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Investigation of the use of foams for silver leaching using the thiosulfate-copper(II)-ammonia system in the context of e-waste recycling

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Abstract

Due to its physical properties, metallic silver is present in numerous electronic wastes. Its recycling requires selective extraction, which involves leaching of silver as the first step. This work focusses on leaching silver with $\text{Cu(II)/NH}_3/\text{S}_2\text{O}_3^{2-}$ which has been widely used for gold leaching. As recently shown for the leaching of copper, using foams whose aqueous phase consists of leaching chemicals is a promising way to reduce the environmental footprint, by improving the metal oxidation thanks to the fast transfer of O_2 from bubble to bubble. In this work, metallic silver samples are dissolved by foams made of $\text{Cu(II)/NH}_3/\text{S}_2\text{O}_3^{2-}$ solution with bubbles composed of $\text{O}_2\text{-N}_2$ mixtures. The main problem of the thiosulfate route is its degradation during metal oxidation hence it requires using large quantities of this reactant. The results obtained for our leaching foams show that the quantity of silver leached per quantity of thiosulfate used is about three times greater in comparison with a solution, which would bring a new solution to this problem. Moreover, we investigate the role of the bubble size and the gas composition (dioxygen partial pressure). Besides we find that the dissolved silver is inhomogeneously distributed between the foam column and the bottom solution, with an accumulation of 90 % of silver inside the foam, hence opening an interesting perspective for an easy separation of silver upon leaching. Comparing several surfactants, we show that only non-ionic surfactant polyoxyethylene oleyl ether, Brij O10, shows satisfying results, while dodecyl trimethyl ammonium chloride most likely binds with silver complexes and triggers a quick collapse of the foams.

Keywords: Silver, Leaching, Foam, Thiosulfate, Copper, Ammonia

1. Introduction

Recycling metals found in e-wastes has become a necessity due to the growing scarcity of a large variety of metals and their use in technologies of the renewable energy transition. Amongst them, silver plays a critical

role in photovoltaics and electrical vehicles. This element is present as its metallic form in numerous electronic devices, with contents estimated as 1300 g/t of printed circuit board (Mishra et al., 2021) or 600 g/t in crystalline silicon photovoltaic modules (Dias et al., 2016). The extraction of silver from these wastes can be performed using a first leaching step, followed by its separation/recovery and its reduction. The leaching of metallic silver has been proposed using several methods based on strong acids/bases with an oxidant, like ammonia/air, nitric acid, sulfuric acid or ozone. The methods used to treat sulfides or gold ores have been studied for decades and have been used more recently for e-wastes recycling (Li et al., 2012). Cyanide is a known efficient chemical, but growing environmental concerns rose in the last decades (Senanayake, 2005b). Thus, developing economically feasible, yet more environmentally friendly and safer alternative to recycle these metals is necessary (Zhang and Senanayake, 2016). Several non-cyanide leaching systems such as thiourea, halides (Br, Cl and I), ammonia and thiosulfate have been investigated in the last few decades (Ritchie et al., 2001; Xie et al., 2021, Aylmore, 2016). Among them, thiosulfate looks particularly promising because of its low toxicity, the biodegradability of its associated salts (Na^+), its relatively high gold recovery capability, the fast leaching rates and the relative easiness to produce on site (Zhang and Senanayake, 2016). Due to economic reasons, most of the research published on leaching using thiosulfate was done on gold while only a few articles deal with silver, although thiosulfate is also known to be a silver complexant (Roldan-Contreras et al., 2020). In addition to thiosulfate, ammonia and copper are commonly added to the leaching liquor (Senanayake, 2005a; Xie et al., 2021). Cu^{2+} ions are used as oxidant-catalyst while ammonia stabilizes Cu^{2+} in solution by complexing it as $\text{Cu}(\text{NH}_3)_4^{2+}$ which prevents the reduction of Cu(II) and thus the oxidation of thiosulfate in solution (Senanayake, 2005b). Ammonia also enables to avoid the precipitation of copper ions in alkaline solution (Xie et al., 2021). The chemical reactions for silver leaching are described in eq. 1-4 (Xu et al., 2017).

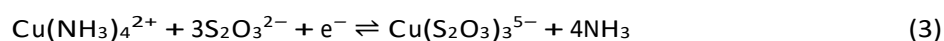
Oxidation of silver:



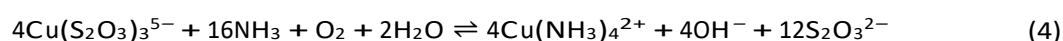
Complexation of silver ions with thiosulfate ions:



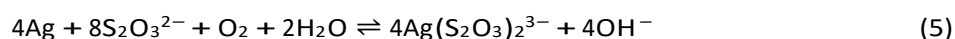
Reduction of Cu(II) into Cu(I) and complexation of cuprous ions with thiosulfate ions:



Regeneration of Cu(I) into Cu(II) by O_2 :

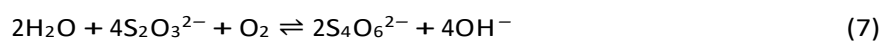
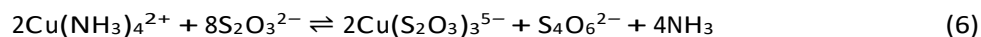


Resulting in balanced eq. 5:



The main limitation of this system is the degradation of thiosulfate which leads to an increase of the quantity of reactant used and hence the cost of the reaction. Moreover, the degradation products (sulfur oxyanions) may

78 have detrimental effects on the silver leaching reaction (Breuer, 2003) and recovery process (Aylmore,
79 2016). Thiosulfate degradation occurs according to eq. 6-7:



82 As can be seen from Equations 6 and 7, copper and ammonia are not consumed in the system but thiosulfate,
83 which acts as a ligand of silver ions is also degraded over time by the tetraamine complex of Cu(II) (eq. 6) and
84 oxygen (eq. 7) (Xu et al., 2017; Jeffrey et al., 2003). Thus, the quantity of silver which can be leached is directly
85 correlated with the quantity of thiosulfate present in solution. Another limitation of this process is the post-
86 leaching decomplexation of silver from thiosulfate, and the possible recovery of thiosulfate reagent, but this is out
87 of the scope of this research (Grosse et al., 2003; Aylmore, 2016). Most of the research activities have focused
88 on investigating the effect of physico-chemical factors such as pH, concentration of reagents, temperature and
89 stirring speed on the leaching of gold using thiosulfate (Senanayake, 2005a; Liu et al., 2020; Deutsch, 2012).
90 Some researchers also tried to leach silver out of printed circuit board (PCB) using the thiosulfate-copper-
91 ammonia system (Li et al., 2012), which demonstrates the potential industrial interest of this system.

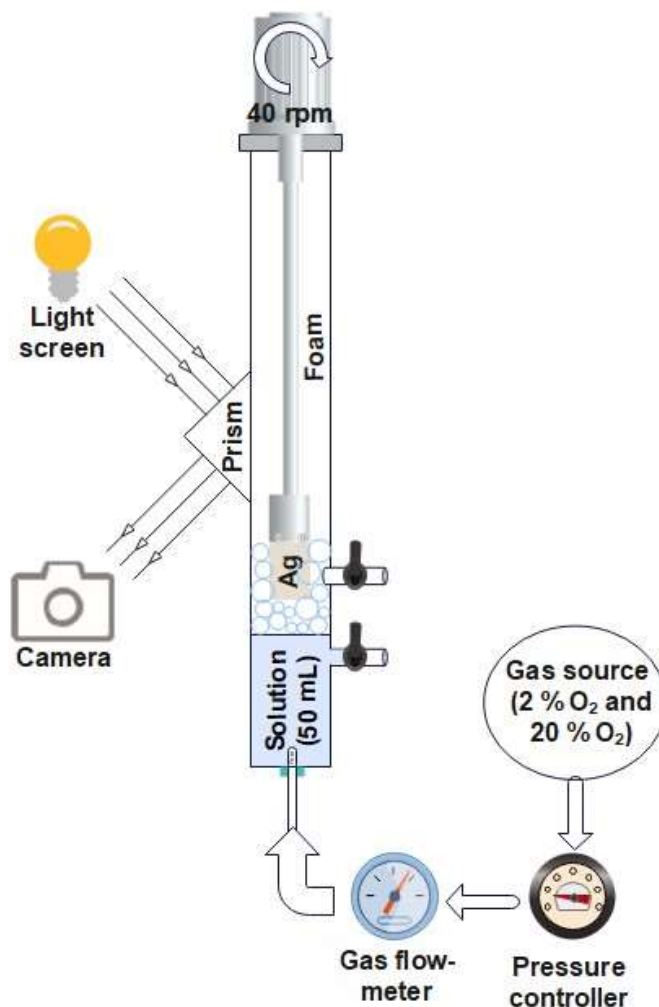
92 In this thiosulfate based reaction, the role of O_2 is crucial as it enables to regenerate Cu(I) into Cu(II) which is the
93 oxidant, therefore we propose in this study the possibility of adding O_2 as bubbles in a foam obtained by foaming
94 the leaching solution in the presence of surfactants. We base our approach on previous results obtained in our
95 group which showed that foams can be used to oxidize copper in a very efficient manner in the presence of H^+
96 ions (Trinh et al, 2021). We showed that the fast transfer of O_2 through the thin films between the foam bubbles,
97 as described by Trinh et al. (2021) enables to increase the kinetics of the oxidation reaction. As a result, foams
98 enable to leach copper about 50 times faster than their solution counterpart (Trinh, 2021) while using 8 times
99 less reactant and water. In the case of silver leaching by thiosulfate, the limiting step for the rate of silver
100 leaching is likely to be the reoxidation of Cu(I) to Cu(II) hence we investigate here whether foams made with
101 bubbles of O_2/N_2 enables to obtain a good leaching of silver in comparison to a solution. We investigate the role of
102 the bubble size, foam liquid fraction and O_2/N_2 composition of the bubbles as well the type of surfactant used to
103 stabilize the foams.

106 2. Materials and methods

108 2.1 Chemicals and column for foam leaching

110 The silver plate (10 cm x 10 cm x 0.25 mm), ammonium hydroxide NH_4OH solution (28 % - 30 % NH_3),
111 copper sulfate, thiosulfate, DTAC (Dodecyltrimethylammonium chloride), DTAB
112 (Dodecyltrimethylammonium bromide), Brij® O10 (Polyoxyethylene (10) oleyl ether), SDS (Sodium dodecyl
113 sulfate), sulfuric acid (95 %-98 %), glycerol, copper and silver standard for Inductive Coupled Plasma-Optical

114 Emission Spectroscopy (ICP-OES)(1000 mg/L) were purchased from Sigma-Aldrich. The 2 % O₂ and 98 % N₂ gas
 115 cylinder (20 L, 200 bar) was obtained from Air Liquide.



116

Fig. 1: Silver leaching experimental setup

117

118

119 The leaching of the silver plate took place in a homemade polycarbonate column of dimensions 30 mm x 30 mm
 120 x 300 mm as shown in Figure 1.

121

122

Table 1: Porous glass frit specifications depending on pore size

Glass frit	Pore size (µm)	Bubble size (µm)	Gas flow (mL/min)	Local liquid fraction (%)
Pore 4	10-16	50-180	135±15	8.8±1.3
Pore 2	40-100	150-420	50±10	2.75±0.25

123

124 The gas (air, i.e. 20 % O₂ or the tailored 98 % N₂ – 2 % O₂) is forced at a controlled flow rate through a 6 mm diameter
 125 porous frit placed in the middle of a 15 mm diameter rubber joint at the bottom of the column. Two porous frits
 126 (Micro filter candles, ROBU18102 and ROBU18104) were used, pore 2 (i.e. 40-100 µm) and pore 4 (i.e. 10-16 µm).
 127 The pore designation controls the pore size hence the bubble size, the gas flowrate needed to produce the foams

128 and the average foam liquid fraction. These conditions can be found in Table 1. The gas volumetric flow rate was
129 provided with a pressure controller (LineUp FlowEZ from Fluigent) and monitored using a gas flow controller
130 (Micrometer Valve Flowmeter from Gilmont Instruments). To measure the foam liquid fraction, images were
131 taken every 10 minutes using a PixelINK camera with a Fujinon (1:1.8 (25 mm), CF25ZA1-S) objective
132 connected to the software PixelINK capture. To allow for a good measurement of the foam liquid fraction a
133 prism was attached to the column with a solution of 0.05 M BrijO10, 0.1 M glycerol and water (replaced weekly)
134 and a light panel as a light source as shown in Figure 1. The local areal liquid fractions were calculated by
135 measuring the ratio of the number of white pixels (liquid) on the total number of pixels (liquid and gas) after
136 binarizing foam pictures using Image J (Trinh, 2020). Average local areal liquid fractions for a specific set of
137 conditions were obtained by averaging areal liquid fractions obtained every 10 minutes. From these areal liquid
138 fractions, volumetric liquid fractions were obtained using the model for polydisperse foams according to eq. 8
139 (Forel et al., 2016):

$$\phi = 0.36(1 - (1 - \phi_c)^{1/2})^2 \quad (8)$$

142 where ϕ is the volumetric liquid fraction and ϕ_c is the areal liquid fraction.

145 2.2 Silver leaching experiment and sampling method

146
147 The silver plate was first washed in sulfuric acid (1 M) to remove surface oxides, dried and weighed (3
148 measurements). The plate was then attached to a stirrer and placed into the column. A 20 mL sample of a
149 solution containing 0.50 mmol of copper sulfate in water, 20 mmol of NH_3 and 0.20 mmol of surfactant was
150 prepared. Its UV-Visible absorbance at 605 nm, A_{ref} was measured three times and was used as a reference for the
151 determination of the Cu(II)/Cu(total) ratio as explained below, where Cu(total) represents the total concentration
152 of Cu(II) and Cu(I). Afterwards, 5.0 mmol of thiosulfate was then added and pH was adjusted to 9.30 with sulfuric
153 acid (1 M). The volume of solution was then completed with milliQ water up to 50 mL so that the initial
154 concentrations are 0.1 M for thiosulfate, 0.4 M for NH_3 , 0.01 M of copper sulfate. The solution was then added
155 to the column and the silver plate was attached to the stirrer and placed in the middle of the column section.
156 A slight flow of gas was delivered before adding the solution to the column (10 mbar for pore 2 and 20 mbar for
157 pore 4) in order to counterbalance the gravity and prevent the solution to flow down through the porous frit.
158 The position of the plate was fixed so that the bottom of the plate was located 6 mm above the solution. To
159 produce the foam, the gas flow was increased to the desired values of flow rate (see Table 1). Once the foam
160 level reached the top of the silver plate, the stirrer was set in rotation at 40 rpm. This is considered to be the
161 time $t = 0$. From $t = 0$ minute to $t = 240$ minutes, a sample of 1.5 mL was taken every 30 minutes from the bottom
162 faucet of the column and its UV-vis absorbance was measured. In one set of experiments, we also took a foam
163 sample from the top faucet of the column. For each of these samples, three UV-vis measurements were performed,
164 the pH was monitored to ensure it remained in the 9.30 - 9.50 range. The samples for ICP-OES analysis were

165 prepared by mixing 0.1 mL of sample and 4.9 mL of 0.4 M NH_3 / 0.1 M thiosulfate solution. Upon completion of
166 these measurements, the sample was added back from the top of the column using a syringe by letting the 1.5 mL
167 solution flow down on one of the walls.

170 2.3 UV-Vis and ICP-OES measurements

171
172 The Cu(II)/Cu(total) ratio can be easily measured by UV-Visible spectrometric measurements (Jeffrey et al.,
173 2003) as cupric $\text{Cu}(\text{NH}_3)_4^{2+}$ solutions are blue and absorb UV-Visible light at a wavelength of 605 nm while Cu(I)
174 solutions are colorless. According to eq. 6, Cu(II) tends to oxidize thiosulfate. Resulting Cu(I) is stabilized by
175 thiosulfate and forms $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$. Thus, we expect that copper will be predominantly in the form of Cu(II)
176 when thiosulfate runs out of solution, that is to say Cu(II)/Cu(total) ratio tends to 1. Although Cu(I) can form
177 complex species with ammonia ($\text{Cu}(\text{NH}_3)_n^+$, $n=1, 2$), it cannot prevent its oxidation to Cu(II) by oxygen (as observed
178 in Eh-pH diagram (Velasquez-Yévenes & Ram, 2022)). Obtaining a robust measurement of the reference absorbance
179 corresponding to Cu(II) being equal to Cu(total) is tricky because the quantity of Cu(II) decreases immediately after
180 the addition of thiosulfate for the benefit of Cu(I). Thus, it has been decided to measure the absorbance A_{ref} of
181 a 20 mL solution containing CuSO_4 and NH_4OH , prepared before the addition of thiosulfate. This solution
182 contains only Cu(II) so it ensures that Cu(II)/Cu(total)=1. Thiosulfate was then added, so that the final volume
183 of leaching solution was 50 mL. The theoretical absorbance A_0 of this 50 mL solution if Cu(total) had stayed in
184 the Cu(II) form can thus be deduced from A_{ref} . From the absorbance $A(t)$ of the solution at a given time t , time
185 evolution of Cu(II)/Cu(total) ratio was obtained by eq. 9:

$$186 \qquad \qquad \qquad \text{Cu(II)/Cu(total)} = A(t)/A_0 \qquad \qquad \qquad (9)$$

188
189 The silver and copper concentrations in solution were determined using ICP-OES. Wavelengths used for the
190 determination of silver and copper concentrations are 328.068 nm and 338.289 (for silver) 327.396 nm and
191 324.754 nm (for copper). Calibration curves (0, 2, 4, 8, 12 and 16 mg/L) were performed before every ICP-
192 OES analysis. Absorbance intensities were measured three times for each sample and averaged concentrations
193 were determined using the calibration curve.

199 3. Results and discussion

3.1 Comparison of silver leaching efficiency in solutions and in foam

It is important to make a comparison between leaching efficiency of (i) a foam, (ii) a solution under continuous bubbling and (iii) a regular solution under no bubbling. The solution was prepared like the foaming solution described in Section 2, except that it did not contain surfactant. Both foaming and bubbling are performed with an air flow rate of 135 mL/min and the foam was produced using pore 2 porous frit leading to foam bubbles of diameter ranging from 150 to 420 μm . The results are shown in Table 2.

Table 2: Comparison of silver leaching efficiency after 4 hours for foam and solutions^a

Method for gas addition	No Bubbling	Bubbling	Foaming ^b
Ag leached in 4 hours (mg)	1.3	42	33
Volume of solution (mL)	200	200	50
Ag leached / added thiosulfate (mmol/mol)	0.6	20	61
Fraction of thiosulfate involved in complexation (%) ^c	0.1	4.0	12.2

- a. All the solutions initially contained: 0.50 mmol Cu(II), 20 mmol NH_3 , 5 mmol $\text{S}_2\text{O}_3^{2-}$ at pH 9.3 at room temperature.
 b. Foaming solution contained 0.20 mmol BrijO10.
 c. Assuming the complexes $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ according to eq. (5).

As shown in Table 2, the mass of silver leached is 1.3 mg when the solution is not bubbled nor foamed, 42 mg when air is bubbled through the solution and 33 mg when the leaching process occurs in the foam. Thus, the foam leaching process yields slightly less silver dissolution than in the bubbling case. However, foaming used only 5.0 mmol of thiosulfate and 50 mL of water which is four times lower than the bubbling case (Table 2). In the foaming case, 61 mmol of silver is leached per mole of initially added thiosulfate, whereas it is only 20 mmol/mol in the bubbling case. We note that in all three experiments thiosulfate is in large excess, as even in the foaming case, only 0.3 mmol of Ag^+ are produced while 5 mmol of thiosulfate were initially introduced. However, the percentage of thiosulfate used for the reaction is 12.2 % for the foaming case against 4 % for the bubbling case. Hence it appears that the foaming case combines two advantages, i. a more efficient use of the reactants combined with ii. a lower quantity of water used. As silver is not entirely leached, an interesting question is whether the unused thiosulfate is still available to participate in silver leaching or whether it has been degraded. As explained in Section 1, thiosulfate can indeed either form a complex with silver ions or be consumed by side-reactions (oxidation by O_2 or by Cu(II) ions). Thus, the evolution of Cu(II)/Cu(total) ratio can be useful to get some insight on the thiosulfate content.

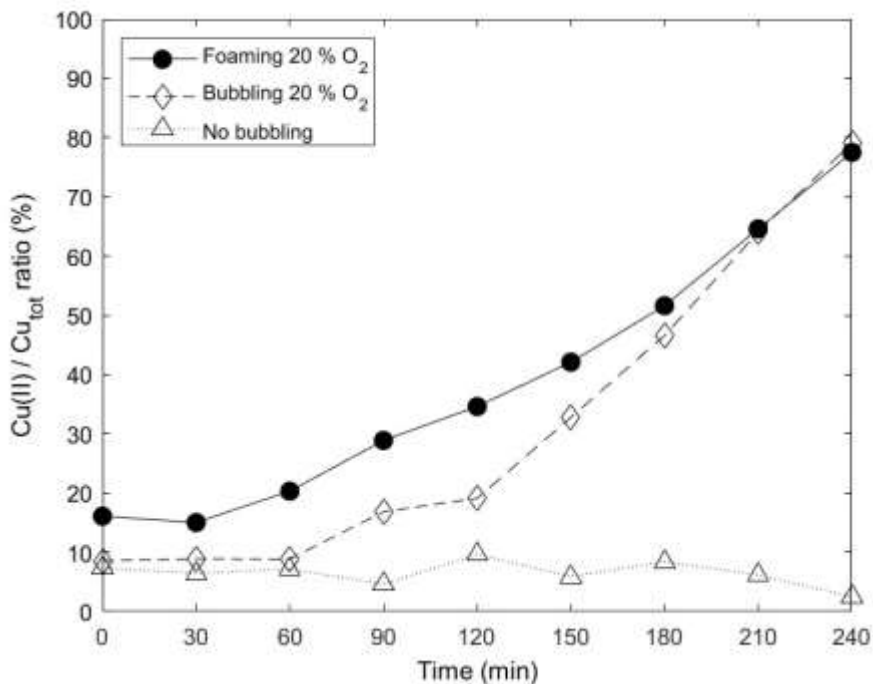


Fig. 2: Evolution of Cu(II) content over time in foam and solutions (see Table 2 for experimental conditions): foaming with 20 % O₂ using Pore 2 (●, full lines), bubbling with 20 % O₂ (◇, dashes), no bubbling (△, thin line).

As explained before, Cu(II)/Cu(total) ratio is indirectly related to the change in thiosulfate concentration evolution, as one expects that Cu(II)/Cu(total) ratio reaches 1 when thiosulfate is no longer present in the solution 2. (Jeffrey et al., 2003). Figure 2 represents the evolution of Cu(II)/Cu(total) ratio over time for bubbling and foaming cases as well as for the experiment with no bubbling. The Cu(II)/Cu(total) ratio increases in the bubbling and foaming experiments whereas it tends to remain constant or even slightly decrease in the standard experiment with no bubbling. This phenomenon can be explained by the fact that the presence of O₂ favors the oxidation of Cu(I) to Cu(II) for the foam and the bubbling solution, whereas Cu(I) is almost not oxidized in the standard solution with no bubbling. Moreover, the little amount of Cu(II) available in solution tends to be reduced to Cu(I) during silver leaching, which might explain the slight decrease observed for the no bubbling case in Fig. 2. This low quantity of Cu(II) ions in solution results in a low leaching efficiency as can be concluded from Table 2. A sufficient input of oxygen is required to obtain the regeneration of Cu(II) ions for fast leaching of silver. Now comparing the foaming and bubbling experiments, one can first notice that after t = 240 minutes, both experiments yield a similar Cu(II)/Cu(total) ratio of about 78 %. The fact that it has not reached 100 % indicates that there is still thiosulfate in solution. If it was not the case, Cu would be exclusively in the Cu(II) form. In principle, the leaching of silver can thus still continue. One can also notice that during the first 200 minutes the Cu(II)/Cu(total) ratio is in the ascending order: no-bubbling < bubbling < foaming (Fig. 2). After 120 min Cu(II)/Cu(total) ratio tends to increase more rapidly (higher slope) in the bubbling case than in the foaming case, which might be due to a faster degradation of the thiosulfate in the bubbling case. Combining these results with the ones shown in Table 2, we

suggest that in the foaming case, there is a better regeneration of Cu^{2+} and a lower of degradation of thiosulfate than in the bubbling case, leading to a more efficient use of thiosulfate for the dissolution of silver.

3.2 Role of the gas composition and pore size

In this section, we investigate the influence of oxygen content in the gas used to produce the bubbles (mixture of O_2 and N_2 with either 2 % O_2 or 20 % O_2) as well as the pore size of the frit used to produce the foams (pore 2 or pore 4). The frit pore size controls the bubble size, as well as the flow rate at which foam is continuously produced and the liquid fraction in the foam as shown in Table 1. The ratio of silver leached per mole of thiosulfate is shown in Table 3 while the time evolution of the $\text{Cu(II)}/\text{Cu(total)}$ ratio obtained with UV-vis measurement is shown in Figure 3.

Table 3 shows that with pore 2, the influence of O_2 content in the foams on silver leaching is high. Indeed, the quantity of silver dissolved per mole of initially added thiosulfate is higher than 61 mmol/mol with 20 % O_2 , while it is around 5.4 mmol/mol with 2 % O_2 . To account for this result, we suggest that a higher O_2 content probably results in a higher regeneration of Cu(II) content which catalyzes the silver leaching reaction, as explained before. Surprisingly, in the case of pore 4, which produces foams with smaller bubbles (Table 1) the quantity of silver leached is almost the same for both 2 % and 20 % O_2 (Table 3). Hence the influence of the O_2 content is different for both pore and bubble sizes.

Table 3: Comparison of silver leaching efficiency after 4 hours for two different gas compositions and two different pore/bubble sizes

Pore designation	O_2 (% v/v)	Ag leached / added thiosulfate (mmol/mol)
4	20	16.8 ± 0.5
2	20	$>61.2 \pm 4$
4	2	$>17.1 \pm 2$
2	2	$>5.4 \pm 2$

In Figure 3 (a) it can be seen that for pore 4 and 20 % O_2 , the $\text{Cu(II)}/\text{Cu(total)}$ ratio increases rapidly to 100 % after 120 minutes meaning that the thiosulfate is completely consumed and that the reaction cannot continue anymore. The silver plate, with dull grey colour initially due to silver etching, presented some silver sulfide crystals at the end of the experiment. This observation can be explained by the reaction between silver ions and sulfide ions, these latter formed due to the disproportionation of thiosulfate (eq. 10) as indicated by Aylmore and Muir (2001).



For Pore 4 and 2 % O₂, the Cu(II)/Cu(tot) ratio is still lower than 20 % at the end of the experiment which means that the reaction can in principle continue. Hence for Pore 4, the quantity of silver leached after 240 minutes is the same for both O₂ contents but in the 20 % case the reaction is over after 240 minutes while it can continue in the 2 % O₂ case. We therefore suggest that for Pore 4 increasing the O₂ content probably leads a faster degradation of thiosulfate. For Pore 2 (Figure 3b), the 20% O₂ case leads to a fast increase of the Cu(II)/Cu(tot) over time but it does not reach 100% after 240 minutes meaning that the reaction can in principle continue.

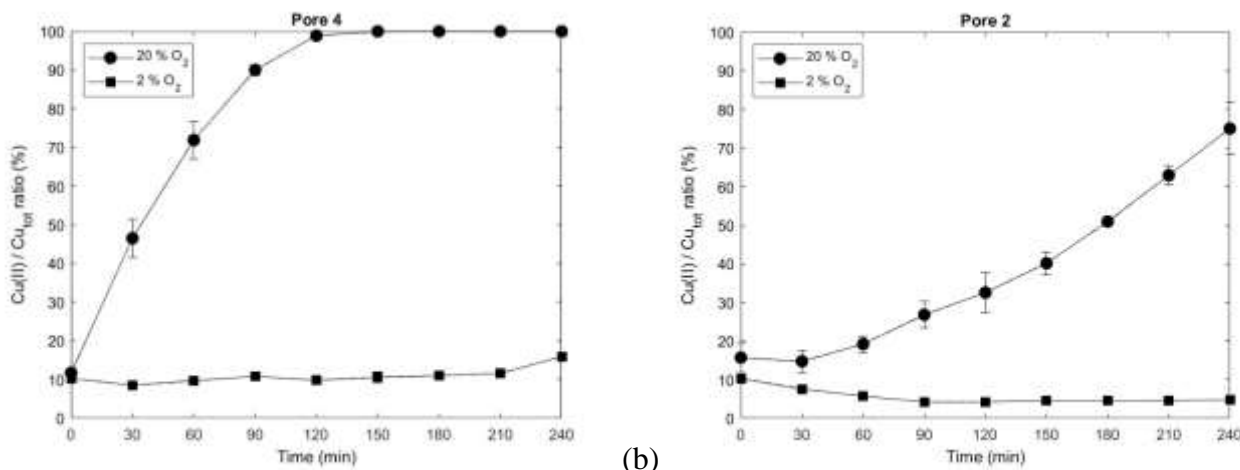


Fig. 3: Evolution of the ratio of Cu(II)/Cu(total) over time for two different gas compositions (20 % O₂ (●) vs 2 % O₂ (■)) and two different bubble sizes (obtained with frits of different pore sizes, (a) Pore 4 vs (b) Pore 2)

To account for the fact that the influence of O₂ content is different for the two pore sizes we compare the flow rates, Q, and total volume, V, of O₂ injected during foaming for the two pore sizes. Indeed, the bubble sizes generated with pore size 4, are higher than the ones obtained with pore size 2; hence the pressure that needs to be overcome to eject the bubbles out of the pores, which corresponds to the Laplace pressure and scales inversely with the bubble size, is higher for pore 4 than pore 2. Consequently the gas flow rate used to keep the foam volume constant throughout the entire experiment is Q=135 mL/min for Pore 4 vs Q=50 mL/min for Pore 2 as shown in Table 1. It impacts the total volume of O₂ injected through the foam during the experiment, which can be estimated according to eq. 11:

$$V(O_2)_{tot} = \%O_2 * Q * t \tag{11}$$

Thus, the total volume of O₂ sent in the foam are estimated for each experiment in Table 4.

Table 4: Comparison of the volume of O₂ sent in the foam in 4 hours for two different gas compositions (20 % O₂ vs 2 % O₂) and two different bubble sizes (Pore 4 vs Pore 2)

Pore designation	O ₂ (% v/v)	V O ₂ (tot) (mL)	Cu(II)/Cu total (%)
4	20	6480	100
2	20	648	75
4	2	2400	15
2	2	240	4

It appears clearly in Table 4 that there is an optimum quantity of O₂ to maximize silver leaching. A low O₂ volume (such as 240 mL or 648 mL) results in limited thiosulfate decomposition as shown by low Cu(II)/Cu(tot) ratio for 2 % O₂ experiments (Figure 3b) and as expected from literature (Jeffrey et al., 2003), but also in low leaching kinetics as the reaction might be limited by the quantity of available Cu(II) which acts as the oxidant. On the contrary, for the highest O₂ volume (such as 6480 mL) thiosulfate consumption is fast because of the fast thiosulfate degradation which results in a low quantity of Ag dissolved (Figure 3a).

To summarize, we find that the volume of O₂ injected in the foams results in two opposite effects, the thiosulfate degradation which has to be minimized and the rate at which the Cu(I) is reoxidized into the oxidant Cu(II) which should be optimized. To this end, two parameters can be optimized, the composition of the gas and the pore size which controls the injection flow rate. Two optimal situations can then be obtained. Using 20 % O₂ at the lowest flow rate (Pore 2), the quantity of silver leached in four hours is the largest. However, this situation leads to a fast although non complete degradation of thiosulfate. Injecting 2 % O₂ using the largest flow rate (Pore 4) is another interesting situation as it leaches less silver but degrades very little thiosulfate. Thus, the quantity of silver leached is lower, but the reaction may be continued over longer times.

The role of oxygen on copper oxidation is well supported by another set of measurements which consists in comparing the Cu(II)/Cu(total) ratio in both the foam and the solution after four hours of experiments (Table 5).

Table 5: Ratio of Cu(II) over total copper concentration for two different foam compositions in both foam and solution phases after 4 hours of experiments

Ratio of Cu ²⁺ /Cu _{tot} (%)	Pore 2, 20 % O ₂	Pore 4, 2 % O ₂
Foam phase	98	44
Solution phase	78	16

This measurement was done for the two optimal situations discussed above, i.e., Pore 2, 20 % O₂ and Pore 4, 2 % O₂. We find that the ratio of Cu(II)/Cu(total) is higher in the foam than in solution in both cases. For Pore 2, 20 % O₂, the Cu(II)/Cu(tot) ratio is 98 % versus 78 % in the solution. For Pore 4, 2 % O₂ however Cu(II)/Cu(tot) ratio is 44 % in the foam and 16 % in the solution. Using ICP-OES we verify that the total quantity

of Cu is identical in both the foam and the solution, which enables to ensure that the largest Cu(II)/Cu(total) ratio in the foams is due to a difference in the degree of oxidation of copper in the foams and not to a difference in the total quantity of copper. We suggest that the largest quantity of Cu(II) in the foams is due to the enhanced transfer of oxygen in the foams which leads to a faster regeneration of Cu(II), higher complexation of thiosulfate with the Ag⁺ ions produced as well as degradation of thiosulfate. Consistently more Cu(II) ions are found in the foams for Pore 2, 20 % O₂ than Pore 4, 2 % O₂ as more oxygen has been sent through the foam generated by Pore 2 than through the foam generated by Pore 4 (see Table 4).

3.3. Concentrating the silver ions in the foams

As oxygen participates in the leaching of silver, it is expected that the production of silver ions is faster in the foam than in the solution. This is due to the faster transfer of O₂ in foam than in solution. We explored the influence of pore size and gas composition on this phenomenon thanks to the measurement of silver concentration with ICP-OES in both the foam phase and the solution across time. To this end, a small foam sample has been taken close to the silver plate every 30 minutes and analyzed. The silver concentrations reported here are therefore local and are not representative of the global foam composition.

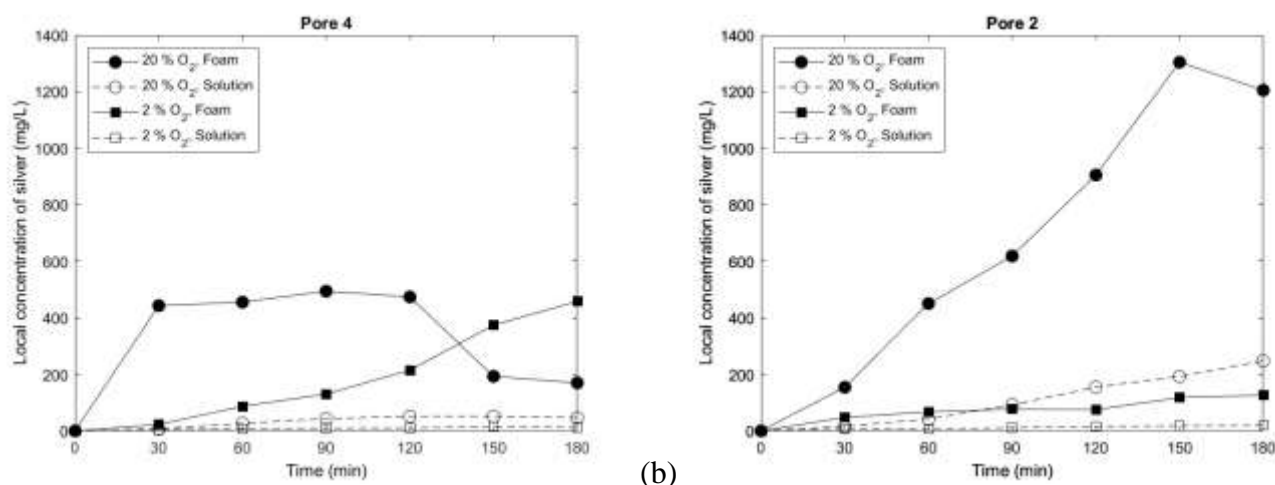


Fig. 4: Local concentration of silver in foam (full symbols (● ■)) and solution (empty symbols (○□)) over time for two different gas compositions (20 % O₂ (●) vs 2 % O₂ (■)) and two different bubble sizes (obtained with frits of different pore sizes, (a) Pore 4 vs (b) Pore 2)

We first focus on the case of Pore 4, 2 % O₂ which was shown to be a promising experiment earlier. Figure 4 (a) shows that the silver concentration in the foam phase increases slowly and continuously over the three hours while the concentration of silver in solution remains small during all the experiment. As explained earlier, the production of silver ions is ensured in the foam because the oxygen content is sufficiently high to rapidly oxidize Cu(I) into Cu(II) and thus rapidly produce silver ions, and sufficiently low to minimize

377 thiosulfate degradation. The highest amount of silver found in the foam with respect to the solution is due to the
378 fact that silver ion production is fast enough not to be entirely compensated by the drainage phenomenon.

379 Let us now turn to the case of the foams produced by pore 2 with 20 % O₂ which was shown before to be
380 promising as it generates the largest amount of Ag⁺ ions per mole of thiosulfate. Figure 4 (b) shows that the local
381 concentration of silver ions continuously increases quickly near the silver plate in the foam until t = 150 minutes
382 and then it decreases slightly. Meanwhile, the concentration of silver ions increases regularly in the solution.
383 In this case, silver leaching is quite fast, as inferred from the high Cu(II)/Cu(tot) ratio presented in Figure 3 (b).
384 After t = 150 minutes, the local concentration of silver ions decreases in the foam, which might indicate that
385 the silver leaching rate decreases. This phenomenon is probably caused by the decrease of available thiosulfate,
386 which is not only consumed by previously leached silver but also by side-reactions.

387 The experiment with Pore 2 frit and 2 % O₂ has been identified before as involving the lowest oxygen content
388 resulting in low silver ion production. The leaching kinetics is indeed slow as inferred from the low Cu(II)/Cu(tot)
389 ratio discussed in Figure 3 and Table 4. Figure 4 (b) confirms that the slow production of silver ions in the foam
390 with time induces a low transfer of the ions in the solution by drainage.

391 Finally, we discuss the experiment performed with pore 4 frit and 20 % O₂ corresponding to the highest oxygen
392 content, which results in fast thiosulfate consumption while not improving the total quantity of silver leached.
393 Figure 4 (a) shows that there is a steep increase in silver concentration in the foam between 0 and 30 minutes,
394 followed by a plateau until t = 120 minutes at which the concentration of silver in the foam drops steeply.
395 Meanwhile, the concentration of silver in the solution phase slightly increases over time but stays very low.
396 These observations can be explained by the fact that leaching of silver is very fast in the foam from the start,
397 as there is immediately a high Cu(II)/Cu(tot) ratio as can be seen in Figure 3a. However, this fast oxidation of
398 Cu(I) into Cu(II) results in a high thiosulfate consumption, which might explain why the local silver concentration
399 does not increase anymore after 30 minutes since drainage compensates the local Ag⁺ production. After t = 120
400 minutes, the Ag⁺ local concentration in the foam drops because thiosulfate runs out of solution and the reaction
401 stops as previously shown in Figure 3a. Thus, no more silver ions are produced and the ions produced earlier
402 progressively drain out of the foam leading to a decrease of the local concentration in the foam. During all this
403 time, the solution phase is enriched in Ag⁺ as the continuous phase, draining through the foams toward the
404 solution contains silver ions.

405 From these results we find that there are higher concentrations of Ag⁺ in the foams compared with the solution,
406 which enables us to foresee a continuous process where the top of the foam column is enriched in silver ions.

3.4. Determination of the optimal surfactant (SDS, Brij O10, DTAC and DTAB)

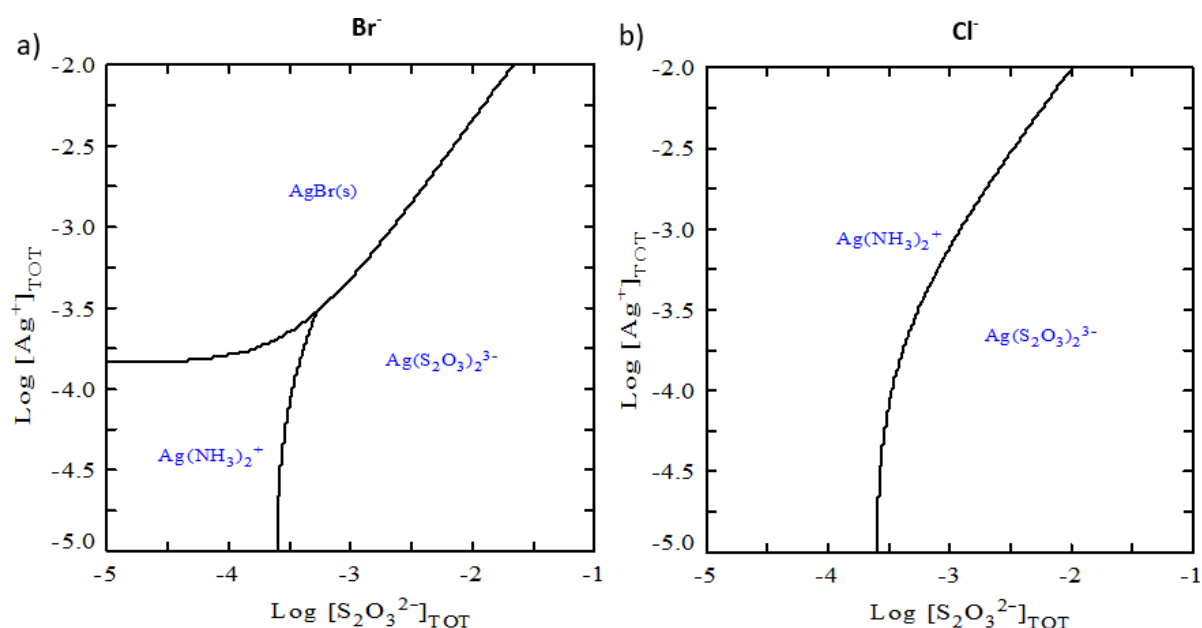
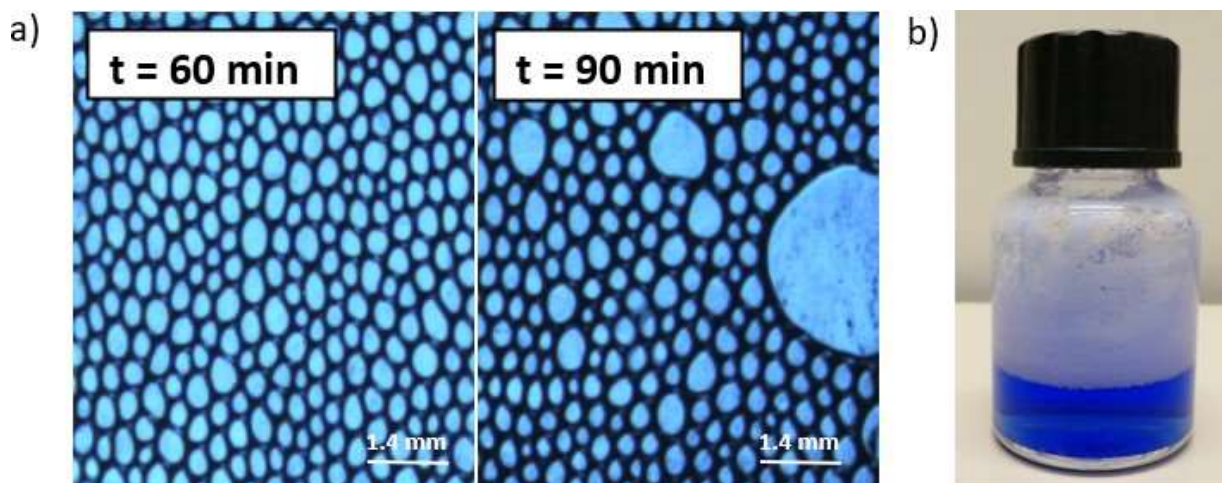


Fig. 5: Predominance diagram of silver at pH 9.3 according to silver and thiosulfate concentrations in the presence of a) Br^- or b) Cl^- 0.01 M.

In the previous results, only the non-ionic surfactant BrijO10 has been used as it was exhibiting relatively good foaming properties. In the following part we extend the study to other surfactants. The use of anionic surfactants such as sodium dodecyl sulfate (SDS) and cationic surfactants such as dodecyl trimethyl ammonium bromide (DTAB) and chloride (DTAC) were investigated for comparison. In figures 5 a) and b), the predominance diagrams of silver species depending on thiosulfate and silver concentration for bromide and chloride ions are plotted. These diagrams are based on Medusa (Chemical Diagrams, Medusa/Hydra for Windows (Visual Basic) developed at KTH) with the following initial conditions: Cu(II) (0.01 M), Br^- or Cl^- (0.01 M), NH_3 (0.4 M), $\text{pH} = 9.3$, $\text{Eh} = 0.22$ (Aylmore and Muir, 2001). At the beginning, the conditions of the experiment are located in the bottom right corner and over time, the reaction conditions are evolving towards the top left corner. According to Figure 5 a), some of the dissolved silver is predicted to be leached mostly under the form of precipitated silver bromide as the thiosulfate is consumed and its concentration is low enough. Indeed, some silver bromide yellow crystals were found in the foam after 2 hours of experiments. Thus, DTAB does not seem to be appropriate to leach silver.

However, according to Figure 5 b), there shouldn't be any silver chloride precipitation with DTAC and silver thiosulfate complexes would preferentially bind to ammonia and / or precipitate with sulfur containing decomposition products of thiosulfate. In practice, no precipitate was found in the foam when using DTAC after 150 minutes of experiment, as expected from the theory. However, the foam collapsed much more quickly, requiring a higher gas flow is required to maintain a stable foam height (gradual increase from 50 mL/min to 80

442 mL/min).



444
445 **Fig. 6:** a) Foam pictures at $t = 60$ min (left) and $t = 90$ min (right) with DTAC, b) Formation of scum
446 when using SDS.

447
448
449 A large heterogeneity in bubble size was observed in the foam with DTAC as shown in Figure 6 a). The foam
450 bubble size is relatively homogeneous at $t = 60$ minutes and becomes quite heterogeneous from $t = 90$ minutes
451 and onwards. At $t = 150$ minutes, no more foam can be produced, and the surfactant loses completely its
452 foaming ability. Knowing that DTA^+ contains only one positive charge, three molecules of DTA^+ should bind to
453 one thiosulfate complex $Ag(S_2O_3)_2^{3-}$, hence forming an electronically neutral complex. This means that 3.4 mM
454 of $Ag(S_2O_3)_2^{3-}$ may be bound with up to 10.2 mM of surfactant, which is about the quantity of surfactant used
455 (10 mM). As no more foam could be produced after $t = 150$ minutes, the loss of surfactant foaming property is
456 assumed to originate from silver complexes binding with DTA^+ . Thus, assuming most of the silver complexes had
457 three negative charges ($Ag(S_2O_3)_2^{3-}$), there must have been about 3.4 mM of $Ag(S_2O_3)_2^{3-}$ in solution at $t = 150$
458 minutes, which corresponds to 18.8 mg of silver. The use of SDS as an anionic surfactant is also inconclusive. It
459 formed a scum as shown in 6 b) and this issue was to be expected in the presence of divalent cations (Cu^{2+}) as
460 suggested by other researchers (Fan et al., 1988 ; Miyamoto, 1960).

461 As a conclusion, none of the surfactants investigated (DTAB, DTAC, SDS) served their purpose as well as
462 BrijO10 did. However, it is important to note that DTAC could be potentially interesting if it were
463 demonstrated to interact with silver complexes as it could facilitate silver separation upon leaching.

464 465 466 **4. Conclusion**

467
468 The long-term objective of our works is to leach silver out of electronic wastes in a more environmentally
469 friendly manner. The copper–ammonia–thiosulfate system has been selected because of the low toxicity and

470 biodegradability of thiosulfate. Oxygen intervenes in the regeneration of Cu(II) complexes from Cu(I)
471 complexes, but side reactions leading to the degradation of thiosulfate species have been identified as the main
472 limitation of this approach using oxygen. Foams based on solution of copper–ammonia–thiosulfate system solution
473 have been evaluated as a potential leaching medium for metallic silver. Measurements of dissolved silver and
474 copper redox state have been performed to follow and characterize the leaching of a silver plate in a foam
475 column. The comparison between experiments with air bubbling and air foaming showed a similar kinetics of
476 silver dissolution, but with a higher efficiency of the foam since a higher amount of leached silver per mole of initial
477 amount of thiosulfate has been measured. The analysis of the foam part and the drained solution has shown
478 that most of Ag(I) remains in the foam, and this enrichment could be exploited in a subsequent separation
479 step. Another result is that decreasing the dioxygen amount injected in the foam allowed to keep a fast
480 regeneration of cupric species while minimizing the degradation of thiosulfate. The optimum can be achieved by
481 tuning both the gas injection flow rate and the bubble gas composition. Several surfactants have been tested, with
482 different results. A non-ionic surfactant (BrijO10) exhibits good foaming properties but it is not expected to have
483 a chemical role in the leaching process. Thus, anionic (SDS) and cationic (DTAB and DTAC) surfactants have been
484 used to evaluate if they could lead to an improvement of the leaching. Foaming of SDS leaching solution has been
485 found troublesome, with the formation of a scum. Electrostatic interactions are expected between dodecyl sulfate
486 ions and Cu^{2+} , what could be the reason for this observation. In the presence of dodecyl trimethyl ammonium,
487 the foam is less stable. It could be explained by the interaction between DTA^+ and anionic thiosulfate species
488 (free or complexed with Ag(I)). Moreover, thermochemical simulations have shown that the silver halide precipitate
489 can be formed only with Br-counter anion. This work is the second demonstration of the potential use of leaching
490 foam to dissolve precious metals from e-wastes, following the studies on copper by Trinh et al., 2021. The
491 main advantage of replacing bubbling approach by foaming is to control the oxygen reactivity. It allowed to increase
492 the leaching kinetics in the case of copper, and to increase the leaching efficiency of silver by the copper–ammonia–
493 thiosulfate liquor. The foam-based leaching media remains largely unexplored, and further studies are needed to
494 fully exploit its potential.

497 Author Contributions

498
499 C.B., G.L. and C.M. conceived the project, G.L. and C.M. supervised the project, C.B. conducted the
500 experiments and wrote the draft. All authors performed data analysis, commented on the work, and reviewed the
501 manuscript.

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504
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