CHAPTER 3

COMPARISON OF DIFFERENT PYRRHOTITE DEPRESSANTS IN PENTLANDITE FLOTATION

3.1 INTRODUCTION

Due to the similarities in mineralogy and chemical composition, and as well as the pyrrhotite collectorless flotation, it is difficult to achieve a clean separation between pentlandite and pyrrhotite. Pyrrhotite rejections has been a long-standing problem in the nickel industry.

Nickel producers have been using a number of different strategies, sometimes in combination, to reject pyrrhotite. These include raising the pH of flotation to partially suppress pyrrhotite floatability (73), introducing separate pyrrhotite rejection circuits which by and large also exploit the fact that pyrrhotite floats poorly in alkaline solutions, and using magnetic separation to remove pyrrhotite from feed or concentrate streams (74, 75). These measures made significant improvements. For example, the pyrrhotite rejection at INCO's Thompson concentrator increased the pyrrhotite rejection from 5 to 60 percent (76). However, none is entirely satisfactory, as high levels of pyrrhotite rejection are invariably accompanied by unacceptable pentlandite losses.

This problem has prompted a search for more efficient ways of separating pentlandite from pyrrhotite. Several new procedures have been devised and some, such as the cyanide method (77) and the reverse flotation methods (78, 79), have been tested extensively. However, all of these new methods have turned out to have deficiencies. They either failed to lower pentlandite losses sufficiently, or they are too difficult or expensive to implement (74, 76). Thus, despite some improvements and much research, the fact remains that no cost effective procedure that gives high pentlandite recoveries and sufficiently selective rejection of pyrrhotite has yet emerged. Much of recent works to reduce SO_2 emissions has, therefore, been focused on sulfur capture and sulfuric acid production during smelting (76).

However, removing as much pyrrhotite as possible in flotation stage using effective pyrrhotite depressants is still a preferred choice for producers because of its low operation cost. Nevertheless, the use of a strong depressant typically entails high pentlandite losses. So looking for a new and better pyrrhotite depressant may be critical to solving the problem.

3.2 LITERATURE REVIEW

Diethylenetriamine (DETA) or some mixture of DETA with other reagents has recently come into commercial use for pyrrhotite depression as described by Kerr et al. (80) and Monticerano et al. (81). According to Yoon et al. (82), DETA works best under oxidizing conditions. After conducting flotation, LIMS, FTIR, XPS studies on the depression mechanism of DETA on pyrrhotite, they revealed that metal ions such as Cu^{2+} , Ni^{2+} and Ag^{+} in the plant water can activate the pyrrhotite flotation. The depressing action of DETA is based on removing the metal ions from the pyrrhotite surface through complex reactions. The activation products formed on pyrrhotite may be sulfides of Ni, Cu, Ag, etc., which are usually insoluble under reducing conditions. Under oxidizing conditions, the activation products may be converted to oxides, whose solubility may be further increased in the presence of DETA. In other words, DETA can improve the separation efficiency only when the feed was oxidized by aerative conditioning.

Kelebek et al. (83) studied pyrrhotite depression using SO_2/DETA combination. They found that DETA by itself failed to produce flotation selectivity with samples from plant and pilot plant streams (Strathcona mill, Canada), which showed relatively high redox potentials. They thought that ferric dihydroxy xanthate and dixanthogen formed on the pyrrhotite surface may be responsible for the poor depression effect when using DETA alone. The use of sulfur dioxide alone has also resulted in a rather poor depression of pyrrhotite. However, the combined use of these reagents has resulted in an efficient and consistent separation of pyrrhotite from pentlandite and chalcopyrite. They proposed a mechanism in which sulfur dioxide acts as a reactive component primarily for the destabilization and/or removal of hydrophobic films on pyrrhotite. Depending on the dosage used, the sulfur dioxide may also help in deactivation of the pyrrhotite surface by decreasing the surface concentration of Ni^{2+}, Cu^{2+} and Fe^{3+} species and increasing that of Fe^{2+} species, while it is transformed into an oxidized state. This provides a highly favorable condition for the action of DETA in converting the pyrrhotite surface from initially a rather hydrophobic state to a mostly hydrophilic state, and so depresses pyrrhotite. In another paper (84), they also proposed that the sulfur dioxide may form a complex, $[Ni(DETA)_2]S_2O_6$, which can adsorb on the surface of pentlandite and pyrrhotite and increases the differences in surface properties when xanthate is added to the system.

INCO also uses the mixture of DETA and SBMS to enhance the depression effect. Despite its effectiveness, DETA is costly to use. To find a replacement for DETA, Cytec Industries Inc. developed several polymeric pyrite/pyrrhotite depressants. Of the various products tested, S-7260 and S-7261 showed the best results in depressing pyrite during coal flotation (85).

The purpose of this research is to investigate the depression effect of two polymeric depressants (S-7260 and S-7261) developed by Cytec Industries by conventional flotation technique, and the possibility of replacing DETA with cheaper polymer depressants in pentlandite pyrrhotite flotation separation.

3.3 EXPERIMENTAL

3.3.1 Mineral Samples

A sample from the rod mill feed at the Strathcona concentrator, Falconbridge Ltd., was used for flotation tests. The ore sample was assayed about 2.5% Ni, 1.4% Cu and 18.6 % S. The ore sample that weighed about 1.2 kg was crushed first in a roller mill to -10 mesh and kept in a refrigerator for further treatment before flotation.

3.3.2 Reagent

Potassium amyl xanthate (KAX) was used as collector for pentlandite flotation. Dowfroth M-254 was used as frother and lime (calcium oxide) was used as pH regulator. Diethylenetriamine (DETA) (99% purity) was purchased from Aldrich Chemicals Co. and used after diluted to 1% solution. SMBS, sodium meta-bisulfite, used combining with DETA, was purchased from Fisher Scientific, NJ and used as received. Two polymeric depressants, i.e., S-7260 and S-7261, were obtained from Cytec and used after diluted to 1% solution. All flotation tests were conducted using tap water with pH adjusted to 9.0 - 9.5 using lime.

3.3.3 Test Procedure

a. <u>Grinding</u>: About 1.2 kg of the ore sample was wet-ground with 0.3 g lime and 780 ml tap water in a steel ball mill for 20 minutes.

b. <u>Magnetic pyrrhotite removing</u>: The mill product was placed in a 4 L flotation cell (or any other cell), and tap water was added to fill the volume. While the slurry was being agitated, a hand magnet was then immerged into the slurry to collect magnetic pyrrhotite on the magnet. This process was repeated until the magnet did not remain any more pyrrhotite. In this way, about 300 g of mineral was removed from the slurry.

c. <u>Flotation</u>: A Denver laboratory flotation machine with a 4 L cell was used in all flotation tests. The rotation speed of the agitator was set at 1500 rpm. The slurry was first aerated for 3 minutes so that the ore sample became oxidized.

After the aerate conditioning, the pH of the slurry was adjusted to 9.0-9.5 by adding lime (about 1.2 g). Then the collector and depressant were added in sequence or combination to the slurry and conditioned for a specific time. The frother is added and the froth flotation started. The detailed flotation procedure would be mentioned when we proceed to the specific test.

d. <u>Assay</u>: Sample of flotation concentrate and tails were collected, dried, weighed, and analyzed for the sulfur, nickel and cupper content in it. Nickel and copper were analyzed by AA, and sulfur was assayed using a Leco Sulfur Analyzer.

3.3.4 Calculation of Mineralogical Composition

The results of the chemical analyses were used to determine the mineralogical compositions of the feed, concentrate and tailings, which in turn were used to determine the pentlandite and pyrrhotite recovery. The following formulas, which were made available through the courtesy of INCO (86), were used to determine mineral contents. In these formulas, the Ni% in pyrrhotite is assumed to be 0.7% on average.

The pyrrhotite contents (*%Po*) were obtained as follows:

$$\%Po = -2.6107 \times \%Cu - 2.4131 \times \%Ni + 2.5857 \times \%S$$

In which *%Ni*, %Cu and %S are the weight percent of nickel, copper and sulfur, respectively. Likewise, the pentlandite content (*%Pn*) is given by the following formula:

$$\%Pn = 0.0513 \times \%Cu + 2.8565 \times \%Ni - 0.0509 \times \%S$$

The pentlandite and pyrrhotite units contained in each concentrate or tailing sample were calculated from the values of the mineral contents. Dividing the units by total units in the flotation feed, the flotation recovery of pentlandite and pyrrhotite were obtained. Adding up the recoveries of all concentrates in a flotation test, an accumulate recovery is obtained and plotted in figures.

3.4 RESULTS AND DISCUSSION

3.4.1 The effect of xanthate on pentlandite – pyrrhotite separation

Figure 3.1 shows the effect of collector (potassium amyl xanthate, PAX) on the selectivity of pentlandite and pyrrhotite separation, and the test procedures are shown in Table 3.1. To establish a baseline, initial tests were conducted without using collector. The open circles represent the results of the collectorless flotation tests, in which froth products were collected as a function of time using only a frother (Dowfroth M-254) in the amount of 20 g/t. As shown, pentlandite and pyrrhotite floated significantly without using a collector. As the pentlandite recovery increased with increasing flotation time, pyrrhotite recovery also gets increased. This finding suggests the following:

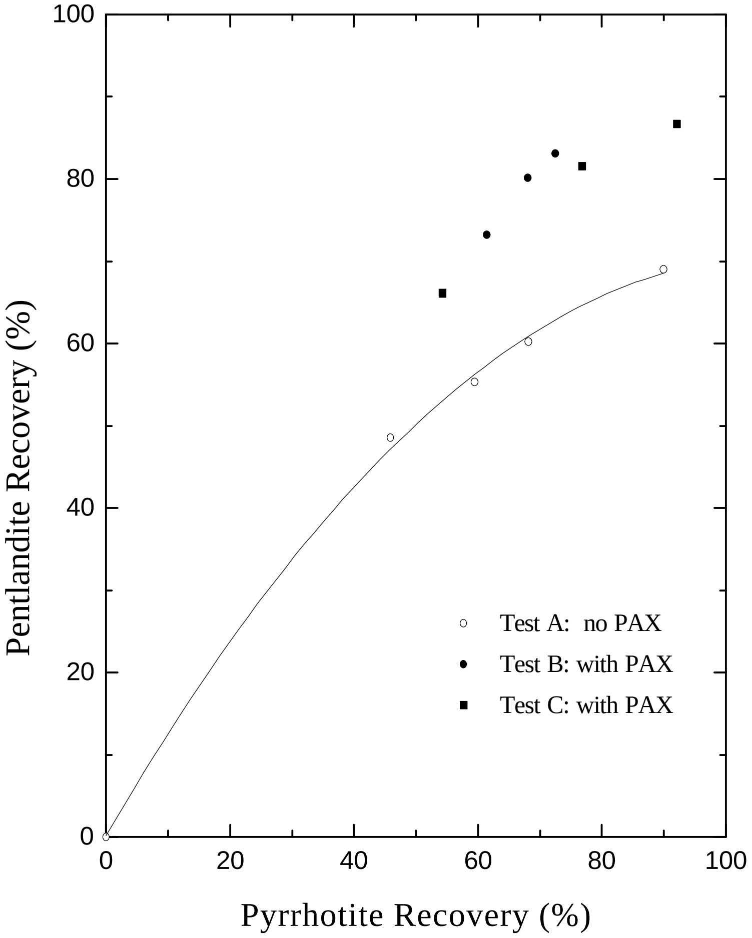

Figure 3.1. The effect of collector (PAX) on the separation selectivity on pentlandite flotation

Table 3.1 Flotation Procedure for Control Tests

(A)

				REAGENT		
operation	time min	% solids	pH	CaO g	PAX g/t	remark
grinding	20	61	6	0.2		
removing mag Po						
aeration	3	25	9.2	1.2		
add frother	1				0	
flotation	7.25					conc.1(0.75), 2(1.5), 3(5)

(B)

				REAGENT		
operation	time min	% solids	pH	CaO g	PAX g/t	remark
grinding	20	61	6	0.2		
removing mag Po						
aeration	3	25	9.2	1.2		
cond. W/PAX	3				260	
flotation	7.25					conc.1(0.75), 2(1.5), 3(5)

(C)

				REAGENT		
operation	time min	% solids	pH	CaO g	PAX g/t	remark
grinding	20	61	6	0.2		
removing mag Po						
aeration	3	25	9.2	1.2		
cond. W/PAX	3				150	
1st flotation	4					conc.1(1.5), 2(2.5)
cond. W/PAX	3				100	
2nd flotation	5					conc. 3

1. Both pentlandite and pyrrhotite float without collector.
2. Pentlandite and pyrrhotite were incompletely liberated from each other.

It is not certain which of the two was more prevalent, but it is likely that both were contributing to the difficulty in rejecting pyrrhotite. If the flotation tests had been conducted on a more finely ground feed, the second mechanism would not have played a significant role.

Hodgson and Agar (87) suggested that pyrrhotite (FeS) oxidizes to iron-hydroxy polysulfide as follow:

$$FeS + H_2O = Fe(OH)[S]^+ + H^+ + 2e \qquad [1]$$

The S^0 species in the polysulfide chain is considered to be responsible for the collectorless flotation, because elemental sulfur (S_8^0) is a well-known hydrophobic entity. In accordance with the work done by Yoon and his co-workers (88) for sulfide minerals in general, pyrrhotite oxidation may be represented by the following reaction:

$$nFeS = nFe^{2+} + S_n^{2-} + 2(n-1)e \qquad [2]$$

where S_n^{2-} is a polysulfide with a chain length of n, which is greater than 2. In a polysulfide chain, the sulfur atoms on both ends have a formal charge of -1, while those in the middle have a formal charge of 0. Only recently, the presence of polysulfide on oxidized sulfide minerals has been confirmed unambiguously by the synchrotron XPS which is substantially more sensitive than the conventional XPS (89).

Note here that the pentlandite recovery vs. pyrrhotite recovery curve shown in Figure 3.1 has a slope of roughly 1 at pyrrhotite recovery below approximately 60%, which means that there is practically no separation between the two minerals. However, the curve bends downward considerably at higher pyrrhotite recovery, indicating that pyrrhotite floats faster than pentlandite at longer flotation times; hence, gives rise to higher recoveries. One possible explanation is that pyrrhotite oxidizes more readily *via* reactions [1] or [2] than pentlandite. The difference in hydrophobicity, induced by superficial oxidation, between the two minerals may be small, but may become more discernible at longer flotation times.

The curve of the flotation results with xanthate has a slope only a little bit higher than 1, which means that there is only very limited separation between the two minerals. Comparing with the base line, the addition of collector (PAX) improved the recovery of pentlandite and pyrrhotite significantly. For example, at 69% pyrrhotite recovery level, the pentlandite recovery was increased from 60% to 80% with the addition of xanthate, represents a 33% improvement. It is clear that the addition of xanthate increased the rate of pentlandite flotation more significantly than in the pyrrhotite flotation, causing an increase in the ratio between the flotation rates for pentlandite and for pyrrhotite. It is the ratio between the flotation rates (or rate constants) that determines the selectivity in flotation and not necessarily the absolute values in flotation rates. Thus, the use of collector is advantageous for improving the selectivity in pentlandite flotation.

3.4.2 Flotation with compound depressant DETA/SMBS

Figure 3.2 shows the results of the flotation tests conducted using the compound pyrrhotite depressants, DETA/SMBS with different dosage of xanthate. Also shown in this figure for comparison are the baseline data, *i.e.*, the flotation results with xanthate only. The test procedures are shown in Table 3.2. When the dosage of xanthate is low, adding depressants did not improve the separation selectivity. As shown in the figure, the results (points A1 to A5) fall a little bit below the base line. Actually, there is no separation with the minerals happening in this case. However, adding more xanthate improved the separation selectivity significantly, as points B1 and B2 that shown in the figure, which has six times xanthate dosage as their corresponding points A2 and A3. From this figure, we can see that, at 36% pyrrhotite recovery level, the pentlandite recovery increased from 45% to 67%, which represent a 50% improvement.

The results also show that the xanthate dosage plays an important role in the depression of pyrrhotite. When the dosage is low, the floatability of both pentlandite and pyrrhotite are low, and adding depressant at this point only shifts the results to the left lower corner in the figure, meaning low pentlandite recovery and low pyrrhotite recovery. Only at higher xanthate dosage, the DETA/SMBS depressant shows significant selective depression on pyrrhotite.

3.4.3 Flotation with polymeric depressant S-7260

Fig. 3.3 shows the results of pentlandite - pyrrhotite separation with the use of polymer S-7260. Also shown in the figure is the base line obtained without using depressants. The test procedure is shown in Table 3.3. It shows that under the condition employed, the use of S-7260 did not improve the selectivity of the pentlandite - pyrrhotite separation, as the points 1, 2, 3, and 4 fall below the base line, except point 5. These results shows that 1) the xanthate dosage maybe too low, and/or (2) the dosage of S-7260 maybe too high. More tests on this polymer should be conducted in the future.

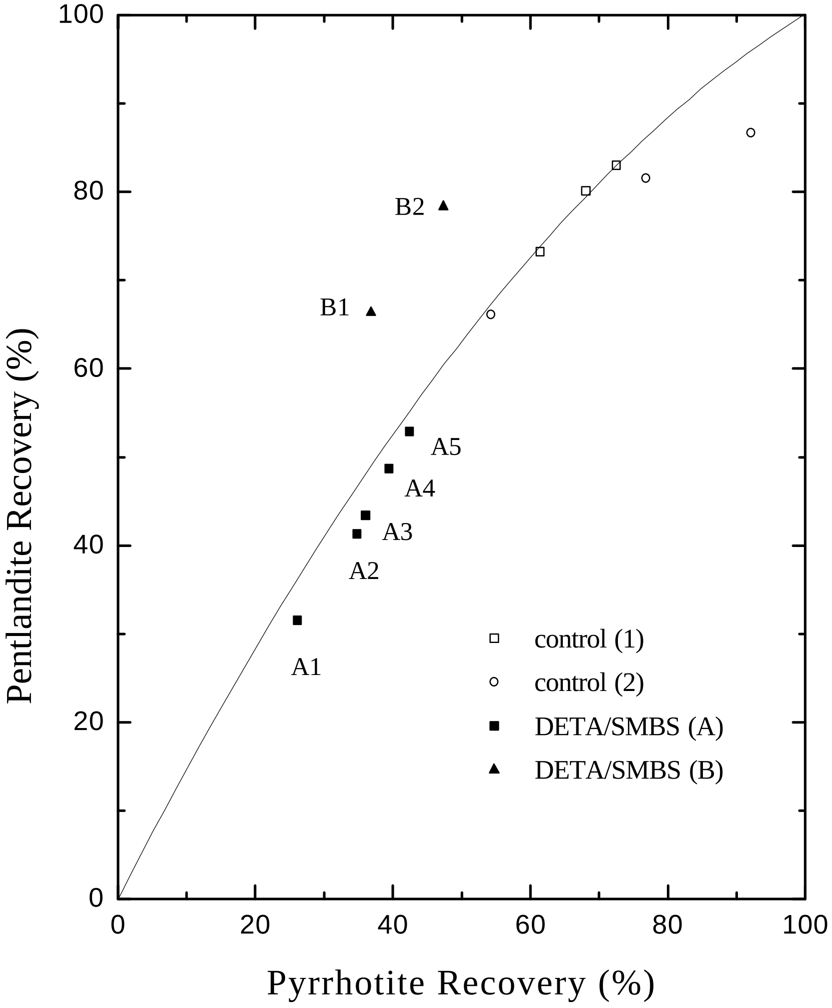

Figure 3.2. The effect of compound depressant DETA/SMBS on the separation selectivity on pentlandite flotation

Table 3.2 Flotation Procedure for DETA/SMBS Tests

(A)

				REAGENT				
operation	time min	% solids	pH	CaO g	PAX g/t	DETA g/t	SMBS g/t	remark
grinding	20	61	6	0.2	5			
removing mag Po								
aeration	3		9.2	1.2				
cond. W/reagents	3				2.5	100	250	condition together
1st ation	2.5							conc.1(1), 2(1.5)
cond. w/reagents	2				5	100	250	
2nd ation	2.5							conc. 3
cond. w/reagents	2				5	50	250	
3rd flotation	7							conc.4
cond. w/reagents	2				7.5	50	250	
4th flotation	13							conc.5

(B)

				REAGENT				
operation	time min	% solids	pH	CaO g	PAX g/t	DETA g/t	SMBS g/t	remark
grinding	20	61	6	0.2	30			
removing mag Po								
aeration	3		9.2	1.2				
cond. w/reagents	3				15	100	250	condition together
1st flotation	3							conc.1(3)
cond. w/reagents	2				30	100	250	
2nd flotation	5							conc. 2(5)

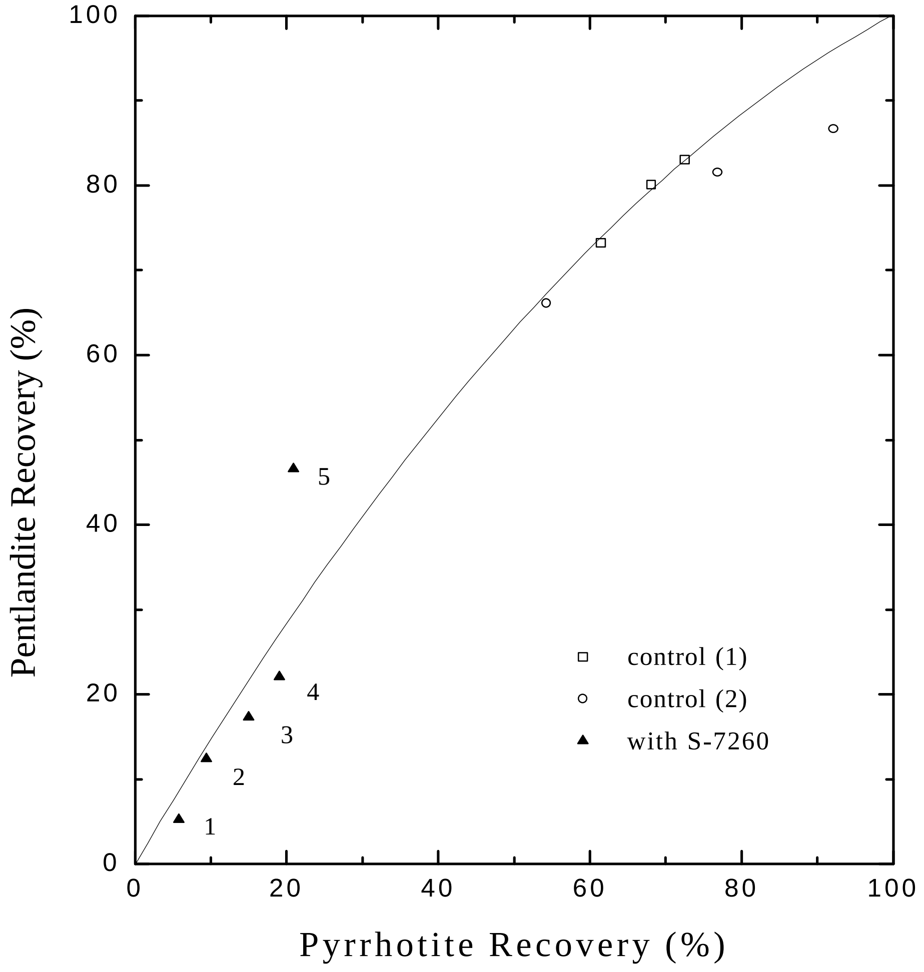

Figure 3.3 The effect of polymeric depressant S-7260 on the separation selectivity on pentlandite flotation

Table 3.3. Flotation Procedure for S-7260 Tests

				REAGENT			
operation	time min	% solids	pH	CaO g	PAX g/t	S-7260 g/t	remark
grinding	20	61	6	0.2	30		
removing mag Po							
aeration	3		9.2	1.2			
cond. w/reagents	3				15	120	condition together
1st flotation	2.5						conc.1(1), 2(1.5)
cond. w/reagents	2				30	120	
2nd flotation	2.5						conc. 3
cond. w/reagents	2				30	60	
3rd flotation	7						conc.4
cond. w/reagents	2				45	50	
4th flotation	13						conc.5

3.4.4 Flotation with polymeric depressant S-7261

Fig. 3.4 shows the results of pentlandite - pyrrhotite separation with the use of polymer S-7261. Also shown in the figure is the base line obtained without using depressants. The test procedures are shown in Table 3.4. Two tests, A and B, were conducted. Test B (points B1 and B2 as shown in the figure) uses the same collector dosage as points A2 and A3 in test A, but with a higher dosage of polymer S-7261. For test A, when the dosage of collector and depressant is low (point A1), it shows a significant improvement over the base line. For example, at 21% pyrrhotite recovery level, the pentlandite recovery increased from 30% to 49%. This represents a 63% improvement. However, this point is still not good enough. Although the pyrrhotite recovery is low (21%), the pentlandite recovery is also less than 50%. As the recovery is increased, as point A2, pyrrhotite recovery also increases, causing a decrease in selectivity. In general, increase in collector and depressant additions causes a decrease in selectivity..

At an appropriate xanthate dosage, a higher dosage of polymer depressant improves the separation selectivity. Point B1, which was obtained at the same dosage of xanthate as point A2 but at a higher dosage of S-7261, shifted to the left side of the figure, which means an improved selectivity. Comparing point B1 with point A2, although the pentlandite recovery (69%) is 15% lower, the pyrrhotite recovery is decreased from 64% to 28%. Point B2 (comparing with point A3) shows a similar trend. The pyrrhotite recovery is significantly decreased (from 77% to 48%) at the expense of only 4% of pentlandite recovery.

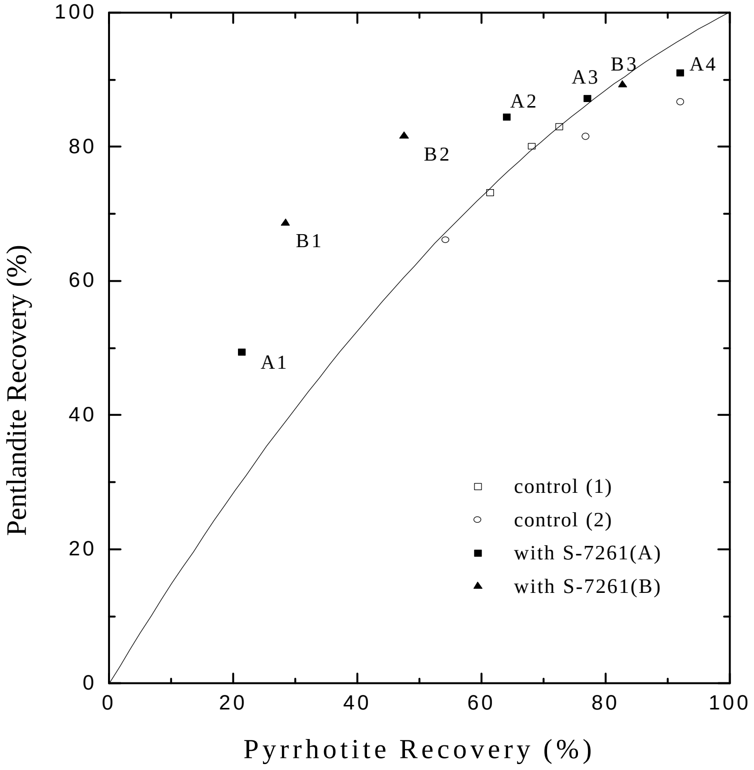

Figure 3.4. The effect of polymeric depressant S-7261 on the separation selectivity on pentlandite flotation

Table 3.4. Flotation Procedure for S-7261 Tests

(A)

				REAGENT			
operation	time min	% solids	pH	CaO g	PAX g/t	S-7261 g/t	remark
grinding	20	61	6	0.2			
removing mag Po							
aeration	3		9.2	1.2			
cond. w/PAX	3				150		condition together
cond. w/S-7261	5					200	
1st flotation	2.5						conc.A1(1), A2(1.5)
cond. w/PAX	3				100		
cond. w/S-7261	5					50	
2nd flotation	3						conc. A3
cond. w/PAX	3				50		
3rd flotation	3						conc.A4

(B)

				REAGENT			
operation	time min	% solids	pH	CaO g	PAX g/t	S-7261 g/t	remark
grinding	20	61	6	0.2			
removing mag Po							
aeration	3	25	9.2	1.2			
cond. w/PAX	3				150		condition together
cond. w/S-7261	5					300	
1st flotation	4.5						conc.B1(1.5), B2(3)
cond. w/PAX	3				100		
cond. w/S-7261	5					100	
2nd flotation	5						conc. B3

3.4.5 Discussion

a. The interaction of xanthate with pentlandite and pyrrhotite

According to Hodgson and Agar (87), the xanthate adsorption mechanisms on pentlandite and pyrrhotite are different. For pentlandite, it was concluded that the xanthate interacts with the mineral and renders it hydrophobic through chemisorption followed by chemisorbed xanthate oxidizing to form dixanthogen. As shown below, the formation of dixanthogen was considered to originate from chemisorbed xanthate on the pentlandite surface:

$$2X^- \rightarrow 2X_{ad} + 2e$$

$$2X_{ad} \rightarrow X_2$$

The formation of dixanthogen would occur concurrently with the adsorption of xanthate on the pentlandite during the progressive oxidation process.

Aeration, or surface oxidation of pentlandite, which may occur via the following reaction (87):

$$Fe_{4.5}\,Ni_{4.5}\,S_8 = Fe_{4.5-x}\,Ni_{4.5-x}\,S_8 + xFe^{2+} + xNi^{2+} + 4xe$$

can also promote hydrophobicity on pentlandite as it forms a more hydrophobic sulfur-rich surface.

Hodgson and Agar (87) showed that xanthate chemisorption does not occur on pyrrhotite. It adsorbs on the pyrrhotite surface through coulombic attraction with the cationic iron (III) site generated through oxidation of the mineral surface as follows:

$$FeS + 2H_2 O = Fe(OH)[S]^+ + 2H^+ + 2e$$

Then, xanthate adsorbson the position site as follows:

$$Fe(OH)[S]+ X^- = Fe(OH)[S] X$$

The xanthate adsorbed as such is further oxidized to dixanthogen by oxygen via a mixed potential reaction:

$$2X^- = X_2 + 2e$$

$$O_2 + 2H_2 O + 4e = 4OH^-$$

Studies show that dixanthogen was the species which conferred hydrophobicity on the surface of pyrrhotite, and its formation was related to the oxidation of pyrrhotite. Thus, the oxidation of mineral was required to produce a suitable site for dixanthogen adsorption. Another research shows that the formation of nickel xanthate facilitated dixanthogen formation.

b. The depression mechanism of DETA

Various forms of nickel and copper ions are released to flotation pulp from sulfides minerals during mining and mineral processing operations. They can be adsorbed on sulfide particles, causing difficulties in flotation. This heavy metal ion adsorption has been confirmed by results obtained with the laser ionization mass spectrometry technique. These surface species will induce xanthate adsorption on pyrrhotite.

According to the research of Kelebek (90), under the Eh-pH conditions for collectorless flotation, DETA forms a variety of chelates with Ni(II) and Cu(II) ions. In the presence of DETA, pyrrhotite will be deactivated owing to the sequestering action of DETA on Ni(II) and Cu(II) ions and its natural reactivation will be minimized (84). Yoon and his co-workers (82) also proved that DETA depress pyrrhotite by chelating the activation metallic ions such as Ni (II), Cu(II), Ag(I), etc.

On the other hand, it appears that DETA may enhance the self hydrophobicity of chalcopyrite and pentlandite by complexing the metallic ions adsorbed on the pentlandite surface and exposing more of the sulfur-rich surface sites for bubble contact in flotation through chelating Ni and Cu ions.

c. The mechanism of pyrrhotite depression with polymers

The adsorption of polymers on mineral surfaces can either be physical or chemical or both. The physical forces include the following:

- Electrostatic forces: these result in the adsorption of polyelectrolyte onto any surface of opposite charge, irrespective of their chemical nature.

- Dipole-dipole attraction forces.
- London-van der Waals forces: in these, neutral molecules or atoms constitute systems of oscillating charges producing synchronized dipoles that attract each other.
- Hydrophobic association: this is characterized by the tendency of nonpolar molecular groups to escape from aqueous phase.

And the chemical forces, which result in chemisorption, include the following:

- Chemical bonding: this is exemplified by reactions of the polymer groups with metallic sites on the solid surface which result in the formation of insoluble compounds by covalent or ionic bonding.
- Coordination bonding: this includes chelating or complex formation resulting in polymer attachment to a surface.
- Hydrogen bonding: in the organic compounds where the hydrogen atom is combined with a strongly electronegative atom (such as O, S, N), the hydrogen atom is able to accept electrons from atoms on the solid surface, such as from the -OH groups of an oxide mineral, resulting in the formation of a hydrogen bond.

In the xanthate/pentlandite or xanthate/pyrrhotite system, the xanthate molecules first adsorb on the mineral surface and are further oxidized to dixanthogen, thus render the mineral surface hydrophobic. When the polymer is added to the system, the polymer molecules adsorb on the mineral surface through the hydrophobic interaction of the hydrocarbon chains between the xanthate molecule and polymer molecules, and thus depress the mineral (pyrrhotite). More tests and spectroscopic studies are necessary to verify this hypothesis.