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Sustainable development in the tinplate industry: refining tinplate leachate with cementation

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Abstract: Tin sludge produced during tin electroplating of steel sheet is an interesting secondary source of tin. Dried sludge usually contains more than 50% tin. Hydrometallurgical sludge treatment consists of several steps, including leaching in hydrochloric acid and electrolytic recovery of tin. The electrowinning process is negatively affected by the presence of impurities such as antimony and bismuth, which can cut overall current efficiency to 11% as well as reducing the quality of recovered tin. It is appropriate therefore to remove these impurities from the leachate before the electrowinning steps. This work studies the refining of leachate using cementation. The experiments were carried out at temperatures of 20, 40 and 60 °C at solid to liquid ratios of 1:60, 2:60, 3:60 and 4:60 using tin and iron dust as cementing metals. The leachates were mixed at a constant rate of 400 rpm during all cementation experiments. Effective removal of impurities was achieved in the case of iron powder cementation at s/l ratio 2:60 and temperature 20 °C. This cementation removed 98.49% bismuth and 99.14% antimony from the leachate solution. Electrolysis efficiency was increased from 11 to 71% after leachate refining. Antimony and bismuth were not detected in the final product obtained from refined electrolyte by means of electrolysis.

Keywords: tin sludge, recycling, hydrometallurgy, cementation, electrolysis

1. Introduction

An essential part of industrial activity is the processing of by-products, including waste. Ideally, waste is generated in a form which allows it to be reused in the process as returnable waste. However, there are also cases where the phase composition makes its use impossible without the application of additional chemical procedures. This type of waste includes sludge formed during the electrolytic tin plating of steel sheets. Tin is an economically important metal in the present day and is used mainly as solder (48%), in chemicals (18%), tinplate (14%) and alloys (5%) (International Tin Association, 2018). The EU consumes up to 55,500 tonnes of refined tin each year, but only 11,500 tonnes is produced locally and the rest is imported, predominantly from Indonesia (35%) and Peru (24%). Such import reliance for refined tin, which is currently at 78%, poses a risk to the sustainable development of EU countries (European Commission, 2017). This risk can be reduced by implementation of circular economy systems in the sectors where tin-containing municipal and industrial waste is generated.

Recovery of tin from municipal waste is relatively successful. The recycling rate for tinned food and beverage cans is 65%. Selective recovery of tin from waste tinned sheets is possible with reverse electroplating (Kékesi et al., 2000). A more complicated type of waste with tin content of about 4% is waste electrical and electronic equipment (WEEE). There is widespread research in the WEEE area, in which the recycling rate of tin is 40%, focusing on hydrometallurgical methods (Cui and Zhang, 2008; Zhang and Xu, 2016; Lundstrom et al., 2017; Willner et al., 2018) with better metal selectivity, but currently industrially-applied methods consist mainly of pyrometallurgical methods. The rate of tin

recovery from other secondary sources is unknown, but the overall rate is 30%. This points to the fact that tin is recovered from industrial wastes less efficiently, which is also reflected in the lower proportion of scientific publications on this topic (European Commission, 2017). Tin-containing industrial wastes comprise dusts and slags from copper production, tin-containing waste water and slags from tinplating processes. Tin recovery has been studied based on copper dust with tin content between 0.4 - 30% (Gudorf et al., 1996), slags with tin content between 0.38 - 0.8% (Soewarno et al., 2014) and industrial water Fe-Sn precipitates by means of leaching in concentrated HCl at low temperatures (Fröhlich et al., 1998).

With tin content up to 60%, tin sludge is a very interesting industrial waste (Urban Kobialkova et al., 2017). This sludge is formed during electrolytic tin-plating of steel sheets. The tin contained in the tinplate solution is gradually oxidized in contact with atmospheric oxygen, and the tin oxides thus recovered settle and are collected at the bottom of the electrolytic cell.

Due to the lower quantities in which this waste is generated, smaller scale and more selective hydrometallurgical treatment methods seem to be more appropriate. Hydrometallurgical treatment consists of leaching, in which tin oxides are leached in HCl (Stefanovicz et al, 1991 and Jumari et al., 2018) or in NaOH (Kawamura et al., 2000), and subsequently tin is electrolytically extracted from the obtained solutions. Problems with this recycling process appear when the sludge contains undesirable impurities such as antimony and bismuth. The presence of these metals negatively affects the purity of the obtained tin and causes complications in electrolytic deposition, where electrode passivation causes significant electrical losses.

In scientific publications there is a lack of information from the study of the removal of antimony and bismuth impurities from tin-containing solutions, and the effects of these impurities on the electrolysis of tin from solution. For that reason, this work studies leachate refining possibilities in order to reduce the negative effect of these impurities in the electrowinning process. Cementation was chosen as the solution-refining method. The effects of different cementing metals, solid to liquid ratios and temperature on impurity removal efficiency were studied. In addition, the use of cementation also allows the selective recovery of antimony and bismuth, which are considered as critical raw materials for the EU, from solid residues after cementation.

2. Materials and methods

2.1. Analytical methods

The chemical composition of input samples, intermediates and products was determined using the AAS method on a Varian Spectrometer AA20+, XRD phase analysis was performed on a PANalytical X'Pert PRO 360 and SEM-EDX analysis was performed on a Mira3 TESCAN. Optical observations were made on a Dino-Lite MZK 1701 digital microscope with 195x magnification.

2.2. Input material

The leachate was obtained by leaching dried and crushed tin sludge (Fig. 1) in hydrochloric acid. The chemical composition of the tin sludge is shown in Table 1.

Optimal leaching conditions for the given type of waste were determined in the previous study for leaching in 4 M HCl at 70 °C for 5 hours and stirring at 300 rpm at a solid to liquid ratio (s/l) of 1:20. More than 99.9% of the tin present in the sludge was leached under these conditions. The chemical composition of the leachate is shown in Table 2 (Urban Kobialkova et al., 2017).

2.3. Cementation

Cementation allows leached metals to be reduced from solutions with higher redox potential by contact with a solid metal with lower redox potential. Comparison of the oxidation-reduction potentials of individual metals is shown in Table 3 (Wright, 2007).

Cementation experiments were carried out in a glass reactor placed in a heated water bath. Tin powder (purity 99.9%, particle size -71 µm) and iron powder (purity 99.9%, particle size -45 µm) were used as cementing metals at s/l ratios of 1:60, 2:60, 3:60 and 4:60. Experiments were performed at 20, 40 and 60 °C. The solutions were stirred at 400 rpm for a period of 60 minutes. The second series of experi-

Table 1. Chemical composition of tin sludge analyzed using AAS (Urban Kobialkova et al., 2017)

Element	Sn	Fe	Zn	Cu	Pb	Ni	Sb	Mg	Bi
Content [%]	63.20	0.57	0	0.07	0	0	0.75	0.06	0.58

Table 2. Chemical composition of the solution after tin sludge leaching

Element	Sn	Fe	Sb	Bi
Concentration [g/dm ³]	31.808	0.4182	0.352	0.153

Table 3. Comparison of oxidation-reduction potentials of individual metals (Wright, 2007)

Ga < Fe < Cd < In < Tl < Co < Ni < In < Sn < Pb < W < H ₂ < Mo < Ge < Sb < As < Bi < Cu

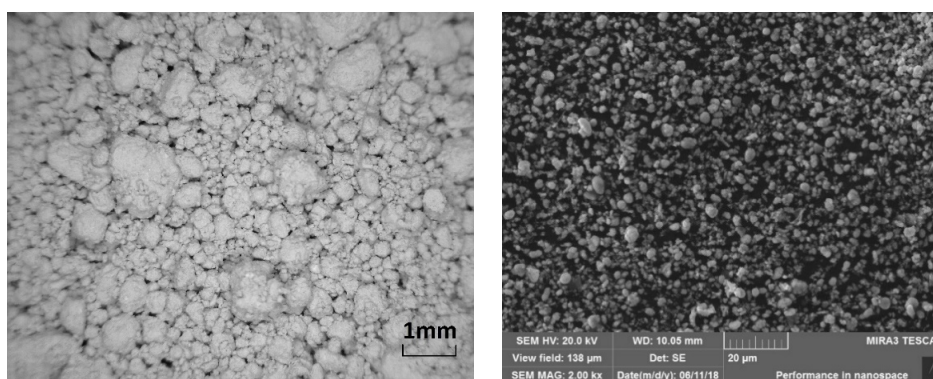
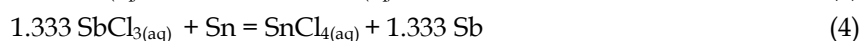
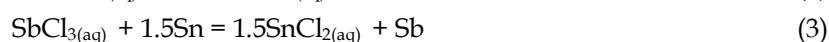
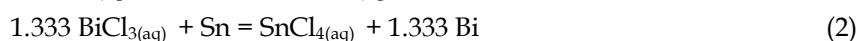
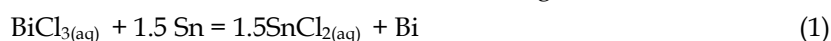


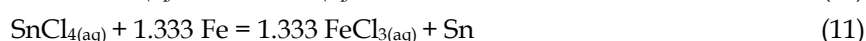
Fig. 1. Optical observation of tin sludge

ments was carried out using iron dust only at 20 °C and the sampling time during this experiment was 10 minutes with an overall duration of 60 minutes.

Cementation process using tin and iron can be described with the following reactions:



During cementation with iron powder, cementation of tin can occur according to reactions (9) – (12), each of which involves tin losses.



2.4 Electrolysis

Synthetic solution, obtained leachate and leachate after cementation were used as electrolytes in these electro-winning experiments. A platinum anode was statically placed while a copper cathode was hung on weighing scales for continuous measurement of the weight changes. Electrolysis experiments with a

total length of 1000 seconds were carried out at 25 °C, a constant current of 0.2 A, stirring at 300 rpm, distance between electrodes 1 cm and submerged cathode area 2 cm².

3. Results and discussion

For efficient electrolytic recovery of tin, it was necessary to remove the antimony and bismuth from the solution, which were leached together with the tin in the preceding tin sludge leaching process. These metals are reduced before tin because of their higher oxidation-reduction potential, which causes a decrease in electrolysis efficiency and in the purity of the tin obtained. For the purpose of removing antimony and bismuth from the solution, cementation was chosen as a cheap and technically less difficult method.

3.1. Cementation

The calculated cementation efficiencies from the comparison of solutions using AAS analysis before and after cementation at 20, 40 and 60 °C and 1:60, 2:60, 3:60, 4:60 s/l ratios for tin dust are shown in Table 4 and for iron dust in Table 5.

The results of both types of cementation indicate that increasing the amount of cementing metal, increasing the total surface on which the substitution reactions of cementation can take place, and raising the temperature have positive effects on antimony and bismuth removal efficiency.

Table 4. Efficiency of tin powder cementation: 60 minutes, 400 rpm

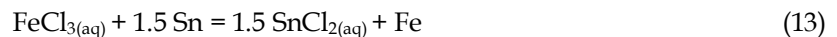
Temperature [°C]	s/l ratio	Cementation efficiency					
		Sb [mM]	Bi [mM]	Fe [mM]	Sb [%]	Bi [%]	Fe [%]
20	1:60	2.67	0.60	4.19	28.08	23.84	29.40
	2:60	0.59	0.09	5.02	84.21	88.50	15.50
	3:60	0.27	0.04	5.30	92.75	95.49	10.73
	4:60	0.33	0.09	5.34	91.17	88.99	10.07
40	1:60	3.48	0.38	4.88	6.27	52.54	0
	2:60	0.32	0.42	5.94	91.51	47.51	0
	3:60	0.01	0.01	5.94	99.62	98.26	0
	4:60	0.01	0.00	5.94	99.63	99.98	0
60	1:60	3.71	0.44	5.94	0.07	44.37	0
	2:60	0.03	0.44	5.94	99.25	44.95	0
	3:60	0.01	0.00	5.94	99.65	99.99	0
	4:60	0.01	0.00	5.94	99.74	99.99	0

Table 5. Efficiency of iron powder cementation: 60 minutes, 400 rpm

Temperature [°C]	s/l ratio	Cementation efficiency				Sn losses	
		Sb [mM]	Bi [mM]	Sb [%]	Bi [%]	[mM]	[%]
20	1:60	0.71	0.37	85.89	60.74	261.14	2.39
	2:60	0.04	0.01	99.14	98.49	256.93	3.98
	3:60	0.05	0.01	99.06	99.2	245.14	8.38
	4:60	0.06	0.01	98.77	98.84	238.23	10.96
40	1:60	0.09	0.00	97.54	99.97	287.42	3.6
	2:60	0.10	0.01	97.22	98.94	273.94	5.97
	3:60	0.09	0.01	97.5	99.03	254.40	11.56
	4:60	0.11	0.01	97.17	98.91	262.49	16.48
60	1:60	0.06	0.00	98.43	99.99	282.54	4.1
	2:60	0.01	0.00	99.65	100	276.81	6.8
	3:60	0.01	0.00	99.79	100	261.81	14.35
	4:60	0.00	0.00	99.93	100	304.94	21.65

The advantage of tin powder cementation is that no other contaminants are added to the solution. The results show that the use of low weight of cementing tin powder does not effectively remove antimony or bismuth from the solution. For effective removal a minimum of 3 g per 60 cm³ solution must be used at 40 °C. The disadvantage of this process is that a large part of the cementing metal is released into the solution due to leaching, and not only due to the substitution reaction of cementation. Although the concentration of tin in the solution is increased by leaching, this process is inefficient as it is necessary to use at least 3 g of pure tin dust, with only 1.86 g of tin leached from tin sludge in the solution. Another disadvantage of using tin as a cementer is its high cost. For these reasons, refining this particular leachate with tin powder proved unsuitable, and in our further research iron powder cementation was studied.

The behavior of iron in solution during tin dust cementation can be described with reaction (13). From the values of standard Gibbs free energy it follows that the reaction has probability and that decrease in the iron content in the solution could occur. Subsequently, iron is leached again into the solution according to reaction (14).



$$\Delta G^{\circ}_{293} = -48.374 \text{ kJ.mol}^{-1}; \Delta G^{\circ}_{313} = -55.467 \text{ kJ.mol}^{-1}; \Delta G^{\circ}_{333} = -62.540 \text{ kJ.mol}^{-1}$$



$$\Delta G^{\circ}_{293} = -44.048 \text{ kJ.mol}^{-1}; \Delta G^{\circ}_{213} = -47.562 \text{ kJ.mol}^{-1}; \Delta G^{\circ}_{233} = -51.516 \text{ kJ.mol}^{-1}$$

Iron powder cementation is advantageous because of its lower cost. In the following electrowinning process, there is no Fe²⁺ to Fe⁰ reduction on the surface of the cathode because its reduction potential (E° = -0.44 V) is lower than that of Sn²⁺ to Sn⁰ (E° = -0.14 V). That means that the purity of the tin recovered should not be affected by the presence of iron in the solution.

Although the purity of the products is not affected, the presence of Fe³⁺ ions can reduce the current efficiency of the process. Oxidation of Fe²⁺ to Fe³⁺ ions may be caused by the presence of dissolved oxygen in the solution and/or by the reaction of iron oxidation at the anode during electrolysis. The Fe³⁺ ions are then reduced on the cathode surface to Fe²⁺ ions. The reduction potential (E° = +0.77 V) of this reaction is higher than that of tin, which decreases the current efficiency of the electrolysis.

In the case of iron powder cementation, it is necessary to find conditions in which antimony and bismuth are removed, but tin remains in solution. Effective removal of impurities from the solution was achieved at ambient temperature using 2 g per 60 cm³ solution. Tin losses under these conditions were 3.98%, antimony removal efficiency 99.14%, and bismuth removal efficiency 98.49%.

By comparing iron dust morphology before cementation (Fig. 2) and after cementation (Fig. 3), the formation of new cemented phases can be observed. According to SEM-EDX analysis the phases on the surface of the iron powder consist mainly of antimony (41.7%) and bismuth (22.4%). It is also possible to observe some cementation of tin, which is undesirable and corresponds to tin losses.

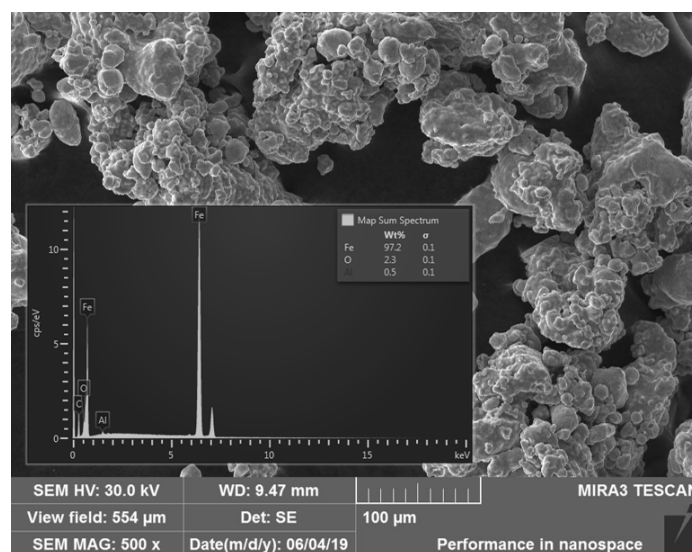


Fig. 2. Morphology and SEM-EDX analysis of iron dust before cementation

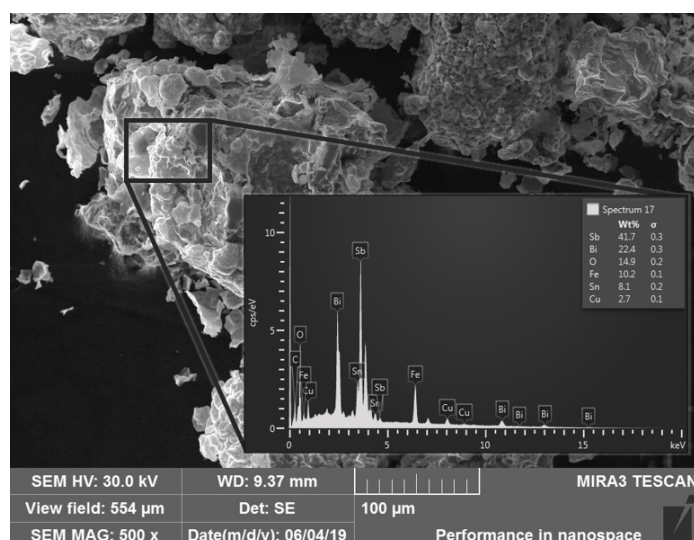


Fig. 3. Morphology and SEM-EDX analysis of iron dust after cementation

In the next step of the cementation process study, experiments were carried out with iron powder only at 20 °C with sampling at 10 minute intervals with a total duration of 1 hour. The effectiveness of bismuth and antimony removal from solution after the individual time intervals is shown in Fig. 4.

The results confirm that 60 minutes of cementation with iron dust at s/l ratio 2:60 and ambient temperature were suitable conditions for removing impurities from the solution. The antimony removal rate from the solution in the first 30 minutes of cementation was higher than in the case of bismuth due to its higher initial concentration. Most antimony was removed after 50 minutes of cementation, but the bismuth was removed after 60 minutes. A comparison of the metal concentrations in the solution before and after cementation is shown in Table 6.

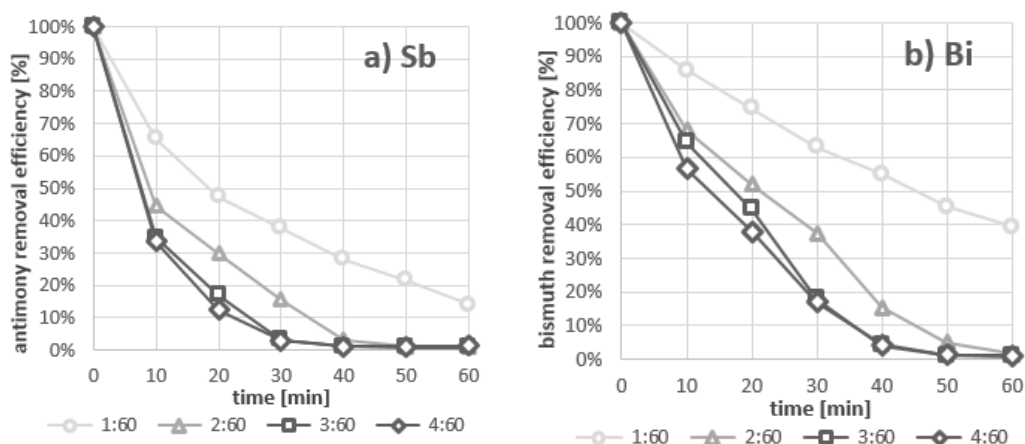


Fig. 4. Efficiency of removal of antimony (a) and bismuth (b) from solution in time at 20 °C

Table 6. Chemical composition of solution after tin sludge leaching and after cementation

Analyte	Sn [g/dm ³]	Fe [g/dm ³]	Sb [g/dm ³]	Bi [g/dm ³]
Solution before cementation	31.8	0.418	0.352	0.153
Refined solution [Fe 2:60, 20 °C]	30.5	3.260	0.005	0.003

3.2. The effect of leachate refining on electrolysis efficiency

Electrolysis experiments were performed in two phases of research using three different electrolytes. The first phase was carried out before the study of solution refining by means of cementation. In these

electrolysis experiments, the use of synthetic electrolyte with comparable tin content without the other undesirable ingredients was compared with electrolysis where tin sludge leachate was used as electrolyte.

Fig. 5 shows a comparison of deposit weights for individual electrolytes at the time from which current efficiency was calculated. While electrolysis using synthetic solution achieved current efficiency of 58% calculated from Faraday's Law (Fig. 6a), electrolysis using leachate achieved only 11%. Due to the higher standard reduction potential of Sb and Bi compared to Sn, these impurities were reduced from the electrolytes prior to tin, causing cathodic passivation (shown in Fig. 6b), and thereby preventing further recovery of tin from the solution. Due to the low current efficiency and reduced purity of the products obtained, the previously-mentioned cementation study was carried out. After the refining study, electrolysis experiments were carried out in the second phase, in which a refined solution was used as the electrolyte, and the current efficiency achieved during this electrolysis was up to 71%. The current efficiency increase resulted from improved electrolyte conductivity due to the presence of Fe ions. On the other hand, the higher current efficiency was not achieved due to oxidation of Fe^{2+} to Fe^{3+} at the anode followed by the reduction of Fe^{3+} back to Fe^{2+} at the cathode.

Increased electrolysis current efficiency can be achieved by increasing the tin concentration in the solution. This can be done by leaching additional sludge with the obtained solution, or by changing s/l ratios in the previous leaching step.

XRD analysis of the electrolytically-obtained tin, shown in Fig. 7, confirms the single Sn^0 phase present. Tin was also analysed by means of AAS, which confirmed that antimony and bismuth were not present in the final product.

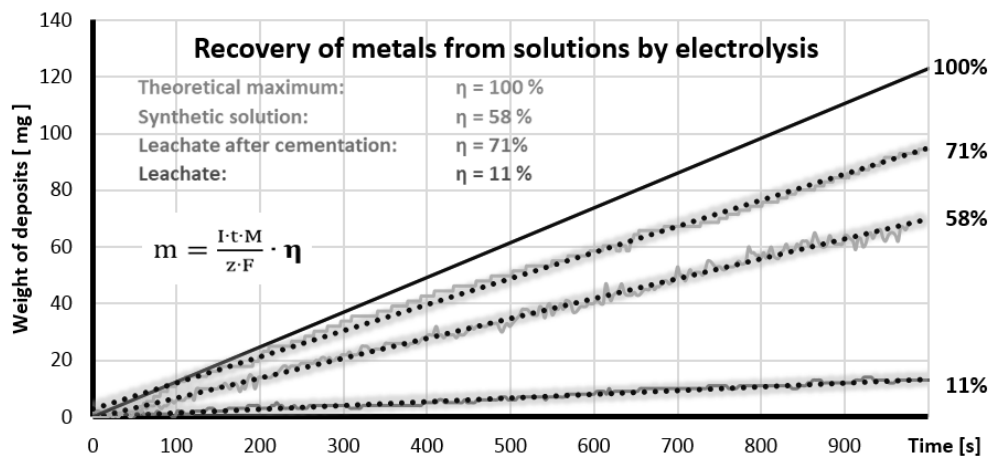


Fig. 5. Cathode weights and current efficiencies of electrolysis using different solutions

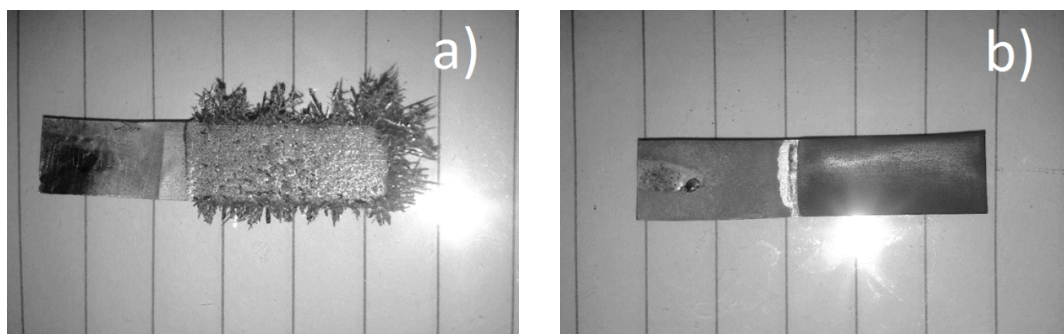


Fig. 6. Optical observations of cathodes after electrowinning using different electrolytes a) synthetic solution, b) leachate before cementation

4. Conclusions

Tin sludge from the electrolytic steel sheet tinning process is an interesting secondary raw material due to its high tin content. In the hydrochloric acid leaching step, impurities such as antimony and bismuth

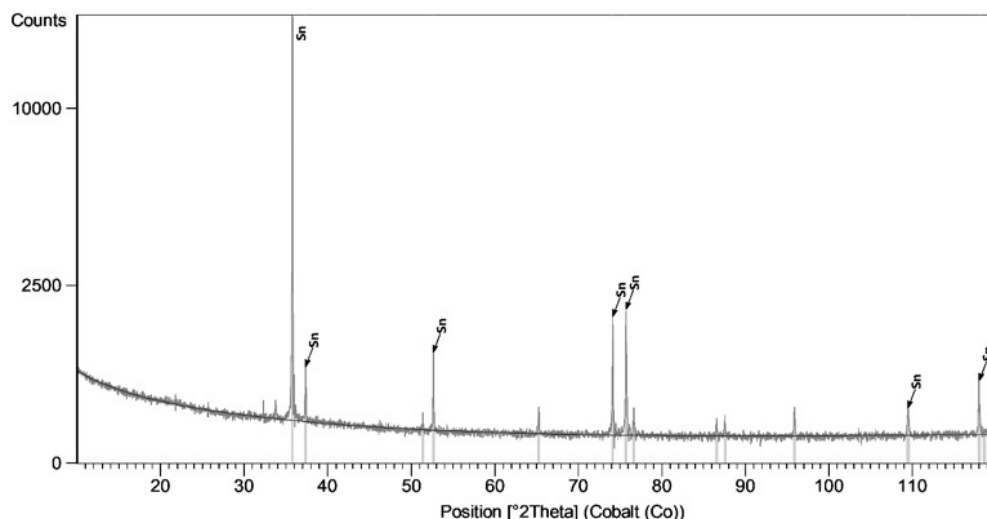


Fig. 7. XRD phase analysis of recovered tin product obtained by electrowinning

are also leached into the solution, which in the next electrolytic deposition step reduces the purity of the tin obtained and the current efficiency of the electrolysis. In this study, the possibilities of refining solutions with cementation after leaching tin sludge were investigated. The experiments revealed the following:

- Increasing the amount of cementing metal and increasing the cementation temperature increases the removal efficiency of Sb and Bi.
- Cementation with tin dust is advantageous because the metal coming from the cementer into the solution does not bring with it any further undesirable impurities.
- In the case of cementation with tin powder at low temperature, iron is also removed from the solution.
- To effectively remove Sb and Bi with tin dust, it is necessary to use up to 3 g for 60 cm³ of solution at 40 °C, whereas only 1.86 g of tin is present in the leachate from the given volume. This means that more tin powder needs to be used for successful leachate refining.
- Iron powder cementation is advantageous because of its low cost, and its presence in solution after cementation does not cause a problem in the next electrowinning steps.
- During cementation with iron dust there is also unwanted removal of tin from the solution.
- Effective removal of impurities from the solution was achieved at ambient temperature using 2 g iron dust per 60 cm³ solution. Tin losses under these conditions were 3.98%, antimony removal efficiency 99.14%, and bismuth removal efficiency 98.49%.
- Due to the removal of impurities by means of iron powder cementation, electrolysis current efficiency was increased from 11% to 71% at a constant current of 0.2 A
- The achieved current efficiency of 71% should be further increased, and thus it is necessary to conduct a separate study for determination of optimum electrolysis conditions, where potentiostatic electrolysis would be performed with applying of tin reduction potential increased by the necessary overpotential.
- XRD of the metal obtained identified tin in metallic form as a single phase, and AAS analysis determined contents of antimony and bismuth below detection level.
- The tin recovered can be used again as a tinplate anode, which closes the loop of the circular economy and promotes sustainable development in the tinplate industry.

Acknowledgments

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