

# CHAPTER 1

## INTRODUCTION

### PREAMBLE

#### 1.1 Coal desulfurization

Coal is an important energy source, providing 57% of the electric power generated in the United States. The combustion of coal, however, can produce a serious environmental threat due to the impurities, especially the sulfur in the coal (1). Coal sulfur mainly exists in three different forms: pyritic sulfur, organic sulfur and sulfate sulfur. Pyritic sulfur, which comes from sulfide minerals, is the major component of coal sulfur. Organic sulfur, which can be found in the forms of mercaptan, sulfide or thio-ether, disulfide, or aromatic systems containing the thiophene ring, is chemically linked to the coal structure rendering physical coal cleaning processes useless in its removal. Sulfate sulfur, which exists in coal due to weathering or oxidation, is present in very small amounts, usually less than 1%. Fresh coals usually contain almost no sulfate sulfur.

Pyritic sulfur in coal includes iron disulfides such as pyrite and marcasite ( $\text{FeS}_2$ ), plus many other inorganic sulfides, i.e. galena ( $\text{PbS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), and sphalerite ( $\text{ZnS}$ ) (2). Differences in the environment, in which pyrite is formed, results in large variations in its morphology and size distribution in coal structure (3). Its occurrences may be found as finely disseminated particles, framboids or groups of individual crystals, and amorphous or structureless pyrite (4).

The new Clean Air Act (5) required that all utilities reduce their emissions to below 1.2 lb. SO<sub>2</sub> /MM Btu and cut the sulfur dioxide emissions by 50% by the year 2000 comparing with present emissions. To meet this requirement, coal must be cleaned before use, and new and effective flotation depressants for coal pyrite must be developed to improve the efficiency in coal desulfurization.

### 1.2 Removing pyrrhotite from pentlandite concentrate

Pentlandite is the major source of nickel. Unfortunately, pentlandite occurs in complex sulfide ores containing other sulfide minerals, such as pyrrhotite and chalcopyrite, and various silicate gangue minerals. Fig. 1.1 shows, as an example, the composition of the Sudbury ore. It contains 5% pentlandite, 20% pyrrhotite, 3% chalcopyrite and 55% silicate. As far as the sulfur in the ore is concerned, the amount associated with pyrrhotite is about 50 times higher than with pentlandite. Smelting nickeliferous pyrrhotite produces large amount of SO<sub>2</sub> but relatively little nickel. As more stringent limits are imposed on SO<sub>2</sub> emissions from smelters, it is necessary to reduce the amount of pyrrhotite in pentlandite concentrate (6, 7). The trend to cut SO<sub>2</sub> emissions is likely to continue and to spread worldwide with the result that efficient rejection of pyrrhotite is becoming increasingly important. So the flotation rejection of pyrrhotite from pentlandite concentrates that are fed to smelters is important in minimizing the sulfur dioxide emissions.

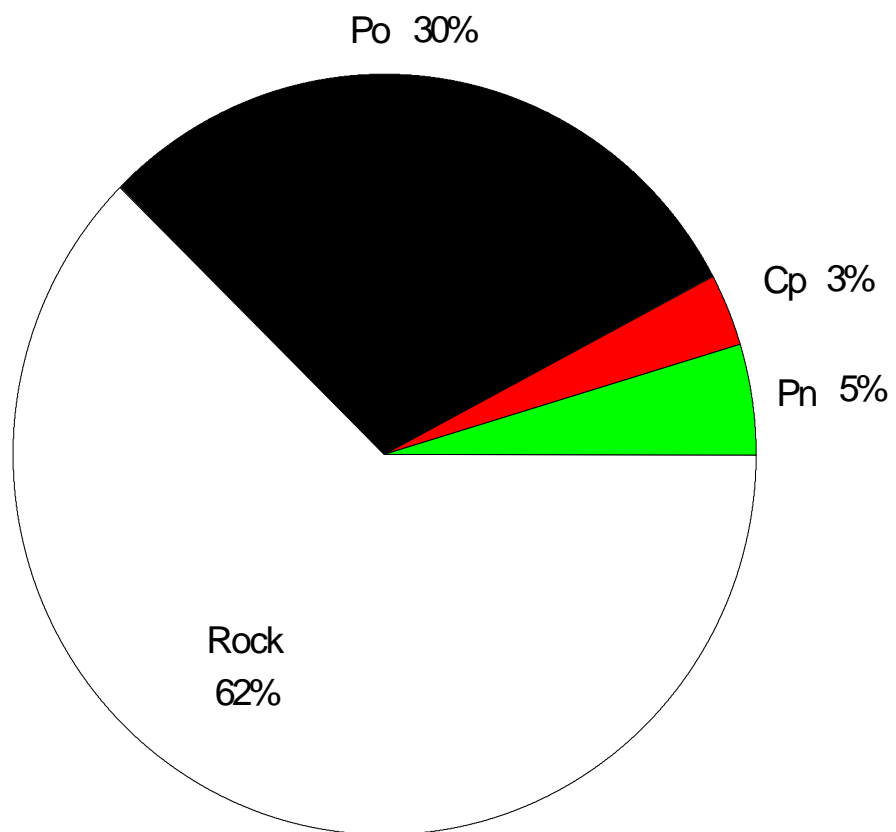


Fig. 1.1 The diagram of composition of Canada Sudbury ore (8).

## **OBJECTIVES**

The main objective of the present investigation is to study the effect of using Cytec polymers as depressants for pyrite during coal flotation and for pyrrhotite during pentlandite flotation. Since the depression mechanism may involve hydrophobic interaction between the hydrophobic moieties of the polymer depressants and the xanthate coated mineral surfaces, hydrophobic force measurements were conducted between gold sphere and gold plate in xanthate solutions using an Atomic Force Microscope (AFM).

The objective of the present investigation is sub-divided into three parts:

1. To evaluate the effectiveness of various polymeric depressants developed by Cytec Industries for the coal-desulfurization. To meet this objective, a series of flotation tests were conducted, in which the performance of 11 polymeric depressants were compared with each other, and then several reagents were selected for further intensive studies to determine the best polymer for pyrite depression and to determine the optimum dosages for flotation separation.
2. To study the effects of using two Cytec polymers for the depression of pyrrhotite, and compare the results with the performance of Diethylenetriamine ( DETA).
3. To measure the hydrophobic forces between xanthate coated gold surfaces using an AFM to identify the species that render the surface hydrophobic.

## **ORGANIZATION OF THE REPORT**

This thesis is organized in the form of independent chapters, each dealing with a particular objective of this investigation. Chapter 2 discusses the depression effect of polymeric depressants on the coal desulfurization using column and conventional flotation techniques. Chapter 3 describes the flotation separation of pyrrhotite from pentlandite, using polymeric depressants and DETA, and their depression effects were compared. In chapter 4, the adsorption mechanism of xanthate on the gold surface was studied using AFM. Chapter 5 and 6 are summary and future work, respectively.

## CHAPTER 2

### COAL DESULFURIZATION USING POLYMERIC DEPRESSANTS

#### **2.1 INTRODUCTION**

##### 2.1.1 Coal preparation

To meet the stringent requirements of the 1990 Clean Air Act Amendments (5), various physical and chemical processes have been developed to remove the various forms of sulfur from coal. Chemical cleaning processes are usually based on the principle of selective oxidation of the organic sulfur over the hydrocarbons. Some of the chemical cleaning processes can also remove pyritic sulfur and ash-forming minerals. The chemical cleaning processes that received more attention in the literature (9, 10, 11, 12) include: the Molten Caustic Leaching (MCL) process, the Mayers process, Oxydesulfurization process, Chlorinolysis, the KVB process and microwave desulfurization. Although many of these processes can remove organic sulfur that can not be removed by physical coal cleaning processes, their cost is high (between \$25 to \$35 per ton) (13) and their applications are limited at present time.

Coal desulfurization by means of bacteria, or biological desulfurization, has also been studied by several investigators. A number of bacteria were found capable of leaching out pyrite (14), or degrading some organic sulfur compounds in coal (15, 16, 17). Some microorganisms, like thiobacillus ferrooxidans, can selectively adsorb on coal pyrite and ash forming minerals, rendering them hydrophilic (18).

Despite the promising application potential for chemical process and biological process, for the removing of pyritic sulfur and ash-forming minerals, physical methods are the best choice considering the economics and effectiveness of the process.

#### 2.1.2. Coal desulfurization by physical methods

The methods of physical removal of ash-forming minerals and pyritic sulfur used today includes: gravity separation, magnetic separation, electrostatic separation, oil agglomeration, flotation, etc. These separation techniques are based on the differences in physical and surface chemistry characteristics, such as specific gravity, magnetic susceptibility, electric conductivity and surface hydrophobicity of coal and coal minerals.

##### 2.1.2.1. Gravity separation technique

Gravity separation, which takes the advantage of the differences in specific gravity between coal and mineral matters (ash-forming minerals and pyrite), are widely used in the coal preparation (19-23). Among gravity separation techniques, dense medium process may be the most prevalent used. Other gravity separation techniques include: centrifugal, jig, landers, etc. Despite its efficiency in ash removal for relatively coarse coal, they are not so useful in fine coal cleaning and coal desulfurization. The reasons are mainly that (1) Gravity beneficiation for coal usually requires feed size larger than 0.5 mm; (2) Sulfur minerals are usually finely disseminated in coal matrix and can be liberated only by grinding to a finer size. To achieve effective coal desulfurization, many U.S. coals must be micronized to free the finely disseminated pyrite particles (24, 25, 26). The small

sizes produced through grinding inhibit the separation of coal and pyrite using gravity techniques as the gravitational effects are lessened. The development of an enhanced gravity concentrator such as Mozley Multi-Gravity Separator (MGS), which is successful to concentrate cassiterite, chromite, etc., shows promise in fine coal treatment (27, 28, 29).

#### 2.1.2.2 Magnetic and electrostatic separation

Since the magnetic properties of pyrite and several other minerals found in coal differ slightly from those of the organic matter, i.e., coal is weakly diamagnetic while pyrite and the ash forming minerals are weakly paramagnetic, there is a possibility of separating these components by magnetic methods (30). However, because the difference in magnetic susceptibility between the components is very small, the separation requires the combination of an intense magnetic field and a large field gradient. The wet High Gradient Magnetic Separation (HGMS) has been applied successfully to fulfill this requirement (31, 32). To improve the separation efficiency, various methods, like agglomerating pyrite, microwave heating and etc., were proposed to improve the magnetic susceptibility of pyrite (30, 32, 33). The dry process was also reported (32).

Electrostatic separation utilizes the difference in conductivity or dielectric properties of coal and minerals to maintain or dissipate an induced charge under dynamic conditions. As a dry process, this technique could circumvent the problems associated with water removal following fine coal cleaning. Its principle lies in that coal is generally less conducting than the ash forming minerals, with pyrite the most conducting (34).



There are two mechanisms for particle charging: corona charging mechanism and triboelectric charging mechanism. In corona charging mechanism, all particles are charged but lose the charge at different rates, depending on their conductivity, and are separated based on the difference in remaining charge. In triboelectric charging (friction or contact), clean coal generally charges positively and ash forming minerals charge negatively to make the separation (35). The second charging mechanism shows more promising applications in recent years (36-39).

#### 2.1.2.3 Oil Agglomeration

Oil agglomeration is a process for removing particles from liquid suspension by selective wetting and agglomeration with a specific oil (40). The process relies on the difference in the surface properties of coal and minerals in slurry. The oil is added to the suspension, which is agitated vigorously causing the oil to be dispersed into droplets. These droplets become attached to coal particles which are essentially hydrophobic in nature. The partially oil-coated particles stick together and form relatively large flocs or agglomerates which can be recovered on a screen. Most mineral particles are unaffected and consequently not recovered. The oil agglomeration method is controlled by a number of factors including the surface properties of the coal and its associated minerals, particle size, type and amount of oil, temperature and pH of the aqueous medium, and the type and intensity of agitation (41). Comparing with flotation, this method offers several advantages (42). First, it can be used to separate and recover even the smallest coal particles. Second, as the oil addition help dewater the product coal. It can produce a

dense, coarse granular product of acceptable strength which makes it easy to separate the coal agglomerates from the ash-forming minerals. It can be applied to oxidized coal and other type of coal which do not respond well to froth flotation. On the other hand, it provides perhaps the only practical means for upgrading extremely fine coal to useful products on a large scale (43). One problem with this method is that while most minerals found in coal are hydrophilic and do not become oil-coated, pyrite is readily wetted by fuel oil and agglomerated due to its weakly hydrophobic surface property. Some methods, such as bacteria treatment (18), or putting the material in a warm alkaline solution with air to oxidize the pyrite surface (44), have been proposed to attack this problem.

#### 2.1.2.4 Flotation

Flotation separation, which is realized using the differences in surface properties of the minerals, is the most widely used physical separation technique in the mineral industry (45). More than 400 million tons of ores treated annually in the US are by flotation (46). This technique has been getting more and more application in coal industry. In today's coal cleaning industry, it is very typical to use flotation separation to clean the coal fine, and it is the only commonly used preparation method that can effectively recover coal particles finer than -200 mesh. Roughly, about 50% of US preparation plants use flotation to process at least a portion of the raw coal feed (47).

In coal flotation, the hydrophobicity difference between coal and other minerals is the driving force to separate pyrite and ash forming minerals from coal. People generally believe that coal is more hydrophobic than the mineral matters in nature, so when the air

bubbles rise through the pulp, the coal is selectively floated and leaving the mineral matter (ash and pyrite) as tailings. However, due to insufficient liberation of pyrite from coal middling (48-52), entrainment and entrapment (53-57) and the surface oxidation of coal pyrite (51, 58, 59, 60), the actual scene is much different. One research showed that the most advanced coal cleaning processes can not reject more than 90% pyrite (61).

Chemical reagents always play a key role in improving the separation efficiency of flotation (62). In sulfide flotation, the flotation behavior of pyrite is well studied and a series of effective pyrite depressants have been developed. However, these depressants do not show effectiveness in coal desulfurization. The reason is that although coal pyrite and mineral pyrite share the same overall chemical formula and crystal structure, their behavior is definitely different. One main cause of these differences appears to be the carbonaceous material in the coal pyrite. This material impregnates the pyrite structure and as a result lowers the apparent specific gravity, increases the porosity, and imparts a dark coloration to the coal pyrite. Another cause may be the different surface chemical property of coal-pyrite with ore-pyrite. According to Lai et al. (58), mineral pyrite is electroactive towards oxygen reduction, while the coal pyrite is not. Chernosky et al. (59) studied xanthate adsorption characteristics of coal-pyrite and ore-pyrite and revealed that there are basic chemical and physical differences in the ore and coal pyrite studied. Their flotation response as a function of pH is drastically different. Another research conducted by Yoon et al. (51) showed that the induction time of coal pyrite was higher by an order of magnitude than those of mineral pyrite. As a result, the coal pyrite did not float well. Their XPS measurements suggested that either the coal pyrite sample had already

contained some oxide/hydroxides before oxidation, or it had oxidized faster than the mineral pyrite. However, in the presence of frother and hydrocarbon collectors, the floatability of coal pyrite increase drastically. The research conducted by Jiang et al. (60) supported Yoon's conclusion. They found that the presence of non-polar collector enhance the floatability of coal pyrite drastically and thereby reducing the selectivity of flotation separation. These reagents may adsorb on the weakly hydrophobic pyrite surface through the hydrophobic interaction force. For lower rank coals which float poorly, large dosage of collector and frother is required to recover the combustible component, pyrite rejection is further deteriorated.

Lots of efforts have been made to find effective coal pyrite depressants to improve the efficiency of coal desulfurization. It is known that to depress coal pyrite, a depressant molecule should adsorb specifically on the surface of pyrite and render the pyrite surface hydrophilic, and thus improve the efficacy of coal desulfurization (63). Numerous coal pyrite depressants have been investigated in the past (64). Classic works by Yancey and Taylor (65) and Zimmerman (66) demonstrated that lime and hydroxyl ion additions decreased the sulfur content of coal froths, while acid additions decreased the ash content. Yancey also found that selected oxidizing and reducing agents were effective as pyrite depressants. Miller (67) reported that lime, coupled with froth sprinkling, decreases the pyritic sulfur and ash content of clean coal significantly. Choudhry and Aplan (68) delineated 11 different depressant systems for the rejection of pyrite during coal flotation. Lots of studies revealed that coal source pyrite was much more difficult to depress than ore pyrite, and the commonly used depressants for ore pyrite were often not effective for

coal pyrite (69), especially when non-polar collectors such as fuel oil and kerosene were used in the floatation of coal. So until today, people still have not found a depressant in coal flotation which can depress pyrite effectively, but still keep a high combustible recovery at the same time. This prompted the study for a more effective pyrite depressants for coal desulfurization.

### 2.1.3. The objective of current research

Polymeric depressants have been used successfully in processing minerals by froth flotation (62). Different functional groups show different depression effects in their applications. In the present study, several functional synthetic polymeric depressants for pyrite were investigated to identify the best function group and to establish optimum dosages on Pittsburgh No. 8 coal and Illinois No. 6 coal samples.

## **2.2 EXPERIMENTAL**

### *2.2.1. Coal samples*

Two coal samples from Pittsburgh No. 8 and Illinois no. 6 seams were used in this investigation. Table 2.1 shows analytical data of the samples. The samples were received as coarse lumps in 1 to 3 inches in diameter. Before flotation tests, the samples were first ground to minus 3/8 inch using a laboratory roll crusher, and then pulverized to 95%

passing 100 mesh in a laboratory hammer mill. The resulting samples were then sealed and stored in a refrigerator at -20° C to minimize oxidation.

Table 2.1. The composition of the coal samples

	Volatile %	Ash %	Total Sulfur %	Pyrite sulfur %	Fixed Carbon %
Pitts. No. 8	37.13	12.58	3.55	1.54	50.38
Illinois No. 6	24.71	44.52	4.87	3.09	31.02

### 2.2.2. Reagents

Kerosene and M-150 were used as collector and frother in the flotation tests, respectively. Polymeric depressants were used as received after diluted in double-stilled water. The eleven different polymeric depressants were essentially polyacrylamides to which various functional groups were attached. Tap water was used in flotation tests.

### 2.2.3. Flotation Procedure

#### a. Column flotation

A 3/4 inch diameter microbubble flotation column with height of 25 inch was used in this investigation. Figure 2.1 shows the apparatus. A coal slurry conditioned with the desired collector and/or depressant was fed to the column using a peristaltic pump (B). Counter current wash water was added to the column through a wash water inlet (D). The flow rate was controlled with a valve and measured through a flow meter (E). The microbubbles were produced by feeding the frother solution from a frother tank (H) to the column by means of a peristaltic pump (I). A portion of the pulp was recirculated from

the bottom of the column along with air through a variable speed centrifugal pump (G) to aid in the formation of microbubbles.

The concentrate froth (product) was collected in the froth launder (J). The tailings were removed from the column through a peristaltic pump (K) at the bottom of the column. By controlling the speed of the tailing pump (K), it was possible to control the height of the froth zone and retention time.

For each test, about 1.5 kg of the ground coal sample was mixed with tap water to prepare a feed slurry at 8% solids (by weight). The slurry was agitated for five minutes before a depressant was added for five minutes of conditioning. After conditioning with a depressant alone, a known amount of kerosene was added, and the slurry was conditioned for another three minutes. When the flotation test is stabilized, i.e., the process reaches a steady state and a stable froth zone is formed, representative samples were taken from the feed, concentrates and tailings stream, respectively. The samples were filtered and dried for analyses.

For the screening tests conducted with the Pittsburgh No. 8 coal sample, depressants were used in the range of 100-500 g/t, while the collector dosage was fixed at 400 g/t. For the Illinois No. 6 coal samples, the dosage rate for the depressants were reduced to 50-300 g/t, but the collector dosage was increased to 800 g/t based on a previous work. M-150 was used as frother in all column flotation tests.

#### b. Conventional flotation

A Denver laboratory flotation machine with a 1.2 L cell was used in conventional flotation tests. For each test, 100 g of the ground coal sample was mixed with 1000 ml tap water and stirred for 5 minutes to prepare a feed slurry. A desired amount of depressant solution was added and conditioned for 5 minutes. Then a known amount of kerosene was added, and the slurry conditioned for another 3 minutes. After that, an appropriate amount of Dowfroth M-150 was added to the slurry before commencing flotation test. The froth product and the tailings were collected, and then filtered and dried to determine their total sulfur, pyritic sulfur, ash and fixed carbon contents.



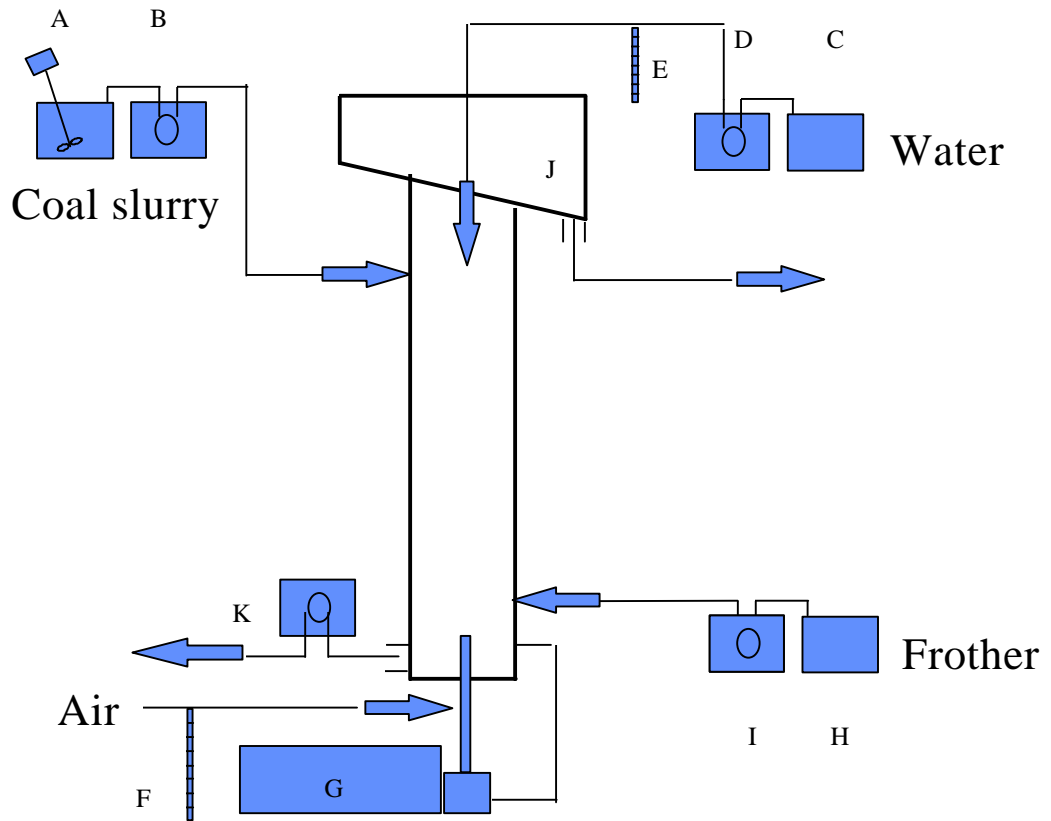


Fig. 2.1. Schematic drawing of flotation column

## **2.3 RESULTS**

### 2.3.1 Effect of Collector Addition on Pyrite Rejection

Fig. 2.2 shows the plots of the total sulfur-rejections vs. combustible recoveries for Pittsburgh No. 8 coal with and without the addition of collector (kerosene). No depressants were added in these tests. It can be seen that the flotation selectivity decreases with the addition of kerosene. Decreased selectivity obtained with the addition of kerosene could be due to the adsorption of the non-polar kerosene molecules on the surface of pyrite, which showed increase the hydrophobicity of pyrite. In this way, the difference between the floatability of coal and pyrite decreased and the flotation selectivity deteriorated.

The effect of collector (kerosene) addition on total sulfur rejection for Illinois No. 6 coal samples is shown in Fig. 2.3. The tests were conducted without using depressant. The results show similar trends as with the Pittsburgh No. 8 coal samples. Comparing with Pittsburgh No. 8 coal sample, the combustible recovery with Illinois No. 6 coal is much lower. This means that the floatability of Illinois No. 6 coal is lower than the Pittsburgh No. 8 coal.

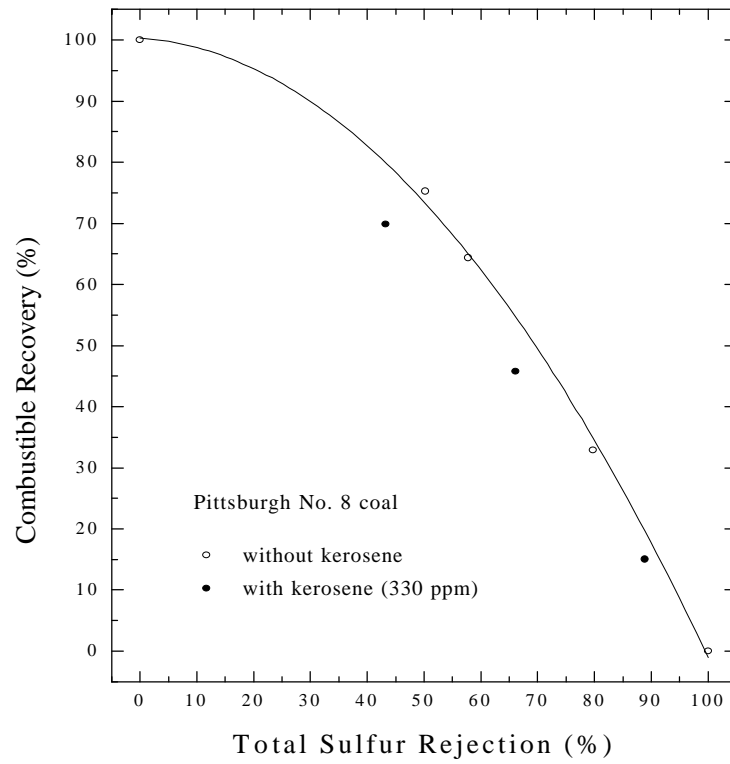


Fig. 2.2 Effect of kerosene addition on the total sulfur rejection from Pittsburgh No. 8 coal samples

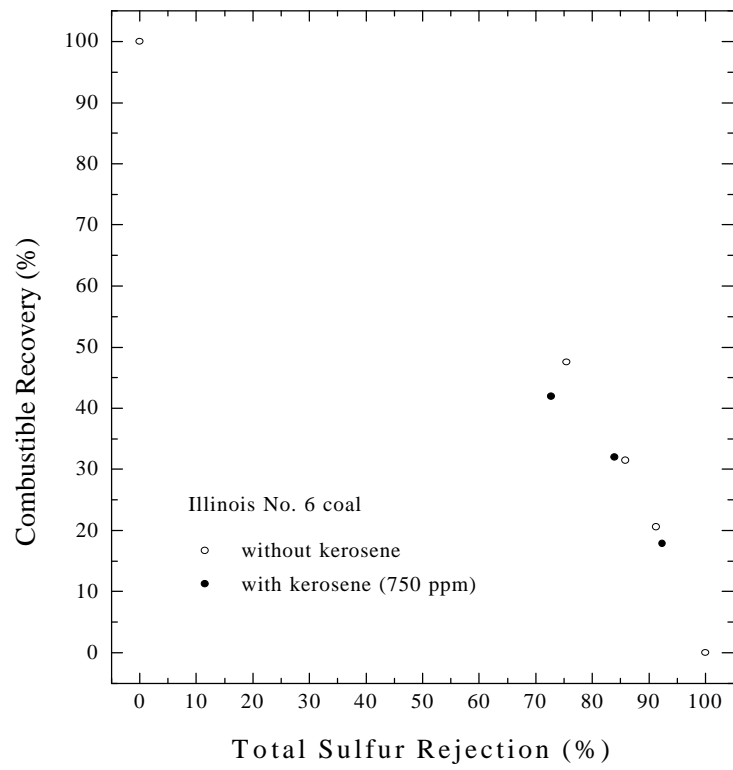
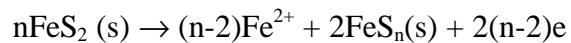


Fig. 2.3 Effect of kerosene addition on the total sulfur rejection from Illinois No. 6 coal samples

### 2.3.2 Effect of Polymer when no Kerosene Added

Fig. 2.4 shows the effect of the 11 polymeric depressants on total sulfur rejection with no kerosene added to the flotation cell for the Pittsburgh No. 8 coal sample. Fig. 2.5 is for Illinois No. 6 coal sample. Based on previous work, the depressant dosage was set at 120 ppm for Pittsburgh No. 8 coal samples and 60 ppm for Illinois No. 6 coal samples, respectively. There was no significant improvement in total sulfur- or pyritic sulfur-rejection observed with the use of any of the depressants. And there is not much difference in coal-pyrite rejection among the 11 polymeric depressants.

There are three factors that may be involved in influencing the flotation behavior of coal pyrite (70). (1) Surface coverage of hydrocarbon content. Scanning electronmicroscope (SEM) analysis indicated a considerable proportion of the hydrocarbon content of coal-pyrite was present on the surface. Systematic scanning of the coal pyrite particles showed that more than 90% of the surface was covered with a thin layer of hydrocarbon. (2) Sulfur enrichment on coal pyrite surface. EDAX determination of the S/Fe stoichiometry of different pyrite showed that coal pyrite had higher sulfur content than mineral pyrite. Sulfur enrichment probably imparts additional hydrophobicity to coal pyrite. (3) Surface oxidation of coal pyrite. According to Yoon (71), coal pyrite may be oxidized by the following mechanism:



in which  $n > 2$  and  $\text{FeS}_n$  represents the iron polysulfides formed on the surface. The  $\text{S}^0$ -like species produced during oxidation constitutes part of the polysulfide chain, and renders the surface hydrophobic. In general, the longer the polysulfide chain, the stronger the hydrophobicity it will have. Although the  $\text{S}^0$ -like species in the polysulfide chain is regarded as rendering the surface hydrophobic, the surface may not be as strongly hydrophobic as expected of  $\text{S}_8$  because of the polar character of the  $\text{S}^{-1}$  ions at the end of each  $\text{S}_n^{2-}$  chain. This consideration may provide an explanation for the relatively low floatability of oxidized coal pyrite. However, the presence of Dowfroth M-150 and kerosene makes the floatability of coal pyrite increase significantly. It is believed that these reagents adsorb on the weakly hydrophobidized coal-pyrite by means of the hydrophobic interaction force.

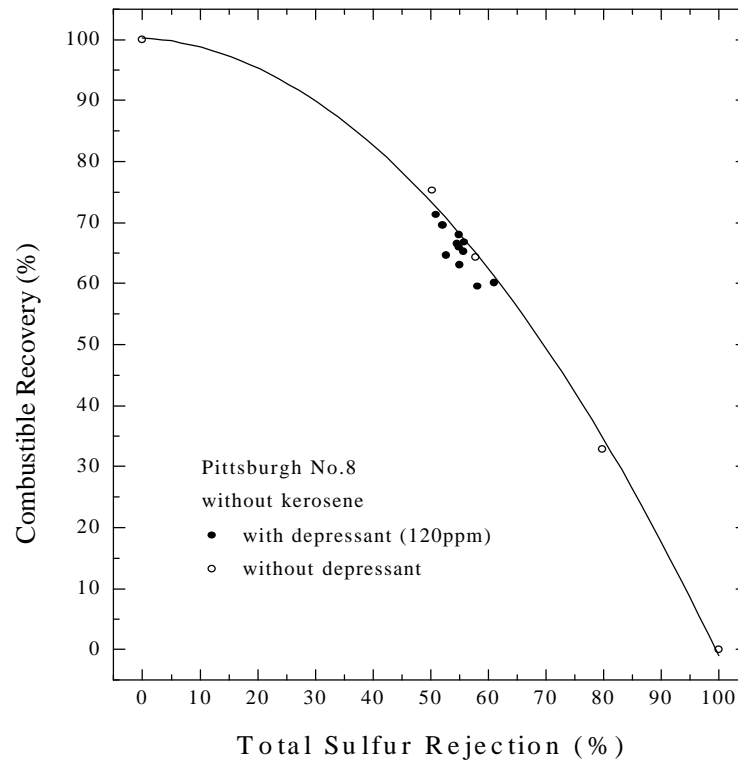


Fig. 2.4 Effect of polymeric depressant on the total sulfur rejection from Pittsburgh No. 8 coal samples. Test number/Cytec reagent number of the reagents used in the tests are as follows: 1/17305-99, 2/17305-185, 3/17305-186, 4/17305-187, 5/17531-153, 6/17531-168, 7/17531-171, 8/17580-2, 9/17580-46, 10/17580-85, 11/17580-101.

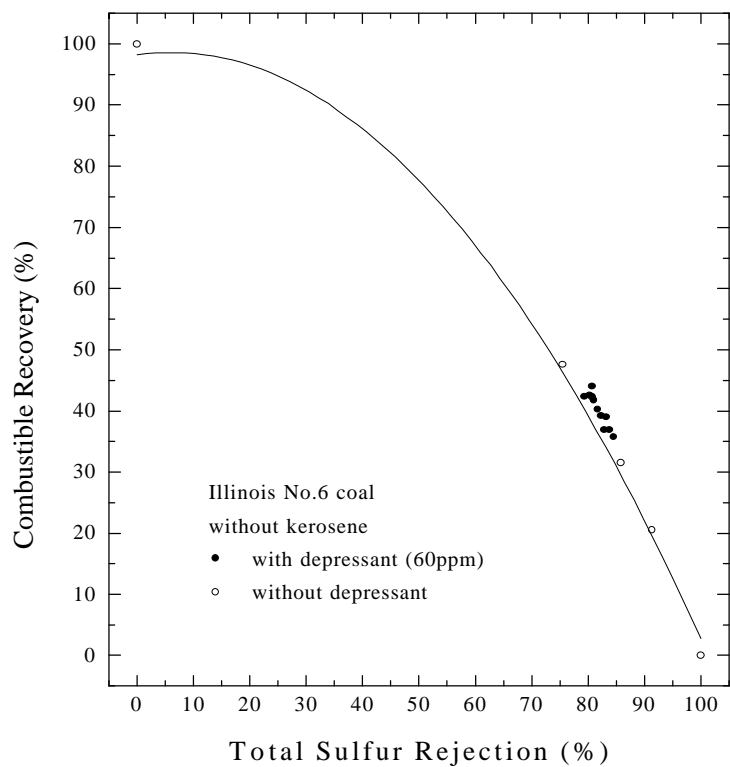


Fig. 2.5 Effect of polymeric depressant on the total sulfur rejection from Illinois No. 6 coal samples. Test number/Cytec reagent number of the reagents used in the tests are as follows: 1/17305-99, 2/17305-185, 3/17305-186, 4/17305-187, 5/17531-153, 6/17531-168, 7/17531-171, 8/17580-2, 9/17580-46, 10/17580-85, 11/17580-101.



### 2.3.3 Depression Effect of Selected Depressants With Kerosene Added

The above results show that: (1) When non-polar kerosene (collector) is not added to the flotation system, the polymeric depressants show no effect in improving coal-pyrite separation efficiency, and (2) The addition of a non-polar collector does have a significant effect on the floatability of coal and pyrite. To study the interaction between polymer and kerosene and identify the best reagents functionality and determine the optimum dosage level, we selected five polymers (i.e., 17305-185, 17305-187, 17531-153, 17580-46, 17580-101) from the eleven polymers. Each of the five polymers represents a specific functionality. Polymer 17580-46 (S-7261), which has the same functionality as polymer 17531-153 but with a much lower molecular weight and a lower functionality percentage, was also selected for further study because it was found to give the best pyrite rejection in microflotation experiments on coal-mineral pyrite mixtures. For Pittsburgh No. 8 coal samples, the flotation tests with all five polymeric depressants were conducted at the dosage range of 100 to 500 g/t. For the Illinois No. 6 coal sample, only polymer 17580-46 (S-7261) was tested with the dosage range from 50 g/t to 300 g/t.

#### a. Pittsburgh No. 8 coal samples

Figure 2.6 shows the plots of combustible recovery vs. the total sulfur rejection for the Pittsburgh No. 8 coal sample, with and without the addition of the selected depressants. At a depressant addition of 100 g/t, most of the reagents showed improved sulfur rejection, except for 17531-153. When the depressant 17580-101 was used (see point A-100 in the Figure 2.6), the sulfur rejection was increased from approximately 18%

to 44%, which represents a 144% increase in total sulfur rejection. Similarly, the depressant 17305-185 increased the sulfur rejection from 15% to 35% (see point C-100 in the figure), which represents an increase of 133%. Depressants S-7261 and 17305-187 also showed a substantial increase in sulfur rejection as shown in Fig. 2.6. It was only the depressant 17531-153 that did not give any improvement in sulfur rejection.

At a depressant addition of 300 g/t, the sulfur rejections were increased at the expense of the combustible recovery for depressants S-7261 and 17305-187. The addition of 300 g/t of depressant 17531-153 (point B-300) resulted in significant sulfur rejection but poor combustible recovery. This suggests that the depressing action of this high molecular weight depressant with the functionality is too strong and has no efficacy in sulfur rejection.

Adding 500 g/t of polymer S-7261 (point S-500), there is no improvement in the separation process. Although the sulfur rejection is very high, the coal flotation is depressed substantially, resulting in a poor combustible recovery. At this high dosage rate, the depressant 17305-185 (point C-500) did not show improvement either.

Based on the data shown in Fig. 2.6, depressants 17580-101, 17305-185 and S-7261 are the reagents showing significant effect for improving sulfur rejection in coal flotation. This suggests that the polymeric depressants 17580-101 and 17305-185 can be used for coal desulfurization for

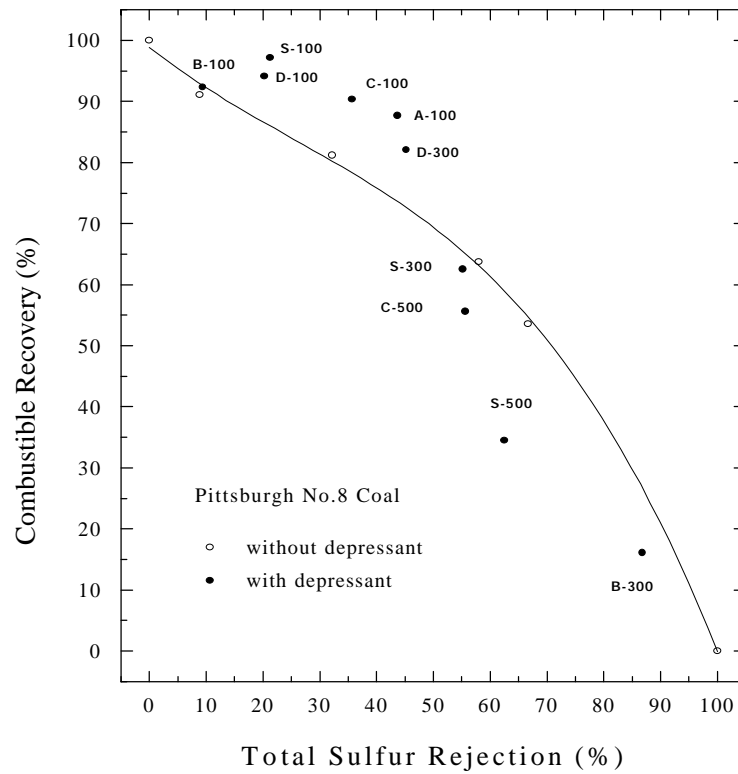


Fig. 2.6 The effect of polymeric depressant on the total sulfur rejection for Pittsburgh No. 8 coal samples. In the figure, the letters stand for the polymers used in the tests (**S**: S-7261; **A**: 17580-101; **B**: 17531-153; **C**: 17305-185; **D**: 17305-187), and the numbers following the letters are the dosage used.

the Pittsburgh No. 8 coal seam. The results also show that the dosage of these reagents should not exceed 300 g/t. At higher dosages, the coal is also depressed along with pyrite. It appears that the use of the high molecular weight depressant with some specific functionality (e.g., 17531-153) is particularly effective in depressing coal, but lowering the molecular weight (polymer S-7261) will improve the flotation selectivity in coal desulfurization.

To further verify the efficacy of the three depressants identified above, pyritic sulfur analyses were conducted for those samples that showed significant improvement in total sulfur rejection. Figure 2.7 shows the pyritic sulfur rejection values obtained as a function of combustible recovery for these reagents at the dosage of 100 g/t. In all three cases, the use of the depressants resulted in a significant increase in pyritic sulfur rejection. This finding suggests that the improvement in total sulfur rejection observed with these reagents (see Figure 2.6) may be attributed to the improved rejection of pyrite from coal. With depressant 17580-101, the pyritic sulfur rejection increased from approximately 30% to 51%, represents a 70% improvement. With depressant 17305-185, the pyritic sulfur rejection increased from approximately 24% to 44%, represents a 83% improvement. A similar result is also observed with depressant S-7261.

The effect of different polymers on the separation efficacy of ash forming minerals from coal is illustrated in Fig. 2.8. At the dosage of 100 g/t, all five reagents tested gave improved ash rejection. The polymers 17580-101 and 17305-185 showed the best ash rejection.

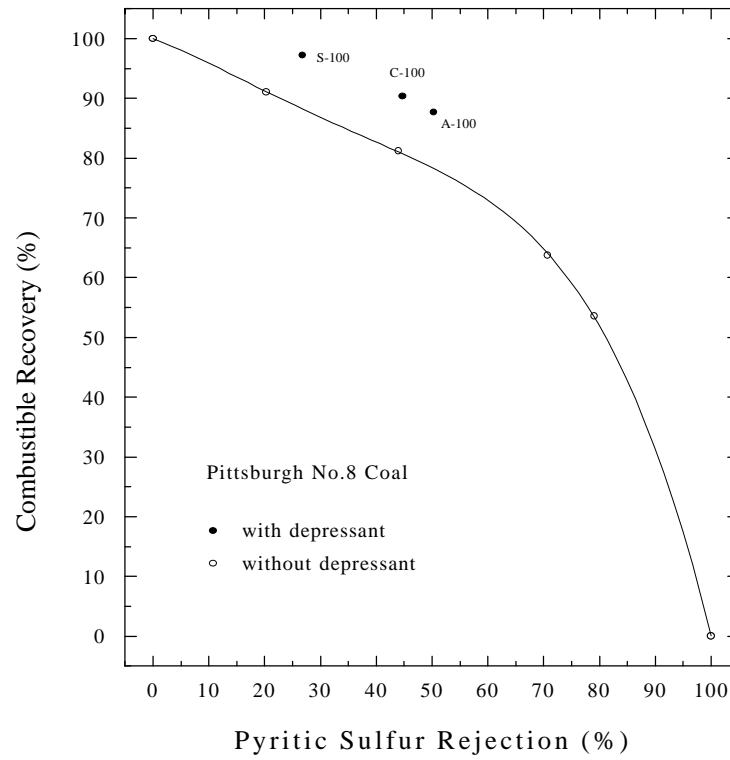


Fig. 2.7 The effect of the selected polymeric depressants on the pyritic sulfur rejection for Pittsburgh No. 8 coal samples. In the figure, the letters stand for the polymers used in the tests (S: S-7261; A: 17580-101; C: 17305-185), and the numbers following the letters are the dosage used.

These two reagents also gave the best total sulfur rejection effect as seen in Figure 2.6. The ash rejection with S-7261 was not as good as the other depressants, but its performance was still better than that with the high molecular weight polymer 17531-153.

At higher polymer dosage (300 g/t), the ash rejection effect gets increased at the expense of lower combustible recovery, but the results are still better than the reference tests without the polymers. At 500g/t, however, both coal and mineral matter are depressed.

According to the test results obtained in the present work, depressants 17580-101 and 17305-185 are very selective at the dosage of 100 g/t for coal pyrite (see points A-100 and C-100 in Fig. 2.6). To verify this finding, two conventional flotation tests were conducted on the Pittsburgh No. 8 coal sample and the results are given in Figure 2.9. As shown, the addition of 100 g/t of 17580-101 and 17305-185 show better separation selectivity than the baseline data obtained without using the depressants. In general, the test results are not as good as those obtained using column flotation, which may be attributed to use of wash water and smaller air bubbles for the column flotation. Nevertheless, there is no doubt that the two depressants are effective in sulfur rejection in coal flotation.

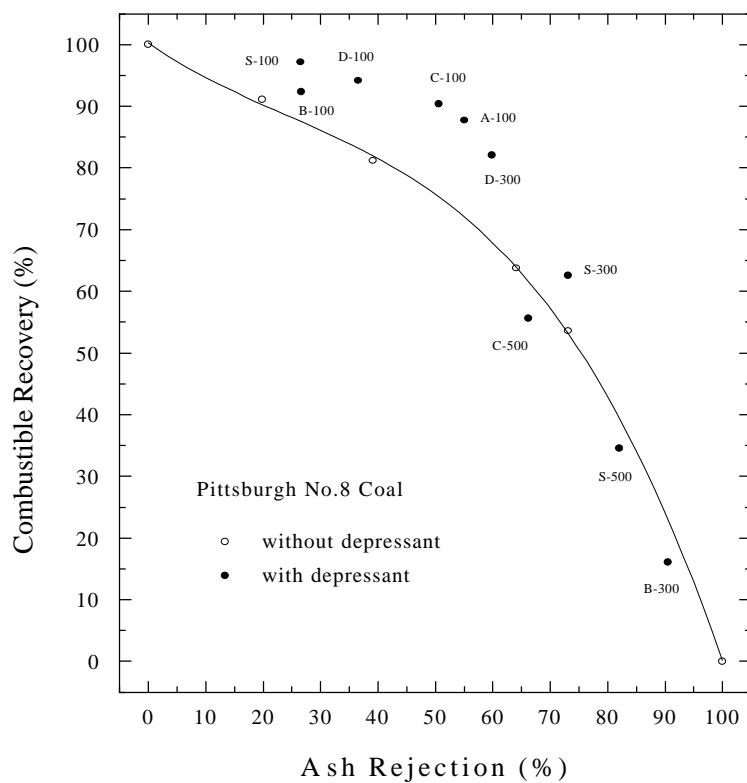


Fig. 2.8 The effect of the selected polymeric depressants on the ash rejection for Pittsburgh No. 8 coal samples. In the figure, the letters stand for the polymers used in the tests (**S**: S-7261; **A**: 17580-101; **B**: 17531-153; **C**: 17305-185; **D**: 17305-187), and the numbers following the letters are the dosage used.

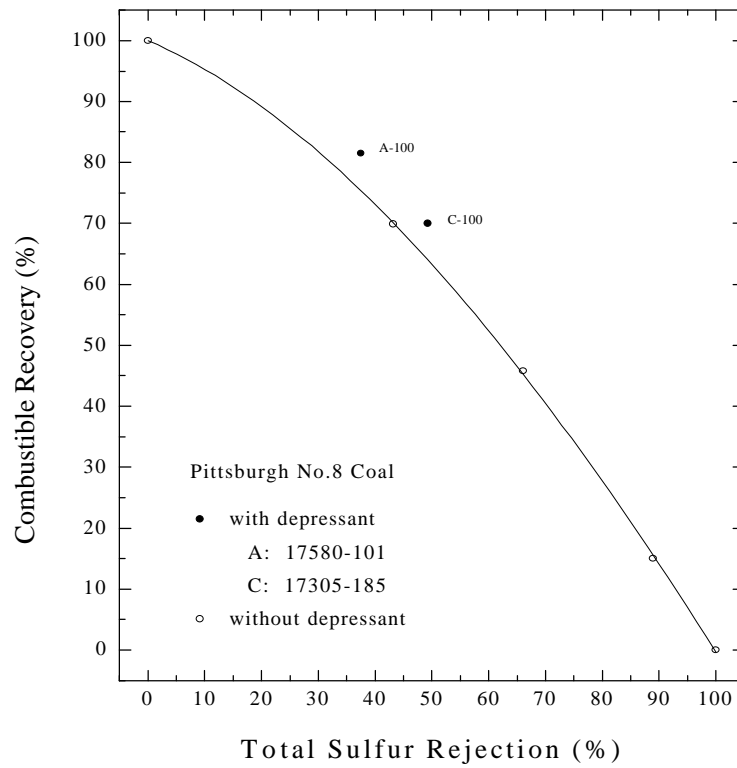


Fig. 2.9 The addition of polymers on the pyritic sulfur rejection for Pittsburgh No. 8 coal samples with conventional flotation technique. The dosage used here is 100 g/t for both polymers.



b. Illinois No. 6 coal samples

Figure 2.10 shows the column flotation test results with and without S-7261 for the Illinois No. 6 coal samples. Since the Illinois No. 6 coal is not as hydrophobic as the Pittsburgh No. 8 sample, the kerosene dosage used was increased to 800 g/t, and the dosage of S-7261 was reduced. The depressant dosages used in these tests were 50, 150 and 300 g/t. At the dosage of 50 g/t, only 15% of the total sulfur was rejected. At 300g/t and 500g/t, the rejections were increased to 41% and 69% respectively, but the combustible recovery was also decreased significantly. Fig. 2.10 also shows the results obtained without the depressants. These points were obtained by changing the feed rate to the flotation column. The data obtained with and without the depressants fall on the same rejection vs. combustible recovery curve, indicating that the use of S-7261 does not have significant effect on the sulfur rejection for the Illinois No. 6 coal samples in the present work.

To understand the cause for the difference in flotation response of the two coal samples (Pittsburgh No. 8 coal and Illinois No. 6 coal) to S-7261, SEM-IPS image analyses were conducted on the flotation feed, concentrates, and tailings. The image analysis data showed that the pyrite particles in the Illinois No. 6 sample are finer and less liberated than those in the Pittsburgh No. 8 sample. Also, most of the middling in the Illinois No. 6 sample contained more coal and less pyrite. These findings may explain the ineffectiveness of the polymeric depressant in removing pyrite from the Illinois No. 6 coal sample.

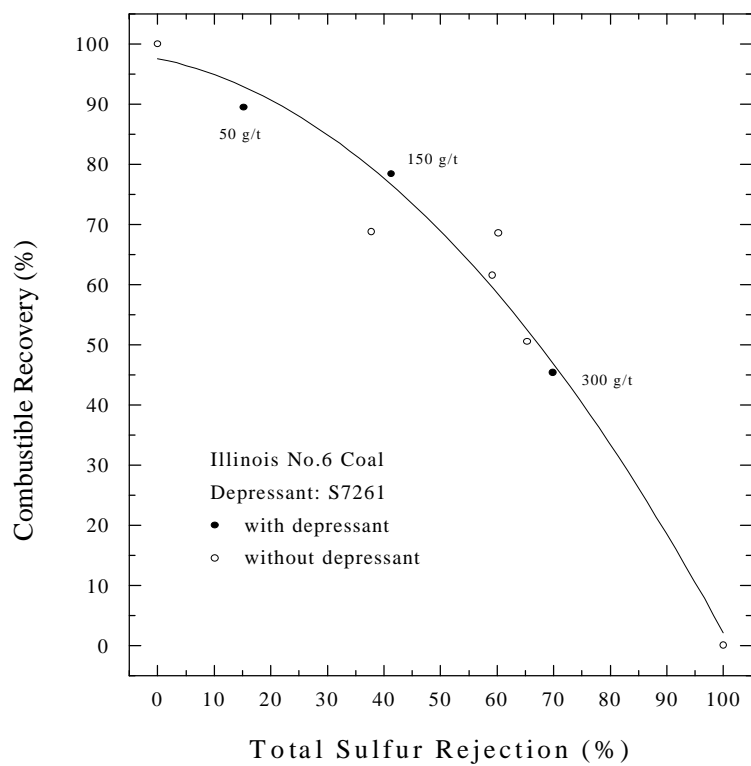


Fig. 2.10 The effect of polymer S-7261 on the total sulfur rejection for Illinois No. 6 coal samples. The numbers are the dosages used in the column flotation tests.

The effect of depressant S-7261 on the ash rejection is shown in Figure 2.11. At 50 g/t, there may be a slight improvement in ash rejection. However, there is no improvement observed at higher dosages comparing with the results when no depressant is added.

The column flotation test data obtained shows that polymeric depressant S-7261 has very limited depression effect on pyrite and ash rejection in Illinois No. 6 coal flotation. At lower dosages, the amount of depressant is not high enough to depress the pyrite present in the coal sample; however, it shows some improvement in ash rejection. At the S-7261 dosage of 300 g/t, the coal is depressed together with pyrite. The optimum dosage for using S-7261 on Illinois No. 6 coal is around 150 g/t.

## **2.4 DISCUSSION**

### 2.4.1. The depression mechanism of polymer reagents

To depress a gangue mineral, the depressant molecules must bear functional groups that (1) can adsorb onto the specific mineral surface and (2) render the surface hydrophilic. The interaction between the functional groups and mineral surface could be one of many types, including opposite charge attraction, hydrogen bonding, or complex formation (62). The strength of the attraction force varies depending on the type of interaction, the surface structure of the mineral particle, and the chemical conditions of the

aqueous medium, such as pH, which may affect the chemical nature of both the mineral surface and the chemical reagents present in the system (72).

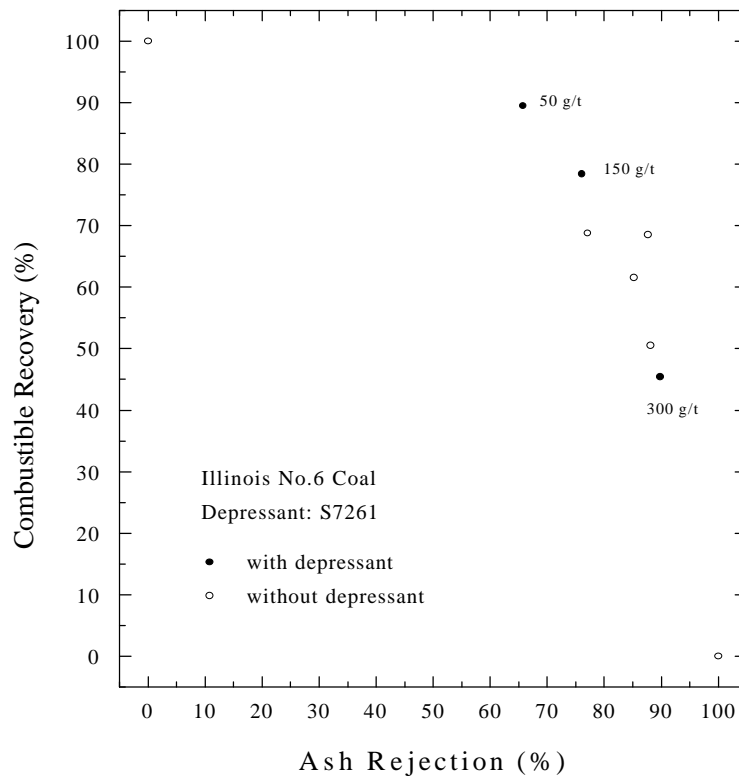


Fig. 2.11 The effect of polymer S-7261 on the ash rejection for Illinois No. 6 coal samples. The numbers are the dosages used in the column flotation tests.

A polymeric depressant molecule is usually a long hydrocarbon chain with at least two kinds of functional groups attached to it. One of them can adsorb or interact with the surface of the mineral which we wish to depress and the another is of hydrophilic nature. So while the former group attached to the mineral surface, the latter one extruded to the aqueous water molecules making the particle hydrophilic. A conceptual model of the interaction between a polymeric depressant molecule and mineral particle is illustrated in Fig. 2.12.

In the present investigation, when the polymers were added to the coal/coal-pyrite slurry, the functionality adsorbs on the surface of coal pyrite, while the hydrophilic group on the main hydrocarbon chain extrudes to aqueous phase and renders coal pyrite hydrophilic. As the main hydrocarbon chain is the same for all the polymers tested in the present investigation, the depression effect of different polymers depends on the attached functionality. The stronger the functionality with coal pyrite, the stronger the depression effect. Polymer S-7261 depresses coal pyrite through hydroxy group. However, polymer 17580-101 depresses pyrite through not only hydrogen bonding between the molecule and particle surface, but also the chemical interaction through sulfur atoms. This makes polymer 17580-101 a stronger depressant compared with S-7261.

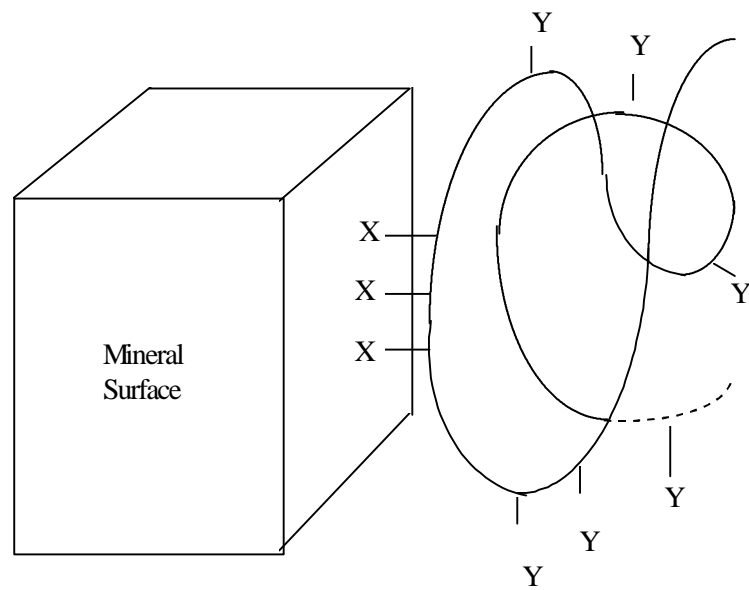


Fig. 2.12. A conceptual model of polymer depression. X and Y are functional groups.