

The Significance of Flotation Frothers Chemical Structure and Fundamental Properties: A Review

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Abstract

Froth flotation is a separation process widely used in the mineral processing industry that depends on differences in particle surface properties to separate valuable materials from undesired gangue. In froth flotation, an addition of a surfactant, acting as frother is usually needed. The basic function of the frother is to produce a swarm of air bubbles, which remain sufficiently stable for the hydrophobic mineral particles to be captured by them. This Paper presents a combination method of a foaming agent-surfactant composition with desirable selectivity and foaming properties. Wherein 1-butanol (C₄H₁₀O) is a main flotation foaming agent, which decides bubble sizes in a collecting area; and tetraethylene glycol (C₈H₁₈O₅) is an auxiliary foaming agent, which affects a rising velocity of the bubbles in the collecting area and a foaming capability in a selected area. Set concentrations of the two components are respectively 60 ppm for the 1-butanol and 120 ppm for the tetraethylene glycol. An addition sequence is the 1-butanol followed by the tetraethylene glycol. The dual advantages of the selectivity and foaming properties of the foaming agent-surfactant composition in the present disclosure are verified through a series of tests, and desirable yields can be obtained in practice.

Keywords

Flotation Surfactants, Critical Coalescence Concentration, Polyglycol, Bubble Size

1. Introduction

Foam flotation is achieved by different effects of different surface properties of

different minerals on liquid and gas in ore pulp [1]-[3]. Wherein bubbles are carriers and mineral grains are bearers. Obtaining stable bubbles through a flotation agent, that is, a foaming agent, is the prerequisite for efficient flotation. The processing capabilities of a flotation machine or a flotation column and economic indexes are directly related to hydrodynamic parameters in a collecting area, such as inflation rates, inflating quantity, bubble sizes and distribution, and the thickness of a foam layer in a selected area or water recovery quantity [4] [5]. Although the above parameters are related to physical characteristics such as a foaming mode of a flotation device, the aperture of a foam maker, a liquid flow state, and air quality, the use of the flotation agent, especially the type of the foaming agent, has a more direct effect on each flotation performance parameter in both areas. The importance of the type and number of the foaming agents in foam flotation has been increasingly recognized in recent years [6].

The difficulties inherent in giving a comprehensive scientific analysis of flotation frothers were in depth analyzed by Wrobel 50 years ago (Wrobel, 1953). The situation 50 years later is not that different and the terms “powerful” and “selective” are still commonly used to describe the properties of these flotation reagents [7]. The frothers that are purchased for commercial use usually come along with the information exemplified by **Table 1**.

Table 1. Flotation frother characteristics as provided by manufacturers.

Property	Frother 1	Frother 2	Frother 2
Molecular weight	200	250	400
Viscosity, cP	7	12	27
Density, g/cm ³	0.970	0.980	0.988
Freeze point, °C	Below -50	Below -50	Below -50
Flashpoint, °F	250	285	325

°F stands for Fahrenheit degrees.

The foaming agent is a heteropolar surfactant, and consists of a polar group and a non-polar group, such that directional adsorption and arrangement can be realized on a gas-liquid interface [8]-[10]. The foaming agent is closely related to the nature of these two groups. The foaming agent mainly has two uses in flotation: providing good hydrodynamic parameters (that is, high selectivity) in the collecting area and providing adequate foam thickness and water recovery quantity (that is, high foaming properties) in the selected area. At present, most of the foaming agents that are of industrial values on an international scale belong to two broad families of compounds: one is fatty alcohol (a chemical formula being $C_nH_{2n+1}OH$) and the other is ether alcohol (a chemical formula being $C_nH_{2n+1}(C_3H_6O)_mOH$ or $C_nH_{2n+1}(C_2H_4O)_1OH$). In an alcohol foaming agent, the most famous is methyl pentanol (*i.e.* Methyl Isobutyl Carbinol (MIBC)), with a chemical structure being $C_6H_{13}OH$; the methyl pentanol has been produced in large quantities in industry; and the methyl pentanol is good in selectivity, such that the methyl pen-

tanol is widely used in metal ore flotation, and has accounted for half of the amount of the foaming agent in the international market. As one of the most famous ether alcohol foaming agents, DowFroth250 produced by DowChemicals is well known in the mineral processing industry. The DowFroth250 has the characteristics of being less in use amount, fast in flotation speed, and more stable in foaming performance. On the international market, the production of ether alcohol and fatty alcohol foaming agents accounts for more than 90% of the total use amount of metal ore flotation foaming agents. The two foaming agents may share a common general formula to represent their chemical structures: $R(X)_nOH$, wherein R represents H or an alkane chain C_nH_{2n+1} , and X represents propylene oxide (PO, or C_3H_6O) or ethylene oxide (EO, or C_2H_4O) [11]. The common plants used frothers are listed in **Table 2**.

Table 2. List of the common plant used frothers.

Common name	Purity	Chemical formula	Molecular weight	HLB
MIBC	Technical	$CH_3CHCH_3CH(OH)CH_3$	102.2	6.1
HEX	Reagent	$C_6H_{13}OH$	102.2	6.0
DEMPH	Technical	$C_6H_{13}OH(EO)_2(PO)$	248.4	6.6
DEH	Technical	$C_6H_{13}OH(EO)_2$	190.3	6.7
MPDEH	Technical	$C_6H_{13}OH(PO)EO_2$	248.4	6.6
(PO) ₁	Reagent	$CH_3(PO)OH$	90.12	8.3
(PO) ₂	Reagent	$CH_3(PO)_2OH$	148.12	8.15
DF-200	Technical	$CH_3(PO)_3OH$	206.29	8.0
DF-250	Technical	$CH_3(PO)_4OH$	264.37	7.8
DF-1012	Technical	$CH_3(PO)_{6.3}OH$	397.95	7.5

HLB is hydrophilic/lipophilic balance value and EO and PO are abbreviations for $-OC_2H_4-$ and $-OC_3H_6-$, respectively.

Identification of the efficacy of the foaming agent should depend mainly on its selectivity and foaming properties. Good selectivity is characterized by stable bubbles, easy to control bubble sizes, and slow rising velocity of bubbles; and good foaming properties are characterized by stable foam layers and large water recovery quantity. Although the foaming agents such as the MIBC and the DowFroth250 are widely used, how to balance high selectivity and high foaming properties, or how to integrate the two characteristics, and adjust one of the frothing agents dosage as needed to independently control selectivity or foaming property, which has always been a difficult point in frothing agent research and selection. Generally, the fatty alcohol foaming agent is good in control of the selectivity but poor in the foaming properties; whereas the ether alcohol foaming agent is good in the foaming properties but weak in the selectivity. If the two foaming agents cannot be balanced, a flotation index cannot be optimized. However, a large number of experiments have proven that by only simply add-

ing and combining two different types of foaming agents, for example, mixing the DowFroth250 and the MIBC cannot provide a 1+1 effect; on the contrary, it may even significantly reduce flotation efficiency. Nevertheless, since the introduction of mixing (or combination) of medicament as a possible direction of research and development application at the Stockholm International Mineral Processing Conference in 1945, mixing of the medicament has attracted attention and rapid development as a simple, easy and effective way [12].

2. Requirements of Foaming Agent-Surfactant Properties

A foaming agent-surfactant composition must achieve a delicate balance between allowing sufficient thinning of the liquid film between the colliding bubble and particle so that attachment can take place in the time frame of the collision and yet provide sufficient stability of the bubble/particle moiety to allow the weakly adhering or mechanically trapped particles of unwanted materials to escape with the draining liquid. A common feature of most commercial frothers is their hetero-polar nature consisting of nonionic polar group exhibiting hydrophilic character coupled with a hydrophobic non-polar hydrocarbon character. This nonionic or neutral character is usually associated with a sufficiently small molecular size so that multiple Van der Waals bonding does not occur in the non-polar portion of the molecule, giving rise to excessively stable froths [13].

The mixed use (also called combined medication) of flotation agents is aimed at improving a synergistic effect between the agents.

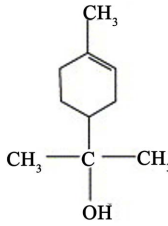
The synergistic effect between the agents may be defined as: in a multicomponent system consisting of two or more than two flotation agents, a flotation index is significantly greater than the sum of indexes of each agent used individually under the same conditions. Compared with a collecting agent, studies on the mixed use of the foaming agent are relative late. The mixed foaming agents are widely used in foreign mine flotation workshops, for example, more than 50% copper mine flotation workshops in America use two foaming agents simultaneously; and some workshops in Zambia use a mixed agent of triethoxybutane and methyl pentanol [9]. A part of the practice has proved that the mixed use of agents can generally obtain better results than used alone. It is to be noted that, not all practices of mixed use of the agents are successful. In most cases, the mixed use of the foaming agents presents no synergistic or anti-synergistic effects. A workshop in Canada once tried a mixed foaming agent of polypropylene glycol and methyl pentanol, resulting in a serious “overflow” phenomenon in the first two cells of a group flotation cell, while the ore liquid levels of the last two cells are decreased without foam generation, thus greatly affecting the final economic and production indicators [11]. There are relatively few types of foaming agents used in China, and the mixed use of the foaming agents is still in a research and initial stage [11].

Using known commercial frothers as standards, tabled as below (Table 3), the general guideline level that is applied to laboratory and plant condition testing

can be stated as follows:

- The stability of the froth formed must be such that a further degree of separation of the valuable mineral from the non-floatable (entrained) materials is obtained in the froth.
- Once the froth containing the valuable mineral is removed, it must break readily for any further treatment.
- It must form a froth of sufficient volume and stability to act as a medium of separation at low concentrations.
- It must possess a low sensitivity to reasonable changes in pH and dissolved salt concentrations.
- It must be readily dispersible (although not necessarily readily soluble) in the aqueous medium.
- It should be relatively cheap, abundant, and environmentally safe for large-scale use.

Table 3. Chemical structures of the selected commercial frothers.

Frother type	Frother family	Frother	Chemical formula	Molecular weight	Code
Alcohol-based type	Aliphatic alcohols	Methyl iso-butyl carbinol	$\begin{array}{ccccccc} \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_3 \\ & & & & & & & & \\ & & \text{CH}_3 & & & & \text{OH} & & \end{array}$	102	MIBC
Alcohol-based type	Cyclic alcohols	α -terpineol		148	Alpha-terpineol
Polyglycol-based type	Polyglycol ether	Dow froth	$\text{CH}_3(\text{C}_3\text{H}_6\text{O})_4\text{OH}$	264	DF-250
Polyglycol-based type	Polyglycol ether	Dow froth	$\text{CH}_3(\text{C}_3\text{H}_6\text{O})_{6.3}\text{OH}$	398	DF-1012

3. New Frothers—A Mixed Foaming Agents

The research of the mixed foaming agents has developed rapidly and formed a system in recent years. A mainstream point of view is that a main foaming agent in the mixed foaming agent determines the basic properties of the bubbles, while an auxiliary foaming agent affects other properties of flotation such as water recovery quantity. During dosage adjustment, the total amount of the foaming agent may be changed, but the ratio of the main and auxiliary foaming agents is generally unchanged. Some new studies have also found that by adding some surfactants that do not have foaming capabilities on their own in a specific foaming agent environment can produce better synergistic effects, for example, the foaming capabilities are much greater than that when such foaming agent is used alone. Many sorting practices prove that, after the agents are combined, compared with the agents used alone, results show that some may improve the rate of recovery, some may improve concentrate grades, and some may improve a flotation rate. The mixed use of the foaming agents may also reduce agent

consumption due to generation of a synergistic effect.

Nevertheless, there are still many shortcomings in the existing research on the mixed use of the foaming agents. Firstly, there is no systematic research on the relationship between a molecular structure of the foaming agent and flotation performance. Only on this basis, a reasonable candidate solution for the type of the mixed foaming agents can be proposed and verified according to intended use. Secondly, there are no means and parameters that can represent the effect of the foaming agent on flotation performance in a broad sense. Most of the existing studies have only been able to demonstrate, in a non-quantizing manner, that a recommended mixed foaming agent solution may produce synergistic effects in a specific mineral sample test, and by finally obtaining the measurement of the ore sample to calculate the concentrate grade, recovery rate, etc., side corroboration conclusions. The method is limited and has no significance for promotion. Third, there is very little research on the mechanism of interaction between the foaming agents.

Intuitively, the assessment of the selectivity and foaming properties of the foaming agents should start from the effect of the molecules of the foaming agents on flotation bubbles, that is: 1) controlling the bubble sizes, and slowing down bubble merging; 2) prolonging the rising velocity of the bubbles and retention time in ore pulp; and 3) improving the stability and water recovery quantity of a foam layer. Measurement and characterization means corresponding to the performance of the foaming agent are completed by using 1) a bubble observation and analysis cabin to measure the sizes D_{32} of the bubbles; using 2) a gas-liquid ratio tester to reflect the rising velocity of the bubbles by measuring a gas-liquid ratio E_g ; and using 3) an automatic water recovery measuring device to monitor a water recovery quantity J_{w0} .

The purpose of studying the mixed use of the foaming agents is to find a foaming agent combination method that may take both high selectivity and high foaming properties into consideration. In some extreme cases, it is even possible to achieve independent control of the selectivity or foaming properties of the main and auxiliary foaming agents/surfactants by adjusting the dosage of the main and auxiliary foaming agents/surfactants.

4. Frothers and Critical Coalescence Concentration

Frother reagents also dramatically enhance gas dispersion in flotation machines, and reduce the size of the bubbles by preventing bubbles from coalescing [9]. The critical coalescence concentration refers to a specific concentration of the foaming agent, that is, as the concentration of the foaming agent increases during flotation, the degree of bubble merging decreases and finally reaches a specific concentration when the bubble merging stops. If the concentration of the foaming agent is lower than the specific concentration during use, the bubbles are unstable, and the sizes are uneven; and if the concentration of the foaming agent is higher than the specific concentration, costs are increased, resulting in

reversal of the performance of the foaming agent to achieve a negative effect.

At formation bubbles tend to coalesce as they grow as two or more bubbles interact and form a single bubble. The size of bubbles affects the performance of flotation process significantly. The bubbles produced in flotation cells with frothers should be generally small—having a size around 0.5 - 2.0 mm. The smaller (compare with the size of bubbles which generated without frother) size of bubbles enhances the efficiency of the flotation process by optimizing the collection of particles. The work suggested that the continued addition of frother has a diminishing effect resulting in the bubble size reaching a limiting value at a sufficiently high concentration called the CCC, the Critical Coalescence Concentration [7]. Although the mechanism by which frothers stabilize the bubble is unclear it was thought that they created hydrodynamic conditions that were favorable to the production of small bubbles. New evidence suggests that they might bind water molecules to a region around the bubble by means of hydrogen bonding, thus making it more difficult for approaching bubbles to get sufficiently close to coalesce, and thus preserving a more stable and smaller bubble size [7]. The CCC value seems to be a property of the frother [6]. At frother concentrations below the CCC, the bubble size tends toward larger values, indicating bubble coalescence as a main mechanism determining the bubble size distribution. On the other hand, at concentrations exceeding the CCC values, bubble size is completely determined by the bubble break-up process. The McGill Bubble Viewer (MBV) can be used for the determination of CCC values by different types of frothers.

The McGill bubble Viewer was developed by researchers at McGill University mineral process group [8]. **Figure 1** presents a schematic of the McGill bubble viewer. The MBV system is used to collect and image bubbles from the aerated flotation cells and the digital images are then processed using available image analysis software adapted specifically for the bubble viewer [1]. More details can be found from McGill mineral processing group.

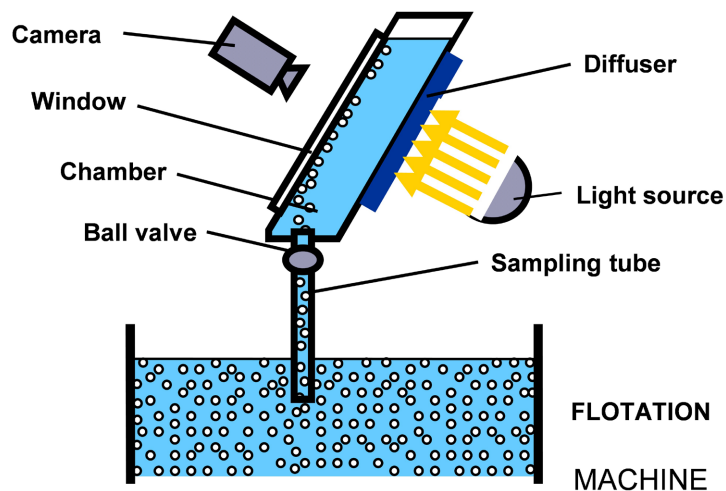
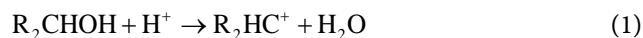


Figure 1. McGill Bubble size measurement equipment.

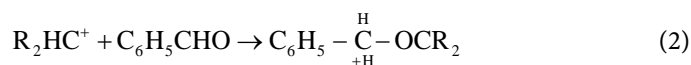
5. Frother Analysis

Due to frothers nature, the reaction is shown by most frothers used in mineral flotation. The two steps of the reaction are:

- Dehydration of alcoholic frother by sulfuric acid,



- The unsaturated hydrocarbon then reacts with the aldehyde to form a colored product.



In acid solution, the product is capable of a resonance (without separation of charge) that accounts for the color.

The procedure can be used on-site to obtain the frother concentration evolution down a bank of flotation cells and frother distribution between pulp and froth phases. The ability to measure the frother directly can help determine the amount and location of frother addition, to assess frother recycled with reclaim process water, and permit further optimization of cell hydrodynamics.

Three plant surveys have been conducted by McGill mineral processing group to date which have proofed the technique. After calibrating with the plant frother and water, sampling, decantation and dilution are generally all that was necessary. For MIBC it was necessary to make the determination promptly as there was evidence of loss over time (sealed samples brought back to MBV showed no detectable frother) probably due to evaporation, which shows the colorimetric method is fairly good and workable.

6. Conclusions

- Frother, which is the one of the flotation surfactants, is the main polymer application in mineral processing area. There are two main groups of frothers distinguished by chemical structure—alcohols based and polyglycol based frothers. Today there are various frothers based on these two groups commercially available to do vary enough in characteristics to effectively allow a plant flotation engineer to select various components together to achieve any reasonable desired result.
- Frother concentration influences initial bubble size generation and stabilizes the froth. The magnitude of anti-coalescence is a function of frother concentration, preserving the concept of a critical coalescence concentration (CCC) as an important aim to achieve.
- The concentration of frother is important for plant control and process optimization in the flotation step of mineral processing. The colorimetric technique is an effective and reliable way to measure the concentration of frothers.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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