

LEACHING BEHAVIOR OF THE ANODE SLIME GENERATED BY THE ELECTROREFINING OF Sn-Ag-Cu ALLOYS

Zoltán Harangi¹, Gábor Nagy², Tamás Kékesi³

¹MSc student, ²PhD student, ³Professor,

Faculty of Materials Science and Engineering, University of Miskolc, Hungary;

kekesi@uni-miskolc.hu

ABSTRACT

The waste material produced in lead-free wave soldering is melted, skimmed and cast into anodes. Anode slime, the by-product of electrorefining in hydrochloric solutions is collected and the basically undissolved silver and copper constituents are removed by selective leaching. The first step is the elimination of metallic tin using HCl of high concentration and temperature, followed by the leaching of the nobler metallic components in HNO₃ under similar conditions. Kinetic study on the leaching behavior of the raw anode slime in both media has shown the optimum conditions. The metallic tin content of the anode slime can be dissolved virtually completely in 10 M HCl at the highest possible temperature of 85 °C, however it takes about 3 hours. On the other hand, silver can be quickly dissolved in about 15 minutes by applying approx. 50% HNO₃ at 90 °C. Combination of the two steps in this order can result in an efficient recycling of the slime by producing relatively pure SnCl₂ and AgNO₃ solutions, respectively. The tin content can be recycled conveniently to the tin electrolysis and the silver containing solution can be used for recovering silver by electrowinning or precipitation.

1. INTRODUCTION

Safety regulations dictated by the relevant European directives (RoHS, WEEE) have excluded the use of lead from tin based soldering alloys, whose recycling is imperative. The most common substitutes are silver and copper [1]. The wave soldering technique is associated with the generation of dross, containing the valuable tin and silver metals. By re-melting the primary dross and after skimming, the molten metal can be cast into anodes and pure tin can be recovered by electrorefining in HCl media [2,3]. Due to the higher electrode potentials, silver and copper are expected to accumulate undissolved in a slime layer formed at the anode surface containing a large amount of metallic particles fallen out of the anode substrate as a result of uneven dissolution. A typical structure of the slime produced with 100 A/m² anodic current density on an anode cast under normal cooling conditions from a tin alloy containing 9% Cu and 3% Ag is shown in the scanning electronmicroscopic (SEM) photographs of Fig. 1a and b. The overall energy dispersive X-ray (EDS) spectrum of the relevant field shows the dominance of the tin-alloy matrix, with precipitated phases dispersed. X-ray diffraction analysis has indicated the presence of the three metals either in solid solution in the elemental and intermetallic (mainly Cu_{6,25}Sn₅ and Ag₄Sn) compound forms. Depending on the composition of the applied electrolyte solution, a varying amount of the CuCl phase can also be detected. The amount of the metallic phase strongly depends on the conditions of anodic dissolution. At high anodic potentials, associated with high anodic current densities, dissolution results in the generation of Sn(IV) species which may in turn react with the metallic particles of the thick slime layer [3,4]:



This by-product can be treated by hydrometallurgical methods to recover the valuable silver and tin components and to separate copper.

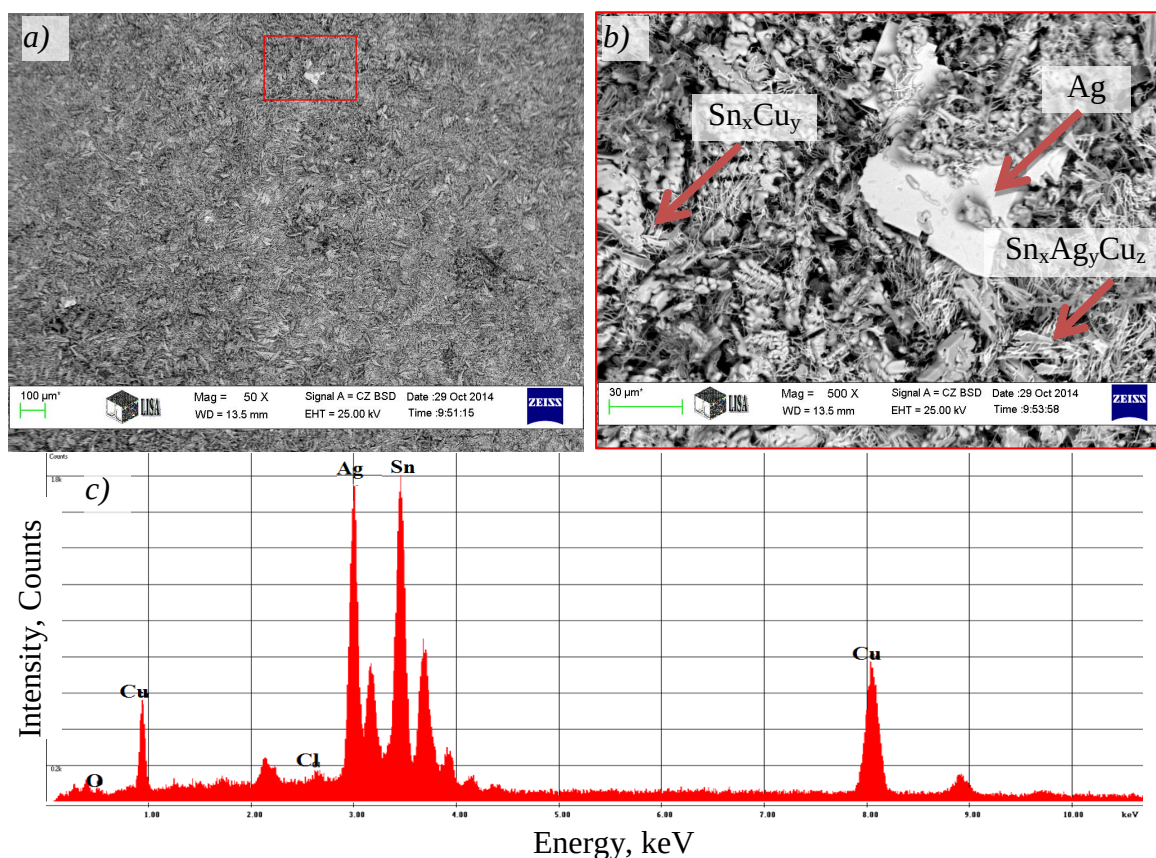


Fig. 1 SEM micrographs of a typical anode slime (a,b) obtained by electrorefining Sn-Ag-Cu anodes in SnCl_2 -HCl solutions, and the relevant overall EDS spectrum (c).

Metallic tin can be dissolved in boiling and concentrated hydrochloric acid [2]. Silver is virtually inert and copper is less likely to dissolve in this medium [5]. Therefore, it is intended to remove as much tin as possible – together with some of copper - by a first step of leaching in HCl. Silver and the remaining part of copper is possible to be leached from the residue of the first leaching step with HNO_3 . Although the practical procedure should be composed of two consecutive leaching steps in the above order, the behavior of the anode slime obtained from the Sn-Cu-Ag anodes enriched in copper was examined directly and separately with either HCl or HNO_3 solutions. The results can be used to design the first and the second steps of the envisaged combined leaching process.

2. EXPERIMENTAL PROCEDURE

In order to see the behavior of the noble components clearly, we have applied a material enriched in copper. It was achieved by fractional crystallization from a $\text{Sn}_3\text{Ag}_0.5\text{Cu}$ (SAC305) melt commonly used in lead-free soldering and coating technology. The composition of the anode was 9% Cu, 3% Ag, the balance made up by tin. It was cast under normal, air cooled conditions. Electrolysis was carried out with a low, 100 A/m^2 anodic current density in stationary solutions of 1 mol/dm^3 HCl and 10 g/dm^3 Sn. As shown in Fig. 2, the slime layer was removed from the surface of the anode, collected,

rinsed, dried at 110 °C in an oven and manually ground to a uniformly fine granular state in a mortar.



Fig. 2 Collecting (a) and mechanical preparation (b) of the anode slime raw material (c).

Samples of 20 g mass were taken from the prepared slime powder and mixed with 200 cm³ hydrochloric acid solution of different concentrations. On the other hand, 2 g slime powder was mixed with the 40 cm³ HNO₃ solutions of various concentrations. The reactor vessels were of 1000 and 250 ml by volume, respectively. The leaching apparatus was equipped with a water cooled reflux condenser to exhaust the evolved hydrogen gas, and the temperature was controlled (± 1 °C) by a thermostated oil bath. Stirring at a constant rate of ~ 600 r.p.m. was applied throughout the experiments. The smaller unit used for the nitric acid experiments is shown in Fig. 3.

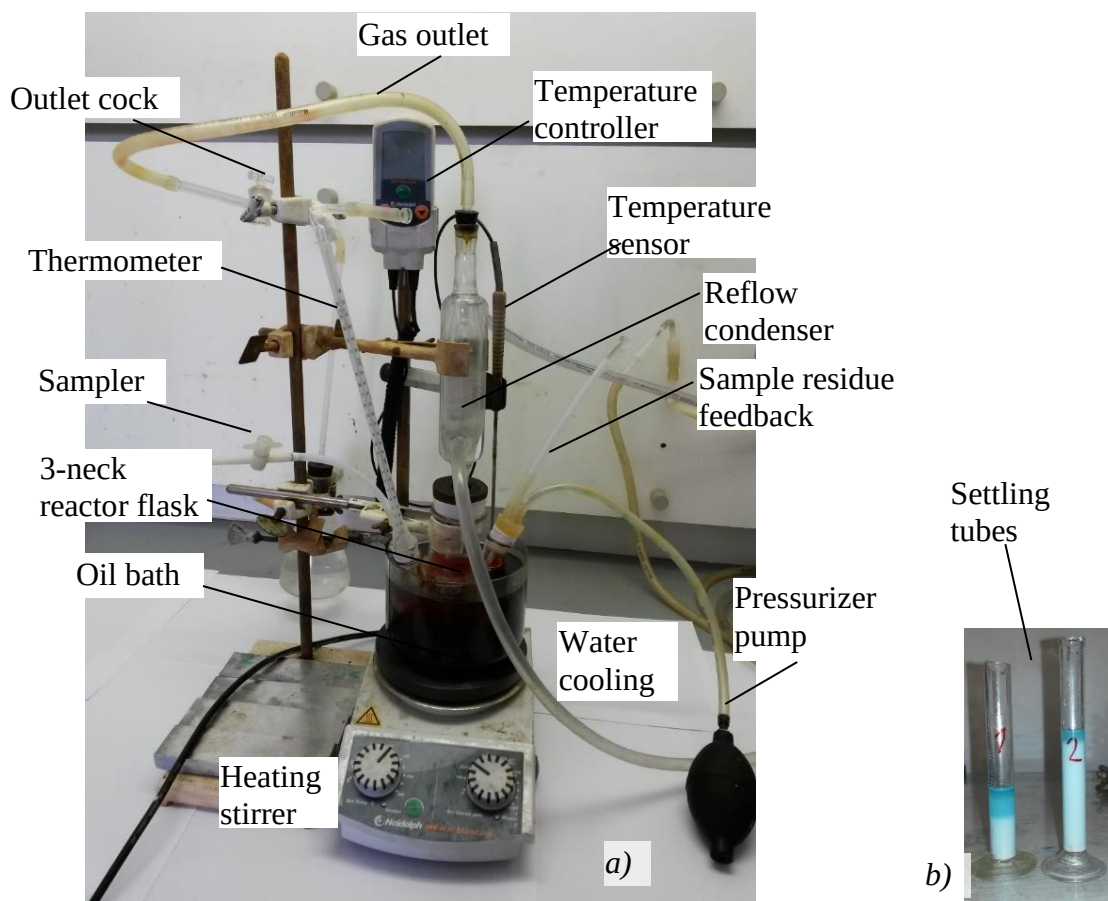


Fig. 3 Experimental apparatus used for the HNO₃ leaching (a) and settling tubes (b).

The available amount of the collected anode slime had to be divided between the two series of experiments with the two different acid solutions. As the major task was finding

the suitable settings for the HCl leaching to achieve an efficient separation of tin and copper from silver, larger slime batches contacted with larger volumes of the solutions, and more parameter settings with higher number of samples were applied than in the case of similar experiments applying HNO₃ solutions. Regular sampling of the solution was carried out by stopping the gas outlet from the reactor, increasing the inner pressure and opening the sampling valve. The collected solution was left settling in a 5 cm³ mess cylinder and samples of 1 cm³ were taken twice for analysis by a micropipette. The rest was returned to the reactor through the feed-back pipe. The removed volume of the solution sample was taken into account in determining the actual volumes in the reactor and the total dissolved masses of the examined metals. In order to define the possible ranges of temperature for the leaching experiments with the HCl and HNO₃ media, the relevant changes of the boiling points were determined by experiments or on the basis of published data [6] preliminarily (Table 1).

Table 1 Measured boiling points of HNO₃ solutions and calculated ones from *published data of HCl solutions*

<i>HCl</i>			<i>HNO₃</i>		
Concentration (25 °C)		Boiling point	Concentration (25 °C)		Boiling point
%	mol/dm ³	°C	cc.HNO ₃ :H ₂ O (Vol.)	%	°C
13.64	4	108	1:3	19	106
19.93	6	110	1:1	39	112
25.93	8	102	2:1	49	115
31.61	10	84	3:1	53	117
36.99	12	55	cc.HNO ₃	65	118

According to former experience [2] in preparing the tin chloride electrolyte solutions, metallic tin can be dissolved only slowly in boiling and concentrated HCl. Therefore, the range of examination for the leaching experiments was selected in a still practicable high HCl concentration range of 6 - 10 mol/dm³ with temperatures above 75 °C in 5 °C steps until 100 °C, except for the 10M HCl solution limited by a lower boiling point. As there was found less change in the boiling points of nitric acid solutions at the examined high (39 - 65 %) concentrations, the entire temperature range of 90 – 110 °C could be applied for all the solutions. The actual experimental parameter settings are summarized in Table 2.

Table 2 The set values of the examined factors in the leaching experiments

Examined material: Anode slime produced with 100 A/m ² on Sn9Cu3Ag anodes					
HCl leaching (max. 360 min)			HNO₃ leaching (max. 60 min)		
Acid conc.(25 °C)		Temperatures	Acid conc.(25 °C)		Temperatures
mol/dm ³	%	°C	cc.HNO ₃ :H ₂ O (Vol.)	%	°C
6	20	75, 80, 85, 95, 100	1:1	39	90, 100, 110
8	26	75, 80, 85, 95, 100	2:1	49	90, 100, 110
10	32	75, 80, 85	3:1	53	90, 100, 110
			cc.HNO ₃	65	90, 100, 110, 118

The experimental step applying HNO₃ had the sole purpose of achieving maximum silver recovery, therefore only silver was analyzed and a smaller number and lower volumes of samples were applied. Although in practice the two different lixiviants should be applied

consecutively, these examinations were carried in parallel with the same anode slime material, in order to obtain preliminary information about the behavior of each of the components in both systems. Further, the residue from the HCl leaching could not always provide the necessary sample mass for continued examination in HNO₃ leaching.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Leaching of the anode slime with either HCl or HNO₃ solutions is characterized by the rate the major components are dissolved. The efficiency of HCl leaching is illustrated by Figs. 4-6 for three HCl concentrations and three temperatures.

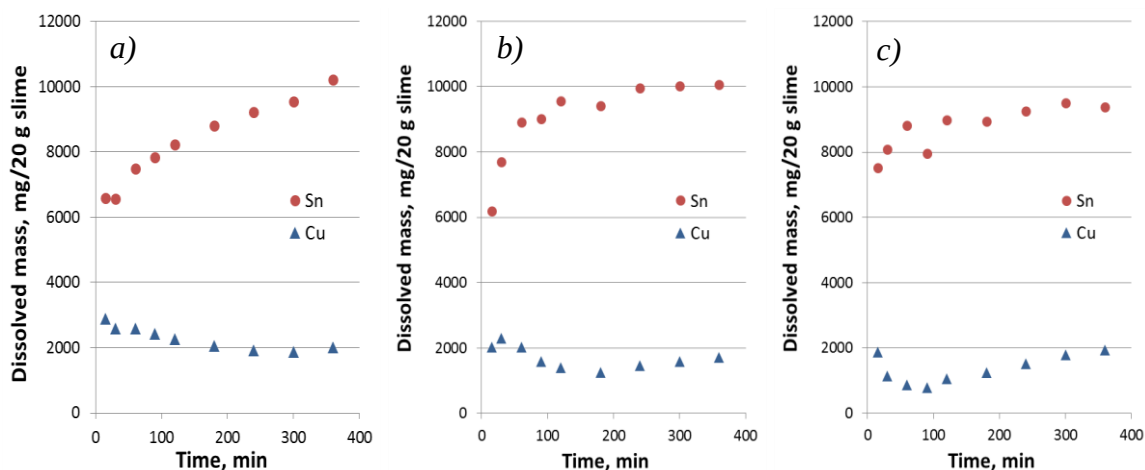


Fig. 4 Leaching of Sn and Cu from the slime with 6 M HCl at 75 (a) 85 (b) and 100 (c) °C

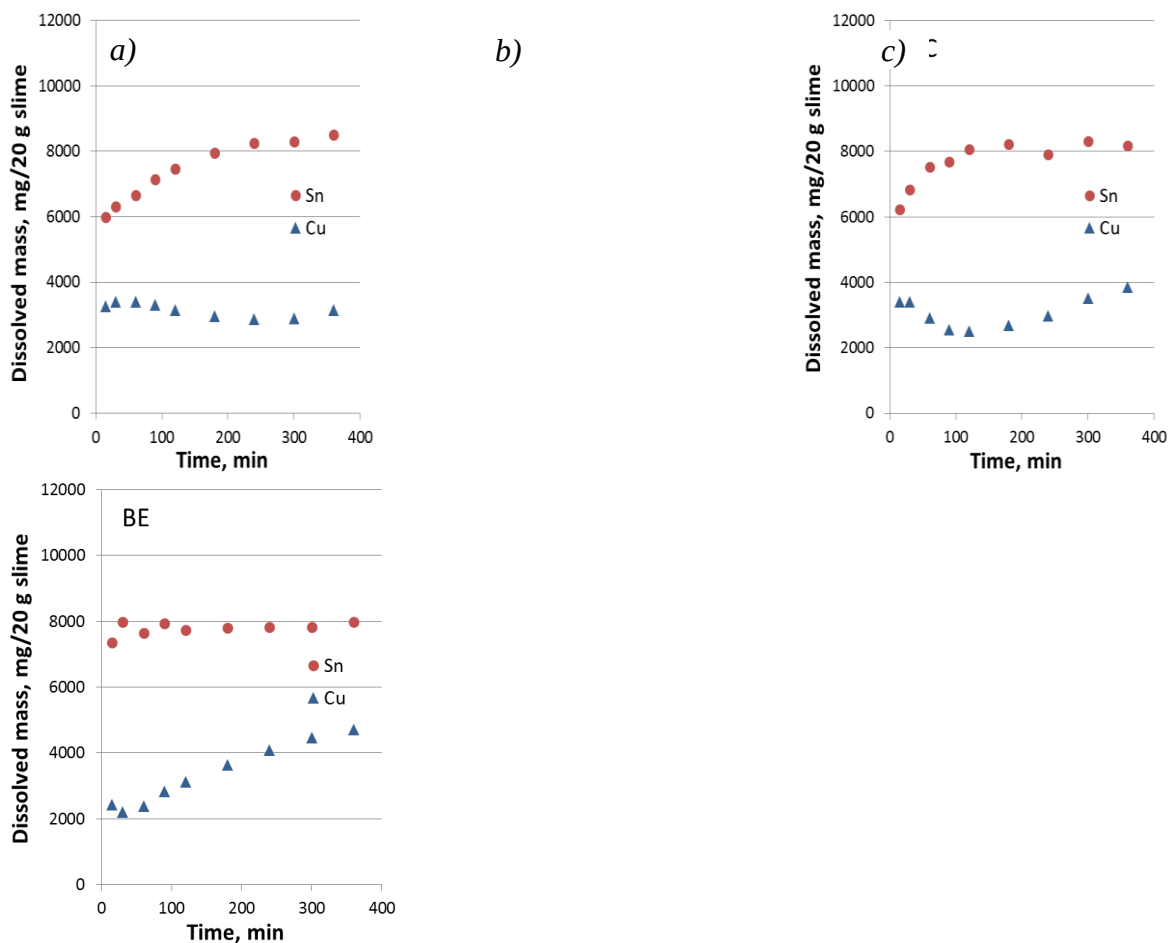


Fig. 5 Leaching of Sn and Cu from the slime with 8 M HCl at 75 (a) 85 (b) and 100 (c) °C

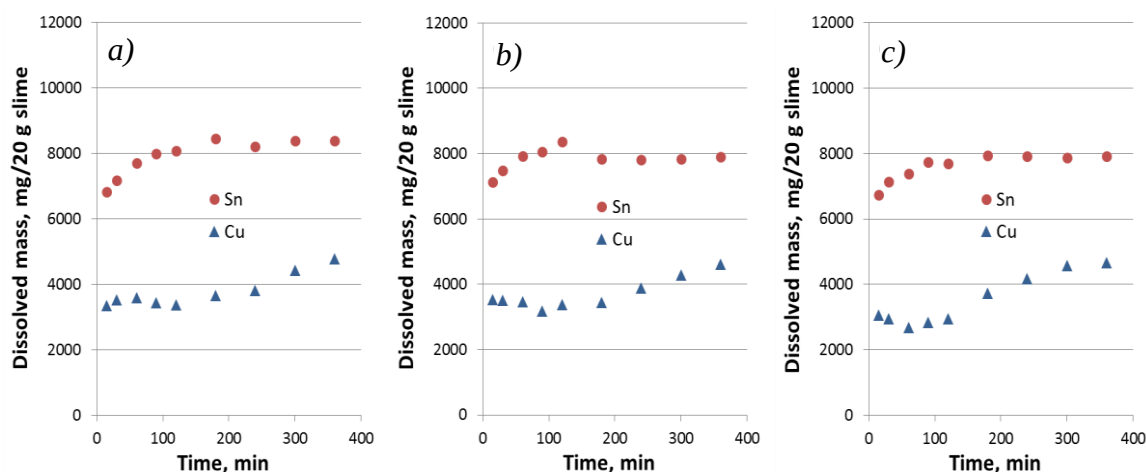
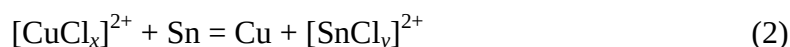


Fig. 6 Leaching of Sn and Cu from the slime with 10 M HCl at 75 (a) 80 (b) and 85 (c) °C. The dissolved amount of tin is relatively slowly increasing with the time of leaching at the lowest examined 75 °C temperature, especially at the lowest examined 6M HCl concentration. An increase of the temperature to 85 °C results in a significant increase in the rate of tin dissolution. However, at the highest examined 10 M HCl concentration, the effect of increasing the temperature above 75 °C is hardly visible. Increasing the HCl concentration in the 6 – 10 M range has a marked effect at the lowest examined 75 °C temperature, but it has little effect on the rate of tin dissolution at higher than 85 °C temperatures. The total amount of the dissolved tin is the highest at the lowest examined 6 M HCl concentration and the lowest examined 75 °C temperature, however the leaching of tin is faster at higher temperatures and higher HCl concentrations. This contradiction can be resolved by the enhanced oxidation of Sn(II) to Sn(IV) at the surface of the solution in contact with air, causing a contrary process of $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ type stannic acid precipitation. The formation of the stannic precipitate is not harmful to the process, as it will stay in the solid state separated from silver, which is to be dissolved in the subsequent step of HNO_3 leaching.

Dissolution of copper is a result of two opposite processes. It assumes the oxidation resulting from air contact, which is seen intensive initially, but the still undissolved tin in the anode slime causes cementation by the



reaction of the chloro-complex copper species of various coordination number (x). However the dissolution of copper increases again as practically all the tin content of the anode slime is dissolved. In 6 M HCl solutions it cannot be seen at 75 °C, but it happens 200 minutes after the start at 85 °C and after 100 minutes at 100 °C. These time intervals are almost halved by raising the HCl concentration to 8M, and the process of copper dissolution is strongly accelerated by further increasing the HCl concentration to 10 mol/dm³. Analysis of silver has proved little dissolution, dispersed in the 1 – 8 mg/20g range only, irrespective of the applied HCl concentration at any of the examined conditions. This amount can be considered negligible in view of the rate of silver dissolution in HNO_3 , as shown in Fig. 7.

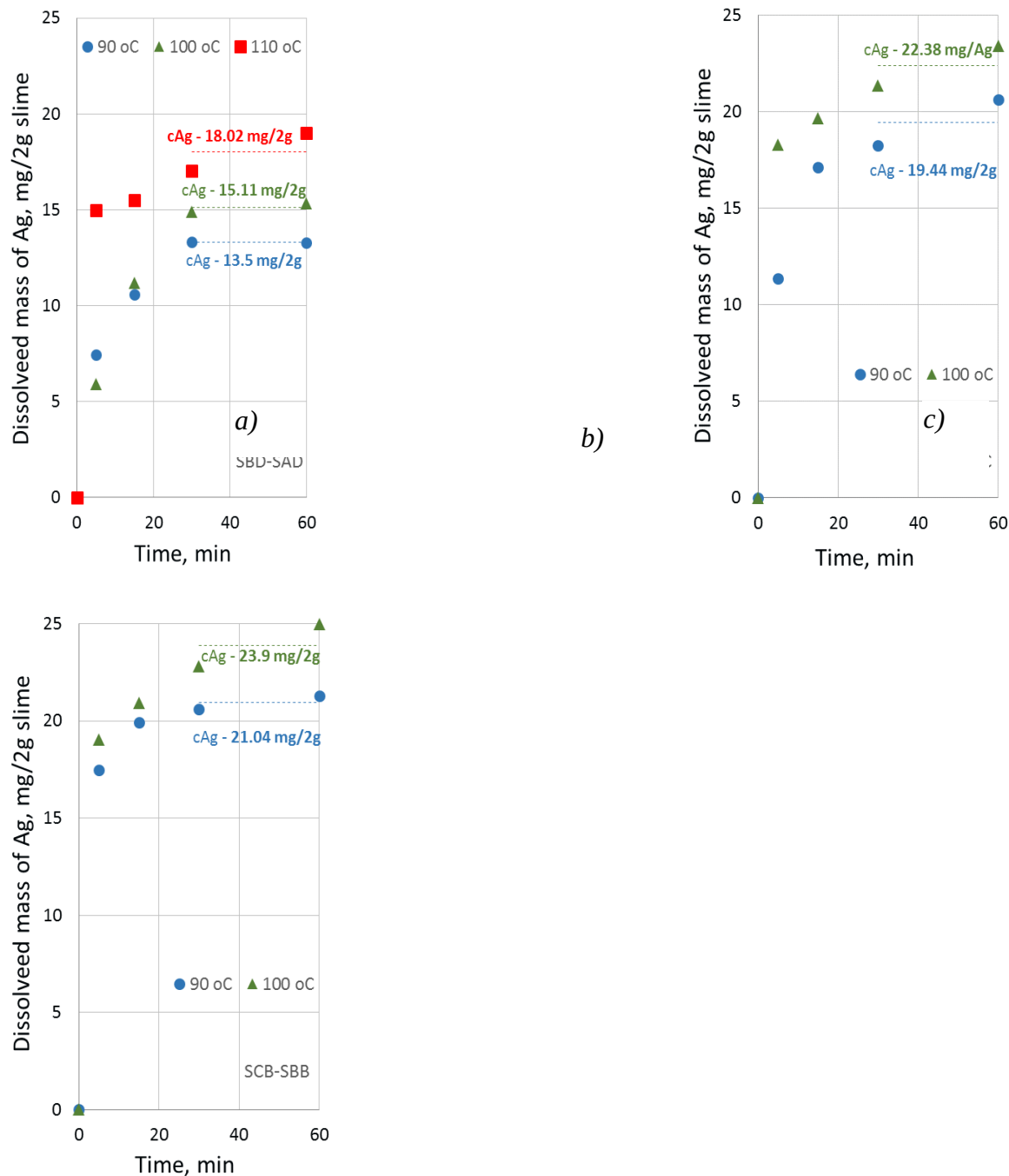


Fig. 7. Dissolution of Ag from the slime in 39% (a) 49% (b) and 53% (c) HNO₃ solutions at different temperatures (marked values represent the average of the last two samples). According to the results of the nitric acid leaching, the rate of silver dissolution from the anode slime considerably increases with every 10 °C step in temperature. A similar increase was found as the concentration of nitric acid in the solvent was raised from 39% to 49% and to 53%. The results of the more concentrated HNO₃ solutions, however, were acceptable only at limited temperatures because high concentration of HNO₃ at high temperature tended to destroy the silicone rubber stoppers of the reactor flask, thereby causing considerable disturbances and losses. The results presented in Fig. 7 are those which can be accepted for this reason. The average amounts of silver dissolved during the last 30 minutes of the applied leaching are marked by the dashed lines and the relevant legends (cAg – average amount of dissolved Ag in mg /2g sample units). Dissolution of

silver in the HNO_3 solutions shows generally faster kinetics than that of tin and copper in the examined HCl solution.

4. CONCLUSIONS

Leaching of the Sn content from the anode slime by HCl can be efficiently completed in about 100 minutes by applying 10 M HCl at higher than 75 °C temperature and vigorous (~600 r.p.m.) stirring. Dissolution of copper, however takes longer time, which can be shortened by applying more oxidizing conditions than simple ambient air contact. Subsequent precipitation of the tin as $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ may happen, however it does not affect the purpose of silver separation, as this precipitate is not soluble in HNO_3 . Silver can be leached efficiently with HNO_3 of ~ 53% in about an hour time applying 100 °C temperature and similarly vigorous stirring. The two leaching steps should be combined - in this order - to achieve selectivity in silver recovery. Tin and copper are removed with HCl in a preliminary step, the filtered and washed residue (together with the incident SnO_2 precipitate) can be leached for silver recovery with HNO_3 .

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