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Leaching foams for copper and silver dissolution : a proof of concept of a more environmentally-friendly process for the recovery of critical metals

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ABSTRACT The recovery of metals from WEEE, Waste from Electrical and Electronic Equipment, is a major challenge to preserve natural resources. Hydrometallurgy, which consists in leaching metals is a promising method but generates large amounts of polluting effluents. In this study we design aqueous leaching foams, composed of 90% v/v of gas and 10% v/v of HCl solution to oxidize and dissolve copper. We take advantage of the oxidizing power of the dioxygen (O_2) present in the air bubbles whose fast transfer through the foams enables an efficient oxidation of copper. We then extend the concept of leaching foams to another gas, ozone, to oxidize silver (Ag). We finally show that using an anionic surfactant to complex cupric ions helps improving the dissolution of the metal. These promising results open new recycling routes for metals contained in WEEE, with a lower environmental footprint.

Introduction

The recovery of the wide variety of metals in WEEE (Waste from Electrical and Electronic Equipment) also called e-waste is becoming a major challenge to preserve natural resources while treating a large amount of waste (1-3). Hydrometallurgy, based on leaching solutions containing oxidants or acids to extract metals, which was traditionally used for the mining industry for ore extraction is also a promising route for the recovery of metals from WEEE (such as Platinum Group metals, Au, Ag, Cu) (4-9). Hydrometallurgy is particularly suitable for local and short scale installations and is therefore an interesting alternative to pyrometallurgy which consists in an energy-intensive process where the wastes are smelted at high temperature (10). Moreover by carefully choosing the leachants used, it is possible to obtain a selective process maximizing the extraction of precious metals while minimizing the extraction of non precious metals (11). The

development of hydrometallurgy is hampered by the fact that this process generates large amounts of polluting effluents such as cyanide or sulfuric acid (12). To address this issue, eco-friendly processes are emerging such as the ones that use eco-friendly leachants (formic acid or potassium persulfate (13) or bioleaching methods, based on microbes eventually combined with chelatants (13). In the present study, we choose another route which consists in reducing the amounts of leaching effluents by developing leaching aqueous foams. Foams are collections of bubbles stabilized by surfactants and contain less than 25% in volume of liquid and therefore appear as a promising way of decreasing the environmental footprint of hydrometallurgy.

Aqueous foams are used in environmentally relevant applications for waste water treatment (14) or nuclear waste retreatment (15-16). These applications rely on flotation, a process which promotes the concentration of impurities at the surface of bubbles and in the liquid films and channels connecting the bubbles, which can then be collected easily as they float at the top of the water sample. The nature of the species that can be concentrated in foams is multiple: ions (17-18), ores (19), minerals (20-21), or proteins (22, 23). A major advantage of foams is that they contain, by definition, between 74 and 99% of air and consequently very little volume of liquid hence they are good candidates for a reduction of effluents volumes during these processes (24). Moreover, foams are remarkably versatile and the surfactant used to achieve their stabilization can be chosen to obtain specific properties, such as in particle or ion flotation processes where ionic surfactants can complex the particles or ions to be recovered which allows a more efficient concentration process (17-23).

In the above applications, the bubble gas, usually air, is not chemically active and is only used to produce bubbles that promote particle flotation. Reactive gases such as O₂ or O₃ may confer some

oxidizing reactivity to aqueous foams that can be useful for applications where leaching is required such as in hydrometallurgy.

In the present study we design leaching foams to oxidize and dissolve metals. We first establish a proof of concept for a standard metal, copper (Cu), using a foam stabilized by a non-ionic surfactant, polyoxyethylene alkyl ether, and containing hydrochloric acid (HCl). We take advantage of the oxidizing power of the dioxygen (O₂) present in the air bubbles and demonstrate that the fast transfer of O₂ through the foams enables a rapid and efficient oxidation of copper. By using ozone (O₃), a gas with a high electrochemical potential, we show that these foams can be applied to the leaching of silver, a more precious metal. Finally we demonstrate that the complexation of cupric ions using an anionic surfactant, sodium dodecyl sulfate (SDS) helps improving the dissolution process of the metal. These promising results open new recycling routes for metals contained in e-waste, with a lower environmental footprint as they would result in a low liquid waste volume and a smaller amount of oxidizing chemicals.

Materials and Methods

The acid solutions are prepared by dilution of concentrated hydrochloric acid (37%, Sigma-Aldrich) or sulfuric acid (Sigma Aldrich) at a concentration of 0,1 or 1 M with MilliQ water (18,2 MΩ.cm@25°C). The nonionic surfactants Brij®O10 (C₁₈H₃₅(OCH₂CH₂)_nOH, n~10 CAS 9004-98-2) and Brij®L23 (CH₃(CH₂)₁₀CH₂(OCH₂CH₂)_nOH, n~23 CAS 9002-92-0) and the anionic surfactant SDS (Sodium dodecyl sulfate, purity ≥ 99,0% CAS 151-21-3) are purchased from Sigma-Aldrich. The gas used are either filtered air, pure nitrogen (supplied by Air Liquide), or a mix between dioxygen and ozone produced by an ozone generator (Anseros DE), ozone generator, COM-AD-01 with a maximum capacity of 4 gO₃/h plugged to a flow controller (Gilmont®) that

ensures gas flowrate around 40 ml/min. When N₂ is used to make the foam, N₂ is bubbled in the solution during 30 minutes to remove dissolved dioxygen. During foaming, air and nitrogen are bubbled into perfluorohexane (C₆F₁₄- CAS 355-42-0 as traces of this water-insoluble gas in the bubbles enable to slow down Oswald ripening and increase the foam stability (24-25). The experiment consists in stirring either a copper plate, (2 cm × 2 cm × 675 μm, purchased at Alfa Aesar, purity 99.9%) or a silver plate (2 cm x 2cm x 250 μm, purity 99.9%, purchased at Sigma-Aldrich) at 40 rpm for five hours (using a RZR 2020 stirrer from Heidolph), in a 3 neck round bottom flask filled with 100 mL of foam or solution. For foam experiments (Figure 1b), 15 mL of the surfactant solution containing HCl or H₂SO₄ are poured into the flask and the gas is then injected through a porous fritted glass (pore diameter: 16-40 μm, supplied by ROBU Glasfilter Geräte GmbH) at a flow-rate of 60 mL/minute for about two minutes to reach a total foam volume of 100 mL, therefore the liquid fraction of the foams is of the order of 15%. The initial bubble diameter is approximately 200 μm is measured by optical microscopy. Because of partial foam collapse, of the order of 10% of the foam volume after 25 minutes, the gas is injected for 20 seconds every 25 minutes to keep the foam volume constant. For solution experiments (Figure 1a), the copper plate is directly stirred into 100 mL of solution. During experiments where air is bubbled in the solution without a surfactant, bubbling is done continuously for five hours at a flow rate of 60 mL/minute. In a set of experiments, the gas atmosphere above the foam or the solution is changed by applying a gentle gas flow above the foam or solution and parallel to their surface. This flow is gentle enough to avoid bubbling or perturbation of the surface.

After five hours, the final mass of the copper or silver plate is subtracted from the initial mass to calculate the total dissolved copper amount ($\Delta m(\text{Cu})$). Samples of 300 μl are also regularly taken in the drained liquid of the foam or directly in solution. They are further diluted with 14.7 ml of

1M hydrochloric or sulfuric acid solution and then analyzed with an ICP-OES (Inductively Coupled Plasma –Optical Emission Spectrometry ThermoScientific ICAP 6300 Duo) spectrometer to measure the amount of copper or silver dissolved above time .

Results and discussion

Oxidation of Copper by O₂ in HCl foams

To evaluate the effectiveness of aqueous foams to oxidize metals and take advantage of the gas contained in the bubbles, we first choose to study the oxidation of a copper plate (Cu) into cupric ions (Cu²⁺) by the dioxygen (O₂) contained in the foam air bubbles in the presence of protons according to the following reaction (1)



To decouple the action of the protons from that of the oxidizing gas, O₂, we choose to acidify the solution with hydrochloric acid (HCl), which is known to be inefficient for the dissolution of metals in the absence of an oxidant. Indeed, metals such as copper are usually dissolved either by using an oxidizing acid such as nitric acid (HNO₃) (26) or by combining a non-oxidizing acid such as HCl or H₂SO₄ with a dissolved oxidant such as Fe³⁺ (27).

We compare the dissolution process of a copper plate stirred in a 3 neck bottle flask containing either 100 mL of a 0.1M HCl solution (Figure 1a) or 100 mL of an aqueous foam obtained by foaming 15 mL of 0.1M HCl solution using a porous fritted glass (Figure 1b). Using Inductively Coupled Plasma, ICP, we measure the concentration of Cu²⁺ ions generated in the foams and in the solution during the experiment from which we deduce the mass of copper dissolved over time (squares in Figure 1c).

a

b

c

Figure 1. Dissolution of a copper plate in a solution and in a foam. (a) Experimental set-up of a copper plate stirred in a 3 neck bottle flask containing 100 mL of a 0.1M HCl solution or (b) 100 mL of an aqueous foam obtained by foaming 15 mL of 0.1M HCl solution. (c) Mass evolution of the Cu plate ($\Delta m(\text{Cu})$) either in 100 ml of a $[\text{HCl}] = 0.1\text{M}$ solution or in 100 ml of foam containing 15 mL of $[\text{HCl}] = 0.1\text{M}$ and $[\text{Brij}^{\text{®}}\text{O10}] = 0.05\text{M}$. The squares are results obtained using ICP experiment while the filled circles are obtained by weighing the copper plate after five hours. In both experiments air is used as atmosphere above the solutions and foams as well as to produce de foam bubbles.

In addition to the ICP experiment, we measure the weight of the copper plate before and after five hours of experiments to deduce the mass of Cu dissolved after 5 hours (circles in Figure 1c). The results obtained by both methods are consistent and they show that the dissolution of the copper plate is much more efficient in the HCl foam than in the HCl solution. After five hours, the mass

of Cu dissolved in the foam is eight times higher than in the solution, while the amount of HCl solution used is almost ten times lower. Knowing the surface of the plate we obtain a rough estimation of the thickness of Cu removed by the leaching foams and find that it is of the order of 125 μm , which is of the same order of magnitude as standard Cu thicknesses on PCBs (ranging between 17 and 170 μm).

We also perform an experiment in which the plate is stirred in a 100 mL HCl solution without any surfactant while air is continuously bubbled through the solution for five hours, using the same porous stick. In that case the amount of Cu dissolved after five hours is only 5 mg, similarly to the case where air is not bubbled in the 100 mL HCl solution. In that case, the air bubbles quickly rise to the top of the flask and probably do not have time to dissolve and transfer toward the copper plate. Comparing the results obtained with and without surfactant enables us to confirm that in the absence of surfactant, even with continuous bubbling, the dissolution process is much less efficient than using foams, for which air is only bubbled for a few minutes over five hours.

From the slopes of the curves presented in Figure 1c, one can see that the reaction rate is higher in the case of the foam than in solution. However the dissolution rate slows down during the process. To determine the reaction limiting reactant, we performed a mass balance (Table 1) to calculate the amount of reactants, H^+ and dissolved O_2 , initially present in the foam and in the solution.

		Initial quantity (mol)	Consumed quantity (mol)
Solution	H ⁺	10 ⁻²	1.5 10 ⁻⁴
	O ₂	2.6 10 ⁻⁵	3.9 10 ⁻⁵
Foams	H ⁺	1.5 10 ⁻³	1.4 10 ⁻³
	O ₂	8 10 ⁻⁴	3.4 10 ⁻⁴

Table 1. Mass balance of the reactants. The number of moles O₂ initially present in the systems is calculated by taking the solubility of the gas in water. In the case of the foam the amount of O₂ corresponds to both the bubbles and the foam aqueous phase. The consumed amount of moles corresponds to the measured mass loss of Cu according to Figure 1c.

The solubility limit of O₂ under ambient temperature and pressure is 2.5 10⁻⁴ M whereas the H⁺ concentration is 0.1 M. These two concentrations are multiplied by the volume of liquid, either 100 mL or 15 mL for the solution or the foam respectively. In the case of the foams, the amount of O₂ present in the foam bubbles, i.e. 85 mL of air containing 21 % of O₂ is of the order of 8 10⁻⁴ M, which is 100 times higher than the amount of O₂ dissolved in the continuous phase, of the order of 2.6 10⁻⁶ M. We then calculate the amount of reactants corresponding to the experimentally measured mass of dissolved copper consumed during Reaction (1). By comparing these sets of

values for the case where the reaction is occurring in a solution, we deduce that protons are in large excess meaning that O_2 is the limiting reactant. Moreover, the amount of O_2 used for the reaction is higher than the amount of O_2 initially dissolved in the solution. Consequently, some O_2 from the atmosphere above the solution dissolves into the solution during the reaction. Performing the same analysis for the foam, we find that O_2 is in excess, owed to the large amount present in the bubbles and that the limiting reactant is H^+ explaining the slowing down of the chemical reaction after 150 minutes in the foam. This first set of experiments shows that foams enable to obtain a better dissolution of Cu than the solutions even when air is bubbled without a surfactant. In the case of solutions, O_2 is the limiting reactant while in foams H^+ is the limiting reactant. We suggest that the dissolution and transfer of O_2 toward the copper plate is faster for foams than for solutions.

To understand how the transfer of O_2 proceeds inside the foams and how it influences the chemical reaction, we perform experiments where air is replaced by an inert gas, Nitrogen (N_2). N_2 is used either to produce the foam bubbles or to control the atmosphere above the foams by introducing a gentle flux in the atmosphere above the foams during the reaction. This protocol allows us to find that the composition of the gas atmosphere above the foams plays a greater role than the gas present in the bubbles. Indeed, when the atmosphere is composed of air and hence, contains O_2 , the mass of oxidized and dissolved Cu is at least ten times higher than in the case of an atmosphere only composed of N_2 , irrespective of the gas used to produce the foam bubbles (Figure 2). As an example, with air bubbles, the amount of dissolved Cu after five hours is only a few mg with a N_2 atmosphere while it is 40 mg using an air atmosphere. Moreover in the two situations where O_2 is present in the atmosphere the reaction kinetics is very similar (not shown), suggesting that a fast transfer of gas between the foam bubbles and the atmosphere proceeds and equilibrates the gas activities across the flask. In other words, the gas atmosphere acts as an infinite reservoir which

controls the gas activity inside the bubbles. Furthermore it suggests that the O_2 transfer through the HCl foams is much faster than in the HCl solutions because it diffuses through the aqueous liquid films between the foam bubbles, which are very thin, usually of the order of tens of nanometers.

Atmosphere	Air	N_2	N_2	Air
Foam bubbles	Air + C_6F_{14}	$N_2 + C_6F_{14}$	Air + C_6F_{14}	$N_2 + C_6F_{14}$
Δm (mg) After 5 hours	43 ± 6	0.9 ± 0.3	6 ± 1	40 ± 8
$[Cu^{2+}]$ (mM) After 5 hours	45 ± 6	1 ± 0.3	7 ± 0.1	42 ± 8

Figure 2. Influence of the foam bubbles and atmosphere gas composition on the copper mass dissolved. The mass of copper dissolved Δm_{Cu} , is obtained by weighing the copper plate after five hours or measuring the cupric ion concentration $[Cu^{2+}]$ using ICP. $[HCl] = 0.1 M$

Extending the leaching foam concept to a noble metal (Ag) and to another reactive gas, ozone (O_3)

This first set of experiments is a proof of concept showing that foams are efficient reaction media for the oxidation of copper by O_2 as they enable the fast transfer of the gaseous reactant through the foam. We now investigate means to extend this concept to noble metals, such as silver (Ag), which is also present in WEEE wastes such as printed circuit boards. We replace the copper plate used in the protocol described above by a silver plate and we use H_2SO_4 instead of HCl to avoid silver chloride precipitation. Indeed silver sulfate is several orders of magnitude more soluble than silver chloride and a simple calculation (not shown) shows that the silver concentration can be higher than 10 mM in presence of 1M sulfuric acid.

When air is used to produce the foams and for the atmosphere above the foams, we do not measure any dissolution of Ag which is in correlation with the electrochemical potential of the silver oxidation. To enable the oxidation of Ag, we use ozone (O_3) a stronger oxidant. As ozone can easily attack the double carbon bond of the surfactant, we replace BrijO10 by Brij®L23 whose hydrophobic chain does not bear a double bond. This surfactant has a life expectancy of a few hours in the presence of ozone (28). To ensure that O_3 is present both in the atmosphere and in the bubbles and to compensate for the foam collapse over time, the O_3/O_2 mixture is injected in a continuous manner using an ozonizer connected to a flow controller to maintain a constant gas flowrate. As shown in Table 2, using a sulfuric acid solution of 0.1 M or 1 M does not change the amount of dissolved silver, about 15 mg after 5 hours. There are very few studies in the literature concerning the leaching of metallic silver by ozone that we can refer to evaluate the efficiency of our process (29-31). Vinals et al. (31) have studied the leaching of a silver powder with ozone dissolved in sulfuric acid solutions. Although the specific surface area of the powder used in their experiments is not given, we use the particle size to convert their results in rates in $mol / (m^2.s)$ of Ag dissolved. Rate values of 2.10^{-6} and $2.10^{-7} mol / (m^2.s)$ were calculated for particles of diameter of 10 μm or 1 μm respectively. In our case, a rate of $10^{-5} mol / (m^2.s)$ can be determined using the surface area of the silver plate, which is at least an order of magnitude higher. This result consolidates the concept of using ozone foams to dissolve silver. Moreover, we note that the low dependency of the leaching rate upon the sulfuric acid concentration (in the 0.1 – 1 M range) that we observe in Table 2 has also been reported by Vinals et al. (32). This result is likely to be due to the large excess of protons compared to dissolved ozone concentration in solution. Indeed the concentration of protons is also much higher than the concentration of dissolved silver and hence its consumption by the dissolution reaction is negligible.

	[H ₂ SO ₄]	Δm _{Ag}	[Ag ⁺]
	(M)	(mg)	(mM)
Solution	1M	9	3
Foam	0.1M	15	6
	1 M	15	6

Table 2. Extension of the leaching foams to a noble metal, silver, Ag using a mixture of O₃ and O₂ for the foam bubbles. Mass of dissolved silver, Δm_{Ag} and silver ion concentration, [Ag⁺] measured in H₂SO₄ solutions and foams after five hours.

Complexing the Cu²⁺ with an anionic surfactant enables to improve the dissolution rate

In the previous section we showed how the efficiency of metal leaching can be enhanced by improving the transfer of the oxidizing gas as a foam is used instead of a solution. Now we explore the potential of surfactants, another indispensable foam component, in the refinement of the oxidizing process. To increase the leaching rate of Cu, we use a surfactant with a better affinity towards Cu²⁺ ions to shift the reaction equilibrium toward the release of Cu²⁺. While the neutral surfactants such as polyoxyethylene alkyl ether are not expected to form complex with Cu²⁺ ions, the use of anionic surfactants such as sodium dodecylsulfate is expected to lead to the complexation of two species with opposite electrostatic charges as shown by several studies in literature.

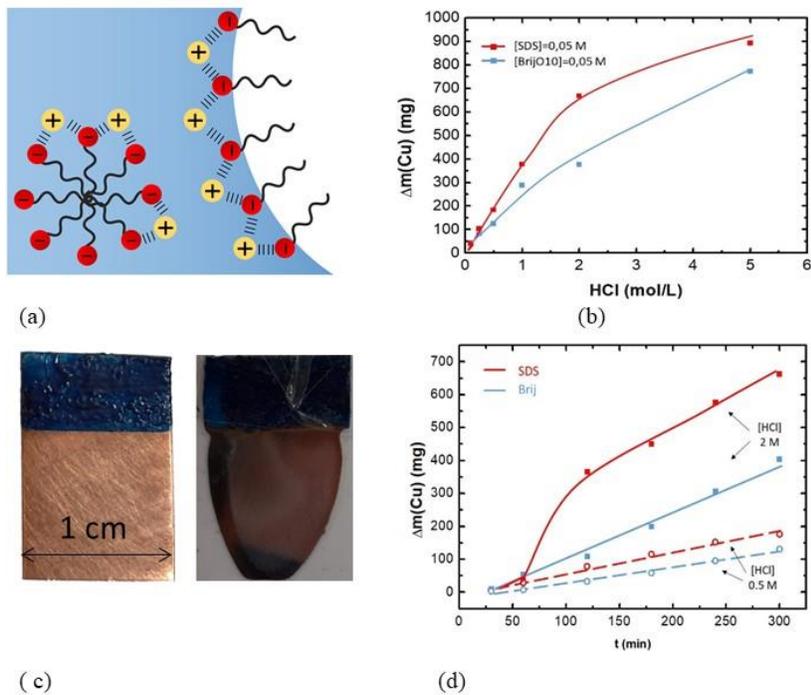


Figure 3. Dissolution of Cu in the presence of complexing surfactants. (a). Schematic drawing of the complexation of Cu^{2+} ions (yellow) with negatively charged SDS micelles in bulk solution and adsorbed SDS at air-water interfaces (b). Mass of dissolved Cu as a function of HCl concentration for a foam containing 0.05 M SDS or 0.05 M BrijO10. (c). Photographic image of the Cu plate before (left) and after (right) five hours of dissolution in 2M HCl and 0.05 M of SDS. (d) Mass of dissolved Cu as a function of time in foams stabilized either by 0.05 M of BrijO10 or 0.05 M SDS and for HCl concentrations of 0.5 and 2 M.

Indeed mixing a cupric salt with SDS is a method reported to synthesize a two-tail surfactants of $\text{Cu}^{\text{II}}(\text{dodecylsulfate})_2$ and interactions between SDS micelles and cupric ions are used for the extraction of Cu^{2+} ions from wastewater in a process called Micelle Enhanced Ultra Filtration (32-34) (Figure 3a). Even though the SDS-Cu^{2+} species are less stable than complexes between Cu^{2+}

and ligands as EDTA or citric acid (30), the interaction is strong enough to promote the ultrafiltration of these cations over a large range of pH.

In Figure 3b, we compare the amount of dissolved Cu^{2+} ions as a function of the HCl concentration for two surfactants, BrijO10 and SDS, at a concentration of 0.05M. For both surfactants, the higher the hydrochloric acid concentration the higher the concentration of dissolved copper. The non-linearity observed at high hydrochloric acid concentration with the SDS foams is probably due the decrease of the surface of the plate (Figure 3c). More interestingly, for every hydrochloric acid concentration, the use of SDS allows a faster copper dissolution of (Figure 3d). We thus demonstrate that the efficiency of the dissolution process strongly relies on the choice of the surfactant used to produce the foams. In addition to the interaction between the SDS micelles and Cu^{2+} ions, it should be noted that the SDS can also interact with the layer of Cu_2O present on the copper sample, with an impact on the dissolution rate. Indeed, the adsorption of SDS on Cu_2O particles has been suggested by Villamil et al. (35) who showed that the protective layer of Cu_2O on a copper electrode is partially dissolved in presence of SDS.

Conclusion

We have demonstrated that aqueous foams can oxidize and dissolve metallic copper in the presence of hydrochloric acid and an oxidizing gas such as O_2 or O_3 . We show that controlling the atmosphere above the foams is crucial, as a fast exchange of gas between atmosphere and bubbles

occurs, probably through the thin liquid films between the foam bubbles. Using foams, we achieve much higher dissolution rates than for aqueous solutions as the reactive gas transfers very quickly through the foams. This method enables to leach and remove a thickness of the order of 175 μm from the copper plate, which is consistent with typical Cu thicknesses in PCBs. Furthermore, using O_3 instead of O_2 enables to extend the leaching foams concept to the dissolution of a noble metal like Ag. Moreover, by replacing a nonionic surfactant by a negatively charged surfactant which complexes the metal ions produced by the reaction, we show that the dissolution rate can be strongly enhanced. Hence, it can be foreseen that a control of the selectivity of the process may be achieved by carefully choosing the surfactant formulation. This work is thus a very encouraging step toward the development of a hydrometallurgical process to recycle metals from electronic wastes based on foams, that is more environmentally friendly than classical hydrometallurgy in solution as it enables a strong reduction the volume of liquid used for the leaching process. From this proof of concept, many other developments can be considered. For example, tailored surfactants can be investigated to extend the synergy with their complexation characteristics. To address WEEE after a grinding step, a new set up designed to leach particles surface could be also studied. Another perspective would be to address other compounds, as metal sulfides, to take advantage of the oxidation by the foam in a leaching step.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SYNOPSIS

Aqueous foams enable to leach metals efficiently because of fast O₂ transfer and they minimize effluent generation.

LIST OF ACRONYMS

Au - Silver

Brij010 - C₁₈H₃₅(OCH₂CH₂)_nOH, n~10

Brij®L23- $(\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}, n \sim 23$

Cu - Copper

EDTA – Ethylenediaminetetraacetic acid

HCl -Hydrochloric acid

ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry)

N₂ - Nitrogen

O₂ – Dioxygen

PCB – Printed circuit boards

SDS - Sodium Dodecyl Sulfate

WEEE - Waste from Electrical and Electronic Equipment

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