MINERAL SEPARATION EFFICIENCY IN FLOTATION DEPENDS, TO AN EXTENT, ON THE TYPE OF FROTHER USED. HUNTSMAN DEVELOPS AND MANUFACTURES UNIQUE FROTHERS WHICH ARE SUITED FOR MINERAL PROCESSING APPLICATIONS. THIS PAPER DISCUSSES THE HUNTSMAN APPROACH TO UNDERSTANDING THE INDUSTRY’S FLOTATION FROTHER REQUIREMENTS TO OPTIMISE FROTHER SELECTION AND INTRODUCE THE HUNTSMAN’S POLYFROTHER® FROTHER RANGE. SPECIFIC CASE STUDIES WHERE THE FROTHERS ARE USED ARE DISCUSSED.

INTRODUCTION

Froth flotation is a process of using bubbles to separate minerals based on their relative affinity for water. Bubbles are induced in the slurry through aeration. Chemistry is used to aid the flotation process and chemical reagents are added to enhance the separation process. The flotation reagents include frothers, collectors, surface modifiers and pH regulators that control physical and chemical conditions of solid, air and liquid phases, respectively.

As described by Harris (1976), the key effect is that of bubble size control by way of preservation of the generated bubble size, which is attributed to the coalescence inhibition by the presence of the frother on the bubble surface. Following this, the frother must stabilize the froth phase. Frothers are also added to create optimal conditions for bubble creation and stability by decreasing the surface tension of the water. Depressants may be added, depending on the ore treated, to assist the hydrophilic particles to stay in the water phase. Clay particles may need to be dispersed to prevent them from attaching to the bubbles. Hydrophobic particles attach to the bubbles and are carried to the surface of the slurry where froth is formed. It is important for these bubbles to have the mobility to carry the mineral to the launder where the concentrate is collected.

Types of Frothers

There are generally three main groups of frothers used in froth flotation.

Alcohol Type

These frothers have a molecular structure that usually includes 5 to 8 carbon atoms in a hydrocarbon chain and their solubility in water is limited. Methyl isobutyl carbinol (MIBC) belongs to this category and is widely used in the industry. The weaker alcohol-type frothers are more selective and typically suited to finer particles. There are three sub-categories under this group: aliphatic, cyclic and aromatic alcohols.
**Alkoxy Type**
These frothers are usually more powerful than alcohols. The alkoxy-substituted paraffin group contains triethoxy butane (TEB) as the main frother in use. These frothers have very low solubility in water.

**Polyglycol Ethers and Polypropylene Glycol Ethers**
These frothers include compounds manufactured by condensation of ethylene, propylene or butylene oxide with or without low molecular weight aliphatic alcohols. They vary from being totally miscible in water to partially soluble, depending on the ratio of hydrophobic to hydrophilic groups in the frother molecule. The degree of selectivity tends to be inversely related to molecular weight. This group of frothers can assist with coarse particle recovery.

**The Role of Frothers**
Frothers in flotation change the interfacial properties by acting at the interface of the gas and liquid. In the separation process, the hydrophobic particles attach to the gas bubble in the slurry and are floated to the froth phase. Bubble size distribution is a factor determining flotation metallurgical response. Bubbles in flotation must not be too large or too small. Insufficient contact time for attachment may result when bubbles are too small. On the other hand, large bubbles change the properties of the water layer surrounding the bubble. Other roles of frothers are to:
- Create finer bubbles, whereby the dispersion of air in the flotation cell also improves;
- Reduce coalescence of individual air bubbles;
- Reduce the rate of bubble rise from the mixing zone to the froth zone;
- Increase the strength of the bubbles and stability of the froth.

**Characteristics of Frothers**
In discussion of frothers, it is important to define the commonly used terminology. Laskowski et al. (2003) characterise flotation frothers as “powerful” or “selective” in their functionality. Selectivity refers to the ability to recover the mineral of interest or attachment of hydrophobic particles to an air bubble, whilst avoiding unwanted gangue particles. Powerful refers to the frothing capacity and froth stability.

Frothers are surface-active agents that provide stability and mobility to the bubble carrying the valuable mineral. Stability and mobility play a significant role in the overall recovery and grade that can be achieved from a flotation cell. Other factors that are influenced by the frother properties in flotation are:
- Flotation kinetics by affecting bubble size;
- Critical coalescence concentration (CCC) – concentration at which increasing the amount of frother leads to no further reduction in bubble size;
- Particle recovery or collecting properties;
- Water recovery and entrainment.

Frothers are categorized by their underlying chemistry and Huntsman has done extensive work in understanding this chemistry to correctly align these products to suitable applications.

**The Interfacial Behaviour of Frother**
Frothers are hetero-polar surface-active compounds containing a polar group (OH, COOH, C=O, OSO₂ and SO₂OH) and a non-polar hydrocarbon capable of adsorbing in the water–air interface. The frother molecules are arranged at the air–water interface such that the hydrophilic or polar groups are oriented in the water phase and the hydrophobic or non-polar hydrocarbon chain in the air phase. The frother concentrates at the interface of water and air bubbles. Figure 1 shows a general structure of a frother molecule indicating orientation at the air-water interface.
As a result of the hetero-polar nature of the frother molecule, which causes adsorption of the frother molecule at the air–water interface, the hydrogen bonding between the water molecules is interrupted and this lowers the surface tension of the water. The effect of frother on surface tension and bubble size was investigated by Sweet et al. (1997). Their tests indicated that the effects of frother on bubble size occurred at frother concentrations much lower than those at which the surface tension was affected. Hence, the effect of frother on bubble size is apparent at very small concentrations of frother in water.

When two bubbles come into contact with each other, the liquid film between them thins and breaks, causing the bubbles to coalesce. When coalescence of bubbles formed in a liquid does not take place in fractions of seconds, the bubbles rise to the surface and aggregate. The point at which three bubbles meet is called a plateau border. Drainage occurs down a network of these borders. At the plateau border, the curvature of the bubble surface is relatively high. The difference between the curvature of the bubble surfaces at the plateau border and that of the flat sides generates a capillary pressure which causes a lamellar water to flow towards the plateau border. This causes them to thin further to a point where they may rupture causing further coalescence. Space between bubbles allows for egress of gangue (non-adhering particles) as well as water drainage.

Coalescence of bubbles is one of the primary reasons that cause hydrophobic particles to detach and return to the liquid zone. A high rate of coalescence may lead to maximum carrying capacity of the froth to a point where further transportation of floatable particles to the concentrate is not possible. The coalescence of bubbles is prevented at a particular concentration, critical coalescence concentration (CCC), which is a measure of the ability of the frother to reduce bubble size and can be controlled by regulating the frother concentration. Coalescence froths with high water contents are mobile and overflow at high rates, giving good recoveries at the expense of low grades. This occurs when the bubbles, on their upward passage from the pulp–froth interface through the froth to the overflow, retain their shape and do not coalesce. The reduction of froth water content by drainage is directly dependent on the degree of bubble coalescence which occurs during their passage upwards through the froth. This, in turn, depends on the stability of the inter-bubble lamellae of the polyhedral structure. It is possible that some valuable solids may be rejected into the draining inter-bubble water during bubble coalescence, and this may also cause an increased bursting rate of the froth bubbles. The degree of coalescence can be regulated by varying the froth dosage.

**Bubble Size**

Bubble size can dramatically affect the flotation process. The bubble size, density and coverage of the particles determine the particle load that a bubble can carry. The lamellae size distribution is not the same as the bubble size distribution and will not only depend on the bubble size but also on the shape of the bubble. Investigations by Cho & Laskowski (2002a, 2002b) indicated that frothers control the bubble size by decreasing the bubble coalescence and that the bubble coalescence can be entirely prevented at frother concentrations exceeding the CCC. As shown in Figure 2, coalescence does not occur at concentrations higher than the CCC.
By measuring the bubble size as a function frother concentration, the CCC can be determined for a given frother. Figure 3 shows the bubble size as a function of concentration for polyglycol frothers and MIBC and Figure 4 shows the curve shifting as a result of increasing the number of PO groups. Also shown in the curves is the CCC.

Figure 2. Schematic diagram of the effect of frother concentration on bubble size (Grau et al., 2005).

Figure 3. Evaluation of CCC values for MIBC, (PO)1 and (PO)2 (Laskowski et al., 2003).
These results indicate that, at concentrations higher than CCC, the bubbles cease to coalesce and the size of bubbles becomes constant and is not affected by the frother concentration. Further to this, is that the ability of these compounds to reduce bubble size improves with increasing number of propylene oxide groups per molecule in series of polyglycol frothers. Frothers that produce finer bubbles also produce more stable froths.

When a frother is introduced into water, its polar groups interact with water molecules to form a hydration shell around such groups. The strength of the film formed due to concentration of frother molecules at the interface are determined by the shell size and hydration energy. The ratio of the hydrophilic to hydrophobic (lipophilic) parts in frother structure is then the determining factor. The balance of these two opposing types of groups is referred to as hydrophilic–lipophilic balance or HLB number. If a chemical structure of a given frother is known, then the HLB number can be calculated using the following equation:

\[
\text{HLB} = 7 + \sum (\text{hydrophilic group numbers}) + \sum (\text{hydrophobic group numbers})
\]

Frothers with lower HLB number are therefore more hydrophobic than those with higher HLB number and hence less soluble in water. The HLB number has the advantage of not accounting for molecular mass. Two frothers of similar HLB numbers, but different molecular mass, will provide different types of froths, and therefore different final grades and recoveries should be expected. Laskowski (2004) plotted the calculated values of the HLB number versus the molecular weight for a given group of frothers, as shown in Figure 5.

Molecular weight and frother molecule structure have also shown to be an important factor in determining what a frother can do in terms of particle size recovery. Klimpel et al. (1988) showed that increasing molecular weight (for a given frother type) leads to a change in the particle size range recovered and in general increased recovery of coarse particles.
An important factor is to know what range of particle size losses are and target an appropriate frother that can help to influence the recovery. Huntsman has developed a tool to assist with the selection of frothers. Figure 6 illustrates this tool used by Huntsman to characterise their POLYFROTH® frother range according to selectivity and strength. POLYFROTH frothers are of diverse chemical types and include polyalkoxy ethers and their combinations with polyalkoxy glycols and alcohols. MIBC is also shown in the diagram. Frothers which fall on the left side of this diagram are known to be selective in flotation, i.e., MIBC and the POLYFROTH 10 series. Frothers on the right side exhibit properties of the strong flotation frothers, i.e., the POLYFROTH 30 and 50 series. Frothers on the left are classified as weaker frothers and can be used in flotation of fine particles, whereas the frothers on the right side are typically polyglycol ethers and have potential to enhance the coarse particle recovery and higher recoveries but a trade-off for selectivity.

Frothers are also classified on the basis of solubility. Frothers which are insoluble or partially miscible in water, like MIBC, fall in the lower section of the chart. The POLYFROTH, frothers falling in this region are denoted by an “H” suffix. Frothers that are miscible in water at all concentrations are located at the top of the chart. The POLYFROTH, frothers in this region are denoted by a “W” suffix.

Such chart is useful in making appropriate frother selection for different mineral systems on the basis of the required froth characteristics and circuit requirements. Matching the correct froth characteristics for a flotation cell or circuit can improve flotation performance and efficiency and prevent over-feeding the reagent.

In addition to standard laboratory batch flotation tests, Huntsman also, on occasion, uses froth stability measurements to aid the diagnosis of froth characteristics and enable the selection of suitable alternative frothers for trial. Froth stability generally refers to the froth (foam) decay process, during which time there is no further generation of gas bubbles. Froth decay is indicated by some visible occurrence, such as froth volume variation, bubble collapse or change in the bubble size. Froth stability and decay experiments can be conducted in a graduated multi-holed sparger column (Zanin...
Grano, 2006) using typical plant flotation feed slurry. In order to quantify the change of the froth, froth volume variation is recorded as a function of time. The faster the change, the less stable the froth. A differential equation can be fitted to describe the rate of froth collapse and the time taken for an equilibrium froth sample to decay to one-half of its original froth height (‘froth half-life’) is used to characterize froth stability. The methodology is based on outcomes of the AMIRA P541 Project (AMIRA, 2008), which Huntsman sponsored and is a useful tool for froth stability characterization as a function of frother type under a range of conditions. Importantly, it allows a useful ranking of frothers as a first approximation to selection for further investigation and testing.

Figure 6. POLYFROTH® frother selection chart.

CASE STUDIES

Two separate case studies where POLYFROTH frothers were selected to replace MIBC frother and a multi-component blended glycol product in copper and copper-gold circuits are discussed.

Case Study 1

Concentrator A: Copper-Gold Ore

Concentrator A processed ore from an open-pit copper-gold deposit averaging 0.9–1.3% copper with chalcocite, chalcopyrite, pyrite and other iron-bearing minerals, and 0.5–0.6g/t Au. Ore processing uses conventional crushing, grinding and flotation with 11 Mt/year throughput capacity. Average recovery was in excess of 90 % for copper and mid-to-high 70s for gold. The concentrator output was in excess of 95 000 t of copper production and 45 000 oz of gold. The concentrator consisted of a single-line process plant with gyratory crusher, semi-autogenous (SAG) and ball milling to a P80 < 200 mm for the rougher flotation feed. The flotation circuit consisted of rougher flotation, rougher concentrate regrind and three stages of cleaning for final concentrate of ~30 % Cu. The incumbent frother was a mixed/blended product predominately consisting of polyethylene glycol butyl ethers and polypropylene glycols (OTX-140). The concentrator had a desire to increase coarse particle recovery in the rougher circuit (50% of losses were identified in the + 212 µm range). It was agreed to go direct to plant trial with POLYFROTH W34 and POLYFROTH W53, which are both polyoxyethylene-polyoxypropylene glycol ethers.
POLYFROTH W34 produces mobile, fluid froths with well-defined froth structure and is suitable for applications requiring intermediate froth stability and good froth control. It offers a good balance between stability and selectivity. It can be considered as an alternative to mid-strength alcohol-based frothers containing blends with polypropylene glycols. POLYFROTH W53 is a robust frother and gives excellent stability and kinetics. With respect to strength, POLYFROTH W53 is a stronger frother than POLYFROTH W34 and would be expected to require lower dosage volumes than OLYFROTH W34 for the same ore being treated.

Case Study 2
Concentrator B: Copper Ore
Copper is mined and processed at Concentrator B from underground copper deposits. The predominant mill feed through this concentrator is chalcopyrite ore at approximate average feed grade of 2.6% Cu. The circuit has two stages of SAG mill grinding in parallel lines consisting of conventional rougher, scavenger, regrind and cleaner banks. All current final concentrate produced at 25% Cu is pumped to a concentrate-handling plant. Typical copper recovery of 89-94% is achieved, depending on line operation and feed grade. Standard laboratory rougher/scavenger testing identified POLYFROTH W22 as a promising frother candidate over the incumbent MIBC.

POLYFROTH W22 frother is a polyoxyalkylene alkyl ether of low molecular weight and represents a crossover from an alcohol frother to an alkyl ether frother in terms of chemical class and properties. It offers a versatile combination of selectivity, hydrophobicity and frothing power and it is these properties that play an integral part in its selection of a frothing reagent in copper ores. Originally developed as an alternative for MIBC in coal flotation, it has become established in the flotation of base and precious metals where it has shown improved metallurgical recoveries for given concentrate grades at lower addition rates than MIBC.

POLYFROTH W22 frother is oil-soluble and partially soluble in water, producing fine bubbles of uniform structure that break down readily in launders. MIBC, in comparison, is a branched alcohol that is sparingly soluble in water and more hydrophobic, producing less tightly knit froths with thin bubble membranes that give more selective froths with less persistence. Whilst these two frothers share some similarities, there are key differences in their efficacy and handling. POLYFROTH W22 exhibits low water carry-over into the concentrate. It is has significantly lower volatility and therefore higher flash point, lower VOC (volatile organic carbon) emissions, toxicity and odour compared with MIBC. The flash point of POLYFROTH W22 frother is over 65°C compared with 39°C for MIBC.

RESULTS AND DISCUSSION
Concentrator A
The plant trials were conducted over five months in three periods of time. Initially POLYFROTH W34 and POLYFROTH W53 were tested in the first two time periods against OTX-140, and then only POLYFROTH W34 was trialed in the third time period, after it was deemed to be the most promising candidate from the first two time periods. In each trial period, the trial frother was run for at least a whole shift (12 hours) to coincide with the site metallurgical shift composite samples.

POLYFROTH W34 frother dosage was similar to the dose rates typically used for the incumbent OTX-140, at 120 mL/min to rougher cell number one and 45 mL/min to rougher cell number five (in order to give enhanced froth stability down the flotation bank). The introduction of POLYFROTH W53 to the circuit required a slightly different operating strategy (i.e., adjustment to cell froth levels and aeration rates) and different reagent dosage regime in order to maintain concentrate grade. POLYFROTH W53 was used at ~20% lower total frother dose.

A summary of the trial timing and metallurgical results for POLYFROTH W34 and OTX-140 frothers during the trial is given in Table I. POLYFROTH W34 gave a +0.7 % increase in recovery. Taking all
the frother trial recovery data for POLYFROTH W34 and OTX-140 in Table I, it is possible to complete
a statistical significance test on this recovery improvement with POLYFROTH W34 via a t-test (two
samples assuming equal variances). Via this t-test, the recovery improvement with POLYFROTH W34
is at a confidence level of 98.4 % (P value of 0.016) and hence it can be concluded to be a real benefit.
Confidence limits can also be placed on recovery benefit with POLYFROTH W34: at a 90 % confidence
level the increase in recovery with POLYFROTH W34 lies between +0.22 and +1.13 % Cu recovery.

Table I. Plant trial results over five months (in three distinct trial periods).

<table>
<thead>
<tr>
<th>Trial number</th>
<th>Frother</th>
<th>Final concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% Cu grade (avg.)</td>
</tr>
<tr>
<td>1</td>
<td>OTX-140</td>
<td>30.53</td>
</tr>
<tr>
<td></td>
<td>POLYFROTH W34</td>
<td>29.59</td>
</tr>
<tr>
<td></td>
<td>POLYFROTH W53</td>
<td>29.40</td>
</tr>
<tr>
<td>2</td>
<td>OTX-140</td>
<td>28.95</td>
</tr>
<tr>
<td></td>
<td>POLYFROTH W34</td>
<td>30.26</td>
</tr>
<tr>
<td></td>
<td>POLYFROTH W53</td>
<td>29.28</td>
</tr>
<tr>
<td>3</td>
<td>OTX-140</td>
<td>29.60</td>
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<tr>
<td></td>
<td>POLYFROTH W34</td>
<td>28.60</td>
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<tr>
<td>Average</td>
<td>OTX-140</td>
<td>29.69</td>
</tr>
<tr>
<td></td>
<td>POLYFROTH W34</td>
<td>29.48</td>
</tr>
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</table>

Plant surveys were also completed during the trial. The data from surveys completed on the rougher
circuit during the first trial period with POLYFROTH W34, POLYFROTH W53 and OTX-140 frothers
are presented in Figure 7. In comparing the survey results, the overall recovery improvement with
POLYFROTH W34 over OTX-140 was ~ +0.5%, while the biggest increase in recovery per size fraction
was seen in the coarse +300 µm fraction, where POLYFROTH W34 was seen to increase the recovery
by nearly 25%.

Figure 7. Plant trial survey results with POLYFROTH W34, POLYFROTH W53 and OTX-140.
The plant trials gave enough information to show that POLFROTH W34 gave an increase in copper recovery and led at first to an extended continuous trial and then adoption as the plant frother for the duration of their open pit mine life.

Concentrator B
The plant trial results from Concentrator B comparing POLYFROTH W22 frother with MIBC plant frother are given in Table II. The results show that with SIBX as the primary collector, greater copper recovery is obtained for POLYFROTH W22 frother, whereas higher selectivity in copper concentrate grade is obtained with MIBC as expected being a weaker frother and more selective.

Table II. Concentrator B plant trial results.

<table>
<thead>
<tr>
<th>Frother</th>
<th>Estimated annual dose (t/a)</th>
<th>Head % Cu (avg.)</th>
<th>Recovery % Cu (avg.)</th>
<th>Grade % Cu (avg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYFROTH W22</td>
<td>150</td>
<td>2.94</td>
<td>92.66</td>
<td>24.93</td>
</tr>
<tr>
<td>MIBC</td>
<td>260</td>
<td>2.85</td>
<td>91.90</td>
<td>25.61</td>
</tr>
</tbody>
</table>

POLYFROTH W22 frother offered clear efficiency gains from a reduction in annual frother usage and operational improvements compared to MIBC, including reduced air rates, greater froth level control and reduced collector dosage.

DISCUSSION
In most flotation circuits, keeping other variables such as air rate and collector dosage fixed, frother concentration can be used to control the kinetics and mass removal rate. Each frother type has a distinct relationship between froth stability, particle loading and kinetics, which will lead to different performance in a circuit. Appropriate selection of frother, carefully considering the stability and selectivity requirements, is a good first step in delivering the required metallurgical performance.

Frother addition rates with POLYFROTH frothers also offer the potential for dose saving; for example, POLYFROTH W22 frother dosage is typically at least 25% lower than MIBC and can reach up to 50% reduction rates in some cases for copper and copper-gold systems. This, in part, is related to the lower CCC of POLYFROTH W22 frother and volatility exhibited by MIBC, which is more susceptible to depletion down the flotation bank than the ether-based products. The more volatile frothers, such as MIBC, can require continual replenishment and staged addition. Failure to maintain frother concentration will result in loss of flotation kinetics, stability and decreased mineral recovery.

The case studies of the POLYFROTH W22 and POLYFROTH W34 frothers presented in this paper have demonstrated these principles and how enhanced froth stability properties, compared with those of MIBC, MIBC-ether blends and other glycol blends, can increase metallurgical performance and provide greater flexibility, circuit control and response across a range of plant conditions. In the cases of Concentrator B, reducing air rates and optimising to lower froth depths to control mass recovery and concentrate flows also led to an improved collector-frother synergy and overall reduced collector dosage. While in the case of Concentrator A, very similar addition rates and circuit control were employed, with the frother giving enhanced recovery.

CONCLUSION
Froth behaviour and characteristics play a significant role in flotation. Huntsman has done extensive research in classifying the POLYFROTH frothers according to fundamental properties in which they offer. These frothers extend the benefits to systems where froth stability and mobility have limited
flotation performance. POLYFROTH frothers have an added benefit of offering improved environmental, health and safety. They have high flash point and low levels of volatility, toxicity and odour.

REFERENCES


