



Synergistic interactions between reagents in sulphide flotation

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Synopsis

Various reagents are added to flotation pulps to manipulate the chemical environment in order to create favourable conditions for the separation of the desired mineral from the unwanted gangue. Interactions occur between these reagents and between the other chemical parameters existing in the flotation pulp which complicate the elucidation of the behaviour of the respective reagents. This paper discusses the roles of the main classes of reagents added viz. collectors, frothers, depressants and activators, as well as the interactions between frothers and collectors. A case study reporting synergistic interactions between thiol collectors in the flotation of pyrite at pH = 4 is included. The use of Potassium n-butyl xanthate (PNBX) and a dithiocarbamate type collector (DTC) were tested both as pure collectors and as components in a collector mixture. In the batch flotation tests sulphur recovery and grade, water recovery, rate of recovery and image analysis of the surface froth were used to evaluate the effect of the mixture on the overall flotation performance. Bubble loading tests showed that the use of the mixture improved the efficiency of the particle collection process by bubbles. Thermochemical measurements of the adsorption of the collectors onto the mineral, indicated the formation of different surface products by the two collectors.

Introduction

The creation of a favourable chemical environment is critical to the overall success of the flotation process. However, due to the complexity of the process and the large number of influential factors and their interactions, it is extremely difficult to ascertain the contribution of each individual factor to the overall flotation performance. Often the interactions between factors mask or confuse the interpretation of the resulting flotation performance. Before the chemistry of the process can be optimised, it is necessary to elucidate the behaviour of each of the factors in mineral slurries.

It is well known in the practice of flotation that mixtures of various collectors often behave with greater effectiveness than would be expected from their individual known characteristics. This phenomenon is a classical example of synergism in flotation in which the combined effect exceeds the sum of the

weighted individual effects. Such phenomena are not only consciously applied by adding mixtures of reagents, especially collectors, but may also occur inadvertently since many industrial reagents are synthesised from less than absolutely pure chemicals, resulting in the presence of small amounts of different product molecules which are often capable of having a positive synergistic effect on the flotation behaviour. Such synergism can have a significant effect not only on the recovery but also on the selectivity of specific minerals in differential flotation. The manner in which reagents interact in order to achieve a synergistic effect is a complex function of their chemical nature as well as their chemisorptive or physisorptive properties. The former will determine whether the chemical composition of the reagent changes when another compound is present through, for example, a dimerisation reaction in the case of thiol collectors. The latter will determine how competitive or synergistic adsorption will influence the ultimate flotation behaviour. The analysis of synergism between reagents in flotation is complicated by the fact that the roles and interactions of the different classes of reagents are difficult to isolate due to the complexity of the flotation process. For example, the frother is added to stabilise the froth zone but can also interact with the collector and affect the performance in the collection zone.

This paper first discusses those properties of pure collectors, frothers, depressants and activators which are pertinent to their potential synergistic behaviour. The interactions between collectors, frothers and each other are then reviewed. The emphasis here is on sulphide minerals but similar effects have been extensively reported in the case of oxide flotation. Finally an hypothesis is proposed to

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explain the synergism observed when mixtures of thiol collectors are used in the flotation of pyrite. This represents a typical sulphide mineral flotation system and will serve to highlight how the various sub-processes of flotation may be influenced in a synergistic manner thus influencing the ultimate flotation performance.

Functional roles of pure reagents

Collectors

The predominant functional role of collectors is to induce hydrophobicity by adsorption onto the desired mineral and they are therefore concentrated at the mineral-water interface. Collectors are heteropolar molecules containing a non-polar hydrocarbon chain, which renders the particle hydrophobic, and a polar group that interacts with the mineral surface.

Collector molecules can be divided into three classes, viz. non-ionic which are largely insoluble and used in the flotation of coal and graphite; cationic which are typically amine salts and used in the flotation of silicates and sulphides in alkaline conditions; and anionic which are used to float basic minerals such as metal oxides and sulphides. Fatty acids are used for the flotation of non-sulphide minerals such as apatite, calcite, feldspar and hematite. Sulphonates and sulphates are used for apatite as their frothing properties limit their usefulness for other systems. Sulphydryl or thiol collectors are used for the flotation of sulphide minerals and, of these, xanthates, first patented in 1925, are still the most widely used¹.

The mechanism of mineral-collector bonding depends on the collector type and the nature and charge of the mineral surface and can occur via physisorption or chemical bonding. There are several modes of chemical interaction of the collector with the mineral surface. In the case of physisorption, the collector does not interact with the mineral surface. The bonds are amorphous and the Gibbs free energy of adsorption is relatively low. In the case of chemisorption, the collector interacts with the mineral surface without movement of the metal ions from their lattice sites and is usually restricted to mono-layer coverage. Surface chemical reactions are accompanied by the movement of metal ions from their lattice sites and multilayers may form. If such a reaction occurs in the bulk solution a hydrophobic surface will only be established if there is bulk precipitation on the mineral surface.

Sulphide minerals are semi-conductors and can react electrochemically with thiol collectors according to the mixed potential model. This involves the cathodic reduction of oxygen and the anodic oxidation of collectors. The electrochemical potential of the system and the thermodynamics of the respective reactions determines the nature of the surface products. Depending on the nature of the surface products formed, the collector can be physisorbed, such as in the case of the neutral dithiolate, or chemisorbed, such as in the case of the metal thiolate. Naturally, when mixtures of collectors are used a combination of these mechanisms and products may occur, resulting in an enhanced flotation performance.

Frothers

Frothers are added to create a dispersion of bubbles in the pulp and stabilise the bubble formation, to create a

reasonably stable froth and to allow selective drainage from the froth of entrained gangue and increase the flotation kinetics. They are non-ionic heteropolar molecules and, unlike collectors, are not associated with particular categories of minerals. The frothing ability of a compound is associated with hydroxyl (-OH), ester (-COOR) and carbonyl (-CO) chemical groups, and commercial frothers can be divided into three main categories, viz. alcohols, alkoxyparaffins, polyglycols and polyglycol ethers. The polar end of the frother molecule forms hydrogen bonds with the water and no mineral-frother bonds are formed. The non-polar end is hydrophobic so that the frother concentrates at the air-water interface and is thus described as being surface active. This affects the surface tension which is a measure of the surface activity of frothers and causes a stable froth to form. In general, increased surface activity results in increased flotability and froth stability.

Depressants

The role of depressants is to reduce the collection of unwanted gangue which consists of typically talcaceous or other oxide minerals. Typical examples include either inorganic salts, such as sodium silicate, sodium sulphite or organic salts, such as polysaccharides, dextrin and starch derivatives, guar gums, carboxymethylcellulose and alginates. Depression is achieved by either enhancing the hydrophilic nature of the gangue surface, by preventing the formation of hydrophobic species or by coating of unwanted slimes on the mineral surface. Mechanisms of depression can also include the formation of large aggregates and the complexation of the collector in solution².

Activators

Activators are specifically added to enhance flotation performance usually by modifying the surface of the particle in some way so as to make it more amenable to interaction with the collector. They may however have unexpected effects, for example, by complexing with other ions in solution and rendering particles less floatable. Copper sulphate, for example, is a well known activator^{3,4}. Under certain circumstances, in sulphide flotation, the copper ions may exchange with other surface ions creating a readily

Notes and abbreviations for Table I

NOTES

1. Reagents tested as components of the mixture are separated by a colon. Where more than two reagents are in the list, all reagents listed have been tested at the all ratios specified in brackets.
2. Ratios are mole ratios.

ABBREVIATIONS

X	xanthate class of reagents
DTC	dithiocarbamate class of reagents
DTP	dithiophosphate class of reagents
MIBC	methyl isobutyl carbinol
MTP	monothiophosphate class of reagents
SMBT	sodium mecaptobenzothiazole
SIBX	sodium isobutyl xanthate
PPG	polypropylene glycol
41G	A propriety frother containing triethoxybutane manufactured by NCP

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Table I

Summary of synergistic effects observed in flotation

Interactions	Reagents (mole ratios tested)	Minerals	Techniques	Benefit of mixture	References	
Collector: Collector Thiol-Thiol	Ethyl, butyl xanthates (2:1; 1:1; 1:2) xanthates, diethyl dithiophosphates (2.1)	Arsenopyrite Galena	Batch flotation Adsorption	Higher rates of recovery at lower dosages and improved coarse recovery. More even adsorption	Plaskin <i>et al</i> ⁷⁻⁸	
	n-Propyl, n-hexyl, cyclohexyl, di propyl dithiocarbamates (10:90; 50:50; 90:10)	Pyrite	Batch flotation	Increased grades and recoveries for all mixtures Optimum ratio 90:10.	Bradshaw <i>et al</i> ⁹	
	Xanthate, dialkyl dithiophosphate	Galena	Adsorption Bubble pick up	Competitive adsorption.	Wakamatsu & Numata ¹⁰	
	Dithiocarbamates: xanthates, dithiophosphates, mecaptopbenzothiazole	Copper sulphides		Best results with dithiocarbamates and other soluble collectors.	Falvey ¹¹	
	Dithiophosphates, xanthates, mecaptopbenzothiazole	Various sulphides	Batch flotation	Improved recoveries due to combined properties. Optimum ratio 70:30.	Mingione ¹²	
	di-iso butyl DTP: SIBX (30:70; 50:50; 70:30) di-iso butyl DTP: SMBT (50:50)	Platinum Group Minerals Pyrite		Improved recovery.		
	Isobutyl xanthate: cyano diethyl dithiocarbamate (12:44):	Chalcopyrite Pyrite	Batch flotation	Increased recovery and grade with 12:44 mixture	Jiwu <i>et al</i> ¹³	
	Dithio-, monothio-phosphates (75:25; 50:50; 25:75)	Mixed copper sulphides	Batch flotation	Optimum recovery at 75:25 due to combination of properties.	Mitrofanov <i>et al</i> ¹⁴	
	Ethyl xanthate : di-ethyl dithiocarbamate (80:20; 66:33; 50:50; 33:66; 20:80)	Hazelwoodite	Adsorption Surface tension Micro flotation	Optimum ratio 33:66 for lower surface tension and increased recovery.	Critchley & Riaz ¹⁵	
	Xanthate : SMBT	Arsenopyrite Gold	Batch flotation	Lower dosage of mixture for better performance	Van Lierde & Lesoille ¹⁶	
Thiol - Anionic	Xanthate : dicresyl dithiophosphate	Copper sulphides	Batch flotation	Enhanced kinetics at lower dosages.	Adkins & Pearse ¹⁷	
	n-Butyl xanthate; dithiocarbamate (95:5; 90:10; 85:15; 50:50)	Pyrite	Batch flotation Bubble loading Thermochemical	Enhanced recovery due to improved collector adsorption and mineral collection.	Bradshaw & O'Connor ¹⁸	
	Ethyl xanthate: sodium Oleate (10:90; 20:80; 40:60; 60:40; 80:20)	Pyrite Gold	Surface tension Contact angle	Optimum mixture ratio 3:1 due to improved adsorption	Valdiviezo and Oliveira ¹⁹	
	Ethyl xanthate : amino acid glycerine	Chalcocite, Galena, Pyrite	Micro flotation	Higher recoveries.	Hanson <i>et al</i> ²⁰	
	Butyl xanthate : hydrolysed polyacrylamide (90:10)	Gold with mixed sulphides	Batch flotation	3% increased recovery (90:10) benefits also at lower dosage.	Orel <i>et al</i> ²¹	
	Ethyl xanthate : alkyl trimethyl ammonium bromide	Pyrite	Surface tension Micro flotation	Mixtures were strong but not selective.	Buckenham & Schulman ²²	
	Collector : Frother	Xanthate : alcohols	Chalcocite	Frothability	Enhanced frothability.	Leja and Schulman ²³
		Ethyl xanthate : α-terpinol	Chalcocite	Adsorption, Film thickness Batch flotation	Increased xanthate adsorption with α-terpinol addition.	Lekki and Laskowski ²⁵
		Ethyl xanthate : diacetone	Copper Ores	Frothability	Only froths in 3 phase	Lekki and Laskowski ²⁵
		Butyl xanthate : 41G	Galena	Contact angle	Contact angle increased	Harris ²⁶
MIBC: thionocarbamate xanthogen formate		Copper sulphides	Batch flotation Plant practice	Better surface distribution. Collector dosage reduced 40% Cheaper but reduced selectivity.	Crozier and Klimpel ²⁷ Klimpel and Hansen ²⁸	
Frother: Frother	Ethyl xanthate : alcohol	No mineral	Surface tension	Improved film characteristics.	Manev and Pugh ²⁹	
	MIBC, pine oil, cresylic acid, ppgs	Copper sulphides	Plant practice	Mixtures used by 37% plants to obtain wider particle size range.	Crozier and Klimpel ²⁷	

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floatable particle, but in different pulp conditions may complex as an hydroxy species and depress the particles^{5,6}. Such effects may be considered synergistic but fall outside the scope of this paper. Another commonly used activator is sodium sulphide or bisulphide which is used as a sulphidising reagent for tarnished or oxidised ores.

Synergistic interactions between reagents

There has been a considerable amount of work done on the effects of mixing reagents in flotation. Table 1 summarises much of this literature with respect to type of reagents mixed, minerals tested, measurements made and the benefits observed.

Collector-collector interactions

The use of mixtures of collectors has long been recognised in plant practice and has been shown to enhance flotation performance. These benefits have been reported for a wide range of collector mixtures (anionic, cationic and non-ionic) and include lower dosage requirements, improved selectivity and rates and extents of recovery and an increase in the recovery of coarse particles. In many cases an optimum ratio of constituent collectors was shown to exist. Dithiophosphates are a class of thiol collectors that are so widely used in mixtures that they are known as promoters^{12,17}.

Using measurements obtained from experimental techniques shown in Table 1 a number of mechanisms have been proposed by various authors to explain the fact that the mixtures give a flotation performance greater than that expected from the contributions of each individual component. These proposals are based on effects related to adsorption of the collectors on the surface of the particle, interactions between the reagents either in the bulk or at the surface or changing froth characteristics and will be considered in this sequence.

When using mixtures of collectors it has often been observed that there is a greater extent of adsorption on the mineral surface. This could either enhance the overall hydrophobicity of the mineral surface or result in an adsorbed surface layer of collector molecules more suitable for frother-collector interactions. The increased mineral hydrophobicity could result from the formation of a more evenly distributed surface species. The change in hydrophobicity can be measured by, for example, changes in contact angle, bubble loading and ultimately the recovery in batch flotation tests. It has also been proposed that, for certain systems, when a mixture of collectors is exposed sequentially to a surface which, by definition, must have a heterogeneous distribution of energetically different sites, the weaker collector will adsorb preferentially on the strong sites and the strongly adsorbing collector, added subsequently, will adsorb on the weaker sites. In this way as many sites as possible are utilised for adsorption thus enhancing the hydrophobicity. Single collector addition may only result in adsorption on strongly adsorbing sites, forming non-uniform coverage and thus a less than optimal adsorption capacity. Such an effect may not be observed if the collectors were pre-mixed before addition thus emphasising the fact that synergism may depend on the sequence of addition as much as on the presence of a mixture.

The grade of the concentrate is largely a function of the

depressant used which affects the froth zone characteristics. The presence of hydrophobic solids in the froth phase will destabilise the froth and result in improved drainage and consequently increased selectivity and grades. The presence of hydrophilic or only slightly hydrophobic minerals can stabilise the froth zone and thereby decrease the grade achieved. The use of a combination of collectors resulting in both physisorbed and chemisorbed surface products can also affect the froth structure and influence the final grade achieved. It is also often observed that enhanced performance is achieved when a strong collector with no frothing properties is used with weaker collector with frothing properties. The former collector increases coarse particle recovery and the latter increases fines recovery. This is however not a true synergistic effect since the combined effect is the sum of the individual effects.

Collector-frother interactions

Before the collision of a mineral particle and an air bubble, adsorbed layers of reagents are present at both interfaces. At the time of collision, there are interactions between these layers which are affected by the nature and charge of the respective molecules. Any associated molecules are anchored to the mineral group by the polar groups of the collector. The strength of this film determines the tenacity of attachment of the mineral to the bubble and the ultimate success of the flotation process. When the molecular associations between frother and collector are suitably balanced the appropriate mechanical properties of the film at the interface are created resulting in good recoveries and grades. If the dosage is too high the molecules would be too densely packed and penetration and successful attachment would not take place. This supports the well-known phenomenon that too high a dosage of reagents can result in reduced recoveries. In this case synergistic interactions between the frother and collector that improved flotation performance at the lower dosages are no longer possible at the higher dosage.

Frother molecules can accumulate at the mineral surface, without enhancing its hydrophobicity, and at the time of collision with a bubble, re-orientate quickly, facilitating mineral-bubble attachment. This produces a stable 3-phase froth and strong tenacity of mineral-bubble attachment. An alternative explanation is that at the mineral-water interface the alkyl chains of frother and collector molecules are held together by van der Waals forces. Frothers are able to form a hydrogen bond with the oxygen atom in the collector molecule. These associations are only formed when a mineral is present^{30,31}. The frother's ability to interact with the collector is thus more significant than its surface activity which is required to produce a stable froth zone. This also explains why detergents are not suitable frothers. It has moreover often been shown that the collector can affect frothing properties and that the frother can affect mineral hydrophobicity.

The surface activity and thus frothability of the frother is very sensitive to the presence of small amounts of other substances, such as impurities or collector molecules. The chemical nature of certain combinations of frothers and collectors may result in interactions occurring at the point of collision between mineral particles and bubbles which have

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been shown to decrease the induction time, increase the attachment efficiency and increase the tenacity of attachment of the mineral to the bubble. The decreased induction time may result in improved kinetics of flotation and increased tenacity of the bubble-mineral bond which will result in better recoveries with less mineral detachment and elutriation.

Frother-frother interactions

It is common practice to use at least two different frothers to get the desired combination of the characteristics of each. For example, a frother with good physical frothing properties when mixed with a frother which interacts with the collector can result in a synergistically improved flotation performance. Mixtures of frothers of differing solubilities can also form more stable froths than either of the pure components. The properties of frothers can sometimes be additive with the mixing of stronger and weaker frothers to form medium strength frothers.

Synergistic interactions between thiol collectors—a case study

Synergistic enhancement of

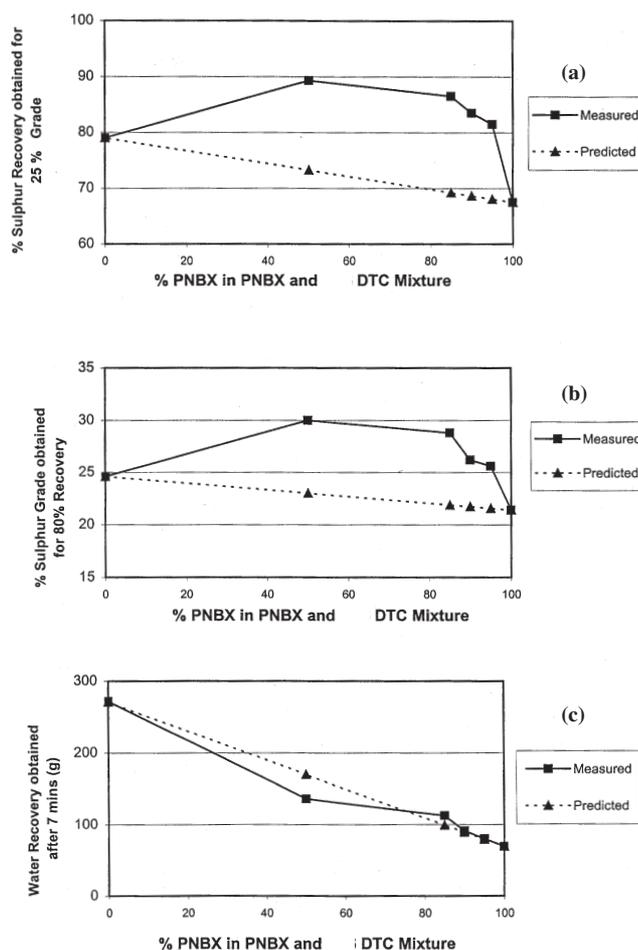


Figure 1—Comparison of measured vs predicted values from linearly additive mole ratio contribution of PNBX and DTC for (a) % sulphur recovery obtained for 25% grade, (b) grade obtained for 80% sulphur recovery and (c) water recovery

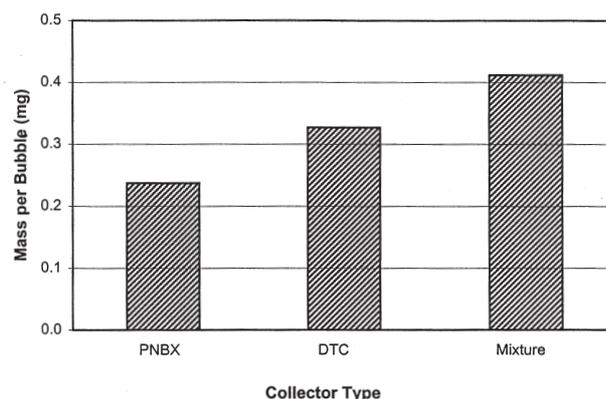


Figure 2—Pyrite loading per bubble with PNBX, DTC and 90:10 mixture of collectors

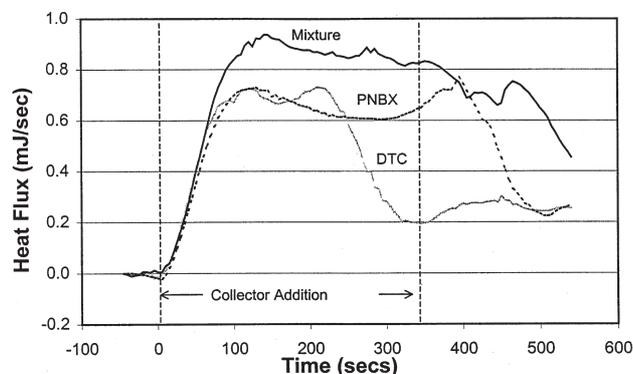


Figure 3—Effect of collector type on enthalpy change

flotation performance has been observed in batch flotation tests with a low grade pyrite ore using thiol collectors at pH = 4¹⁸. The collectors tested were potassium n-butyl xanthate (PNBX) and an alkyl dithiocarbamate (DTC). Performance was analysed using grade-recovery data as well as water and mass recoveries and the rate of sulphur recovery. The froth surface was analysed using digital image analysis. In all experiments the total molar concentration of collector was constant.

Figure 1 shows the batch flotation results as represented by

- the sulphur grade at 80% recovery,
- the sulphur recovery at 25% grade and
- the water recovery, all as a function of mole ratio of components.

It is clear that the grades and recoveries are greater than would be expected from a merely linearly additive effect and are synergistically enhanced. Obviously pure collectors may not show linearity with respect to dosages but in the present case the dosages were in the range where these differences were minimal. The change in water recovery however was linearly proportional to the molar contribution of the components and clearly the synergistic effect was only influencing the behaviour of the solid particles. Digital image analysis of the froth showed that when the mixture of collectors was used the froth was more mobile and the froth surface bubble size was larger. This may be due to the

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frother-collector interactions, decreasing froth stability, increasing drainage of entrained material and increasing the grades obtained.

In order to elucidate the mechanisms of synergism, the extent of bubble loading and the heats of adsorption were measured for the respective collectors and collector mixtures using pure pyrite at pH value of = 4. Figure 2 shows that increased bubble loading resulted from the use of a mixture of collectors and Figure 3 shows that when a mixture of collectors was used there was a stronger adsorption than in the case of the pure xanthate, where multilayer adsorption of dioxanthogen is indicated, and in the case of dithiocarbamate where pseudo-monolayer adsorption is indicated.

In this example the synergistic effect observed is attributed to increased mineral hydrophobicity which is thought to be due to the weakly adsorbing dioxanthogen adsorbing in multilayers around the strongly adsorbing dithiocarbamate which acts as a sort of anchor on the surface of the mineral particle. The ultimate result is an increase in bubble loading, an improvement in froth characteristics and a greater grade and recovery.

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