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Leaching foams: toward a more environmentally-friendly process for the recovery of critical metals from electronic wastes

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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 effluents which need to be collected and concentrated. 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 (O₂) 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 valuable 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 processes, based on leaching solutions containing oxidants or acids to extract metals, were traditionally used for the mining industry for ore extraction, is also a promising route for the recovery of metals from WEEE (4-9). Hydrometallurgy is particularly suitable for local and short scale installations and presents a high efficiency and selectivity for the purification of metals. This process is therefore an interesting alternative to pyrometallurgy which consists in smelting the waste at high temperature so that it is highly energy consuming and generates off gases that can be toxic (10). Even though hydrometallurgy is less environmentally hazardous than pyrometallurgy, its development is hampered by the large amounts of liquid effluents that need to be collected and treated. In this context, aqueous foams which are collection of bubbles stabilized by surfactants and contain less than 10% of liquid appear as a promising way of decreasing the environmental footprint of hydrometallurgy.

Aqueous foams are used in environmentally relevant applications for waste water treatment (11) or nuclear waste retreatment (12-13). 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 (14-15), ores (16), minerals (17-18), or proteins (19, 20). A major advantage of foams is that they contain more than 90% v/v of air and very little volume of liquid hence they are good candidates for a reduction of effluents volumes during these processes. Moreover, foams are remarkably versatile and the surfactant used to achieve their stabilization can be chosen so as to give specific properties, such as in particle or ion flotation processes where ionic surfactants can complex the particles or ions to be recovered from a solution (14-20).

In the above applications, the gas, usually air is not chemically active and is only used to produce bubbles that promotes particle flotation. Nevertheless, reactive gases such as O_2 or O_3 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 (O_2) present in the air bubbles and demonstrate that the fast transfer of O_2 through the foams enables a rapid and efficient oxidation of copper. By using ozone (O_3), 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 concentrated sulfuric acid (Sigma Aldrich) with MilliQ water (18,2 M Ω .cm@25°C). The nonionic surfactants Brij®O10 (C₁₈H₃₅(OCH₂CH₂)_nOH, n~10) and Brij®L23 (CH₃(CH₂)₁₀CH₂(OCH₂CH₂)_nOH, n~23) and the anionic surfactant SDS (Sodium dodecyl sulfate, purity \geq 99,0%) 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, the solution is beforehand bubbled during 30 minutes to remove dissolved dioxygen. During foaming, air and nitrogen are bubbled into perfluorohexane (C₆F₁₄) as traces of this water-insoluble gas in the bubbles enable to slow down Oswald ripening and increase the foam stability (21-22). The experiment consists in stirring either a copper plate, (2 cm \times 2 cm \times 675 μ m, purchased at Alfa Aesar, purity 99.9%) or a silver plate (2 cm x 2cm x 250 μ m, purity 99.9%, purchased at Sigma-Aldrich) at 40 rpm for five hours, in a 3 neck round bottom flask filled with 100 mL of foam or solution. For foam experiments (Figure 1b), 15 mL of the HCl or H₂SO₄ solution are poured into the flask and gas is then injected through a porous fritted glass (pore diameter: 16-40 μ m, supplied by ROBU Glasfilter Geräte GmbH) to reach a total foam volume of 100 mL. The initial bubble diameter is approximately 200 μ m is measured by optical microscopy. Because of foam collapse, the gas is injected every 25 minutes to keep the foam volume constant. For solution experiments (Figure 1a), the copper plate is directly stirred into a volume of 100 mL of solution. For both cases, the gas atmosphere above the foam or the solution can be changed by applying a gentle flow through the flask necks.

After five hours, the final mass of the copper or silver plate is subtracted from the initial mass to calculate the total dissolved copper quantity ($\Delta m(\text{Cu})$). 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 spectrometer to measure the quantity of copper or silver dissolved above time.

Results

Oxidation of Copper by O_2 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 metallic copper, (Cu) into cupric ions (Cu^{2+}) by the dioxygen (O_2) 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, O_2 , 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 (HNO_3) (23) or by combining a non-oxidizing acid such as HCl or H_2SO_4 with a dissolved oxidant such as Fe^{3+} (24).

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 in 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 Cu^{2+} 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).

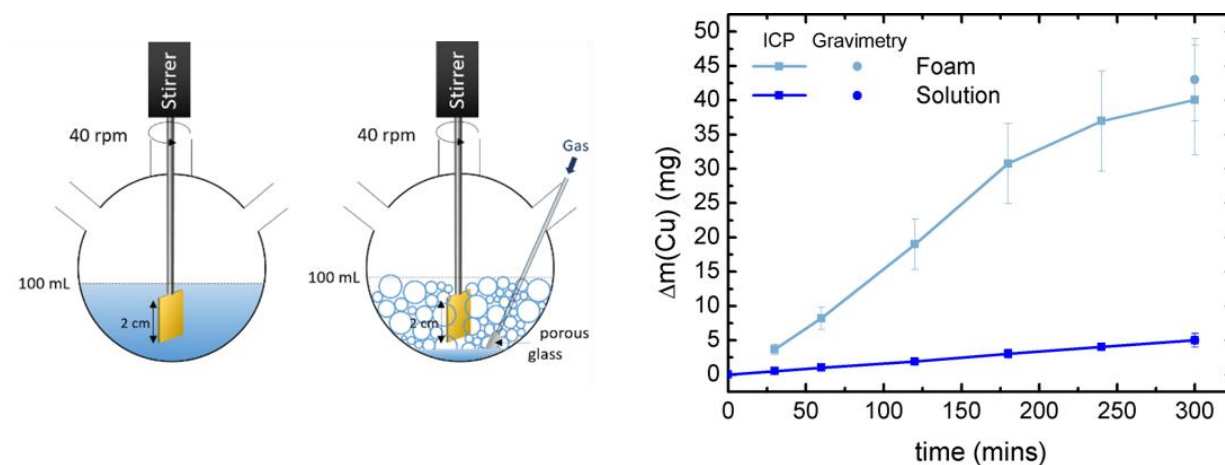


Figure 1. Dissolution of a copper plate in a solution and in a foam. (a) Experimental set-up of a copper plate stirred in a 3 neck bottle flask containing 100 mL of a 0.1M HCl solution or (b) 100 mL of an aqueous foam obtained by foaming 15 mL of 0.1M HCl solution. (c) Mass evolution of the Cu plate ($\Delta m(\text{Cu})$) 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 $[\text{Brij}^{\text{®}}\text{O}10] = 0.05\text{M}$. 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.

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 but it 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 O₂, 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 1©.

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 and 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 O_2 dissolved in the continuous phase, of the order of $2.6 \cdot 10^{-6}$ 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 quantity 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.

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 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 (Table 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 O₂ 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.

Gaz composition

Bubbles	Atmosphere	Δm_{Cu} (mg)	[Cu ²⁺] (mM)
Air	Air	43 ± 6	45 ± 6
N ₂	N ₂	0.6 ± 0.3	0.06 ± 0.03
N ₂	Air	39 ± 8	41 ± 8
Air	N ₂	5 ± 1	0.5 ± 0.1

Table 2. Influence of the 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 [Cu²⁺] using ICP. [HCl] = 0.1 M

Extending the leaching foam concept to a noble metal (Ag) and to another reactive gas, ozone (O₃)

This first set of experiments is a proof of concept showing that foams are efficient reaction media for the oxidation of copper by O₂ 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 H₂SO₄ instead of HCl to avoid silver chloride precipitation. 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 (O₃) a stronger oxidant. As ozone can easily attack the double carbon bond of the surfactant, we replace BrijO10 by Brij®L23 which hydrophobic chain does not bear a double bond. This surfactant has a life expectancy of a few hours in the presence of ozone (25). To ensure that O₃ is present both in the atmosphere and in the bubbles and to compensate for the foam collapse over time, the O₃/O₂ 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 3, 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 (26-28). Vinals et al. (28) 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⁻¹ of Ag dissolved. Rate values of 2.10⁻⁶ and 2.10⁻⁷ mol.m⁻².s⁻¹ were calculated for particles of diameter of 10 μm or 1 μm respectively. In our case, a rate of 10⁻⁵ mol/s/m² 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 3 has also been reported by Vinals et al. (29). 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] (M)	Δm _{Ag} (mg)	[Ag ⁺] (mM)
Solution	1M	9	0.8
Foam	0.1M	15	9
	1 M	15	9

Table 3. Extension of the leaching foams to a noble metal, silver. 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 2. 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 (29-31) (Figure 2a). 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 2b, 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 2c). More interestingly, for every hydrochloric acid

concentration, the use of SDS allows a faster copper dissolution of (Figure 2d). 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. (32) 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 showed that controlling the atmosphere above the foams is crucial, as a fast exchange of gas between atmosphere and bubbles occurs. Using foams, we achieve much higher dissolution rates than for aqueous solutions as the reactive gas transfers very quickly through the foams. 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, we foresee that the surfactant formulation may enable to achieve a selectivity of the process for a targeted metal to be recovered. 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.

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Author Contributions

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SYNOPSIS

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

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