic compounds for example. In this case the nobler element does not precipitate in the anode sludge but is deposited at the cathode, the amount of anode sludge decreases as shown in Figure 11. The second risk of high potentials is that some of the ignoble elements present in the electrolyte deposit also at the cathode. The presented influence of the oxygen content is quite strange. It could be expected that with elevated oxygen contents in the anode the amount of anode sludge will increase because of a higher probability of Cu_2O in the anode, reacting according to equations 2 and 3. Having excluded copper as component in the anode sludge this effect has been suppressed (Figure 9), but including copper in one of our previous models (Figure 10), the expected effect can be seen.

$$Cu_2O + 2H^+ \rightarrow 2Cu^+ + H_2O \qquad (2)$$
$$2Cu^+ \rightarrow Cu\downarrow + Cu^{2+} \qquad (3)$$

Reason for the contrary effect of oxygen based on the final model is due to a lower precipitation of arsenic (Table 4). This effect is generally smaller than the increased copper precipitation and therefore superimposed in Figure 10.
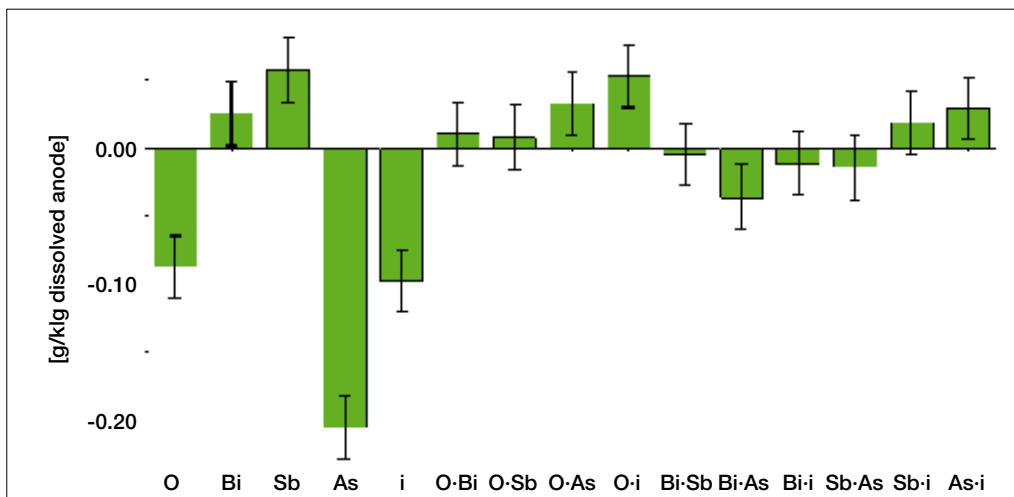

Fig. 9:
Coefficient plot of the specific anode sludge formation (model excludes the copper content)
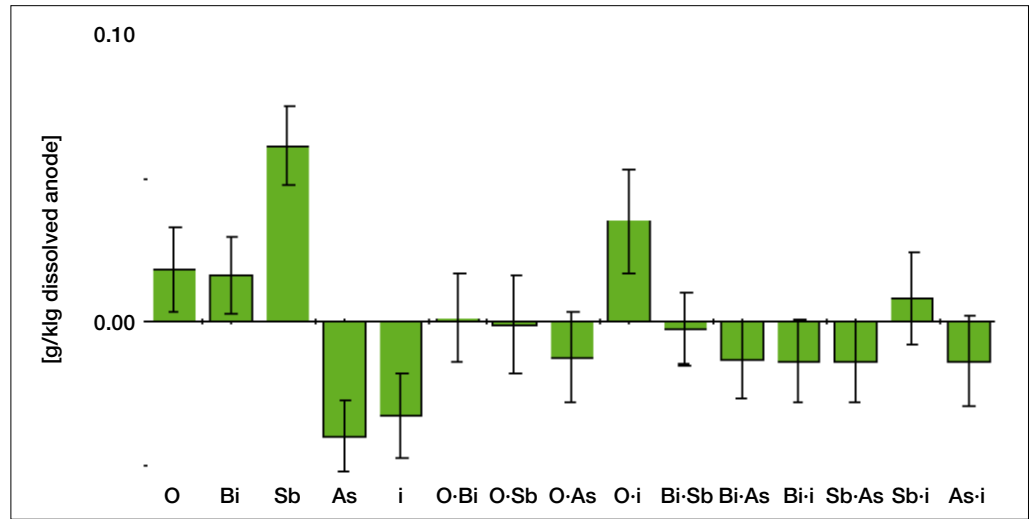
Fig. 10:
Coefficient plot anode sludge formation (model including copper)

Table 4: Average amount of As transferred to anode sludge in g/kg dissolved anode (all anodes with the same chemical composition except the oxygen content)

Anodic current density [A/m²]	As in anode sludge [g/kg dissolved anode]		
	1000 ppm O in anode	2000 ppm O in anode	4000 ppm O in anode
191	0.66	0.63	0.58
300	0.48	0.47	0.46
409	0.37	0.36	0.35

Reasons for the reduced arsenic precipitation could not securely be detected.

Comparing Figure 9 and Figure 10 it is evitable that the influence of all other factors is principally the same, just the accuracy is higher for the model without copper (74 % in contrast to 50 %), factor combinations with small influences could be determined as well and the predictability of the anode sludge amount is a lot more accurate using this model.

The factor combinations O·As, O·i and As·i can be clearly determined to raise and the Bi · As combination to lower the amount of anode sludge. From Table 4 it can be seen that a rising O·i value is lowering the precipitation of As in the sludge, so this factor is mainly increasing the precipitation of other components like for example antimony. But the present results do not allow identifying clearly which elemental distributions are effected by all this factor combinations, so an explanation for this phenomenon is not possible yet. A detailed analysis of the distribution coefficients and the factors influencing them will be presented in part III of this publication series.

4.4 Prediction of the anode sludge formation

Based on the effects presented in Figure 9 the anode sludge formation was investigated further with special respect to chemical composition and anode current density, shown in Figure 11 and Figure 12. The forecast of the specific anode sludge formation in g/kg of dissolved anode mass within
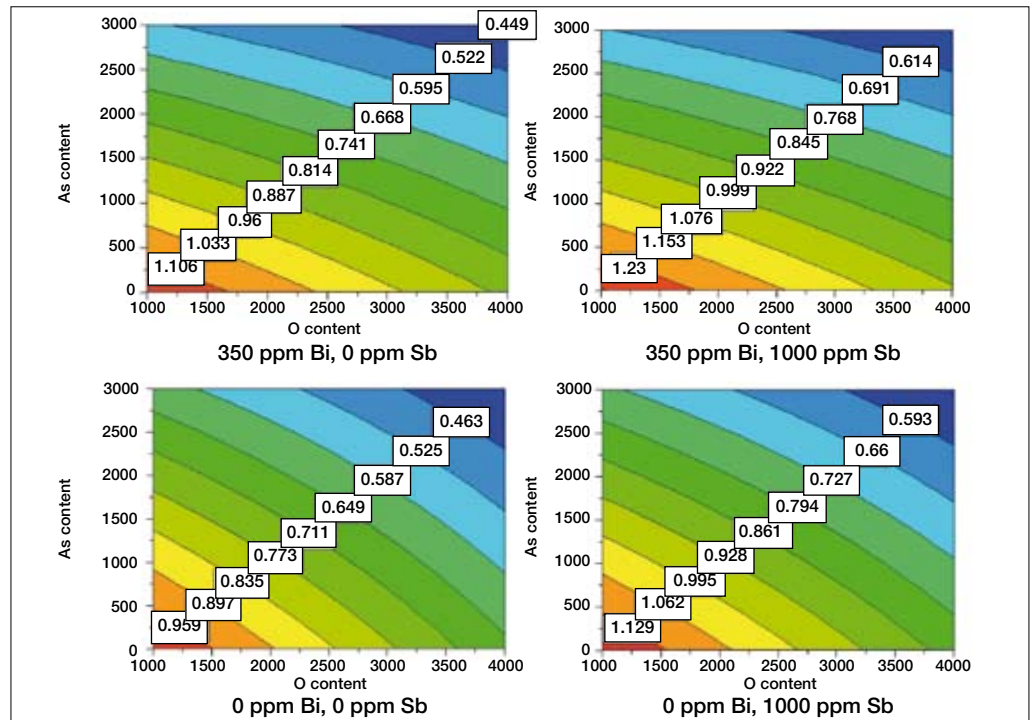

Fig. 11:
Response prediction plot for anode sludge formation in g/kg of dissolved anode mass depending on its oxygen and arsenic levels at 300 A/m² (two different Sb and Bi levels)

1700 Ah electrolysis "time" at 300 A/m² depending on the Sb-, As- and Bi-content in ppm is displayed first (without taking into account the copper content). It is quite obvious that the amount of anode sludge produced is increasing for increasing antimony concentrations from 1.10 g/kg dissolved anode at 0 ppm Sb to 1.23 g/kg at 1000 ppm Sb for anodes containing 350 ppm Bi, 1000 ppm O and 0 ppm As. These values are decreasing at higher oxygen and arsenic concentration down to 0.45 g/kg and 0.54 g/kg at 3000 ppm As and 4000 ppm O. At 0 ppm Bi all these values are again decreasing as can be seen from Figure 11.

In a second figure the influence of the current density on the anode sludge formation is displayed. According to Figure 12 the amount of anode sludge produced for anodes with industrial typical oxygen concentrations of 2000 ppm is strongly dependent on the arsenic concentration of the anodes and the current density. At 191 A/m² the value changed from 0.76 g/kg dissolved anode for anodes with 3000 ppm As to about 1.25 g/kg for anodes without As contamination, at 300 A/m² the value decreased to 0.66 g/kg respectively 1.05 g/kg and at 409 A/m² to 0.56 g/kg respectively 0.85 g/kg. Values for other anode compositions at different current densities can also be taken from Figure 12.

The presented model can only predict the amount of anode sludge produced during electrolysis when taking the copper content not into account. It was not possible to forecast the amount or the concentration of copper in the anode sludge due to the mentioned problems of metallic copper portions in anode sludge. As an estimate the copper content for anodes with approx. 2000 ppm O, up to 3000 ppm As and up to 350 ppm Bi will vary at 191 A/m² between 2.2 and 2.6 g/kg dissolved anode for anodes without Sb, 2.5 and 3.1 g/kg at Sb concentrations of about 500 ppm and 2.8 and 3.5 g/kg at Sb concentrations of approx. 1000 ppm. At 300 A/m² these values reduce to 2.0 to 2.2 g/kg respectively 2.2 to 2.7 g/kg and 2.5 to 3.1 g/kg. At 409 A/m² this values are further decreased to 1.4 to 1.7 g/kg respectively 1.7 to 2.3 g/kg and 2.3 to 3.0 g/kg.

The reasons for the insufficient model fit for the amount of anode sludge were mainly due to difficulties determining the exact amount of anode sludge, unpredictable metallic copper concentrations and changing conditions during the tests (for example final acid concentrations from 135 g/l to 182 g/l H_2SO_4).

5   Summary

In this work the dissolution characteristics of lab-scale produced copper anodes with various combinations of Cu-Ag-Ni-As-Sb-Bi-O were investigated. Main focus was the influence of As, Sb, Bi, O and the current density on the dissolved anode mass respectively the anode current efficiency. For a better assessment of the experimental results 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.

The anode current efficiencies varied between 100.4 % and 103.7 % depending on the anode composition. The factor with the highest impact is oxygen, which influence is approximately four times higher than the influence of As respectively As·O and even higher than the influence of Bi·Sb. Oxygen is increasing the dissolved anode mass by forming chemical soluble metal oxides. This is also the reason for the smaller but also increasing effect of As·O and Bi·Sb (formation of Cu-Sb-Bi-oxides). As shows a contrary effect, as it occurs in the anode partly in solid solution, allowing it to be electrochemically dissolved before copper. Unlike copper it is forming trivalent ions and therefore the dissolved mass per Ah is declining. The current density might have a small decreasing effect on the dissolution behaviour, but this effect is not significant enough in our trials. Several prediction charts were designed forecasting the dissolution of anodes within the parameter set. Generally the specific anode dissolution degree varies between 1.19 g/Ah and 1.22 g/Ah. Anodes with industrially typical oxygen concentrations of maximum 2000 ppm show a maximum dissolution value of 1.21 g/Ah. This leads to about 110 kg dissolved anode mass in seven days at 300 A/m² with 1.8 m² surface and As contents up to 3000 ppm, Bi concentrations up to 350 ppm and Sb concentrations up to 1000 ppm.

In the second part of this work the main focus was on the generated amount of anode sludge 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 and additional 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 seems to have no impact.
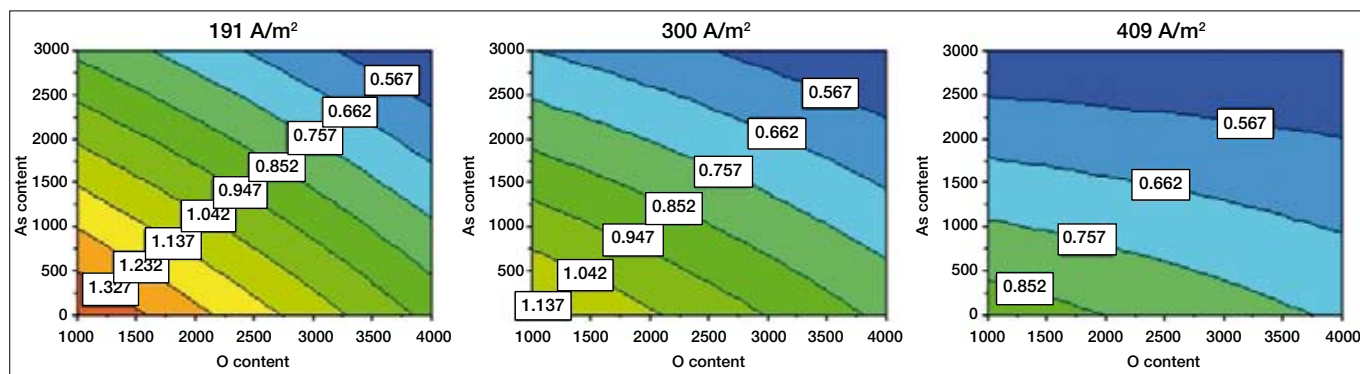

Fig. 12: Response prediction plot for anode sludge formation in g/kg of dissolved anode mass depending on its oxygen and arsenic levels at different current densities (500 ppm Sb and 150 ppm Bi)

Investigating the factors influencing the amount of anode sludge revealed that it is influenced by a lot of factors, mainly by As and partly by O and the current density. Arsenic and current density lower the specific amount produced, oxygen only if calculations exclude copper in the slime. Additional to that Bi and Sb were determined as factors increasing the amount of anode sludge slightly, but Bi only if it is not present in combination with As in the anode. Also the factor combinations As·O, O·i and As·i appear to increase the amount of anode sludge to some extend.

The amount of anode sludge produced for anodes with an industrial common oxygen concentration of 2000 ppm varied at 191 A/m² from 0.65 g/kg for anodes with 3000 ppm As to 1.25 g/kg for anodes without As. At 300 A/m² this values decreases to 0.58 g/kg respectively to 1.13 g/kg. Finally at 409 A/m² the amount of anode sludge reached values of 0.38 g/kg respectively 0.65 g/kg for anodes without As. It was not possible to forecast the amount or the concentration of copper in the anode sludge due to unsystematically contents of metallic copper from disproportion anode reactions and cathode copper losses to anode sludge. As an estimate it was found that the copper content for anodes with approx. 2000 ppm O, up to 3000 ppm As and up to 350 ppm Bi will vary at 191 A/m² between 2.2 and 2.6 g/kg for anodes without Sb, 2.5 and 3.1 g/kg at Sb concentrations of about 500 ppm and 2.8 and 3.5 g/kg at Sb concentrations of approx. 1000 ppm. At 300 A/m² these values are reduced of about 12 % and at 409 A/m² of about 21 %.

The chemical composition of the anode sludge is strongly dependent on the distribution of the individual elements into sludge and electrolyte, so in the third part of this publication series in World of Metallurgy – ERZMETALL the distribution coefficients of the relevant elements will be calculated and analysed regarding their dependency on the anode composition. Based on these coefficients the interactions of the accompanying elements As, Sb, Bi and O will be assessed.

Acknowledgement

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