Challenges in the Electrolytic Refining of Silver –

Influencing the Co-Deposition through Parameter Control

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1 Abstract

Due to the high standards for silver in electronic uses, it is essential to control the behavior of the main impurities such as copper or palladium during the electrolytic refining. In regard to palladium, it is indispensable to control its complete transition into the anode slime. Established silver refining processes are currently operated with parameters that favor the silver cathodic deposition. Usually this requires a high precious metal stock and leads to low space-time yields. Parameter research studies show the possibility of changing these parameters to achieve a more efficient process without decreasing the silver grades. This research leads to the use of less pure electrolyte systems and more contaminated anodes. This also enables the use of increased current densities and accordingly increased production capacities. The research depicts the influence of the anode alloy, electrolyte composition, as well process parameters like current density and pH on the electrorefining. The applied electrode potential and therefore the applied current density shows great influence on the dissolution behavior of more noble metals than Ag at the anode. At the cathode, the applied current density influences the co-deposition of less noble metals, such as Cu. This phenomenon is based on the Nernst equation. The pH of the electrolyte system and thus the acid concentration influences the solubility behavior of the impurities. This leads to an influence on their concentration in the electrolyte and their co-deposition on the cathode.

2 Introduction

From an economic point of view, it becomes more and more relevant to use less pure electrolyte systems and insert more contaminated anodes into the refining process. This is based on the otherwise high necessary silver stock. Additionally, economic reasons cause an increase in current densities and accordingly an increase in production capacities and a decrease in refining duration. Therefore, the impurity behavior needs to be controlled and influenced during the electrolytic refining process.

Basic electrolysis parameter through which the process can be influenced and controlled are the current density, hence the applied potential on the electrode, the acid concentration in the electrolyte, as well as the anode and electrolyte composition.

The paragenisis of silver in copper ores as well as the use of sterling silver as main jewelry alloy leads to high Cu contents in the crude silver anodes. Moreover, the use of silver palladium alloys in electrics and electronics leads to increasing Pd contents in the crude anodes. This explains the main impact these two elements have on the electrorefining and specifies the vital importance of considering their behavior and impact in the electrorefining process. Furthermore, the electrochemical similarity of Ag and Pd can lead to further economical disadvantages. The Pd content in the electrolyte needs to be monitored precisely in order to not be deposited on the cathode and therefore be handled as a loss. This research therefore identifies possible parameter ranges which allow a high grade silver production with less economic impacts.

3 Background

Electrolysis is a process which can be handled on different complexity levels. There are many parameters that show a great influence on the product. Furthermore, the parameters even have different and/or increased impact due to interdependencies on each other. [1]

Independent of the silver origin, it is indispensable to refine silver electrochemically. This is necessary to produce high grade silver with an impurity content less than 0.01 wt.-%. These grades are needed especially for industrial use purposes. Furthermore, the silver electrolysis enables to separate the contained precious metals such as Au or PGM's. In the electrorefining, the crude silver anodes are dissolved in a nitric acid, silver nitrate solution and the

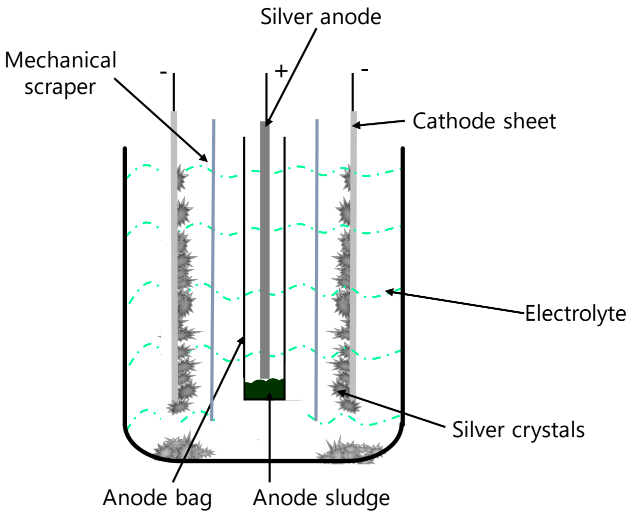

Figure 1 Möbius Silver Electrolysis Cell [8]

fine silver is deposited on stainless steel cathodes. A typical cell arrangement, as shown in figure 1, is the Möbius cell[1]. Operating parameter such as $AgNO_3$ concentration, amperage or electrolyte temperature are set in a way, that ideally the less noble metals (e.g. Cu, Pb) will stay dissolved in the electrolyte. The more noble metals (e.g. Au, Pd, Pt) will not dissolve and pass into the anode slime. The anode slime is collected in anode bags around the dissolving anode. Under optimal conditions, only fine silver (purity > 99.9 %) will deposit on the cathode. An advantageous condition for the electrolytic deposition of Ag is the large potential difference between Ag and Cu (0.5 V). Thus, Cu should theoretically not co-deposit on the cathode. The containing Au and PGM's, however, are either insoluble in the electrolyte or have a too large standard potential and hence remain in the anode slime. Pd though behaves in a slightly different way. The higher the content of Ag in the electrolyte and the lower the current density, the purer is the deposited fine silver. [3, 4, 5, 7, 8, 10, 11, 12]

3.1 Copper Co-Deposition

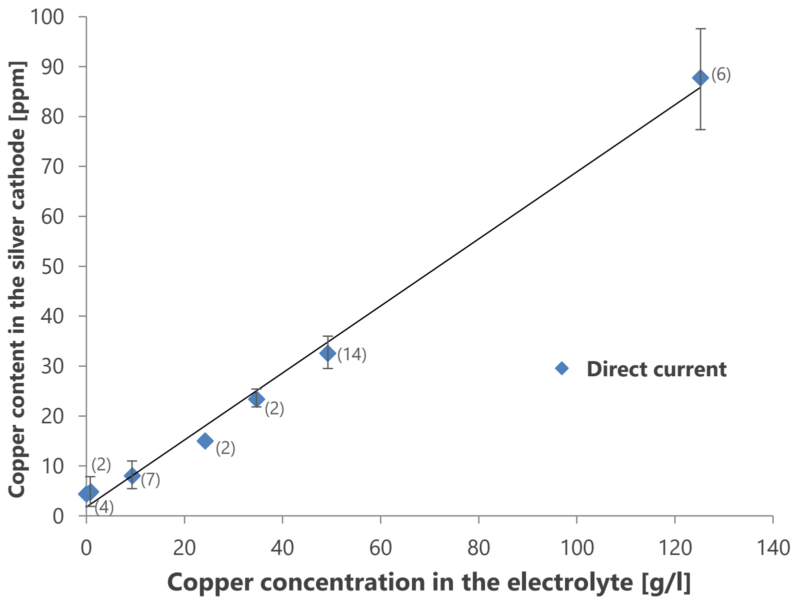

Figure 2 linear correlation of cathodic Cu co-deposition on the Cu concentration in the electrolyte (basic parameter: $c_{Ag} = 100$ g/l, $c_{HNO3} = 1$ g/l, $i_{cathode} = 550 – 600$ A/m^2, $T_{Electrolyte} = 25±1$ °C; set in brackets: quantity of trials to calculate mean value) [17]

Looking at the standard potential of Cu ($Cu/Cu^{2+} = 0.345$ V and $Cu/Cu^{+} = 0.522$ V), it is apparent that during electrorefining of Ag, Cu will mostly dissolve into and enrich in the electrolyte. Partial occurrence of Cu in the anode slime can be detected. This is more or less due to oxidic Cu present in the crude silver anodes. Theoretically, Cu should not be co-deposited on the Ag cathode, even when applying high current densities. Nevertheless, during operation, cathodic Cu co-deposition is always observed. This leads to the necessity of monitoring and controlling the Cu content in the electrolyte. Studies clearly depict a direct correlation of the Cu content in the electrolyte to the Cu co-deposition as shown in figure 2. However, it is also apparent that the electrolytic Cu concentration can rise up to 50 – 100 g/l until it results in a significant Cu deposition (> 50 ppm) on the cathode. This co-deposition on the cathode can either be electrochemically or due to an inclusion of Cu salt in the cathode silver. [2, 3, 13, 15–18, 21]

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[1] The dominant cell type in Europe is the Möbius cell, whereas in northern America and for anodes with high Au contents, the Balbach-Thum cells are preferred. Due to the cell construction, Möbius electrolysis only can handle up to 6-wt. % Au, while anodes containing 20-wt.% Au can be inserted in Balbach-Thum cells. [3, 9]

This shows the need to determine critical limits for Cu in the electrolyte as well as in the anodes due to anodic Cu dissolution. Ag anodes with a high Cu content also lead to high Cu impurity in the cathodes through the enrichment of Cu in the electrolyte (as discussed above). Moreover, in high Cu containing anodes (Cu > 30%, cf. [22]) cementation of Ag from the electrolyte can occur. This cemented Cu collects in the anode slime and therefore leads to Ag losses. Nevertheless, the critical Cu limits basically depend on the required purity of the cathodes. Three basic mechanism can lead to Cu impurity in the cathode based on high Cu contents in the electrolyte:

- electrochemical co-deposition,
- inclusion of Cu containing electrolyte in the cathode crystals,
- hydrolysis reaction[2] of Cu salts and their subsequent precipitation as hydroxide during washing process of the fine silver crystals.

These mechanisms can be applied to all contained less noble elements in the electrolyte. Further studies depict a negligible influence of other electrolyte parameter such as cathodic current density variation (250 – 3000 A/m^2) or the electrolyte temperature on the Cu content in the cathode. [2, 8, 10, 13, 17, 18, 22]

3.2 Palladium Co-Deposition

Pd, however, shows a certain electrochemical similarity to Ag (standard potential 0.810 – 0.830 V). This leads to a definite Pd dissolution into the electrolyte during the electrorefining. Due to the small difference in the standard potential to Ag, small Pd concentrations lead to Pd co-deposition on the cathode. Ag rich electrolytes (min. 60 g/l Ag) as well as low acid concentrations can counteracted to this effect, as Pd (as well as Pt) preferably dissolves in electrolytes with low pH values. When looking at the dependency of the Pd concentration in the electrolyte on the content in the crude anode silver, a direct relation is visible. Plus, the Pd content in the cathode, directly connects to the Pd in the electrolyte. Both phenomena are displayed in figure 3. Research illustrates that even high Pd contents in the anodes (0.05 – 0.27%) do not necessarily lead to high Pd co-deposition. Even with this high Pd concentration, fine silver with < 3 ppm Pd and < 5 ppm Cu can be achieved. This is based on the use of slightly contaminated electrolytes (< 20 mg/l Pd) and high pH values. Studies of Cu-Ni-PGM alloys show, that in these alloys the PGMs occupy atomic places. Therefore, parts of the alloy are more noble than others. This leads to a higher dissolution potential of these parts, than the rest of the crystal. When polarizing anodically, this part accordingly is not dissolved and remains as amorphous and very fine component in the anode slimes (very fine atomic agglomerations without crystalline structure). [2, 13, 17, 24, 25, 20, 23]

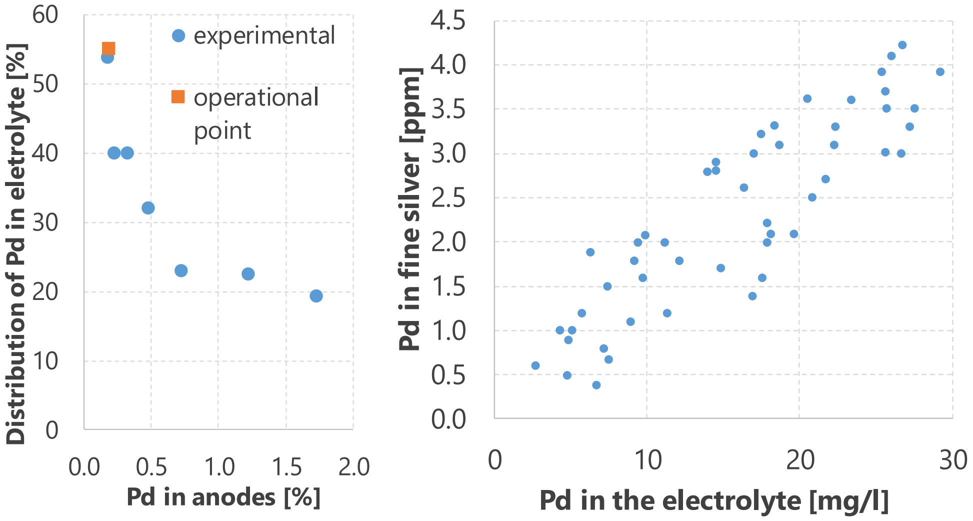

Figure 3 Dependence of the Pd transition into the electrolyte on the Pd content in the anodes (left) and Ag quality depending on the Pd concentration in the electrolyte (right); both [18]

3.3 Process Consideration and Research Strategy

The ultimate goal of the process improvement is to reduce the necessary metal stock while ensuring the required product purity. In silver refining electrolysis, Pd is a challenge which shall not be underestimated as the standard

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[2] Hydrolysis can occur during the washing process of fine silver, and therefore be accordingly eliminated by washing with acidified water followed by washing with a neutral hot water. [17]

potential of Pd (E_0 = 0.987 V) is very close to Ag (E_0 = 0.799 V). Cu accumulates in the electrolyte and is also a challenge due to a co-deposition at the cathode when exceeding certain values that are too high in the electrolyte. Consequently, the electrolyte is continuously checked on the Cu content. When reaching certain limits, the electrolyte is exchanged. During the electrolysis process, the Ag concentration decreases while Cu increases. This offers two alternatives for handling the electrolyte; an entire removal of the electrolyte as soon as the Cu content in the cathode exceeds the specifications or a continuous exchange of part of the electrolyte. The latter results in a more uniform operational management and is therefore the preferable process handling. Cu in the electrolyte has indeed disadvantageous effects on the cathode product purity, but the presence of Cu ions increases the conductivity of the electrolyte. Hence, a certain presence of Cu ions during the process is desirable. This compensates for the loss of conductivity due to the decrease of the silver content (based on the created misbalance when anodically dissolving Cu^{2+}-ions while depositing Ag^+-ions on the cathode). The nitric acid content in the electrolyte should remain constant and the HNO_3 content of the electrolyte should not be too high (approximate value pH of 1.5 to 2.5). Otherwise this can lead to increased dissolution of Pd. [2, 3, 9, 13]

The following table 1 displays an overview on published processing data of industrial silver electrolysis. Based on this table 1, the investigated parameter in this research were defined. The main focus lay on investigating high Cu (up to 100 g/l) and Pd (up to 1.4 g/l) contents in the electrolyte (and for Pd also in the anode) in order to still ensure a high grade silver production with moderate current densities and pH values whilst decreasing the Ag concentration in the electrolyte.

Table 1 Overview on published processing data for industrial silver electrolysis

Reference		**[8]**	**[13]**	**[6]**	**[12]**	**[14]**	**[15]**	**[16]**	**[9]**	**[3]**	**[17]**	**[18]**	**[19]**		**[20]**
i [A/m^2]	**anode**	400	400-500	1000	< 1000					400 – 500		360	500	430	1435 *
	cathode		460-500			300						335			645*
Ag concentration electrolyte [g/l]		50	>60		100 – 150	150	60 – 160		80 – 100	50	100	60	40	130	150 – 200
Cu concentration electrolyte [g/l]			max. 50 – 80			max. 45	60	max 60	5 – 10		15 – 50	3 - 5	35	10	
Pd electrolyte												20 mg/l			
final electrolyte [g/l]		Ag: 50 Cu: 100							Ag: 30 – 40 Cu: 70						
anode mass [kg]		15	3.9 – 4.2	45		21.77 (48 lbs)									12
anodes	**Ag [%]**	98			95 - 99	86 – 92					>99 %				99.30
	Cu	1 %				0,5 – 1									0.4 – 0.6
	Pd					0.16 – 0.18%									68± 19 ppm
	Au [%]	0.50				8 – 9									0.04 – 0.07
Temperature electrolyte [°C]		45			<55	32						45 – 55			35 – 50
pH/ c_{HNO_3}						1 – 1.5	1.5 – 2.5		1 – 20 g/l	10 g/l	1 g/l	5 g/l	3.8	2 g/l	2.5 g/l
Anode rest [%]		5 – 10				15			25						
Current efficiency [%]		95			98 – 99										

* calculated value from amperage and number anodes under the assumption that 60% of the surface are active

4 Experimental Validation

All experiments were conducted in an electrolytic refining laboratory cell, which is displayed in figure 4. The basic parameters are presented in table 2. During the experiments, the acidic concentration, the anodic current density and the Ag-, Cu- and Pd-concentration in the electrolyte as well as the Pd- concentration in the anode was varied. The main idea was, to increase the maximum Cu and Pd content in the electrolyte, as well as the maximum Pd content in the crude silver anodes. The main goal was to still produce high grade silver (> 99.9%) even with the stated unfavorable conditions.

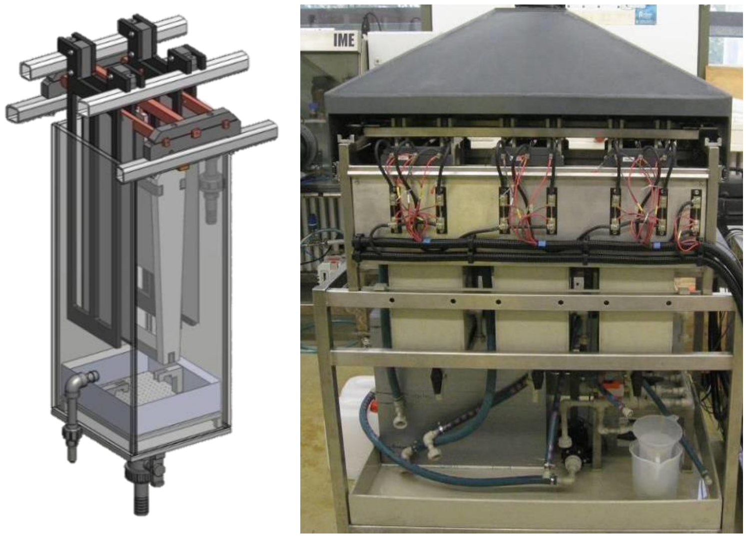

Figure 4 Laboratory Ag electrorefining cells (3 cells in total) at IME Aachen

Table 2 Basic parameter

Parameter	**Value**	**Electrolyte composition (varied values)**		**Anodic composition**	
Anodes/cathodes per cell	1 / 2	Ag	65 – 120 g/l	Ag	96.5%
$V_{electrolyte}$ per cell	~ 27 l	Cu	45 – 98,6 g/l	Cu	3%
electric charge per cell & trial	~ 580 Ah	Pd	0 – 1 g/l	Pd	0.05% (varied 0.01-0.1%)
Cathodic current density	335 – 535 A/m^2	HNO_3	0.6 – 10 g/l	Au	0.01%
Other Parameter					
Anodic current density	500 – 800 A/m^2	electrode distance anode-cathode	70 mm		
End of trials approx. i_A	660 – 1060 A/m^2	Active anode surface*	25.7x 10 x 2 cm		
Cathode active surface	15.6 cm x 30.5 cm	Electrolyte temp.	35 °C		
Cathode material	Stainless steel				

5 Results and Discussion

Taking into consideration the studied impurities Cu and Pd in Ag anodes, ideally Cu should dissolve and enrich in the electrolyte whereas Pd should be insoluble and pass completely into the anode slime.

Figure 5 presents the Pd concentration in the anode slime depending on different electrolyte compositions (with unvaried Pd impurity in the used anodes). The Pd content in the anode slime shows a significant dependence on its concentration in the electrolyte. Whereas the Cu content in the anode slime also shows a dependency on the Pd concentration in the electrolyte. With increasing Pd concentration in the electrolyte, the Cu content in the anode sludge decreases. Consequently, one can assume that palladium is anodically dissolved parallel to the Ag during electrolysis. Subsequently it reacts through cementation with the metallic Cu (or even Ag) present in the anode sludge according to the equation below. The structure of the anode sludge supports this assumption, since Cu only appeared as metal in the anode sludge.

$$\mathrm{Pd}^{2+}_{\mathrm{electrolyte}}+\mathrm{Cu}^{0}_{\mathrm{anode\ sludge}}\rightarrow\mathrm{Pd}^{0}_{\mathrm{anode\ sludge}}+\mathrm{Cu}^{2+}_{\mathrm{electrolyte}}$$

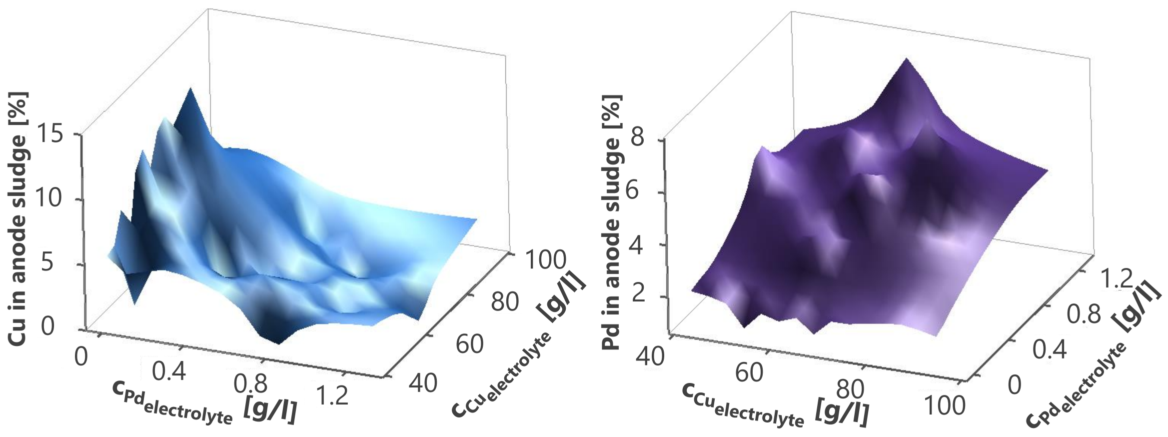

Figure 5 Illustration of Cu (left) and Pd (right) content in the anode slime as a function of Cu and Pd electrolyte concentration (Ag influence on Cu and Pd anode sludge concertation was negligible at this point)

The subsequent figure 7 shows this dependence of the Pd and Cu content in the anode sludge on the Pd concentration in the electrolyte, without taking into account the concentrations of Cu and Ag in the electrolyte. In this diagram, the discussed influence becomes even more apparent.

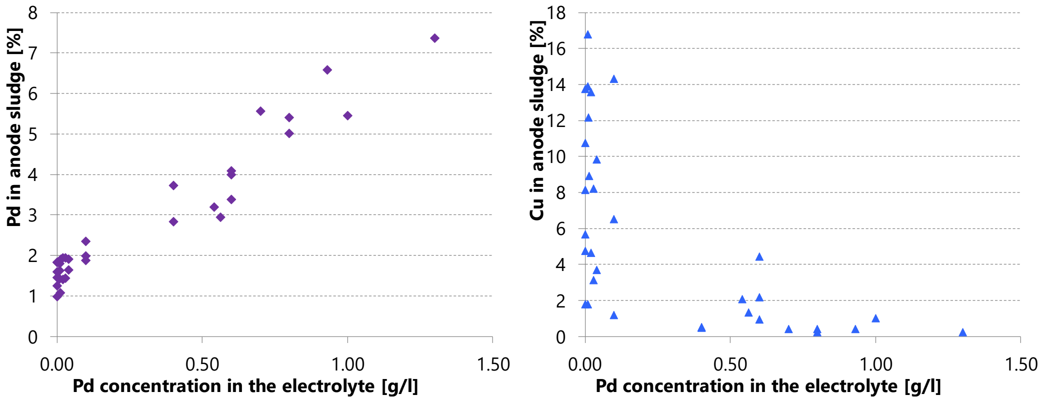

Figure 7 Influence of Pd concentration in the electrolyte on the Pd (left) and Cu (right) content in the anode slime

With an increasing Ag concentration in the electrolyte, it basically can be observed, that the Cu co-deposition slightly decreases. An increasing Cu concentration in the electrolyte on the other hand leads to a slight increase in Cu co-deposition. If only the dependence of the Cu concentration in the produced fine silver on the Cu content in the electrolyte is applied, the figure 6 can be generated. With increasing Cu concentration in the electrolyte, a tendency of increasing Cu concentration in the cathode can be seen, regardless of the Ag electrolyte concentration. It is also apparent, that this is not a distinct linear dependency, rather a co-influence with the Ag electrolyte concentration. Whether the Cu concentration in the cathode is based on electrochemical deposition or rather based on electrolyte inclusions, cannot be clarified. Investigations of fine silver crystals via microprobe and SEM analysis were not able to identify whether Cu electrochemically alloyed in the silver matrix or was present as electrolyte inclusion. This is due to the detection limits of the used analysis and the low Cu contents reached in the fine silver (< 100 ppm).

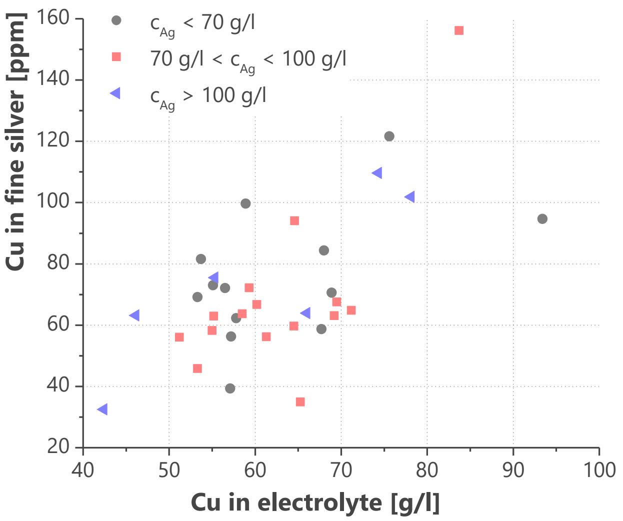

Figure 6 Influence of the Cu concentration in the electrolyte on the Cu content in the fine Ag in electrolytes containing 60 – 100 g/l of Ag (parameter: c_{HNO3} = ~ 3 g/l, i_a = 700 A/m^2)

The effect of the Pd content in the anode on the Pd and Cu concentration in the produced fine Ag as well as the electrolyte concentration is presented in figure 8. It is noticeable that elevated Pd contents in the anode lead to both increased Pd and Cu concentrations in the produced fine silver. This is based on the effect that an elevated palladium content in the anode should increase the anode potential. This causes a higher cathode potential and thus an increased deposition of Cu and Pd. Moreover, Pd contents > 1 g/kg in the anode (green in figure 8) lead to higher Pd contents in the electrolyte (>0.5 g/l) and therefore also in the fine silver due to the dependency of the activity on the concentration of Pd in the electrolyte.

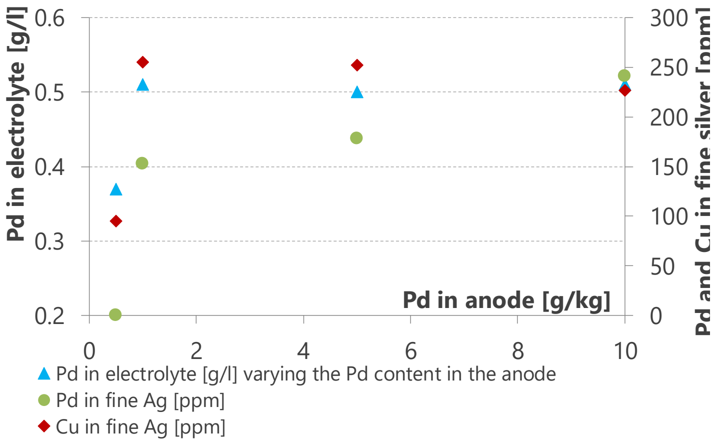

Figure 8 Fine silver composition as well as palladium concentration in electrolyte depending on the Pd content in the anode

Figure 9 shows the generated results of the experiments dealing with the influence of the current density and the acid concentration on the Pd co-deposition. It can be seen that the acid concentration in the electrolyte is the main influence factor. Consequently, a higher acidity results in an increased Pd co-deposition on the cathode. This is based on the strong dependence of the Pd solubility in the electrolyte on the p. The higher the acid content is, the greater concentrations of palladium in the electrolyte are reached. It can be concluded accordingly that the acidity is more or less an indirectly relevant parameter, whereas the palladium concentration in the electrolyte is crucial for Pd co-deposition. The anodic current density on the other hand tends to show a minor influence. Based on these results in order to not exceed critical Pd contents in the fine silver, the acid concentration generally should not extent 7 g/l.

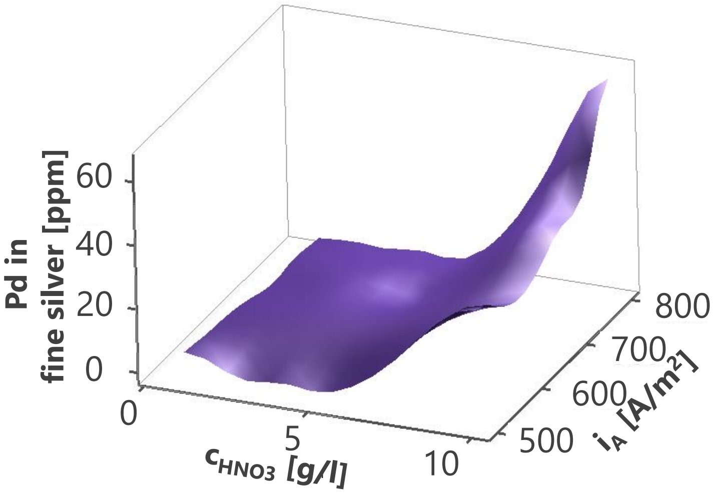

Figure 9 Pd co-deposition dependent on the anodic current density and acid concentration

6 Conclusion

Concluding all test parameters, with respect to their influence on the copper content in produced the fine silver, the following figure 10 can be obtained. It is distinct that, although the copper concentration in the electrolyte is a non-negligible factor, an elevated palladium content in the anodes and a high acidity as well as high current densities also adversely affect the copper co-deposition. At least when the copper and silver concentrations in the electrolyte are almost at an equal level. This leads to the general conclusion, that in order to ensure low copper levels in the produced fine silver, the palladium content in the crude anodes should not be too high. Moderate current densities (i_a up to 600 A/m^2) and acid concentrations enable to operate electrolytic refining of silver with copper contaminated electrolyte without jeopardizing the silver quality.

Overall, the experimental results demonstrate, that the pH of the electrolyte system shows a great influence on the behavior of Pd. At least in a range of anodic current densities from 500 – 800 A/m^2 and a nitric acid concentration from 1 – 10 g/l. Consequently, it is indispensable to monitor the pH for an electrolyte refinery if the production rate and thus the current density shall be increased. However, monitoring and controlling the pH is a complex topic especially on a production site. One possibility is to add a manual acidic concentration titration in the electrolyte analysis. In order to continuously monitor the pH, an electrolyte resistant pH electrode can be included into the electrolyte flow streams.

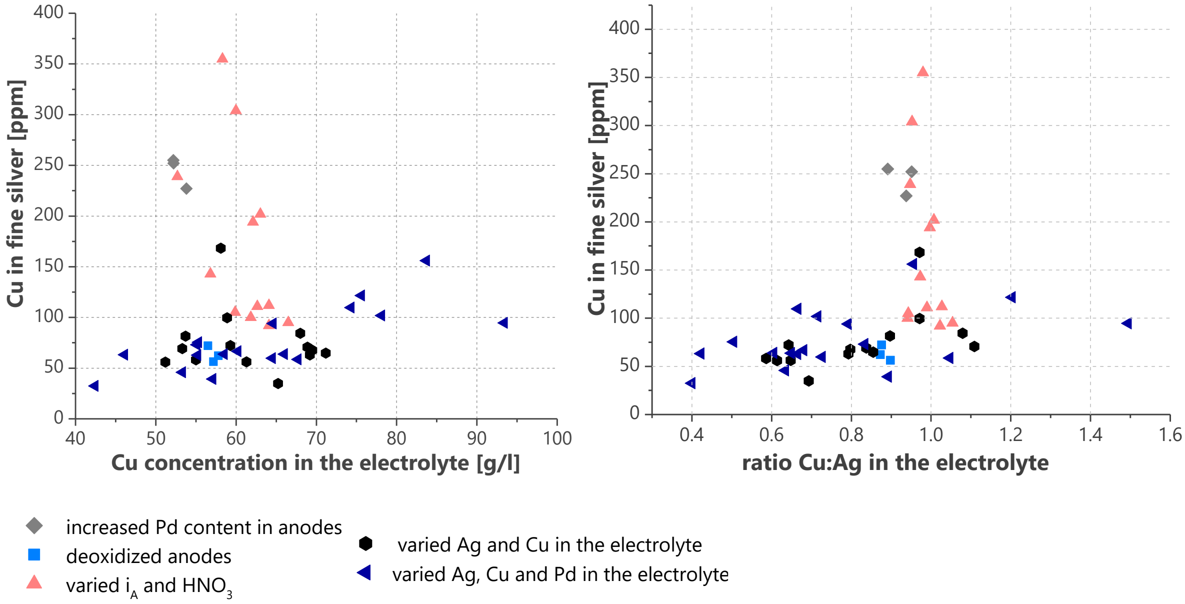

Figure 10 Influence of the copper concentration in the electrolyte (left) and of the copper to silver ratio in the electrolyte (right) on the copper content in the fine silver as a function of the varied experimental parameters

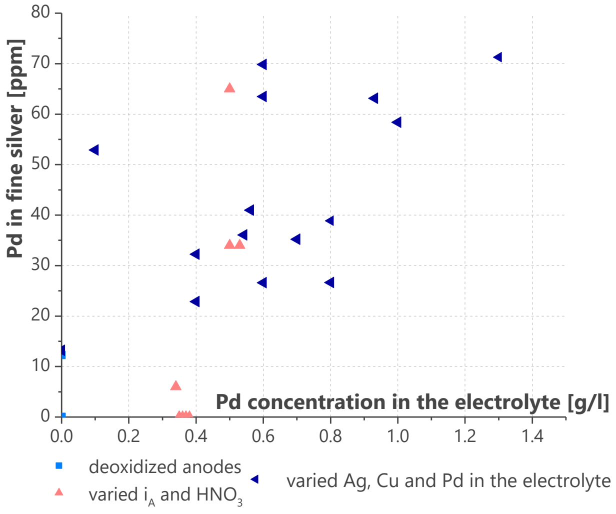

Figure 11 Influence on the palladium content in the fine silver depending on the palladium content in the electrolyte as well as the acid concentration

As exemplified above, one of the main influence parameter on a palladium co-deposition is the palladium content in the crude anode. Concluding the varied parameter, figure 11 is prepared. This figure does not consider an elevated palladium anode concentration in order to identify other influencing parameter. Therefore, figure 11 prevails dependencies of the palladium content in the produced fine silver as a function of the palladium concentration in the electrolyte and therefore also the pH.

These results furthermore indicate that monitoring the palladium content in the anode and the electrolyte, as well as the acidity are essential for controlling the behavior of palladium. Ensuring low acid concentrations and thus higher pH during the refining, process lead to low palladium co-deposition. If, however, heavily palladium contaminated anode shall be inserted in the process, the use of separate anode and cathode chambers as a suggestion can be recommended. To avoid the contact of palladium-rich electrolyte and the cathode altogether, an intermediate palladium precipitation from the anolyte and a fine filtration is suggested. Afterwards this purified electrolyte can be supplied as a catholyte in the cathode chamber.

This research study is part of the authors dissertation thesis “Behavior of Copper and Palladium in the Electrolytic Refining of Recycling Silver”, to reach the academic degree Dr.-Ing.

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