Foam Separation of Metal Ions and the Potential ‘Green’ Alternative to Solvent Extraction

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Foam separation has been applied to recover or remove various substances from dilute aqueous solutions in various industries because it is an environment- and cost-friendly process. The literature has been reviewed focusing on the separation of metal ions. From an operational point of view, various methods are discussed for the removal of metal ions from solution, and on the selective recovery of a specific target metal ion. The former applications are designed to purify industrial effluents, and the performance of foam separation is well proven. The latter examples are aimed at recovering valuable metals, which has been shown to be difficult due to the inherent problem of contamination in foam separation. An operation mode was developed to overcome this problem and to enhance the selectivity for separating a specific target metal from solutions containing multi-metals. The method, called continuous counter-current foam separation, was developed, and its performance was demonstrated by the experimental results for Ga(III) separation. Since both high selectivity and recovery was obtained by this method, foam separation is potentially a “solvent-free” alternative to solvent extraction.

1. Introduction

Foam separation [1-10] has been widely used in industry for recovering valuable materials, and also for removing impurities or toxic substances from aqueous solutions. Among the targets to be treated are surfactants [11-21], proteins [22-28], microorganisms including bacteria and viruses [29, 30], dyes [9, 31], other organic substances including plastics [7, 32-35], ores [36-55], metal ions [56-105], colloidal particles [106-108] in pretreatment in mining and for analytical chemistry, or in the emission control of sewage and industrial effluents. Since foam separation enables operation with space-saving simple equipment with low energy input and operational cost, the process is regarded as an efficient method with a low impact on the
In the operation of foam separation, foam [109-117] is generated by introducing air continuously into an aqueous bulk solution, and the foam bed is formed above the solution surface in a column. As the foam rises through the column, interstitial liquid between adjacent foam bubbles is drained out by gravity, and the liquid content in the foam bed decreases in the upper part of the column. At the top of the column, foam collapses and is collected in a reservoir as foamate. A surface-active reagent (surfactant) is usually added to the solution to enhance both foam production and foam stability. When target species are surface-inactive, reagents for collecting the target substance or conditioning the solution would be added to modify the surface of the target substances. The basic separation mechanism is the preferential distribution of the target substance between the foam surface and the bulk solution. Solutes with a low affinity for the surface are washed out by gravitational drainage, while solutes with a strong affinity are preferentially concentrated on the surface of the foam. As the foam bed ascends in the column, however, the drainage decreases and a small amount of interstitial liquid, which contains the non-target species at the same concentration as the bulk solution, is collected as the foamate. In other words, there is an intrinsic trade-off relationship between the yield and selectivity for the target substances in foam separation [83, 87]. This is a major disadvantage of the foam separation process in comparison with solvent extraction, where non-target species are preferentially removed in a multistage operation. Many attempts have been made to overcome this problem by adding a reflux [13, 15, 17], operating in multi-stage mode [14, 20, 102], installing various partitions in the column [18, 19, 21, 74] and incorporating ultrasonic generation [79, 101].

For the application of foam separation in hydrometallurgy [1], Lemlich proposed a classification of adsorptive bubble separation methods into two categories i.e. foam separation and non-foaming adsorptive bubble separation [119, 120], depending on the stability of the bubble as shown in Figure 1. The latter includes solvent sublation and bubble fractionation. Foam separation is further divided into two sub-categories of froth flotation and foam fractionation. While the former method deals with solid particles or precipitations, the latter covers soluble complexes with surfactants/collectors. For metal recovery, froth flotation is used widely. Froth flotation has several subcategories such as ion flotation, precipitate flotation and sorptive flotation. In ion flotation, ionic targets are precipitated and their recovery enhanced by adding

![Classification of adsorptive bubble separation methods (Lemlich, et al. 1968)](image-url)
a counter-ionic surfactant as a collector. In precipitate flotation, precipitates are formed by adding neutralizing alkali agents. Sorptive flotation utilizes colloid or solid sorbents to collect target solutes. Sorbents to be added are colloidal Fe(OH)$_3$, natural zeolites, activated carbon, and so on.

In industrial applications, foam or bubbles are typically produced by three techniques; induced air flotation (IAF) [8, 46, 48], dissolved air flotation (DAF) [8, 46 48, 57, 72] and jet cell flotation (JCF) [8, 46, 108]. IAF utilizes a mechanical force to form bubbles with a combination of a high-speed agitator and an air injector. This method is usually employed in the mineral processing and petrochemical industries. While in DAF, bubbles are formed by reducing the surrounding pressure of water pre-saturated with air; this method is widely adopted in effluent treatment. In JCF, which is a modified version of DAF, bubble/particle aggregates are formed by injecting a jet of a mixture of air and the feed solution into the bulk solution under high pressure. The Jameson cell is a well known JCF apparatus and has been applied in mineral processing and for effluent treatment.

In this review, the use of foam separation will be focused on the recovery/removal of metal ions. From this standpoint, techniques are reviewed from two points of view; firstly purification of solutions containing metals, and secondly selective metal recovery. The former aims to remove most metals from solution. Three types of operation are described in section 2.1. While for the latter, various methods are proposed to separate a specific metal, and the techniques are summarized in section 2.2. The method developed by the authors is introduced in section 3. It is referred to as continuous counter-current foam separation (abbreviated as CCFS hereinafter) [91, 94, 95, 104], which achieves both high selectivity and recovery of a specific metal target. Typical experimental results for CCFS for Ga(III) separation from a solution containing multi-metals are presented.

2. Foam separation of metal ions

2.1. Metal removal from aqueous solutions: solution purification

This type of operation is generally performed in industrial wastewater treatment to reduce metal concentrations to appropriate levels. There are many reports on separating various types of metals from synthetic solutions and real wastewaters. Techniques applied are ion flotation, sorptive flotation and precipitate flotation. The following are typical examples of the applications.

Lazaridis et al. [88] compared the three types of flotation in treating aqueous effluents containing Cu, and reported that the removal efficiency was in the order of ion flotation > sorptive flotation > precipitate flotation. An economic evaluation of the sorptive flotation using a DAF apparatus was also presented. Polat and Erdogan [96] applied counter-ionic surfactants as metal collectors in ion flotation for removing metal ions. Although they attempted the selective separation of Cu from a solution containing Cu, Zn and Ag, their mutual separation was unsuccessful. Doyle [86] carried out ion flotation tests and found that the selectivity for metals depends on the ionic valence and radius of metals, the surface tension of aqueous solutions of the metals and surfactants and so on. Doyle also compared the performance of ion flotation with other unit operations such as solvent extraction and ion exchange; for concentrated metal solutions,
the performance of ion flotation was relatively poor. Aiming at removing toxic arsenic minerals from pulp solutions, Ma and Bruckard [52] studied the possibility of using ion flotation. They concluded that pre-oxidization of the mineral ores is essential and the addition of a reagent is required to suppress contamination by cuprous species.

Medina et al. [90] investigated precipitate flotation of Cr(III) from dilute solutions using sodium dodecylsulfate (SDS) as the anionic collector. Parameters influencing the separation performance were the zeta potential and floatability of chromium hydroxide precipitates. Maximum removal was obtained at around the isoelectric point of the precipitates. Tessele et al. [72] reported on the flotation of Hg, As and Se ions from effluents in the gold cyanidation process. Through precipitation with sodium dithiocarbamate, followed by coagulation with LaCl$_3$ and flocculation with Bufloc 606 polymer, more than 98 % of the metals were removed from the effluents.

Capponi et al. [107] studied the sorptive flotation of several metals such as Al, Cd, Cr and Pb in synthetic solutions using colloidal Fe(OH)$_3$ as the sorbent. This method was also applied to electroplating wastewater on a pilot scale; the metal concentrations in the treated water were reduced to below the regulation values. Feris et al. [46] investigated several combinations of sorbent and metal in sorptive flotation, along with a performance comparison with DAF, IAF and JCF for oil removal. Koyanaka [99] and Shakir et al. [106] successfully applied sorptive flotation to radioactive metals such as $^{137}$Cs, $^{144}$Ce, $^{60}$Co, $^{106}$Ru, $^{65}$Zn, $^{95}$Zr, $^{89}$Sr and $^{90}$Sr using colloidal Cu$_2$[Fe(CN)$_6$]$_3$, Fe(OH)$_3$, Al(OH)$_3$ and Co(OH)$_3$ as the coprecipitants. More than 98 % removal was obtained for $^{137}$Cs, $^{144}$Ce, $^{60}$Co, $^{106}$Ru, $^{95}$Zr, $^{90}$Sr and $^{65}$Zn, and for $^{89}$Sr the removal was over 90 %. They have shown the advantage of this method over conventional chemical precipitation and ion exchange.

2.2. Selective metal recovery from aqueous solutions

To enhance the selectivity in the mutual separation of metal ions, reagents having a specific affinity for the target metal were added to the foam separation system. The same strategy is used in solvent extraction except for the presence of a surfactant, which is an essential component in foam separation. Some studies use functional surfactants which have an affinity for the target metal, and other studies use collectors or conditioners as cosurfactants. In the latter cases, the additional dosage makes the process complicated because of the requirement to recover those chemicals before discharging the effluents. The following are applications aimed at recovering valuable metal ions from solutions containing multi metal ions.

Gold is a common target in selective foam separation, and several studies have been conducted on its recovery from synthetic solutions and/or mineral processing streams. Galvin et al. [66] investigated ion flotation of the aurocyanide anion, Au(CN)$_2^-$ using cetyltrimethylammonium bromide, (CTAB) from synthetic solutions containing the dicyanoargentate anion, Ag(CN)$_2^-$ as a contaminant. A separation factor of 8 was obtained for the recovery of gold from solutions containing large quantities of silver. Galvin et al. [69] also carried out a field trial for ion flotation of gold cyanide from heap (in situ) leaching solutions at a pilot scale. A gold recovery of over 80 % was obtained while 80 % of the reagent was successfully reused.
Nicol et al. [67] adopted ion flotation for the recovery of gold as the aurocyanide anion, \( \text{Au(CN)}_2^- \) from heap leaching solutions. Over 90% recovery using CTAB was achieved, and thus could be increased by up to 100 times in a multistage operation; the resultant foamate was sent to an electro winning process. The cost of the equipment and the operating cost was estimated to be lower than that for the existing adsorption processes using resin ion exchanger and activated carbon.

As for other valuable metals, attempts have been made by Marczenko and Kalinowski [118] for the recovery of \( \text{Pt(SnCl}_3)^3^- \) with basic dyes, and by Berg et al. [119] for the separation of \( \text{IrCl}_6^{2-} \) and \( \text{RhCl}_6^{3-} \) from hydrochloric acid solutions using hexadecyltripropylammonium (HTPAB) through ion flotation followed by solvent sublation. In both cases, separation was possible but the performance was poor. Miller et al. [47] reviewed ore flotation of pyrrhotite containing platinum group of metals, PGMs using xanthate derivatives as collectors. Due to the lack of stability of the ore hydrophobicity, the system was difficult to operate practically. Hernandez-Exposito et al. [93] investigated the ion flotation of Ge from leaching solutions of a fly ash using dodecylamine as the collector. Although complete recovery of Ge was achieved, considerable amounts of contaminants such as Ni, As and Sb were included in the final foamate even under optimum conditions. The content of GeO\(_2\) in the roasted final product was reported to be 53%. Charewicz and Grieves [58] carried out a selective flotation trial for the metal oxoanions \( \text{HReO}_4 \), \( \text{H}_2\text{MoO}_4 \), \( \text{H}_2\text{CrO}_4 \), \( \text{H}_2\text{WO}_4 \) and \( \text{HVO}_3 \) in a batch mode from synthetic hydrochloric acid solutions using a cationic surfactant, hexadecyldimethylbenzylammonium chloride (HDMBAC). The selectivity for the target did not achieve a level of practical interest.

Although a number of trials including adding reflux or operating with multistage apparatus have been made, highly selective separation was difficult to achieve with foam separation. However, for the percent recovery of the target, relatively high values were obtained in some studies. Furthermore, the separation performance in continuous mode was lower than in the batch mode due to insufficient contact between the metals, the collector and the surfactant. The results clearly demonstrate this problem in conventional foam-separation and there seems to be much room for performance improvement.

3. Continuous counter-current foam separation

3.1 Enhancement of selectivity by controlling liquid flow in the foam

To improve the selectivity of foam separation, we have proposed an operation mode, continuous counter-current foam separation (CCFS), wherein the metal and the surfactant solutions are simultaneously injected into the rising foam bed. The surfactant used has a high affinity for the target metal. Figure 2 shows the schematic diagram of the CCFS apparatus (b) along with that of a conventional one (a): CCFS features gradual injection of metal and surfactant solutions into the foam bed. The air is supplied to the bulk solution through a gas distributor to make the foam bed which moves up the column. A metal-free base solution containing a surfactant is continuously fed in at the bottom of the column.

In CCFS, the surfactant and the metal solutions spread in the bed and eventually flow downward against the foam flow. When the downflow of the metal solution encounters foam which comes from the bottom, the target metal in the solution is preferentially adsorbed onto the surface of the foam. As the metal
solution flows down, the target is continually adsorbed on the surface. Finally, almost all the target is loaded onto the foam surface. Non-target metal ions are contained in the interstitial liquid in the foam bed even though they are not adsorbed on the foam surface. To scrub the non-target metal ions in the interstitial liquid, a surfactant solution was introduced in the upper part of the injection point of the metal solution. The downflow of the surfactant solution takes the non-target metal ions downward. Even if a portion of the target metal on the foam surface was stripped by the downflow of the surfactant solution, it would be re-adsorbed on the surface while flowing down to the bottom. Overall, the target metal is brought upward along with the foam bed, and non-target metals move downward along with the downflow. Such a counter-current behavior of the target metal and the non-target metals is similar to multi-stage operation in solvent extraction.

The foam bed in CCFS is divided into three zones depending on the function as shown in Figure 3. Two zones from the bottom correspond with steps in a solvent extraction (SX) process. The adsorption zone, which is below the injection point of the metal solution, is regarded as forward extraction in SX. The target metal is adsorbed on the foam surface in CCFS, while in SX, it is preferentially distributed to one phase. The scrubbing zone is below the injection point of the surfactant solution, wherein the non-target metal ions in the interstitial liquid are washed out by the downflow of the surfactant solution. Supplying the surfactant solution also enhances foam stability. This zone corresponds to scrubbing in SX. In the enrichment zone of CCFS, the target metal is concentrated because the solvent, water in this case, is drained-out by gravity while the target metal stays at the foam surface. This enrichment is a significant advantage of CCFS. In SX,
enrichment can be attained by back extraction into a smaller amount of solution or by evaporating the organic solvents. Since CCFS is operated in a column configuration, the zone heights are easily adjustable depending on requirements by changing the position of liquid injection. Furthermore, the column requires only a small installation area. Mixer-settlers need a large area to accommodate many vessels for multistage operation. Also, the emission of organic solvents vapors to the atmosphere should be carefully controlled.

The surfactants used in our studies are nonionic types, poly(oxyethylene) nonylphenyl ethers HO(CH₂CH₂O)ₙ-C₆H₄C₉H₁₉, (abbreviated as PONPE), where n is the EO number [121-130]. In Figure 4 the affinity of PONPE10, which has 10 EO units is illustrated for various metals for different HCl concentrations. The affinity was compared with the percent extraction of the metal in a solvent extraction test using PONPE10 as the extractant [129]. Highly selective affinity of PONPE 10 for Au, Ga and Fe was observed, while a negligibly small affinity was found for other metals. The extracted metals are trivalent and are present as HAuCl₄, HGaCl₄, and HFeCl₄. Whereas the selectivity was little affected by the number of the EO units of PONPE, the stability of the foam

Figure 3. The three zones in the foam bed for CCFS and the corresponding operations in the SX process

Figure 4. Extraction of metal ions with PONPE10 in chloroform
varied with the EO number. PONPE with 20 units (PONPE20) gave appropriate foam stability for CCFS.

3.2. Comparison of CCFS with conventional foam separation and solvent extraction

As an example, the results for Ga(III) separation with CCFS using PONPE20 as the surfactant were used to compare the performance of CCFS with that of conventional foam separation and SX [104]. The feed solution contained Ga(III), Fe(III), Cu(II) and Zn(II), and the initial concentration of each metal was 20 ppm. Since only a trace amount of Cu(II) and Zn(II) was recovered in the foamate with CCFS, the major contaminant for Ga(III) recovery was Fe(III). The performance was evaluated using the concentrations of Ga(III) and Fe(III). For evaluation, the percent recovery (R), the separation factor (Sp) and the enrichment (En) of Ga(III) are defined by the following equations.

\[
\begin{align*}
R_{mi} &= 100 \left( \frac{F_{mi}}{M_{mi}} \right) \\
Sp_{mi} &= \frac{[Ga]_{mi}}{[Ga]_{fd,ini}} \\
En &= \frac{[Ga]_{f}}{[Ga]_{fd,ini}}
\end{align*}
\]

where \(F\) and \(M\) are the respective volumetric flow rates of the foamate and the metal solutions, and the subscripts, \(mi\), \(f\), \(fd\), and \(ini\), refer to the metal ions, foamate, metal (feed) solution and initial values, respectively.

The change in the percent recovery of Ga(III) and Fe(III) with the concentration of hydrochloric acid is shown in Figure 5 for the three operation modes, CCFS, NS and Con. NS refers to an operation where only the metal solution is fed to the foam bed. Con represents the mode shown in Figure 2(a). No solutions were injected into the bed, and the solution of the mixture of the metal and the surfactant was used as the base solution. In CCFS, the recovery of Fe(III) is successfully suppressed while almost all the Ga(III) is recovered in the foamate. For the NS mode, the Fe(III) curve is located at significantly higher values compared to the curve for the CCFS mode. The trend shows clearly the rinse effect of supplying the surfactant solution. While in the conventional mode, Con, the separation is obviously low because of the insufficient contact between the target and PONPE due to the dilution. Comparison of Ga(III) recovery between Con and NS shows the advantage of

![Figure 5](image)

Figure 5. Percent recovery of Ga and Fe for different operation modes (Kinoshita, et al. 2011)

![Figure 6](image)

Figure 6. Comparison between CCFS and SX for the separation of Ga from Fe (Kinoshita, et al. 2011)
feeding the metal solution into the foam bed. The separation factor for Ga(III)/Fe(III) and the enrichment ratio of Ga(III) in the three operational modes are summarized in Table 1. Values underlined show the highest value of each parameter. The highest separation factor is obtained from CCFS, while the enrichment for CCFS is relatively low because of the two liquids fed into the foam bed. Improvement in the enrichment will be obtained by making the enrichment zone longer. The results from Figure 5 and Table 1 indicate an optimum HCl concentration of 6 M, for separating Ga(III) from Fe(III) with CCFS.

Figure 6 compares the percent recovery of Ga(III) and Fe(III) in CCFS with the percent extraction of both metals with PONPE in SX using chloroform as the diluent [129]. The separation of each extraction curve suggests that multi-stage extraction is required for separating Ga(III) from Fe(III). Furthermore, it is not practical to use chloroform as the diluent. No organic solvent is required in CCFS, and good separation was obtained in a single unit simply by introducing air and solutions in the column.

<table>
<thead>
<tr>
<th>Mode</th>
<th>CCFS</th>
<th>NS</th>
<th>Con</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow rate of metal sol.</td>
<td>0.35 cm$^3$/min</td>
<td>0.35 cm$^3$/min</td>
</tr>
<tr>
<td></td>
<td>Flow rate of surfactant sol.</td>
<td>0.25 cm$^3$/min</td>
<td>none</td>
</tr>
<tr>
<td>4 M HCl</td>
<td>3.7</td>
<td>0.05</td>
<td>1.3</td>
</tr>
<tr>
<td>5 M HCl</td>
<td>38</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>6 M HCl</td>
<td>67</td>
<td><strong>3.6</strong></td>
<td><strong>2.8</strong></td>
</tr>
<tr>
<td>7 M HCl</td>
<td>13</td>
<td>3.4</td>
<td>2.2</td>
</tr>
<tr>
<td>8 M HCl</td>
<td>4.0</td>
<td>2.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

### 3.3. Recovery of gallium from a leach liquor from zinc refinery residues

The feasibility of CCFS for recovering Ga(III) from an industrial waste, zinc refinery residue has been studied. The residue was leached with 6.0 M HCl to obtain the leach liquor. The leach liquor was conditioned by dilution and addition of ascorbic acid to reduce Fe(III) to Fe(II). The resulting solution was used as the feed solution for CCFS to recover Ga(III). The metal composition is shown in Table 2. The concentration of Ga is relatively low and the iron concentration is very high, so Ga recovery will be difficult. The experimental results for the optimum operating conditions in CCFS are summarized in Table 3. The percent recovery of Ga reaches 100 % and extraordinarily high separation factors for Ga are obtained against Zn, Al, As, In and Cu. The factor against Fe is 860 which is reasonably high. For comparison, the result for SX using PONPE10 as the extractant is also shown in Table 3. The same feed solution was treated by SX using a single stage forward extraction step followed by 5 scrubbing stages with 4.5 M HCl solution and finally back extraction with water. The separation factor for Ga against Fe is 72, which is lower than CCFS and the percent recovery of Ga is 71 % mainly because of the loss in scrubbing stages. The comparison of the results for CCFS and SX highlights the excellent performance of CCFS in the selective recovery of the target metal from metal mixtures. From the aspect of chloride hydrometallurgy, Ga SX has attracted attention [131,132], and studies using amines [131] and TBP proved the potential.
However, a major problem to be overcome is coextraction of Fe, In and other impurities. Since CCFS is an organic solvent-free, simple operation and has the potential of low reagent inventory due to the nature of the surfactant working as the target collector, this method provides a ‘green’ alternative option for metal separation.

| Table 2. Composition of feed solution prepared from a leach liquor from a zinc refinery residue |
|---------------------------------|-----|-----|-----|-----|-----|-----|
| Element | Ga | Fe | Zn | Al | As | In | Cu |
| Conc. [ppm] | 12 | 1500 | 3100 | 1400 | 600 | 320 | 87 |

| Table 3. Separation performance of CCFS and SX in Ga recovery |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|
| R<sub>Ga</sub> [%] | En [-] | Sp<sub>Fe</sub> [-] | Sp<sub>Zn</sub> [-] | Sp<sub>Al</sub> [-] | Sp<sub>As</sub> [-] | Sp<sub>In</sub> [-] | Sp<sub>Cu</sub> [-] |
| CCFS | 100 | 3.2 | 860 | 25000 | 20000 | 15000 | 5100 | 3300 |
| SX | 71 | 0.7 | 72 | 62000 | 7700 | 340 | unmeasurably high | unmeasurably high |

4. Conclusion

From an operational viewpoint of foam separation, studies on metal separation have been reviewed for the applications for the bulk removal of metals and also to recover a specific target metal from a metal mixture. The problem of selective separation in conventional foam separation was highlighted, and a method to overcome the problem was proposed. The high performance of the selective separation of Ga(III) from a multi-metals solutions by the method of continuous counter-current foam separation, CCFS using PONPE as a surfactant was proven in examples of the separation from a synthetic feed solution as well as from a real leach liquor from a zinc refinery residue.

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