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Development of New Frothers through Hydrodynamic Characterization of Frother Chemistry

F. Cappuccitti[1]
J. A. Finch [2]

[1] Flottec, LLC
115 Route West, Suite F1000
Mountain Lakes, New Jersey, USA, 07046
Tel/Fax: (973) 394 0864

fcappuccitti@flottec.com

[2] Department of Mining, Metals and Materials Engineering
3610 University Street
McGill University
Montreal, QC, Canada, H3A 2B2
Tel: 1 (514) 398-4755
Fax: 1 (514) 398-4492

jim.finch@mcgill.ca

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ABSTRACT

Much progress has been made over the last several years in the ability to measure flotation cell hydrodynamic parameters in both the laboratory and plant. These techniques have allowed fundamental research to proceed to determine the effects that frother chemistry has on the main hydrodynamic parameters (gas hold up, bubble size) as well as on the amount of froth generation and water content of froth. A research program was begun that brought together a team consisting of private companies and a University with expertise in hydrodynamic characterization (McGill), flotation reagent applications (Flottec) and chemical synthesis (Sasol N.A.) with the purpose of characterizing frother chemistries with two goals in mind: Determine which frother chemistry can provide optimized cell hydrodynamics; and, create new frother chemistries with specific hydrodynamic properties.

This paper describes the key steps that were taken that led to the development of new frother chemistry for use in flotation.

The first step was the characterization of the major frother chemical families in a two phase system. The parameters measured were gas hold up, bubble size, froth height and water carrying rate at different concentrations and gas velocities.

Analysis of the data indicated that definite patterns existed between frother chemistry and hydrodynamics and showed that frothers could be grouped into classes. More importantly, by modifying known frothers through chemical reaction it was shown that these frothers could be moved from one class to another. As a result of this better understanding of the interdependence of hydrodynamic and chemical properties, a new frother chemistry was proposed that was predicted to perform similarly to MIBC.

The new frother was synthesized and hydrodynamic testing confirmed that the chemical performed similar to MIBC. Laboratory flotation tests were conducted on two different ore types that also confirmed the similar performance of the new chemical and MIBC. Subsequently, the new product was placed on a plant for a short period of time. The results showed that the product was an excellent frother but increased the flotation rate slightly more than MIBC at the same addition rate.

Further research showed that the new frother chemistry was a family of products. By changing the reaction the resultant products could be made to be slightly weaker or stronger than MIBC but that this chemistry cannot provide hydrodynamic/froth characteristics similar to strong frothers like glycols and glycol ethers. Further work is planned to conduct longer plant trials to confirm the efficacy of this new frother family.

INTRODUCTION

The frother plays several key roles in the flotation process. Frothers help establish the proper hydrodynamics within the pulp in the flotation cell (bubble size, gas hold-up, etc) and create froth on top of the pulp that has the stability to hold the collected minerals, allow drainage of water, be mobile enough for removal then decaying quickly to assist downstream operations (such as pumping).

A large number of compounds have froth producing properties but cannot be used as flotation frothers because their hydrodynamic, frothing or decay properties do not provide adequate operability for the flotation process. The most widely used commercial frothers are: a) natural oils such as terpineol (as in pine oil) and cresols, b) $C_5 – C_8$ aliphatic alcohols, c) polypropylene glycols and their alkyl ethers, d) mixed ethers, aldehydes and ketone co-products of oxo alcohol production, e) alkoxyalkanes such as TEB (tri-ethyl-butane).

Most of the known frothers do not possess all the desired properties, and operators must make trade offs when choosing a frother, such as the need to use a persistent frother to last throughout the flotation circuit which may result in froths that do not decay and cause pumping problems. Attempts to improve the performance of frothers have focused on blending known frothers to derive synergies and offset the detrimental properties, as well as the modification of known frothers by reactions with alkylene oxides to increase their power.

A literature search shows that little to no research has been done to invent novel frother chemistries using alcohols that are not already known frothers. Most of the work has focused on reaction products of either C_5 alcohols and above with ethylene, propylene and butylene oxides or polyalkyl glycols and their ethers reacted with the same alkylene oxides (Klimpel, 1996). A need exists for better performing (e.g., to achieve particular hydrodynamic or froth properties) and less expensive frothers.

A novel class of frothers is introduced here resulting from the reaction of aliphatic alcohols C_1 (methanol) to C_4 (butanol) and mixtures thereof with between 0.2 moles to 5 moles of ethylene oxide. They correspond generally to the formula
$R_1 – O – (CH_2CH_2O)_nH$, where R_1 is a straight or branched chain C_1 to C_4 alkyl radical and n is between 0.2 – 5. The new frothers have their own set of hydrodynamic and froth properties that depend on the amount of ethylene oxide reacted with the alcohol. They will provide operations with another choice of frothers to optimize the hydrodynamic and froth characteristics and improve performance.

The background to the development of the new frother chemistries is described. This starts with introducing hydrodynamic parameters to characterizing frothers, which led to identifying new frothers as potential equivalents to MIBC, and ends with the resulting laboratory batch and plant test work.

HYDRODYNAMIC MEASUREMENTS

Hydrodynamic characterization of aerated reactors, like flotation cells, typically involves relationships among bubble size, gas hold-up (fraction of gas in a gas slurry mixture) and superficial gas velocity (volumetric gas flow rate per unit cross-sectional area of cell). Extensive plant evaluations have established the utility of hydrodynamic characterization of flotation machines (Nesset et al., 2006) and revealed the significant impact of frother. The use of these same relationships to characterize frothers derived from this observation.

Rather than a flotation cell and presence of solids a simpler start is to use a bubble column and air-water. The basic set-up is shown in Figure 1 and versions are described in some detail in Quinn et al. (2006), Azgomi et al. (2006) and Moyo et al. (2006). The columns employed are typically 10 cm in diameter and some 200 cm high equipped with a porous sparger to disperse the air and instrumented to measure air flow rate, determine gas hold-up from conductivity or pressure (as shown in Figure 1), and bubble size using the McGill bubble viewer technology. The unit can be run batch or with continuous overflow, which is usually recycled to the 'make-up' tank.

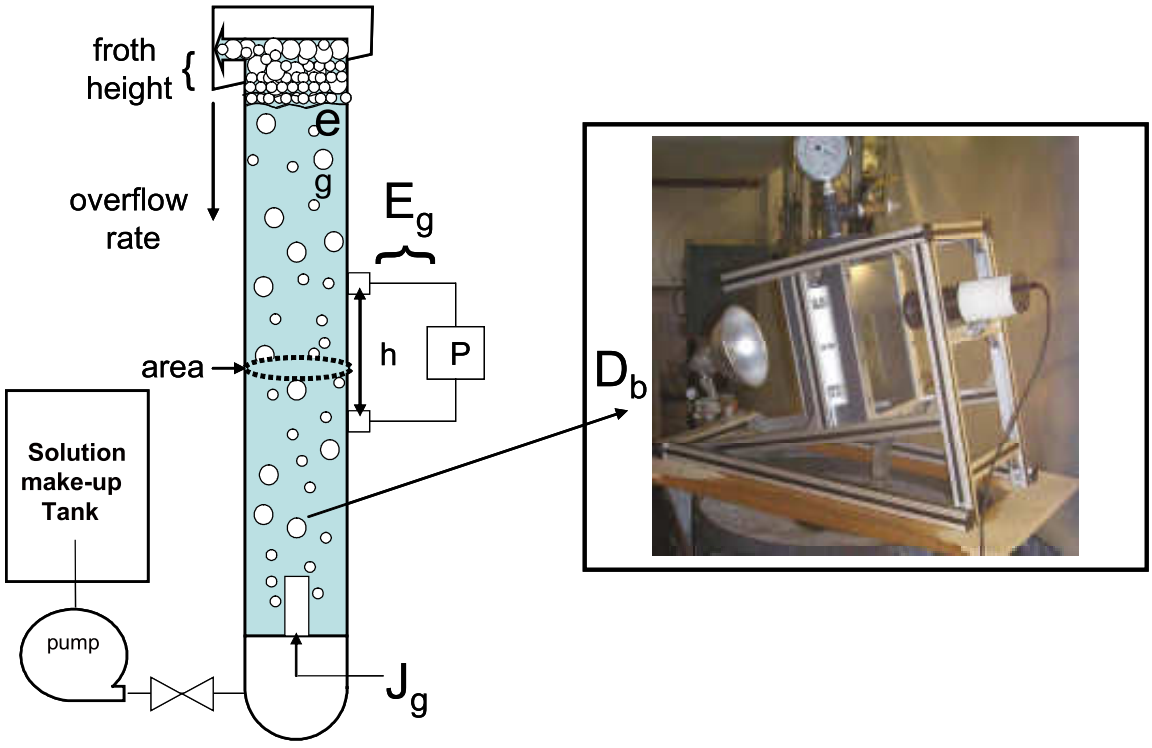

Figure 1: The basic bubble column set-up to measure gas holdup, E_g (using differential pressure, P over distance h), bubble size, D_b, using the McGill bubble viewer (the inset shows the viewer which is actually on the top of the column), froth height, overflow rate and gas velocity, J_g

Hydrodynamic characterization of frothers consists in measuring bubble size and gas hold-up as a function of concentration at set gas velocity[1] and sparger porosity. Figure 2 shows an example of the mean bubble size and gas hold-up as a function of concentration. It is evident that the two measurements are related, as expected because as bubble size is decreased (by adding frother) the bubble rise velocity decreases and the amount of gas retained in the column (i.e., literally the gas is 'held up') increases. Because of this relationship and the fact that gas hold-up is simpler to measure and is effectively on-line most frother characterization work uses gas hold-up.

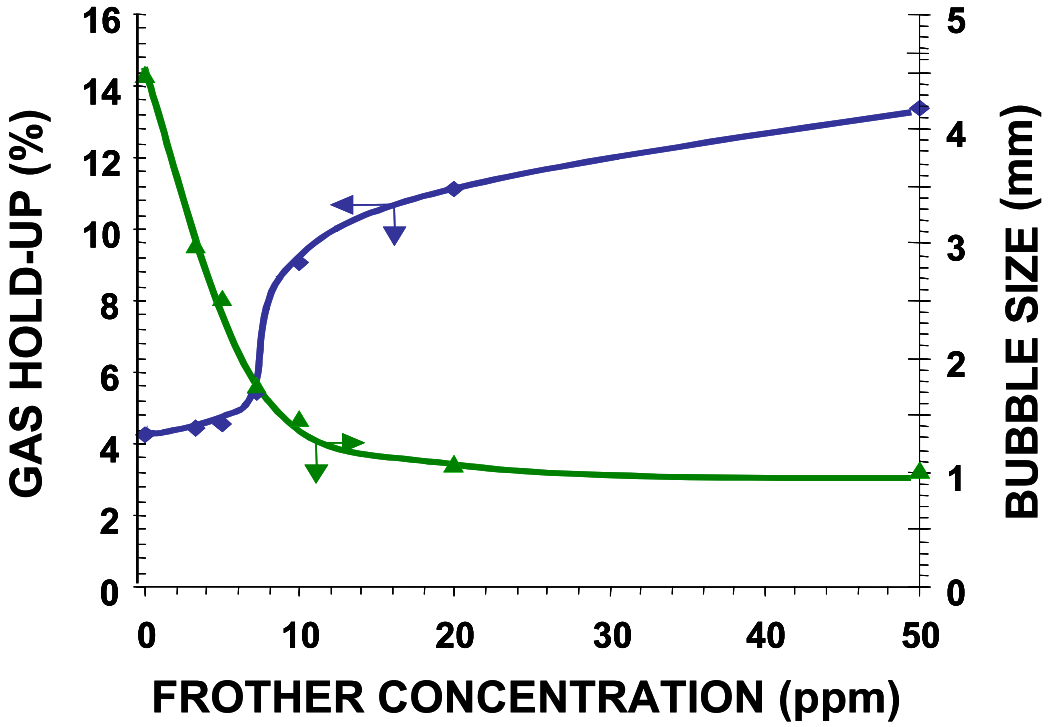

Figure 2: The general relationship between gas hold-up and bubble size as a function of frother concentration (MIBC in this case)

DEVELOPMENT OF FROTHER CHARACTERIZATION TECHNIQUES

Overflow rate vs. gas hold-up

The first approach was to run in continuous mode with a controlled froth depth (7 cm) and measure the froth overflow rate to investigate correlations against gas velocity, bubble size (below the froth) and gas hold-up. The result was the observation that frothers could be grouped in 'families' according to the dependence of overflow rate on gas hold-up (Moyo et al., 2006). Figure 3 summarizes this for all the frothers tested.

[1] Just the term 'gas velocity' will be used from hereon rather than 'superficial gas velocity'.

From the perspective of characterization key points emerging from Figure 3 are:

- In order of increasing overflow rate (for a given gas hold-up) the ranking corresponds to the qualitative understanding that the glycols give more watery froths than the alcohols (Cytec, 2002)
- Increasing chain length for alcohols and number of propylene oxide groups for glycols increases overflow rate
- For alcohols, overflow rate depends on chain length independent of branching (compare MIBC and n-hexanol)
- Adding an ethoxy (2 carbon) makes a C 6 alcohol perform like a C 8 alcohol

It was the last observation that set in motion a train of thought that by modifying (e.g., by ethoxylation) an alcohol in one family it could be moved to another. That is, a new class of frother chemistries could be created.

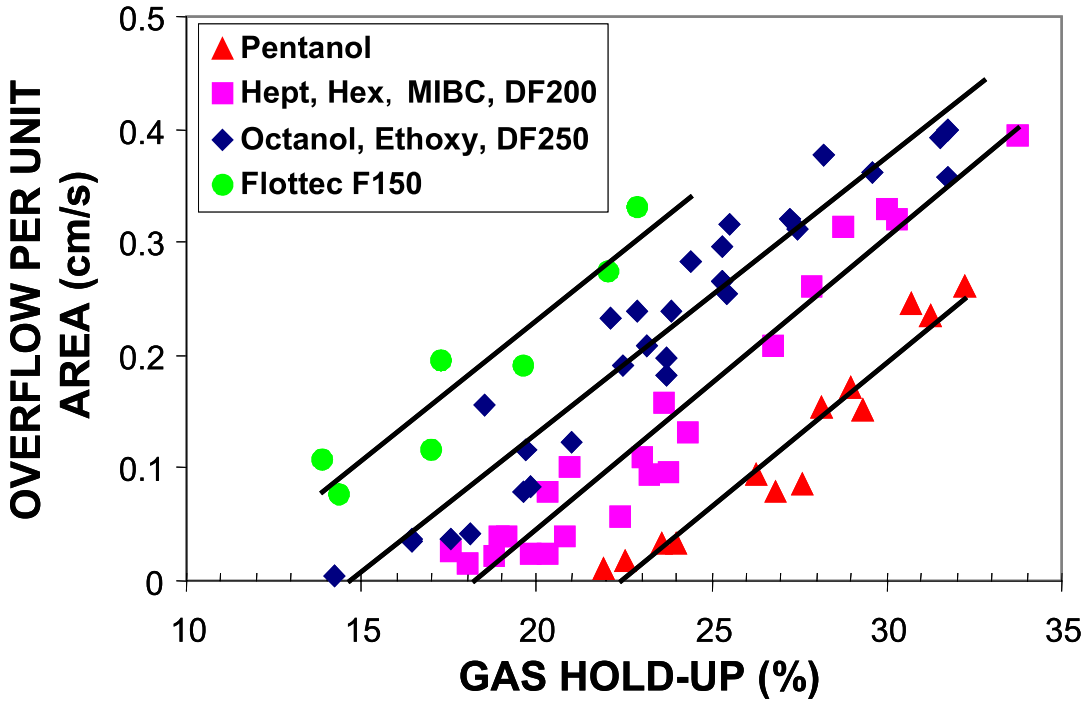

Figure 3: Overflow rate (per unit area of column) as a function of gas hold-up for the series of frothers tested by Moyo et al. (2006) showing the 'families' (note, 'ethoxy' refers to ethoxylated hexanol)

Gas hold-up vs. froth height

The overflow technique proved inconvenient as the measurement was not on-line and frother concentrations much higher than used in flotation practice (typically < 10 ppm) were required to establish a 7-cm froth depth in some cases (e.g., more than 30 ppm was required for MIBC). An attraction was that the technique included both a hydrodynamic property (gas hold-up) and a froth property (overflow rate).

Follow up work established that gas hold-up vs. concentration by itself (Figure 4) ranked the frothers in the same order as in Figure 3, pentanol through to F150 and the concentration range now was close to practice (Azgomi et al., 2006). These relationships could be established running the column batch giving an opportunity to measure steady state froth height at the same time.

The combination of gas hold-up and froth height proved an effective characterization tool opening the way to a comprehensive yet manageable evaluation of the established frothers and the proposed new chemistries. Figure 5 gives an example of a characterization chart, froth height vs. gas hold-up at a given frother concentration (10 ppm in this case).

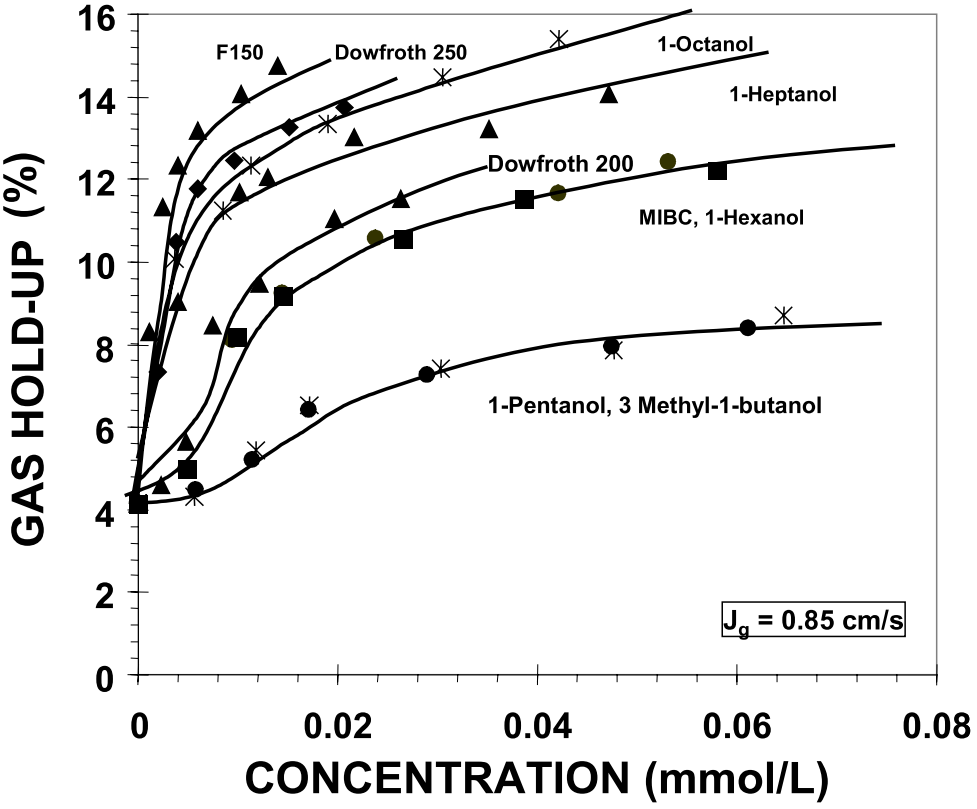

Figure 4: Gas hold-up as a function of concentration for series of frothers tested by Azgomi et al. (2006) (Note: 1, the same ranking of frothers occurs as in Figure 3; 2, for reference 0.04 mmol/L MIBC is ~ 4 ppm)

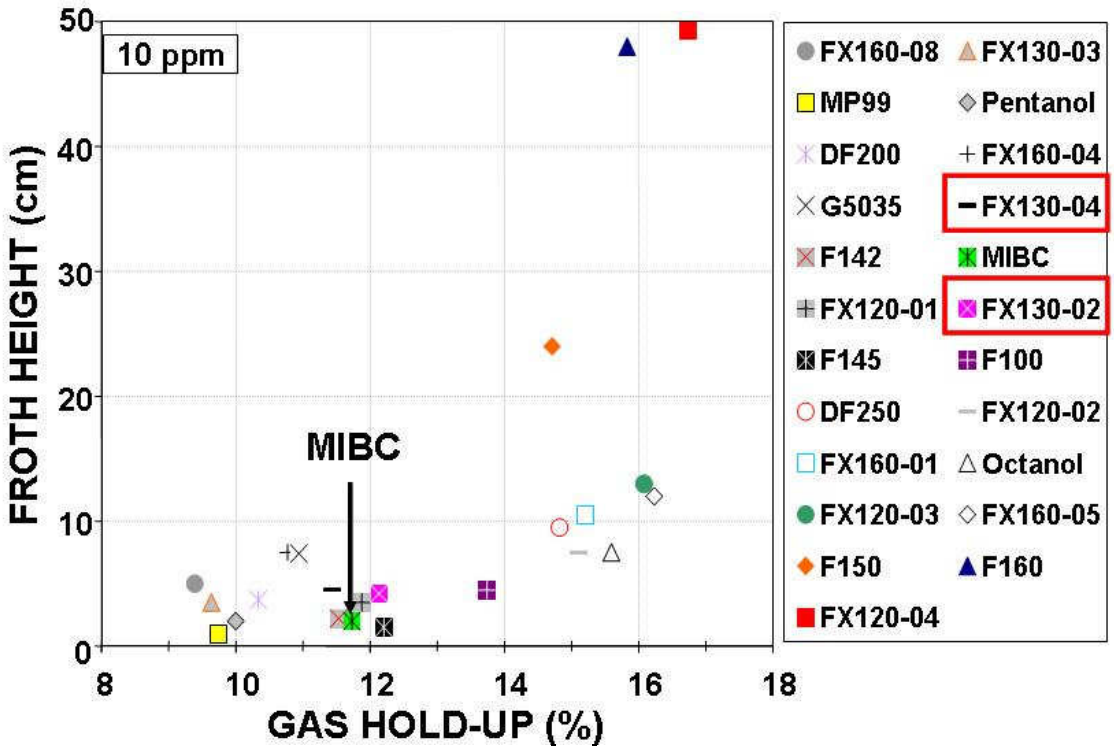

Figure 5: Chart of froth height as a function of gas hold-up for a series of known and new frother chemistries

Finding an equivalent to MIBC

The trend in Figure 5 shows most of the frothers (and all the alcohol frothers) give little froth height but provide a wide range of gas hold-up (and by inference bubble size). Those giving high gas hold-up also tend to give high froth height, this height increasing significantly for some frothers, all in the glycol class. One possible use of the chart is to suggest an alternative to one frother by finding another that gives similar gas hold-up and froth height at the same concentration.

Using MIBC as an example, from inspection of the chart, two frothers are close, FX130-02 and FX130-04. These represent two in a series of reaction products of n-butanol with ethylene oxide. This is the FX130 series with the second figure coding the number of ethoxy groups added (although not the actual number of moles).

To test the equivalence, Figures 6 and 7 show gas hold-up vs. concentration and froth height vs. concentration, respectively. These indicate that FX130 chemistries give similar hydrodynamic and froth properties to MIBC.

The next step was laboratory batch testing to evaluate the new FX130 chemistries.

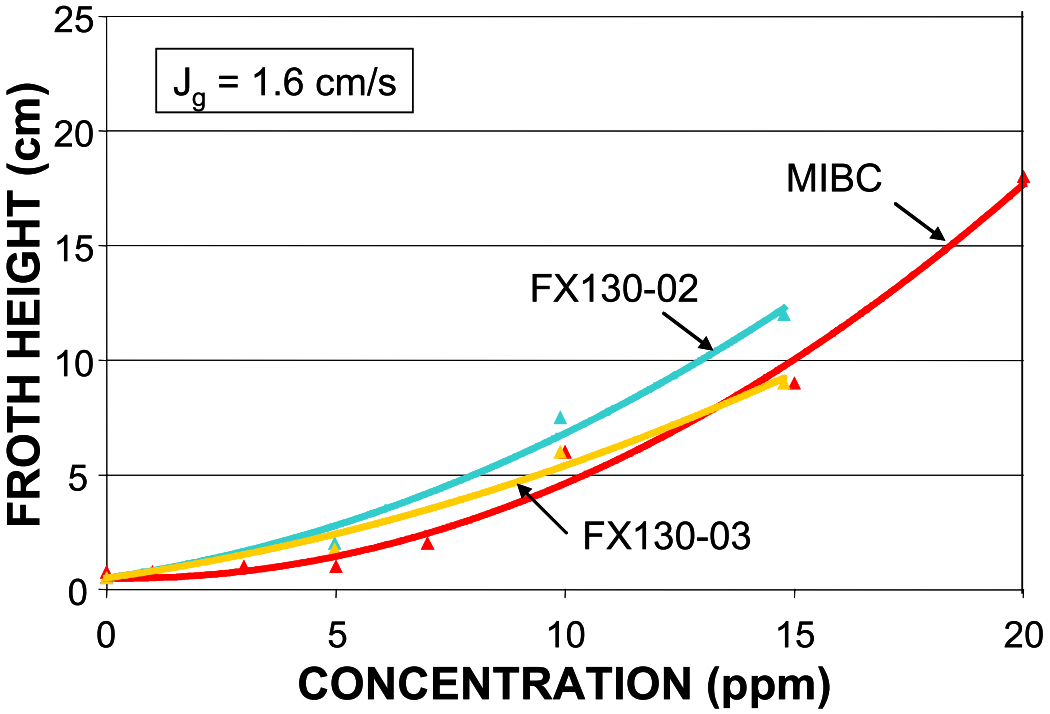

Figure 6: Froth height as a function of concentration for two FX130 chemistries relative to MIBC

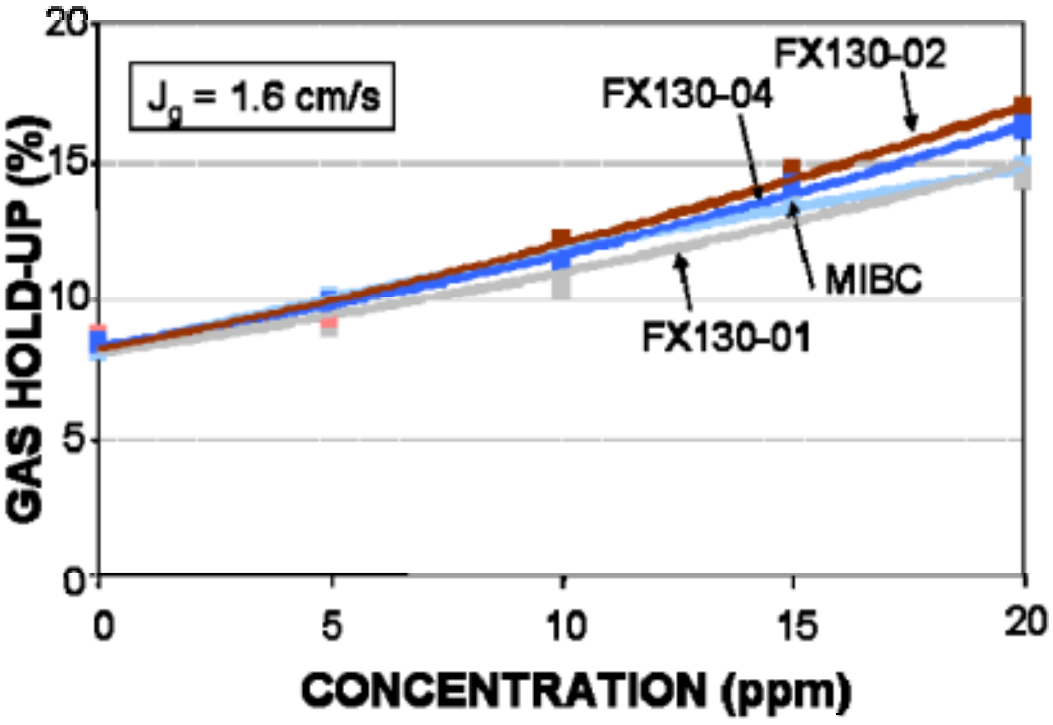

Figure 7: Gas hold-up as function of concentration for three FX130 chemistries relative to MIBC

Flotation testing of FX130 chemistries

Batch Testing

Batch tests were performed on two ore samples, one from Canada (Cu/Au) and one from Doe Run (Pb/Cu/Zn). The results for the Canadian example are summarized in Table 1.

Table 1: Comparison of MIBC and FX130-01 on the Canadian ore
Conditions:
Charge: 2kg
Grind Fineness: 80% passing 140µm
Pulp Density: 22% solids
Collector Dosage: 2g/t PEX, 3g/t 3477 added in the mill)
Frother Dosage: 125g/t
pH: Natural (pH 7.8)
Results:

No.	Frother	Dosage (g/t)	Tails Grade		Recovery (%)[1]	
			Au (g/t)	Cu (%)	Au	Cu
1	MIBC	125	0.21	0.048	59	71
2	FX130-01	125	0.21	0.046	61	70
3	MIBC	125	0.22	0.059	56	63
4	FX130-01	125	0.23	0.060	55	67

[1]based on calculated head

The conclusions are that the FX130-01 is equal to MIBC in the recovery of gold and copper.

Figure 8 shows the Doe Run test results for Pb (a), and Cu (b). (In this case n-hexanol instead of MIBC was employed but they are known to give similar performance); again, the results with FX130-01 are similar.

The comparison was sufficiently encouraging to risk a plant test.

Plant testing

Frother FX130-02 was substituted for MIBC for a 1-hour trial at Doe Run's Buick mill. About 20 minutes after the switch there was no visible change. At the end of the test the kinetics in both the Pb and Zn circuits appeared to have increased and the froth seemed more foamy. Overall metallurgy showed no change (Table 2). This indicates the substitution was successful, and that the differences in flotation rate and froth quality could be compensated by addition rate. And, important from the viewpoint of acceptability, there was no alcohol smell.

There was insufficient supply of reagent to prolong the test but these preliminary findings lend further support to the fact that FX130 chemistries can substitute for MIBC. More extensive proving will be performed in the near future.

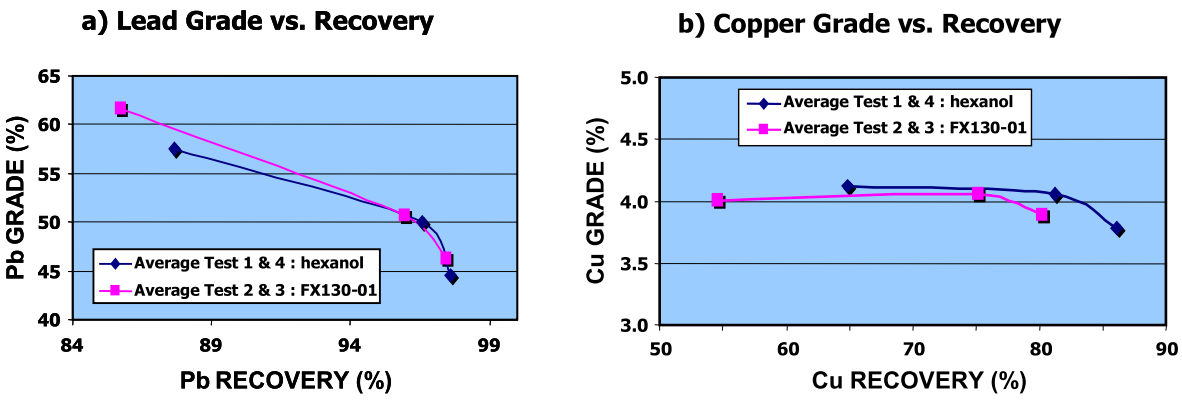

Figure 8: Results of lab tests on Doe Run ore sample

Table 2: Results of 1-hour plant of FX130-02 at Doe Run Buick mill (12:00-1:00 pm)

Stream	Grade (%)[1]		Recovery (%)	
	Pb	Zn	Pb	Zn
Before test (11:50 am): MIBC @ 85 ml/min				
Mill Feed	9.9	0.9		
Pb Conc.	77	0.53	95	
Zn Conc.	2.1	57.3		78
At end of test (1:00 pm): FX130-02 @ 82 ml/min				
Mill Feed	11.1	0.9		
Pb Conc.	78.4	1.4	97	
Zn Conc.	0.44	60		65
1 hour after test (2:10 pm): MIBC @ 85 ml/min				
Mill Feed	11.3	0.8		
Pb Conc.	78.2	1.5	96	
Zn Conc.	1.96	57.3		70

[1] From on-stream analyzer

DISCUSSION

The frother characterization procedure employed here combines a hydrodynamic property, gas hold-up, and a froth property, froth height, measured on a two-phase system. These two parameters are monitored as a function of frother concentration and can be presented as 'charts' of froth height vs. gas hold-up at a given concentration. This recognizes the dual function of frothers: control of conditions in the pulp and the froth. Other techniques continue to emphasize just frothing properties (e.g., shake test (Wang and Yoon, 2006)) or do not clearly differentiate between the two functions. For instance, the dynamic foamability index (Laskowski, 2003), being based on volume expansion upon aeration, actually includes the contribution of gas hold-up below the foam[2]. The proposed technique is straightforward, requiring only a bubble column

[2] Foam is often the term used for two-phase froths

with pressure taps to give gas hold-up and a ruler for froth height, while measuring parameters which are clearly associated with the two functions. It made tractable the reliable evaluation of quite an exhaustive list of known and new frother chemistries. Any drift over time (e.g., due to sparger blockage) was readily detected by testing standard strength frother concentrations at intervals in the program. A draw back at this stage is that the absolute values of gas hold-up and froth height depend on the gas velocity and the type of sparger used. (The procedure also relies on Montréal tap water although there is evidence that the quality may vary sufficiently to affect bubble properties (Sam et al., 1996).) Reliance, therefore, is on the relative position (ranking) of a frother but it is anticipated that a numeric index can be derived from the relationships that would provide a unit of frother 'strength'.

The work identified distinctive characteristics of frother types. The alcohols tend to give relatively low rate of change in gas hold-up with concentration compared to the glycols (Figure 4). This may convey an advantage to the alcohols in that close control over concentration is not demanded to maintain acceptable hydrodynamic conditions. On the other hand, the glycols more readily generate froth than alcohols (Figure 5) which may prove an advantage in some situations.

The work illustrated an application of the characterization tool: identifying FX130 chemistries as potential substitutes for MIBC. The subsequent laboratory and plant evaluation established that the choice performed as anticipated. This supports the original notion that characterization in the two-phase system (i.e., no solids) is an adequate place to start. Apart from the fact that no universal choice of a 'standard' solid is likely, the impact of solids has to be considered with respect to the two frother functions. In general, solids do not greatly alter the bubble size produced (Nesset et al., 2006) but, by common experience, in both laboratory and plant, solids can establish substantial froth even with frothers that are poor froth producers on their own at typical flotation dosages, like MIBC (Indeed, solids can also do this with salt solutions that again produce little froth on their own (Quinn et al., 2006).) Recent work by Pugh (2006) emphasizes that hydrophobic particles alone are capable of generating froth.

The new frother chemistries emerging from this work will expand the options available to operators to achieve the target hydrodynamic and froth conditions in the on-going search or optimum flotation conditions.

CONCLUSIONS

Frothers perform two major functions in flotation: helping set hydrodynamic conditions in the pulp phase (bubble size, gas hold-up, etc) and froth properties (stability, water content, etc). The evolution of a method of characterizing frothers based on these functions using gas holdup and froth height in a two-phase (air-water) bubble column is described. The method revealed the various frother 'families' and showed that frothers could be chemically altered to move from one family to another. This led to the invention of a new class of frothers based on the reaction product of an aliphatic alcohol C_1 (methanol) to C_4 (butanol) with between 0.2 moles to 5 moles ethylene oxide. Examples of the new frothers based on butanol as potential alternatives to MIBC

(the F130 series) were proved in laboratory batch and plant test work. The new frother class opens up additional options for selecting conditions to optimize flotation.

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