XVI International Mineral Processing and Recycling Conference
28-30 May 2025, Belgrade, Serbia

DOI: 10.5937/IMPRC25091P

Original research article

HOLLOW DROP BUBBLES A PROPOSED NEW TECHNOLOGY FOR OPTIMIZED METAL EXTRACTION VALIDATED IN THE LABORATORY

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ABSTRACT – A new technology for solvent extraction has been developed. This innovation, Hollow Drop, merges flotation with solvent extraction by using air bubbles coated with an insoluble extractant material. While the concept of coated bubbles is not new, our work focuses on advancing this idea by generating a swarm of coated bubbles to scale up the process.

Experimental tests were conducted using dissolved copper solutions, SX extractants, Iodine solutions, and Kerosene, achieving copper recoveries of 70% with aqueous-to-organic (A/O) ratios of 17. These results demonstrate that the coated bubble process can operate continuously and holds promise for industrial-scale implementation.

Keywords: Solvent Extraction, Hollow Drops, Coated Bubbles, Reactive Oily-Bubble.

INTRODUCTION

Taggart first introduced the concept of organic-coated hollow droplets [1]. He proposed that oil-coated hollow droplets could serve as effective collectors of hydrophobic particles, a theory later supported by Misra and Anazia(Misra & Anazia, 1987), through their study on the flotation of ultrafine carbon. Their research showed that the binding time of an oil-free hollow droplet to carbon, initially 88 ms, was significantly reduced by the encapsulated droplet in oil to 5 ms. These findings highlight that coated hollow oil droplets accelerate mass transfer at the interface and enhance the recovery of the target metal."

In the flotation of sulfide minerals, Liu [3] adapted this concept to reduce the unwanted recovery of gangue particles and the organic collector's consumption. In this experiment, an organic collector, which is used in flotation, is dissolved in Kerosene, which is mixed with air and passed through a porous glass to produce a reactive oily bubble [4,5].

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The reactive hollow droplet concept can also be applied to conventional solvent extraction. In this approach, the organic coating of the reactive hollow droplet extracts the metal ions of interest. Chen et al. first introduced this idea. [6] It is known as 'Air-Assisted Solvent Extraction' (AASX). The most common non-conventional SX technologies can be summarized as (i) air-assisted solvent extraction (AASX), (ii) technology based on gas compression where solvent extraction is through dissolved nitrogen in a pre-dispersed solvent (DNPDSE) or columnar flotation technology (CEF) and (iii) technology based on the gas without compression (GWC).

Air-assisted solvent extraction (AASX) uses bubbles coated in organics, which are bubbled through a continuous aqueous phase to enhance the mass transfer process. The difference in density between the coating agent and the aqueous phase allows for the fast separation of phases. [6–8]. The coating agent on the bubble is thermodynamically stable based on the spreading coefficient between the surface tension of the different layers. [9–11]. Dissolved nitrogen in a pre-dispersed solvent technology uses compressed air to generate an organic blend of extractant, which is then introduced into the aqueous phase. [12–14] This approach's objective is similar to that of coated bubble technology, where increasing the bubbles' surface area and buoyancy leads to improved performance compared to traditional methods.

Rahmati's research used the last gas technology without gas compression (Rahmati et al., 2019, 2020, 2024). They proposed creating a foam layer of organic material and air in a separate column. A Venturi tube system passes this foam layer, which is mixed with a high-speed aqueous solution. The resulting mixture then moves through a separating column, where the charged organics are removed at the top.

In this experiment, two solvent extraction processes were carried out. One used a copper solution of 5gr/lots of copper and Kerosene-containing extractant Oximes (90% LIX and 10% Cytoximes). The second experiment used an Iodine solution at 1,5gr/lt of Iodine, and Kerosene was used as an extractant.

EXPERIMENTAL

Device

The equipment developed to carry out the solvent extraction process using a swarm of coated bubbles consists of 4 special zones, listed from bottom to top:

- **Discharged organic zone (Zone I):** Here, a porous air injector generates bubbles, either micro-bubbles or macro-bubbles, which promote foam creation at the top of the discharged organic zone.
- **Coated bubble generator zone (Zone II):** In this zone, a porous filter has been placed, which traps the organic phase in its pores using a difference in hydrophobicity and drags it through an upward air stream.
- **Extraction mixer zone (Zone III):** The solvent extraction via bubbles occurs. These bubbles ascend through the aqueous phase, which contains the metal ions of interest to be extracted.

- **Settler zone (Zone IV):** Due to the bubbles' gaseous core, they rise in the aqueous phase, reaching the Settler zone where the bubbles break, letting go of their organic coat.

Materials

The solutions were used in the solvent extraction column using coated bubbles. The samples were obtained at various times following the logic of chemical kinetics, and then they were analyzed using spectrophotometric techniques. The summary of reagents is in Table 1

Table 1 Reagents used in the experiments

	Copper extraction	Iodine extraction
Reagents	Analysis grade copper sulfate, 99% purity	KI and KIO_3 at 98% purity
PH Modifier	Sulfuric acid at 99% purity	Sulfuric acid at 99% purity
Organic solvent	Kerosene	Kerosene
Extractant	90% LIX and 10% Cytoximes	

Methods

The timings between each kinetic reaction sample were defined first for the methodology. The timings are as follows: 1, 2, 3, 5, 8, 13, 21, and 34(minutes). Samples were taken from the aqueous solution to determine the amount of extraction over time. The test conditions for the experiments are in Table 2.

Table 2 Conditions for experiments

	Copper extraction	Iodine extraction
Air Flows(slpm)	0.87 1.1 1.74	0.87 1.1 1.74
PH	2,1	2,23
Aqueous flow(ml/min)	300	300
O/A	17.89	20

The Spectronic 20D spectrophotometer, configured with a wavelength of 640nm, was used for the spectrophotometry tests for copper solutions. This equipment has a transmittance accuracy of 0.1% and a precision of 98%, for the iodine redox volumetric method was used.

RESULTS AND DISCUSSION

Different extraction percentages were obtained from the analyses, reaching up to 97% in 34 minutes for the maximum condition of Jg of 2 and 90% for the minimum condition of Jg; the extraction percentages are found in the following graph.

Although a higher extraction was obtained at higher Jg, high turbulence was generated due to the chum turbulent state, producing an organic entrainment of 5% in the analysis samples. In comparison, at a lower Jg, the bubbly flow condition was better attained with a drag of less than 1%. The results for copper and Iodine are shown in Graphs 1 and 2.

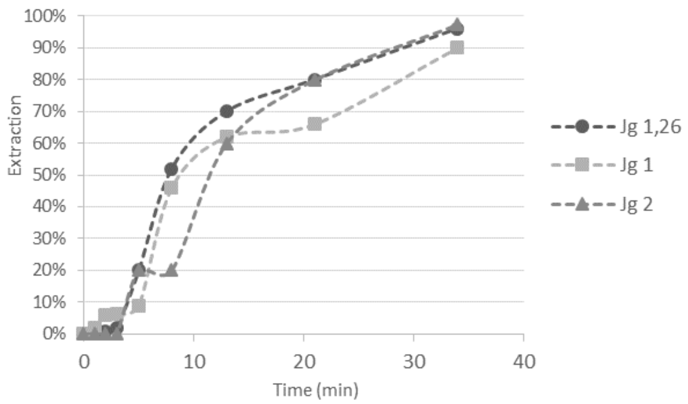

Figure 1 Copper extraction experiments

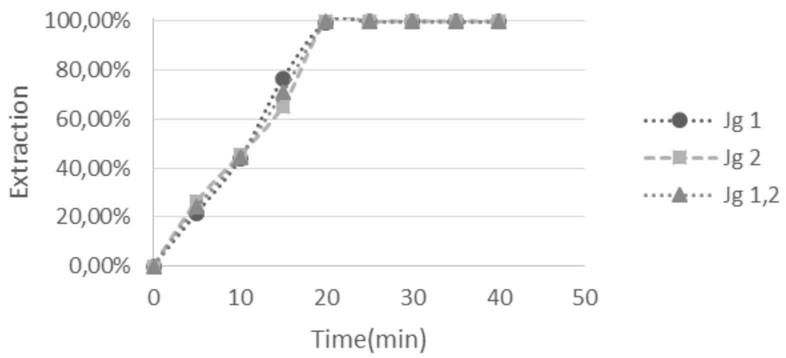

Figure 2 Iodine extraction experiments

Figures 1 and 2 show the extraction percentage in time of each experience. Copper extraction occurs more slowly than iodine extraction. This can be explained because in copper extraction, the rate is dependent on the extractant molecule. In contrast, in iodine extraction, the rate is controlled by the Iodine affinity in kerosene. In both cases, an almost 100% extraction was achieved using coated bubbles, Iodine is a polar compound that is only sparingly soluble in water. Its solubility in water is reported to be 0.34 g/kg at 25 °C and 0.549 g/kg at 40 °C. However, Iodine dissolves well in organic solvents like benzene, carbon disulfide, ethyl acetate, and ethyl alcohol. The resulting solutions typically exhibit red, violet, or brown colors.

To estimate the rate constant for extraction reaction, a first-order reversible equation according to equation 1 was used for copper, and a first-order non-reversible equation according to equation 2 was used for Iodine. Results for Iodine are in graph 3 and for copper in graph 4.

$$Ln\left(\frac{C_s - C_{s,eq}}{C_s^0 - C_{s,eq}}\right) = -(k) * t \quad (1)$$

$$Ln(C_s) = -(k) * t + Ln(C_0) \quad (2)$$

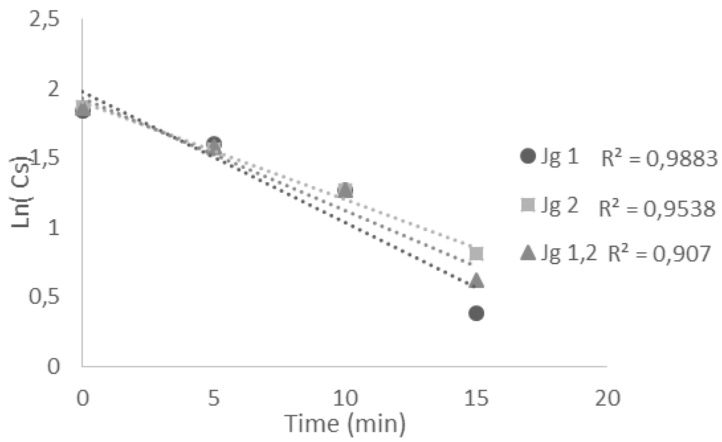

Figure 3 Iodine rate constant

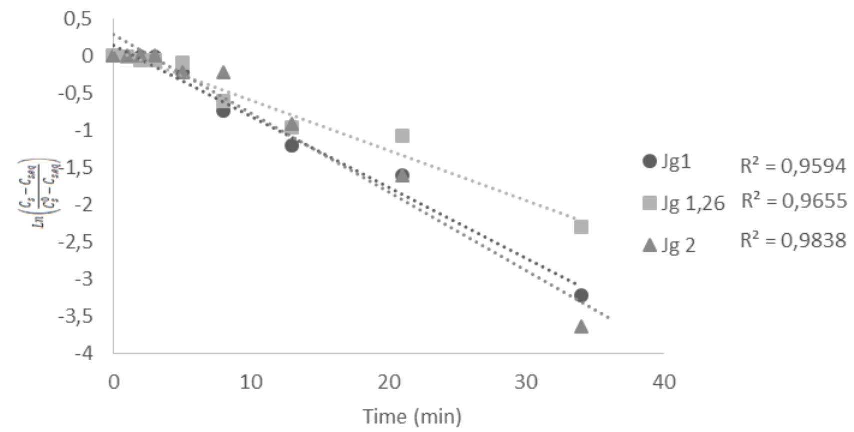

Figure 4 Copper rate constant

CONCLUSION

By designing and constructing a columnar flotation device, we successfully implemented a continuous process that generates a stable coated bubble swarm. This process was employed to achieve air-assisted solvent extraction of copper using a mixture of Kerosene and extractant at a 25% v/v concentration. T and extraction of Iodine from a solution using Kerosene as extractant.

Detailed extraction calculations demonstrated that our system could consistently produce a stable coated bubble swarm, resulting in up to 97% copper extraction efficiency. This was achieved at superficial gas velocities of 2 cm/sec, with an aqueous-to-organic phase volume ratio of 18, indicating that the system performs effectively under these conditions.

Despite these promising results, it is essential to note that our technology is still in the exploration phase. More extensive scale-up tests are required to refine the process and identify the ideal parameters, particularly for the aqueous ratio, gas superficial velocity, and feed flow rates. We constructed a functional system for generating a coated bubble swarm that is simple, efficient, and does not require moving parts or complex equipment, representing a notable advancement in the field.

ACKNOWLEDGEMENT

The authors wish to acknowledge the material support provided by Seven-C Project SpA and the financial support provided by Universidad Católica del Norte.

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