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Propriedades de Espuma no Desempenho da Flotação Catiônica Reversa de Minério de Ferro

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PPGEM

Tese intitulada **"Propriedades de Espuma No Desempenho da Flotação Catiônica Reversa de Minério de Ferro"**, área de concentração: Tecnologia Mineral, apresentada pelo candidato **Vanderson Eney de Matos**, para obtenção do grau de Doutor em Engenharia Metalúrgica, Materiais e de Minas, aprovada pela comissão examinadora constituída pelos seguintes membros:

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RESUMO

A flotação catiônica reversa tem sido amplamente utilizada na concentração de minérios de ferro. A eficiência do processo depende fortemente das características da fase espuma, que por sua vez é função do sistema de reagentes químicos utilizados. Espumantes são surfactantes responsáveis pelo controle das propriedades da espuma através da redução da tensão superficial da água, prevenção da coalescência de bolhas e estabilização da espuma. Coletores e modificadores têm funções distintas, mas interferem também nas propriedades da espuma interagindo com os espumantes e/ou atuando nas diversas interfaces do processo. O objetivo deste trabalho foi investigar a influência dos reagentes nas propriedades de espuma da flotação catiônica reversa de minério de ferro, através de estudos simulando as interações nas interfaces bifásica líquido-gás e trifásica líquido-sólido-gás, via ensaios fundamentais e aplicados. Eteraminas acumulam as funções de coletor e espumante na flotação catiônica reversa de minério de ferro. Suas formas estruturais eterdiamina e etermonoamina possuem características específicas que induzem efeitos distintos na formação e estabilidade da espuma, justificando a diferença de seletividade entre elas. Resultados demonstram que a eterdiamina apresenta melhor flotabilidade do quartzo puro em ensaios de microflotação, para ambas as concentrações e valores de pH avaliados. Comparando-se com etermonoamina, valores superiores de seletividade foram encontrados com a eterdiamina na flotação de um minério de ferro em experimentos de bancada. Essa superioridade está relacionada à maior recuperação metalúrgica da eterdiamina atribuída ao menor arraste hidrodinâmico (*entrainment*) das partículas finas de hematita, provocado pela formação de espumas mais secas e estáveis, superando a vantagem da etermonoamina em relação à geração de bolhas menores. Além disso, a combinação de reagentes espumantes específicos às eteraminas potencializaram o desempenho da flotação através de melhoria na seletividade. A substituição parcial das eteraminas por espumantes, normalmente mais baratos, apresenta melhor custo e benefício, entretanto a combinação entre a eterdiamina e a etermonoamina apresentou os melhores resultados.

Palavras-chave: Espumas de flotação. Eteraminas. Espumas bifásicas. Espumas trifásicas. Espumantes. Minério de ferro. Flotação catiônica reversa.

ABSTRACT

Reverse cationic flotation has been widely utilized in the concentration of iron ores. The efficiency of the process strongly depends on the characteristics of the froth phase which is function of the used system of chemical reagents. Frothers are surfactants responsible for the control of the froth properties by the reduction of the water surface tension, prevention of bubbles coalescence and froth stabilization. Collector and modifying agents perform different functions, but they also interfere on the froth properties interacting with frothers and acting at the different interfaces of the process. The objective of this study is to investigate the influence of reagents on the froth properties of the reverse cationic flotation of iron ore, by means of studies simulating the two-phase liquid-gas and three phase liquid-solid-gas interfaces, using fundamental and applied experiments. The structural formulas etherdiamine and ethermonoamine possess characteristics that induce distinct effects on froth formation and stability, justifying the difference in selectivity. The results demonstrated that etherdiamine imparts better floatability of pure quartz in microflotation tests at both concentrations and pH levels evaluated. In comparison with ethermonoamine, higher selectivity levels were achieved with etherdiamine in bench scale flotation of an iron ore. This superior performance was attributed to the greater metallurgical recovery of etherdiamine attributed to the lower hydrodynamic entrainment of fine hematite particles, caused by the formation of drier and more stable foams, overcoming the advantage of ethermonoamine to generate smaller bubbles. Besides that, there is a wide diversity of reagents that act exclusively as frothers. The combination of etheramine-specific frothers reagents potentiated flotation performance through improved selectivity. The replacement of etheramine by frothers, normally cheaper, presents better cost and benefit, however the combination between etherdiamine and ethermonoamine showed the best results.

Keywords: Flotation froths. Etheramines. Two-phase foams. Three-phase froths. Frothers. Iron ore. Reverse cationic flotation.

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ROTEIRO DA TESE

A tese é estruturada sobre a forma de capítulos, onde o capítulo 1 apresenta a introdução geral do assunto e o capítulo 2 aborda o arcabouço teórico da tese, abrangendo os principais aspectos das propriedades da espuma no processo de flotação, focado nos fundamentos do processo, uso de reagentes espumantes e suas interações com coletores e modificadores na formação e estabilidade de espuma. Os objetivos gerais e específicos da tese são descritos no capítulo 3.

Os diferentes materiais, equipamentos e métodos utilizados no desenvolvimento do trabalho são apresentados no capítulo 4 e estão descritos especificamente em cada artigo publicado/submetido, apresentados nos capítulos 7 a 10 supracitados.

No capítulo 5 são sumariados os principais resultados deste trabalho, seguidos pelas conclusões (capítulo 6), relevância dos resultados e sugestões para trabalhos futuros inerentes ao tema. As referências da literatura consultadas neste trabalho (arcabouço teórico do capítulo 2) estão organizadas no tópico referências bibliográficas, anterior ao capítulo 7.

Os capítulos 7 a 10 apresentam em detalhes e de forma independente os resultados obtidos, discutidos através de artigos publicados (Artigo A, B e C) e proposto para submissão (artigo D), conforme descrições a seguir:

- Artigo A – "*Analysis of Quartz Floatability Using Design of Experiments*": Estudo comparativo do efeito das formas estruturais etermonoamina e eterdiamina na flotabilidade do quartzo puro através de ensaios de microflotação e aplicação de planejamento fatorial de experimentos.
- Artigo B – "*Etheramine: Foam/Froth Stability and Selectivity in Iron Ore Flotation - Part 1 - Two-Phase Systems*": Avaliação do efeito das eteraminas nas propriedades de espuma bifásica (*foam*) através da caracterização das suas funções estruturais e desempenho em testes de flotação focados nas interface líquido-gás.
- Artigo C – "*Foam/Froth Stability and Selectivity in Iron Ore Flotation - Part 2 – Three-Phase Systems*": Avaliação das eteraminas nas propriedades de espuma trifásica (*froth*) e seu efeito na seletividade da flotação catiônica de um minério de ferro, em testes focados nas interfaces envolvendo sólido, líquido e gás.
- Artigo D – "*Effects of Surfactants Combination in Iron Ore Flotation*": Investigação das propriedades de espuma dos espumantes tipo álcool (MIBC) e poliglicol (DF1012),

comparado às eteraminas e seus efeitos na seletividade da flotação, quando substituindo parcialmente os coletores.

Ao final de cada capítulo contendo os artigos, estão descritas as referências bibliográficas citadas especificamente em cada sessão.

1 INTRODUÇÃO

A eficiência do processo de flotação aplicada como técnica de concentração de minerais depende fortemente da escolha adequada do sistema de reagentes. Coletores, modificadores e espumantes são funções distintas atribuídas aos reagentes, que atuam simultaneamente nas diferentes interfaces presentes no processo, controlando as propriedades superficiais das partículas sólidas, a tensão superficial da água, a dispersão do ar, o comportamento fluidodinâmico da polpa, o estado de agregação e dispersão das espécies minerais e a formação, estabilidade, tamanho das bolhas e conteúdo de água da espuma.

A flotação catiônica reversa utilizando aminas como coletores e amidos como depressores é consagrada como o método mais eficiente e amplamente utilizado na concentração de minério de ferro de baixo teor. No entanto a evolução do desenvolvimento de reagentes na flotação catiônica reversa de minério de ferro (FCRMF) é lenta e baseada em empirismo, premissas práticas e suposições generalistas que perduram ao longo de décadas, sendo poucas vezes desafiadas ou questionadas.

Frequentemente a escolha dos reagentes é definida pelo custo unitário do produto em detrimento de performance, negligenciando o uso de produtos alternativos ou inovadores. A disponibilidade de formulações químicas para cada função dos reagentes é quase ilimitada, mas a aplicação na prática permanece conservadora e restritiva.

O controle das características da fase espuma no processo de flotação requer o uso de espumantes, uma vez que líquidos puros não geram espumas. A formação, estabilização e persistência/extinção de espumas na concentração de minerais por flotação são cruciais para êxito na eficiência desse processo.

O uso de espumantes específicos em processos convencionais de flotação é clássico e os estudos e desenvolvimentos nessa área são amplos e crescentes na última década. No entanto, na flotação catiônica reversa de minério de ferro a função espumante recebe atenção secundária ou é quase inexplorada, em face de uma simplificação de processo, na qual a amina exerce as funções coletora e espumante concomitantemente. Apesar de funcional, essa prática limita a eficiência do processo.

As eteraminas são surfactantes catiônicos que em meio aquoso e pH alcalino se dissociam por protonação em espécies iônicas (coletores) e moleculares (espumantes). Alguns autores relatam que a máxima eficiência do processo é obtida quando o sistema atinge o equilíbrio, ou seja, onde espécies moleculares e iônicas coexistem em concentrações equivalentes.

Etermonoaminas e eterdiaminas apresentam efeitos distintos no desempenho da flotação, em função das suas características estruturais, mas a descrição e distinção desses efeitos nas características das espumas ainda não estão claramente explicadas. Além disso, não há estudos abordando as propriedades das espumas formadas pelas eteraminas, comparadas àquelas formadas por outros tipos de espumantes, que garantam que as primeiras sejam a alternativa de melhor desempenho para esse processo, em termos de controle da espuma.

A escolha dos espumantes adequados, utilizados da forma correta, pode ampliar a seletividade do processo, aumentar a produtividade e/ou reduzir o custo operacional, através da redução do consumo específico dos reagentes ou por serem, geralmente, mais baratos que as aminas.

O principal papel dos espumantes na flotação é reduzir o tamanho de bolhas na espuma através da prevenção da coalescência, uma vez que, teoricamente, bolhas menores exercem melhor desempenho na flotação, pelo aumento da probabilidade de colisão partícula-bolha. Os espumantes também têm a função de facilitar a dispersão de ar dentro de bolhas, estabilizar e dar mobilidade a espuma.

A geração das espumas de flotação se dá pela adsorção dos surfactantes na interface líquido-gás, gerada pela injeção do ar em uma polpa mineral em suspensão. No primeiro estágio, as bolhas unitárias estão separadas por um filme líquido constituído por uma camada solvatada, com propriedades diferentes daquelas vindas da água livre.

O contato entre duas bolhas vizinhas provoca o afinamento da camada lamelar e o próximo estágio envolve a remoção de líquido das camadas hidratadas em contato. Dependendo da natureza dessa camada de hidratação, a qual reflete o tipo de surcfatante utilizado, a drenagem e a coalescência podem ser rápidas (álcoois) ou o filme pode ser mais persistente (poliglícois). A drenagem da água também é governada pela gravidade e por efeitos de capilaridade.

Classicamente, o processo de flotação tem sido dividido entre as fases de polpa e espuma. Na flotação catiônica reversa de ferro, os minerais de ganga, compostos principalmente por quartzo (SiO_2) e ou outros silicatos, são coletados pela fase espuma, enquanto os minerais portadores de ferro, principalmente hematita (Fe_2O_3), magnetita (Fe_3O_4) e goethita (FeOH), são concentrados na fase polpa.

As zonas de polpa e espuma definem tanto a qualidade do concentrado quanto a eficiência ou produtividade do processo. As propriedades dessas duas zonas incluem a hidrodinâmica da polpa, a taxa de coalescência das bolhas na espuma, a taxa de água no overflow e a dispersão/recuperação do ar.

Essas propriedades dependem não só do tipo e concentração dos reagentes, mas também da natureza física, química e mineralógica das partículas minerais, bem como das interações reagente-partícula e potencialmente das interações partícula-bolha.

A zona de espuma contribui para o processo promovendo transporte das partículas minerais hidrofóbicas para o overflow e rejeitando o aprisionamento das partículas hidrofílicas, por drenagem dessas, de volta para a zona de polpa. O aprisionamento ou transporte não seletivo de partículas sólidas prejudica o desempenho da flotação e está intimamente associado à recuperação de água no flotado. A Figura 1.1 apresenta de maneira esquemática os mecanismos de transferência de partículas via coleta por flotação e arraste hidrodinâmico entre as zonas de polpa e espuma e seus respectivos transporte para fora do sistema (célula de flotação).

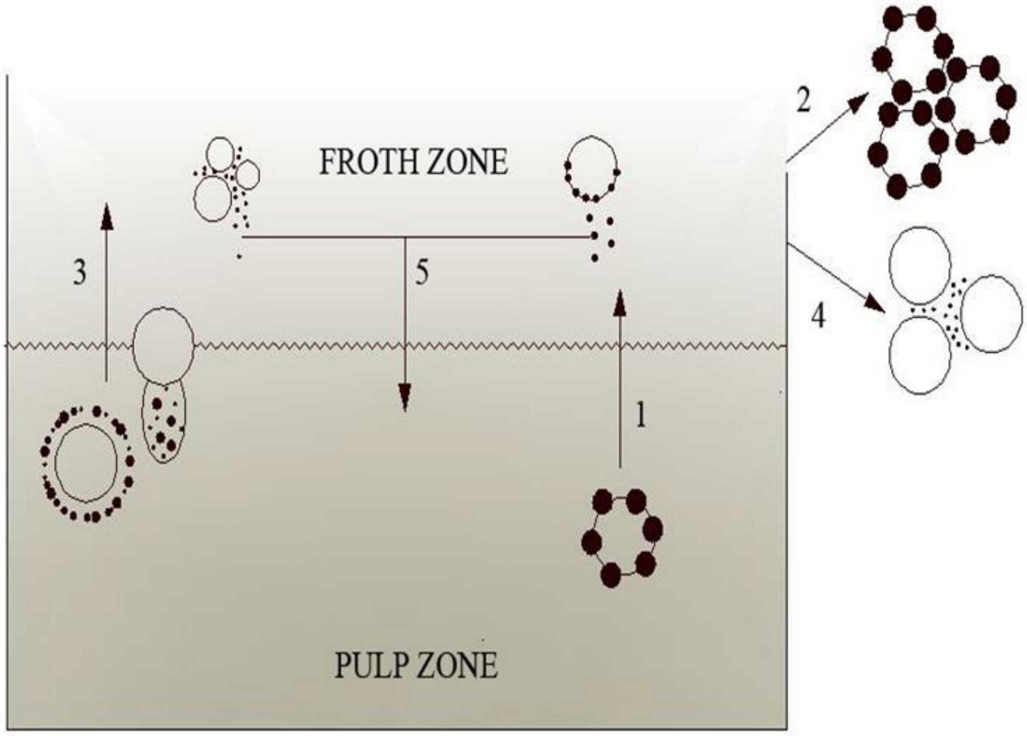

Figura 1.1 - Mecanismos de transferência das partículas minerais liberadas na célula de flotação (SAVASSI, 1998).

Na flotação catiônica reversa de minério de ferro, o aprisionamento é definido pelo arraste hidrodinâmico de partículas finas contendo ferro para o rejeito, provocando aumento na perda metálica de partículas de hematita, principalmente aquelas com características especularíticas.

As propriedades da espuma e da polpa, governadas pela presença dos surfactantes, interferem também em etapas subsequentes de separação sólido-líquido, necessárias ao processo de beneficiamento mineral. A atuação desses surfactantes no decaimento da tensão superficial da água altera a eficiência de processos de sedimentação, recuperação de água, filtragem, secagem e consequentes fases de transporte e disposição de produtos. Buscar sinergias entre o uso dos reagentes na flotação e seu efeito colateral nos processos supracitados é fundamental, essencialmente diante do cenário desafiador de uso restrito de água e máxima segurança na disposição de rejeitos de mineração.

2 ARCABOUÇO TEÓRICO

Este capítulo apresenta o arcabouço teórico da investigação, abordando o uso dos reagentes de flotação, contextualizando as propriedades da espuma.

2.1 Flotação

A flotação é o processo de concentração de minérios mais eficaz tanto do ponto de vista tecnológico quanto econômico para a produção de concentrados de ferro (FILIPPOV et al., 2010). A versatilidade desse método é comprovada pela aplicação em diversas classes minerais, em amplas faixas granulométricas (LIMA et al., 2013). Este processo é considerado diferenciado, em relação às demais técnicas concorrentes de concentração, porque a propriedade diferenciadora que o caracteriza pode ser induzida pela utilização de reagentes químicos que alteram as características superficiais das partículas minerais em relação à hidrofobicidade, e probabilidade de adesão dessas com bolhas durante colisões no interior da célula de flotação, permitindo a separação seletiva do mineral de interesse (MATOS et al., 2015).

A técnica compreende métodos distintos de processo que são convenientemente adequados às características e conteúdo dos minerais e aplicação do produto. Estes métodos são classificados como flotação aniônica direta de óxidos de ferro, e flotação reversa, que por sua vez é subdividida em flotação aniônica de sílica ativada e flotação catiônica reversa (HOUOT, 1983; ARAUJO et al., 2005; FILIPPOV et. al., 2014). Houot (1983) inclui neste grupo a floculação seletiva de lamas associadas com a flotação aniônica ou catiônica da sílica. Mowla et al., (2008) relataram o uso de flotação reversa de hematita, para remoção de ferro de minerais industriais como areia, feldspato caulinizado (*China clay*) e feldspato como uma outra categoria. Dentre esses métodos, a flotação catiônica reversa de quartzo destaca-se como a mais importante, crítica e amplamente utilizada técnica de concentração de itabiritos para a produção de pellet feed de alta qualidade (HOUOT, 1983; ARAUJO et al., 2005; VIEIRA & PERES, 2007; MA et al., 2011, LIMA et al., 2013; FILIPPOV et al., 2014), também chamados superconcentrados.

A distribuição de tamanhos (granulometria) das partículas é a principal variável em processos de tratamento de minérios. Trahar (1981) relatou que a recuperação de partículas grossas na flotação é mais sensível ao meio químico em comparação com a de partículas mais finas. Vieira & Peres (2007) discutiram os dois principais desafios enfrentados na flotação catiônica reversa de quartzo, utilizada na concentração de óxidos de ferro, relacionados ao tamanho das partículas: (i) – partículas grossas de quartzo não respondem bem à ação coletora das aminas; (ii) – partículas finas e ultrafinas portadoras de ferro não respondem bem à ação depressora dos amidos de milho gelatinizados. Lima et al., (2013) citaram que a flotação de minérios de ferro é realizada com a alimentação de partículas na faixa de tamanho entre 10 e 150 μm. Estes autores realizaram ensaios de flotação com três frações granulométricas de um minério de ferro itabirítico e concluíram que a flotação em separado das frações grossa e fina indicaram aumento de 3% na recuperação metálica, com redução no teor de SiO_2 no concentrado, comparado à flotação em conjunto dessas frações, com aumento de 30% na dosagem de coletor e redução de 20% no consumo de depressor. Atualmente a flotação é multiestagiada, sendo finos e grossos tratados separadamente em equipamentos diferentes (colunas e células mecânicas, respectivamente).

O desempenho da flotação catiônica reversa é potencializado quando a polpa é previamente deslamada (eliminação de partículas inferiores a 10 μm). Este efeito é mais sensível na flotação catiônica reversa em relação à flotação aniônica (HOUOT 1983, MA et al., 2011). Partículas muito finas são deletérias para o processo de flotação provocando o efeito *slimes coating* (perda de seletividade pelo recobrimento das partículas por lamas) e consumo excessivo de reagentes (ARAÚJO et al., 2005). Rocha et al., (2010), no entanto, obtiveram bons resultados de recuperação metálica (80% na flotação) e qualidade de concentrado ($\%SiO_2<1\%$) utilizando altas dosagens de depressor, na flotação catiônica reversa de uma lama de minério de ferro (D_{90}=10,9 μm; 86% passante em 7,1 μm).

Em todos os casos, a seletividade do processo é governada pelo uso adequado de reagentes químicos, ativos nas interfaces presentes no processo. A flotação direta utiliza ácidos graxos saturados (QUAST, 2006) e ácido oleico (QUAST, 2016) como coletores e silicato de sódio como depressores de ganga silicatada. Os reagentes mais utilizados na flotação catiônica reversa são as eteraminas, atuando como coletores das partículas de quartzo, e os amidos naturais, exercendo a função de depressores das partículas de óxido de ferro (ARAÚJO et al., 2005; PEARSE, 2005; FILIPPOV et al., 2010; MATOS et al., 2015).

2.2 Reagentes de Flotação

A utilização de reagentes na flotação de minerais possui um papel fundamental no desempenho do processo. Nakhaei & Irannajad (2017) classificam os tipos e a quantidade de reagentes como a parte mais importante para a seletividade do processo de flotação.

Esses produtos químicos atuam nas propriedades interfaciais das fases presentes, exercendo funções distintas que garantem versatilidade na aplicação da técnica de concentração mineral por flotação. A complexidade do sistema de reagentes utilizados no tratamento de minério de ferro usualmente envolve coletores, espumantes, depressores, dispersantes, ativadores e reguladores de pH.

Revisões da literatura sobre o uso de reagentes na flotação são recorrentes, abordando os mais complexos mecanismos envolvidos nas interações entre os diferentes minerais e os mais diversos tipos de reagentes (ARAUJO et al., 2005; PEARSE, 2005; BULATOVIC, 2007; QUAST, 2016; NAKHAEI & IRANNAJAD, 2017).

Este capítulo descreve as funções dos reagentes no processo de flotação e suas interações, focado nos coletores catiônicos utilizados na flotação reversa de ferro e os espumantes, amplamente utilizados nos processos de flotação, mas pouco explorados na concentração de minério de ferro.

2.2.1 Coletores

Coletores são os reagentes mais importantes para qualquer sistema de flotação (NAKHAEI & IRANNAJAD, 2017). A escolha do tipo de coletor utilizado depende do tipo de minério e da rota de beneficiamento selecionada, e é tão importante para a flotação que classifica e dá nome ao processo. Coletores aniônicos são utilizados na flotação aniônica direta e reversa de minério de ferro, enquanto os coletores catiônicos são utilizados no processo mais amplamente empregado: a flotação catiônica reversa de minério de ferro (FCRMF).

Os coletores aniônicos podem ser divididos em carboxilatos, hidroxamatos, sulfonatos e thiois. Essa classificação é baseada na estrutura do grupo solidofílico (oxidril, hidroxil, sulfidril ou carboxil). Ácidos graxos, ácidos resinílicos, alquil sulfatos ou sulfonatos, ácidos oleicos, oleatos de sódio e xantatos são os coletores aniônicos mais aplicados nessa categoria de flotação.

Coletores catiônicos, como aquilaminas primárias graxas, eteraminas e sais quaternários de amônia, são utilizados principalmente na flotação de quartzo e silicatos. A dodecilamina (DDA) é o coletor de quartzo mais comum, devido sua forte habilidade de coleta desse mineral (LIU, 2015).

Quimicamente, aminas orgânicas primárias, secundárias e terciárias são bem conhecidas, pelo uso na síntese intermediária de surcfatantes catiônicos, anfotéricos e não iônicos, dependendo do tipo de composto usado na derivação do produto. Esses derivados geram uma série de propriedades funcionais distintas para as aminas que incluem atividade superficial, solubilidade, reatividade e equilíbrio ou moderação.

Essa versatilidade expande potencialmente as possibilidades de aplicação das aminas na flotação, principalmente na flotação catiônica de minério de ferro. Uma alternativa interessante seria a proposição de diferentes espumantes não iônicos a base de amina, permitindo a melhoria das características das espumas no processo que utiliza eteraminas e potencialmente sais quaternários de amônia.

Patra et al., (2018) relataram o *design*, síntese e análises de um novo coletor à base de poliamina, proposto para a flotação de minerais aluminosilicatos contidos em um minério de ferro indiano fino (partículas majoritariamente menores que 30 μm), rico em goethita e caolinita. Os resultados mostraram que os níveis de sílica no concentrado foram reduzidos significativamente com o novo coletor. Estes autores reforçaram a importância do emprego da modelagem molecular para a proposição de novos coletores, específicos para a flotação de minérios com características específicas.

As aminas graxas e seus derivados são a base para produção de eteraminas, sendo que as aminas primárias e os sais quaternários de amônia também podem ser utilizados como coletores catiônicos na flotação reversa de oximinerais (ARAÚJO et al., 2005; PEARSE, 2005; MA et al., 2009; FILIPPOV, 2010; FILIPPOV, 2014).

As etermonoaminas ou N-alquiloxipropilamina [$R–O–CH_2–CH_2–C–NH_2$] são obtidas através da reação de adição de um álcool graxo com acrilonitrila, formando éter nitrila. Esse produto é então hidrogenado cataliticamente a alta pressão formando a etermonoamina. Analogamente, o produto da reação sequencial das etermonoaminas com acrilonitrila, formando uma éter-nitrila, seguida de hidrogenação, produz a eterdiamina ou N-alquiloxipropil-1,3-propanodiamina [$R–O–(CH_2)_3–NH–(CH_2)_3–NH_2$] (Vieira e Peres, 2007).

Segundo Araujo et al., (2005), a inserção do grupo polar $(O\text{-}CH_2)_3$ entre o radical R e a cabeça polar NH_2 da amina primária, caracterizando a função éter que classifica as eteraminas (Figura 2.1), melhora a solubilidade do reagente, facilitando o seu acesso às interfaces sólido-líquido e líquido-gás. As eteraminas são fornecidas como acetatos ou sais quaternários de cloretos parcialmente neutralizados com ácido acético ou ácido clorídrico, respectivamente.

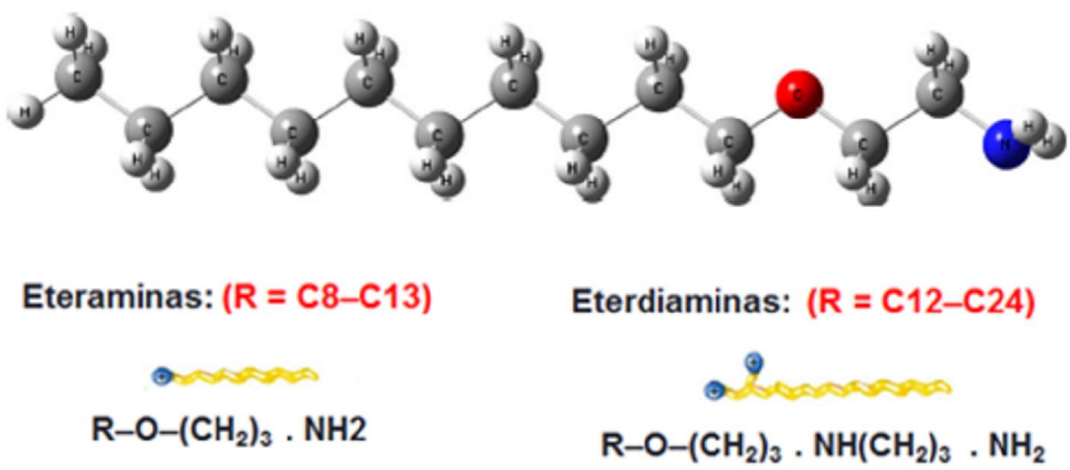

Figura 2. 1 - Estrutura molecular das eteraminas.

As aminas se ionizam em solução aquosa por protonação segundo a equação $RNH_2(aq)+H_2O=RNH_3^{+}+OH^{-}$ (BULATOVIC, 2007). A dissociação é sem dúvidas a propriedade mais importante das aminas quando aplicadas na flotação. Monoaminas e diaminas possuem perfis diferenciados de curvas de dissociação entre os compostos moleculares e iônicos (SMITH & AHANTAR, 1976; e ARI, 2001). A forma iônica é solúvel e se adsorve facilmente sobre a superfície do quartzo predominantemente por um mecanismo de atração eletrostática, já que a superfície do mineral está carregada negativamente em valores de pH superiores a 2,5. As espécies moleculares agem também como espumantes, conferindo elasticidade à película interlamelar na espuma, aumentando a seletividade da separação. No momento da adesão partícula-bolha ocorre a interpenetração entre as espécies coletor e espumante, fazendo com que também as espécies com papel espumante permaneçam adsorvidas ao quartzo. Smith & Scott (1990) sugeriram que uma amina funciona melhor como coletor, em um valor de pH em que as espécies iônicas e moleculares estão presentes em quantidades aproximadamente iguais.

Diaminas são coletores de quartzo mais fortes que as monoaminas para comprimentos de cadeias comparáveis. (SCOTT & SMITH, 1991; MA et al., 2009). Os valores inferiores (mais ácidos) de pKa da diamina em relação à monoamina e a dupla carga polar da diamina promoveram flotação mais forte do quartzo, quando uma diamina de 12C foi comparada à uma monoamina 12C (SMITH & SCOTT, 1991). Algumas vezes esta constatação é extrapolada arbritariamente para os minerais silicatados sem evidências experimentais (SCOTT & SMITH, 1992), entretanto Ma et al., (2009) contrariaram esta afirmação indicando que a química de flotação da caulinita é totalmente diferente do quartzo, de tal forma que a eterdiamina não induziu nenhuma flotação na caulinita enquanto a etermonoamina causou uma forte flotação desse mineral. Eteraminas são mais eficazes na flotação reversa de certos tipos de minérios de ferro, enquanto, para outros tipos, melhores resultados foram obtidos com eterdiamina (PAPINI et al., 2001; ARAÚJO et al., 2005; FILLIPOV et al., 2010). Vieira & Peres (2007) observaram que eterdiaminas foram mais efetivas na flotação de partículas grossas e médias de quartzo, enquanto as etermonoaminas apresentaram melhor desempenho na flotação das partículas finas. Matos (2017) realizou experimentos de flotação em bancada com amostras de minério de ferro, apresentando resultados que demonstraram que a eterdiamina é mais seletiva para a flotação de grossos enquanto a etermonoamina é mais eficiente para a flotação de finos.

Normalmente as etermonoaminas comerciais utilizadas na flotação reversa de ferro têm cadeia hidrocarbônica entre 8 e 12 carbonos enquanto as eterdiaminas possuem cadeias entre 12 e 18. A influência do comprimento de cadeia hidrocarbônica (4C a 18C) na recuperação de quartzo, utilizando acetatos de aquilaminas, foi explorada por Fuersternau et al., (1964). Os resultados mostraram que as aquilaminas com comprimentos de cadeia maiores exigem concentrações menores para obtenção de um mesmo nível de recuperação de quartzo na flotação. Na flotação direta de hematita, Quast (2006) explorou o desempenho de ácidos graxos saturados, com comprimentos de cadeia de C_6 a C_{18}. Além do comprimento, as cadeias hidrocarbônicas dos coletores utilizados na flotação podem ser lineares ou ramificadas oferecendo novos elementos de investigação sobre o desempenho desses reagentes.

2.2.2 Modificadores

A classe dos reagentes modificadores é a mais ampla em termos de classificação de subfunções compreendendo os depressores, dispersantes, ativadores e controladores de pH. De maneira geral, qualquer reagente que não seja um coletor ou espumante pode ser classificado como um modificador e chamado de aditivo de flotação.

Matos (2017) relatou que os depressores, pela sua importância no processo de flotação reversa, deveriam ser destacados em uma classe específica, uma vez que estes são os responsáveis por manterem as espécies de interesse concentradas na polpa, garantindo a qualidade e recuperação metálica na flotação reversa.

Diversos polímeros orgânicos naturais ou sintéticos podem ser aplicados como depressores em processos de flotação de minerais (PEARSE, 2005; NAKHAEI & IRANNAJAD, 2017). Araujo et al., (2005) relataram o uso de amidos naturais de milho e mandioca na prática industrial da FCRMF. Outras fontes naturais de amidos como batata, arroz, sorgo, trigo, inhame entre outros demonstram potencial técnico para a função, mas sua aplicação ainda se restringe a estudos e pesquisas (KAR et al., 2013, SHRIMALI & MILLER, 2016) que não identificaram ainda diferenciais técnicos ou econômicos que justifiquem a sua aplicação na prática.

Outras fontes de polímeros depressores como carboximetilcelulose (CMC), goma guar, lignossulfonatos, poliacrilamidas e ácido húmico são propostos como alternativas potenciais para substituição total ou parcial dos amidos, na concentração de minério de ferro por flotação (TURRER, 2007; DOS SANTOS & OLIVEIRA, 2007).

Wiese & Harris (2012) relataram que o uso de altas dosagens de depressores, necessárias ao processo, resulta em uma significativa redução na estabilidade das espumas de flotação, podendo restringir a recuperação de sólidos no flotado, com consequente redução da recuperação dos minerais de valor. Na flotação reversa de ferro isso seria equivalente a reduzir a taxa de flotação de sílica, produzindo concentrados com baixa pureza. No entanto, o estudo mostra que essa estabilidade da espuma pode ser melhorada pelo aumento na dosagem do espumante. Esses autores avaliaram ainda a interação entre dois diferentes depressores (goma guar e carboximetilcelulose) com um poliglicol espumante simples (Dowfroth 200) e outro mais forte (Dowfroth 250), evidenciando efeitos distintos nos teores e recuperações de cobre e níquel obtidos nos ensaios de flotação em bancada.

Amidos são polissacarídeos utilizados como depressores universais de minerais de ferro na flotação catiônica reversa de minério de ferro. O conteúdo dos polímeros amilose e amilopectina, além de caracterizar os diferentes tipos de amido, são determinantes na performance da flotação.

Matos (2017) apresentou resultados demonstrando a superioridade de um amido com 100% de amilopectina na seletividade da FCRMF. Estes resultados foram atribuídos à maior eficiência de floculação da amilopectina, ausência de adsorção da amilopectina na superfície do quartzo e ausência de interações amina amilose (clatratos). No entanto, estudos sobre a influência do tipo de amido e suas diferenças estruturais nas características da espuma, e sua relação com o desempenho do processo de flotação, ainda não estão disponíveis na literatura.

2.2.3 Espumantes

Espumantes são reagentes surfactantes não iônicos, que desempenham múltiplos papéis na flotação como facilitar dispersão de ar dentro de bolhas, prevenir a coalescência entre bolhas (redução do tamanho de bolha), estabilizar e dar mobilidade à espuma, reduzir o tempo de contato partícula-bolha e acelerar a taxa de flotação (GRAU et al., 2005; MELO & LASKOWSKI, 2006; NAKHAEI & IRANNAJAD, 2017; DRZYMALA & KOWALCZUK, 2018; KOWALCZUK et al., 2018).

Geralmente os espumantes são compostos heteropolares orgânicos, incluindo produtos químicos naturais como óleo de pinho, ácido cresílico e reagentes sintéticos, como metil isobutil carbinol (MIBC) e éteres de poliglicol. Idealmente, os espumantes devem possuir pouca ou nenhuma propriedade de coleta e vice-versa, para que ambas as funções possam ser controladas separadamente.

De acordo com a teoria da penetração de Leja-Schuman (LEJA & SCHUMAN, 1954), os espumantes acumulam-se preferencialmente na interface líquido-gás e interagem com as moléculas de coletor adsorvidas nas partículas sólidas, durante as fases de colisão e adesão partícula-bolha. Segundo Cho & Laskowski (2002), espumantes mais eficientes na redução do tamanho de bolha produzem espumas mais estáveis.

2.3 Classificação dos Espumantes

As propriedades dos espumantes dependem de muitos parâmetros, incluindo estrutura química, concentração e habilidade de interagir com água, sólidos e outros reagentes coletores e modificadores. Existem muitas classificações de espumantes, propostas na literatura, que dependem das características e do sistema físico-químico que se deseja explorar (BULATOVIC, 2007; KHOSHDAST & SAM, 2011; KOWALCZUK & DRZYMALA, 2017; DRZYMALA & KOWALCZUK, 2018).

A literatura clássica oferece abordagens mais simplistas ou objetivas de classificação de espumantes, baseadas nos grupos químicos, solubilidade, acidez/alcalinidade ou funções básicas dos espumantes (GAUDIN, 1957; DAVIES, 1957; DUDENKOV e GALIKOV,1969; Leja, 1982; CROZIER, 1992; LASKOWSKI, 1998; BULATOVIC, 2007). A extensa literatura disponível sobre o uso de espumantes tradicionais disponibiliza várias informações sobre alguns dos álcoois, poliglicóis e outros surfactantes ou compostos de aplicação consagrada na flotação de sulfetos e carvão, principalmente minérios de cobre, níquel, ouro, zinco, chumbo, platina e grafita.

Os álcoois são geralmente considerados como espumantes fracos, de baixa atividade superficial, que produzem espumas relativamente pouco espessas e secas (sem carreamento de água) e de persistência reduzida. Sua ação espumante aumenta com o comprimento da cadeia hidrocarbônica (máximo 6 ou 7 carbonos). O MIBC (metil isobutil carbinol) é o mais conhecido espumante nesse grupo.

Já os espumantes do tipo poliglicóis formam uma classe ampla de estruturas e pesos moleculares variáveis, que produzem espumas espessas e molhadas, mais estáveis e persistentes. Dowfroth 250 (DF250) e Flottec 150 (F150) são exemplos desses poliglicóis (ZHANG, 2016).

Zhang et al., (2012) caracterizou trinta e seis espumantes, através da correlação entre a concentração crítica de coalescência (CCC_{95}) e seu balanço hidrofílico-lipofílico (HLB). Estes reagentes foram subdivididos em três famílias: álcoois alifáticos ($C_nH_{2n+1}OH$), polipropileno glicol alquiléteres ($C_nH_{2n+1}(OC_3H_6)_mOH$) e polipropileno glicol ($H(OC_3H_6)_mOH$), em relação ao grupo aquil (representado pelo número de átomos de carbono n) e número de grupos oxi-propileno (representado por m).

A diversidade de características, métodos de medição e forma de avaliar as propriedades dos espumantes tem sido ampliada em outros estudos recentes, gerando sistemas mais completos e complexos de classificação, que permitem selecionar produtos multifuncionais e/ou múltiplos produtos para uma mesma função ou aplicação específica.

Khoshdast & Sam (2011) classificaram espumantes levando-se em consideração a sensibilidade ao pH, a solubilidade, as propriedades de coleta, seletividade e poder de espumação. Estes autores também descrevem a existência de novas classes como os espumantes modificados e os bioespumantes. Segundo Melo & Laskoviski (2006), os espumantes, dependendo do seu efeito na flotação, são comumente classificados como seletivo ou potente. Drzymala & Kowalczuk (2018) propuseram um esquema de classificação dos espumantes que subdividem, primariamente, as possibilidades de avaliação desses produtos em quatro grupos: (i) estado puro; (ii) solução aquosa; (iii) sistema solução aquosa/gás; e (iv) sistema solução aquosa/gás/sólidos. A distinção das formas de classificação dos espumantes proposta por esses autores, subdividida em 5 categorias baseadas no número de dimensões necessárias para a classificação, está apresentada na Tabela 2.1.

Tabela 2. 1 – Sistema de classificação de espumantes baseado nos quatro sistemas físicos e número de valores numéricos usados para classificação (DRZYMALA & KOWALCZUK).

Sistema	Classificação	Tipo de Parâmetro
Estado Puro	(a) orgânico, inorgânico (composição elementar)	Qualitativo
	(b) álcool, não-álcool (estrutura química)	Qualitativo
	(c) sólido, líquido, gás (estado físico do reagente puro)	Qualitativo
	(d) Balanço Hidrofílico-lipofílico (HLB)	Unidimencional
	(e) HLB vs. Peso molecular (PM)	Bidimensional
Solução aquosa	(a) ácido, neutro, alcalino (sensibilidade ao pH)	Qualitativo
	(b) solubilidade	Unidimencional
	(c) ponto de fulgacidade	Unidimencional
Solução aquosa/Gás	(a) atividade na superfície, surfatante (tensão superficial vs. concentração)	Bidimensional
	(b) inclinação de tensão superficial	Unidimencional
	(c) concentração crítica de coalescência (CCC)	Unidimencional
	(d) retenção de gás (gas hold-up)	Unidimencional
	(e) índice de flotabilidade dinâmica (DFI)	Unidimencional
	(f) DFI vs. CCC	Bidimensional
Solução aquosa/Gás/Sólido	(a) eficaz, neutro, prejudicial, superdosado (recuperação vs. concentração)	Qualitativo
	(b) eficaz, neutro, prejudicial, superdosado (recuperação vs. tensão superficia	Qualitativo
	(c) concentração crítica de coalescência (recuperação vs. concentração)	Unidimencional
	(d) K_{50} (cinética)	Unidimencional
	(f) Força (baseado em graficos recuperação-recuperação)	Unidimencional
	(f) seletividade (baseado em graficos recuperação-recuperação)	Unidimencional
	(g) recuperação vs. constante cinética)	Bidimensional
	(h) força e seletividade (DFI vs. CCC, HLB vs. PM)	Correlação gráfica
	(i) gráficos cartesianos (x-y) ou triangulo de Gibbs	Tridimensional

2.4 Fase polpa e fase espuma

A cinética de flotação envolve processos de transferência de massa localizados na fase polpa (colisão e adesão partícula-bolha, e transporte do agregado partícula bolha para a fase espuma) e outros na fase espuma (recuperação de partículas da fase espuma para o flotado). Todos esses sub-processos dependem fortemente do tamanho de bolha e da estabilidade de espuma (ZHANG, 2016). Se a espuma não for suficientemente estável, bolhas mineralizadas que atravessam a camada de espuma se rompem prematuramente, provocando o retorno dessas partículas para dentro da polpa. Por outro lado, espumas muito estáveis podem resultar no excessivo arraste não-seletivo de grandes massas de partículas hidrofílicas na espuma, reduzindo a seletividade do processo (CHO, 2001).

Segundo Zhang (2016), as zonas de polpa e espuma são os principais componentes da flotação na definição tanto da qualidade do concentrado final quanto da eficiência ou produtividade do processo (recuperação do metal de interesse). A importância das propriedades dessas duas zonas, a qual inclui a hidrodinâmica da polpa, a taxa de coalescência das bolhas na espuma, a taxa de água no overflow e a taxa de distribuição do fluxo de ar, tem sido reconhecida de forma crescente. Essas propriedades não são dependentes apenas do tipo e concentração dos espumantes utilizados, mas também da natureza (física, química e mineralógica) das partículas minerais presentes no sistema de flotação, bem como das interações espumante-partículas e potencialmente das interações partícula-bolha. Neste contexto, incluem-se ainda as interações dos espumantes com os demais reagentes presentes no sistema de flotação.

A zona de espuma contribui para o processo promovendo transporte das partículas minerais hidrofóbicas para o overflow e rejeitando o arraste das partículas hidrofílicas através da drenagem dessas, de volta para a zona de polpa (ZHANG, 2016).

2.5 Tamanho de bolha (CCC)

Segundo Grau et al., (2005), o efeito mais dramático dos espumantes na flotação vem da redução do tamanho de bolhas. O efeito do espumante no tamanho de bolha resulta de sua habilidade de prevenir a coalescência entre bolhas.

O aumento na dosagem do espumante reduz gradativamente o diâmetro das bolhas até uma concentração particular, chamada concentração crítica de coalescência (CCC), a partir da qual a coalescência é completamente prevenida. O conceito de CCC foi introduzido por Cho & Laskowski (2002 a, b). Esses autores propuseram a determinação gráfica do valor de CCC, através do traçado de duas assíntotas pelos dados experimentais, uma aproximando os dados de baixa concentração, onde ocorre a redução acentuada do tamanho das bolhas, e outra assíntota horizontal aproximando os dados de alta concentração de surfactante, onde esses tamanhos são relativamente constantes (Figura 2.2). O rebatimento do ponto de encontro dessas duas assíntotas ao eixo da concentração define a CCC. Essa abordagem requer um número suficientemente grande de pontos na região de baixa concentração, e o patamar horizontal, na região de concentrações mais elevadas, frequentemente não é facilmente determinado.

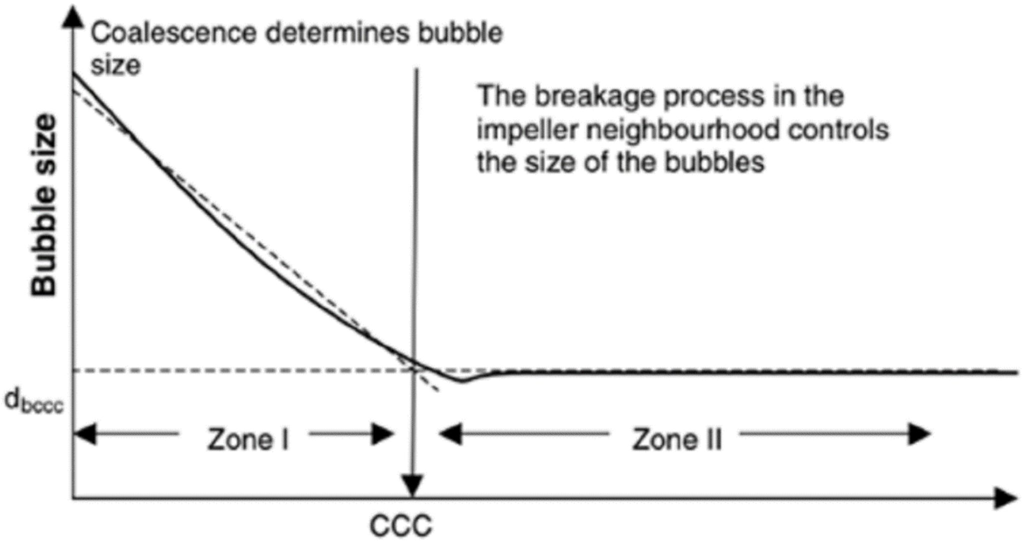

Figura 2. 2 - Diagrama esquemático do efeito da concentração de espumante no tamanho de bolha em uma célula de flotação (GRAU et al., 2005).

Em função da subjetividade no método gráfico proposto por Cho & Laskowski (2002, b), Finch et al., (2008) propuseram um método alternativo para estimar a concentração crítica de coalescência, baseado na equação de modelo ajustado, descrita abaixo:

$$D_{32} = D_L + (D_0 - D_L).\exp(-b.c) \qquad \text{(Equação 1)}$$

Onde D_{32} é o diâmetro médio de bolhas de Sauter, D_L é o menor tamanho de bolhas de Sauter nas concentrações mais elevadas, D_0 é o tamanho de bolha médio de Sauter na concentração c=0, b é a constante de decaimento e c é a concentração de surfatante. Rearranjando a equação 1 tem-se que:

$$\frac{D_{32}-D_L}{D_0-D_L} = \exp(-b.c) \qquad \text{(Equação 2)}$$

Finch et al., (2008) definiu a concentração crítica de coalescência como a concentração de surfactante na qual a diferença entre o dímetro médio D_{32} e o menor diâmetro de bolha obtido D_L é 5% da diferença entre tamanho médio de bolhas inicial D_0 e o menor tamanho D_L., onde tem-se o seguinte desenvolvimento:

$$0{,}05 = \exp(-b.c) \qquad \text{(Equação 3)}$$

$$\ln(\,0{,}05) = (-b.c) \qquad \text{(Equação 4)}$$

$$c = \ln(\,0{,}05)/b \qquad \text{(Equação 5)}$$

A concentração crítica de coalescência, obtida pelo procedimento de ajuste de modelo proposto por Finch et al., (2008) é comumente chamada CCC_{95}.

A medição do tamanho de bolhas em função da concentração de surfactante permite a determinação do diâmetro médio de bolhas ou diâmetro de Sater (D_{32}). Este, por sua vez, pode ser correlacionado a outras variáveis importantes da flotação, como velocidade superficial do ar (Jg), hold-up do ar (εg) e fluxo superficial de área de bolhas (Sb). Grau et al., (2005) compararam os tamanhos de bolha gerados por três espumantes de pesos moleculares distintos, utilizando dois medidores diferentes (UCT *bubble size meter* e HUT *bubble sizer analizer*) e encontraram resultados comparáveis. Alguns autores utilizaram ainda um método matemático experimental chamado de *drift flux*.

Amini et al., (2013) avaliaram o tamanho de bolhas em função da velocidade do impelidor em duas células mecânicas de flotação de 5 e 60 litros, geometricamente similares. Os resultados mostraram que o aumento da velocidade do impelidor reduziu o tamanho das bolhas geradas na célula de 5 litros, enquanto para a célula de 60 litros a velocidade não afetou o tamanho de bolhas. Estes autores introduziram o conceito de energia cinética turbulenta (TKE) para explicar a diferença de comportamento provocada pelo tamanho da célula, justificando a inconsistência dos dados prévios da literatura.

A determinação do tamanho de bolhas na fase espuma, através da análise de imagens, é proposta por muitos métodos, destacando-se os algoritmos de detecção de bordas, segmentação e espectro de textura (ALDRICH et al., 2010). A abordagem por espectro de textura seria o método mais susceptível a variação da iluminação nas imagens, adequado a operações em espaços abertos e sujeitas a iluminação ambiente.

Silva (2012) avaliou a influência de algumas variáveis nas propriedades visuais de espuma em colunas de um circuito industrial de flotação catiônica reversa de minério de ferro, através de análise de imagem por espectro de textura.

Os resultados qualitativos de tamanho de bolhas, medido na espuma, mostraram que bolhas maiores foram consideravelmente melhores que bolhas menores para a qualidade do concentrado obtido, ou seja, bolhas maiores resultaram em um concentrado com menor teor de sílica e com uma menor variabilidade, vide Figura 2.3 (SILVA, 2012). Esse autor ressalta, entretanto, que não é possível afirmar que o aumento contínuo no tamanho de bolhas acarretaria diminuição no teor de sílica no concentrado. Além disso, as relações entre o teor de ferro no rejeito e as propriedades da espuma da coluna não foram consideráveis em função de limitações da montagem de câmeras no circuito avaliado.

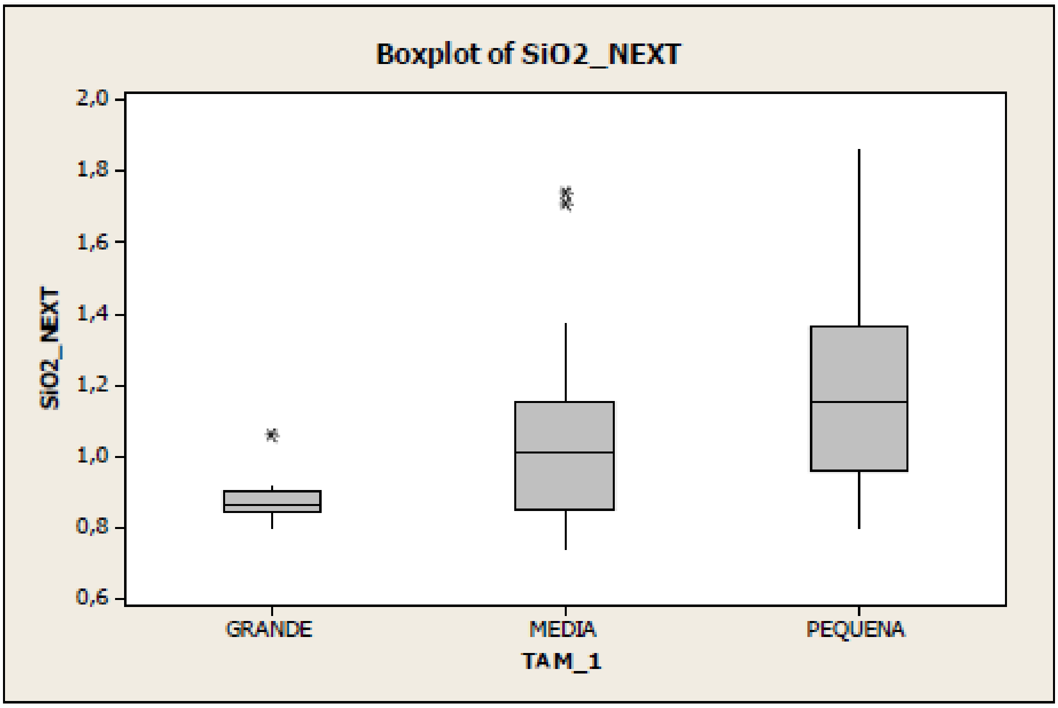

Figura 2. 3 - *Box plot* de teor de sílica no concentrado em função do tamanho de bolha (SILVA, 2012).

2.6 Estabilidade de Espuma

Devido à sua natureza heteropolar, o espumante se adsorve na interface ar-água resultando na diminuição da tensão superficial da água, estabilizando a espuma quando atinge o topo da polpa. Se as bolhas estourarem quando atingirem esse ponto, qualquer mineral que elas carreguem voltará para a polpa. O papel principal do espumante é estabilizar a espuma formada por tempo suficiente para que o concentrado (no caso da flotação direta) seja removido da célula de flotação. Uma vez removida da célula, a espuma deve quebrar para permitir que as partículas minerais sejam repolpadas novamente para processamentos posteriores.

O ar disperso em um líquido sob a forma de bolhas constitui um sistema termodinamicamente instável, tendendo ao colapso e à forma segregada mais estável (Baltar 2021). O processo de flotação exige que estas bolhas tenham alta mobilidade e um tempo de vida suficiente para realizar as etapas de colisão, adesão e transporte que governam sua eficiência, expressa na equação a seguir:

$$E_f = E_c*E_a*E_t.$$

Segundo Baltar (2021), a estabilidade de espuma pode ser avaliada em termos de capacidade de espumação (estabilidade dinâmica), de tempo de persistência/colapso (estabilidade estática), e/ou pela determinação do percentual de água removida (água flotada) na espuma, seja ela bifásica (*foam*) ou trifásica (*froth*).

Quando três bolhas ou mais se encontram, há a formação de um “reservatório” nessa interseção, delimitada pela região definida como bordas de Plateau. A maior parte da água na espuma está contida na região dessas bordas, e apenas uma fração mínima reside nas camadas lamelares (ZHANG, 2016). A velocidade de escoamento da água contida nessas regiões, provocando o afinamento das camadas de proteção da bolha, caracteriza a estabilidade da espuma. O afinamento da película até a espessura crítica de ruptura que inicia o contato entre bolhas resulta em coalescência se a velocidade é lenta ou o colapso, se for rápida. Essa velocidade é função principalmente da estrutura química do espumante.

O movimento do líquido junto da interface gás-líquido durante o afinamento da película que recobre a superfície da bolha cria um gradiente de tensão superficial, deslocando as moléculas dos espumantes, em um movimento elástico conhecido como Efeito Marangoni (TAN et al., 2005). Esse efeito de relaxação, diferente para cada tipo de espumante, dificulta o escoamento do líquido livre retardando o afinamento da camada que recobre a bolha, aumentando por consequência a estabilidade da espuma.

2.7 Arraste

O conteúdo de água associada à interface líquido-gás, necessária à estabilização da espuma, é crescente com o aumento da dosagem ou concentração do espumante em sistemas bifásicos. A perda de partículas finas de ferro no rejeito da flotação catiônica reversa pode ser correlacionada a essa taxa de recuperação de água no flotado, que por sua vez depende das características das espumas, controladas pelos tipos de espumantes utilizados.

No processo de flotação, arraste é o processo mecânico (ou hidráulico) de transferência de massa pelo qual partículas minerais da região superior da polpa, suspensas na água contida na região entre bolhas de uma espuma de flotação, são transferidas para o concentrado (flotação direta). Tanto partículas minerais hidrofóbicas quanto hidrofílicas sofrem arraste hidrodinâmico, especialmente as mais finas (WANG et al., 2015; LIMA et al., 2016). Segundo Neethling & Cilliers (2009), arraste de ganga na espuma do concentrado (no caso, da flotação direta) é um fator importante no desempenho das células de flotação devido à diluição do material de interesse e redução no teor do produto final.

É bem estabelecido que o arraste é proporcional à recuperação de água na espuma (THORME et al., 1976, TRAHAR, 1981; MELO & LASKOWSKI, 2007; WIESE & HARRIS, 2011), sendo que há uma relação crescente não linear nas baixas recuperações de água, seguida por uma relação linear nas recuperações mais altas, (ENGELBRECHT & WOODBURN, 1975; ZHENG et al., 2006). Esta relação está apresentada na Figura 2.4 para partícula de sílica abaixo de 12 e acima de 41,6 μm. A proporcionalidade entre a frações de ganga e água recuperadas são denominadas de fator de arraste simbolizado por *Ent* (SUBRAHMANYAM & FORSSBERG, 1988; KIRJAVANEN, 1996).

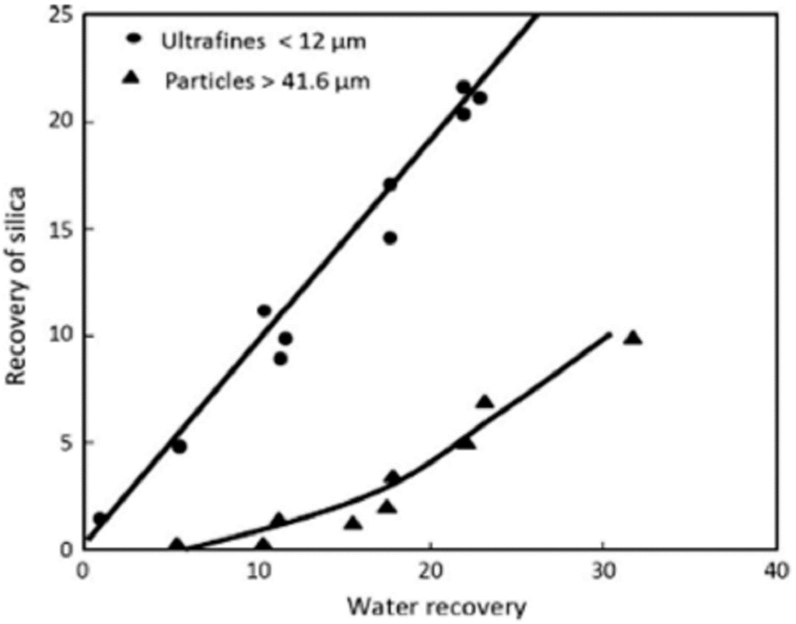

Figura 2. 4 - Recuperação de sílica em função da recuperação de água (ENGELBRECHT & WOODBURN, 1975).

O fator de arraste ou grau de arraste (*ENT*) é definido como a razão entre a recuperação de espécies sólidas arrastadas e a recuperação de água. O fator de arraste tem sido modelado utilizando relações empíricas (ENGELBRECHT & WOODBURN, 1975; KIRJAVANEN, 1996; SAVASSI et al., 1998; CILEK & UMUCU, 2001; ZHENG et al., 2006), simulações detalhadas (NEETHLING & CILLIERS, 2002 a,b) e modelos teóricos (NEETHLING & CILLIERS, 2009).

Na quase totalidade dos casos fica evidente que o fator de arraste é significativamente dependente do tamanho de partículas. A exceção é um modelo alternativo apresentado por Stevenson et al., (2007). Normalmente o arraste hidrodinâmico não é significativo para partículas maiores que 50 µm, sendo este limite dependente das propriedades da espuma (SAVASSI et al., 1998).

Além do tamanho de partículas, o grau de arraste de partículas em função da recuperação de água depende do percentual de sólidos, da densidade das partículas, da velocidade do rotor/ impelidor, da taxa de fluxo de ar, da altura da espuma, do tempo de residência da espuma, da reologia, da dosagem do espumante e da hidrofobicidade da partícula (WANG, 2015).

3 OBJETIVO

3.1 Objetivo Geral

Avaliar a influência das propriedades de espuma na eficiência do processo de flotação catiônica reversa de minério de ferro, via testes bifásicos (líquido-gás) e trifásicos (sólido- líquido-gás).

3.2 Objetivos Específicos

Avaliar as diferenças entre as espumas formadas pelos coletores convencionais etermonoamina e eterdiamina e seus efeitos na seletividade no processo de flotação catiônica reversa de minério de ferro. Diferenciar a ocorrência de flotação verdadeira e arraste hidrodinâmico.

Investigar o efeito de diferentes tipos de surfactantes espumantes nas características da espuma e o seu desempenho no processo de flotação.

Avaliar a otimização do processo de flotação pela substituição parcial do coletor pelo uso de espumantes distintos, e pela mistura entre eteraminas.

Avaliar a correlação entre a recuperação de água na espuma e o arraste hidrodinâmico de partículas finas de ferro na recuperação metalúrgica e qualidade do concentrado produzido, na presença de diferentes combinações do sistema de reagentes (espumantes/coletores).

4 MATERIAIS E MÉTODOS

Os materiais, equipamentos e métodos utilizados na execução experimental da pesquisa estão apresentados nos tópicos seguintes. Foram realizadas análises para caracterização das amostras minerais utilizadas e testes fundamentais e aplicados, simulando o processo de flotação na ausência (ensaios bifásicos) e presença (ensaios trifásicos) de sólidos. A metodologia é baseada em técnicas analíticas e procedimentos laboratoriais referenciados na literatura, em estudos recentes que investigam as propriedades da formação e estabilização de espumas.

4.1 Materiais

Dentre os diversos reagentes comerciais disponíveis foram escolhidos aqueles de uso consagrado e de compatibilidade econômico-financeira que viabilize sua aplicação na flotação de minério de ferro. Foram avaliadas as diferenças entre os efeitos de duas eteraminas (Etermonoamina e Eterdiamina) e dois espumantes com características estruturais distintas.

Os espumantes da série Dowfroth (Dowfroth P-series) são produtos baseados na família química glicol, amplamente utilizados e relatados na literatura. Estes espumantes são indicados para uma grande variedade de aplicações, recomendados particularmente para sistemas de flotação de minerais sulfetados de cobre, zinco, chumbo, ouro e cobre/níquel. DF250 é recomendado particularmente para partículas médias e finas enquanto DF400 e DF1012 são sugeridos para partículas médias e grossas, tais quais a avaliadas nesse estudo. O MIBC é um álcool espumante moderado recomendado para sistemas de flotação de partículas médias e finas. Todos os regentes foram preparados em soluções aquosas de 1% p/p.

Para a realização dos testes denominados trifásicos (sólidos-líquido-gás) foram utilizadas amostras de quartzo puro (98,90% SiO_2) e um minério de ferro (44,30% Fe), provenientes de uma mina do quadrilátero ferrífero, previamente caracterizados, em relação às características físicas, químicas e mineralógicas. A relação dessas amostras minerais, com os respectivos resultados da análise química quantitativa está apresentada na Tabela 4.1.

Tabela 4. 1 - Relação das amostras minerais disponíveis para o estudo.

Amostras	**Fe (%)**	**SiO_2 (%)**	**Al_2O_3 (%)**	**P (%)**	**CaO (%)**	**MnO_2 (%)**	**MgO (%)**	**PPC (%)**
Quartzo	0,57	98,90	0,14	0,003	0,00	0,00	0,09	0,05
Minério de Ferro	44,30	34,16	0,35	0,032	0,01	0,04	0,01	2.02

Os testes bifásicos foram realizados utilizando água deionizada, também devidamente caracterizada (pH = 6.89; C = 1.23 µS and T = 1.42 NTU).

4.2 Métodos

Os métodos aplicados nesse trabalho foram adaptados ou baseados nas metodologias descritas na literatura consultada, conforme referenciado. Na primeira fase foram realizados os testes chamados bifásicos (interface líquido-gás). Em paralelo foram realizados ensaios fundamentais, exploratórios e comprobatórios, na presença de partículas minerais (testes trifásicos, sólido-líquido-gás). Além desses ensaios auxiliares foram realizados para ampliar a investigação e discussão. Esses métodos e respectivos equipamentos são elencados a seguir:

- Ensaios de microflotação, em tubo de Halimond, apresentado na Figura 4.1. (LIU et al., 2015).
- Medida de tamanho de bolhas e dispersão de ar, utilizando *buble sizer* da UCT, vide Figura 4.2 (GRAU et al., 2005; ZHANG et al., 2012; LIMA et al., 2016).
- Testes bifásicos de estabilidade de espuma, em células de flotação em bancada e quantificação da massa de água contida na espuma (Figura 4.3-a), através do uso de provetas graduadas (Figura 4.3-b) e balanças de precisão (MELO & LASKOWSKI, 2006; WIESE & HARRIS, 2011).
- Testes de flotação em bancada com minério (Figura 4.4-a) para estudos de cinética de flotação e determinação de seletividade (MELO & LASKOWSKI, 2007; WIESE & HARRIS, 2011; NGOROMA et al., 2013; MATOS, 2017).
- Medidas de tensão superficial, figura 4.5 (ATRAFI & PAWLIK, 2016).

As Figuras 4.1 a 4.5 apresentam imagens de alguns dos equipamentos utilizados para a realização dos testes descritos nessa seção.

Figura 4. 1 - Montagem experimental do Tubo de Halimond modificado, pHmetro e cronômetro.

Figura 4. 2 – (a) Medidor de tamanho de bolhas Bubble Sizer APBS. (b) Montagem com o equipamento acoplado à célula de flotação em bancada.

Figura 4. 3 – (a) Célula de flotação em bancada e (b) serie de provetas graduadas para determinação de estabilidade de espuma via testes bifásicos (líquido-gás).

Figura 4. 4 – (a) Célula de flotação em bancada para realização de testes trifásicos (sólido-líquido-gás). (b) – detalhe das amostras de concentrado e rejeito após filtragem e secagem.

Figura 4. 5 – Tensiômetro Kruss K10ST.

O planejamento dos testes, validação e tratamento dos dados foi feito via metodologia estatística DOE (*Design of Experiments*), com determinação de curvas, superfícies de resposta e regressões lineares, via software Minitab 17®. Este método permite a simulação e otimização das variáveis significativas do processo e uma boa avaliação de resultados, via gráficos comparativos.

Os materiais e métodos empregados são detalhados nos capítulos 10, 11, 12 e 13.

5 RESULTADOS E DISCUSSÃO

A eterdiamina é mais eficiente que a etermonoamina tanto pela sua capacidade de coletar partículas de quartzo por flotação verdadeira, quanto pelo controle do indesejado arraste hidrodinâmico das partículas de hematita na espuma. Esses resultados foram comprovados via ensaios de microflotação de quartzo puro e testes de flotação em bancada com a amostra de minério.

A espuma mais seca, estável e persistente formada pela eterdiamina permite maior recuperação metálica de ferro associada ao atendimento da qualidade estabelecida do concentrado. Dessa forma a eterdiamina, como coletor, é classificada como mais seletiva, comparada à etermonoamina, considerada mais potente, por atingir sua seletividade máxima em uma dosagem inferior. Essa definição se opõe à mesma classificação, quando aplicada às características espumantes desse surfactante, avaliadas em testes bifásicos, onde a etermonoamina foi mais seletiva por produzir bolhas menores, mas requerendo maior concentração mínima para completa prevenção da coalescência entre bolhas (concentração crítica de coalescência - CCC) em relação à eterdiamina, neste caso definida como mais potente.

As diferenças estruturais entre as eteraminas e suas espumas formadas também é evidenciada na avaliação do uso de espumantes específicos (álcoois e poliglicóis) substituindo parcialmente esses coletores na flotação. Esses espumantes produzem bolhas menores (teoricamente favoráveis à flotação) e espumas com maior conteúdo de água (que provoca a perda metálica por arraste hidráulico).

Os testes mostraram que o uso de espumantes não-iônicos associados às eteraminas é mais eficiente para a FCRMF comparado às eteraminas puras. Esse efeito é potencializado pelas combinações Eterdiamina-DF1012 e Etermonoamina-MIBC com substituição de 10% da amina pelo espumante. Nos testes com mistura, no entanto, a alternativa mais eficiente foi a mistura entre a eterdiamina e a etermonoamina, sempre com a eterdiamina em maior participação. O melhor desempenho das misturas entre surfactantes e suas especificidades é explicada pela coadsorção entre as moléculas mais compatíveis, tanto na interface líquido-gás (formação da espuma) quanto sólido-gás (coleta de quartzo).

Os resultados obtidos são apresentados e discutidos em detalhe nos capítulos 10, 11, 12 e 13.

6 CONSIDERAÇÕES FINAIS

O uso de reagentes na flotação requer conhecimento do efeito desses nas propriedades de espuma, como requisito para controle da eficiência do processo.

O conteúdo de água na espuma é um indicador eficiente da estabilidade de espuma no desempenho da flotação. Espumas mais secas (ou drenadas) inibem a perda metálica de ferro fino no rejeito por arraste hidrodinâmico, permitindo a obtenção de recuperações metálicas mais elevadas.

Etermonoaminas e eterdiaminas possuem características estruturais diferentes que provocam efeitos distintos nas propriedades da espuma e consequentemente na eficiência da flotação catiônica reversa de minério de ferro.

Eterdiaminas exerceram melhor flotabilidade do quartzo comparada a uma etermonoamina nas faixas de dosagem e pH testados.

Etermonoaminas produzem bolhas menores que favorecem a colisão partícula bolha e a coleta das partículas, enquanto a eterdiamina previne a coalescência entre bolhas em uma concentração crítica de coalescência (CCC) menor.

Por outro lado, as eterdiaminas produzem espumas mais secas ou drenadas que inibem o entranhamento não seletivo de partículas na espuma e favorecem a flotação verdadeira do quartzo, garantindo uma melhor seletividade comparada ao efeito mais potente da etermonoamina.

Espumantes não-iônicos produzem bolhas menores que as eteraminas, formando espumas com elevado conteúdo de água. As propriedades das espumas formadas pelo uso de diferentes tipos de espumantes associados às eteraminas em proporções adequadas melhoram o desempenho da flotação, sendo que a compatibilidade entre moléculas (Etermonoamina-MIBC e Etherdiamina-DF1012), potencializam a seletividade. A combinação eterdiamina-etermonoamina apresentou resultados ainda melhores, demonstrando que as propriedades de adsorção/coadsorção dos surfactantes nas interfaces líquido-gás (formação e estabilização de espuma) e sólido-gás (adesão e coleta de partículas) tem o mesmo nível de importância para o desempenho da flotação.

RELEVÂNCIA DOS RESULTADOS

Os resultados obtidos esclarecem o efeito das principais características da espuma no desempenho da flotação catiônica de minério de ferro, em relação à utilização de surfactantes distintos atuando como coletores e espumantes.

O estudo definiu a eterdiamina como melhor reagente para FCRMF, utilizada em conjunto com espumantes ou com a etermonoamina, o que permite redução do custo específico dos reagentes, uma vez que a estes reagentes tem menor custo e o uso combinado deles com a eterdiamina oferece maior produtividade.

Benefícios adicionais são obtidos quando se opera de forma mais eficiente, seja pela menor produção de rejeito em função da maior recuperação metalúrgica e pela maior recuperação de água no processo. Isso gera mais tempo de vida útil para as estruturas de disposição de rejeito, menor custo no manejo e consumo mais sustentável do recurso mineral e hídrico.

SUGESTÃO PARA TRABALHOS FUTUROS

Avaliar a influência do tipo de mineral e tamanho de partículas na estabilização da espuma.

Investigar a influência do tipo de reagente depressor nas características de espuma e sua relação com a eficiência do processo.

Avaliar o efeito das variáveis operacionais na formação, estabilização e ação da espuma no processo de flotação.

Investigar o efeito da qualidade da água na formação das espumas.

Avaliar a influência de alguns dos reagentes testados, em processos de separação sólido-líquido.

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7 ARTIGO A - Analysis of quartz floatability using design of experiments

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ABSTRACT

Quartz floatability in cationic reverse flotation depends on the suitable choice of surfactant type and the conditions under which they are applied. The design of experiments (DOE) allows the evaluation of process variables, in a structured and independent way, with statistical validation and a limited number of tests. Tests of microflotation of quartz, in the size range -150 +75 µm, using factorial design of experiments, showed that etherdiamine leads to higher level of quartz floatability than ethermonoamine, favored by increase in collector concentration, at the high level of pH tested (11.0). Floatability values above 90% were achieved with the use of 3 mg/L of etherdiamine for both pH levels, while with ether monoamine the target was reached only at pH 11.

7.1 – Introduction

The major routes used in iron ore concentration are froth flotation and magnetic separation. Low intensity magnetic separation was intensively applied to concentrate magnetic taconites in the USA. Froth flotation was then introduced for concentration of non magnetic taconites. In Brazil, the production of iron ore concentrates from itabirites started in 1972 with the use of WHIMS (wet high intensity magnetic separation). The decrease of iron grade in the ROM (run of mine) ore, the more complex associations of iron oxides with gangue minerals, and the more strict specifications of the iron and steel making industry induced a gradual replacement of WHIMS by flotation or a combination of both techniques (Silva et al., 2017).

The flotation routes viable for use in iron ore concentration are direct flotation of iron oxides and reverse quartz flotation, either via the anionic route after surface activation or the cationic one (Araujo et al., 2005; Filippov et al., 2014). The reverse cationic flotation of quartz is the most widely utilized in the beneficiation of low grade iron ores, such as the Brazilian itabirites, for the production of high quality pellet feed (Araujo et al., 2005; Vieira and Peres, 2007; Filippov et al., 2014). The anionic flotation is widely applied to low grade Chinese ores.

Froth flotation is a concentration process in which the differential property is induced by the adsorption of reagents onto the surface of mineral particles and other interfaces present in the system. Reagents control the hydrophobicity of the mineral particles rendering possible the selective separation.

The collectors currently used are ether amines partially neutralized with acetic acid (forming etheramine acetate), divided in two classes: ethermonoamines ($R\text{-}O(CH_2)_3NH_2$) and etherdiamines ($R\text{-}O(CH_2)_3NH(CH_2)_3NH_2$). In aqueous medium, at alkaline pH, these cationic surfactants dissociate via protonation in ionic and molecular species, also being able to play the role of frother (Bulatovic, 2007). The equilibrium between ionic and molecular species concentrations is a pH value defined as pKA (Ari 2001; Mhonde, 2016).

Matos (2017) investigated the performance of ethermonoamine and etherdiamine in the bench scale flotation of a low grade iron ore in two size ranges: coarse (d_{50} = 70 µm) and fine (d_{50} = 20 µm). For both size ranges lower SiO_2 grade in the concentrate was achieved with ethermonoamine, while etherdiamine yielded a higher iron metallurgical recovery. Vieira e Peres (2007) conducted column flotation tests using pure quartz in three size ranges (coarse -297 + 150 µm; medium -150 + 74 µm; fine -74 + 38 µm) and ethermonoamine and etherdiamine as collectors. Etherdiamine was more effective in the flotation of medium and coarse particles, while a better performance of ethermonoamine was observed in the case of fine particles.

Araujo et al., (2005) reported that “blending di-amines and mono-amines is usual practice in a large concentrator to achieve low silica contents in the concentrate”.

Reverse cationic flotation of itabirites iron ores is considered a well established plant practice in operation since 1978. Nevertheless the number of chemical, physical, and physicochemical variables is large and neither the individual effect of most of them nor the effects of their interactions are well known.

The following variables, among other, are relevant for the understanding of the complex reverse cationic flotation of iron ores (Nagaraj, 2005; Filippov, 2014; Matos, 2017):

i. collector: ethermonoamine, etherdiamine, modified etheramine, ether amines blends, dosage; chain length;
ii. depressant: source of starch (corn, cassava, sorghum, other), degree of purity, composition (amylopectin:amylose ratio), carboxymethylcellulose, guar gum, synthetic polymer;
iii. use of tailored frothers for specific action;
iv. pH: action on the dispersion degree, pKa of the collector;

v. mineralogical composition of the ore;
vi. particles size range in the pulp.

The design of experiments provides the conduction of tests in a structured way. The variation of independent variables are under control, providing the evaluation of their influence on the response variables with a small number of tests.

Successful application of the technique was reported by Feng and Aldrich (2004), who evaluated the influence of operation parameters, such as pulp temperature, collector dosage, pulp pH, and grinding condition (dry or wet) on the flotation of apatite via multilinear regression.

This investigation aims to provide preliminary information on this complex universe of effects addressing the variables amine type, amine concentration, and pH and their interactions on the floatability of quartz.

7.2 – Materials and Methods

The quartz samples were hand collected in the Iron Quadrangle, Minas Gerais state, Brazil, comminuted and screened in laboratory sieves. The fraction in the size range between 75µm and 150µm was washed in tap water, without addition of any chemicals and purified with a hand magnet. The results of the quantitative chemical analysis were: 98.90% SiO_2; 0.81% Fe_2O_3; 0.14% Al_2O_3.

The evaluated collectors were ethermonoamine PA14F-30 and etherdiamine M73, supplied by Air Products, as acetates (neutralization degree ND=30%). The solutions were diluted to 0.5% w/v with distilled water. A 1% (w/v) NaOH solution, also diluted with distilled water, was used for pH control.

The microflotation tests were conducted in a modified Hallimond tube apparatus illustrated in Figure 1. Both fractions (floated and unfloated) were dried, filtered, and weighed in analytical balance model AUW220D/SHIMADZU (d=0.1 mg/0.01 mg) for determination of floatability. The tests were designed according to a DOE 2^3 (Table 1), in which the defined variables and levels were collector type (ethermonoamine and etherdiamine), collector concentration (1 and 3 mg/L), and flotation pH (10 and 11). Quartz floatability was defined as variable response. The tests followed random sequence and the statistical analysis of data used the software Minitab 17.

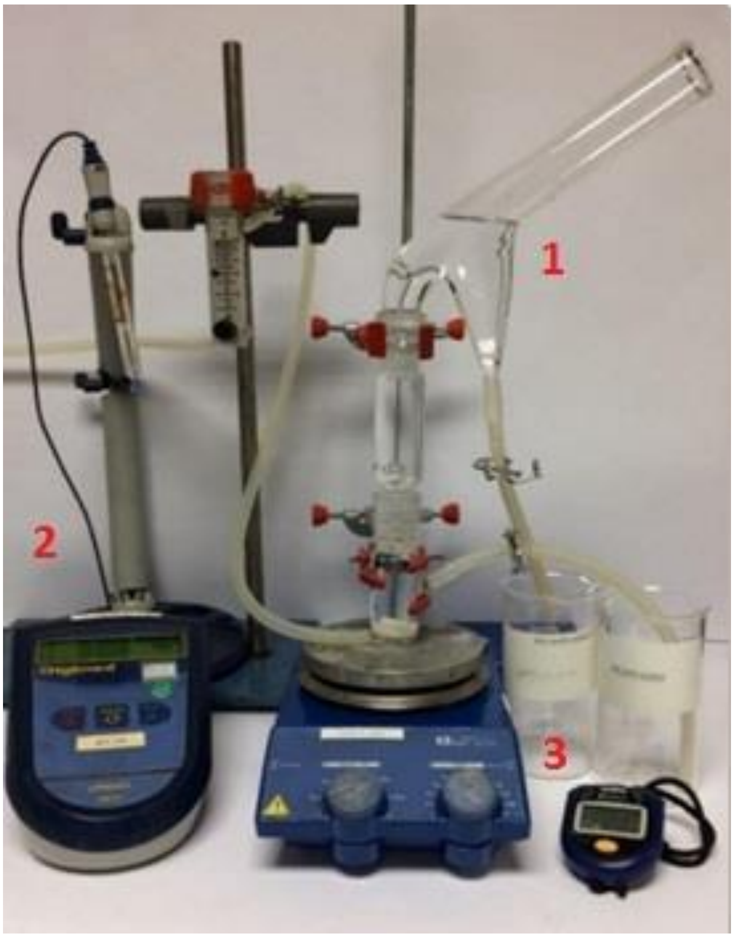


Figure 1 – Experimental apparatus of microflotation tests: 1 - modified Hallimond tube supplied by Hialoquímica, 2 – pHmeter Digimed, 3 - timer Technos.

Table 1. Design ofexperiments

Stand Order	**Seq Order**	**Collector Type**	**Collector Conc. (mg/L)**	**pH**
4	T01	Etherdiamine	3	10
8	T02	Etherdiamine	3	11
1	T03	Ethermonoamine	1	10
7	T04	Ethermonoamine	3	11
2	T05	Etherdiamine	1	10
3	T06	Ethermonoamine	3	10
5	T07	Ethermonoamine	1	11
6	T08	Etherdiamine	1	11

7.3 – Results and Discussion

The results of all tests, with respect to the variable collector type, amine concentration, and pH are shown in Table 2, and can be visualized in the vertices of the cube plot in Figure 2.

Table 2. Data and results of tests

Seq Order	Initial mass (g)	Floated mass (g)	Bulk mass (g)	Quartz Floatability (%)
T01	1.00489	0.92539	0.07087	**92.89**
T02	1.00159	0.93613	0.06406	**93.60**
T03	1.00404	0.42112	0.57230	**42.39**
T04	1.00368	0.90987	0.08292	**91.65**
T05	1.00602	0.75681	0.24604	**75.47**
T06	1.00357	0.86197	0.13613	**86.36**
T07	1.00597	0.56995	0.45261	**55.74**
T08	1.00132	0.82856	0.16380	**83.49**

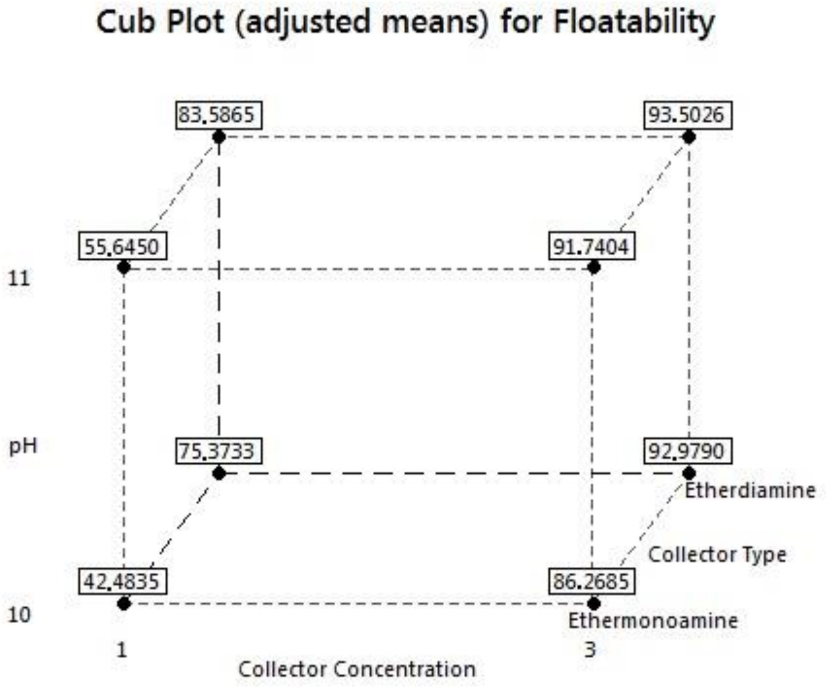


Figure 2 – Cube plot of the adjusted means for floatability.

The results shown on the Pareto plot indicate that all tested variables and their interactions are statistically significant for the response, considering a 95% confidence interval. This analysis is based on the absolute value of the effects (reference line = 12.7) for factorial experiments without replicates, defined by the Pseudo Standard Error (PSE) of the Lenth method. All variables and their interactions present standard effects above this value, as can be observed in the Figure 3. The sequence of significance is: collector concentration, collector type, interaction collector concentration /collector type, and pH.

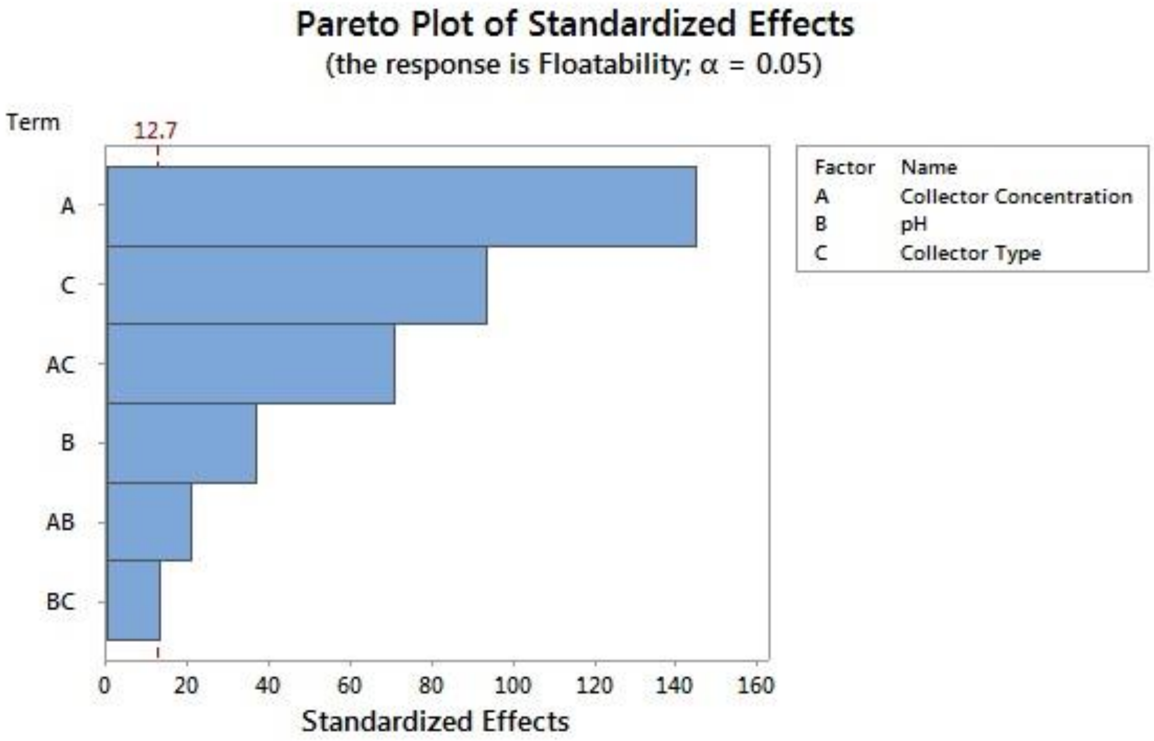


Figure 3 – Pareto plot of the standardized effects.

The DOE method allows the modelling of quartz floatability (QF) as a linear regression function (Equation 1) of tested variable collector type (CT), collector concentration (CC), pH and their interactions.

$$QF = C + \alpha_1 CT + \alpha_2 CC + \alpha_3 pH - \beta_1 (CT * CC) - \beta_2 (CT * pH) - \beta_3 (CC * pH) \qquad \text{Equation (1)}$$

Where,

C – constant;

α_1, α_2, and α_3 – linear coefficient of variables

β_1, β_2, and β_3 - linear coefficient of interacting variables.

Equation (2) presents the linear regression equation for the floatability with respect to coefficient values for the tested variables and their first order interactions, with a regression order of 99.98%. For the calculation of floatability, (-1) is used for ethermonoamine and (1) for etherdiamine.

$$\text{Floatability} = -101.74 + 47.73 \cdot CT + 53.80 \cdot CC + 14.532 \cdot pH - 6.5448 \cdot CT \cdot CC - 2.474 \cdot CT \cdot pH - 3.845 \cdot CC \cdot pH \qquad R^{2} = 99.98\% \qquad \text{Equation (2)}$$

The analysis of the main effects, considering adjusted means, shows that etherdiamine leads to higher floatability levels in comparison with ethermonoamine and that the floatability increases with the high amine concentration and for the high pH levels, as observed on Figure 4. This effect is explained by the higher adsorption density of etherdiamine on the quartz surface, due to the presence of the additional NH cationic group and extra pair of electrons with respect to ether monoamine. There are differences in the dissociation of the collectors, but there are no reliable references in literature for the pKa of the reagents utilized (Ari 2001; Mhonde, 2016).

The results are similar to those achieved by Vieira and Peres (2007) for the same size range, but the comparison is not possible due to the fact that equipment, reagents, and concentrations were not the same. Ma et al., (2009) investigated the floatability of kaolinite ($Al_2Si_2O_5 (OH)_4$), silicate that is present in iron ores, reaching the conclusion that ether monoamine in the acidic pH ranges and high concentrations yields high floatability in opposition to the low or nihil floatability with ether diamine.

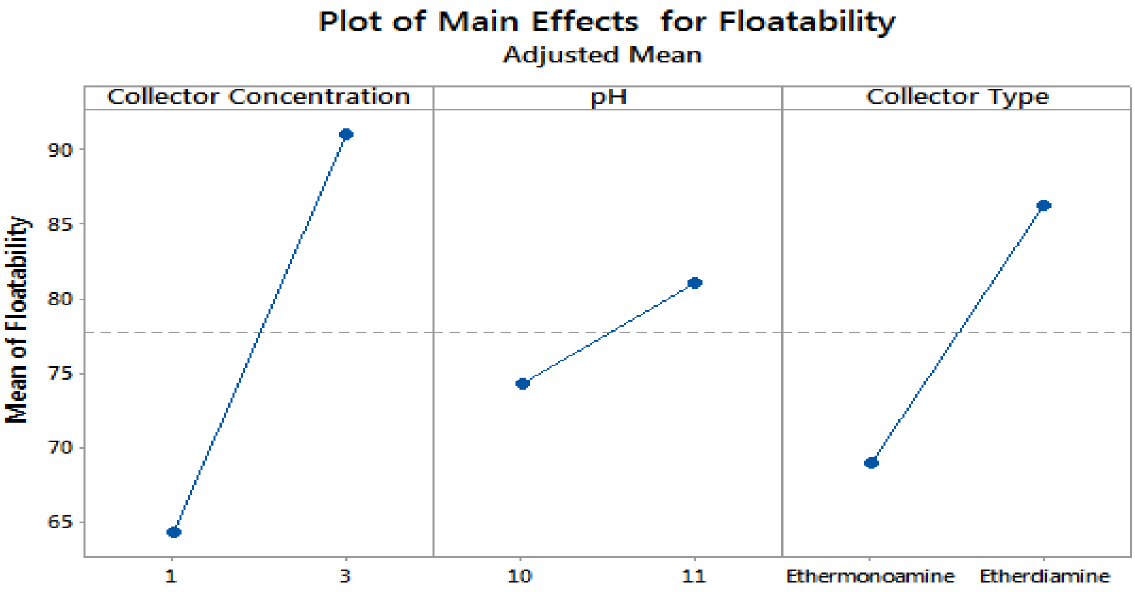


Figure 4 – Plot of main effects of the adjusted means for floatability.

Plots of interactions among the variables are presented in Figure 5, where stratified plots in function of collector concentration and pH clearly show that etherdiamine was more effective than ethermonoamine.

The DOE allows the building of over imposed contour plots, providing the identification of areas where a certain level of floatability may be achieved as a function of the tested variables. In Figure 6, one may observe regions where floatability levels above 90% may be achieved with the use of ethermonoamine (white area in Figure 6.a) and use of etherdiamine (larger white area in Figure 6.b).

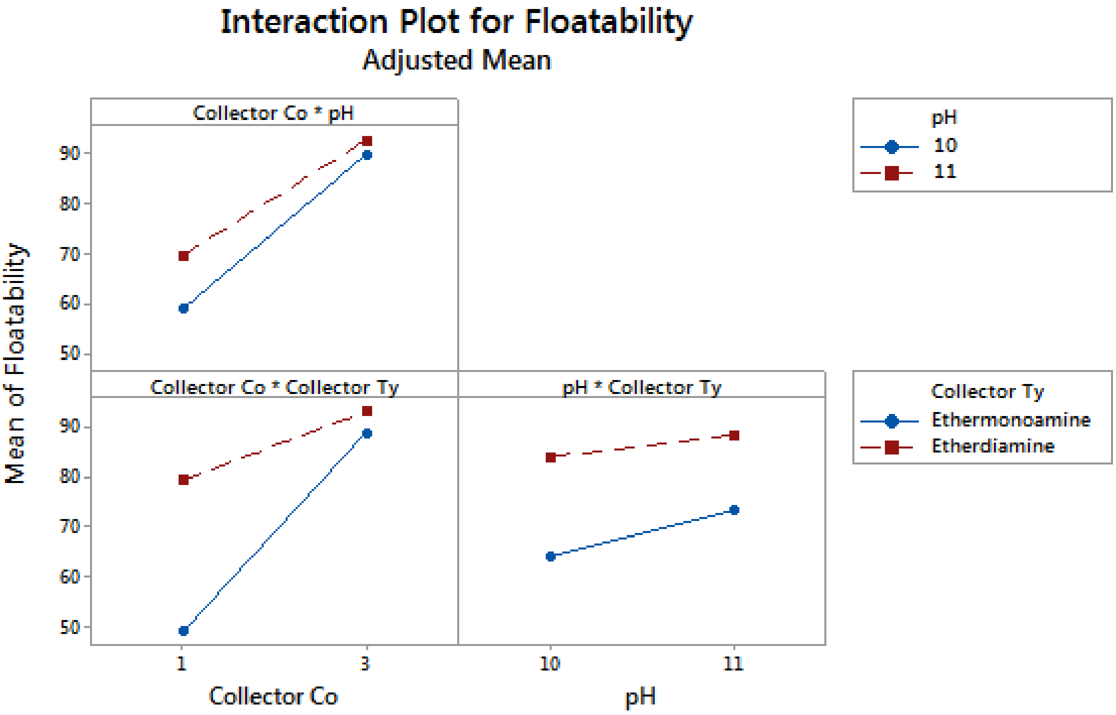
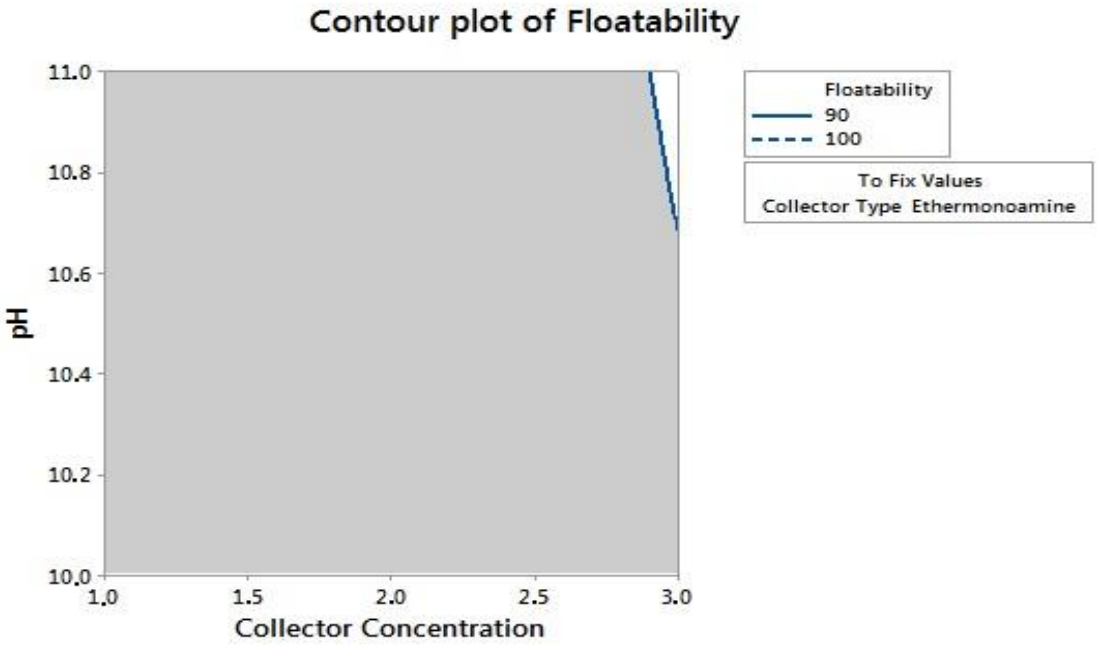
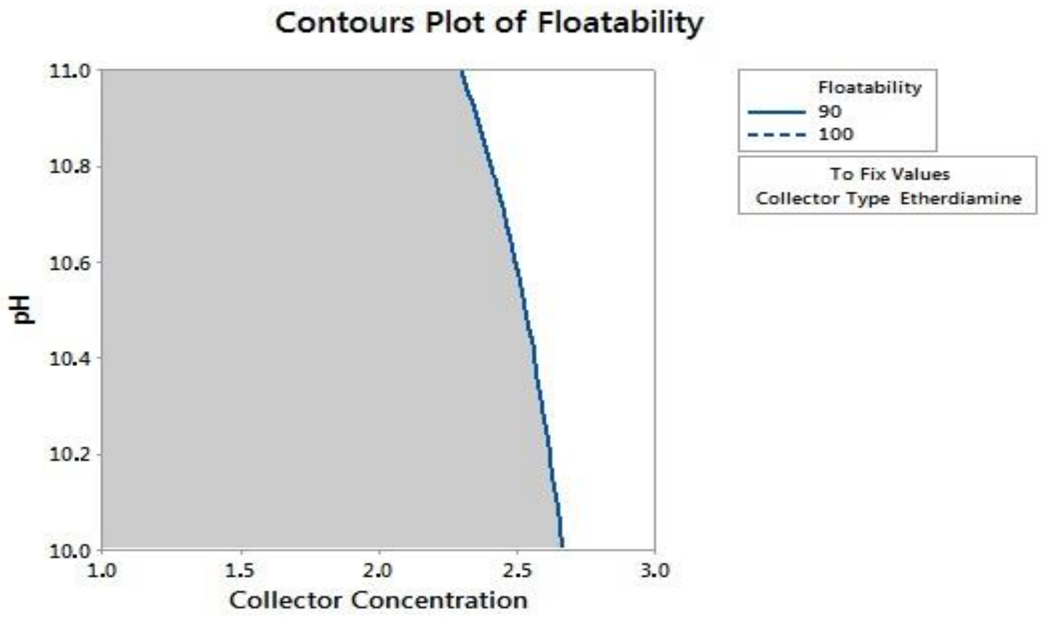


Figure 5 – Plot of the adjusted means interaction for floatability.



(a)



(b)

Figure 6 – Plot of superimposed contours of floatability against amine concentration and pH: a) – Ethermonoamine; b) – Etherdiamine.

The use of the DOE methodology has proved to be efficient to evaluate multivariable issues, providing a lot of structured information from a small number of tests.

7.4 – Conclusions

The floatability of quartz is significantly affected by the variables of the amine concentration (1 and 3 mg/L), collector type (ethermonoamine and etherdiamine), pH (10 and 11) and their primary interactions. This response may be modeled by the linear regression:

$$\mathrm{QF} = \mathrm{C} + \alpha_1\mathrm{CT} + \alpha_2\mathrm{CC} + \alpha_3\mathrm{pH} - \beta_1(\mathrm{CT} * \mathrm{CC}) - \beta_2(\mathrm{CT} * \mathrm{pH}) - \beta_3(\mathrm{CC} * \mathrm{pH})$$

Quartz achieves higher floatability levels with etherdiamine than with ether monoamine, due to structural differences between the reagents. The floatability increases for the high levels of concentration and pH.

Floatability levels above 90% were easily achieved with etherdiamine at the concentration 3 mg/L for both pH values. This target was achieved by ethermonoamine for the concentration 3 mg/L and pH 11.

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8 – ARTIGO B - Etheramines: Foam/Froth Stability and Selectivity in Iron Ore Flotation. Part I: Two-Phase Systems

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ABSTRACT

Etheramines are quartz collectors and also play a role as frothers in cationic reverse flotation of iron ores. While the adsorption of this surfactant on quartz surface has been widely investigated, the impact of its foam/froth properties on the selectivity in iron ore flotation has not yet been addressed in detail. The structural differences between ethermonoamine and etherdiamine result in distinct adsorption and frothing properties, offering versatility in the concentration of hematite. This study addressed the effect of the etheramine type on flotation selectivity, focused on the analysis of frothing properties. The characterization of the surfactants in the pure state and in two-phase systems (liquid/air) was conducted to investigate the behavior of etheramines concerning foam forming and stabilization. The surface tension measurements showed greater activity of etherdiamine at the liquid–air interface in comparison with ethermonoamine, which was more effective to prevent bubble coalescence and produce smaller bubbles, despite the reagent’s higher critical coalescence concentration. Ethermonoamine presented faster foamability for concentrations greater than the observed critical coalescence concentration values as well as greater water recovery in foam, whereas the double NH_2 group and higher molecular weight imparted strong lipophilic character to etherdiamines, producing drier, voluminous, and more stable foams, with longer lifetime. These results are fundamental for the evaluation of three-phase systems, which will be presented in a subsequent paper.

Keywords: Etheramines; foam formation; foam stability; bubble size.

8.1 - Introduction

Brazilian iron ore concentrates have a high price in the transoceanic market of direct reduction and blast furnace pellets. Reaching the required impurities grade results in low metallurgical recovery, which is an even greater challenge as the iron ore industry faces a steady decrease of iron content in the run of mine. In the concentration of iron ores, flotation is the most important technique, in which etheramines are widely used as quartz collectors, but also playing a role as frothers. Several studies explain the adsorption of the surfactant on quartz surface, whereas foam/froth properties of the reagent, also important for collision, adhesion, and transport probability in flotation (and consequently selectivity, grade, and recovery), have not been examined in detail.

The last two decades were rich in publications addressing characteristics and fundamental properties of foaming and frothing of different nonionic surfactants, basically alcohol and polyglycol types, in different flotation systems (Cho and Laskowsky 2002; Grau, Laskowski and Heiskanen 2005; Melo and Laskowski 2006; Zhang et al. 2012; Zhu et al. 2019). However, few investigations addressed properties of ionic surfactants, such as fatty acids (Atrafi and Pawlik 2016, 2017), and, according to our knowledge, references on foamability of etheramines are not available.

Amines are weak bases, which dissociate by protonation in aqueous medium under acidic and moderately alkaline pH ranges (Bulatovic, 2007). These surfactants are widely used in plant practice as quartz collectors in reverse flotation to concentrate iron ores (Araujo, Viana and Peres 2005; Filippov, Severov and Filippova 2014; Nakhaei and Irannajad 2018; Zhang et al. 2019). The ionic species adsorb onto the negatively charged quartz surface, whereas the molecular species adsorb at the air/liquid interface acting as a frother.

Fatty amines were used in the past (Uwadiale 1992). Smith and Scott (1990) stated that primary fatty amine adsorption on quartz is pH-dependent. In the pH range of full flotation, surface precipitation takes place when the amine solubility limit is exceeded within the quartz solution interface. The application of quaternary ammonium-based ionic liquids was reviewed by Sahoo, Rath and Das (2019). Aliquot 336 yielded 97% quartz recovery and 8% hematite recovery in tests with pure minerals.

Novel collectors, such as bio-collectors and innovative formulations, have been investigated and proposed as alternative reagents (Patra et al. 2018), however etheramines are still the most successful biodegradable collectors used in plant practice in the reverse cationic flotation of iron ores. Papini, Brandão and Peres (2001) concluded that etheramines perform better than fatty amines in the reverse flotation of an itabirite

Brazilian iron ore. They concluded that etheramines perform better than fatty amines, ethermonoamine yielded higher recovery than etherdiamine, and the performances were reverted when the amine is blended with fuel oil. Also, the functional ether group O(CH2)3 represents an advantage by improving the solubility of these surfactants (Araujo, Viana and Peres 2005).

Although ethermonoamines are generally used because of its low cost, understanding from use of reagents should con- sider overcoming challenges as reducing water consumption and tailing generation, starting with foam control. Etherdiamines have distinct effects on the flotation performance as a function of their structural characteristics (Matos et al. 2019).These effects depend on process variables and intrinsic characteristics of ores or minerals to be separated (Matos 2017; Vieira and Peres 2007). Etherdiamine, containing two polar sites, can adsorb onto more surface sites than ethermonoamine, which has similar molar weigh, although just this is not sufficient to enhance the floatability. The characteristics of the hydrocarbon chain and their effects on the water/air interface, or froth phase, are as important as the ionic properties.

Vidyadhar, Kumari and Bhagat (2014) reported that mixed cationic/anionic collectors should present good results on flotation. Nakhaei and Irannajad (2018) stated that blending diamines with monoamines is a usual plant practice in a large Brazilian concentrator.

The performance of amines is impaired by the presence of Ca^{2+} in the flotation pulp. Good results were achieved by Lelis, da Cruz and Fernandes Lima (2019) by complexation of the interfering ions with EDTA.

All chemicals present affect collector adsorption and froth properties. Depressants, widely starches, complete the reagent’s system in iron ore flotation (Rath and Sahoo 2020). One of the first studies on the interaction of amine and starch in quartz flotation was conducted by Hendriks and Smith (1972). Complex formation was suggested for the mutual adsorption effects of fatty primary amine and starch.

Pure liquids are not capable to form stable foam due to their high surface tension. The use of heteropolar molecules (surfactants) reduces the surface tension, resulting in the formation of more stable bubbles. The frother also contributes to bubble stabilization by strengthening the interfacial membrane which protects the wall of the bubble against hydrodynamic efforts. The surface tension decreases and foaming increases with the surfactant concentration and chain length, whereas the molecular structure defines the hydrophilic-lipophilic character (HLB) of the surfactant (Davies 1957; Tan, Zhang and Finch 2018).

The ability of a frother to form foam is a two-phase event, whereas the formation of froth during flotation is a three-phase phenomenon (Kowalczuk and Drzymala 2017). The effect of frothers on the foamability and foam stability is monitored by the bubble size, air dispersion, bubble half-life time, water recovery, and many other measurements.

This study compares the differences in performance of one ethermonoamine and one etherdiamine commonly used in iron ore flotation plant practice, comprising surfactants characterization in the pure state and solutions, and foam properties in two-phase systems. Foam stability, bubble size, kinetics of foam formation, and wettability interfere directly with the selectivity of these surfactants in the reverse flotation of iron ores, which will be presented in Part II of this study.

8.2 - Materials and Methods

8.2.1 – Materials

The surfactants ethermonoamine PA14F-30 (isodecyloxypropyl amine) and etherdiamine M73 (isotridecyloxypropyl-1,3-diaminopropane), supplied with the highest available purity (≥99.5) by Air Products (actual Evonik, USA), were used in this study. These cationic surfactants are alkyethylene etheramine acetates with branched hydrocarbon chain and neutralization degree of 30%. Ethermonoamine PA14F-30 ($C_{10}H_{21}$) has molecular weight of 225 g/mol whereas etherdiamine M73 ($C_{13}H_{27}$) has molecular weight of 330 g/mol.

In the experiments, the pH was controlled by using caustic soda (NaOH). Deionized water (pH = 6.89; C = 1.23 µS and T = 1.42 NTU) was used to prepare all 1% (w/v) reagents solutions and to conduct the two-phase tests

8.2.2 – Methods

The total amine value (TAV) and the degree of neutralization were evaluated in duplicate, via titration with ethyl alcohol and KOH (potassium hydroxide). The total amine value is the number of milligrams of potassium hydroxide equivalent to the basicity of 1 g of sample.

The surface tension measurements of surfactant solutions were performed in a K10ST tensiometer (±0.5 mN/m) from Krüss, Germany, using the Du Nouy ring method. All tests were conducted at approximately 21 ± 2°C, with 20 ml samples, measured five times after flame treatment of the platinum plate ring, in order to remove organic contamination.

Bubble size measurements were conducted in an APBS MK4 Anglo Platinum Bubble Sizer apparatus connected to the flotation machine and under similar conditions of foam formation. For each test condition, 25–35 photographs were analyzed using image analysis software provided by Stone Three Mining (South Africa). This software performs the statistical analyses to calculate the mean Sauter diameter (d32).

Foam was generated in a 3.9 L cell of a laboratory Wemco flotation machine, using a 3 L pH adjusted aqueous solutions (water and reagents at pH = 10.5), at specific concentration. The solution was stirred at 1250 rpm during 1 min, then the air, at constant flow rate, was introduced and the foam was collected in individual recipients at subsequent 30 s intervals. Each foam aliquot was weighed in analytical balance (±0.01 mg) to generate kinetic curves of cumulative water retained in the floated fraction. Replicates of these tests were conducted to measure foam volume and its gradual extinction at time every 60 seconds, using a 2000 mL graduated glass cylinder (±6 mL) and a chronometer. The difference in half initial foam volume (Volume50) and its time, here defined as LF50 deter- mine the foam stability parameters.

The tests were designed according to a DOE 2^2 (Table 1), in which the defined variables and levels were amine type (ethermonoamine and etherdiamine) and frother concentration (10 and 15 mg/L). These concentrations were chosen because they are greater than CCC values for both etheramines, found from the bubble size measurements. Mass recovery, kinetic constant (k), Volume 50, and Lifetime 50 were defined as response variable. The tests followed random sequence and the statistical analysis of data used the software Minitab 18.

Table 1. Design of experiments.

Seq Order	Etheramine Type	Concentration (mg/L)
1	Etherdiamine	10
2	Etherdiamine	15
3	Ethermonoamine	10
4	Etherdiamine	10
5	Ethermonoamine	10
6	Ethermonoamine	15
7	Etherdiamine	15
8	Ethermonoamine	15

8.3 - Results and Discussion

8.3.1 - Amines characterization

The molecular weight (MW), hydrophilic–lipophilic balance (HLB) and activity at the water–air interface (surface tension) are relevant parameters to characterize the differences between surfactants and their effects on foam/froth formation, stabilization, and drainage during flotation.

The structural formula of etheramines allowed the calculation, as proposed by Davies (1957), of the HLB values of ethermonoamine (6.87) and etherdiamine (5.45). In the HLB range from 4 to 10, both reagents are classified as frothers (Drzymala and Kowalczuk 2018). The double NH_2 group present in etherdiamine is responsible for its stronger lipophilic character (less affinity by water), showing better drainage in foam formation, for consequence, than ethermonoamine. Other physical chemical properties such as TAV (analyzed), density and acidity of etheramines (specified by the supplier) are essential for quantitative performance of frothers. These parameters are presented in Table 2.

Table 2. Etheramines properties: Molecular Weight (MW), Total Amine Value (TAV), density, pH and Hydrophilic Lipophilic Balance (HLB).

Amine type	MW(g/mol)	TAV	Density (kg/l)	pH	HLB
Ethermonoamine	225	244.4	0.85	10.25	6.87
Etherdiamine	330	331.0	0.87	9.97	5.45

Figure 1 shows that both reagents present strong tensoactive action, although etherdiamine is slightly more effective than ethermonoamine regarding the reduction of water surface tension. Surfactants with longer hydrocarbon chain present stronger surface activity than those with lower molecular weight, either in the case of ionic or nonionic molecules, as results found by Atrafi and Pawlik (2016).

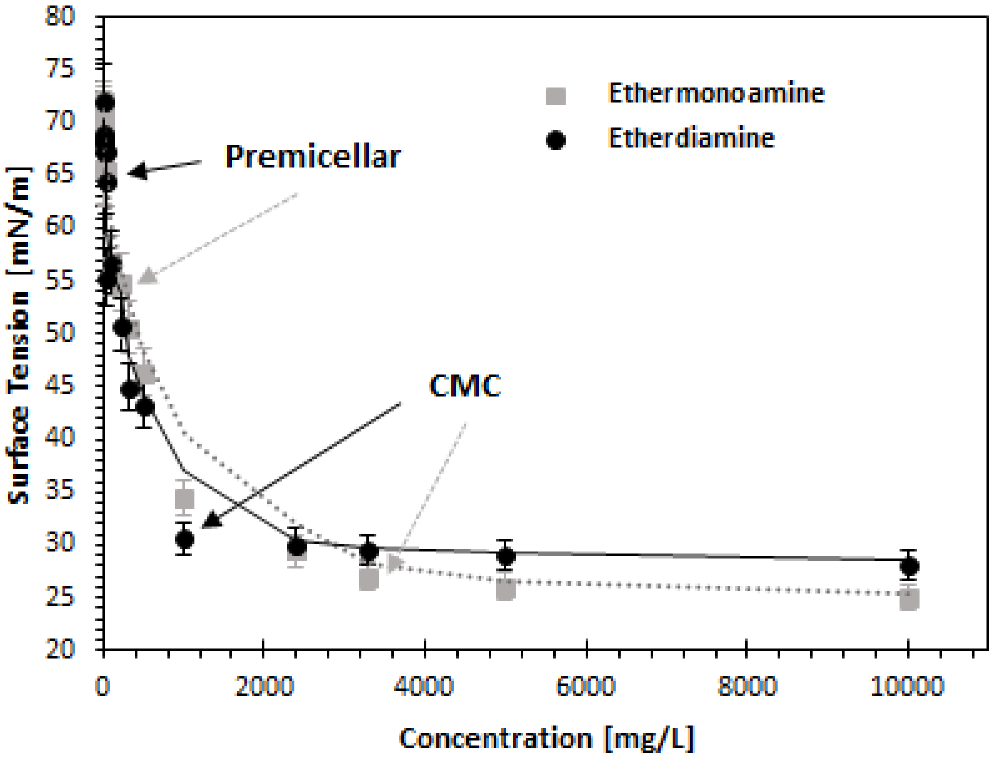

Figure 1. Surface tension isotherms with indication of premicellar and CMC points, for ethermonoamine and etherdiamine at 21°C.

As shown in Figure 1, the ethermonoamine and etherdiamine critical micelle concentration (CMC) are 3300 and 1000 mg/L, respectively.

Grau, Laskowski and Heiskanen (2005) stated that static surface tension should not be directly utilized in the analysis of the properties of dynamic systems, such as foams, due to the Marangoni effect (Tan et al. 2005a). However, it is important to characterize a surfactant action regarding foamability (Tan et al. 2005b). Lower surface tension increases the foamability of a solution from the perspective of surface energy (Wang et al. 2015).

8.3.2 - Two phase tests

8.3.2.1 - Bubble Size

The increase in frother concentration reduces the average bubble size by coalescence prevention, up to a particular point, where a plateau is established. Above this point, coalescence is completely prevented. Cho and Laskowsky (2002) defined this point as critical coalescence concentration (CCC) and proposed drawing two asymptotes to define it, as shown in Figure 2(a).

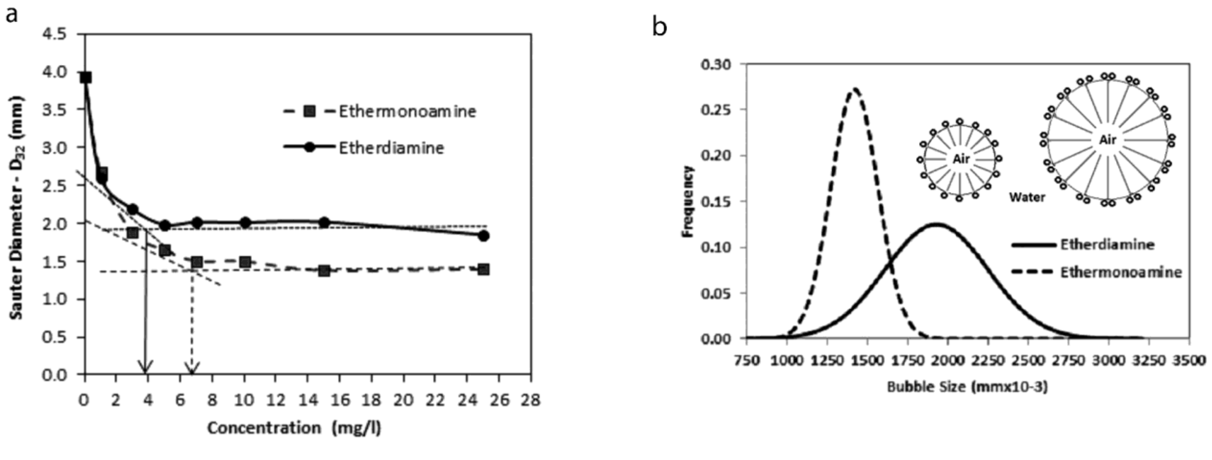

Figure 2. (a). CCC curves for ethermonoamine and etherdiamine at 10–25 mg/L. (b). Normal distribution of bubbles sizes at 10–25 mg/L for ethermonoamine and etherdiamine.

Figure 2(b) presents the Normal Distribution Curves of mean Sauter diameters for etherdiamine and ethermonoamine at concentrations ranging from 10 to 25 mg/L (concentration after CCC). Ethermonoamine produces smaller (1.38 ± 0.03 mm) bubbles with less variability in size distribution in comparison with etherdiamine (2.02 ± 0.05 mm), considering a 95% confidence interval. Finer bubbles increase the collision probability of particle/ bubble, favoring mineral floatability. Also, the Figure 2 (b) presents a schematic representation of different etheramines adsorbed in air-water interface forming the bubbles.

8.3.2.2 - Water content

The measurement of water content in the floated flow allows the determination of the foamability and the foam stability in two-phase flotation tests. The DOE study compared the water mass recovery and its kinetic to evaluate foam formation, foam volume, and its half lifetime to define stability. The statistical analyses of results indicated that both variables (etheramine type and concentration), at tested levels were significant, considering 95% confidence interval.

Figure 3 presents water recovery as a function of etheramine type and concentration. The foam formed by ethermonoamine induces greater water recovery, which is potentialized by higher concentration. The water content in the floated fraction depends critically on the frother concentration (Malysa 1998), and an increased amount of water associated with the liquid/ gas interface stabilizes the foam, which thus becomes more voluminous (Melo and Laskowski 2006).

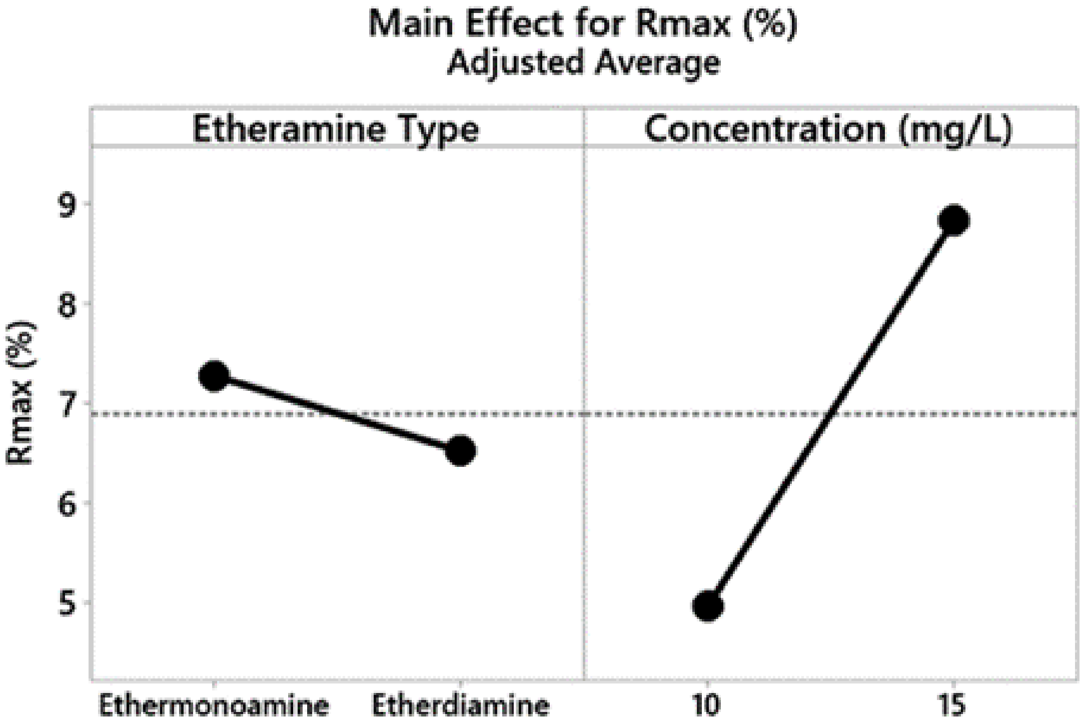

Figure 3. Cumulative water recovery in the foam (R_{max}).

The wet foam formed by ethermonoamine overdosage promotes hydrodynamic motion, dragging more water to the foam phase during the test whereas, for etherdiamine, the drainage of foam was more intense. This distinct and remarkable characteristic can be due to the hydrophilic–lipophilic balance and interfacial tension differences between each surfactant, previously discussed.

The differences between foam properties originated using ethermonoamine and etherdiamine are qualitatively illustrated in pictures in Figure 4. The assemblies of spherical bubbles, separated by thick liquid wall in ethermonoamine foam (Figure 4 right) are characteristic of wet and unstable foams (Leja 1982; Melo and Laskowski 2006). At picture, is possible see that this foam is less viscous and voluminous and has smaller macro bubbles. In other hand, foams produced by etherdiamine (Figure 4 left) can be classified as metastable or dry, exemplified by bubbles with polyhedral shape and only slightly curved liquid film.

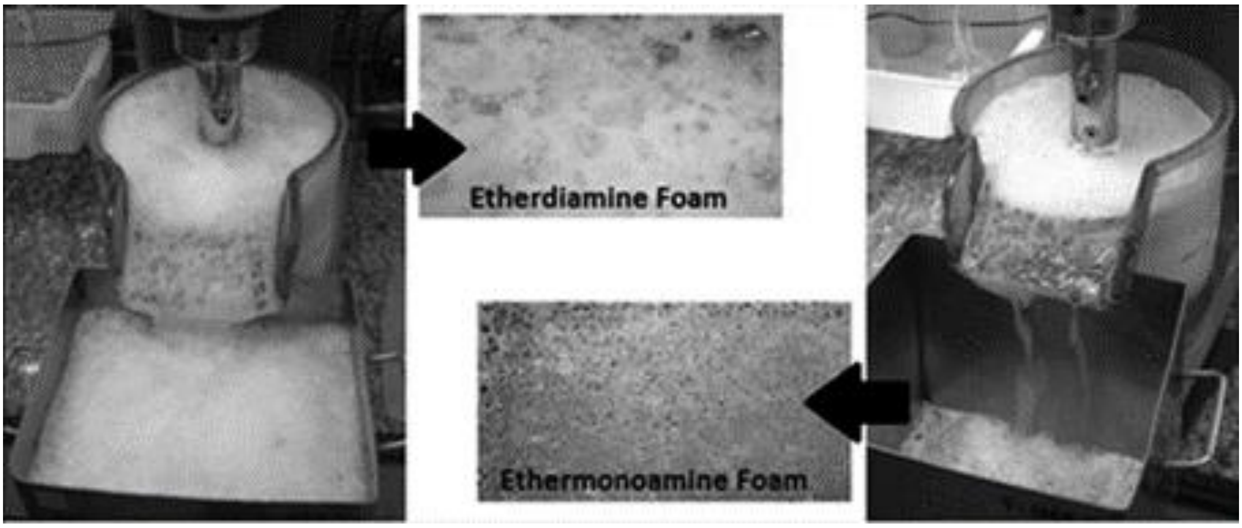

Figure 4. Example of stable and dry foam formed by etherdiamine and wet and unstable formed by ethermonoamine (15 mg/L).

Atrafi and Pawlik (2017) reached similar results evaluating fatty acid solutions, quantified by TOC (total organic carbon). These authors observed that shorter chain surfactants (hexanoate and laurate) produced wet foams with very low concentration of surfactant accumulated in the foam phase, in contrast with sodium oleate, which produced stable dry foams, attributed to greater adsorption at the gas-liquid interface.

Neethling, Lee and Cilliers (2003) developed a fundamental model to predict water recovery from unstable ($\alpha < 0.5$) and stable ($\alpha \geq 0.5$) foams, in which α represents the recovery of air by uninterrupted bubbles. The equations depend on rheological parameters such as kinetic viscosity, liquid density, gravitational constant, in addition to the bubble diameter, which square is inversely proportional to the water recovery. The evaluation of the equations confirms the results found, since the greater recovery of water from the unstable foam of ethermonoamine presented smaller bubbles and requires an additional multiplier parameter as a function of α.

8.3.2.3 - Kinetics of Foamability

Most flotation related processes, including foamability, follow the so-called first order kinetic equation:

$$R = R_{max}[1 - exp(-kt)] \qquad \text{Equation 1}$$

where, R is the cumulative mass recovery in the froth (%), R_{max} is the ultimate cumulative flotation recovery (%), k is the first order kinetic constant (s^{-1}) and t is the flotation time (s). Applying the method of local efficiency (Drzymala, Ratajczak and Kowalczuk 2017; Ratajczak, Drzymala and Kowalczuk 2016) at t=0 (graphically represented in Figures 5:

$$\left.\frac{dR}{dt}\right|_{t=0} = R_{max} \cdot k \qquad \text{Equation 2}$$

Figure 5 shows that ethermonoamine presented faster kinetics in comparison with etherdiamine, and that greater constants are observed at higher amine concentration.

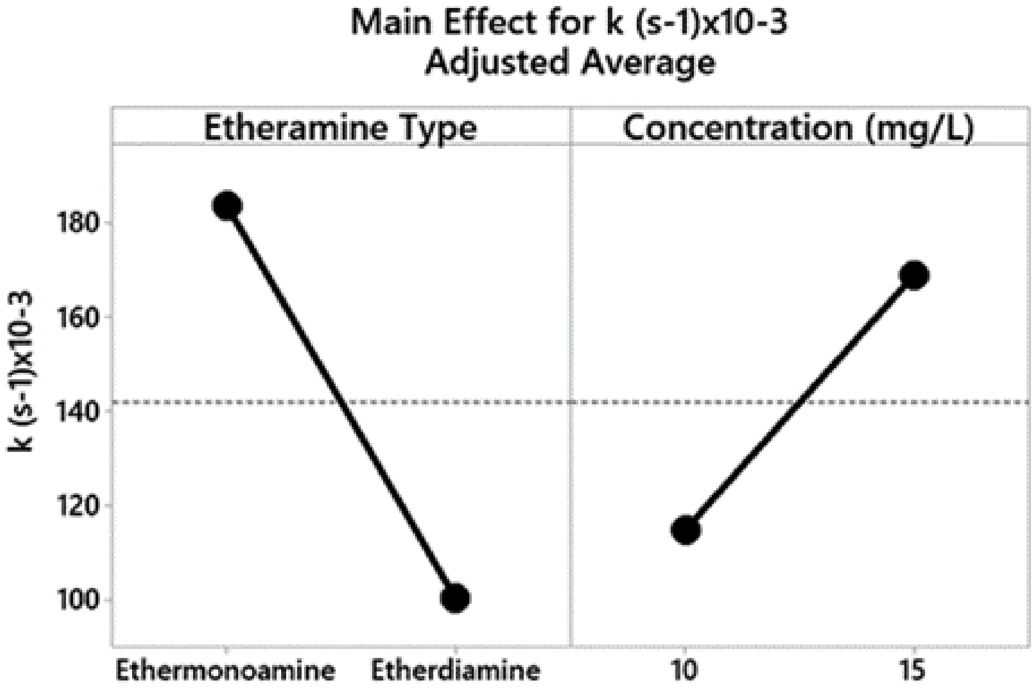

Figure 5. Kinetics of foamability for etheramine type and concentration.

8.3.2.4 - Foam Stability

The foamability is a dynamic process and part of the water that stabilizes the foam suffers drainage. The action of specific surfactants could either hold the bubbles' structure or later, collapse the foam, which determines the lifetime or foam stability.

Figures 6 and 7 show the difference in half initial foam volume (Volume50) and its time, here defined as LF50, between ethermonoamine and etherdiamine and the considered concentrations. This concept can be used for any foam volume reduction. Etherdiamine forms greater volume of foam with longer lifetime. According to Tan et al. (2005b), the foamability increases with the frother concentration, then reaches a maximum plateau region, and decreases above this well-defined concentration range. It explains why the higher tested concentration reached higher volume with lower lifetime. The foamability and water content are also function of the gas flow rate, which was held constant in this study.

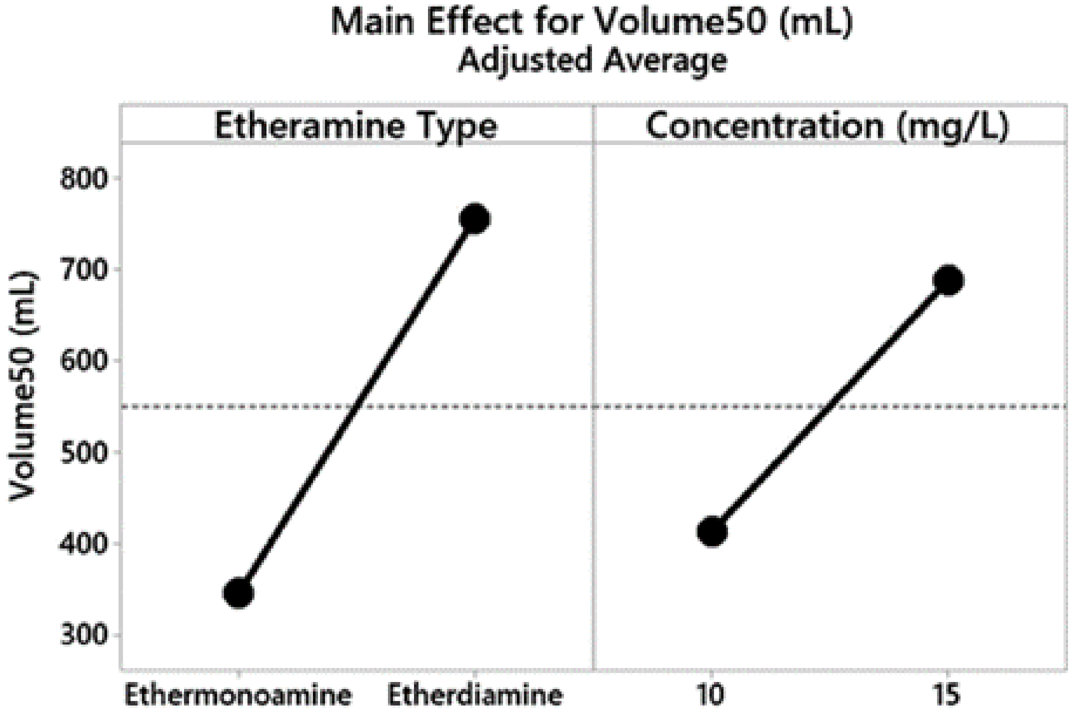

Figure 6. Half foam volume (Volume50).

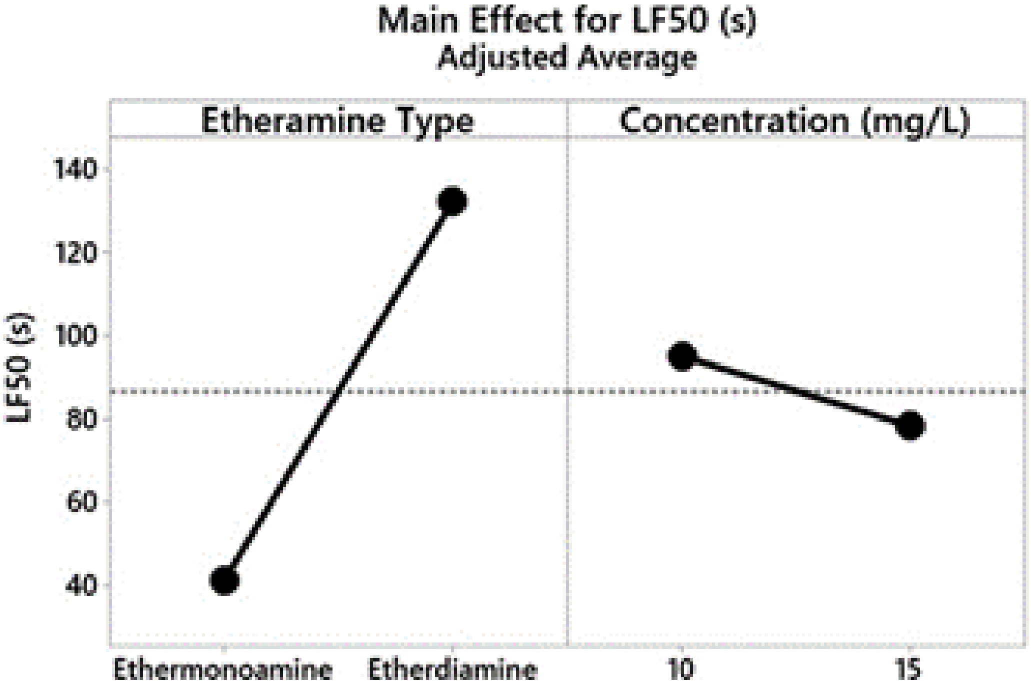

Figure 7. Lifetime of foam volume (LF50).

As expected, the faster and wetter foam from ethermonoamine have shorter lifetime. The foam produced by ethermonoamine extinguishes completely at 180 s, whereas remaining foam is present after 600 s with etherdiamine as shown in Figure 8. The higher hydrophilic character of ethermonoamine promotes premature collapse of bubbles, reducing the stability of foam in opposition to the etherdiamine behavior, which promotes greater elasticity in its bubbles lamellar layers and Plateau Borders generated.

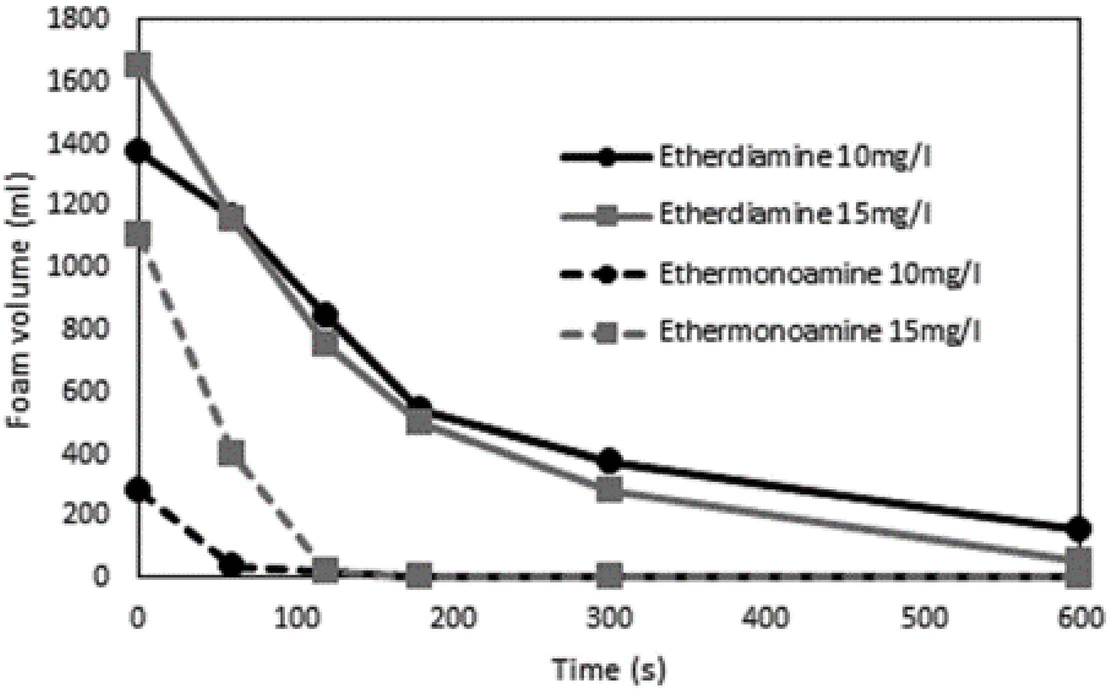

Figure 8. Foam stability for ethermonoamine and etherdiamine.

Finally, the ability of etherdiamines to form bubbles with thinner, well-drained, and better elasticity walls, makes them more resilient to the three stages of particle collection (collision, adhesion, and transport) inherent to the flotation process, compared to smaller bubbles formed by ethermonoamine.

8.4 - Conclusion

The results in this study indicate that the different structural characteristics of ethermonoamine and etherdiamine define their effect on foamability and foam stability. Etherdiamine presents stronger lipophilic character and higher molecular weight than ethermonoamine, whereas the latter produces smaller bubbles at faster formation rates and presents higher critical coalescence concentration than etherdiamine. The higher molecular weight, lipophilic character, and surficial activity of etherdiamine generates, at greater intensity and slower kinetics, more stable, drier, and persistent foams compared to ethermonoamine. In the next step of this study (Part II), these remarkable differences in the stability of foams produced by ethermonoamine and etherdiamine will be evaluated in three-phase tests to clarify their impact on the selectivity in the reverse cationic flotation of iron ore.

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9 – ARTIGO C - Etheramines: Foam/Froth Stability and Selectivity in Iron Ore Flotation. Part II: Three-Phase Systems

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ABSTRACT

Part I of this investigation, addressing two-phase systems, showed that etherdiamine produces more stable and dryer foams, whereas smaller bubbles are formed with faster kinetics by ethermonoamine. These remarkable differences in foam stability, attributed to the distinct chain length and consequent hydrophilic–lipophilic balance, influence froth properties, and may affect the selectivity of reverse cationic flotation of iron ores. The investigations conducted in this paper evaluated the effect of froth properties on the selective flotation recovery of a Brazilian iron ore from the Iron Quadrangle. The results showed that etherdiamine presented faster kinetics of froth formation but the recovery of water and solids in the froth was lower than that achieved with ethermonoamine. The water recovery was closely related to nonselective transport of solid particles in the froth by entrainment. The etherdiamine ability to form more stable and dryer froth reduced the entrainment of fine iron-bearing particles in the froth (tailings), improving the metal recovery in the concentrate (bulk), as the iron loss was directly proportional to the water recovery in the froth and the reagent presented lower entrainment factor than the ethermonoamine. In addition, the drier froth from etherdiamine is responsible for greater quartz true flotation, rendering this collector a more selective effect on flotation in spite the more powerful effect of ethermonoamine

Keywords: etheramines; froth; entrainment; water and iron recovery; selectivity index

9.1 - Introduction

The reverse cationic flotation is the most important process to concentrate iron ore from countries like Brazil, Canada, United States, China, Russia, India, and Chile (Lima, Valadão and Peres 2013; Peres et al. 2009), showing advantages and disadvantages in relation to direct flotation and anionic reverse flotation. Several process routes, iron ore characteristics and reagent types used maintain cationic reverse flotation for iron ore as an active research field (Zhang et al. 2019). Ethermonoamine is still the most widely used collector in this process because its lower cost, or the lack of knowledge about how to use more efficient alternatives. The power and consumption of amines depends on their chain length (Uwadiale 1992). Sahoo, Rath and Das (2019) have indicated ionic liquids (IL) as collector com- pared with conventional dodecylamines used on iron ore flotation.

The application of etheramines as quartz collector is widely cited in literature review (Filippov, Filippova and Severov 2010; Matos et al. 2019; Nakhaei and Irannajad 2018; Uwadiale 1992; Zhang et al. 2019), however, in the reverse cationic flotation of iron ore, etheramines play another critical function as frother. Previous results of this research (Matos et al. 2021) addressing two-phase system showed how the structural differences between ethermonoamine and etherdiamine affect the foam formation and stability.

Industrial froth flotation systems may be divided into pulp zone (bulk phase) and froth zone (Zhang 2016), the latter defining the concentrate quality and the process efficiency or productivity. The properties of these two zones include the pulp hydrodynamics, the bubble coalescence rate in the froth, the water overflow rate, and the air dispersion. These properties depend not only on frother type and concentration, but also on the physical, chemical, and mineralogical nature of the mineral and on particle-surfactant and bubble–particle interactions. Water quality deserves special concern regarding the presence of multiple valence cations (Lelis, Da Cruz and Fernandes Lima 2019). Also, particles in the coarse and fine size ranges impart different effects on the properties of the pulp and froth zones (Farrokhpay, Filippov and Fornasiero 2020; Matos 2017).

The froth phase is responsible for the selectivity of the process, promoting the transport of hydrophobic mineral particles to the overflow and rejecting the entrained hydrophilic particles, by drainage, back to the pulp zone (Zhang 2016). The control of formation, stabilization, persistence, and extinction of froth is critical to the flotation efficiency.

The ability of a frother to form foam is a two-phase parameter, whereas the formation of froth during flotation is a three-phase phenomenon. Moreover, most flotation systems are multiphase, containing more than one solid species (Kowalczuk and Drzymala 2017; Wills and Finch 2016). Frother type and dosage are the main parameters responsible for froth formation and stability in flotation systems. Froth properties and their effect on entrainment were addressed in many studies in the last decade (Lima et al. 2016; Neethling and Cilliers 2009; Wang et al. 2015; Wiese and Harris 2012; Zhang 2016).

Entrainment is a nonselective hydrodynamic process of mass transfer, by which the water flow carries solid particles to the floated product. The mechanism of this process starts by turbulent motion of dispersed bubbles and suspended mineral particles in the pulp zone, followed by entrapment or confinement of finer particles (unable to suffer drainage) into in Plateau boarder and bubble lamellar surface, formed at froth zone (Wang et al. 2015). According to Neethling and Cilliers (2009), entrainment of a gangue mineral in the froth affects the performance of direct flotation as it dilutes the concentrate. Similarly, in the reverse flotation of iron ore, the entrainment of valuable mineral in the froth (iron loss in tailings) reduces the iron recovery in the concentrate (bulk).

Entrainment occurs simultaneously along with true flotation. The effects of hematite true flotation and hydrodynamic drag in two Brazilian industrial circuits were reported by Nykänen et al. (2018). Both valuable and gangue minerals experience entrainment. Three mechanisms have been proposed to describe the mass transfer from pulp to froth by entrainment:

- Boundary Layer Theory – Transport of mineral particles in the bubble lamella, or the thin hydrodynamic layer of water surrounding the bubble (Bascur and Herbst 1982; Gaudin 1957; Hemmings 1981; Moys 1978).
- Bubble Wake Theory – Transfer of water including mineral particles in the wake of an ascending bubble (Smith 1985; Yianatos et al. 1988).
- Bubble Swarm Theory – Squeezing upward of particles due to the buoyancy of the bubbles swarm (Smith and Warren 1989).

Several factors affect entrainment in flotation systems, such as water recovery, solids concentration in the pulp, particle size, impeller speed, particle density, gas flow rate, froth height, froth retention time, rheology, and froth structure (Wang et al. 2015). Entrainment can be evaluated using different methods, which are based on experimental measurements (Ross 1989; Trahar 1981; Warren 1985) and modeling by direct estimation (Maachar and Dobby 1992; Moys 1978; Neethling and Cilliers 2002), or on the use of classification functions and water recovery (Bishop and White 1976; Kirjavainen 1992; Ross and Van Deventer 1988; Savassi et al. 1998; Yianatos and Contreras 2010; Zheng et al. 2005).

The recovery of water in the floated fraction is closely related to nonselective transport of solid particles by entrainment or hydrodynamic drag (Lima et al. 2016; Melo and Laskowski 2006; Wiese, Harris and Bradshaw 2011). The water content at the liquid–air interface, necessary to stabilize the foam, increases with frother concentration. The loss of fine iron particles in tailings of reverse cationic flotation may be related to water recovery, which depends on froth characteristics controlled by the frother type and also on the mineral’s particle size and morphology (Kowalczuk et al. 2018).

Froth stability, kinetics of froth formation, and water content interfere with the true flotation and the entrainment factor, affecting directly the selectivity of these surfactants in the process of quartz removal and hematite concentration. This investigation evaluated the performance of ethermonoamine and etherdiamine in the reverse cationic flotation of one Brazilian iron ore, based on froth characterization in bench-scale studies.

9.2 - Materials and Methods

9.2.1 - Materials

Ethermonoamine PA14F-30 (MW = 225 g/mol, HLB = 6.87) and etherdiamine M73 (MW = 330 g/mol, HLB = 5.45) were used as collector-frother. The iron ore reverse cationic flotation requires the use of starch as depressant and an adequate pH level (Hendriks and Smith 1972; Rath and Sahoo 2020). Sodium Hydroxide (NaOH) was used for cassava starch gelatinization and pH control. Deionized water (pH = 6.89; C = 1.23 µS and T = 1.42 NTU) was used to prepare all 1% (w/v) reagents solutions and to conduct the flotation tests.

The sample is primarily a hematite ore (69% hematite, 9% Goethite, 2% Magnetite, 19% Quartz) collected in the Brazilian Iron Quadrangle (Mariana, MG). The material was previously comminuted, deslimed (with NaOH at pH = 9.5), filtered, dried, homogenized, and sampled. The flotation experiments were conducted using the size fraction ranging from 10 µm to 150 µm (D50 = 70 µm). The results of chemical analyses conducted by X-Ray Fluorescence (XRF) and the size distribution are presented in Table 1 and Figure 1, respectively:

Table 1: Chemical composition of the iron ore sample.

Sample	**Fe**	**SiO_2**	**Al_2O_3**	**LOI (Loss on Ignition)**
Iron ore	44.30%	34.16%	0.35%	2.02%

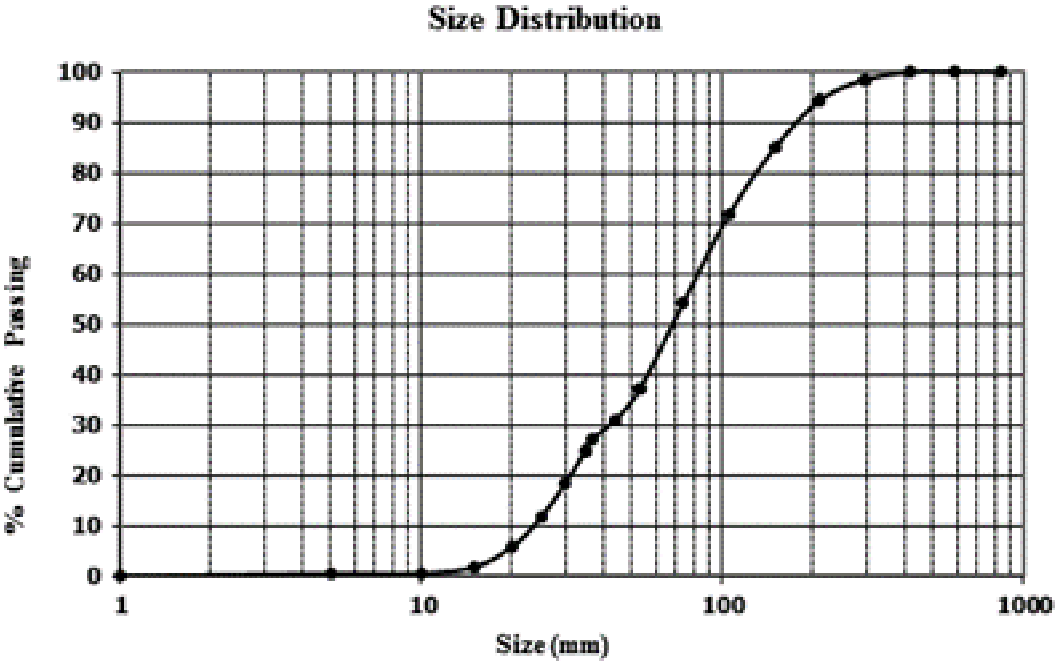

Figure 1. Size distribution of the iron ore sample.

9.2.2 - Methods

The flotation tests were performed in bench scale, within 10 days after comminution, following standard procedures described by Matos (2017). The experiments were conducted in a Wemco machine equipped with a 3.9 L cell, using 1.5 kg iron ore aliquots to form 50% solids (w/w) pulps with deionized water. The pulp was conditioned at 1200 rpm, initially with starch for 3 minutes and then with amine for 1 extra minute. The amine dosage ranged from 25 to 100 g/t to be compatible with the conditions applied in plant practice and those utilized in correlated studies. Then, it was diluted to 42% solids for flotation. The froth was collected at different time intervals to generate kinetic curves. In the sequence, tailings aliquots and the remaining concentrate were weighed in an analytical balance (±0.01 mg), filtered in vacuum filters, dried at 105° C, weighed again and chemically analyzed using XFR.

In the metallurgical balance, the mass recovery (MR) and iron recovery (R_{Fe}) in the concentrate, quartz rejection (R_{SiO_2}) and iron loss (L_{Fe}) in the tailings, and Gaudin selectivity index (SI) are calculated using Equations (1) -(5):

$$RM = \frac{dried\ final\ concentrate\ (solids)}{cumulative\ dried\ floated\ mass\ (solids) + dried\ final\ concentrate\ (solids)} \tag{1}$$

$$R_{Fe} = RM \text{ x} \left(\frac{\%Fe\ Concentrate}{\%Fe\ Feed}\right) \tag{2}$$

$$R_{SiO2} = (100 - RM) \text{ x} \left(\frac{\%SiO2\ Tailing}{\%SiO2\ Feed}\right) \tag{3}$$

$$L_{Fe} = 100 - R_{Fe} \tag{4}$$

$$IS = \sqrt{\frac{R_{Fe\ in\ concentrate} \times R_{SiO2\ on\ tailing}}{(100 - R_{Fe\ in\ concentrate}) \times (100 - R_{SiO2\ on\ tailing})}} \tag{5}$$

9.3 - Results and Discussion

9.3.1 - Frothability

Flotation rate is limited by the particle-bubble collision and subsequent attachment of the particle to the bubble, in the quiescent flotation, and by the destruction of the bubble- particle aggregates, in the turbulent conditions (Ahmed and Jameson 1989). Kinetic curves describe the flotation frothability through the values of the ultimate recovery Rmax (final froth recovery) and kinetic constant (k) of the process, obtained from the first-order kinetic equation Equation (6):

$$R = R_{max}(1 - e^{-kt}) \tag{6}$$

where R is the froth recovery and t is the flotation time.

Table 2 presents the found values, where froth formation with etherdiamine was faster, producing lower mass than that with ethermonoamine, for dosages above 50 g/t. The frothability of ethermonoamine was almost constant, in increased from 25 to 75 g/t and then decreased above 100 g/t, indicating hemi-micelles formation.

Table 2: Kinetic parameters (k and R_{max}) for etherdiamine and ethermonoamine.

	Etherdiamine		**Ethermonoamine**	
Dosage (g/t)	**R_{Max} (%)**	**k (s^{-1}) x10^{-3}**	**R_{Max} (%)**	**k (s^{-1}) x10^{-3}**
25	15.70	33.3	40.63	43.7
50	34.30	62.7	45.05	44.1
75	38.45	90.3	48.81	51.4
100	43.14	72.7	49.12	54.6

9.3.2 - True Flotation and Entrainment

Froth is a mixture of air, water, and solids of different composition. The transport of solids to the froth phase is due to true flotation and/or entrainment. Both hydrophobic and hydrophilic solids suffer entrainment, which strongly depends on the water recovery the full range of dosages tested, whereas that of etherdiamine in the floated fraction (Nykänen et al. 2018; Wang et al. 2015), whereas only hydrophobic particles should undergo true flotation. According to Wang et al. (2015), and based on the Warren Method (Warren 1985), Equations (7) and (8) allow the calculation of recovery by true flotation and entrainment, respectively, using mineral recovery versus water recovery, that is essentially from kinetic test data:

$$R_M = F_M + e_M \times W_{water} \tag{7}$$

$$R_G = e_G \times W_{water} \tag{8}$$

R_M and R_G are the cumulative recoveries of valuable (hydrophobic) and gangue (hydrophilic) minerals, respectively, W_{water} is the water recovery after a given time, F_M refers to the value of mineral recovery when water recovery is zero, representing the recovery by true flotation. The coefficients e_M and e_G are the entrainment degrees for the hydrophobic and the hydrophilic minerals, respectively. Considering that the system under investigation consists of reverse cationic flotation of quartz, this is the hydrophobic mineral (gangue) and hematite is the hydrophilic mineral (valuable).

Applying the adapted Warren Method for each collector dosage, it was possible to estimate the desired quartz true flotation (Figure 2) and the iron entrainment degree (Figure 3), for both etheramines, as presented at examples with 50 g/t in respective figures.

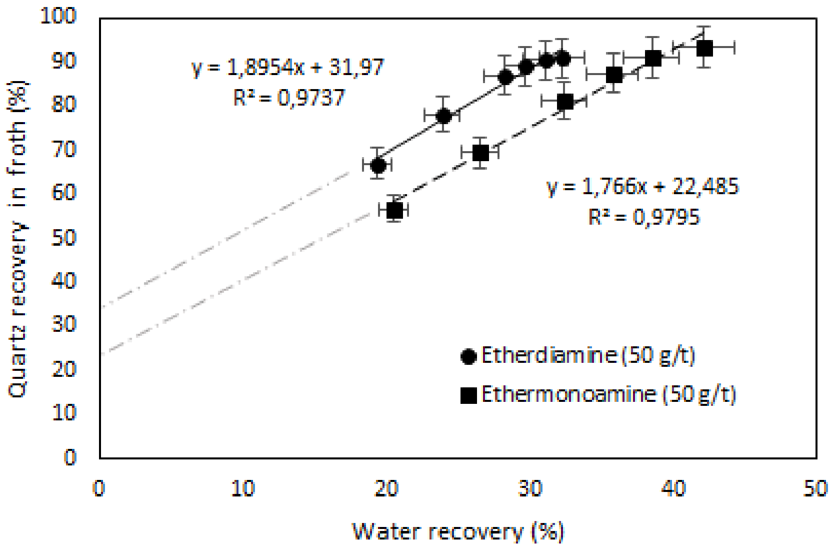

Figure 2: Quartz true flotation according to the adapted Warren Method.

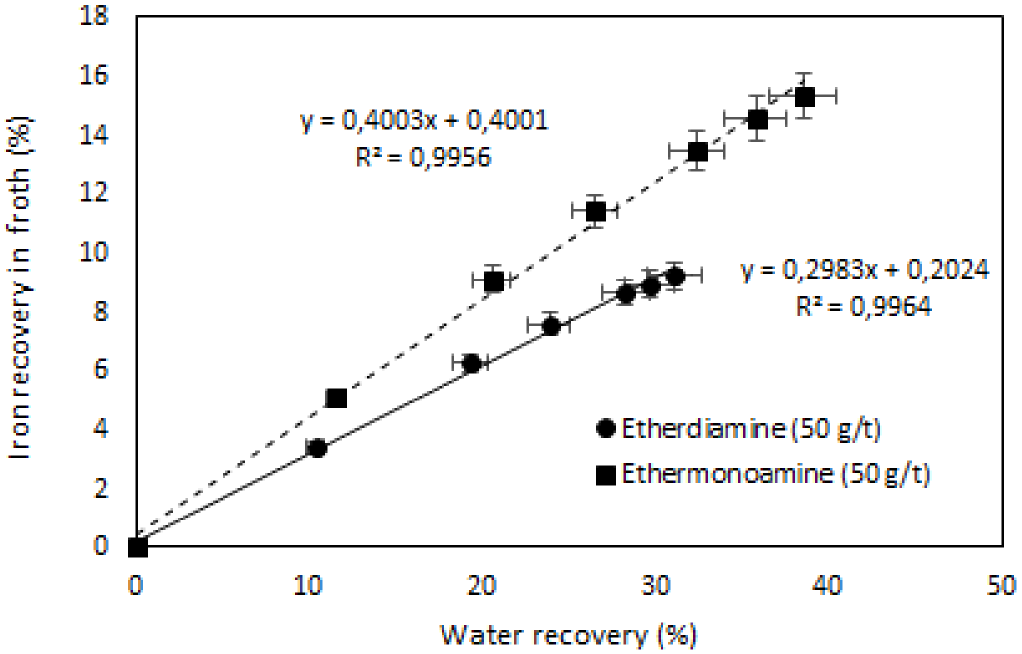

Figure 3: Iron entrainment degrees according to the adapted Warren Method.

The results show that the greater quartz true flotation from etherdiamine in comparison with ethermonoamine confirm investigation conducted by Matos et al. (2019), which showed that etherdiamine induced higher quartz flotability than ethermonoamine, performing microflotation tests in Hallimond Tube. The authors explained this effect by the greater adsorption density of etherdiamine, forming a stronger layer onto the quartz surface, due to the presence of the additional NH^+ cationic group and extra pair of electrons in comparison with ethermonoamine. Filippov, Filippova and Severov (2010) reached similar results comparing a primary monoamine with an etherdiamine.

Flotation efficiency depends of particle-bubble collision, adhesion, and transportation (Yoon and Luttrell 1989). Despite the ethermonoamine produces smaller bubbles which increasing the collision probability, the etherdiamine induces drier and more stable, intensive, and persistent foam/froth, improving the probability of adhesion and transport between bubbles and the hydrophobized quartz promoting the consequent higher true flotation. On the other hand, Figure 3 indicates that, at a 50 g/t collector dosage, the unwanted entrainment of iron in the froth is greater for ethermonoamine (0.41) in comparison with etherdiamine (0.31). Ethermonoamine generates wetter froth that drags and confines the finer hydrophilic iron particles in its larger Plateau’s borders and lamelar surface, against drier froth from etherdiamine.

Table 3 shows the results of iron entrainment degrees and quartz true flotation for both reagents, at different dosages. Besides the frother type and dosage, the entrainment factor depends on particle characteristics (size, density, shape, and hydrophobicity), hydrodynamic parameters (air flow rate, impeller speed), pulp composition (solids percentage and rheology), and froth properties (height and residence time) (Wang et al. 2015). These conditions were kept constant during the experiments.

Table 3: SiO_2 true flotation and Fe entrainment degree for etherdiamine and ethermonoamine.

	Etherdiamine		**Ethermonoamine**	
Dosage (g/t)	**Quartz True Flotation (%)**	**Iron Entrainment Degree**	**Quartz True Flotation (%)**	**Iron Entrainment Degree**
25	10	0.18	25	0.32
50	32	0.30	22	0.40
75	31	0.40	17	0.48
100	23	0.43	13	0.52

Figure 4 presents the correlation between water recovery and iron loss for each etheramine. As a drier froth favors the true flotation of hydrophobic quartz particles and the drainage of hydrophilic hematite particles back to the pulp, the figure shows the wetter froth produced by ethermonoamine resulting in greater iron loss in the tailings, in contrast with etherdiamine behavior. Despite hematite particles being denser than quartz, its finer size, specular shape, and hydrophilic surface is more susceptible for entrainment mechanism, impairing flotation performance.

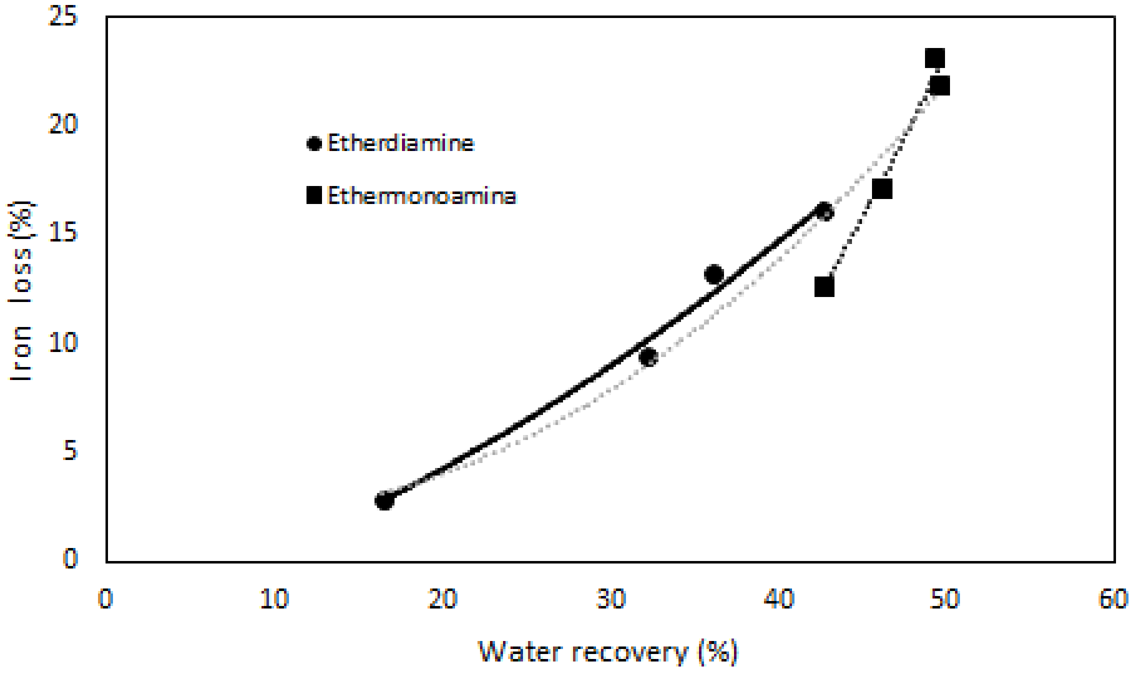

Figure 4: Iron loss as a function of water recovery in the froth for etherdiamine and ethermonoamine.

9.3.3 - Selectivity

Different approaches can be used to evaluate flotation performance, either using individual parameters or combining them in calculations and graphs. In practice, it is common to evaluate the flotation performance by comparing valuable metal grade (iron) and its metallic recovery or yield (mass recovery) in metallurgical balances. Table 4 presents the flotation results with the two etheramine types, using dosage as an incentive parameter.

Table 4: Metallurgical balance of the bench scale flotation tests with etherdiamine and ethermonoamine.

Amine	**Dosage (g/t)**	**% Mass Recovery**	**%Iron Recovery**	**%Iron Grade**	**%Silica Rejection**	**%Silica Grade**	**Gaudin's Selectivity Index**
Etherdiamine	**25**	85.28	97.15	50.18	38.43	25.60	4.62
	50	62.49	90.56	64.23	91.70	4.70	10.29
	75	58.14	86.79	65.74	95.71	2.64	12.10
	100	56.11	83.89	66.43	96.77	2.02	12.49
Ethermonoamine	**25**	62.12	87.39	61.67	85.34	8.51	6.35

	50	56.30	82.87	65.05	94.53	3.46	9.15
	75	52.19	78.16	66.14	97.22	1.90	11.19
	100	51.00	76.83	66.05	97.13	2.03	10.60
Standard Error		**(±0.41)**	**(±0.40)**	**(±0.17)**	**(±0.39)**	**(±0.21)**	**(±0.22)**

Table 4 shows that, for dosages above 50 g/t, etherdiamine is more selective than ethermonoamine. This can be explained by the greater floatability of quartz with etherdiamine in comparison with ethermonoamine (Filippov, Filippova and Severov 2010; Matos et al. 2019) and confirmed by results of true flotation associated with lower iron loss by entrainment presented in Table 3.

Despite the iron loss by entrainment, the increase in water recovery in the froth improves the selectivity index due to greater quartz recovery (silica rejection) by drag or entrainment. However, the interdependence between SI and water recovery occurs in different ranges of water recovery for each etheramine, as presented in Figure 5. In other words, the iron loss, despite being undesired, may be necessary to achieve satisfactory Selectivity Index values. Ethermonoamine and etherdiamine present these specific behaviors because of their distinct frothing properties.

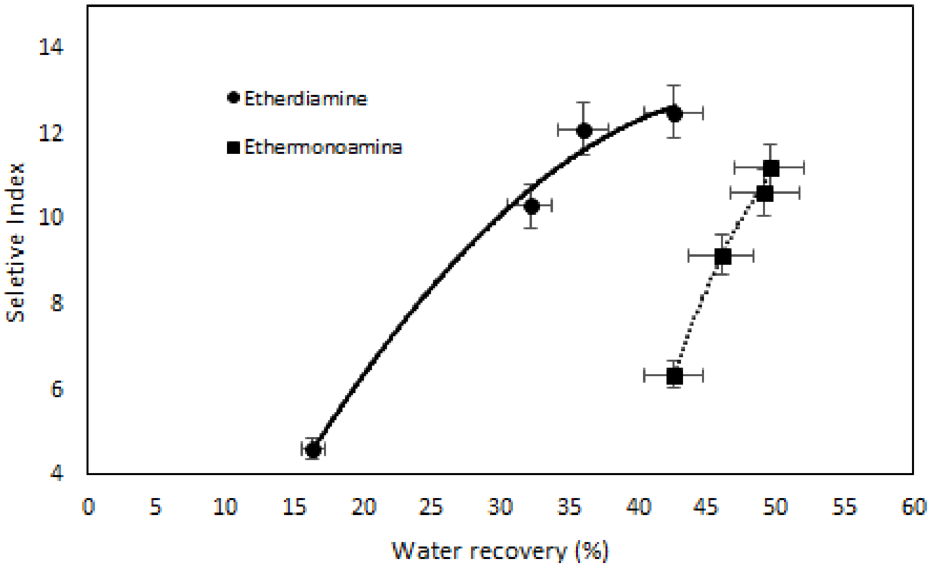

Figure 5: Gaudin’s Selectivity Index versus water recovery in the froth.

Gaudin’s SI can lead to confusion in the performance analyses of some cases, as the same value can represent distinct grades and recoveries. Better selectivity indices can be used to evaluate flotation performance, where the minimum and maximum values should be clearly defined. While Galdin’s SI is a nondimensional number varying between 0 and ∞ (Gaudin 1957), the Fuerstenau Index shows values from 0 to 100, where 50 represents no selectivity, below 50 indicates degrading and above 50 indicates upgrading, being 100 an ideal upgrade (Drzymala 2006; Fuerstenau 1991). The Fuerstenau upgrade curves, in Figure 6, shows quartz recovery as a function of iron recovery for etherdiamine and ethermonoamine. In this approach, selectivity F (%) and power P (g/t in this case) classifies the frothers efficiency (Drzymala and Kowalczuk 2018; Kowalczuk and Drzymala 2017). The results show that etherdiamine is more selective although ethermonoamine is more powerful, requiring less dosage to achieve the condition of its best selectivity.

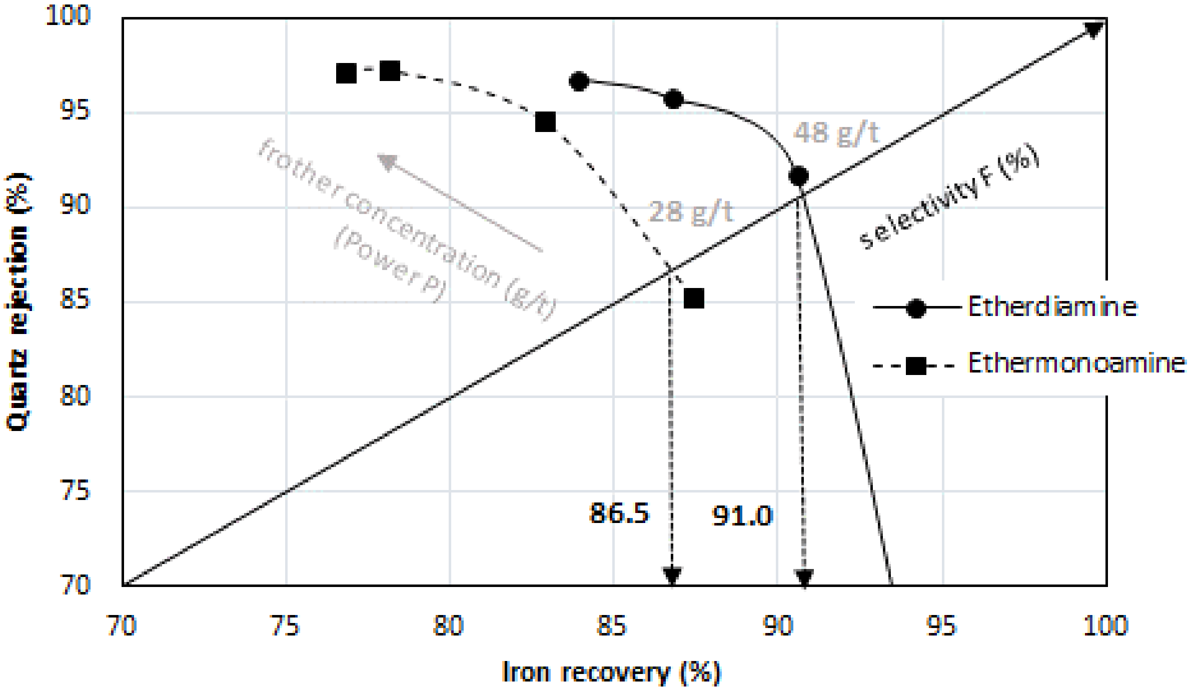

Figure 6: Fuerstenau’s Graphic correlating quartz rejection and iron recovery.

9.4 - Conclusion

In three-phase tests, etherdiamine yielded better flotation selectivity in comparison with the more powerful ethermonoamine. The use of etherdiamine allows obtaining higher levels of productivity for the same concentrate specifications, compensating its eventual specific consumption or higher cost, once etherdiamine is 20–40% more expensive than ethermonoamine. Etherdiamine induced lower iron loss due to lower water recovery in its drier froth. Besides the gains in process performance, this conveniently contributes to environmental issues such as reducing water consumption and the tailings generation and disposal. The froth properties achieved with etherdiamine favor true flotation of quartz and inhibit hematite entrainment. The results confirm that the froth properties of etheramines are as critical to the reverse cationic flotation of iron ores as their collector role. This understanding expands knowledge about the processing of increasingly complex ores, such as those found in the Brazilian Iron Ore Quadrangle.

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10 – ARTIGO D – Effects of Surfactants Combination in Iron Ore Flotation

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Highlights

- Frothing has not been played by specific frothers in cationic flotation of iron ore
- Frothers surpass etheramines in reducing bubble size and increasing foamability
- The partial replacement of the etheramines by frothers improved the selectivity
- The compatibility of molecular weight explains the improved selectivity
- The replacement of etherdiamine by 10% of ethermonoamine showed the best result

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ABSTRACT

Frothing plays a crucial role in mineral froth flotation. However, the use of only frothing reagents is not common in the reverse cationic flotation of iron ores because etheramines, the commonly applied collectors, also play this role. In alkaline aqueous solution, etheramines dissociate as ionic (collector) and molecular (frother) species, simplifying the chemical system. Despite practical and functional, this practice is limited once etheramines are less efficient to form foam and more expensive than conventional frothers, *e.g.*, alcohols and polyglycols. This study investigated the comparative effects between non-ionic frothers and cationic etheramines on foam properties in two phase systems, and the combination of these etheramines and frothers in three phase systems in comparison to single etheramines and their mixtures. The results show that the frothers DF1012 and MIBC produce smaller bubbles and more stable foams than the single ethermonoamine or etherdiamine. The partial replacement of etheramines by non-ionic frothers reduced the silica content in the concentrate, improving flotation selectivity at specific mixture condition of collector substitution for each frother type, despite decreasing the iron metallurgical recovery. The substitution of etherdiamine by polyglycol at 10% w/w produced the best result in the cationic/non-ionic surfactants comparison, although the mixture of etherdiamine and ethermonoamine yielded the highest selectivity, because of the synergistic effect on froth stability and mineral surface adsorption.

Key words: Frothers, etheramine replacement, collector mixture.

10.1 - Introduction

Froth flotation is the most important process to produce superconcentrates from low-grade oxidized iron ores. The efficiency of the process strongly depends on bubble size and froth stability, requiring the use of frothers. The flotation dynamics involves the collision and adhesion between bubbles and mineral particles in the pulp phase and the transportation of the aggregate to the froth phase. The froth zone contributes to the process by promoting transportation of hydrophobic mineral particles to the overflow and rejecting the drag of hydrophilic particles (Zhang, 2016). If the froth is not stable enough, mineralized bubbles break prematurely, causing these particles to move back to the pulp. On the other hand, very stable foams can result in excessive entrainment (Cho, 2002; Melo and Laskowski, 2006).

Entrainment is the hydraulic mass transfer process by which mineral particles (both hydrophobic and hydrophilic, especially the finer ones) are transferred to the overflow, impairing the flotation performance (Wang et al., 2015; Lima et al., 2016; Neethling and Cilliers, 2009). It is well established that entrainment is proportional to the recovery of water associated with the liquid-gas interface, required for the stabilization of the foam (Thorme et al., 1976, Trahar, 1981; Melo and Laskowski, 2007; Wiese et al., 2011; Engelbrecht and Woodburn, 1975; Zheng et al., 2006; Subrahmanyam and Forssberg, 1988; Kirjavanem, 1996). The properties of the pulp and froth zones depend not only on the dosage and type of frothers, but also on their interaction with other reagents and their action on each interface present in the flotation system.

Several studies have explored the chemical system of iron ore froth flotation, including the role of collectors, modifiers, and frothers (Araujo et al., 2005; Quast, 2017; Nakhaei and Irannajad, 2017; Pattanaik and Venugopal, 2018; Rath and Sahoo, 2020). Frothers are non-ionic surfactants that play multiple roles in froth flotation, such as to facilitate foam/froth formation, disperse the air inside bubbles, prevent the coalescence between bubbles (bubble size reduction), modify the structure of films between bubbles as well as solid particles and bubbles, regulate the hydrodynamic properties of the pulp phase, stabilize and impart mobility to the foam, reduce the particle-bubble contact time and accelerate the flotation rate (Grau et al., 2005; Melo and Laskowski, 2007; Zhou et al., 2016; Drzymala and Kowalczuk, 2018; Kowalczuk et al., 2018). Their application is well established in the flotation of sulphides, mainly copper, nickel, gold, zinc, lead, and also of coal, platinum, and graphite ores (Nyabeze and McFadzean, 2016; McFadzean et al., 2016; Huang et al., 2019), but is still poorly explored in the Reverse Cationic Flotation of Iron Ore (RCFIO).

The properties of frothers depend on their chemical structure, concentration, dosage, ability to interact with water, and other flotation reagents (Kowaczuk and Drzymala, 2017). The classic literature addresses the classification of frothers by the direct way, based on chemical groups, hydrophilic-lipophilic balance (HLB), solubility, acidity/alkalinity, and their basic functions (Gaudin, 1957; Davies, 1957; Dudenkov and Galikov,1969; Leja, 1982; Crozier, 1992; Bulatovic, 2007). Their functional classification, on the other hand, is extensive and depends on the characteristics and the physicochemical properties of the system one wants to explore, especially the effect on foam/froth properties and flotation selectivity (Bulatovic, 2007; Khoshdast and Sam, 2011; Drzymala and Kowalczuk, 2018). According to Melo and Laskowski (2006), frothers are commonly classified as either powerful or selective, depending on their effect on froth flotation.

Comparative studies have explored frother classes with distinct characteristics, commonly the alcohols and polyglycols. Alcohols are generally considered as weak frothers, with low surface activity, which produce dry, thin foams with reduced persistence. Their foaming action increases with the length of the hydrocarbon chain (usually including 5 to 8 carbons). Methyl-Isobutil-Carbinol (MIBC) is the most known and widely used frother in industrial applications in this category. Polyglycol-type frothers, on the other hand, constitute a wide class of structures and variable molecular weights, which produce thicker, wet, more stable and persistent foams. Dowfroth series are examples of these polyglycols (Zhang, 2016).

Sometimes the traditional and new collectors are exploited just regarding adsorption properties in surfactant-mineral collection as the effective mechanism in the reverse anionic or cationic iron ore flotation (Weng et al., 2013; Huang et al., 2014; Fan et al., 2020; Luo et al., 20021; Silva et al., 2021; Cheng et al., 2022; Rocha et al., 2022). Amines have often been used to obtain highly pure pellet feeds in the cationic reverse iron ore flotation, eliminating quartz impurities by overflow, however, the main problem associated with these collectors is related to the control of frothing properties and the high cost of amine (Kapiamba and Kimpiab, 2021). Etherdiamine imparts better quartz floatability in comparison with primary monoamine or ethermonoamine (Vieira and Peres, 2007; Filippov et al., 2014; Matos et al., 2017; Matos et al., 2019; Matos et al., 2021.b), but its cost is higher.

According to Pattanaik and Venugopal (2018), the systematic understanding of the mineralogical composition, association between the different minerals and surface characteristics are pre-requisite for proper selection of the reagent regimes in direct or reverse flotation. For the iron ores containing kaolinite, gibbsite and clays as impurities, improved flotation chemistry understanding needs to be developed for such ores. The presence of deleterious slimes and clay, characteristics of these ores, increases the pulp viscosity and flocculation phenomena, affecting froth stability (Farrokhpay and Bradshaw, 2012, Farrokhpay et al., 2016). These challenges require further studies on the use of frothers associated with specific other reagents to assure finer bubbles and stable froth on several conditions imposed by each iron ore flotation strategy.

The combination of differently structured surfactant molecules and its effects on froth flotation has been mentioned in several studies addressing non-ferrous minerals (Dey et al., 2014; Ngoroma et al., 2013). For iron ore flotation, different applications, such as anionic-anionic collectors, anionic-cationic collectors, and ionic-nonionic surfactants became common in reverse anionic and cationic flotation to increase solubility in order to reduce collector consumption and improve metallurgical results (Rao et al., 1997, Filippov et al., 2010; Vidyadhar et al., 2012; Filippov et al., 2014; Fan et al., 2020). The design of reagent system needs detailed research evaluating the use of surfactants with additional of cationic groups (e.g., dicationic and tricationic), and specific, selective and cost-effective reagents for kaolinite and gibbsite for beneficiation of high-alumina iron ore fines, as suggested by Pattanaik and Venugopal (2018). Therefore, this research was focused on optimizing the flotation chemical system, clarifying the effect of frothers partially replacing the etheramines collectors on the selectivity of reverse cationic flotation of iron ores. The improvements from this optimization can bring relevant contribution to reach superconcentrate specification (for RD pellet feed) with high level of recoveries, maximize the use of natural resources, generate lesser residues, and contribute for the sustainability of the industrial process.

10.2 - Materials and Methods

The two-phase tests were conducted with deionized water (pH=6.89; C=1.23 µS and T=1.42 NTU). The investigated surfactants (table 1) were the etheramines PA14F-30 and M73 supplied by Evonik, widely investigated by Matos et al. (2021.a, 2021.b), the frother MIBC (methyl isobutyl carbinol), of the aliphatic alcohol group, and Dowfroth 1012 (mono-alkyl ether of propylene oxide), representing the polyglycol family. In the flotation bench scale tests, cassava starch was applied as depressant in bench flotation test and caustic soda (NaOH) was used as pH regulator. All the chemicals were prepared with 1% p/v of concentration. The iron ore sample was collected in the Brazilian Iron Quadrangle (Mariana, MG). The material was previously comminuted, deslimed, and characterized via chemical and granulometric analyses.

Table 1: Molecular Weight (MW) and Hydrophile-Lipophile Balance (HLB) of surfactants used as collector and frothers.

Name	Chemical Formula	MW(g/mol)	HLB	Reference
Ethermonoamine	$R\text{-}O(CH_2)_3NH_2$	225	6.87	Matos et al., (2021.a)
Etherdiamine	$R\text{-}O(CH_2)_3NH(CH_2)_3NH_2)$	330	5.45	Matos et al., (2021.a)
MIBC	$CH_3CHCH_3CH(OH)CH_3$	102	6.1	Laskowski (2004)
DF1012	$CH_3(PO)_{6.3}OH$	397.95	7.5	Laskowski (2004)

Bubble size measurements were conducted in an APBS MK4 Anglo Platinum Bubble Sizer apparatus connected to the flotation machine and under similar conditions of foam formation. For each test condition, 25-35 photographs were analyzed using the image analysis software provided by Stone Three Mining (South Africa). This software performs the statistical analyses to calculate the mean Sauter diameter (d_{32}).

The surface tension measurements of surfactant solutions were performed in a K10ST tensiometer (Krüss, Germany), using the Du Nouy ring method. All tests were conducted at approximately 21 ± 2°C, with 20 mL samples, measured five times after flame treatment of the platinum plate ring, in order to remove organic contamination.

Foam was generated in a 3.9 L cell of a laboratory Wemco flotation machine, using a 3 L volume of pH adjusted aqueous solutions (water and reagents), at specific concentration. The solution was stirred at 1250 rpm during 1 min, then the air, at constant flow rate, was introduced and the foam was collected in individual recipients and weighed.

The bench flotation tests were conducted in a Wemco machine equipped with a 3.9 L cell, using 1.5 kg iron ore aliquots in 50% solids (w/w) pulps. The pulp was conditioned at 1250 rpm, initially with starch for 5 minutes and then with the collector and frother solutions for 1 extra minute, when it was diluted to 42% solids for flotation. The froth was collected for 3 minutes to ensure that all foam generated was exhausted. In the sequence, tailings aliquots and the remaining concentrate were weighed in analytical balance, filtered in vacuum filters, dried at 105°C, weighed again and chemically analyzed using FRX. The metallurgical balance (minerals recovery, rejection, and selectivity Index) was calculated using equations reported by Matos et al. (2021.b).

10.3 - Results and discussion

10.3.1 - Mineral characterization

Figure 1 shows the X-Ray diffractograms (XRD) for the iron ore sample, which identified the mineral phases hematite, quartz and goethite.

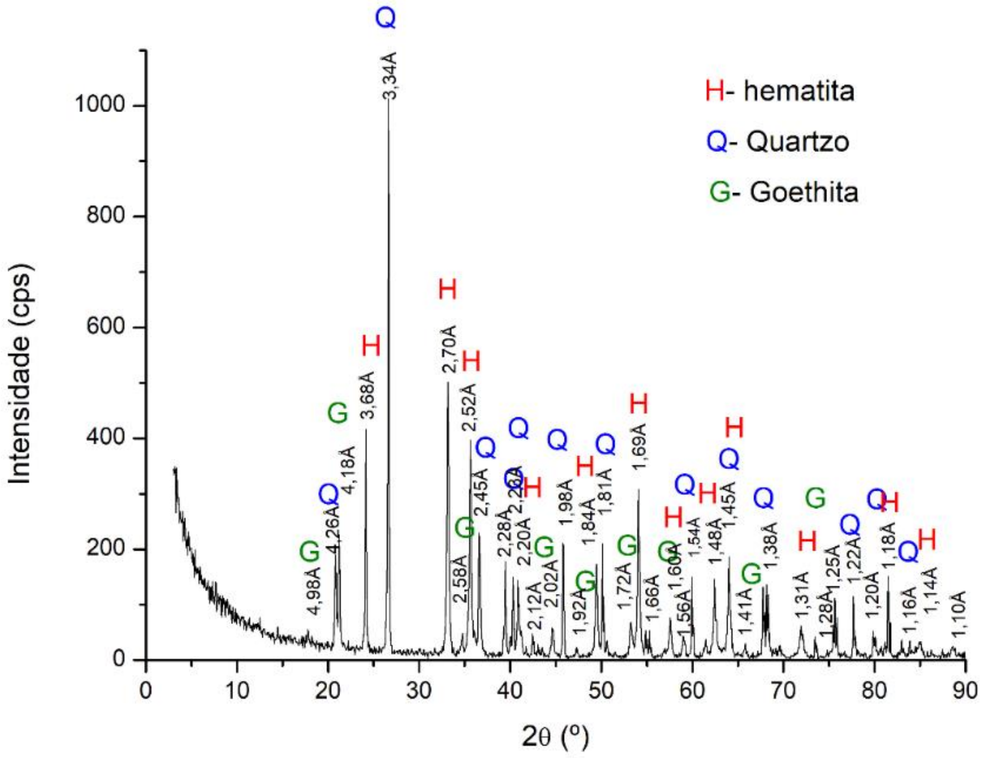

Figure 1: X-Ray Diffraction for the iron ore sample.

Table 2 shows the quantitative results of the contents of each element, obtained by X-Ray Fluorescence (FRX). The target of froth flotation was to concentrate the iron grade from 45% to 67% through reducing the SiO_2 content from 34% to values below 2%.

Table 2: Chemical composition of the iron ore sample.

Fe (%)	SiO_2 (%)	Al_2O_3 (%)	P (%)	CaO (%)	MnO_2 (%)	LOI (%)
44.30	34.16	0.35	0,032	0,01	0,04	2.02

The physical characterization of the sample presented the values of the size distribution (figure 2) of the ore used in the flotation tests. The results show that the sample has a D_{50} of 70 µm and about 85% of the material below 150 µm, sizes suitable for the flotation process. Furthermore, one can observe that the material is practically free of slime (particles less than 10 µm).

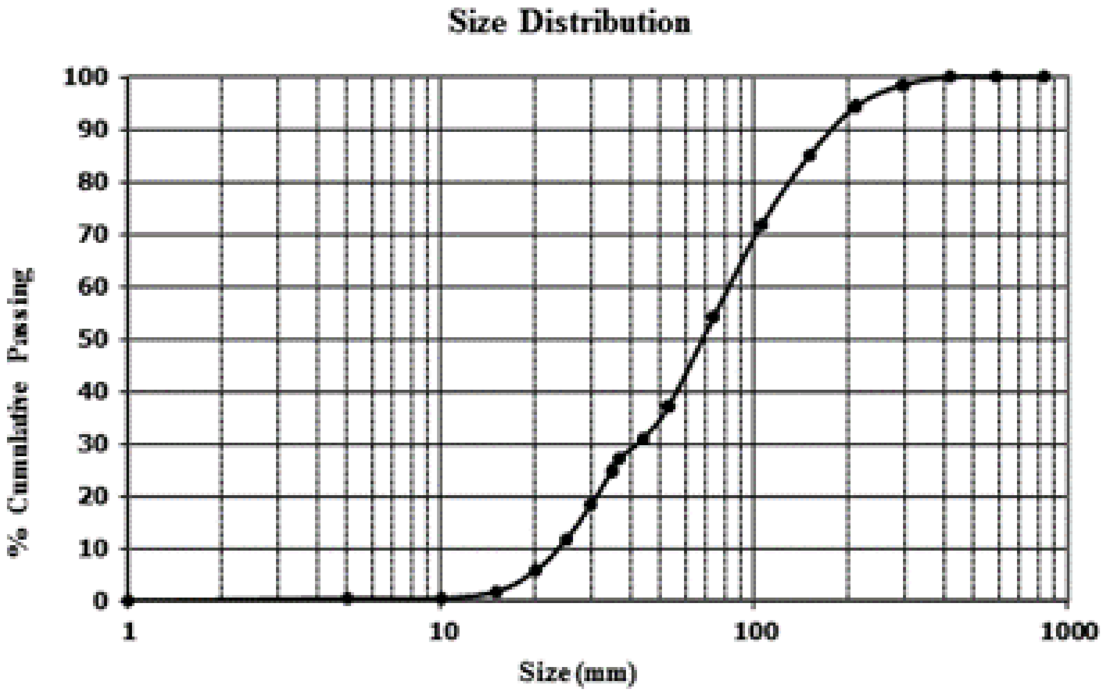

Figure 2. Size distribution of the iron ore sample.

10.3.2 - Two-phase tests

The efficiency of frothers is related to their ability to reduce the bubbles size through coalescence prevention and to formation of stable foams.

10.3.2.1 - Bubble size

Smaller bubbles induce higher probability of bubble-particle collision and attachment and strongly contribute to quartz flotation in the reverse cationic flotation of iron ore. On the other hand, finer bubbles have larger interfacial area, causing water to accumulate into the foam. Increasing frother dosage gradually reduces the bubbles diameter until a particular concentration, called critical coalescence concentration (CCC), from which coalescence is completely prevented (Cho and Laskowski, 2002).

According to Matos et al. (2021.a), ethermonoamine produces smaller bubbles at higher CCC, than etherdiamine, because of its lower molecular weight. Figure 3 shows that frothers, DF1012 and MIBC, clearly induce finer bubbles than both etheramines, presenting CCC values at approximately 6 and 11 ppm, respectively, similarly to the results observed by Laskowski (2003); Gupta et al. (2007); and Castro et al. (2013). As for the amine samples, CCC values were observed at 5 ppm, for etherdiamine, and 8 ppm, for ethermonoamine.

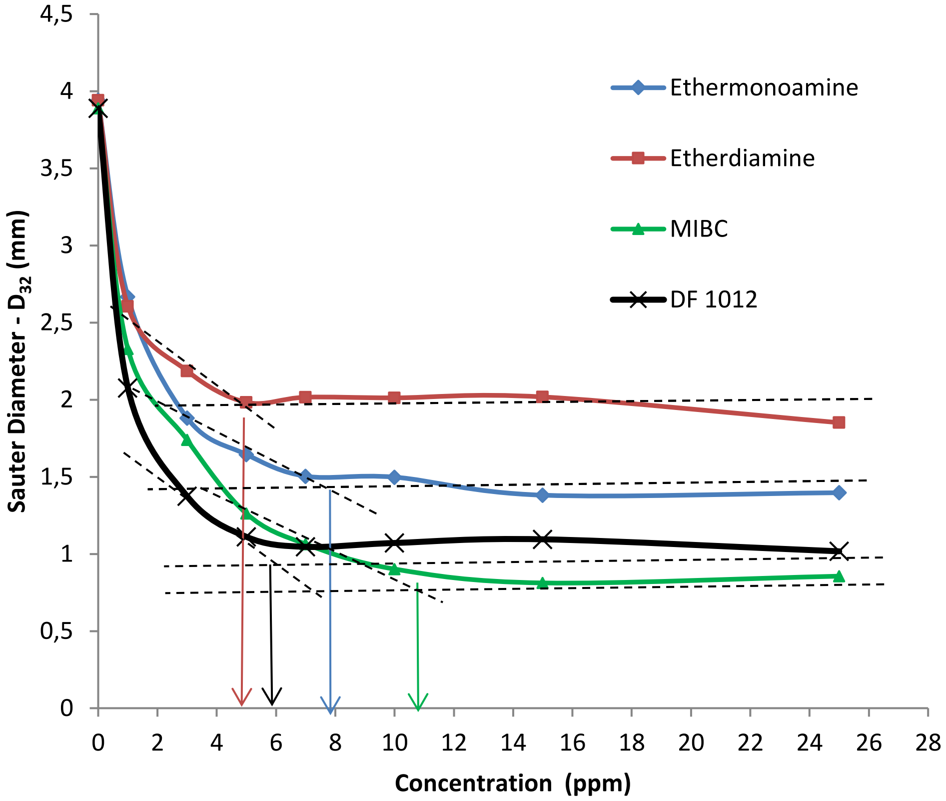

Figure 3. CCC curves for the tested etheramines and frothers.

Bubble size measurement allows the determination of the mean bubble diameter or Sauter diameter (d32). This can be correlated to other important flotation variables, such as surface air velocity (Jg), air hold-up (εg) and surface bubble area flow (Sb). Figure 4 shows the bubble population distribution curves for each surfactant tested at a concentration of 15 ppm for a 95% confidence interval.

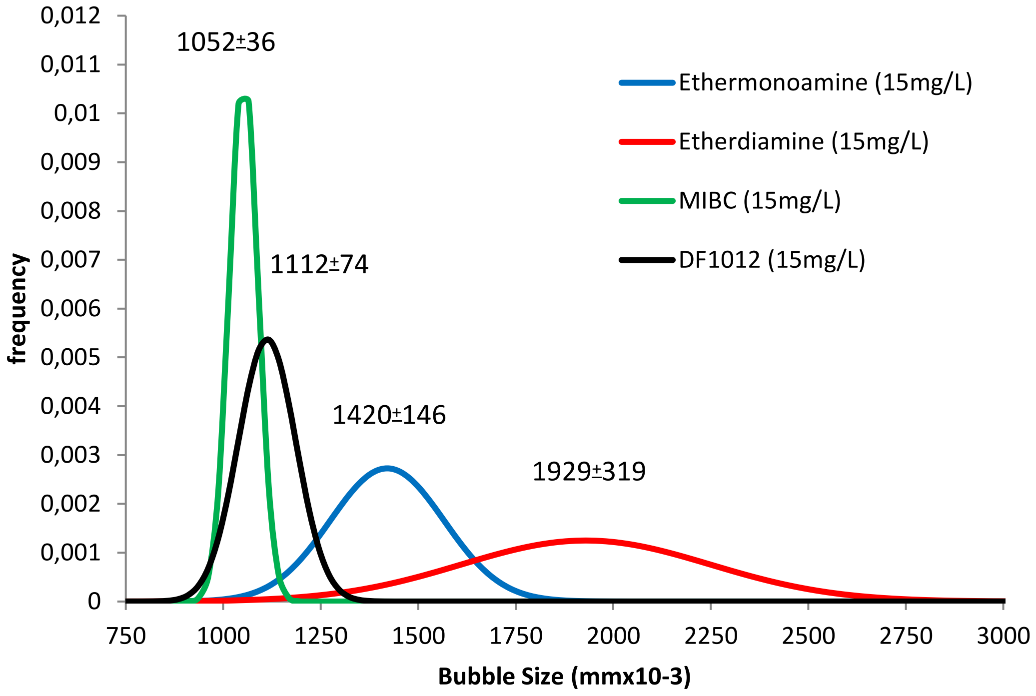

Figure 4: Normal distribution of bubbles sizes at 15 mg/L for etheramines and frothers

Laskowski (2003) classified frothers with low CCC as powerful, whereas the selective frothers produce smaller bubbles. Using this classification, DF1012 is powerful and MIBC is selective. Comparing just the etheramines, acting as frothers, etherdiamine can be classified as more powerful and ethermonoamine as more selective.

10.3.2.2 - Foam Stability

Foam is a two-phase system (liquid-gas), while froth is a three-phase system (liquid-solid-gas). The foam stability primarily depends on type and concentration of the frother, whereas regarding the froth, the size and surface properties of solid particles also determine its stability.

Stable foams prevent premature disruption of the particle-bubble aggregate, ensuring the complete transport of hydrophobic particles to the overflow. On the other hand, very stable foams can result in excessive non-selective drag of large masses of hydrophilic particles into the froth, impairing flotation selectivity (Cho, 2002; Melo and Laskowski, 2007; Zhang, 2016).

Figure 5 shows the results of water recovery as a function of surfactant concentration in the foam for frothers and amines. The frothers produced larger volumes of water in the foam than those yielded by etheramines, causing greater foamability.

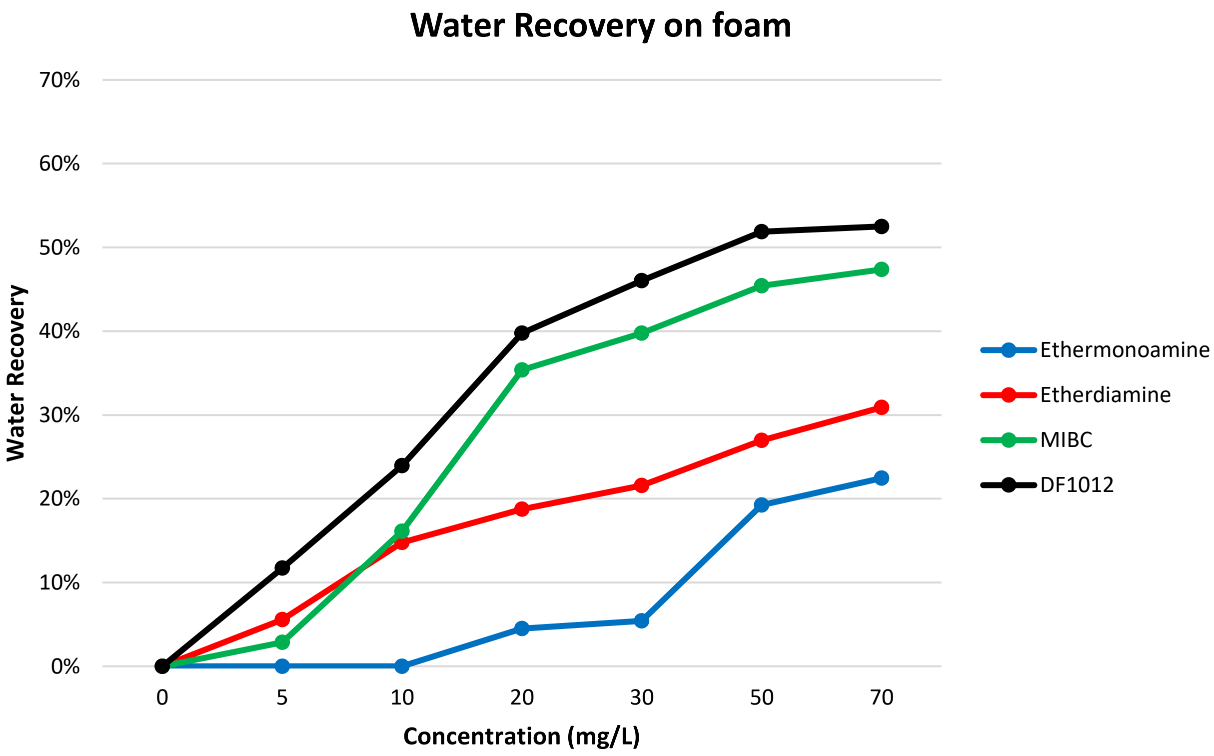

Figure 5: Water recovery in foam in function of surfactants concentration.

The balance between the foam mass or water content and its stability is a kinetic function dependent on the bubble formation times, reaching a certain height and volume of the foam followed by its drainage. The results presented in the figure 5 characterize the water content according to its mobility at the time of collection and the operational and geometric parameters of the test. The foamability is defined as the capacity of the surfactant to form foam, where the foam stability or foam durability is described by variations of foam height or volumes with time, immediately after foam generation (Malysa and Lunkenheimer, 2008; Karakashev et al., 2021).

The appearance and stability define foams as unstable or metastable. The unstable or wet foams are characterized by spherical bubbles separated by thick liquid walls. Their lifetime is short, just persisting when the gas flow is passing through the solution. On the other hand, the dry and metastable foams are more persistent, characterized by bubbles with polyhedral shapes, separated by planar or slight curved fine liquid film (Melo & Laskowski, 2006).

According to Laskowski et al. (2003), powerful frothers such as DF1012, yield metastable foams, whereas more selective frothers, like MIBC, produce unstable foams. Matos et al. (2021.a) presented results in which ethermonoamine formed wetter foams in two-phase tests, compared with etherdiamine. In the evaluation carried out with an iron ore (three-phase tests), this effect was confirmed (Matos et al., 2021.b).

Based in this classification, it was expected that MIBC and ethermonoamine would present larger water content than DF1012 and etherdiamine, respectively. However, the characteristics of high foamability with low froth stability, observed during the investigation, explain the results showed in figure 5, once the shorter lifetime of unstable foams from the MIBC and ethermonoamine was not enough to reach the height needed for transferring and collecting.

Excess water in the foam promotes the entrainment effect of hydrophilic fine iron particles in the froth and this metallic loss compromises the iron recovery. Once most of the water in the foam is contained in the Plateau Boarders and only a tiny fraction resides in the lamellar layers, surfactants that produce wetter foam will carry unwanted hydrophilic particles into the froth phase in the flotation process. The effect of water content in the foam on flotation performance must be confirmed in tests in the presence of solids.

Non-ionic surfactants had a lower capacity to reduce the water surface tension compared to etheramines, as shown in figure 6. These differences also justify the larger water content in the gas-liquid interfaces formed by frothers compared to etheramines.

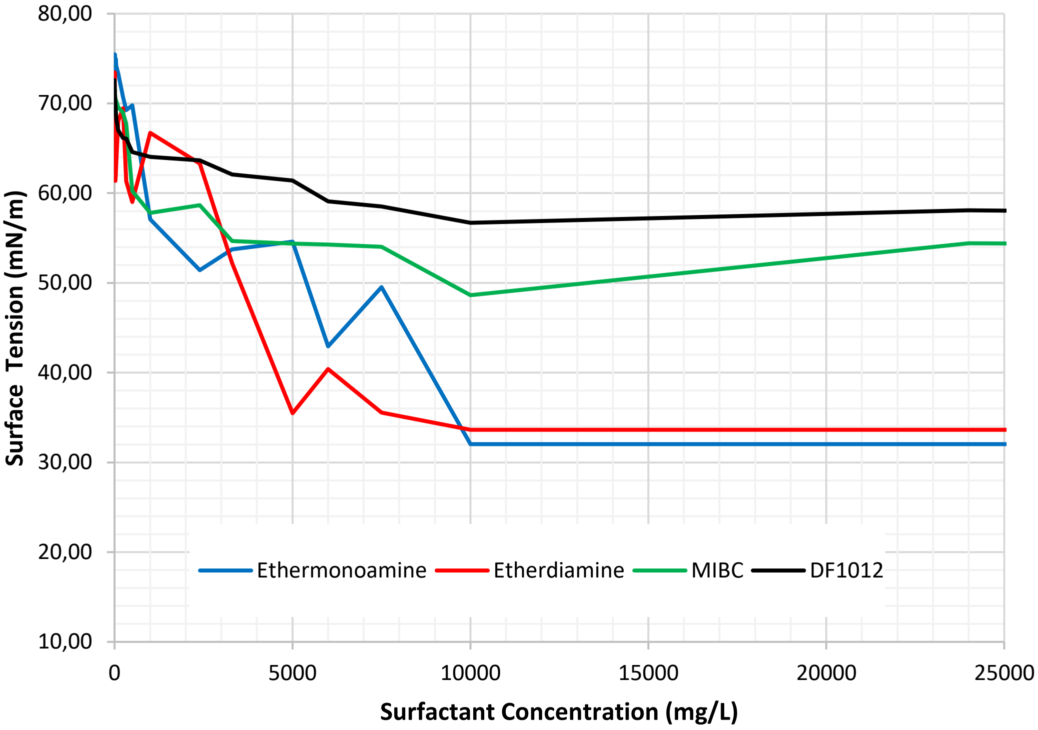

Figure 6. Surface tension isotherms for surfactants at 21°C.

10.3.3 - Three-phase tests (Bench flotation)

Despite better foamability and smaller bubble size on the froth, the non-ionic frothers do not collect quartz by true flotation, due to the lack of effective adsorption onto the negative quartz surface, in contrast with the cationic surfactants etheramines. Adsorption of frothers on the surface of naturally hydrophobic particles is attributed to Van der Walls interactions between the hydrophobic part of the frother molecule and the hydrophobic surface of the mineral particle (Zhang, 2016). Although possible in the studied system, this adsorption is considered weak and insufficient to maintain the stability of the bubble-particle aggregate needed to carry out flotation. The results presented in figure 7 confirm that non ionic frothers MIBC and DF1012 did not act as collector (quartz rejection and selectivity index close to zero), unlike etheramines, which presented quartz rejection above 90% and selectivity index greater than 10. However, the frothers promoted iron loss by non selective entrainment of fine particles. Once the hematite is hydrophilic at flotation conditions, the higher HLB of DF1012 promotes greater water recovery in the froth than the MIBC, inducing higher iron loss. The results with etheramines indicated similar effect. The drier froth produced by etherdiamine induced lower iron loss by entrainment in comparison with ethermonoamine (Matos, 2021.b).

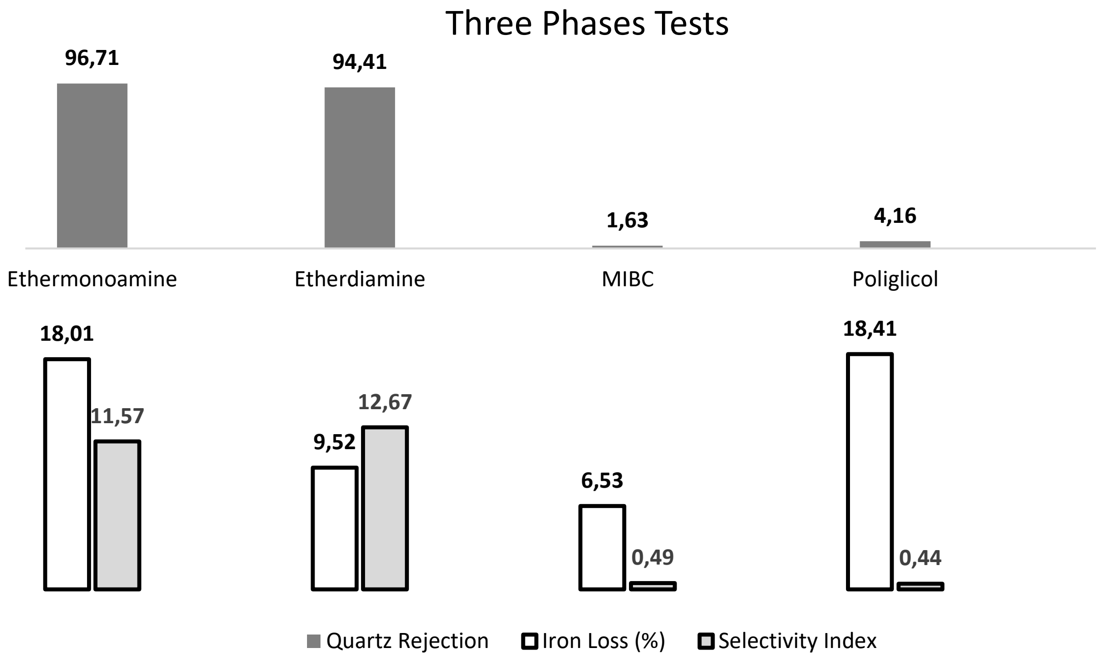

Figure 7: Comparative results of quartz rejection, iron loss and Selectivity index between ionic and non-ionic surfactants.

Figure 7 also shows better selectivity with etherdiamine in relation to ethermonoamine, due to its ability to reduce iron loss in the floated tailings (greater metallic iron recovery in the concentrate), despite the higher quartz rejection achieved with ethermonoamine, replying the results reported by Matos et al. (2021.a, b). The authors related that the distinct structural characteristics of these etheramines affect both their adsorption on the mineral surface and the formation and stabilization of the foam/froth. Despite smaller bubbles produced by ethermonoamine, increasing particle-bubbles collision and flotation probability, the dryer and more stable froths of etherdiamine reduce iron loss by fine hematite entrainment. Also, the selective etherdiamine demonstrated higher capacity to promote quartz true flotation in comparison to the powerful ethermonoamine.

Figure 8 shows a schematic comparing the differences between non-ionic frothers and cationic etheramines as function of bubble size and water content in the lamellar bubble surface, and their interaction with hydrophobic (quartz) and hydrophilic (hematite) mineral particles. The comparative quadrants of the figure shows that etherdiamine induces the larger bubbles radius with finer interlamellar layers, inducing greater flotation of hydrophobic particles and lesser entrainment of hydrophilic particles than ethermonoamine, MIBC and DF1012. Also, Figure 8 illustrates how the non-ionic frothers cannot collect the hydrophobic particles, due to a thicker interlamellar layer.

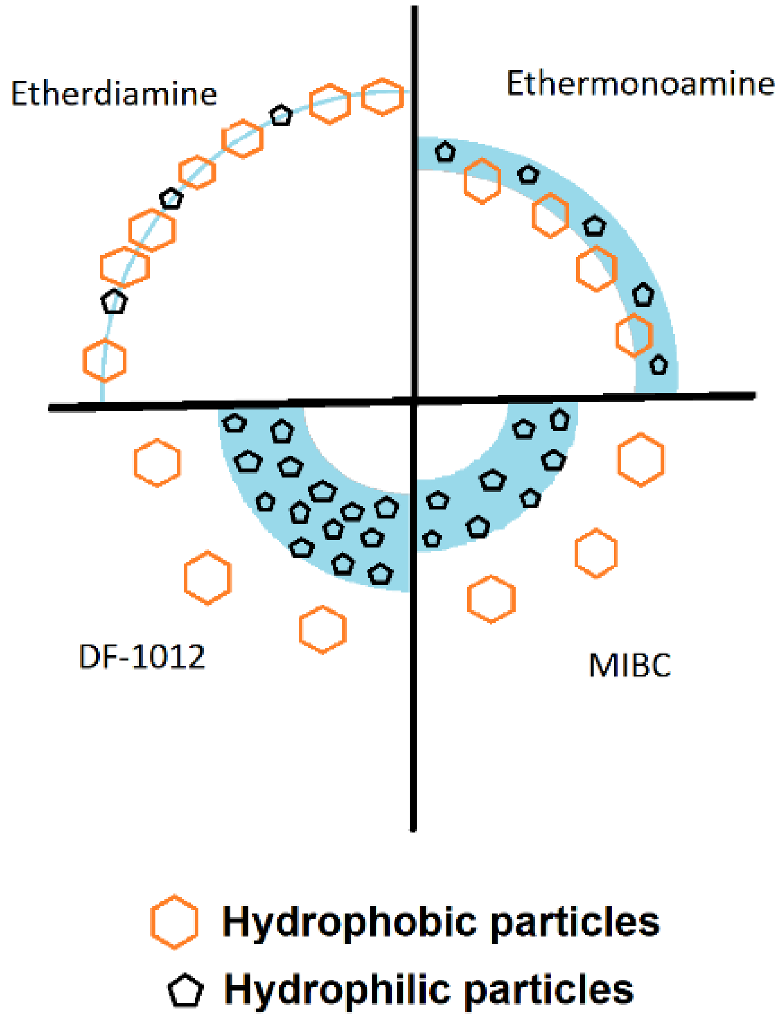

Figure 8. Schematic representation of bubble size and water in lamellar surface for the different surfactants and its interaction with the hydrophobic and hydrophilic particles.

It is important to clarify the distinction between surfactants classification acting as collector or frothers. Powerful collectors require lower dosages to obtain its maximum efficiency, whereas the selective collectors are those which achieve the best efficiency values. On the other hand, frothers are classified as powerful when they result in lower CCC values, whereas a selective frother reaches smaller bubble size. In this sense, the ethermonoamine is a powerful collector and a selective frother, while the etherdiamine is a selective collector and a powerful frother.

10.3.3.1 - Frothers-Collectors Interaction

The interaction between the hydrocarbon chains of the frother and the collector in solution occurs at both, the liquid-gas and the solid-liquid interfaces, providing greater foaming intensity and better hydrophobization of the mineral surface. According with Leja & Schuman (1954), the frother interacts with collector molecules adsorbed on the solid particles during the particle-bubble collision and adhesion steps. The coadsorption of the cationic collector and the non-ionic frother reduces the electrostatic repulsion between the polar heads of the surfactants, also improving the immobilization of their non-polar tails. This increases the stabilization of the particle-bubble adsorption, reducing the probability of detachment of the aggregate during transportation, increasing the flotation efficiency. The coadsorption of neutral molecules with ionic collector increased mineral flotation in several mineral-reagents systems (Rao & Forssberg, 1997). Liu et al. (2015) reported that the coadsorption of diamine and a short-chain alcohol on the surface of quartz occurs through hydrogen bond-type interactions, reinforcing the electrostatic adsorption between the collector and the mineral.

The complete results of the bench flotation tests are shown in table 3. The effects of amine type, frother type and collector replacement grade are presented in relation to concentrate quality parameters (%Fe_C and %SiO_2_C), recovery of each mineral (iron in the concentrate and silica in the tailings), and overall performance, measured by the Gaudin Selectivity Index (SI).

First, the wetter foams formed by non-ionic frothers (DF1012 and MIBC), compared with that produced by etheramines, were responsible by the lower metallurgical recovery of etheramines-frothers combinations in comparison with single etherdiamine. For this same reason, the DF1012-etheramine combinations yielded lower recoveries when compared with the MIBC-etheramine mixtures. However, these combinations between cationic and non-ionic surfactants resulted in greater selective index than those with cationic collectors alone, enhancing the concentrate quality (lower silica content), mainly in the etherdiamine-DF1012 case.

Table 3: Bench flotation results

Colector Type	"Frother" Type	Replacement (%)	%Fe_C	%SiO2_C	%Fe_R	Mass Recovery	Iron Recovery	Quartz Rejection	SI
Ethermonoamine	-	0	66,58	1,86	19,48	57,11	81,99	96,71	11,57
	MIBC	10	66,32	1,86	18,76	57,63	82,78	96,73	11,92
	DF1012	10	66,30	1,79	19,69	57,04	81,72	96,86	11,75
	Etherdiamine	10	66,30	1,75	19,18	57,74	82,52	96,89	12,14
	MIBC	20	65,76	2,06	17,00	58,56	84,53	96,43	12,16
	DF1012	20	65,46	2,26	17,43	57,79	83,72	96,22	11,45
	Etherdiamine	20	66,25	1,71	18,16	58,40	83,67	96,95	12,77
Etherdiamine	-	0	65,67	2,89	11,98	63,40	90,48	94,41	12,67
	MIBC	10	65,64	2,53	13,04	61,87	89,09	95,34	12,93
	DF1012	10	65,94	1,88	15,94	60,40	86,32	96,56	13,31
	Ethemonoamine	10	66,15	1,95	14,06	60,53	87,83	96,49	14,08
	MIBC	20	65,53	2,85	12,56	62,25	89,59	94,72	12,42
	DF1012	20	66,56	1,90	16,38	59,36	85,59	96,53	12,87
	Ethemonoamine	20	66,16	1,86	14,69	59,47	86,85	96,76	14,04

Figure 9 shows that partially replacing amine collector by frother improved the selectivity index. Once the frothers produce smaller bubbles, improving particle-bubbles collision probability, it was expected that the combination between frothers and etheramines would increase quartz recovery in the froth, reducing the SiO_2 content in concentrate. This fact clearly occurred with etherdiamine-Dowfroth1012 mixture, achieving SiO_2 content below 2% (see table 3), reference in bench tests for specification of pellet feed superconcentrates. In addition to the better performance, the replacement offers an opportunity of costs reduction, since frothers are normally less expensive than etheramines. Corona-Arroyo et al. (2015) presented results demonstrating smaller bubble size and CCC reduction when frother-DDA blends were compared to the separate use of collector and frothers (MIBC and Polyglicol F507).

Second, the performance distinction between ethermonoamine and etherdiamine is also evident when they are combined with the alcohol or polyglycol frothers. Ethermonoamine produced better selectivity in combination with MIBC, whereas the propylene glycol DF1012 was more effective to improve the etherdiamine performance. The mentioned benefits from collector-frothers coadsorption occurs more effectively for surfactants with similar hydrocarbon chain length, which justifies the better performance of etherdiamine with the higher molecular weight frother DF1012, while ethermonoamine performed better with the short-chain alcohol MIBC.

Figure 9 also shows that the mixture of etherdiamine and ethermonoamine yielded the highest selectivity, because of the synergistic effect on froth stability and mineral surface adsorption. Nogueira et al. (2022) related the occurrence of synergistic effects of a binary mixture 1:1 (ethermonoamine:etherdiamine) on quartz floatability on microflotation tests and on silica reduction on bench flotation of iron ore. In the results presented in table 3, the etheramine mixtures dead to an average silica reduction of 7% and 34%, in the replacement of ethermonoamine and etherdiamine, respectively, when compared to the tests with pure collector.

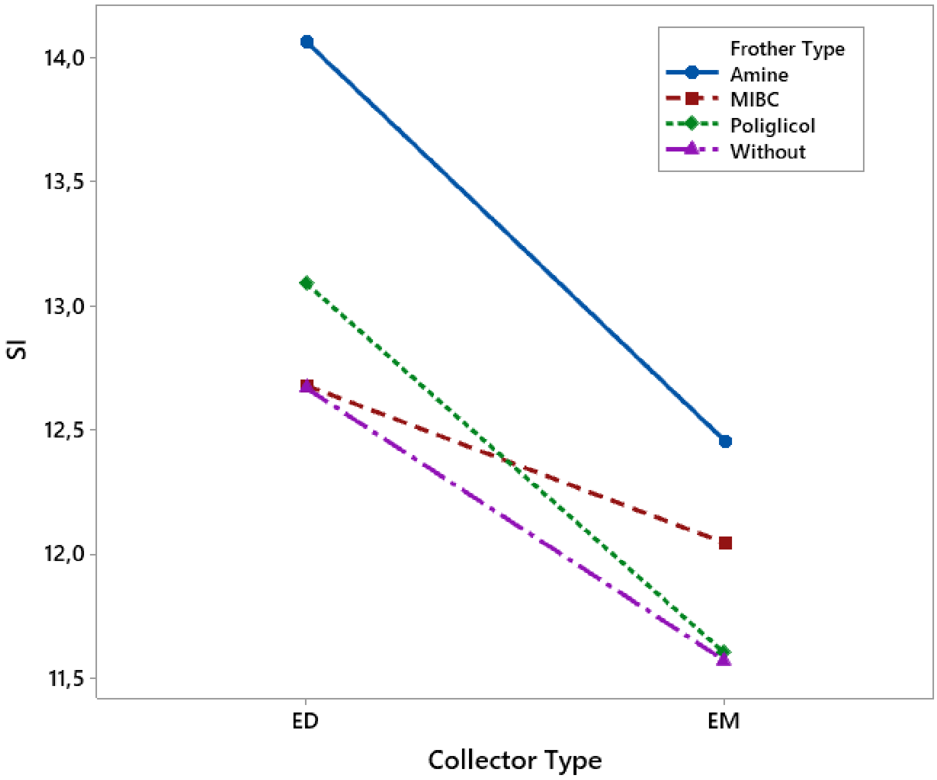

Figure 9: Selectivity Index for the etheramines and its replacements by frothers and one each other.

Finally, the ratio of each surfactant has been found to be decisive in the reverse cationic flotation performance. Silva et al. (2008) indicated the efficacy of replacing up to 10% in weight of the amine collector by a commonly used straight chain alcoholic frother, measured by the increase in iron recovery and separation efficiency. Kapiamba & Kimpiab (2021) reported the benefits to replace more than 10% of amine collector EDA3 by a polypropylene glycol methyl ether (Senfroth 200). From 10 to 50% replacement, the global flotation performance was improved, although resulting in a pronounced entrainment of fine hematite, which indicated the need to investigate alternative reagents. Figure 10 shows that 10% replacement was more effective to increase the selective index with etherdiamine, while greater values were achieved with ethermonoamine at 20% replacement.

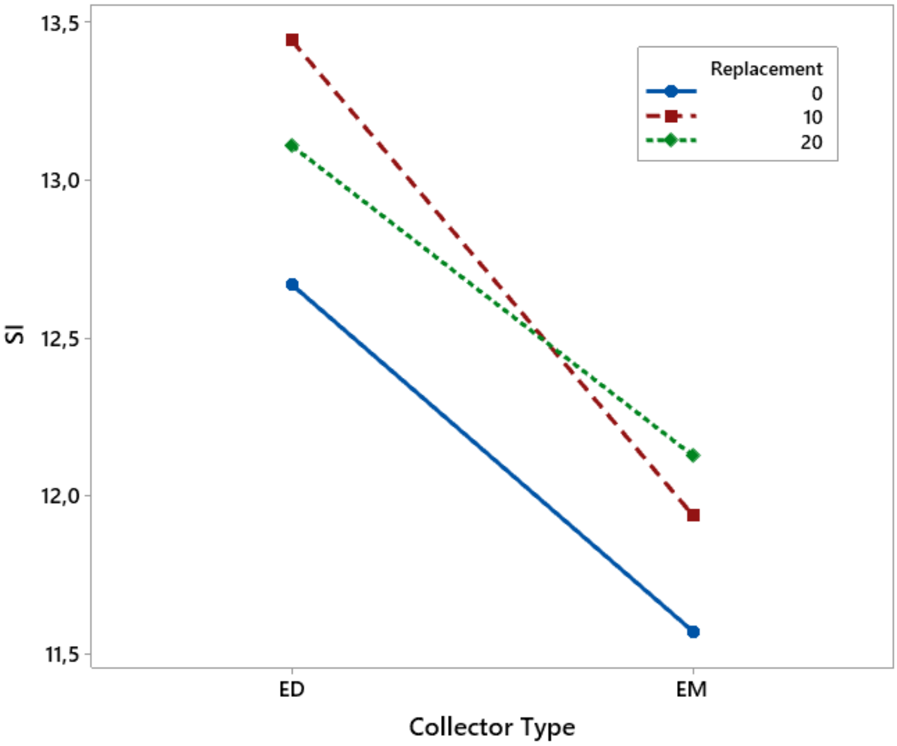

Figure 10: Selectivity Index in function of etheramines replacements rate.

It is important to emphasize that the partial replacement of the cationic collector by the non-ionic frothers represents not only the effects of improving the foam properties, but also the reduction in the presence of the cationic surfactant agent primarily responsible for adhesion by electrostatic adsorption. The improvement in froth properties by specific frothers, and their weak coadsorption, is not enough to offset the collector need, especially because the etherdiamine is less powerful than ethermonoamine (Matos et al., 2021.b).

Since most of the industrial application of reverse cationic flotation of similar iron ores uses pure ethermonoamine on its process, the optimized combination of 90% etherdiamine plus 10%

of DF1012 or ethermonoamine could reaches the same concentrate quality, providing 6% improvement in production concomitantly with 8% reduction in tailing generation, based on the mass recovery results from table 3.

10.4 - Conclusion

The challenge in iron ore flotation performance is the balance between the high level of quartz recovery with the minimum iron loss in the froth. The strategy in chemicals used should consider an optimum combined system to perform the simultaneous functions assigned to the reagents. Non-ionic surfactants MIBC and Dowfroth 1012 are more efficient than etheramines acting as frother, due to their capacity to reduce bubble size and higher foamability. For this reason, the partial replacement of the etheramines collector by these frothers improved the selectivity of the reverse cationic flotation of iron ore at specific combinations ethermonoamine-MIBC and etherdiamine-Dowfroth 1012. The compatibility of molecular weight and its effect on co-adsorption on liquid-gas and solid-gas interfaces explain these observations. However, the replacement of more selective etherdiamine by 10% of the powerful ethermonoamine showed the best result due to the synergistic effect on froth stability and mineral surface adsorption.

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