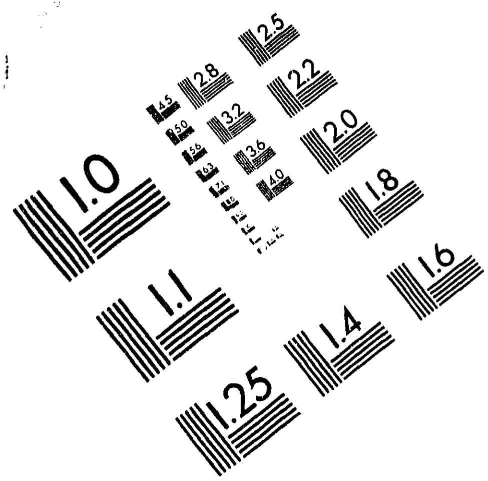

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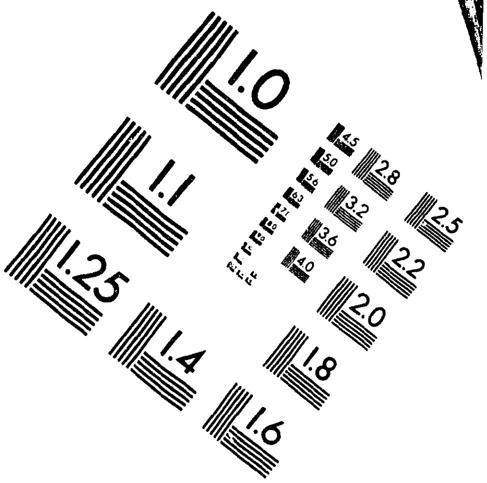

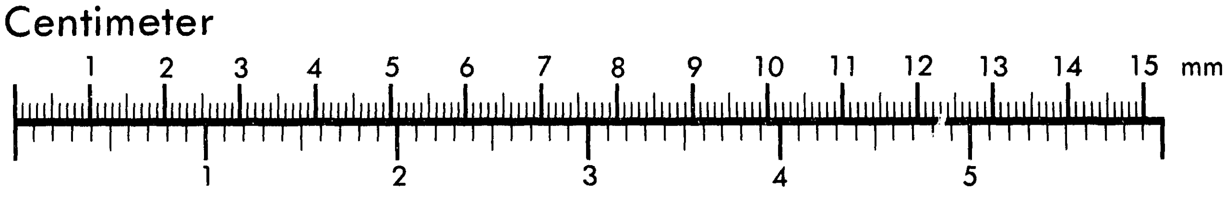

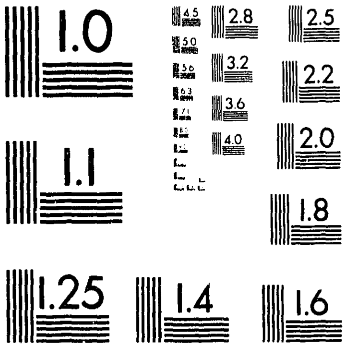

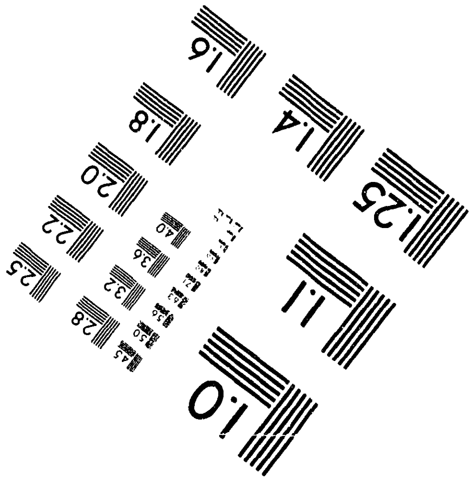

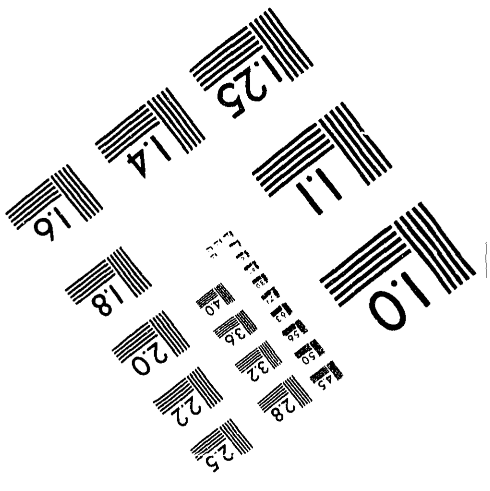

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FINAL REPORT

ON

REMOVAL OF ORGANIC AND INORGANIC SULFUR FROM OHIO COAL BY COMBINED PHYSICAL AND CHEMICAL PROCESS

TO

Ohio Coal Development Office
Ohio State Department of Development
Columbus, Ohio

Grant Agreement No. CDO 1R-86-78/91

BY

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PROJECT SUMMARY

This project consisted of three setcions. In the first part, the physical cleaning of Ohio coal by selective flocculation cf ultafine slurry was considered. In the second part, the mild oxidation process for removal of pyritic and organic sulfur was investivgated. Finally, in the third part, the combined effects of these processes were studied.

The physical cleaning and desulfurization of Ohio coal was achieved using selective flocculation of ultrafine coal slurry in conjunction with froth flotation as flocs separation method. The finely disseminated pyrite particles in Ohio coals, in particular Pittsburgh no.8 seam, make it necessary to use ultrafine (-500 mesh) grinding to liberate the pyrite particles.

Experiments were performed to identify the "optimum" operating conditions for selective flocculation process. The results indicated that the use of a totally hydrophobic flocculant (FR-7A) yielded the lowest levels of mineral matters and total sulfur contents. The use of a selective dispersant (PAAX) increased the rejection of pyritic sulfur further. In addition, different methods of floc separation techniques were tested. It was found that froth flotation system was the most efficient method for separation of small coal flocs.

The results showed that the optimum flocculant (FR-7A) concentration was 5-20 mg/l while the most effective PAAX concentration was at 200 mg/l. Furthermore, it was found that grinding coal for 3 hours in a ball mill resulted in the liberation of most of the pyrite particles.

Operating the selective flocculation at the aforementioned conditions, over 80% of pyritic sulfur and over 60% of mineral matters rejections were obtained with 85% coal recovery. Therefore, raw coal with 16% ash and 3.6% total sulfur contents (1.25% organic sulfur content) could be cleaned to 4% ash and 1.8% total sulfur contents. The economic assessment of the selective flocculation/froth flotation process resulted in 62% rate of return on the investment in comparison with that of only froth flotation process. The selective flocculation/froth flotation process has the potential near-term commercialization and adaptation to existing coal preparation plants. The environmental impacts of this process were considered and found to be minimal.

This project also aimed at developing a mild chemical cleaning technique for removing organic and pyritic sulfur from high sulfur coals. This technique was conducted at room temperature and atmospheric pressure, using an inexpensive commercial chemical, potassium permanganate ($KMnO_4$), as the oxidizing reagent. The oxidation process was followed by a

washing step with a complexing reagent or dilute acid, also at atmospheric pressure and room temperature, to remove the undesirable precipitates and loosely held sulfates produced during the oxidation.

To achieve the project objectives, investigation on the following tasks were conducted: 1) the conceptual feasibility of the process and effects of important process parameters; 2) removal of oxidation products during the washing step; reagents for removing the oxidation precipitates. 3) characterization of chemically treated coal products at various phases of the process; 4) conceptual flowsheet development; and 5) preliminary economic and environmental assessments.

The results obtained indicate that permanganate oxidation followed by a washing step would be very promising approach as it can remove substantial amounts of both pyritic and organic sulfur from coal and therefore has high technical and commercial potentials. More than 80% pyritic sulfur rejection and 33% organic sulfur removal with over 90% Btu recovery can be achieved through one step oxidation 15% $KMnO_4$ followed by one washing step with 14% HCl. Generally, up to 50% of organic sulfur removal and over 90% pyritic sulfur removal can be expected through two to three washing steps. The characterization and washing studies showed that the precipitates formed during the oxidation step were successfully removed through the washing step. Preliminary economic assessment suggested that the cost of the chemical cleaning would be about $11.24/ton clean coal. Environmental impacts of this process were briefly studied and it was shown that this process should be environmentally sound.

The advanced physical cleaning by selective flocculation was integrated with the mild chemical process. The test results indicated that the combined process is technically and economically feasible. With one step treatment by the combined process, clean coal containing less than 0.9% total sulfur and about 4% ash with 12,500 Btu/lb content could be obtained, and the overall coal recovery was over 81%. The preliminary economic assessment indicated a gross project of $4.5/ton of clean coal.

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PART I

PHYSICAL CLEANING OF OHIO COAL BY SELECTIVE FLOCCULATION OF ULTRAFINE COAL SLURRY

I.1 INTRODUCTION

In order to appreciate the complexity of the task of desulfurization of Ohio coals, in particular Pittsburgh no. 8 seam, one has to know the characteristics of this coal. Since in physical desulfurization, for the most part, the pyrite particles are removed, the size, shape, and distribution of pyrite particles in the coals are of extreme importance. There are several studies to determine these characteristics of the Ohio coals.

In a comprehensive study, Kneller and Maxwell (ref. 15) reported that there was a marked increase in the volume distribution of microscopic pyrite within the size range of -32 to 4 micron with the average size at the range of 16 to 8 micron. Specifically, they reported that Pittsburgh no. 8 seam coal which is the most abundant type of coal in Ohio, has over 70% by volume of its microscopic pyrite (-840 to 1 micron range) below 32 micron size. This findings clearly indicate that for any pre-combustion desulfurization method, especially any physical technique, for pyrite particles to be accessible, the coal has to be ground to very fine size, e.g., -500 mesh (-25 micron). Therefore, ultrafine cleaning techniques must be utilized to effectively remove the pyrite.

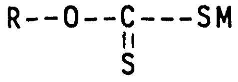
Selective flocculation of ultrafine coal slurries is one of the most promising techniques available. This process has been utilized commercially for cleaning and extracting other minerals such as iron ore, potash and kaolin. The main steps involved in the selective flocculation are to first liberate the impurities from the ore structure by grinding it to appropriate size and then by exploiting the surface chemical differences of the impurities and the ore, selectively agglomerate the desired mineral particles into flocs while leaving the remainder of the mineral particles dispersed. The third critical step is the flocs separation method. The simpliest method is sedimentation of the heavier flocs, however, in some cases sedimentation may not be very effective due to the complex physical properties of the impurities in the raw ore.

There are many parameters that can affect the performance efficiency of the selective flocculation process. This efficiency can be measured by the final upgrading and recovery of the clean ore. In the following paragraphs, a brief discussion of several investigations are provided which will give a better insight to the problems and the methods for solving them.

Perhaps the most important factor in selective flocculation is the flocculant chemical. The flocculant is typically a long chain polymer or co-polymer which can have one to three million average molecular weight. The back-bone of the polymer is usually a long chain saturated hydrocarbon chain different functional group attached. Two factors determine the selectivity of the flocculant: the size or molecular weight of the flocculant and the affinity of the functional groups to the desired minerals, their proportionality, and arrangement along the hydrocarbon chain. Attia (12) presented the structure of some of the commercially available flocculants having selective affinity for coal which were also used in this study. He also tested these flocculant for their deashing effectiveness. These functional group can be totally hydrophobic, totally hydrophilic or partially hydrophobic. The ionic characteristics of these groups determine whether the flocculant is anionic, cationic or non-ionic. In addition to these electro-chemical properties, the functional groups can also have specific chemical affinity with some of the minerals. Therefore, one can design a flocculant for a specific purpose, if one knows the surface chemical properties of the ore and its associated impurities. In fact, Attia (1987) reported ways and means of designing of selective polymers for colloid separation by selective flocculation. For example, he reported that for organic colloids, selective adsorption may be achieved through hydrophobic bonding with the hydrophobic groups on the polymer. Thus, one may conclude that for flocculation of coal ultrafine slurries a totally hydrophobic flocculant is most effective, since most of the mineral matters are hydrophilic. However, the pyrite is also partially hydrophobic, hence, a new method should be used for rejection of pyrite.

This method which is used in this study is based on selective dispersion of the liberated pyrite particles. Before the flocculation process, the particles in the slurry must be well dispersed to reduce the entrapment of undesirable mineral matter. In order to enhance the dispersion of pyrite and other ash minerals, dispersing agents are used. The use of a selective dispersant such as polyxanthate (or PAAX) should improve the dispersion of pyrite particles and the selectivity of coal flocculation process.[2]

Xanthate compounds are widely used as mineral collectors and flotation reagents for sulfide minerals. The basic structure of a xanthate-containing compound is:



$$\mathrm{R{-}{-}O{-}{-}\underset{\underset{S}{\|}}{C}{-}{-}{-}SM}$$

where R can be an alkyl hydrocarbon group and M is a monovalent metal such as sodium or potassium.[3]

High molecular weight xanthates such as cellulose xanthates have been used as flocculants for processing of sulfide minerals. Attia[4] extensively studied the production and characterization of cellulose xanthate for selective flocculation of copper minerals and other metal oxides.

However, the use of xanthate-containing polymeric dispersants has been recently reported to enhance the dispersion process of ultrafine pyrite particles in coal desulfurization process using selective flocculation method.[2,5] The xanthated reagent is used as a selective dispersion reagent to enhance the performance of the flocculation process.

Attia[2] reported that the procedure for preparation of PAAX. The xanthation process is a reversible reaction, therefore, seldom does the reaction go to completion which means that not all the carboxylic acid groups are xanthated.

The dispersion process involves the adsorption of short chain xanthate-containing polymeric molecules on the active sites of the pyrite particles. Such adsorption depresses the flocculant adsorption by pyrite, increases the hydrophilicity of the pyrite, and enhances the electrical double layer repulsion of pyrite particles. Therefore, during the flocculation step the pyrite particles have little or no affinity towards the flocculant molecules and stay dispersed in the slurry while the coal particles agglomerate and are separated afterwards. A clear picture of adsorption bonding mechanism is yet to be developed for the polyxantthate, although there are several reports indicating the formation of unstable dixanthogen-coating around pyrite particles with low molecular weight xanthates.[3,6-8]

The other important factor in performance efficiency of selective flocculation is the liberation size and the size distribution of the particles in the slurry. As it was discussed earlier, the size distribution of the slurry determines whether all the undesired impurities are liberated. In addition, the average size, and size distribution is a measure of the total surface area of the particles in the mixture. Of course, the total weight of particles or slurry concentration is also positively proportional to the surface area of the mixture. In general, the higher the surface area the more flocculant molecules are required for flocculation of the mixture.

There are several important process parameters which can affect the selective flocculation. In recent study by Driscoll (9), some of these parameters were studied to define the "optimum" performance of the selective flocculation. The parameters investigated were: velocity gradient (mixing rate), polymer dispersion time, rate of polymer addition, polymer stock solution concentration, slurry pH, slurry solid content, and floc conditioning time. The results of this work was used as the initial point of investigation for the present study. Some of the parameters listed above already have more pronounced effect than the others. For example, pH and slurry content are more important than the flocculant stock solution concentration as long as the same operating conditions are kept.

The objective in this part of the work was to investigate the technical and economical feasibility of the selective flocculation for cleaning and desulfurization of an Ohio coal. Therefore, a systematic study was designed to determine the important parameters both fundamental and process oriented. Three basic factors were involved; namely, the liberation size, the effect of chemical reagents, and the floc separation method. Adsorption experiments and surface property characterization tests such as zeta-potential measurements, and pore size distribution were performed with pure minerals to provide us with the essential knowledge to explain the physical effects observed with the raw coal and to direct us to the determine the "optimum" conditions for performance of selective flocculation.

In the following section, a complete description of measurement methods and experimental techniques are presented. In addition, a full description of the chemicals and minerals used in this study are reported. In the next section, the results of the different experiments are summarized for comparison and contrast which is followed by a discussion of the results and their implications in a commercial scale process. Later, the environmental impact and waste handling of the suggested process are considered. The toxicity of the chemicals and the method to overcome these problems are also discussed in that section. The techno-economic assessment answers whether the process is economically feasible and its potential advantages and disadvantages. Finally, the conclusions and recommendation are presented.

I.2 EXPERIMENTAL TECHNIQUES

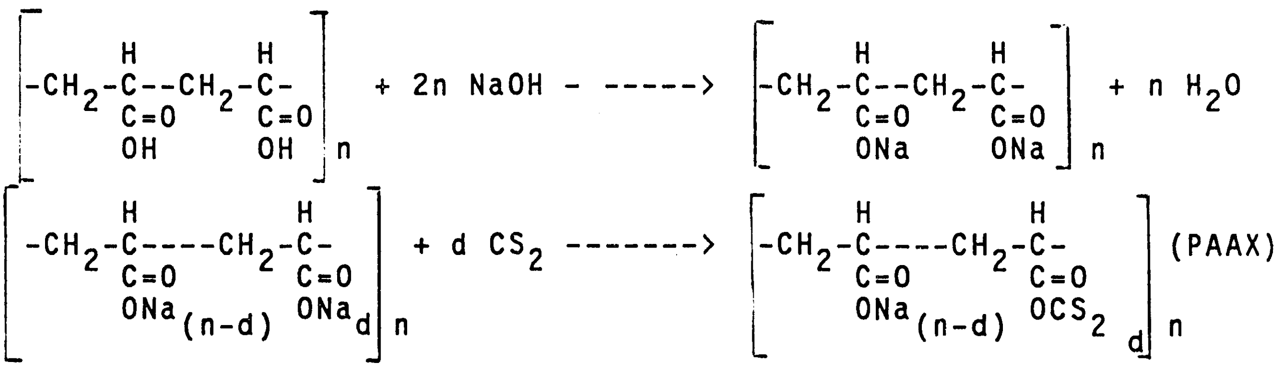
In the following section, a detailed description of the preparation and analysis of all the chemicals and reagents used in our tests, experimental procedures for each set of experiments, and the list of all the minerals and their properties which were used in our experiments are given.

Note that due to the large volume of the work performed and the relatively long period of time from the beginning to the end of the project, the properties of the raw coal (mainly Pittsburgh no. 8) varied rather drastically. It is also not adequate to use the average values to characterize all the coals used here since the initial percentage of impurities can directly affect the quality of the clean product.

Chemicals

Preparation of Polyxanthate Dispersant (PAAX)

The sodium salt of polyacrylate-acrylodithiocarbonate, or in short PAAX, is formed by reacting carbon disulfide (CS_2) with sodium polyacrylate as shown below:



$$\left[-CH_2-\underset{\underset{OH}{C=O}}{\overset{H}{C}}--CH_2-\underset{\underset{OH}{C=O}}{\overset{H}{C}}-\right]_n + 2n\ NaOH \longrightarrow \left[-CH_2-\underset{\underset{ONa}{C=O}}{\overset{H}{C}}--CH_2-\underset{\underset{ONa}{C=O}}{\overset{H}{C}}-\right]_n + n\ H_2O$$

$$\left[-CH_2-\underset{\underset{ONa_{(n-d)}}{C=O}}{\overset{H}{C}}----CH_2-\underset{\underset{ONa_d}{C=O}}{\overset{H}{C}}-\right]_n + d\ CS_2 \longrightarrow \left[-CH_2-\underset{\underset{ONa_{(n-d)}}{C=O}}{\overset{H}{C}}----CH_2-\underset{\underset{OCS_{2\ d}}{C=O}}{\overset{H}{C}}-\right]_n \ (PAAX)$$

Unfortunately, the above reaction sequence is complicated by the formation of by-products such as mono- and tri-sodium thiocarbonate and dixanthogens. Moreover, being an unstable compound at low pH and room temperature, xanthate group easily decomposes to CS_2 and its initial sodium salt. Consequently, the reaction conditions such as temperature and stochiometric ratio of the reactants must be well defined for the optimum production of PAAX. The experimental range of the different parameters are listed in Table I.1

Table I.2 lists the optimum conditions for production of PAAX. The PAAX was prepared by reacting polyacrylic acid (PAA)

Table I.1 The Ranges of Variables for the Reaction Parameters Investigated.

Temperature: 15-50°C
Stochiometric ratio: 1.0: 1.5: 0.15 to 1.0: 8.0: 17.0 wt. ratio of PAA:NaOH: CS_2 (weight basis)
Reaction Time: 1 to 5 hours
pH: 11 to 12.5
1% to 15% polyacrylic acid solution

Table I.2 The Optimum Reaction Parameters for Production of PAAX.

Temperature: 15°C
Stochiometric Ratio: 1.0: 1.5: 4.0 wt. ratio of PAA: NaOH: CS_2
Reaction Time: minimum 5 hours
pH 12.5
15% polyacrylic acid solution

---

with average molecular weight of 1800 to 5000 with NaOH, and CS_2 in 1.0:1.5:4.0 weight ratio, respectively (or molar ratio of 1.0:2.76:4.22). Polyacrylic acid (PAA) was obtained from Polysciences, Inc., Warrington, PA.

PAAX Preparation Procedure. The general procedure for PAAX preparation which also used for determining the optimum conditions was as follows. 3 grams of 50% wt. aqueous-PAA stock solution were dissolved in 10 ml distilled water to make a 11.5% PAA solution. Subsequently, 2.2 grams of NaOH were added to the dilute polyacrylic acid solution. The mixture was then stirred until all of the NaOH was dissolved which resulted in a clear and colorless solution. This solution was cooled down to 15°C in a constant temperature water bath shaker, and 5.6 grams of CS_2 were slowly added to the solution. A reflux condenser was mounted at the top of the reaction vessel to condense and reflux any CS_2 vapor. In approximately 30 minutes the clear solution changed to a pale yellow mixture. As the reaction time increased, the color of the mixture became darker and eventually the color turned orange. After about 5 hours, the reaction was stopped and the excess CS_2 was removed by decantation.

Purification of PAAX. The purification of the product involved basically only one single step which can also be repeated several times for obtaining cleaner product. 100 ml of ethanol was added to the reaction mixture upon which a viscous orange layer rapidly percipitated to the bottom of the reaction vessel, while the bulk of the reaction mixture dissolved in alcohol and formed a somewhat yellow liquid. The volume of the percipitated viscous layer was about 2 ml which was approximately equal to the volume of added PAA from stock solution (50% wt.).

The yellow liquid layer contained most of the ethanol-soluble compounds which also included excess NaOH in the reaction mixture and some of the immiscible CS_2. The excess CS_2 and NaOH react with the ethanol to form sodium ethyl xanthate. However, the immiscible orange layer contained most of the polyxanthate dispersant. The mixture was then separated by decantation or through separatory funnel. The polyxanthate product which also contained approximately 50 to 60% (by volume) water was a very viscous and adhesive gel similar to viscoelastic materials. Treatment by ethanol can be repeated several times to extract excess water and any residual by products of the reaction.

Storage of PAAX. Since xanthate compounds are not stable at room temperature and susceptible to thermal decomposition, the product was kept under refrigeration. Nevertheless, it was observed that upon dilution of the polyxanthate product in water, the orange color of the solution gradually changed to pure yellow even at the refrigeration condition within approximately three weeks period. The change in the color of the solution directly correlated with the reduction in the UV-absorbance level which indicated the gradual decomposition of the PAAX.

However, it was also observed that when the product was not diluted and maintained refrigerated at its original concentration after the purification step, the color did not change or fade. The UV-absorbance level of diluted solution also indicated that the concentration of the PAAX did not change significantly when it was stored at high concentration and under refrigeration for over 6 weeks.

Characterization of PAAX. Characterization of the product for its composition and concentration was made by using UV/Visible light Spectroscopy technique. The spectrophotometer systems used in the experiments were a Bausch&Lomb Spectronic model 2000 and Beckman model DU 701 UV-VIS spectrophotometer. The results are discussed in the following sections.

At low concentrations (2 to 50 mg/ℓ), light absorbance of xanthate group at wavelengths of 302-304 nm is approximately linear. Therefore, using known concentrations of the polyxanthate solution, a caliberation curve for UV-absorbance versus PAAX concentration can be determined. The concentration of the PAAX product in unknown solutions was determined by appropriate dilution of small amount of PAAX and measuring the absorbance at the characteristic peak (302-304 nm).

The degree of xanthation of PAAX was calculated by measuring the xanthate concentration in PAAX solution of known PAA concentrations. The xanthate concentration was determined from a calibration curve made with known concentrations of low molecular weight xanthate compounds such as potasium amyl xanthate and sodium isopropyl xanthate.

Stability Analysis of PAAX

UV-Spectrophotometry of PAAX. The analysis of polyxanthate dispersant showed three distinct aborbance peaks at 378, 304, and 212 nm. The UV-spectrum indicated a lower absorbance peak at about 224-227 nm which is shadowed by the strong absorbance at 212 nm. Figure I.1 shows the UV absorbance characteristic for PAAX solution. Shown also in Figure I.1 is the UV absorbance of sodium polyacrylate which has multiple peaks at 210 to 225 nm.

Also shown in Figure I.2 is the UV absorbance of sodium ethylxanthate which was formed during the purification process. This low molecular xanthate compound was formed by the reaction of ethanol with excess NaOH and CS_2 as described previously. Note the absence of the peak at 212 nm.

These results were compared with the UV analysis for pure sodium isopropyl and potassium amyl xanthates which showed sharp absorbance peaks at 380-384, 301.3-304., and 227 nm.[3]

The strong absorbance peak at 212 nm for PAAX is the result of the unreacted carboxylate groups present in the polymer chain. The pure xanthate compounds and the purified PAAX were also used to caliberate the absorbance of UV light for the concentration and the decomposition rate. Based on the absorbance peak at 304 nm, it was found that there is a linear relationship between aborbance and the xanthate concentration for

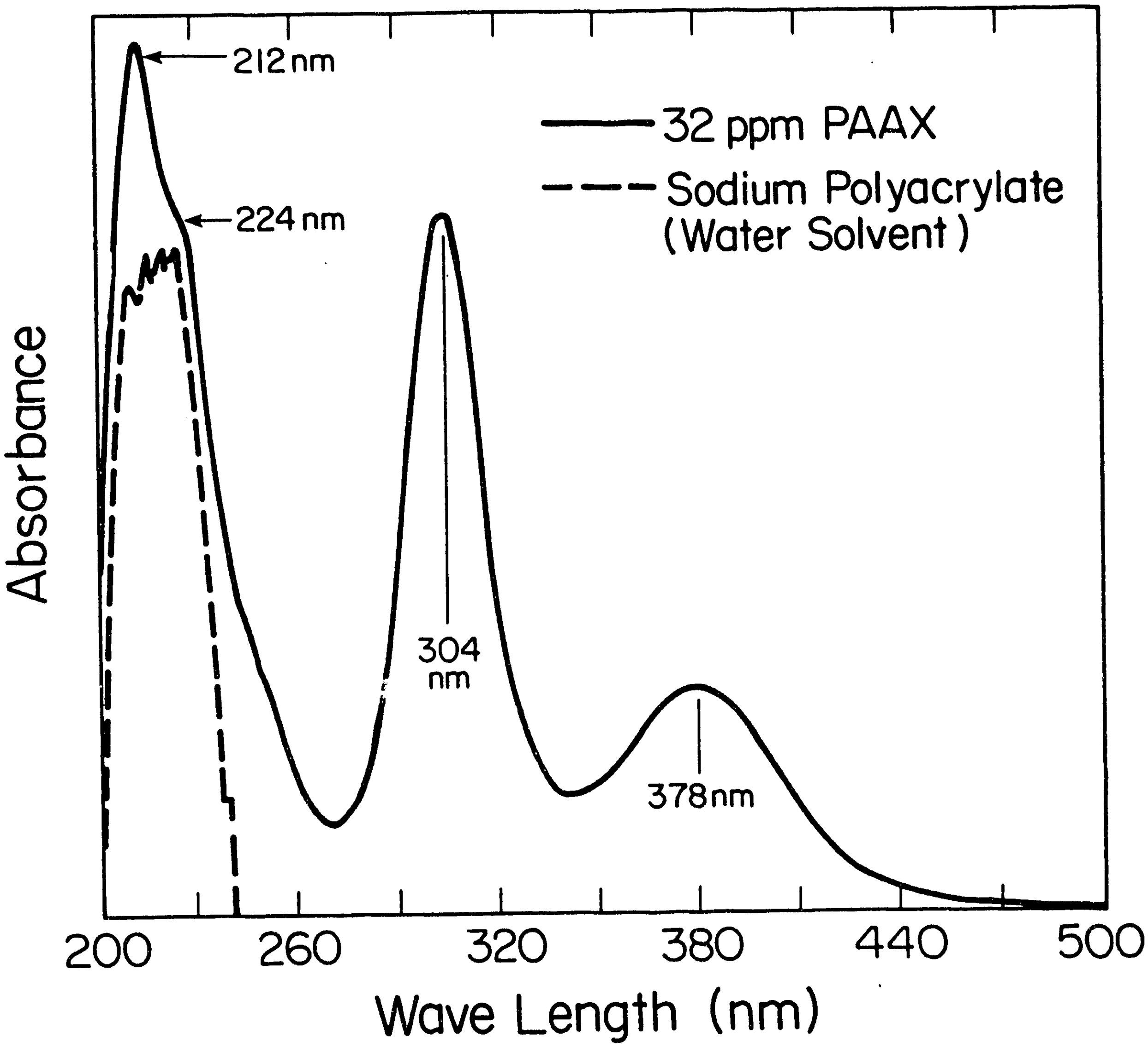


Figure 1.1 UV Absorbance characteristics of Sodium Polyacrylate and Polyxanthate Product for at Reaction Temperature of 15oC and Reaction Time of 5 hrs.

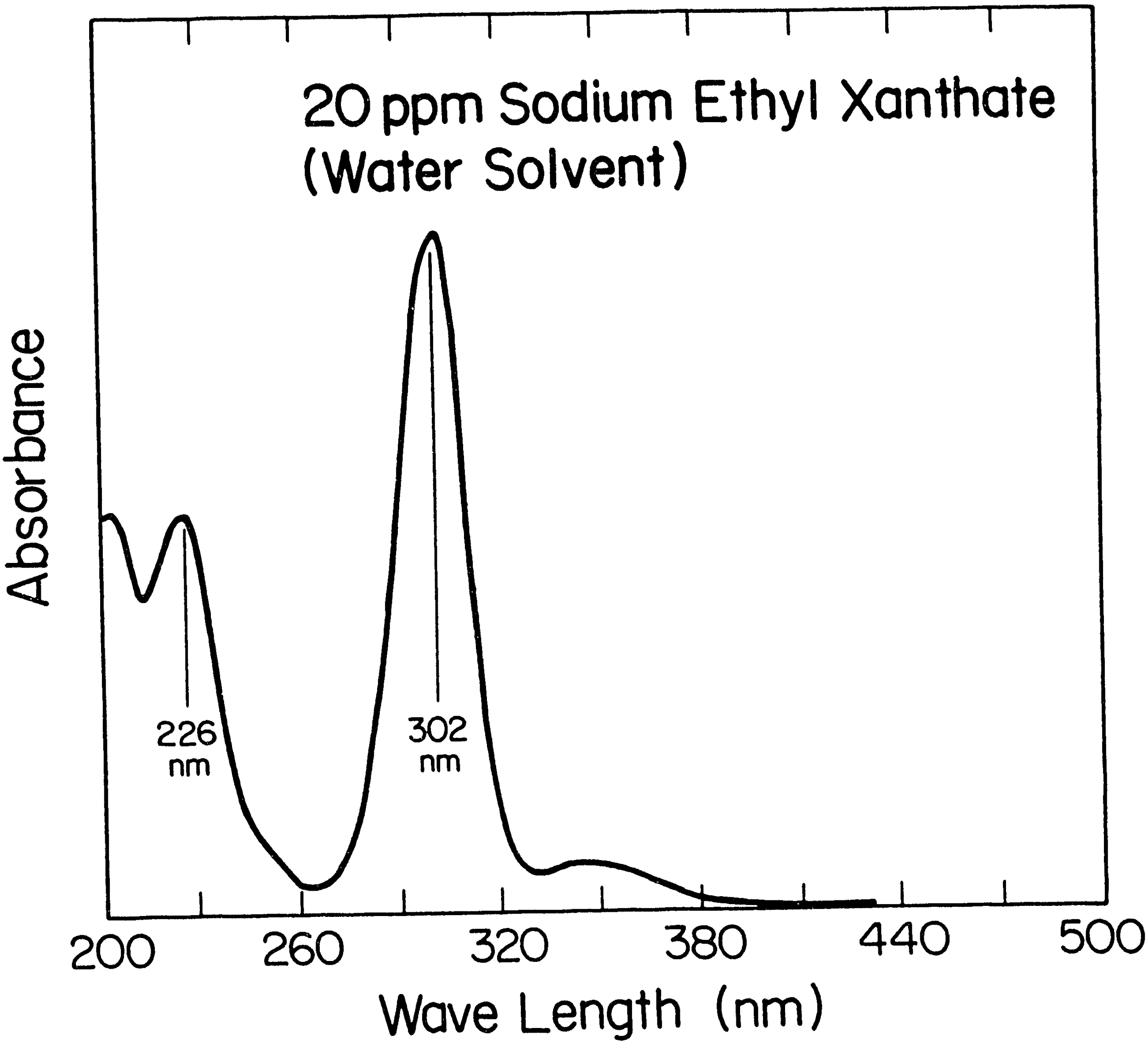


Figure 1.2 UV Absorbance Characteristics for Sodium ethyl xanthate.

concentrations of less than 50 mg/ℓ for both PAAX and the low molecular weight xanthate.

Effect of Reaction Temperature and Reaction Time. Analysis of the reaction products whose reaction temperatures were maintained above 25°C showed strange behavior. The UV-analysis of these reaction products exhibited consistently an initial peak at 318 nm which gradually leveled off to 307 nm as shown in Figure I.3. Similarly, the UV-absorbance level also decreased with the drifting wavelength as shown in Figure I.4. The same phenomenon was observed for the products of the experiments whose reaction time were less than 2 hours at reaction temperatures of 12 to 20°C. It should be noted that this behavior was observed at low concentrations of the reaction products (approximately 5 to 10 mg/ℓ of the crude PAAX), however the pH of the solution was maintained above 10.

The exact nature or structure of the chemical compound responsible for this phenomenon is not known at the present time. However, the formation of intermediate complex is believed to be responsible. This is evident in the relatively quick stabilization of the product upon dilution in water.

In addition, at higher temperature, the characteristic peak for tri-sodium thiocarbonate compound was also observed at 332 nm, whereas the low temperature products did not indicate the formation of tri-sodium thiocarbonate.

Markedly, the polyxanthate products of the low temperature reaction (13 to 20°C, 5 hrs.) showed considerably

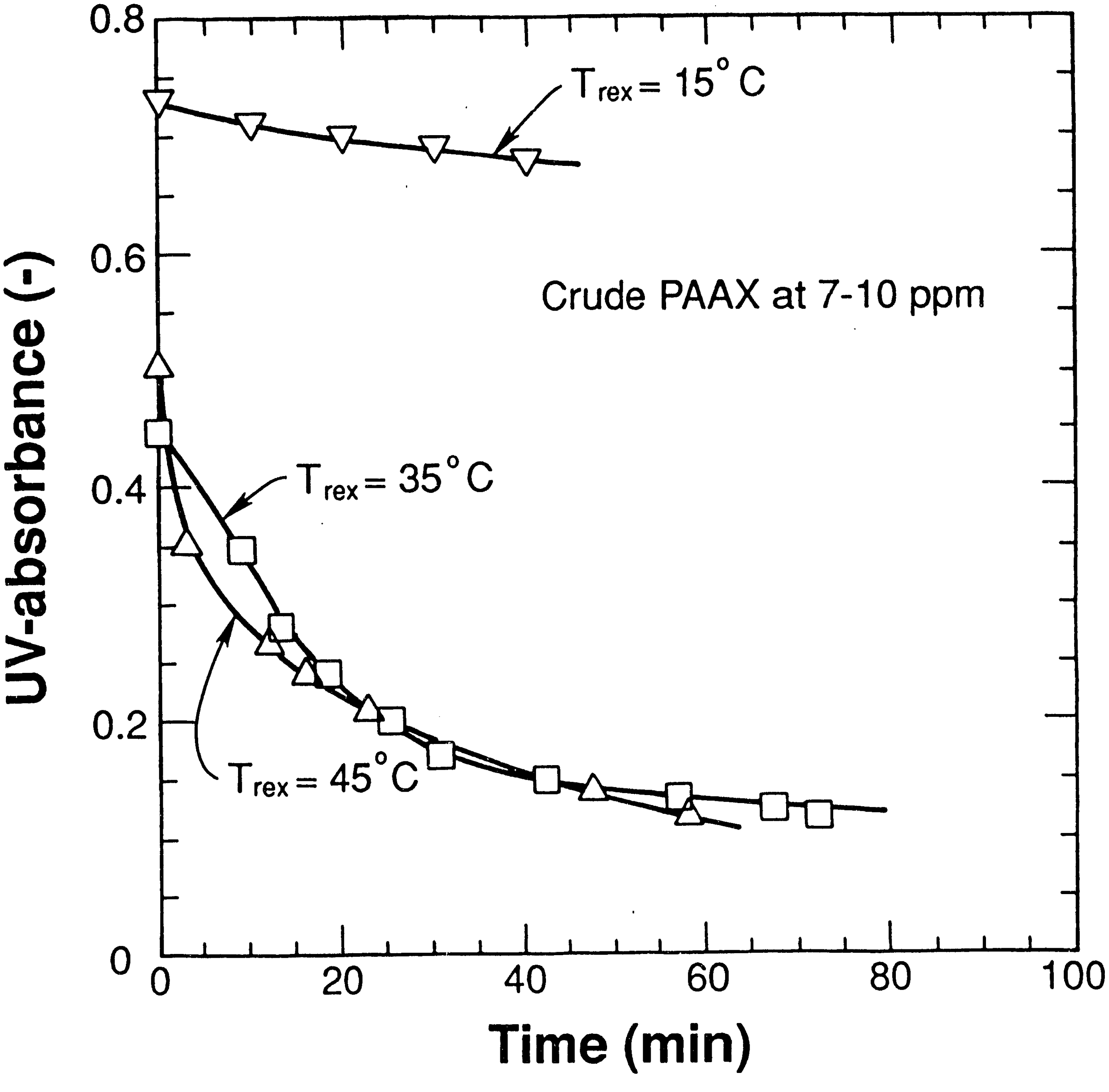


Figure 1.3 Effect of Reaction Temperature on the Decomposition of PAAX Products of of 15, 35 and 45oC.

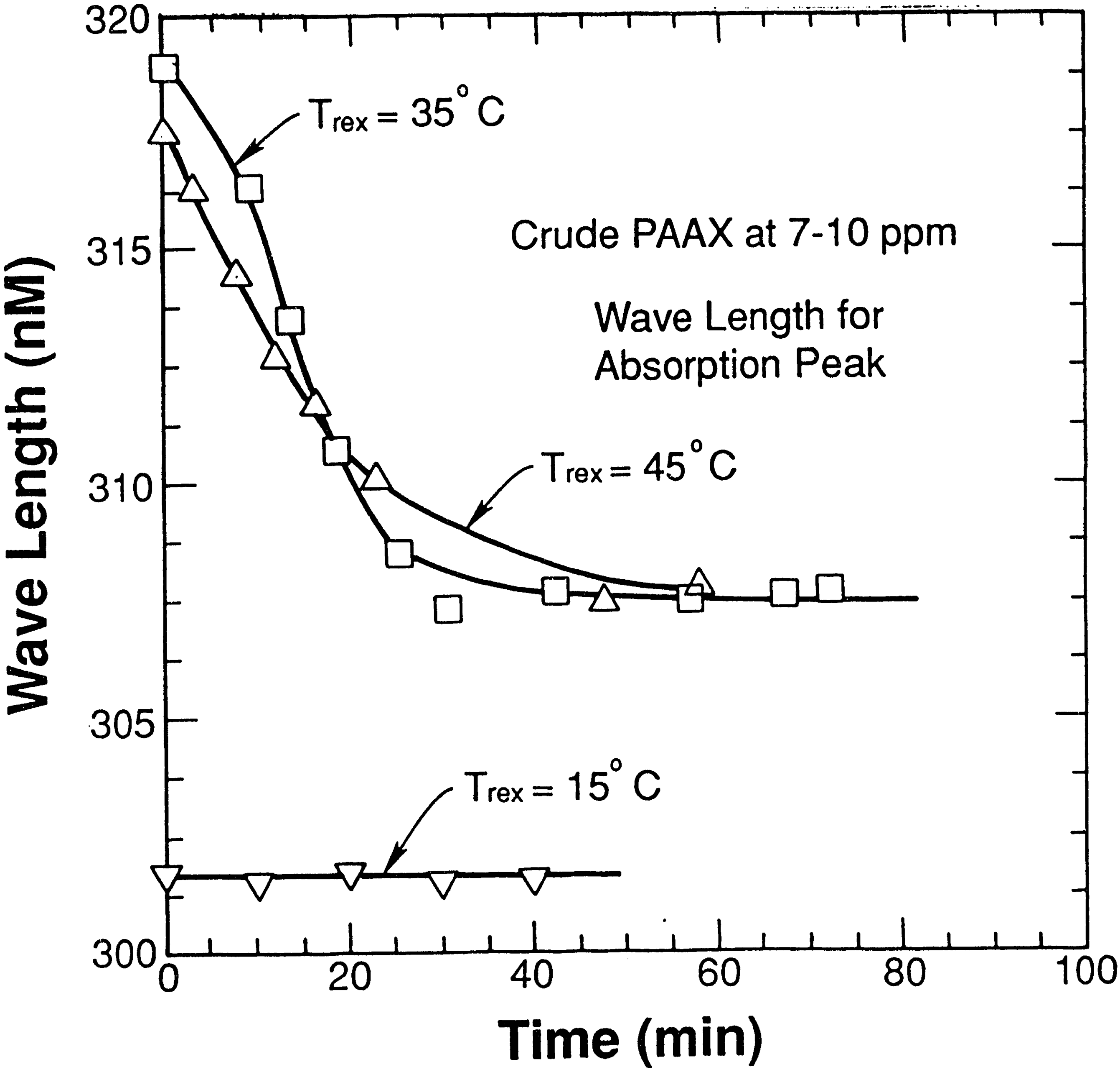


Figure 1.4 Effect of Reaction Temperature on the Stability of the Characteristic UV-Absorbance Peak for PAAX Products. Reaction Times were: 5 hours for 15°C, 2 hours for 35 and 45°C Reaction Temperatures.

more stable behavior and higher absorbance at the same dilution rate which means a higher degree of xanthation.

Effect of CS_2 Dosage. Figure I.5 shows the effect of initial dosage of CS_2. As was expected, the higher dosage of CS_2 resulted in a higher degree of xanthation. However, excessive dosage of CS_2 is not recommended since after a certain amount of CS_2 dosage, the xanthate group concentration did not increase significantly and further addition of CS_2 would merely prolong the purification process. It should be noted that the optimum amount of CS_2 dosage is a function of the reaction temperature and the reaction time. Therefore, the results of one set of reaction conditions could not be employed to predict the dosage for a different reaction conditions.

Attia[4] reported similar findings for the xanthation of cellulose. The comparison of 40 wt% initial CS_2 to cellulose dosage with 400 wt% CS_2 dosage indicated a significantly higher xanthate content and also more uniform substitution of xanthate group. The reported results are compatible with the data obtained in these experiments. As shown in Figure I.5, the xanthate concentration increased approximately by a factor of four when the initial CS_2 / PAA wt. ratio increased from 1 to 4 which, in terms of degree of xanthation of carboxylate groups in the polymer chain, means an increase of 5 to 35 percent.

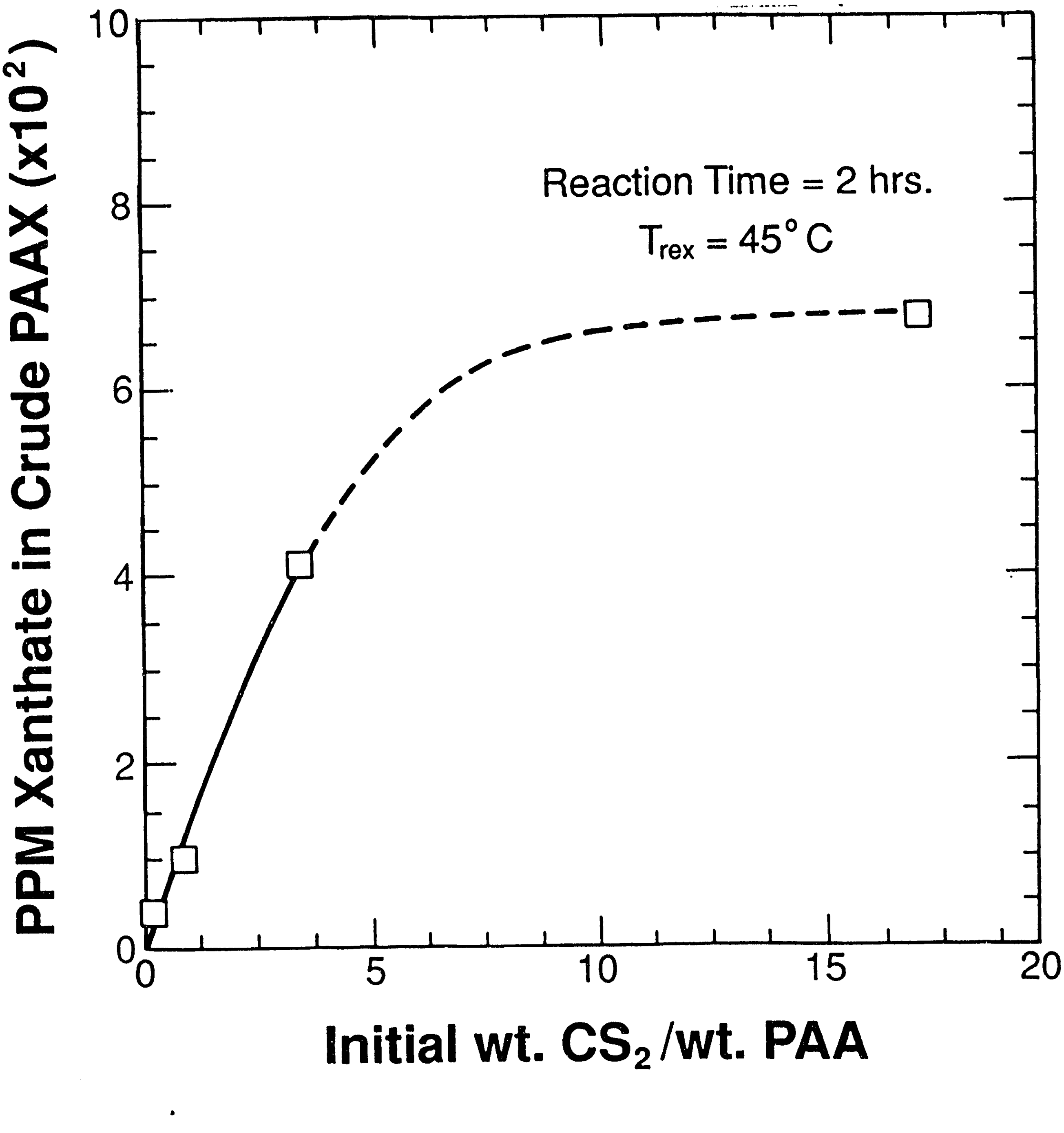


Figure 1.5 Effect of Initial CS_2 Dosage On Xanthation of Polyacrylic Acid.

Nevertheless, as discussed before, excessive dosage of CS_2 is not recommended since it can complicate the purification step.

General Dispersant (SMP).

The general dispersant used in all the flocculation and in some of the adsorption experiments is sodium meta-phosphate (SMP) which has the chemical structure of

$$(Na\ PO_3)_x \cdot NaO$$

where x=13. This chemical is a very strong dispersant due to the presence of a large number of negatively charged ions of PO_3^- in each molecules. The appropriate amount of SMP was added to the coal before grinding such that when the coal slurry was diluted, the concentration of SMP was 200 to 300 ppm. SMP was purchased from Fisher Scientific company.

Flocculants

FR-7A. FR-7A is a type of totally hydrophobic polymer, provided by Calgon Corp., Pittsburgh, Pennsylvania. The exact chemical structure of this polymer is an industrial proprietary information and cannot be revealed. Since this polymer is specifically emulsified, it can well disperse in water. The molecular weight of FR-7A is believed to be slightly less than one million. However, it was observed that the FR-7A polymeric colloid cloud tends to migrate to the anode under an electropheresis cell. It seems that FR-7A appears weakly anionic.

The calibration of FR-7A concentration vs. turbidity was made using the nephelometric method (see following section), and a very good linear relationship was found as follow:

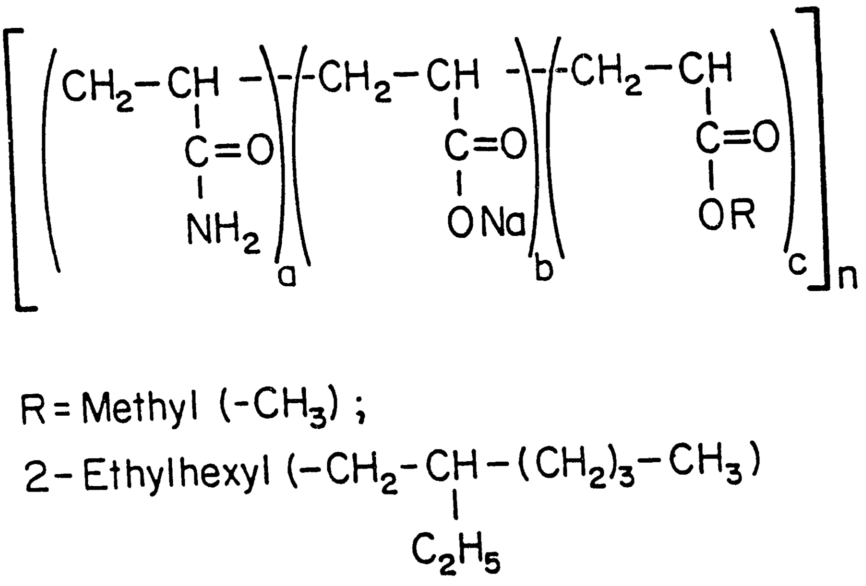
mg/l of FR-7A = NTU/2.34

Also, it was found that this calibration relationship is independent of solution pH.

F1029-D and F1029-J. These flocculant are both partially hydrophobic co-polymers. They were manufactured by DKS Company in Japan. Figure I.6 shows the chemical structure of both flocculants. Note the ratios of a, b, and c groups can directly affect the selectivity of the flocculant. The higher the a and b the more hydrophilic is the flocculant, and thus, it is less selective. The average molecular weight of both F1029-D and J were three million. The a/b ratio for D was 85.5 and for J was 60.23 .

Minerals

The coal used in this study was Pittsburgh Number 8 coal seam and Upper Freeport coal (used mostly for adsorption tests), obtained from the R&F Coal Company, Lamira preparation plant, Warnok, Ohio. The coal was obtained in large chuncks which were crushed to average size of 5 to 7 mm. The crushed coals were either directly used for the experiments (both adsorption and flocculation tests) or pre-cleaned using heavy liquid separation (tri or tetrachlorethylene, S.G.=1.6 or 1.3) technique. The float was collected, filtered and washed with acetone and then dried at 104°C for five hours. It should be noted that the



R = Methyl ($-CH_3$) ;

2-Ethylhexyl ($-CH_2-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-(CH_2)_3-CH_3$)

Figure I.6 Structure of Partially Hydrophobic Flocculants Series F1029 Co-polymer. The proportions of the various units are as follows: (a) Acrylamide = 55-85%; (b) Sodium Acrylate = 0-15%; (c) Hydrophobic Units R = 10-40%. (Attia, 1987) change in surface properties of the coal due to heavy liquid separation is insignificant specially when the float is ground to minus 500 mesh (-25 micron).

The coal slurry was prepared by grinding one kilogram of coal in two kilograms of distilled water which had a pH of approximately 10, and 3000 mg/ℓ SMP. The high SMP concentration was used so that when the slurry was diluted to 5% to 10% solids, the SMP concentration would be 300-600 mg/ℓ. The coal was ground to minus 500 mesh (-25 micron) in an attrition mill supplied by the Fort Pitt Mine Machine Co., Pittsburgh, Pennsylvania and/or in a ball mill.

Pyrite at 99.3% purity from Hunzala, Peru, and the arigillaceous shale mineral were supplied by Ward's Natural Science, Inc., NY. Each of them was attritioned to very fine (the majority below -500 mesh) and stored in the refrigerator.

Characterization of samples. The total sulfur contents of the coal samples were measured by a Sulfur Determinator, Model SC132, manufactured by LECO Co., and the ash contents were measured by an Isotemp Programmable Ashing Furnace, Model 497, Produced by Fisher Co., respectively. The measurements followed the ASTM procedures [ref.10].

The surface areas of the samples of coal, pyrite and shale were determined using an Accusorb 2100E manufactured by Micromeritics Instrument Corporation, Norcross, Georgia.

A Laser Zee(tm) Model 501, Manufactured by Penkem, Inc., Bedford Hills, New York, was employed to measure the zeta potential (the potential at the shear plane of the electrical double layer) of colloidal particles by determining the rate at which these particles move in a known electric field. From the measured zeta-potentials, the point of zero charge (pzc) of each sample was derived.

The particle size, and size distribution of the coal slurries were measured by the Microtrac particle size analyzer using laser diffraction suppling by Leeds and Northrup Corp. Small samples of a well mixed slurry were used to perform the size measurements.

Table I.3 lists the analyzed data of ash and total sulfur contents, surface area and pzc of the samples used in the adsorption experiments. These data indicate that: a) the prepared shale powders were very fine, which was due to the over-attrition; b) the pzc of pyrite is almost the same as the coals', which means that they have similar surface electrostatic properties.

Procedure of Adsorption Determination

The general procedure for conducting the adsorption study consists of five steps.

The first step was sample preparation. The selected fresh mineral solids (coal, pyrite and shale) were finely ground separately then were stored uder refrigeration to minimize

Table I.3 Analyses of the samples which were used in adsorption

Sample	Ash (%)	Tot. S (%)	Surface Area (m^2/g)	pH of pzc
Upper Freeport coal (after heavy liquid separation at 1.3 s.g.)	3.5	1.80	2.615	6.7
Pittsburgh No. 8 coal (after heavy liquid separation at 1.3 s.g.)	4.2	2.67	3.5	7.1
Pyrite	----	----	3.578	7.1
Shale	----	----	7.422	2.1

surface oxidation. The subsequent step was adsorption of the chemicals on the selected minerals. The specific chemical (FR7A or PAAX) was added to a solid/liquid mixture at the desired conditions for a certain time to allow the chemical molecules to adsorb on the solid particles' surfaces. The third step was solid/liquid separation. For coal flocs, the separation could be conducted easily through filtration. For pyrite and shale minerals, membrane filtration was performed using membranes with pore size less than 0.2-0.45 micron. Measurement of the residual chemical concentration in the liquid was made. This concentration was corrected by comparing it with that of standard or calibrated ones. Finally, it was data computing. From the difference in concentration between the initial and residual solutions, the quantity of adsorbed chemical could be derived. Then, according to the measured data of surface area, the adsorption density of the chemical on a mineral of known surface area could be determined.

Determination of FR-7A concentration. Two techniques were employed for measuring the polymer concentration in residual solution. These were: nephelometry and uv-vis spectrophotometry.

The nephelometric method was found to be directly applicable to the FR-7A polymer because this polymer is supplied as an oil in water emulsion. A Nephelometer, Model 21, manufactured by Monitek Inc., Hayward, California, was employed for the turbidity measurement. A standard solution with a turbidity 4.3 NTU provided by the manufacture was used for calibration of the nephelometer. The range of measured turbidity with this instrument was 0.01 to 200 NTU. The caliberation curve for FR-7A is shown in Appendix B.I.

Selective Flocculation Experiments

Table I.4 summarizes all the chemicals and conditions which were used for selective flocculation of the coal slurries. In the following sections each parameter is discussed in more detailed.

Figure I.7 shows the basic steps in the flocculation experiments. After heavy liquid separation, the coal particles were ground and then a 5 wt% slurry mixture was prepared. The coal slurry was first agitated for five minutes at a shear rate of 425 sec^{-1}(approximately 700 rpm), and the pH was adjusted to the desired value. When the experiment involved the use of PAAX, PAAX was added at the beginning of the experiment to the slurry

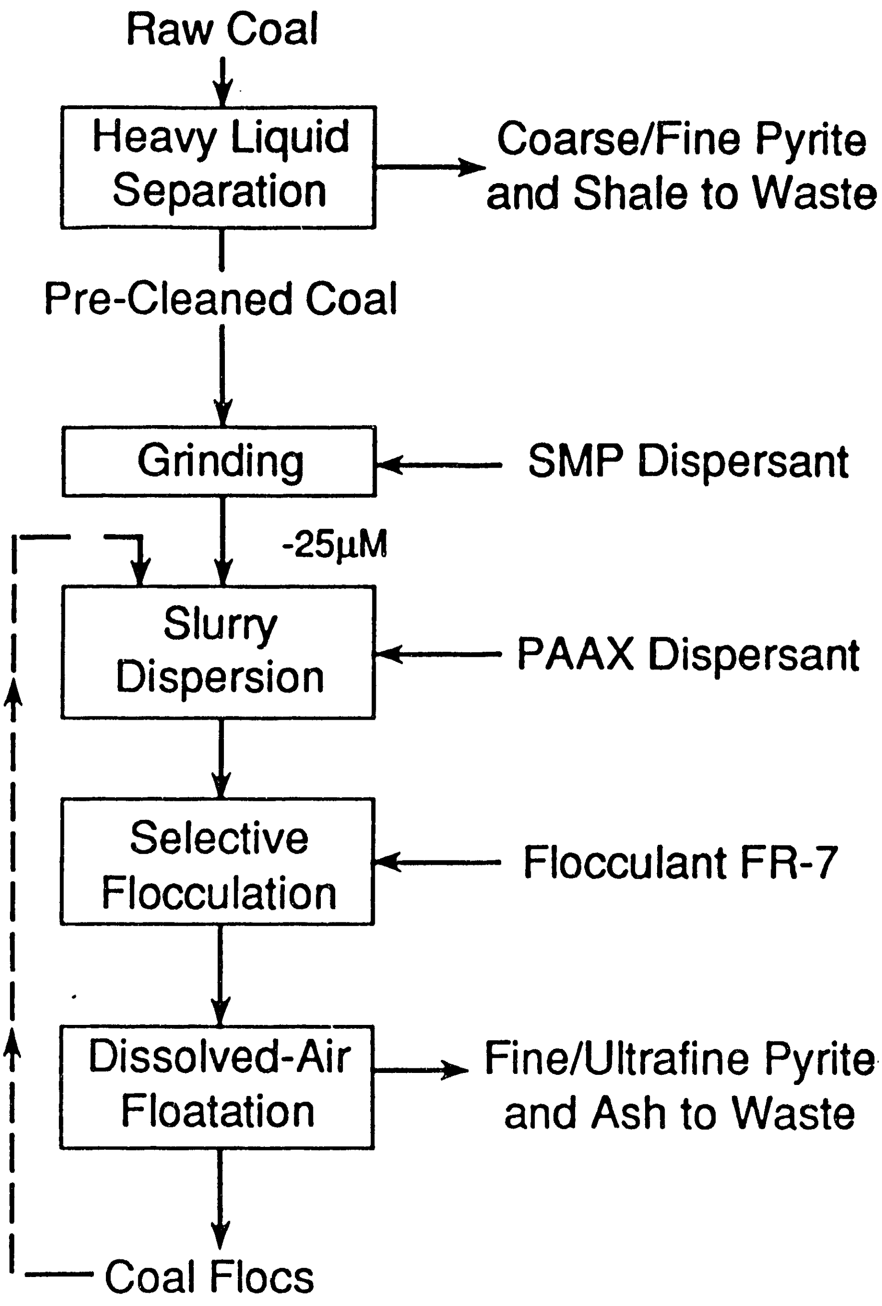


Figure 1.7 Experimental Scheme of Selective Flocculation of Coal Slurries.

Table I.4 The Ranges of parameters for Selective Flocculation experiments

Dispersants:	Sodium meta phosphate General dispersant Kept at 300 ppm
	PAAX as selective dispersant Varied from 50 to 500 ppm
Flocculants:	F1029-D, F1029-J, FR-7, and FR-7A 5 to 100 ppm
Slurry concentration:	4.5 to 10% wt. solid
Slurry type:	Raw coal Pittsburgh no. 8 Pre-cleaned coal Pittsburgh no. 8 Synthetic mixture (mixture of measured amounts of pre-cleaned coal, pyrite and shale)
Agitation:	700 to 1000 rpm for polymer mixing 100 to 250 rpm for flocs conditioning
Flocs separation:	Sedimentation (1, 2, or 3 steps) Dissolved-air flotation (1 and 2 steps) Froth flotation (1 and 2 steps) Combination of sedimentation and flotation
Grinding:	Attrition 30 minutes (25% solid) Ball mill 1 to 17 hours (50% solid)
pH:	5 to 11

and then the pH was adjusted. This is done because the crude PAAX stored in very basic pH solution with approximately 2-3% NaOH concentration. The slurry was conditioned with PAAX at 425 sec^{-1}shear rate for 10 minutes. Varied amounts of flocculant was added over one minute interval, and was allowed to mix for one minute. The shear rate was then reduced to 170 sec^{-1}, and the flocs were allowed to condition for three to five minutes. The mechanism of selective flocculation is shown in Figure I.8.

The flocs were separated by different methods as listed in the previous Table I.4. Most frequently, flotation (either dissolved-air or froth flotation) was used. The main advantage of either of these separation processes is that the flocs do not settle, so the pyrite which is not dispersed by the PAAX will not report with the flocculated fraction. The equipment used to study dissolved air flotation is shown in Figure I.9. It consisted of a sealed vessel (1) connected to a long cylinder column (2) filled with packing (3). The lower end of the column was connected to a stirred vessel (4) which was used as flotation cell. The system was allowed to stand at 620 kPa (75 psig) for five minutes to allow air dissolution to come to an equilibrium. In addition to hydrophobic flocculant, 0.82 kg/ton of methyl isobutyl carbinol (MIBC) was used as the flotation reagent.

A Galligher flotation machine was used for froth flotation test. The cell has a capacity of 1.5 liter and mixing was conducted at 1000 to 3000 rpm.

Finally, multiple cleaning stages were tested by performing one and two step selective flocculation-flotation or flocculation-sedimentation-flotation tests. For this set of experiments, the flocs from the first cleaning stage were re-dispersed under high shear rate mixing, and then re-flocculated.

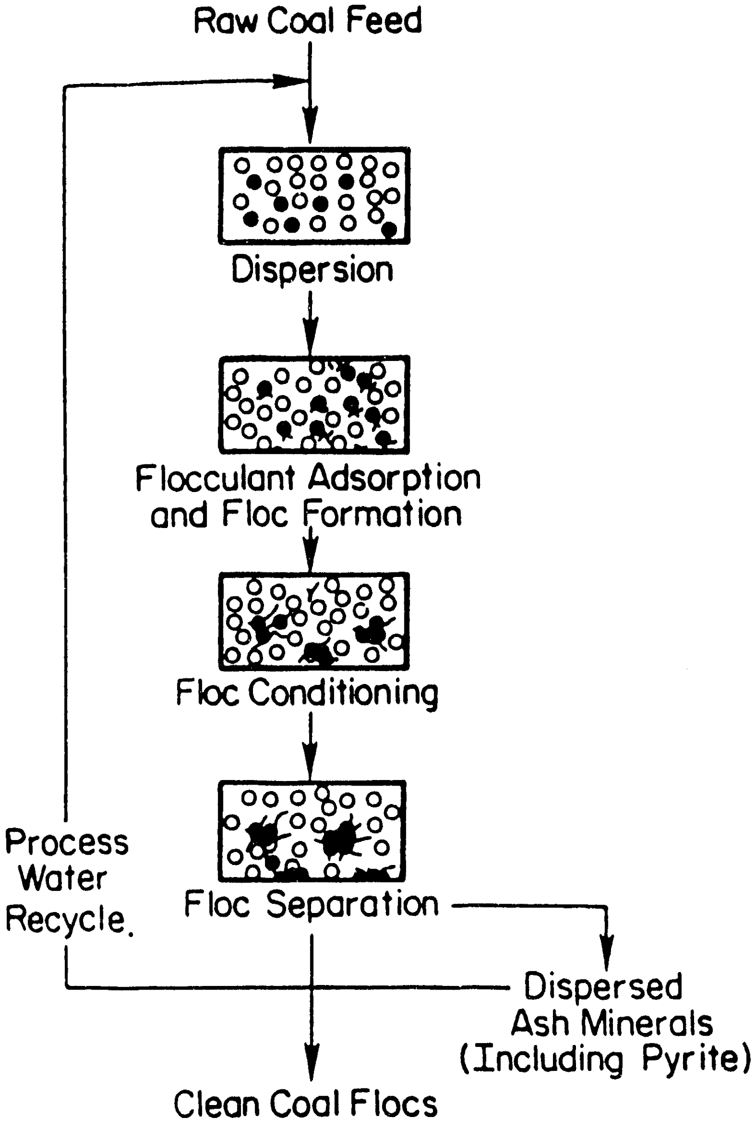


Figure 1.8 Mechanism of Selective Flocculation of Coal Slurries.

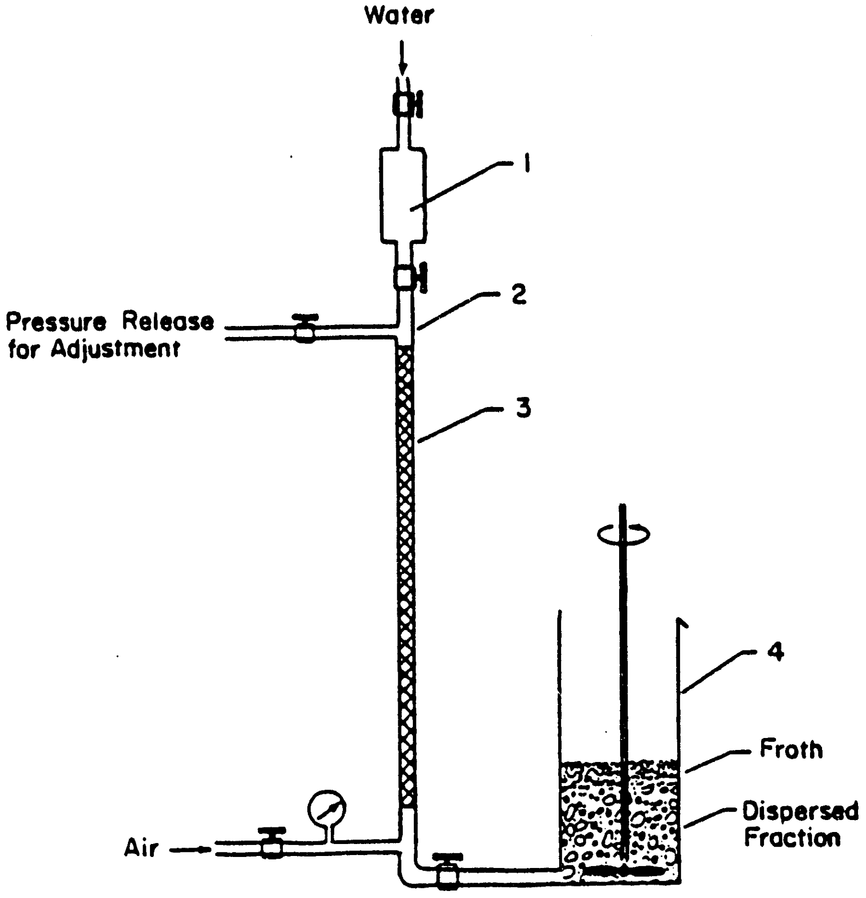


Figure 1.9 Dissolved-Air Flotation Apparatus.

I.3 RESULTS AND DISCUSSION

Adsorption Experiments

Adsorption of FR-7 on minerals

Kinetics of Adsorption of FR-7A. The purpose for studying the adsorption kinetics of FR-7A was to find out the time for adsorption to attain equilibrium. Adsorption kinetics of FR-7A were conducted at various levels of pH and initial FR-7A concentration. The results as illustrated in Figs. I.10, I.11, and I.12 indicate that the time for adsorption to attain equilibrium are about 8 hours for the Upper Freeport coal, about 4-5 hours for pyrite, and about 5-6 hours for shale. However, the adsorption equilibration time was taken as 12 hours. This equilibration was used in the subsequent tests for establishing adsorption isotherms.

Adsorption Isotherms of FR-7A. The tests to establish the adsorption isotherms were performed at various pH levels and initial FR-7A concentrations below 250 mg/l. The experimental data on the adsorption isotherms are summarized in Figure I.13 for the four mineral samples respectively. The obtained results indicate that:

a) The adsorption isotherms appear to be the Langmuir adsorption type [ref. 14].

b) Adsorption density of FR-7A was influencedby pH: at acidic pH FR-7A adsorbed significantly on all minerals. The adsorption

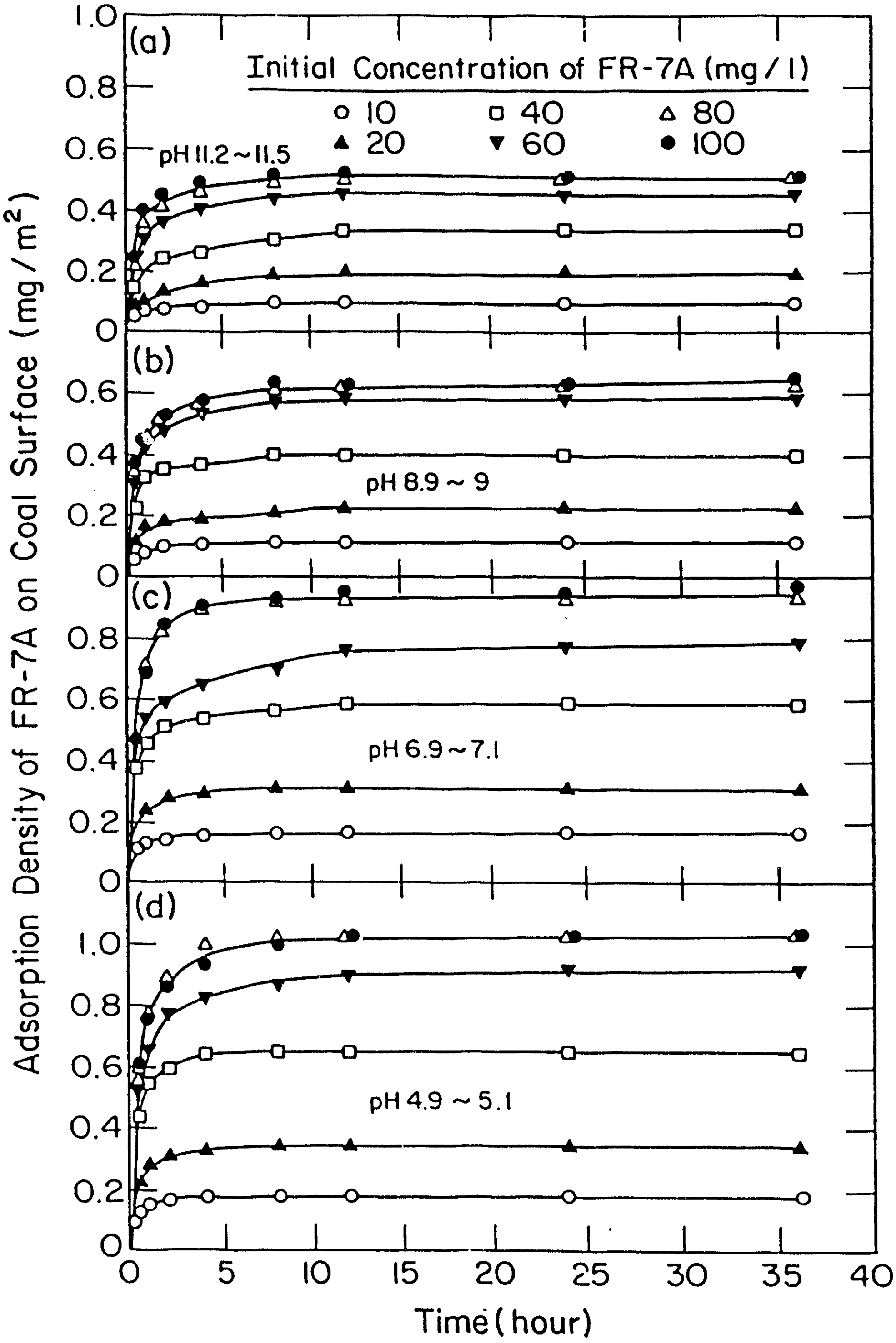


Figure 1.10 Adsorption kinetics of FR-7A molecules on the Upper Freeport coal at various pH values and initial FR-7A concentration

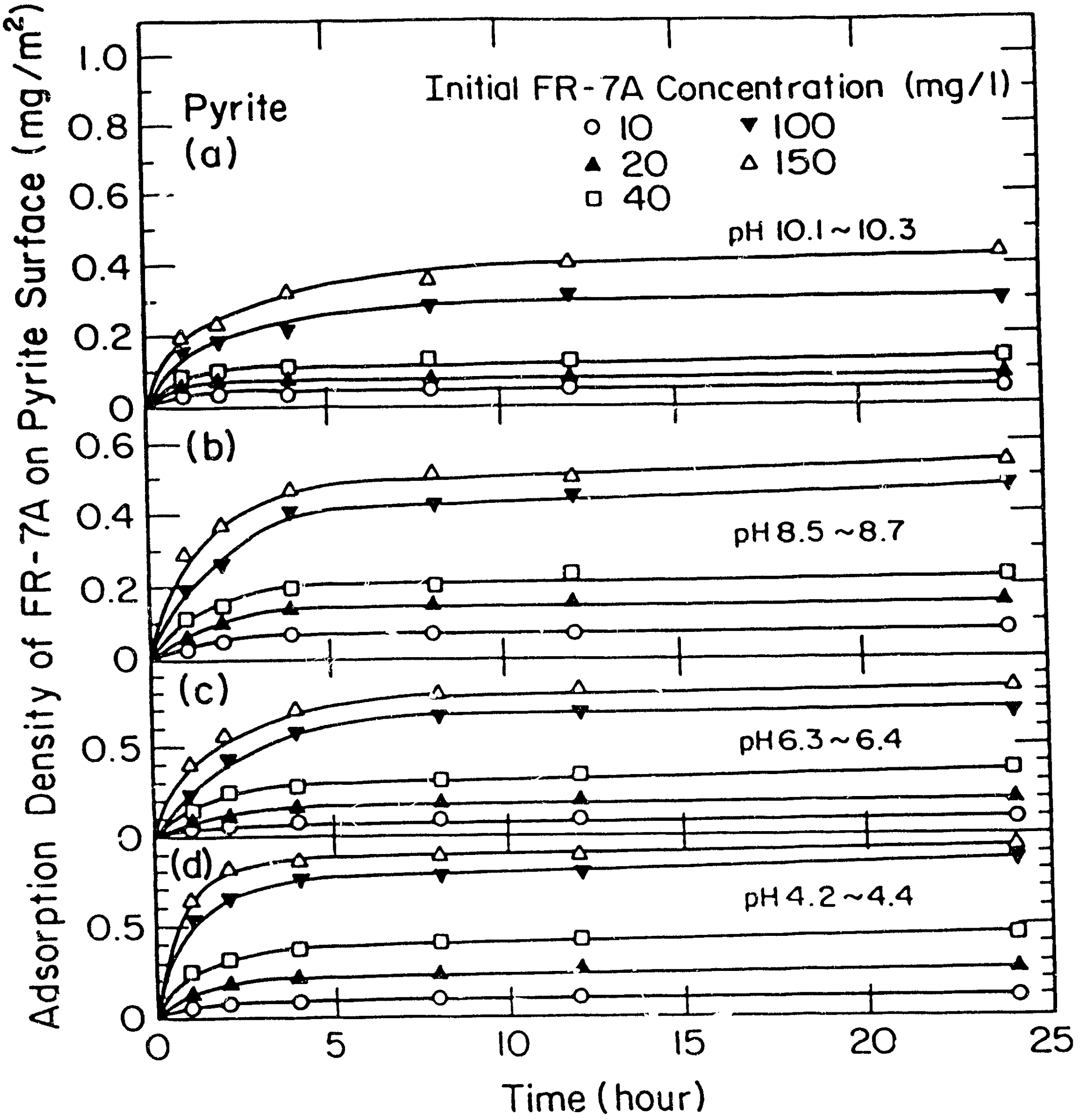


Figure 1.11 Adsorption kinetics of FR-7A molecules on pyrite at various pH values and initial FR-7A concentration

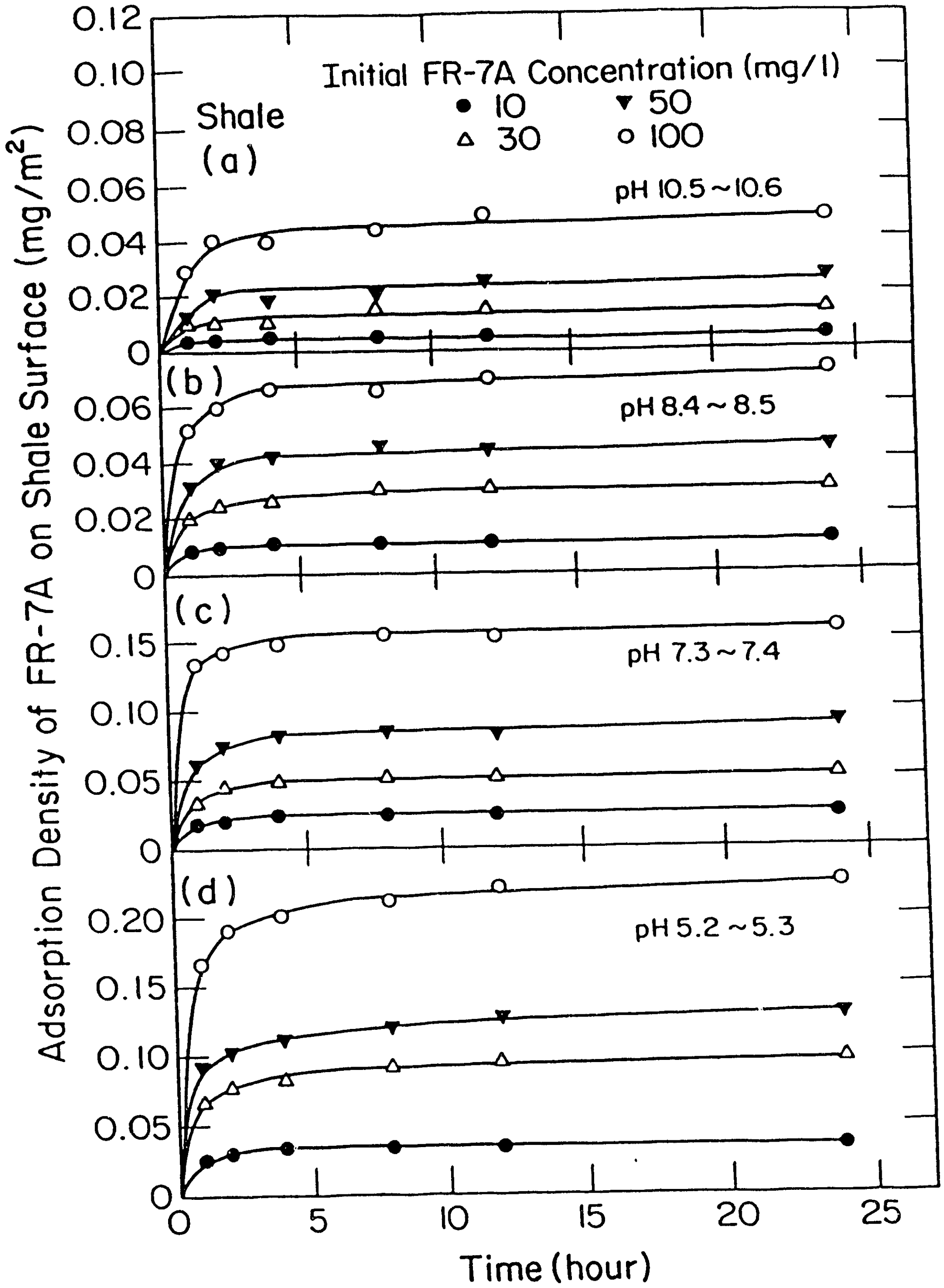


Figure 1.12 Adsorption kinetics of FR-7A molecules on shale at various pH values and initial FR-7A concentration

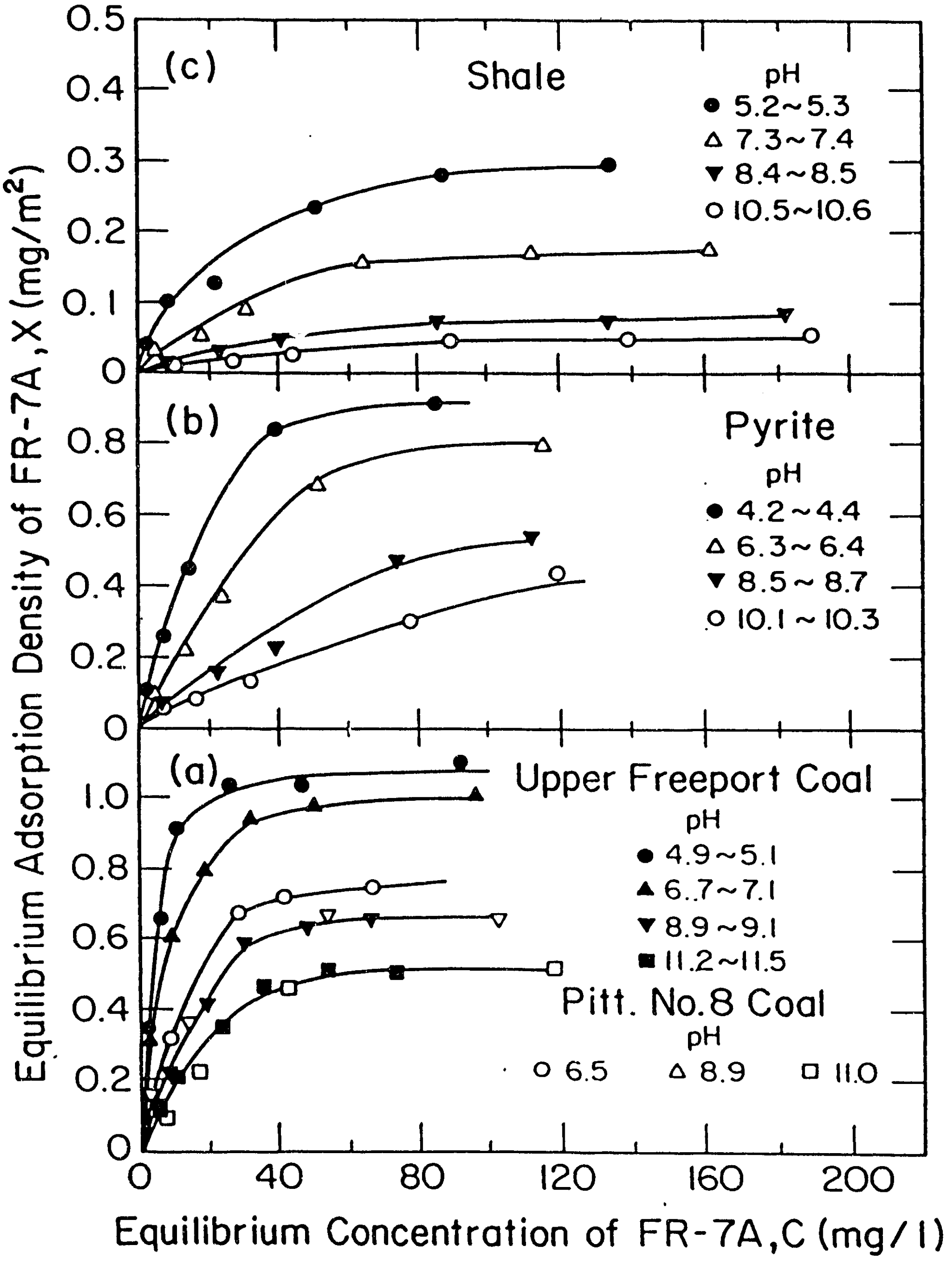


Figure 1.13 Adsorption isotherms of FR-7A on the Upper Freeport coal, Pittsburgh No. 8 coal, pyrite and shale at various pH

densities (mg/m^2) are 1.1 for coal, 0.9 for pyrite and 0.3 for shale. However, above pH 8.5, FR-7A adsorption on shale was very small (i.e.; less than 0.1 mg/m^2), while its adsorption on coal and pyrite was still high (0.6 and 0.5 mg/m^2). Figure I.14 shows the comparison of adsorption isotherms of FR-7A on the different minerals at pH between 8.5-9.0. The curves clearly indicated that FR-7A has a high affinity to coal then to pyrite, due to the natural hydrophobicity of coal and pyrite. The affinity of FR-7A to shale is poor because of the natural hydrophilicity of shale.

<u>Effect of pH on Adsorption of FR-7A</u>. Figure I.15 illustrates the equilibrium adsorption density of FR-7A vs. pH. This figure confirms the observations mentioned above. This adsorption behavior suggests that both the electrostatic and hydrophobic bonding mechanisms are operative in acidic media, while the hydrophobic bonding is the main mechanism for adsorption in alkaline media.

<u>Effects of SMP on Adsorption of FR-7A</u>. Figure I.16 shows the effect of SMP on the electrokinetic properties for the Upper Freeport coal, pyrite and shale respectively. The figure illustrated that by increasing SMP concentration, the zeta-potentials of the minerals became more negatively charged. This was likely due to the adsorption of metaphosphate anions on the mineral surfaces. However, when SMP concentration was higher than 300-400 mg/l, the zeta-potentials of the minerals did not increase any further. This implied that adsorption reaches a

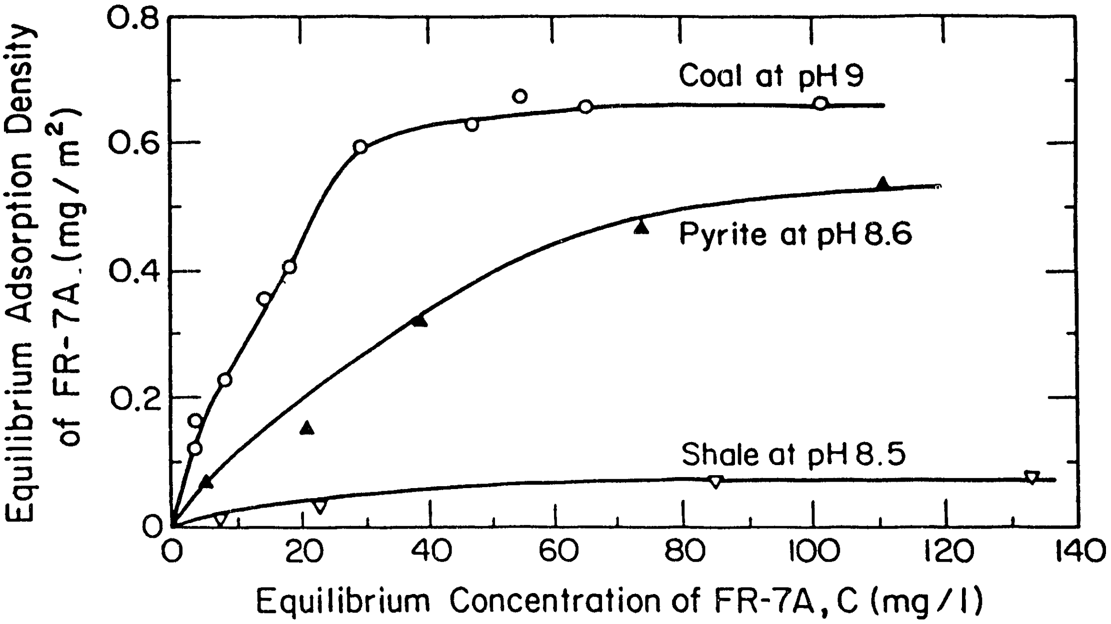


Figure 1.14 Comparison of adsorption isotherms of FR-7A on coal, pyrite and shale at pH 8.5-9.0

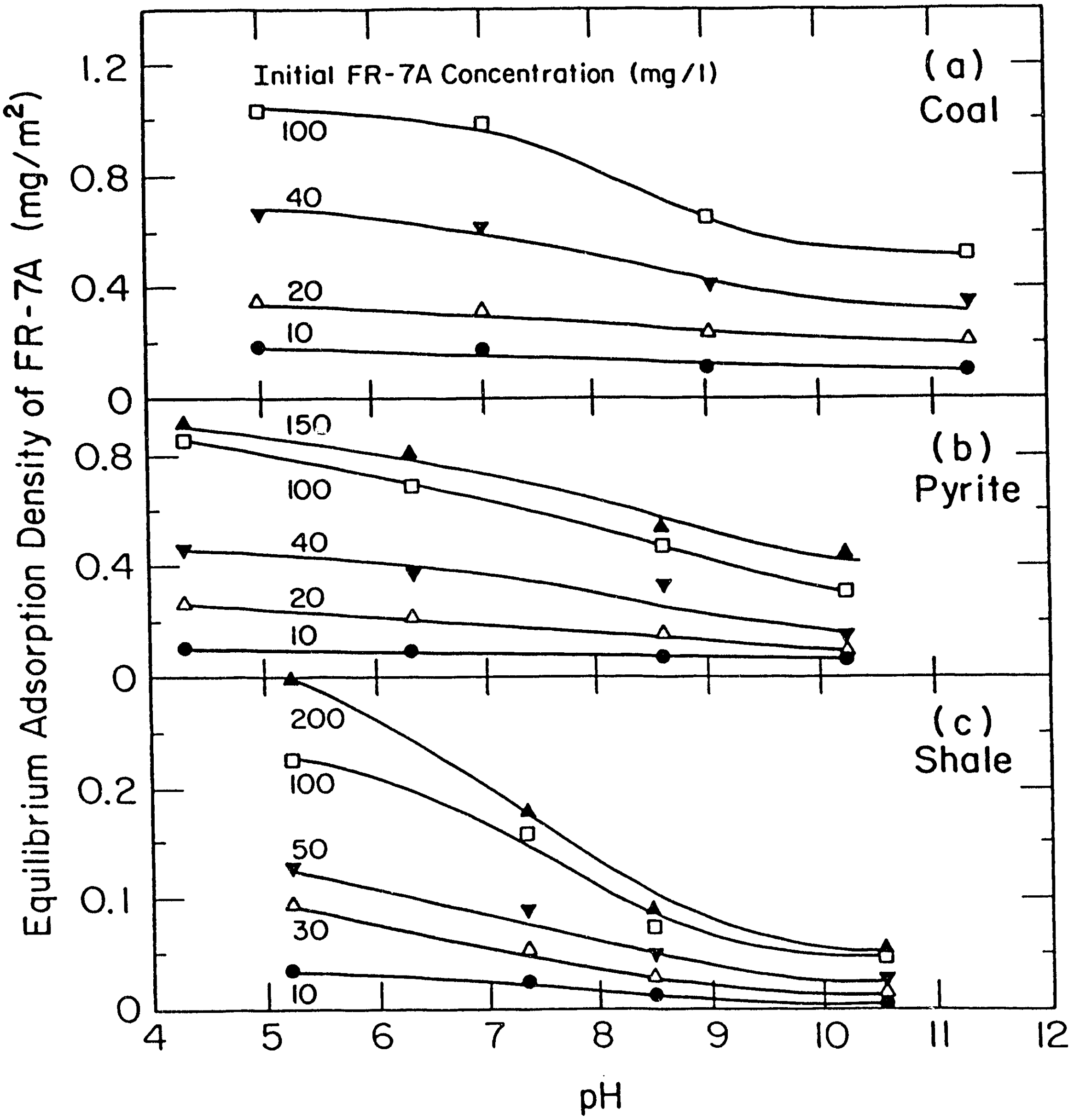


Figure 1.15 Effect of pH on the adsorption density of FR-7A molecules on the Upper Freeport coal, pyrite and shale (Note: the expanded scale for the graph on shale is different from those on coal and pyrite)

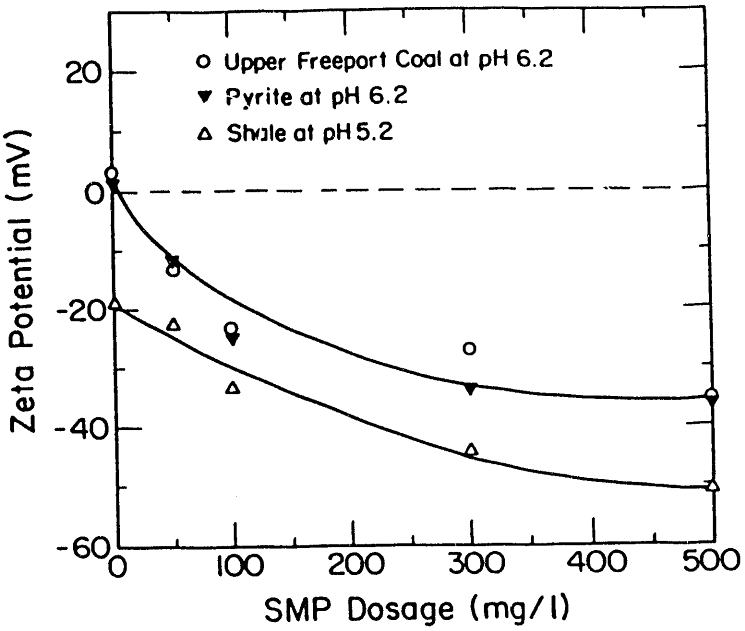


Figure 1.16 Effect of SMP dosage on the electrokinetic properties of the Upper Freeport coal, pyrite and shale

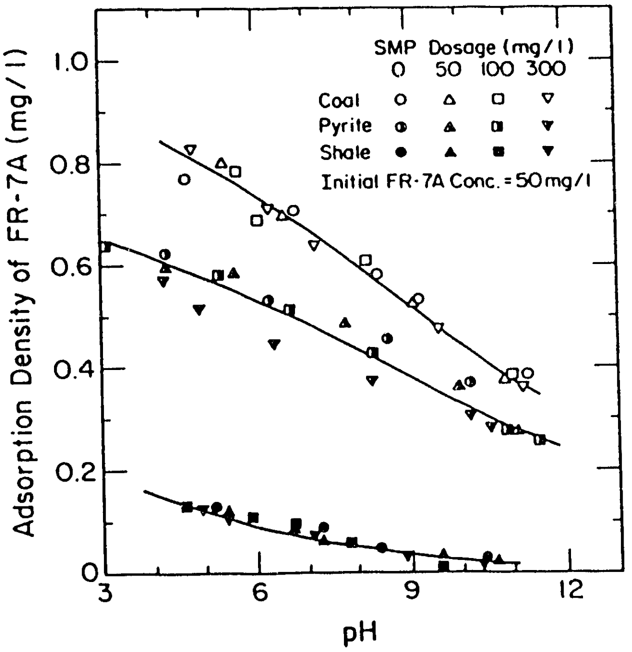


Figure 1.17 Effect of SMP on adsorption density of FR-7A on the Upper Freeport coal, pyrite and shale at various pH

saturation level akin to langmuir monolayer coverage of the mineral surface.

Since the presence of SMP leads the mineral surface to be more electrically negative, the adsorption of FR-7A on coal and other minerals should be reduced or even inhibited due to electrostatic repulsion between the solid surface and the anionic FR-7A molecules. However, the results illustrated in Figure I.17 indicated that SMP did not influence the adsorption in any way. This might be due to the relative ease of displacing SMP ions on the surface with FR-7A molecules which have much higher free energy of adsorption than the weakly held SMP ions.

Adsorption of PAAX on Coal Minerals

Kinetics of PAAX adsorption. This study was aimed at determining the time needed for PAAX/minerals interface to attain adsorption equilibrium. The results, in Figure I.18, indicated that the equilibration time for Upper Freeport coal and shale was 4 hours and for pyrite it was 8 hours. However, in the conduct of adsorption isotherms, the equlibration time was taken as 12 hours. Also, it can be seen that the adsorption density of PAAX on pyrite was about 6 times higher than that on coal and on shale.

Adsorption isotherms of PAAX. The purpose of the tests discussed in this section was to determine the adsorption isotherms of PAAX, i.e., the relationship between adsorption density and equilibrium PAAX concentration. A set of tests was performed at pH 11.2 where a certain dosage of PAAX solution was mixed with a

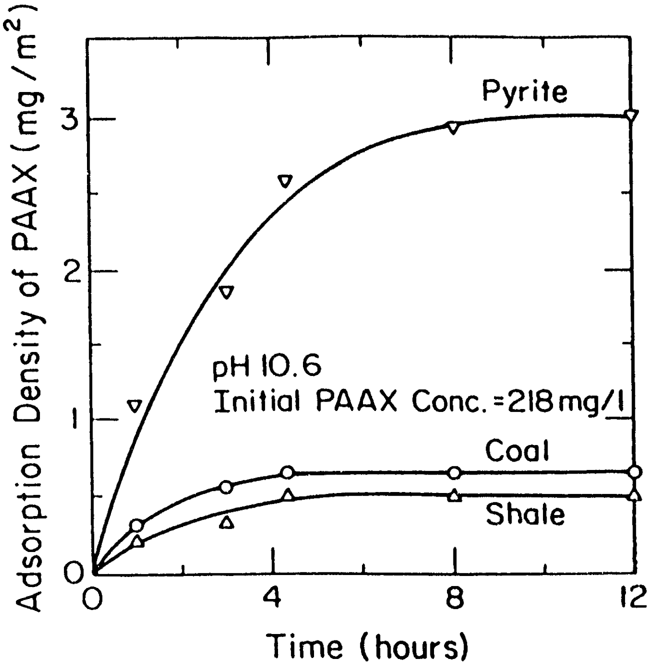


Figure 1.18 Adsorption kinetics of PAAX on the Upper Freeport coal, pyrite and shale at pH 10.6

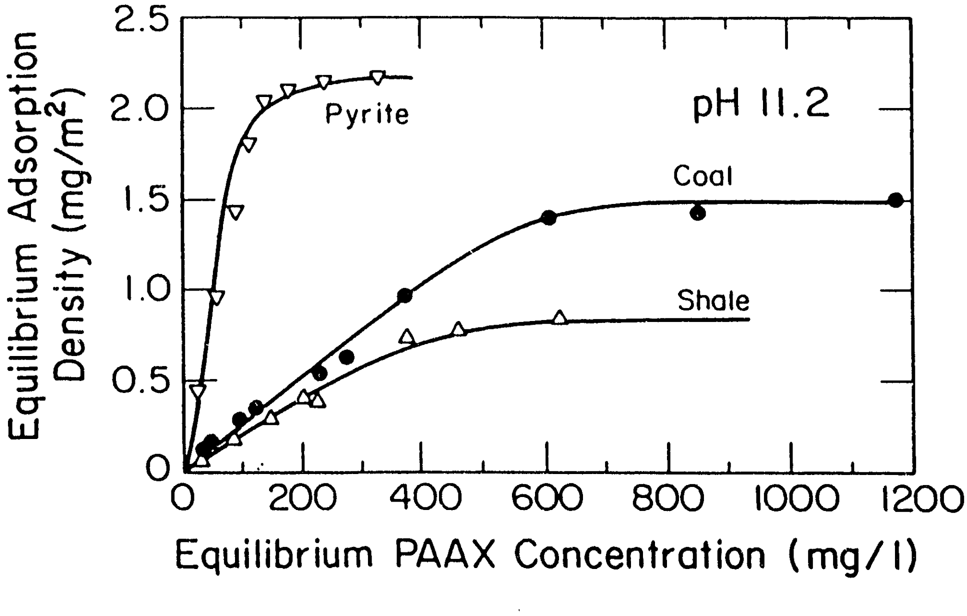


Figure 1.19 Adsorption isotherms of PAAX on the Upper Freeport coal, pyrite and shale at pH 11.2

certain amount of mineral solids at 1 or 2% solid content. The mixture was allowed to stand for 12-13 hours to attain adsorption equilibrium.

It can be observed from Figure I.19 that the adsorption density of PAAX on pyrite was about 8 times higher than that on the Upper Freeporc coal, and shale at the lower concentration range (i.e. less than 350 mg/liter initial concentration of PAAX). As the PAAX concentration was increased to much higher levels, its adsorption density on coal and shales gradually approached that on pyrite. Usually, the dosage of PAAX in selective flocculation is controlled at about 200 mg/l. Therefore, we expect that PAAX would selectively adsorb on pyrite in preference to coal and shales and consequently, enhance the pyrite's dispersion.

Effect of Adsorption of PAAX on zeta-potential. In Figure I.20 were shown as function of adsorption density. The results indicated that when the PAAX adsorption was relatively low, i.e.;below 350 mg/liter, the zeta-potential of each of the minerals became more negative with increasing PAAX adsorption.

Effect of SMP on PAAX adsorption. In this set of tests, the mineral slurry was mixed with pre-determined amounts of PAAX and SMP at pH 10.5. The initial PAAX concentration was adjusted at 266 mg/l, and SMP dosage was at 0, 50, 100, 200 and 500 mg/l respectively. The slurry was conditioned for about 12-14 hours. Adsorption density of PAAX were in the same manner mentioned

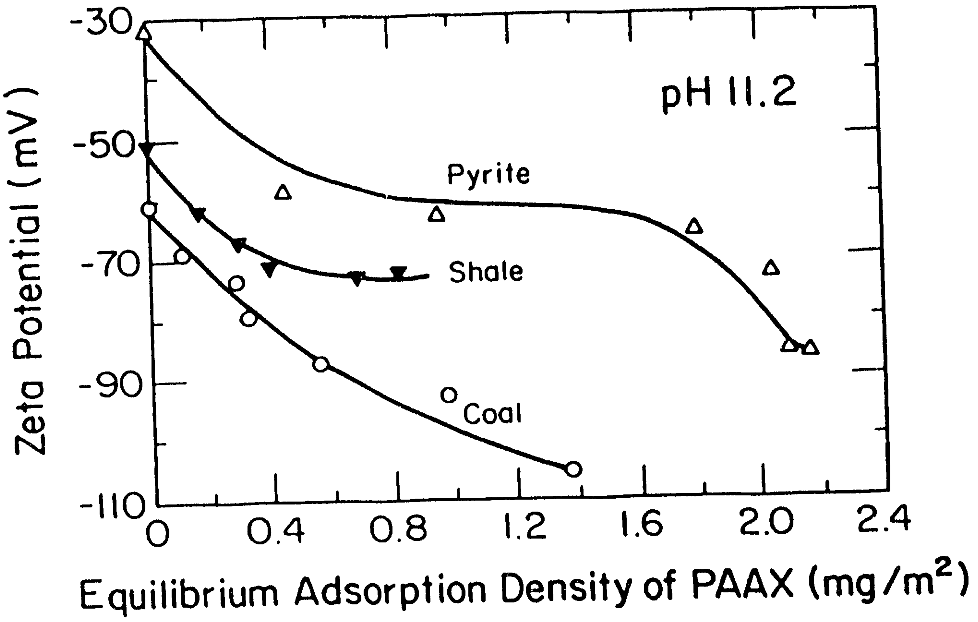


Figure 1.20 Effect of adsorption of PAAX on zeta-potentials of the Upper Freeport coal, pyrite and shale at pH 11.2

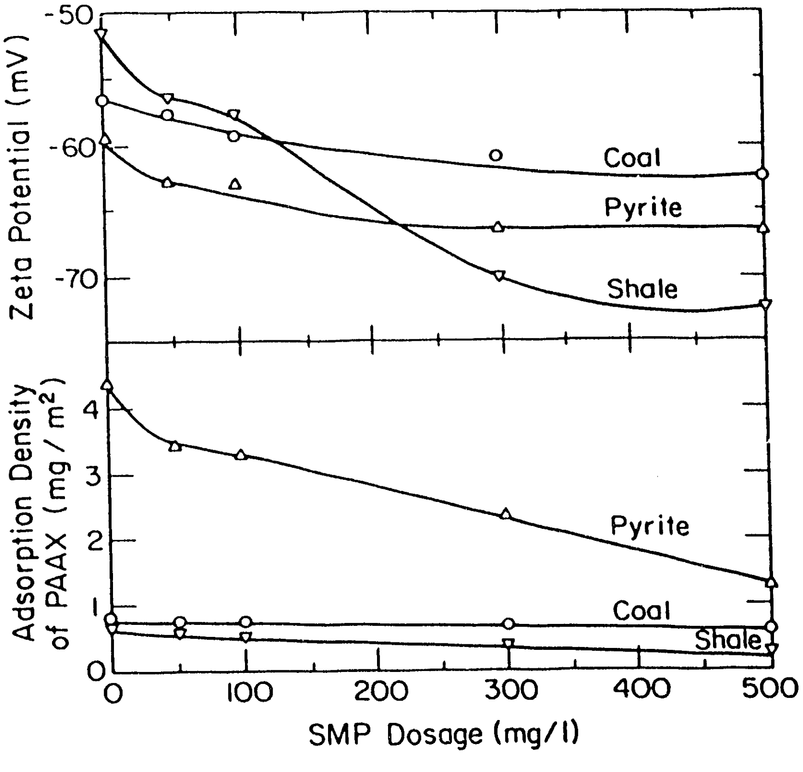


Figure 1.21 Effect of SMP dosage on (a) adsorption of PAAX, and (b) zeta-potential of the Upper Freeport coal, pyrite and shale at pH 10.5

earlier. Correspondingly, the zeta-potentials were measured in the presence of different concentration of SMP.

In Figure I.21, the relationship is shown between the adsorption density of PAAX on the minerals vs. SMP dosage. Also, shown on this figure were the zeta-potential of the three minerals as a function of SMP dosage.

In the case of the adsorption on the Upper Freeport coal, the results indicated that the existence of SMP only slightly affected the PAAX adsorption. The reason could be attributed to the relatively poor affinities of both PAAX and SMP to coal.

For the adsorption of PAAX on shale, it can be observed from the graph that SMP causes a decrease in the adsorption of PAAX. As discussed in Section 4.5, SMP has a high affinity to shale. In a mixed solution of SMP and PAAX, therefore, SMP molecules would be more likely to adsorb on shale particle than PAAX.

An interesting observation was that SMP also significantly affected the adsorption of PAAX on pyrite, eventhough PAAX had a high affinity to pyrite. This was probably due to competitive adsorption between both SMP and PAAX molecules.

Summary

The main observations for adsorption studies of FR-7A and PAAX on two coals, pyrite and shale, can be summarized as follows:

a) FR-7A Adsorption

1) Adsorption of FR-7A on the four samples at relatively low concentration followed a Langmuir type adsorption.

2) The time for attaining "equilibrium" adsorption of FR-7A was as short as 8 hours for the Upper Freeport coal, 6 hours for shale and 5 hours for pyrite. However, the longer period of 12 hours was allowed for adsorption studies to ensure attaining "true" equilibrium.

3) Since coal is naturally hydrophobic, it had the highest adsorption density of FR-7A as it was expected. Because the pyrite was also partly hydrophobic, the adsorption of FR-7A on pyrite was also relatively high. For naturally hydrophilic shale, the adsorption of FR-7A on shale was poor, as expected. Generally, the affinity sequence of FR-7A to the minerals in a coal slurry is: coal > pyrite >> shale. That means FR-7A ishould be highly selective for coal in deashing process, but it would not be effective for pyrite rejection.

4) The adsorption of FR-7A on the minerals was significantly affected by pH. At acidic condition, more FR-7A molecules are adsorbed on the minerals, thus reducing its selectivity towards coal. The adsorption density for each mineral, however decreased noticeably with increasing pH, but more so for shale than for coal, thus enhancing FR-7A selectivity towards coal.

5) It was found that the adsorption of SMP would cause the solids surface to be more negative probably due to the adsorption of

metaphosphate anions. However, due to the relatively high affinity of FR-7A to coal, the presence of SMP had almost no effect on the adsorption of FR-7A on coal, and only caused a slight decrease (about 5-7%) in the adsorption density of FR-7A on shale and pyrite.

b) PAAX Adsorption

1) The time to attain adsorption "equilibrium" of PAAX was about 4 hours for Upper Freeport coal and shale, and about 7 hours for pyrite.

2) The adsorption density of PAAX on pyrite was found to be about 8 times than that on the Upper Freeport coal and shale. This indicated that the affinity of PAAX to pyrite was much higher than that to coal and shale.

3) The adsorption of PAAX induced the surfaces of the minerals take more negatively charged.

4) It was found that at an initial PAAX concentration of 266 mg/l and pH 10.5, the adsorption density of PAAX on the minerals decreased with increasing SMP dosage. The sequence of the effect of SMP on the PAAX adsorption on the minerals was:
pyrite >> shale > Upper Freeport coal. Meanwhile, at the same conditions, the magnitudes of the zeta-potentials of the minerals increased with increasing SMP dosage.

Selective Flocculation For Coal cleaning and Desulfurization

Experiments were performed to determine the "optimum" conditions for deashing and desulfurizing Pittsburgh no.8 coal by using selective flocculation method. In order to increase the desulfurization rate and selectivity of the flocculants, the surfaces of pyrite particles were modified by a partially xanthated hydrophilic compound (PAAX) used as the selective dispersant. Therefore, seven series of experiments were performed to establish the effects of operating parameters such as flocculant concentration and type, PAAX concentration, pH, particle size and grinding time, and the interaction between these parameters. In addition, experiments were performed to find an efficient technique for separation of the coal flocs. This work included multi-step cleaning and/or combination of several separation technology in a multi-step process.

Following is the summary of the results of these experiments and the effects of different parameters. In all the results reported here, the percent ash and pyrite sulfur rejections were based on the material balance of the tests and not merely on the final analyses of feed and clean coal.

Selection of Flocculant Reagent

Four different flocculants were tested (i.e.; FR-7A, FR-7, F1029-J, and F1029-D). The selectivity of each flocculant was measured with respect to its ability to reject mainly mineral matters (or ash forming minerals) and pyrite. Then these values were compared to the coal recovery which in essence was the BTU recovery of the process.

In these sets of experiments synthetic slurry was used to ensure the liberation of pyrite and ash mineral matters. The slurry was prepared from a measured amount of pre-cleaned coal (by heavy liquid separation s.g.=1.3). The coal was then ground in the attrition mill for 25 minutes. Following this measured amount of finely ground pyrite and shale were mixed with the coal slurry and then the mixture was completely blended in a ball mill for approximately one hour. The synthetic slurry contained 25.% ash forming minerals, and 5.13% total sulfur of which 1.25% was organic sulfur.

Two techniques were employed to separate the flocs. In the first method a single step of froth flotation was used. The second method was a combination of single step of sedimentation followed by re-dipersion of the flocs at high shear rate and then reflocculation followed by another sedimentation step.

The results of these experiments are listed in Table I.5. A comparison of the results indicated that the two step sedimentation set generally yielded lower recovery than the one step flotation set of experiments. The reason was that when flocs separation was done by sedimentation, a significant amount of the coal (or carboniferous materials) remained suspended in the dispersed phase. Moreover, the results indicated that the total sulfur contents in the sedimentation tests were generally higher than the total sulfur obtained in one step flotation

Table I.5 Effect of different flocculants on coal recovery and rejection of ash and pyrite

Sepn. Steps	pH	Flocculant		Total S	Pyr. S Rejection	Ash	Ash Rejection	Recovery
		Type	Conc. (ppm)	(%)	(%)	(%)	(%)	(%)
1,FF	7.5	FR-7A	10	3.98	46.26	10.64	67.87	87.02
1,FF	7.5	FR-7	10	3.96	46.85	11.27	64.95	89.40
1,FF	10.5	F1029-J	10	4.24	41.60	10.03	68.94	88.88
1,FF	10.5	F1029-D	10	4.93	29.23	13.04	60.23	84.58
2,SED	7.5	FR-7A	10+5	4.26	55.78	10.17	72.99	59.18
2,SED	7.5	FR-7	10+10	4.25	72.50	10.73	84.41	41.35
2,SED	10.5	F1029-J	7+10	5.30	49.81	10.83	78.72	55.50
2,SED	10	F1029-D	5+10	6.26	52.48	19.76	70.27	40.05
2,SED	10, 7.5	F1029-D FR-7A	5 10	6.02	22.47	17.36	55.26	68.44

FF - froth flotation, SED - sedimentation

Table I.6 Comparison between the effect of different flocculants on coal recovery and rejection of ash and pyrite using a two-step separation technique (sedimentation + froth flotation)

pH	Flocculant		Total Sulfur	Pyr. S Rejection	Ash	Ash Rejection	Recovery
	Type	Conc. (ppm)	(%)	(%)	(%)	(%)	(%)
7.5	FR-7A	10+10	2.4	73.21	7.56	84.76	79.05
7.5	FR-7	10+10	2.49	69.58	7.62	83.76	83.15
10	F1029-J	5+2	4.15	21.75	10.50	75.38	87.34

experiments. Liberated pyrite particles, being 4 to 5 times denser than the coal, can settle as fast (if not faster) or co-settle with the coal flocs ;thus, resulting in an increase in the total sulfur content of the flocs. However, when the ash content of the sedimentation experiments were contrasted with the flotation results, there was no appreciable difference.

Therefore, a Collective survey of the results indicate that the separation technique was the cause of the discrepancies. In other words, one may conclude that the flocs separation by sedimentation method is not an efficient technique for selective flocculation process when pyrite is present.

In Table I.6 the results of different flocculants are listed. The experiments with FR-7 and FR-7A generally resulted in cleaner flocs with modest recoveries. In addition, there is no significant difference between FR-7 and FR-7A. However, one can clearly see the flocs formed by F1029-D have the highest total sulfur and mineral matters content, and lowest recovery, ash rejection and pyritic sulfur rejection rates. On the other hand the use of F1029-J flocculant resulted in modest ash and sulfur contents, and coal recoveries.

A second set of experiments were performed to verify the results of the first experiments. Similar methodology was used to prepare the slurry, however, a different separation technique was devised for separation of the flocs. This technique consisted of first step separation after flocculation by sedimentation followed by re-dispersion and reflocculation processes. The flocs formed in the second step were the separated by froth flotation technique in the preceding step.

The results are shown in Table I.7. The results clearly indicated that FR-7A was more effective towards rejecting mineral matters and pyrite. This is quantitavily shown by higher ash and pyritic sulfur rejection rates. However, F1029-J resulted in the lowest rejection rates but higher recoveries.

FR-7 and FR-7A are both totally hydrophobic flocculants with very similar structure. The results obtained by using either of these flocculants are also similar. Therefore, one may conclude that there is no significant difference between the FR-7 and FR-7A flocculants. However, as it was shown in the previous sections (materials and methods), F1029-D and F1029-J flocculants are only partially hydrophobic. They both contain similar functional groups and have nearly the same molecular weight (3 million). However, the ratio of the hydrophilic groups in F1029-D is by 20% higher than that in F1029-J.

There are actually two factors working simultaneously in favor of FR-7A flocculant. The first is obviously the higher hydrophobicity of the molecule. The second factor is its smaller size. The molecular weight of FR-7A is only one million.

Recalling the results form the adsorption characteristics of FR-7A on minerals. It was concluded that the FR-7A is adsorbed strongly on the coal surface and to lesser degree on the pyrite surface, however, FR-7A does not have a strong affinity towards shale. Therefore, it is possible that some pyrite particles incorporated themselves in the flocs structure. However, this kind of association is not completely a random process. Rather it is a complex function of surface and hydrodynamic forces which are prevelant during the selective adsorption/flocculation process. For example, fast rate of flocculation could produce large flocs and entrap unwanted particles. From the adsorption studies, it was clear that FR-7A also adsorbs on pyrite which would cause it to co-flocculate with coal. The presence of PAAX or any other suitable dispersant should reduce the adsorption of FR-7A on pyrite. The flocculation is also a function of adsorption energy which is directly proportional to the number of adsorption bonds of the hydrophobic groups onto the surface of the minerals. Therefore, the size (or the molecular weight) of the flocculant is a very important factor since it determines the number of hydrophobic groups. The larger the molecular weight, the more possibility of pyrite association. However, by the same reasoning, a small flocculant can result in low recoveries due to fewer number of the bonds formed with the desired minerals.

Selection of the Dispersant Reagent

Two types of selective dispersants were tested in the these experiments. The dispersants were Polyacrylic acid (PAA) and PAAX. Three sets of experiments were performed to investigate the effect of each dispersants.

In the first set synthetic slurry was used with 30.04% ash content and 3.86% total sulfur content of which 1.25% was organic sulfur. The coal flocs were separated through a two step process of sedimentation followed by froth flotation. The results are shown in Table I.8.

The results clearly indicated that there was a net positive effect of the dispersant on the rejection levels of mineral matters and pyrite. There was some interaction between the type of flocculant and the dispersant effect. The results presented here show that selective flocculation is more effective iently with the totally hydrophobic flocculants FR-7A than with F1029-J.

The second set of experiments was performed to differentiate between PAA and PAAX; hence, no flocculant was used and the coal was separated through single step of froth flotation. The results are shown in Table I.9.

As expected, PAAX showed a more pronounced affinity towards pyritic particles; thus resulting in higher level of ash and pyritic sulfur rejections with higher recoveries while PAA acted as unselective dispersant for all particles.

The third set of experiments was performed to identify the "optimum" dosage of PAAX. In these experiments, pre-cleaned coal was used and ground for 18 hours in a ball mill to ensure the liberation of minerals. The results of these experiments are shown in Table I.10.

In agrrement with previous experiments, these results indicated PAAX has a significant effect on both the ash and pyritic sulfur rejection levels. Moreover, it is also clear that

Table I.7 Effect of selective dispersant on selective flocculation of fine coal slurry

pH	Flocculant Type	Flocculant Conc. (ppm)	Dispersant Type	Dispersant Conc. (ppm)	Total S (%)	Pyr.S Rej. (%)	Ash (%)	Ash Rej. (%)	Recovery (%)
7.5	FR-7A	10+10	--	--	2.40	73.21	7.56	84.76	79.05
7.5,10	FR-7	10+10	PAAX	0+100	2.45	71.91	7.60	84.54	78.81
7.5	FR-7A	10+10	PAA	0+130	2.30	74.92	6.86	85.76	80.47
10	F1029-J	5+2	--	--	4.15	21.75	10.50	75.38	87.34
7.5,10	F1029-J	5+2	PAAX	0+100	3.90	30.25	13.40	69.59	82.69
10	F1029-J	5+2	PAA	0+130	4.17	18.95	11.12	73.18	90.28

Table I.8 Comparison of the effect of different dispersants

pH	Dispersant Type	Dispersant Conc. (ppm)	Total Sulfur (%)	Pyr. S Rejection (%)	Ash (%)	Ash Rejection (%)	Recovery (%)
10.5	PAAX	100	2.20	76.46	8.50	80.68	87.07
10	PAA	130	2.65	62.31	13.06	69.45	86.69

Table I.9 Effect of the interaction between FR-7A and PAAX on coal recovery and rejection of ash and pyrite using froth flotation

pH	FR-7A Conc. (ppm)	PAAX Conc. (ppm)	Total Sulfur (%)	Pyr. S Rejection (%)	Ash (%)	Ash Rejection (%)	Recovery (%)
10.3	50	200	1.91	72.49	3.55	68.30	89.50
10	--	200	1.91	78.08	3.02	78.80	70.84
10	50	--	2.06	68.24	4.11	66.16	82.50

the use of FR-7A flocculant ahead of flotation, increases the coal recovery significantly. This is due to the fact that in flotation process particle size directly affect the recovery. The optimum size for flotation is approximately 200 micron. However, the unflocculated slurry has an average size of approximately 5-10 micron; therefore, when no flocculant was used, some degree of cleaning was observed but the recovery was low. In contrast, when flocculant was used the particle size especially the coal particles sizes are increased thus increasing the recovery of the process. Therefore, one may conclude that using PAAX and FR-7A can result in cleaner coal with relatively high recovery even for ultrafine slurries.

Selection of The Flocs Separation Method

The technique used to separate the flocs is an important element of the selective flocculation process. Ideally, the separation process should be such that it does not break or disintegrate the flocs structure. Its design should be compatible with the selective flocculation process. In other words, uses the same fundamental surface chemical principals for separation. Naturally, design of such a process was beyond the scopes of this project. However, several methods were tested to establish the significant effect a good separation process might have on the outcome of the results.

Several techniques were used to separate the flocs; namely, dissolved-air flotation (DAF), sedimentation, and froth flotation (FF). In some experiments several trials were done to combine one or two of these processes.

Dissolved-Air Flotation (DAF). A synthetic slurry with a liberated materials was prepared to test this method. The slurry contained 21.6% ash and 4.92% total sulfur with 1.25% organic sulfur.

A single step of DAF and a two step process of sedimentation followed by DAF were employed. The results which are shown in Table I.11, indicated that the DAF system could not separate the flocs. This was due to the fact that the there was not enough air dissolved in the water and the bubble size was too large and the air and water flow floated virtually everything. Thus, as the results indicate the concentrate (or the flocs) had nearly the same levels of ash and total sulfur. In addition, the recoveries were low.

The results shown here do not necessarily indicate that DAF system is not compatible with the flocculation process. In fact, DAF can be a good candidate for flocs separation, however, the system used in this study was poorly designed and was unable to efficiently dissolve the required amount of air into water.

In fact, in earlier experiments where a different design and considerably more efficient dissolved-air flotation system was used, significant desulfurization and de-ashing of an ultafine coal slurry of pre-cleaned Pittsburgh no.8 coal was achieved. However, the coal used in these experiments had

Table I.10 Effect of dissolved-air flotation on floc separation

Sepn. Mehtod	pH	Flocculant Type	Flocculant Conc. (ppm)	PAAX Conc. (ppm)	Total S (%)	Pyr.S Rej. (%)	Ash (%)	Ash Rej. (%)	Recovery (%)
DAF	9.5	FR-7	10	--	4.75	53.30	20.29	54.07	45.22
DAF	9.5	FR-7	10	100	4.71	41.27	18.87	45.58	64.49
DAF	10.5	F1029-J	10	--	4.96	16.49	16.08	38.59	82.61
SDM+ DAF	10.5/ 9.5	F1029-J FR-7A	10 10	0 100	4.87	41.22	15.05	58.54	59.39
Feed	--	--	--	--	4.92	--	21.63	--	--

DAF - dissolved air flotation, SDM - sedimentation

Table I.11 Comparison of different techniques for coal floc separation after selective flocculation

Separation Mehtod	pH	FR-7A Conc. (ppm)	PAAX Conc. (ppm)	Total S (%)	Pyr.S Rej. (%)	Ash (%)	Ash Rej. (%)	Recovery (%)
2-SDM *	7.5	10+5	--	4.26	55.78	10.17	72.99	59.18
2-SDM+FF **	11.0	40+10+0	200+200+100	2.60	70.00	5.12	86.19	62.67
SDM+ FF ***	7.5 10.0	10 10	-- 100	2.45	71.91	7.60	84.54	78.81
FF **	7.5	10	--	3.98	46.26	10.64	67.87	87.02
FF **	11.0	10	200	1.87	80.19	7.16	73.19	86.51
2-FF **	11.0	5+5	200+100	2.02	84.24	4.44	89.25	62.45

* The synthetic slurry contains 24.47% ash and 5.13% total sulfur.

** The synthetic slurry contains 19.93% ash and 3.71% total sulfur.

*** The synthetic slurry contains 30.04% ash and 3.86% total sulfur.

unusually low organic sulfur (about 0.7%) and 2.6% total sulfur and about 6.5% ash contents.

Tables I.12 and I.13 show the results of these earlier experiments with one and two step selective flocculation. Note that 200 ppm of PAAX was used in conjunction with dissolved air flotation as the floc separation technique. It can be seen that using a single step selective flocculation, the total sulfur content was reduced from approximately 2.6% to 1.6% and the pyritic sulfur was reduced from 1.9% to 0.95%. The ash content of the pre-cleaned coal was reduced to 3.9% with a coal recovery of 93% . This is very close to the super-clean coal level. The use of the second step of the selective flocculation produced a clean coal that had a total sulfur content of 0.95%, and pyritic sulfur content of 0.2% , i.e. about 90% removal of the ultrafine pyrite was achieved. The ash content of the cleaned coal in these tests was 2.5%, while the recovery was still above 90% .

These results clearly indicated that a less turbulent hydrodynamic conditions such as the one exists in the DAF system could reduce the hydraulic entrainment of finely dispersed pyrite in the solution. Consequently, the heavier pyrite particles setteled slowly while the fine air bubbles is attached to small coal flocs and float them to the top of the flotation cell. Unfortunately, the old DAF system could not be used due to the malfunction in the system.

Table I.12 Selective Flocculation - Dissolved-Air Flotation Cleaning of Precleaned Pittsburgh No. 8 Coal Using One Step Flocculation/Dissolved-Air Flotation.[*]

	ANALYSIS%				DISTRIBUTION%		
Product	Weight	Ash	Coal	Total Sulfur	Ash	Coal	Total Sulfur
Flocs	91.8	4.74	95.26	1.67	56.8	94.7	57.5
Dispersed	8.2	40.52	59.48	13.81	43.2	5.3	42.5
Feed	100.0	7.66	92.34	2.66	100.0	100.0	100.0
Flocs	91.4	3.48	96.52	1.64	40.5	95.7	54.3
Dispersed	8.6	54.66	45.66	14.65	59.5	4.3	45.7
Feed	100.0	7.65	92.35	2.76	100.0	100.0	100.0
Flocs	88.8	3.79	96.21	1.73	44.0	92.5	52.2
Dispersed	11.2	38.24	61.76	12.25	56.0	7.5	47.8
Feed	100.0	7.65	92.35	2.91	100.0	100.0	100.0

Table I.13 Selective Flocculation - Dissolved-Air Flotation Cleaning of Precleaned Pittsburgh No. 8 Coal Using Two Steps Flocculation/Dissolved-Air Flotation.[*]

	ANALYSIS%				DISTRIBUTION%		
Product	Weight	Ash	Coal	Total Sulfur	Ash	Coal	Total Sulfur
Flocs	85.5	2.83	97.17	0.94	30.5	90.3	29.3
Dispersed 1	6.9	42.52	57.48	13.48	36.6	4.3	33.9
Dispersed 2	7.6	34.23	65.77	13.27	32.9	5.4	36.8
Feed	100.0	7.94	92.06	2.74	100.0	100.0	100.0
Flocs	88.1	2.40	97.60	0.97	30.1	92.4	30.3
Dispersed 1	5.8	56.90	43.10	14.77	47.2	2.7	30.4
Dispersed 2	6.1	26.01	73.99	18.17	22.7	4.9	39.3
Feed	100.0	7.03	92.97	2.83	100.0	100.0	100.0
Flocs	86.2	2.25	97.75	0.87	25.7	91.2	26.6
Dispersed 1	6.0	45.88	54.12	13.30	36.1	3.5	28.4
Dispersed 2	7.8	37.07	62.93	16.21	38.2	5.3	45.0
Feed	100.0	7.57	92.43	2.81	100.0	100.0	100.0

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[*] Note that the old DAF system was used in these experiments and the organic sulfur content of the coal was unusually low at 0.7%.

Flocs Separation by Sedimentation/Froth Flotation. Table I.14 shows a selected sample of results using different separation techniques. These techniques were used after the flocculation and formation of the coal flocs.

Two step sedimentation method was used for separation of flocs with different type of flocculants (refer to Table I.11). In general, this method resulted in low recoveries. In addition, the total sulfur content in the flocs was high due to co-settling of the pyrite particles (refer to Tables I.11 and I.14).

The use of a two steps sedimentation followed by one step froth flotation with high dosages of flocculant improved the situation, however, the recovery was still low.

One step sedimentation followed by one step froth flotation was also tested. The results indicated a modest improvement in ash and sulfur rejection as well as the coal recovery.

Flocs Separation by Froth Flotation. From the previous experiments, it was clear that the reason for low recoveries and high sulfur contents was in the sedimentation step(s) where most of the small flocs were lost and the pyrites co-settled. Therefore, single step froth flotation was used to separate the coal flocs after formation and coniditioning of the flocs. The results are shown in Table I.15. It is immediately clear that the recovery , the pyritic sulfur rejection levels were significantly increased. However, the ash rejection level was decreased.

Table 1.14 Effect of FAAX on floc separation with a single step froth flotation

Chemicals	pH	Pyr. S Rej. (%)	Ash Rej. (%)	Recovery (%)	Remarks
200 ppm PAAX	11	82.90	85.60	57.20	*
200 ppm PAAX + 10 ppm FR-7A	11	80.09	73.19	86.51	*
200 ppm PAAX	10	78.08	78.80	70.84	**
No PAAX + 50 ppm FR-7A	10	68.24	66.16	82.50	**
200 ppm PAAX + 50 ppm FR-7A	10	72.49	68.30	89.50	**

* The synthetic slurry contains 19.93% ash and 3.71% total sulfur.

** The Pittsburgh No. 8 coal after heavy liquid separation contains 9.63% ash and 3.29% total sulfur.

Table 1.15 Effect of PAAX concentration on coal recovery and rejection of ash and pyrite in the presence of FR-7A with single and double step floc separation techniques

PAAX Conc. (ppm)	Sepn. Method	FR-7A Conc. (ppm)	Ash (%)	Total Sulfur (%)	Pyr.S Rej. (%)	Ash Rej. (%)	Coal Recovery (%)
100	1 step	50	3.89	2.00	69.63	66.80	85.83
	2 steps	50+50	3.70	2.39	71.13	80.33	52.64
200	1 step	50	3.55	1.91	72.49	68.30	89.45
	2 steps	50+50	3.55	2.23	73.38	79.79	57.63
300	1 step	50	4.20	2.04	68.22	64.39	84.63
	2 steps	50+50	4.74	2.58	63.44	72.56	57.41
400	1 step	50	3.96	2.23	62.64	68.20	86.60
	2 steps	50+50	3.72	2.32	71.00	78.77	58.89
500*	2 steps	60+40	5.84	2.19	70.22	61.22	67.25

* 400 ppm of PAAX was added in the first step, and 100 ppm of PAAX was added in the second step

Two step froth flotation process was also used. The results indicate that lower ash and sulfur content were obtained but the coal recovery was also lower.

Effect of PAAX Dispersant

Three sets of Experiments were performed to study the effect of PAAX on the pyritic sulfur rejection and to determine the optimum dosage of PAAX.

Synthetic slurry was used in the first set of the experiments. The coal slurry was ground in a ball mill for 18 hours. The ash content was 19.93% and the total sulfur was 3.71% with 1.2% organic sulfur. In these experiments no flocculant was added and the slurry was maintained at pH 11. A single step of froth flotation was used to separate the the coal. Basically, in these experiments PAAX was used as a dispresant agent for pyrite.

Figure I.22 shows the effect of PAAX concentration on the recovery and the rejection levels of ash and pyrite. In general, addition of PAAX decreased the recovery and increased the ash and pyrite rejection. As it was shown in the adsorption experiments PAAX can also adsorb on coal; therefore, as the PAAX concentration is increased some of the PAAX will adsorb on coal and results in dispersion of coal and lowering of the recovery. From the Figure, one can observe that at 200 ppm concentration of PAAX, the highest level of pyritic sulfur and ash rejections were obtained.

The second set of the experiments aimed to study the effect of PAAX in the presence of flocculant. These experiments

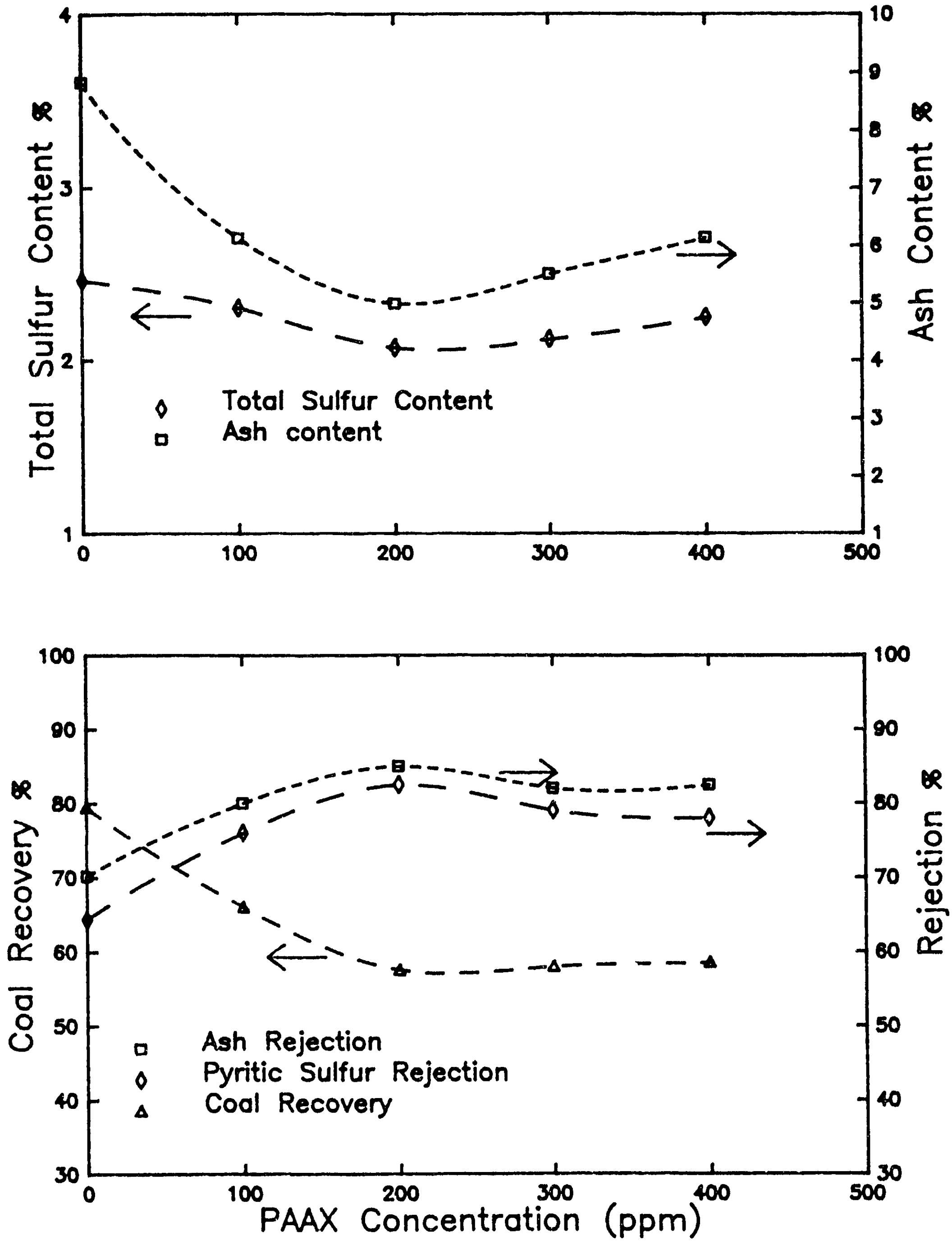


Figure I.22 Effect of PAAX Concentration as a Pyrite depressant in Froth Flotation Process. The experimental conditions are : pH = 11, FR-7A = 0.0 dosage, single step froth flotation.

were done with pre-cleaned (heavy liquid separation s.g.=1.6) coal Pittsburgh no.8 seam. The coal was ground for 18 hours in a ball mill. The feed had 9.63% ash and 3.29% total sulfur (organic sulfur was 1.25%).

Since the slurry was ultrafine (3-6 micron), 50 ppm FR-7A was added to for all the tests. A single step froth flotation was used for flocs separation and pH was maintained at 10.3 .

The results are shown in Figure I.23. At 200 ppm dosage of PAAX optimum level of rejection and recovery was obtained. At higher concentrations PAAX begins to disperse coal as well, thus, resulting in lower recoveries.

Comparison of Figures I.22 and I.23 suggests that the presence of FR-7A flocculant improves the process performance. Furthermore, the optimum dosage of PAAX is 200 ppm.

Table I.15 shows the effect of both PAAX and FR-7A on the process parameters using one step froth flotation as the flocs separation method. From these results, one can conclude that the usage of PAAX and flocculant significantly improves the recovery and the mineral matters content of the concentrate.

In the third set of experiments the effect of PAAX and FR-7A concentrations using two steps separation techniques was studied. The dosage of PAAX and FR-7A were equally divided between two steps except for the last experiments where it was indicated. In the first step sedimentation was used to separate the flocs. The flocs were then re-dispersed under high shear

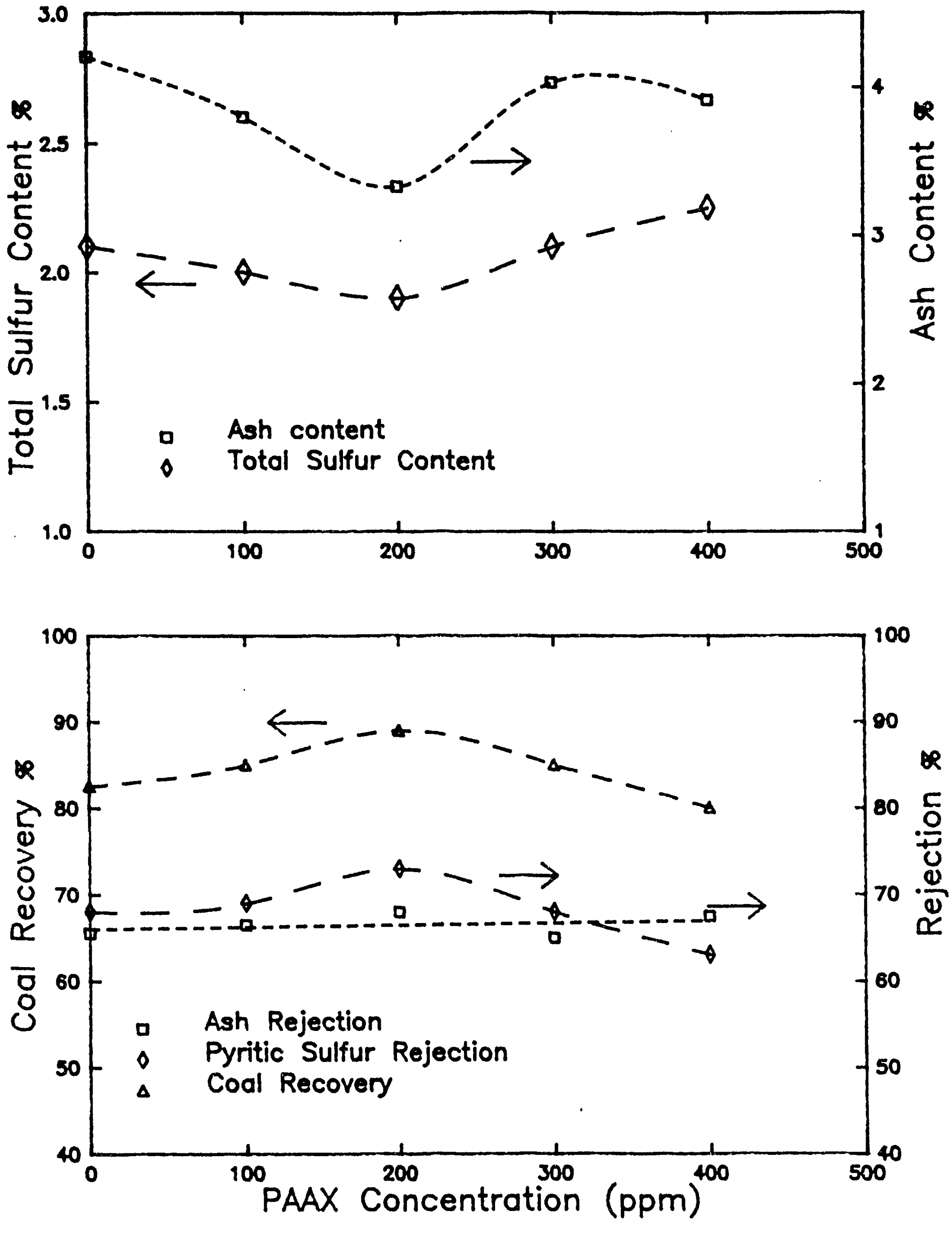


Figure I.23 Effect of PAAX Concentration on the Flocculation Parameters. The experimental conditions are : pH = 11, FR-7A = 50.0 ppm, single step froth flotation.

rate and then re-flocculated. The secondary flocs were then separated by froth flotation.

The single step froth flotation resulted in higher recovery and lower total sulfur and ash contents. Again there was a significant amount of the coal was lost in the sedimentation step. It was also clear that the during the sedimentation step pyrite particles were co-settled with flocs and increased the total sulfur content of the secondary feed. Consequently, in the second step the actual sulfur content of the slurry was increased.

From these discussions, one can conclude that PAAX has a significant positive effect on the pyrite rejection. The Presence of PAAX decreases the coal recovery somewhat. However, the addition of FR-7A flocculant improved the recovery. Finally the optimum dosage of PAAX was about 200 ppm.

Effect of Slurry pH

pH of the slurry can have a significant effect on the selectivity of the flocculant and the coal recovery. A series of experiments was performed to investigate the effect of pH on the flocculation process. Pittsburgh no.8 seam was used in these experiments. The raw coal was ground for 18 hours in the ball mill to obtain an average particle size of 3 micron. The feed had 16.14% ash and 3.97% total sulfur with 1.25% organic sulfur content. In all the experiments, the concentrations of SMP, PAAX, and the flocculant FR-7A were maintained at 300, 200, and 50 ppm, respectively. The pH range was from 5 to 11.

Figure I.24 shows the results obtained in these experiments. It should be noted that PAAX readily decomposes to when used in acidic media. Therefore, in reality at the lower pH range, there was no effect of PAAX. From the results it is clear that the recovery slightly decreased as the pH increased to 10. However, beyond pH 10, there was a sharp decrease in the recovery. The reason can be explained in terms of the adsorption and surface charge characterization of the minerals discussed earlier in this section. The higher the pH of the slurry is the more negatively charged the surface of the coal and other minerals become. It was shown earlier that the ZPC of the shale, pyrite and coal were at pH 2.5, 5.5, and 7, respectively. Therefore, at high pH of 11 all the minerals (coal, pyrite and the mineral matters) should be negatively charged and the agglomeration tendencies of these minerals should be very low. In addition, when the particle size is small (3-6 micron), the resulting flocs would still be small (10-15 micron). Consequently, these two factors combined would result in a low recovery of coal flocs.

Effect of Flocculant Concentration

From the very beginning, it was noticed that the formation of large visible large flocs was a function of the total surface area and size of the particles in the slurry. Therefore, the required amount of flocculant needed for formation of large flocsis inversely proportional to the particle size.

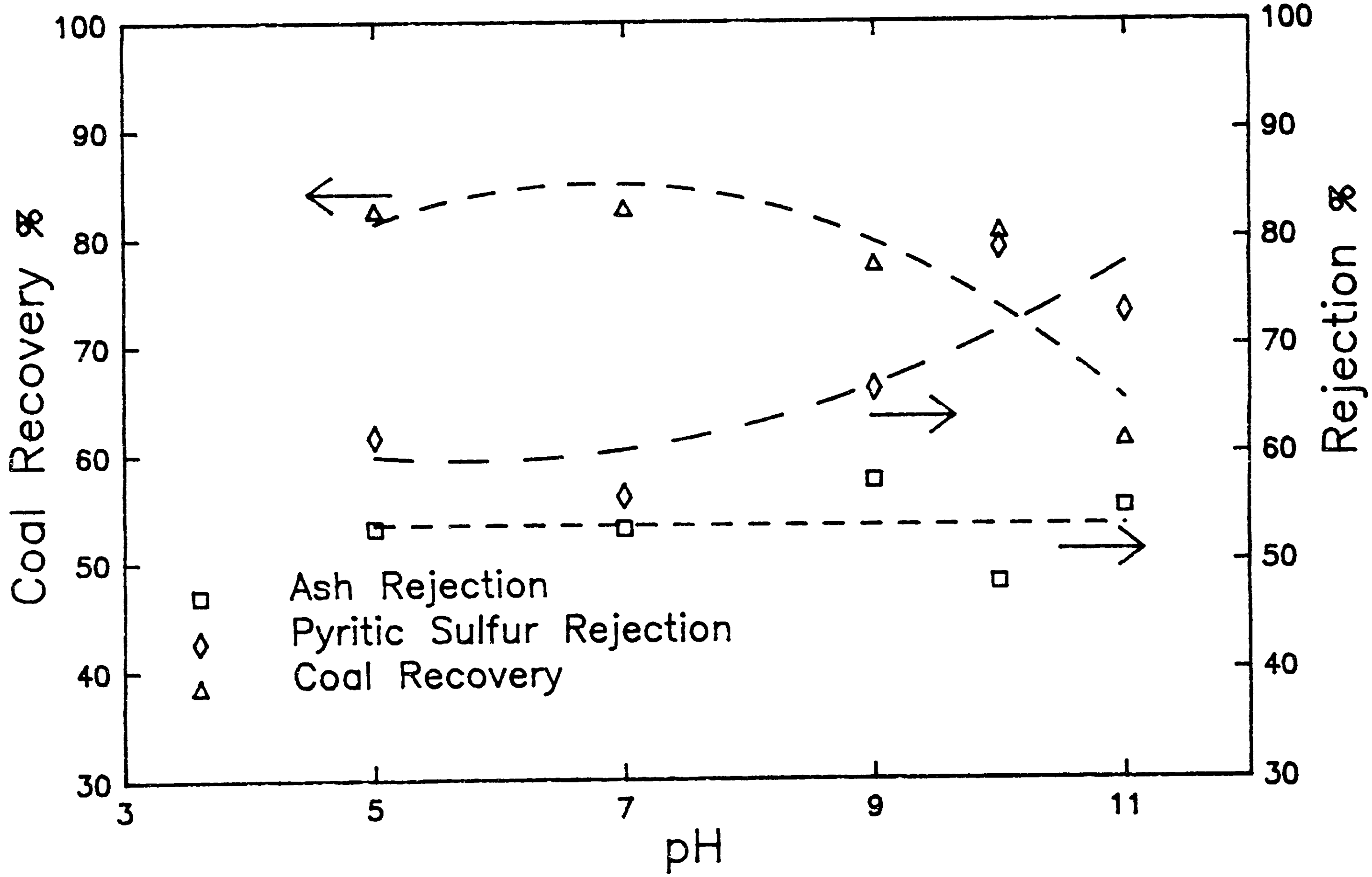


Figure I.24 Effect of Slurry pH on the Flocculation Parameters. The experimental conditions are : FR-7A = 30 ppm, PAAX= 200 ppm, single step froth flotation.

In order to study the effect of flocculant concentration ultrafine slurry with over 80% of the particles less than 8 micron of raw Pittsburgh no.8 coal was prepared. The slurry concentration was also maintained at about 7 to 8%. The feed contained 15.54% ash and 3.97% total sulfur with 1.25% organic sulfur. The pH was maintained at 10. The PAAX concentration was kept constant at 200 ppm.

It was visually observed that from 40 to 100 ppm FR-7A concentration, visible flocs were formed. As the FR-7A dosage decreased, the flocs size became noticeabily smaller.

The results of this experiments are shown in Figure I.25. The trends observed here were very interesting. At zero FR-7A condition, the rejection levels of ash and pyrite were about 45 and 70%. However, there was an increase in the rejection levels as the dosage of FR-7A was increased to 50 ppm witha maximum rejection at 5 ppm. Beyond 50 ppm the rejections actually started decreasing while the coal recovery increased.

From the adsorption characteristics of the minerals tested earlier, this behavior was expected. It was shown that FR-7A can be adsorbed to lesser extent on the pyrite and shale minerals. Therefore, at lower concentrations of FR-7A, most of the flocculant would be adsorbed on coal. FR-7A being a totally hydrophobic polymer, acts as a strong flotation collector reagent which can also increase the coal size. However, at higher FR-7A dosage, some of the flocculant also adsorbed on the undesired minerals and increased their flotability which decreased the

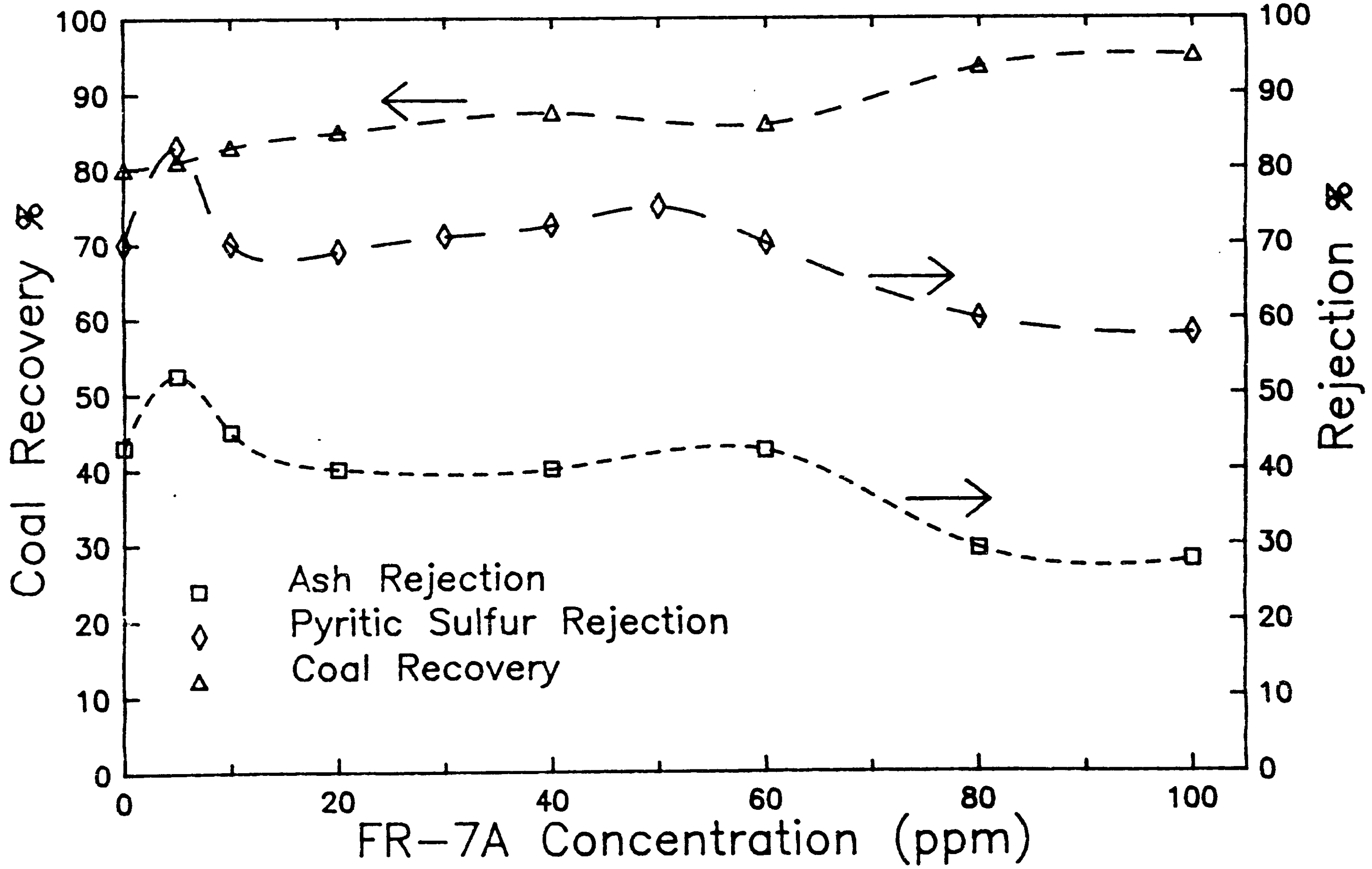


Figure 1.25 Effect of FR-7A concentration on the Flocculation Parameters. The experimental conditions are: PAAX= 200 ppm, single step froth flotation, pH = 10.

rejection levels. It is also possible that at higher dosage of FR-7A some of the minerals and pyrite were entrapped and/or associated in the structure of the coal flocs which naturally explains the decrease in the rejection levels. It should be noted that in the froth flotation cell, the large flocs are broken to smaller sizes due to the high mixing rate in the cell; hence, the effect of flocculant on the particles size can not be completely obtained by this separation method.

It seems that at higher concentrations (over 60 ppm), there was a larger decreasing trend in the rejection levels while the recovery rate is also increasing more significantly. This trend indicate that there is a threshhold or an onset of perhaps indiscriminate (total) flocculation of the slurry although the flocculant is totally hydrophobic.

The results indicate that at low flocculant dosage, there is a net positive effect on the recovery and the rejection levels. However, this effect diminishes as the dosage of flocculant increases. In these experiments at dosages of 5 to 10 ppm, the highest levels of rejection were observed. This results can have significant economical benefits in an industrial scale operation since lower dosages of flocculant are required for optimum operating conditions.

Effect of Particle Size and the Grinding Time

The particle size and the grinding time can have a significant effect in any mineral process. In the previous sections, in order to eliminate the liberation size factor the slurry was ground for more than 18 hours. The particle size distributions of these slurries were indeed at the liberation size of the pyrite particles.

Clearly for any low-value mineral such as coal, it is not economical to consume too much energy and capital investment for grinding. Therefore, a series of experiments were performed to determine the grinding time and the effect of particle size distribution on the overall process parameters.

In these experiments natural coal (Pittburgh no.8) was ground in a ball mill. At intervals of 1, 2, 3, 4, and 18 hours samples were drawn for the flocculation experiments and the particle size analyses. Of course, additional, water was added to maintain the charge of the ball mill approximately constant throughout the experiments. The feed had 10.58% ash, 3.0% total sulfur and 1.17% organic sulfur.

The results of the particle size distribution versus grinding time are shown in Figure I.26. In Figure I.27 the flocculation results are presented.

From Figure I.26, it is clear that there was a significant effect on the duration of grinding and the size distribution. While there was only 25% of the particles under 10 micron after one hour of grinding, in two hours this amount was increased to 55% and over 75% for 3 , 4 and 18 hours. From the data, it is also obvious that there was no significant difference in particle size distribution for grinding beyond 3 hours.

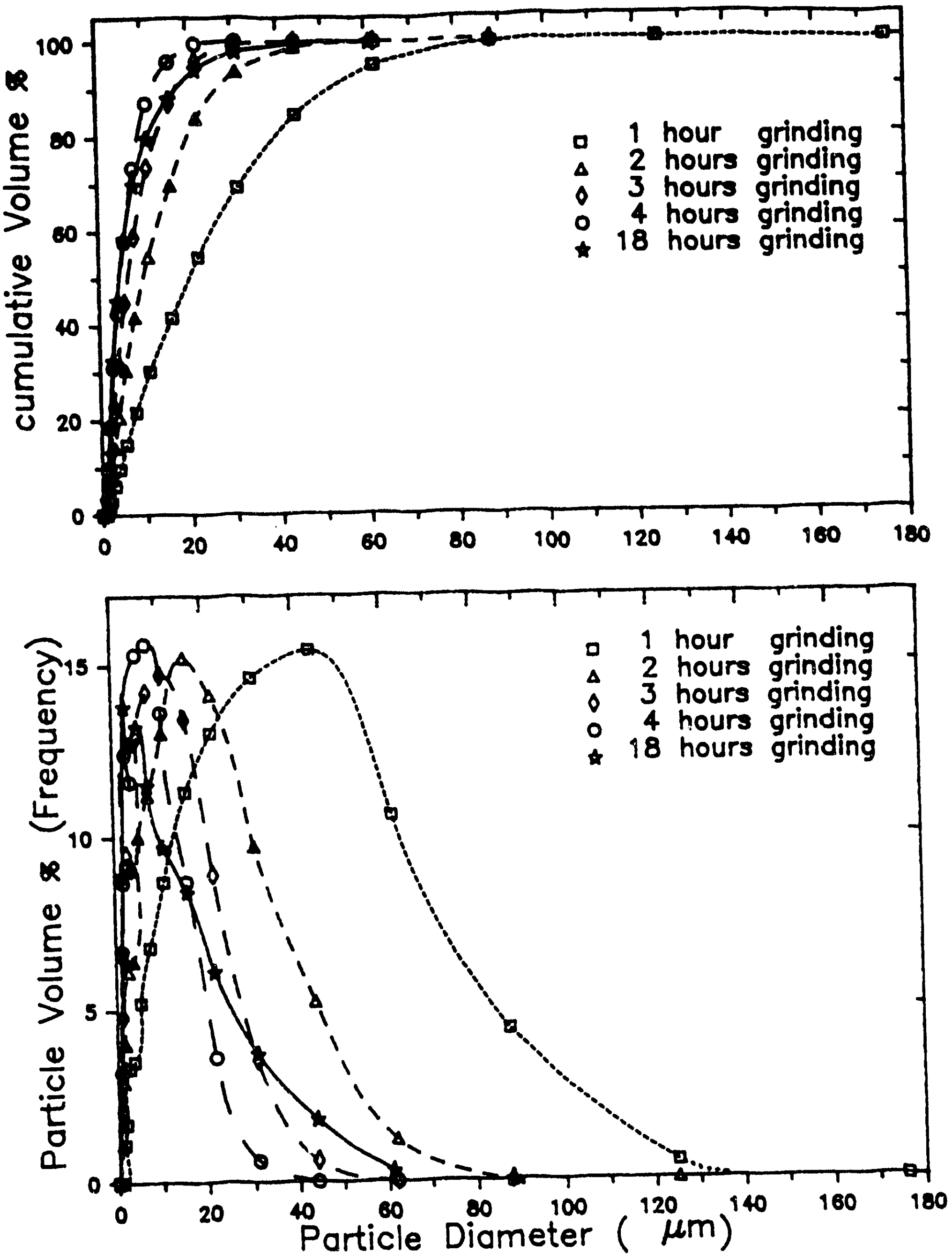


Figure 1.26 Frequency and Accumulative Particle Size Distributions of Pittsburgh No.8 Seam Coal.

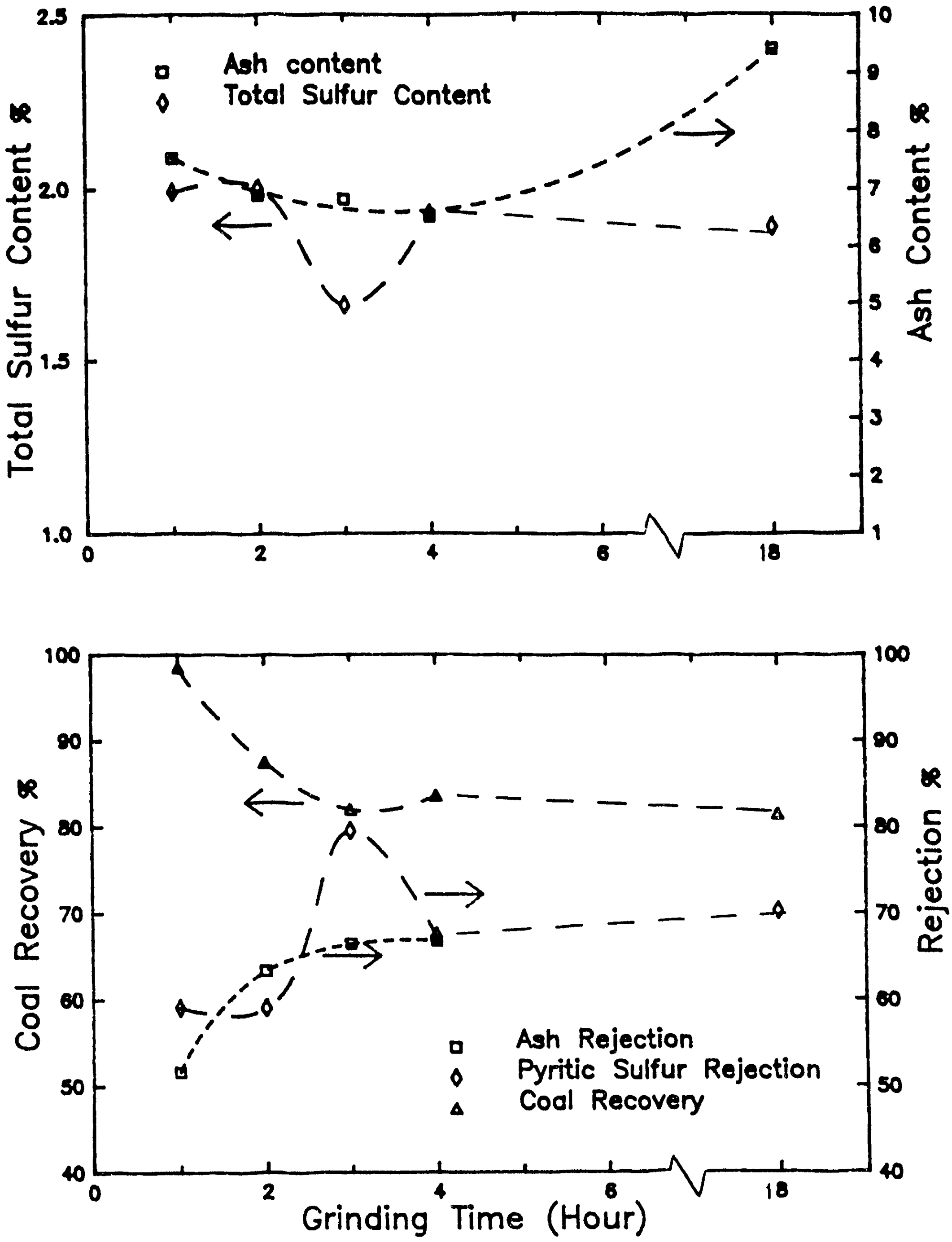


Figure 1.27 ·Effect of Grinding Time and/or Particle size Distributions on the Selective Flocculation Parameters. The experimental conditions are: FR-7A = 20 ppm, PAAX = 200 ppm, pH = 10, single step froth flotation.

As it is shown in Figure I.27, the particle size distribution had a significant effect on the recovery, and the rejection levels. In fact, during the experiments, a very significant change in the flocs size was observed. As the grinding time increased the flocs size noticeabily decreased. In fact, for one hour grinding slurry, the flocs size were so large that it was initially thought that total flocculation had occurred.

From the data it can be observed that the ash rejection level (from 52% to 66%) and the recovery (from 99% to about 81%) are leveling off after three hours of grinding time. It should be noted that the mineral matters actually increased due the errosion of iron oxide from the balls and the mill surface into the slurry after 18 hours of grinding. This was clearly evident from the brown color of the mineral matters after ashing procedure. Therefore, the last data point for the ash rejection was not presented here.

However, the pyritic sulfur rejection followed an interesting trend. There was nearly no significant difference between the pyritic sulfur rejection from one to two hours grinding. This implied that only coarse pyrite particles have been rejected and most of the pyrite particles were still trapped in the coal floc structure. This result was a clear indication of what Kneller and Maxwell reported with regards to the pyrite size distribution in Pittsburgh no.8 coal. After, three hours of grinding the average particle size was about 8.5 microns. Over

65% of the particle under 10 micron and 37% under 4 micron. Therefore, a majority of the pyrite were liberated and at the same time the coal particles were still not too fine to be lost in the dispersed phase. As the grinding time increased there was no more significant liberation of pyrite, however, there was significant increase in the percentage of the ultrafine coal. Consequently, the new surfaces generated were due to the grinding of the liberated minerals. The net result was the formation of smaller flocs size to the extent that hydrodynamic factors in the flotation cell became significant. The liberated pyrite has been ground to finer sizes which can be easily entrained with the net flow of the liquid with froth.

The results of this set of experiments clearly indicated that there is an optimum size distribution for desulfurization of the ultrafine coal. A significant portion of the pyrite was entrapped as very small particles in the coal floc structure. The results also showed that with three hours of grinding in a ball mill, the desired size distribution for the liberation of pyrite particles could be obtained. Over 80% rejection of the pyritic with over 80% recovery of the coal were achievable with this process.

Summary of the Findings

1) It was found that the totally hydrophobic flocculants FR-7 and FR-7A have the highest selectivity towards coal compared with F1029-d and f1029-J.

2) The preparation and characterization of PAAX was studied and a procedure for producing PAAX was determined.

3) The optimum level of PAAX concentration was found to be 200 ppm.

4) A single step of froth flotation used for floc separation resulted in highest coal recovery (80 to 90%), with over 60% pyritic sulfur rejection, and 50% mineral matters rejection.

5) Particle size, and size distribution have a significant effect on the flocculant performance. Three hours of grinding in ball mill resulted in the appropriate size distribution, pyrite liberation, and highest level of sulfur removal.

6) The optimum pH for this slurry was 10.

7) The lower level of dosage of the flocculant FR-7A is recommended. The results indicated that at 5 mg/liter concentration, the highest rejection levels of pyrite and mineral matters were obtained.

I.4 ENVIRONMENTAL IMPACTS

A brief discussion on the environmental impacts of the proposed process is presented in this section. Moreover, the available data on the possible toxicity of the chemical are also discussed. Finally, some recommendations are made for waste management from selective flocculation process.

Hazardous Properties and Environmental Impacts of the Chemicals

Sodium Metaphosphate. SMP is an inorganic compound with little human toxic hazard. In fact, in many household products such as detergents a small amount of it is present. However, SMP may have a negative impact to some of the life forms (mostly fish) that live in the streams, rivers, or lakes. The phosphates in the SMP actually increase the growth of microscopic living organism such as bacteria, algea, fungi, and also vegetation and plants life forms, therefore, resulting in depletion of oxygen content of the water. Consequently, animal live forms which are dependent on the dissolved oxygen in the water will die.

However, in the proposed process, there will be very little release of this chemical into the environment. Since the water is recycled in the process, most of the SMP will remain within the coal cleaning plant.

Poly Acrylic Acid Xanthate (PAAX). Little is known about this specific compound since it is manufactured in our laboratory and it not commercially in use yet. However, we can obtain some useful information by looking at the polymer carbon chain and its functional groups.

Short chain xanthates are commercially used in many industries such as textile industry. Xanthates are also used in the flotation of many metal sulfides (PbS, ZnS, etc.). Therefore, PAAX will not be a new compound and there are established ways and means to deal with it. However, as it was discussed, PAAX as the selective dispersant reagent will be recycled with the process water. The recycle of PAAX is not only an environmental issue but also a very significant economic factor. We believe initially the cost of PAAX will be significant and one of the ways to keep this cost low is to recycle it with process water in the plant. There are also several operating advantages in doing so as it was discussed earlier in the previous section. It should be also noted that PAAX is highly soluble in water and as long as a good water recycle design is used there will be no environmental impact due to the use of PAAX.

Although polyacrylic acid is a skin irritant, the neutralized form of it (sodium salt of the acid) does not have that property. Thus, as far as standard industrial safety measures are adhered to, there should not be any human hazard. However, the process is operating at basic pH (about 8 to 9), therefore, the equipment and the instruments in use must be corrosion resistant .

Flocculant FR-7A. Since the chemical structure of this polymer is a proprietary information of Calgon Company, we can not discuss its chemical properties in details. However, this polymer is used commercially in paper industry. In addition, the company did not inform us of any possible hazard, and in the past two years that we have been working with it, there was no problem with using it. However, as it was shown in the adsorption experiments most of this polymer is adsorbed on the coal. In addition, the amount used in the experiments are less than 50 mg/liter. It is expected that in the industrial operation the dosage of the flocculant can be further decreased to less than 5 mg/liter. Therefore, there will be little if any that remain in the solution and as it was discussed before the solution (water) is recycled. Since the polymer is mostly hydrophobic, it will be easily burned with the coal and also it will not result in an increase in the emission of any of the hazardous combustion gas (i.e., NO_X or SO_2).

In summary, the chemicals and their amounts used in this process can be categorized as relatively safe with little or no adverse impact on the environment. The recycled process water naturally can take care of most of the possible problems and also it will benefit the enconomic aspect of the process.

Waste Management

This is a rather difficult problem which not only faces this particular process but also any coal preparation plant in Ohio and in the United States in general. Considering a plant with a capacity of one million tons of coal per year, a conservative estimate of 90% recovery of the process will yield in about hundred thousand tons of waste which is not very large for a preparation plant. However, in the process of several years that can be significant.

There are several methods to dispose of the waste. The conventional method is to dispose of the waste in the landfills and specifically the area that the coal is being mined. However, this method although very cheap can result in many serious problems such as acid mine run offs and contamination of under ground water sources, nearby streams and rivers. Unfortunately, this method is widely used in the midwest mining area and has resulted in many problems to the wild life and the some farming and residential communities.

There is however a relatively cost effective way for treatment of the waste. The waste of the process contains approximately 10% pyritic sulfur, 20 to 30% mineral matters. The pyritic sulfur can be taken care of by a bioleaching process commonly used in many other mining industry such as copper and lead bioleaching by Thiobacillus ferrooxidans microorganism. The waste can be dumped in the bioleaching pools and eventually the pyrite is oxidized to form soluble sulfates. The by product of this is sulfuric acid which can be extracted and be used or sold. The remaining waste is mostly mineral matters (30 to 40%) and coal which can be safely dumped in the landfills. This remaining waste can actually be very valuable since now some of the rare metal compounds in the coal structure are highly concentrated and it may almost economical to extract some of those. It is also possible to burn or incinerate the remaining coal and use its energy for part of the plant.

On the other hand, there have been several successful waste disposal and land reclamation methods used on commercial scale and on demonstration projects. Several examples are given in Part II.

These processes for handling the waste require a modest amount of capital investment. However, they are highly efficient and during the life time of the plant they will pay for themselves by the savings and/or profits which can be made out of them.

I.5 Economic Assessment of Ohio Coal Desulfurization Using Selective Flocculation Process

As it was discussed in the previous sections, Ohio coals contain a high amounts of finely disseminated pyrite particles. By some estimation more than 50% of pyritic sulfur is associated with these ultrafine pyrite size (less than 75 micron). In our study the analysis of Pittsburgh no.8 coal resulted in an avergae value of 16% mineral matters content, 4.% total sulfur content, and 2.8% pyritic sulfur content.

The experimental results indicate that 70 to 80% of the pyrite can be removed in a single step of cleaning by using the proposed selective flocculation process and froth flotation as flocs separation method. However, the coal slurry has to to ground to -500 mesh (-25 micron). The recommended industrial scale process flow-sheet is shown in Figure I.28.

Since there is no similar commercial process with which we can compare our process, several assumptions and estimation were made. The following discussions outline the method used to estimate the cost imposed by selctive flocculation process.

Cost Estimation for Selective Flocculation to Produce One Million tons of clean coal/year

It was assumed that the flocculation process can be implemented into an existing froth flotation process with some minor modification. Therefore, there will be two additional

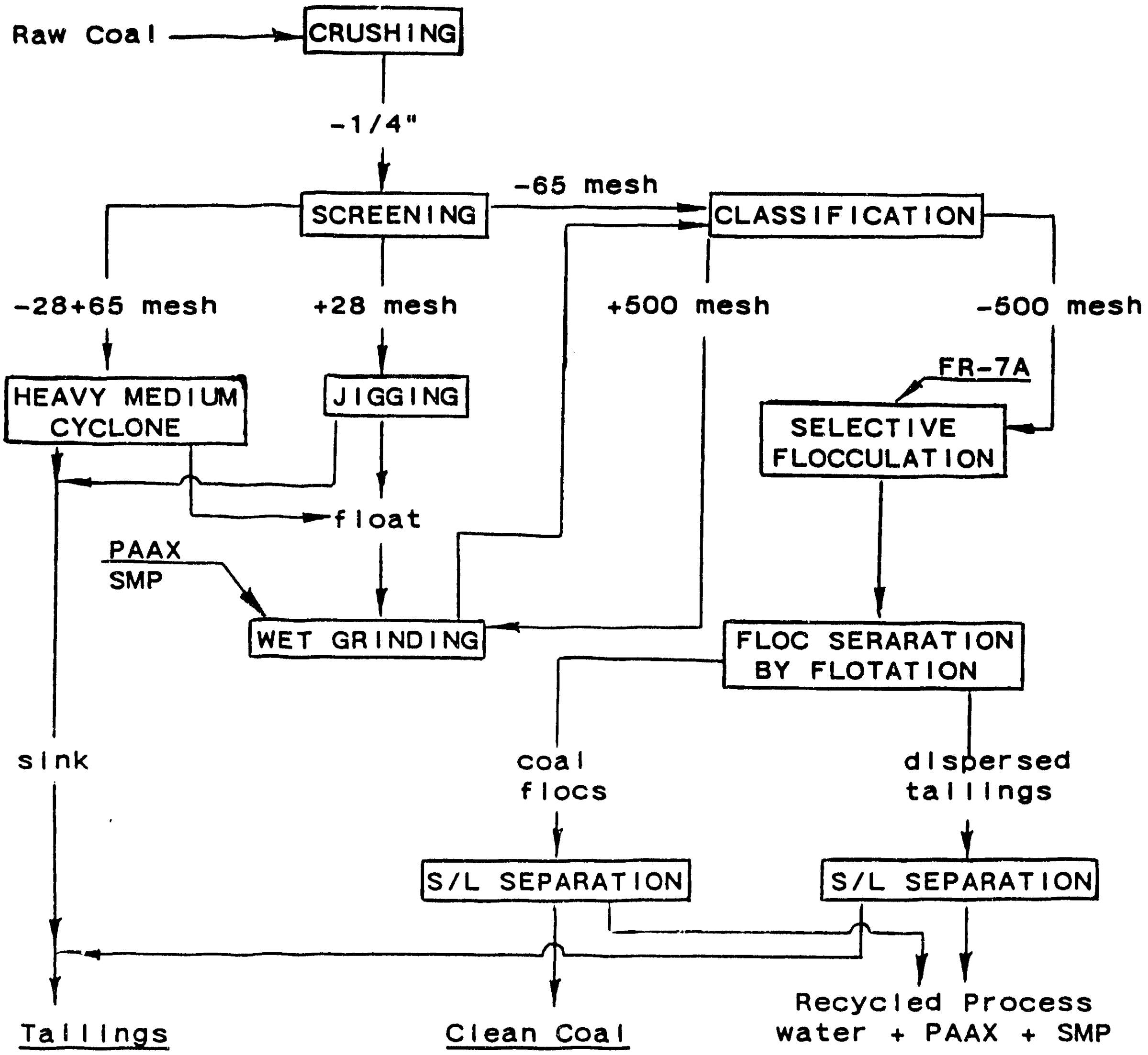


Figure 1.28 Recommended Flow sheet Diagram for Selective Flocculation/Flotation Process.

changes in an industrial circuit for froth flotation process. The first modification is the extra grinding facilities required to produce a -325 or -500 mesh slurry. In this analysis, we compared selective flocculation which is integrated in a flotation plant to flotation only plant which treats -200 mesh coal slurry. Furthermore, there will be the extra units and operating costs associated with the selective flocculation ahead of flotation unit. Therefore, the cost due to flocculation process is the summation of these two additional changes. The benefit on the other hand, is the increase in the value of the final coal product.

In all these analyses, it was assumed that the average plant capacity is one million tons of coal per year. The cost of a froth flotation plant with this average capacity is listed below. This information was obtained from McNally Pittsburgh Engineering, Wellstone, Ohio.

- Crushing and grinding circuit cost to -200 mesh (-74 micron) without heavy medium separation:

Capital Investment	$ 10 million
Operating Cost	$ 2 million/yr

- Capital and operating costs for flotation and associated processes

Flotation chemicals, waste treatment,diposal, dewatering, and etc. :

Capital investment	$ 8 million
Operating Cost	$ 10 million/yr

- Total processing cost per ton of coal

Plant life:	10 yrs.
Comminution cost:	$ 3 / ton

Flotation circuit:	$ 10.8 / ton
Total cost of flotation	$ 13.8 / ton

Note that these estimations are for a flotation circuit using -200 mesh slurry without using the heavy medium separation (HMS) circuit. Assuming that there is a HMS process before comminution, clearly the capital cost will increase. However, the coarse pyrite and silica particles (hard particles) will be eliminated. Consequently, the mill capacity will increase, the operating cost for comminution process will decrease, and the life time of the equipment will increase. In addition, The HMS process will improve the final value of the product by removing the coarse size impurities (1% of pyritic sulfur and 7% of the mineral matters).

Therefore, the advantages of the HMS process naturally subsidize the extra investment. In any event, the cost associated with the HMS will be still equal in both the flotation and the flocculation/flotation processes. This implies that there is no change in the magnitude of the cost difference between the flotation process and the flocculation/flotation process.

Now assuming there is a HMS process before grinding and flotation processes, the coal to the comminution process has 3.0% total sulfur and 9.% ash content. As a result of grinding to -74 micron only 40% of the remaining pyrites are liberated (i.e., 0.74% pyritic sulfur). Flotation can remove about 40 to 50% of the liberated pyrite (or 0.38%). Therefore, the final product has about 2.62% total sulfur, and 6% ash content with 90% coal recovery.

For the proposed flocculation/flotation circuit, the coal has to be -25 micron. It is assumed that as a result there will be a 50% increase in the comminution cost.

- Total comminution cost for the flocculation/flotation circuit

Capital cost of comminution (costant)	$ 10 million (10 years)
or	$ 1 / ton
Operating cost	$ 3 / yr
or	$ 3 / ton
Total comminution cost	$ 4 / ton

The residence time of the slurry in the selective flocculation process is about 5 minutes which implies that a small mixing tank or on-line mixer is required for this process. Attia (ref. 16) calculated the operating cost for the bio-conditioning process with 10 minutes residence time. It was found that this cost is about $ 0.89 / ton. In the flocculation process the residence time is shorter and there is no need for the auxiliary equipment used for the bio-conditioning. However, there is the operating cost for chemical used in this process (FR-7A, SMP and PAAX). Approximately 130 tons of FR-7A and 2,500 tons of PAAX are required. However, PAAX can be recycled. As a result, it can be assumed that the total addition cost of selective flocculation is $ 1 / ton of coal. Therefore, the total cost of proposed process is:

Total cost = Comminution + Selective Floccuation + Flotation

or;

Total proposed process cost = (\$ 4 + \$ 1 + \$ 10.8) / ton
= \$ 15.8 / ton

The produced coal will have 1.8% total sulfur and 3.55% ash content. the recovery of the coal will be 85%. The market price of coal is determined by the quality of the coal (i.e., Btu, ash and sulfur content). The current prices of different type of coals in Ohio are obtained from the coal outlook^{TM}(ref. 17). According to these market prices:

Coal with 2.5% total sulfur = \$ 30/ ton

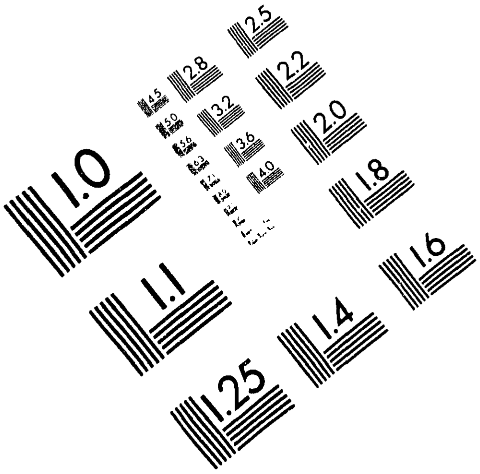
Coal with 1.8% total sulfur = \$ 35/ ton

The net profit will be:

Gross Profit = (35 - 30) - (15.8 - 13.8)
= 5 - 2
= \$ 3 / ton

Table I.16 Summary of the Economical Assessment.

	Flotation	S. Flocculation/Flotation
Clean Coal	2.62% T.S, 7% ash	1.8% T.S., 3.55% ash
Coal Price	\$ 30 / ton	\$ 35 / ton
Total Cost	\$ 13.8 / ton	\$ 15.8 / ton
Recovery	91 %	83 %
Coal yield	81 %	78.7 %
ton feed/ton clean coal	1.22	1.27



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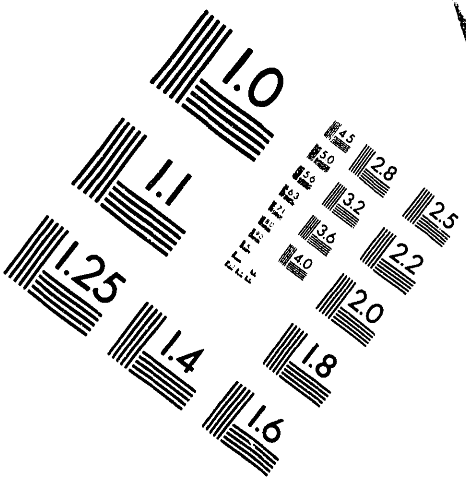

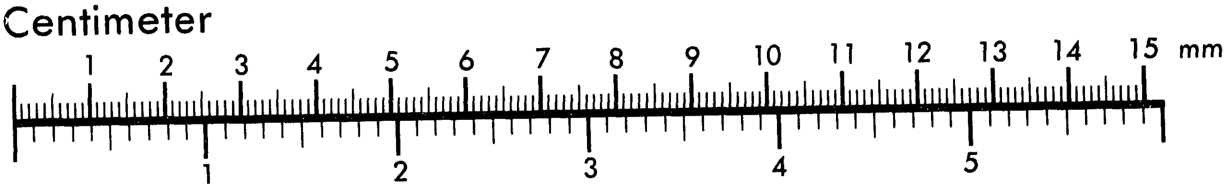

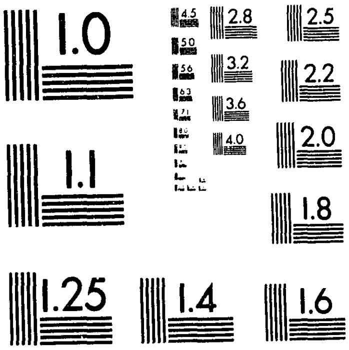

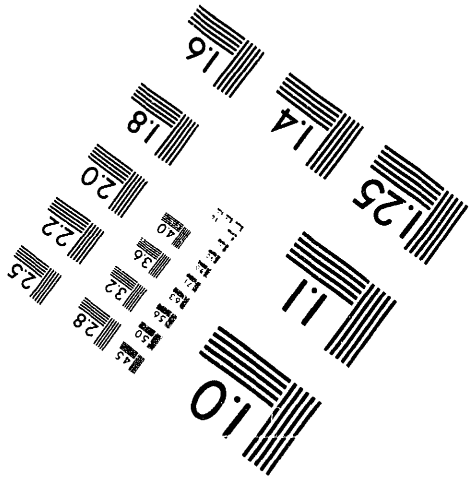

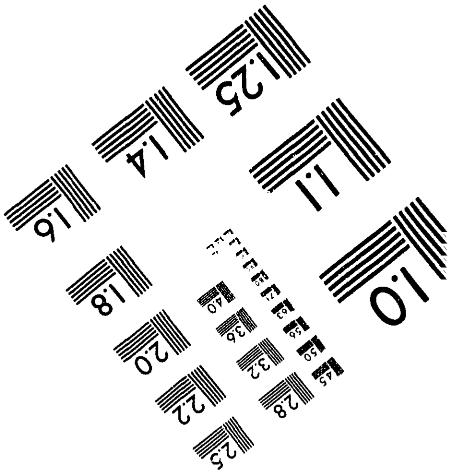

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Note that the coal price estimates presented here are relatively less than the prices paid by either Ohio Power Co. (AEP) or Ohio Valley Electric Corp for even higher sulfur and ash content coals (ref. 17).

Final Assessment

a) Increase in income due to selective flocculation:

$$I_2 - I_1 = \$\ 35 \times 0.787 - \$\ 30 \times 0.81$$
$$= \$\ 3.24 / \text{ton}$$

b) Increase in total cost due to selective flocculation:

$$C_2 - C_1 = \$\ 15.8 - \$\ 13.8 = \$\ 2 / \text{ton}$$

c) Investment income ratio = 2 / 3.24 = 1 : 1.62

i.e., for each $ 1 invested in selective flocculation, $ 1.62 in income will be returned. In other words, the rate of return on investment (ROI) was 62%. This value indicate a highly profitable process.

I.6 CONCLUSIONS AND RECOMMENDATIONS

Based on the test results mentioned in this report, the following main conclusion can be made:

1) Selective flocculation process appears to be technically, environmentally, and economically feasible for deep cleaning and desulfurization of Ohio coal. The process has the potential of near-term commercializationa and can be adapted to existing coal preparation plants with only minor retrofits.

2) Fundamental interfacial studies confirmed the validity of the process concepts. Thus, the flocculant (FR-7) used was selective towards coal, while the PAAX dispersant proved selective towards ultrafine pyrite. This allowed the simultaneous removal of ultrfine ash and pyrite while recoveries of the clean coal as agglomerates. The size of this agglomerates can be controlled which will enhance the dewatering and handling behaviors of the cleaner coal.

Recommendations:

1) Further study of the implementation of the selective flocculation to several types of Ohio coal is recommended.

2) Further research work should be conducted to find a more efficient method for flocs separation since the high turbulance in the flotation system adversely affects the clean coal product.

3) A pilot study of the proposed process is recommended before commercialization of the process.

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PART II

REMOVAL OF ORGANIC SULFUR FROM OHIO COAL BY MILD CHEMICAL PROCESS

INTRODUCTION

The high sulfur content of Ohio coals imposes a severe limitation on their utilization, since the level of sulfur oxide gases emitted from the combustion of these coals is higher than that recommended by the U.S. Environmental Protection Agency. Removal of sulfur from high sulfur coals before combustion would therefore help greatly to eliminate this problem.

It is known that many Ohio coals are characterized by a relatively high organic sulfur content with varying proportions which in some cases represents about 50% of the total sulfur. Since the organic sulfur is an integral part of coal matrix it cannot be removed by physical techniques. Only chemical and/or biochemical treatments can selectively destroy the sulfur compounds present in the coal matrix, rendering the sulfur amenable to extraction by leaching [1].

Since inorganic sulfur (namely pyrite) can be removed in large measure by advanced physical cleaning techniques, there is a need for a chemical cleaning technique capable of removing this organic sulfur and residual pyritic sulfur from Ohio coal. Hence, this study is relevant and consistent with the objectives of the Ohio Coal development Office.

Conventional Chemical Processes: A brief review:

The reported chemical cleaning processes for coal include: (1) the Battelle Hydrothermal Coal (BHC) process, (2) the mayer's (TRW) process, (3) Oxydesulfurization (Ames, PETC, LOL) processes, (4) Chlorinolysis (JPL) process, (5) KVB process, and (6) Microwave Desulfurization [2-5]. The treatment conditions, and sulfur reduction of these techniques are listed in Table II.1.

TABLE II.1. Examples of the chemical desulfurization processes

Process	BHC	TRW	LOL	PETC	Ames	JPL	KVB	GE
Method	Caustic leach	Acid leach	Oxygen/ ammonia leach	Air/ water leach	Oxygen sodium leach	Chlorine/ water leach	Dry oxidation	Microwave caustic leach
Reagents	NaOH $Ca(OH)_2$	$Fe_2(SO_4)_3$, H_2O, O_2	O_2, H_2O	Air, H_2O	O_2, H_2O	Cl_2, H_2O	O_2, N_2, NO	H_2O, NaOH
Pressure (atm)	39-84	Atmospheric	10-20	34-68	14	Atmospheric	Atmospheric	Atmospheric
Temp (C)	250-400	90-130	130-350	180	150	50-100	100	250-300
Pyritic sulfur reduction (%)	90	90	90	90	90	90	90	95
Organic sulfur reduction (%)	40	0	25	45	50	50	40	60
Status	Pre-Pilot	Pilot plant	Inactive	Bench scale	Bench scale	Bench scale	Inactive	Bench scale

In recent years, molten caustic leaching process-TRW Gravimelt process has been developed by DOE's chemical-coal-cleaning program [6]. The TRW Gravimelt process basically consists of treating coal with molten caustic (NaOH or a NaOH/KOH mixture) at 370-390°C for 1-3 hours. The treated coal is then washed consecutively with water, dilute acid, and again with water. This process has been shown by TRW and other workers to remove 90% or more of the mineral matter, all of the pyritic sulfur, and 50% or more of the organic sulfur from most coals studied. C. W. Fan and his coworkers [7] recently conducted a three-step leaching treatment with ferric and cupric salt solutions at 200-300 °C and then with sodium carbonate at 330°C and finally with boiling hydrochloric acid. Both organic and inorganic sulfur were removed with up to half of the organic sulfur was extracted. In another study, pyritic sulfur and organic sulfur form dibenzothiophene could be removed with Manganese, ferromanganese at 580°C [8].

Most of the processes discussed above were successful in achieving 90% pyritic sulfur rejection and 25% to 50% organic sulfur removal. Some of these chemical processes have been developed to pre-pilot plant scale or pilot plant scale such as BHC and TRW processes, but none has been commercialized. These methods are not universally applicable, but are rather suitable for special applications, because they use costly and sometimes corrosive chemicals and are carried out under extreme conditions of high temperature and pressure. In addition, the high temperature treatment may alter the properties of the coal itself and destroy its caking tendency. For example, the PETC oxydesulfurization process was carried out at high temperature 180-200°C and high pressures 34-68 atm achieving the removal of almost all of the pyritic sulfur and up to 45% of the organic sulfur. However, the caking properties of the coal were destroyed in this high temperature oxidation [2].

Mild Chemical Oxidation Process

Mild chemical oxidation processes such as the one investigated in this project are typically conducted at room temperature and atmospheric pressure and use inexpensive commercial oxidizing reagents. The mild chemical oxidation of organic sulfur using sodium hypochlorite has been tested in the laboratory on several coals. Sodium hypochlorite, NaOCl, is known to oxidize various organic sulfur functionalities. It was used for this purpose in research conducted by the petroleum industry early in this century to remove sulfur from crude oil and petroleum distillates [9-11] and in refining petroleum naphta solutions [12,13]. More recently, NaOCl was used by Chakrabartty [14-16] and Mayo [17,18] in the oxidative dissolution of coal for the purpose of studying coal structure. These efforts, however, were not concerned with the removal of organic sulfur.

The desulfurization process was based on mixing the coal slurry with the bleach solution at room temperature and atmospheric pressure. The oxidation process was followed by a washing step using warm to hot water or sodium carbonate solution. A detailed description of this process is given in two recent publications by Taylor [20]. According to Brubaker and Stoices, the treatment of coal with the bleach solution has preferentially decreased the organic sulfur by 10-42%, and most of the sulfatic sulfur, while the pyritic sulfur was apparently the least affected by this treatment. Up to 58% reduction of total sulfur was reported. In this treatment, they found it advantageous to pre-condition the coal sample with Ammonium hydroxide, NH_4OH and wash the coal with hot sodium carbonate after the oxidation with the hypochlorite. These steps were repeated as necessary to effect a higher degree of desulfurization. Boron and Taylor used float sink to separate coarsely liberated ash and pyrite, followed by mild oxidation with sodium hypochlorite at elevated temperatures. Organic sulfur removal approached 30% and coal Btu recovery was greater than 70%. The results they obtained indicated that sodium hypochlorite treatment is a promising approach because it removed up to 30% of organic sulfur under the ambient conditions. However, it was at an early stage of development and it removed only the sulfatic and organic sulfur, the pyritic sulfur remained almost unchanged.

Another mild desulfurization process ultrafine coal cleaning was reported recently [21]. The technical feasibility of a two step process to remove inorganic and organic sulfur as well as mineral matter from a high sulfur Illinos #6 coal was examined. the first step was fine grinding of the coal to an average particle size of 2 microns followed by a physical demineralization. Subsequent chemical treatment with aqueous $CuCl_2$ or $FeCl_3$ solutions under mild conditions. Total sulfur removal varied up to 65% for the $CuCl_2$ reaction, and 60% for reaction with $FeCl_3$. About 23% of organic sulfur was removed with

$CuCl_2$. This process did not remove much organic sulfur. In addition the residual copper removal was difficult, the heating value of coal decreased after desulfurization, and the energy consumption for obtaining the ultrafine size coal would be higher.

Permanganate Desulfurization

Recently we have developed a mild oxidation process, for the removal of organic sulfur and residual pyritic sulfur from Ohio coal using potassium permanganate as the oxidizing agent. The conceptual feasibility and important parameters of this process were investigated. The results obtained indicated that this chemical oxidation technique was successful in achieving 90% pyritic sulfur rejection and up to 50% organic sulfur removal.

The oxidation process is conducted at room temperature and atmospheric pressure and uses an inexpensive commercial chemical reagent potassium permanganate. potassium permanganate is a powerful oxidizing agent in either alkaline or acid media [22]. In alkaline solution, purple permanganate is quickly reduced to the green manganate, which later deposits brown manganese oxide. The overall half-reaction is [22]:

$$MnO^-_4 + 2H_2O + 3e \text{ ---> } MnO_2 + 4OH^-; \qquad E = +1.23 \text{ Volts}$$

potassium permanganate would be expected to oxidize various organic sulfur functionalities such as sulfides, mercaptans and thiophehes in the coal to related sulfates.

In addition to organic sulfur forms, the inorganic sulfur in the form of pyrite can also be oxidized by the following reaction [19];

$$FeS_2 + 8H_2O \text{ ---> } Fe^2 + 2SO_4^{-2} + 16H^+ + 14e^-; \ E = -0.362V$$

In alkaline solutions, the oxidation of pyrite and organic sulfur follows the following equation [2]:

$$8FeS_2 + 30NaOH \longrightarrow 4Fe_2O_3 + 14Na_2S + Na_2S_2O_3 + 15H_2O$$

The oxidation process is followed by washing step with complexing reagent or dilute acid at atmospheric pressure and room temperature also, to remove the side-product precipitates. This process appears to be more promising than other chemical processes since it does not require high capital and operating expenses for maintaining high pressure, temperature and chemicals recovery. It has advantage over the mild oxidation with sodium hypochlorite, because it is more effective for removing organic sulfur and it can remove 90% of pyritic sulfur at the same time. Furthermore, potassium permanganate is less expensive than sodium hypochlorite and other chemicals used in some chemical processes such as copper chloride, ferric chloride, ferric sulfate, etc.

During chemical oxidation conducted with $KMnO_4$, the permanganate is reduced to insoluble brown manganese dioxide [22]. Another possible precipitate during oxidation is jarosite $KFe_3(SO_4)_2(OH)_6$ [23] which is a basic alkali sulfate.

In order to remove these precipitates of MnO_2 and jarosite, a washing step following the oxidation step was conducted at room temperature and atmospheric pressure using dilute complexing reagent, inorganic acid or organic acid. Thus, the integrated approach would enable the removal of both organic and pyritic sulfur as well as the precipitates. The research program on the proposed process was conducted on coal samples pre-prepared by heavy liquid separation as shown on the following diagram.

The specific objectives of this study were: 1) to investigate the feasibility of removing organic sulfur from Ohio coal using potassium permanganate at room temperature and atmospheric pressure; and 2) to investigate the important process parameters and "optimize" reaction conditions for both oxidation and washing steps in order to achieve maximum organic sulfur removal and Btu recovery.

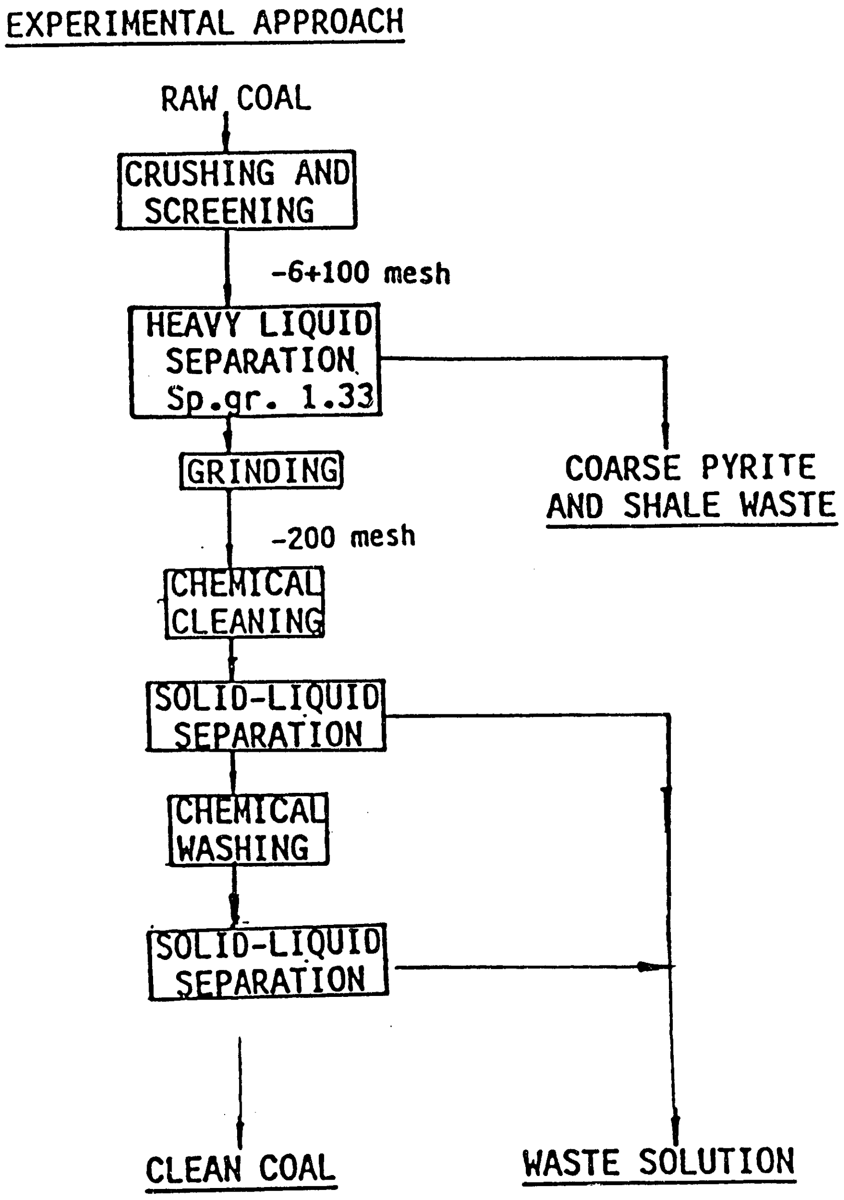


Figure II.1. Permanganate coal cleaning approach

EXPERIMENTAL TECHNIQUES

Materials:

Coal Sample Preparation: The coal samples utilized in this study were from the Pittsburgh No.8 Seam and were kindly supplied by R & F Coal Company, Lamira Preparation Plant, Warnock, Ohio. The raw coal samples were crushed and screened to the size range of -6 +100 mesh (-2800 +150 microns) and were pre-cleaned by heavy liquid separation using 1,1,1,-Trichloroethane with a specific gravity of 1.33. To eliminate the effects of the residual 1,1,1,-Trichloroethane on coal surface properties, the float coal products were washed with acetone and were dried overnight in an oven at 100°C to evaporate the organic solvent. Three pre-cleaned coal samples were prepared in this way from different fresh raw coal samples at different periods during the project. The ash and sulfur contents of these three coal samples

TABLE II.2. Ash and sulfur contents of the Pittsburgh No. 8 coal samples before and after heavy medium separation

Sample	Ash %	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%
Raw coal #1	13.8	3.58	2.82	0.02	0.74
Pre-cleaned by heavy liquid	4.4	1.78	1.04	0.02	0.72
Raw coal #2	15.8	3.86	2.80	0.02	1.04
pre-cleaned by heavy liquid	5.4	1.98	0.92	0.002	1.06
Raw coal #3	16.1	3.97	2.70	0.02	1.25
pre-cleaned by heavy liquid	5.8	2.26	0.96	0.04	1.26

before and after heavy liquid separation (pre-cleaning) are listed in Table 2-2. The pre-cleaned coal samples were ground to -200 mesh (-74 microns) before use in the chemical oxidation experiments.

Chemical Reagents: The oxidizing reagents, such as 4%-6% solutions of high purity sodium hypochlorite, crystals of potassium permanganate, hydrogen peroxide, ammonium persulfate and potassium persulfate, and the washing reagents, such as the complexing reagent EDTA, hydrochloric acid, nitric acid, sulfuric acid, ascorbic acid, oxalic acid and citric acid were all analytical grade chemicals made by different manufacturers and were obtained from Fisher Scientific Company, Chemical Manufacturing Division, Cincinnati Ohio, U.S.A. Solutions of the chemicals were made at the required concentrations.

Procedures

Chemical oxidation: The experiments were carried out in a batch mode at room temperature and atmospheric pressure. Twenty or forty grams of -200 mesh (-74 micros) pre-cleaned coal sample were placed into a 500 ml or 1000 ml beaker containing an aqueous solution of the oxidizing reagent of the desired concentration. The volume of the queues solution was varied to obtain the required solids content. Mixing of the coal slurry with the reagents was accomplished with a magnetic stirrer or a variable speed impeller mixer for one or one and half hour. The variable speed impeller used was T-line mixer, model 102, supplied by Sepor Inc. Wilmington, California, U.S.A. The pH of the solution was measured and adjusted during the oxidation reaction using Chemcadet pH/mv meter, supplied by Cole-Parmer Instrument

Company, Chicago, Illinois. At the end of the oxidation period, the reaction mixture was filtered on a Buckner Funnel, and was washed repeatedly with distilled water until the pH of the filtrate was neutral. Unless mentioned otherwise, the oxidation period was one hour.

A series of oxidation treatment tests was conducted on the pre-cleaned coal sample #1 for evaluating the following variables:

(1) Types of oxidizing reagent;

(2) Concentration of potassium permanganate (2, 4, 6, 8 and 10%);

(3) Oxidation time (0.5, 1.0, 1.5, 2.0 and 2.5 hours);

(4) Agitation speed (645, 825, 935, 1010 and 1100 rpm);

(5) Solid content (10, 20, 30 and 40% wt.);

(6) Number of oxidation steps (1, 2, 3); and

(7) PH of the reaction slurry (6 to 12).

Washing of oxidation products: The filter cake was transferred to a 500 ml beaker or flat-bottom flask equipped with a condenser, where it was re-slurried to the required solids content, with an aqueous solution of the washing chemical at the desired concentration. The slurry was continuously stirred using a magnetic stirrer for one hour. The washing temperature was maintained by a temperature controlled water-bath when the washing was conducted at higher levels than room temperature. The washed slurry was filtered in a Buncher Funnel, dried at 75-80^{o}C overnight and was analyzed for all forms of sulfur, ash content and Btu.

A series of washing tests were conducted on the chemically oxidizing coal for evaluating the following variables:

(1) Types of washing reagent (water, $Na_2(CO)_3$, complexing reagent EDTA, HCl, HNO_3, H_2SO_4, ascorbic acid, oxalic acid, citric acid);

(2) Temperature of the washing step with distilled water (22, 35, 50, 65 and 80°C);

(3) Concentration of the HCl and HNO_3 (7 and 14%); and

(4) Number of oxidizing/washing steps (1, 2, and 3).

Ultrasonic dispersion was intermittently employed during oxidation and washing steps using Branson Ultrasonic Cleaner. Particle size of coal before and after using ultrasonic dispersion was determined by Microtrac Particle Size Analyzer (Leeds & Northrup Company).

Analyses

Total sulfur in coal was determined by LECO automatic sulfur titrator model 532-500 and LECO Sulfur Determinator Model SC 132. Pyritic sulfur and sulfate sulfur were determined according to the recommended ASTM procedures. The sulfate sulfur was analysed using gravimetric method in which the sulfate ion was precipitated and weighed as barium sulfate. Pyrite was extracted quantitatively by dilute nitric acid. The extracted iron was determined by atomic absorption techniques using Perkin-Elmer Model 3030. Organic sulfur was calculated by subtracting the sulfate and pyritic sulfur from the total sulfur in the coal.

Ash contents were determined by Fisher Isotemp Programmable Ashing Furnace Model 497 according to the standard ASTM procedure.

Btu value of the coal was determined by using parr Oxygen Bomb Calorimeter.

Chlorine content of coal was determined using Bomb Combustion procedure and Titration with silver nitrate according to the standard ASTM D 2361-85 procedure.

Sample Characterization technique

X-ray diffraction, automated image analysis, density determinations and microscopic methods were used to characterize certain properties of raw coal, pre-cleaned coal, chemically oxidized coal and chemically washed coal.

The matrix density of the coal was calculated by determining the weight in air and the weight in kerosene of the coal sample. This method described by Nuhfer and others [24], utilizes vacuum impregnation of the ground coal with kerosene of known specific gravity. The matrix density of the coal can be found to within 0.02 g/cc.

Vitrinite reflectance and pyrite size parameters were determined using a Leitz Textural Analysis System, supplied by E. Leitz, Inc. Rockleigh, New Jersey 07647. This instrument, commonly referred to as an automated image analysis system is capable of reproducing vitrinite reflectance value in oil to within 0.02 percent reflectance. Coal pellets used for the vitrinite reflectance determinations were polished in accordance with ASTM Method 2792. A total of 80 fields, each encompassing 2256 square microns and equally distributed over the pellet's surface in a grid-like pattern were used for the reflectance measurements. Average gray-level values determined by the AIA for vitrinite were converted to reflectance values (in oil) using glass standards. The glass standards used had reflectance values slightly below that of the vitrinite being measured.

Geometric mean pyrite sizes and pyrite size distributions were determined by AIA. Pyrite sizes are based on the equivalent circular diameter (ECD) of the cross-sectional areas of the pyrite grains detected by the image analyser on surface of the polished coal pellet. Geometric means of the pyrite size distributions were found by graphic methods [25].

X-ray diffraction analysis of low temperature ashing products of different coal samples were performed by using Novelco X-ray diffractometer, Mark II, Phillips Electronic Instruments, Mahwah, new Jersey 07430. Low Temperature Asher is Model IPC 1003B-248AN, supplied by Branson International Plasma Corporation, Hayward, California 94544. The ashes from these samples were ground to minus 200 mesh, carefully packed in aluminum slide holders and X-rayed from 2° 2θ to at least 60° 2θ.

The microscopic examination of samples was performed to recognize pyrite and aggregates in coal by using Leitz MPU 2 microscope, E. Leitz, Inc., Rocklergh, New Jersey 07647.

Manganese content of the coal was determined by powdered coal leaching with concentrated hydrochloric acid for one hour, and then collecting and diluting the filtrate. The extracted manganese was determined by atomic absorption techniques using an air acetylene flame in a model 3030 Atomic Absorption Spectrophotometer manufactured by Perkin-Elmer, Norwalk, Connecticut.

RESULTS AND DISCUSSION

FEASIBILITY OF ORGANIC AND INORGANIC SULFUR REMOVAL BY THE MILD CLEANING PROCESS:

Selection of oxidizing agents

The conceptual feasibility of coal desulfurization by mild chemical treatments was tested with pre-cleaned coal sample #1 using several different oxidation reagents at room temperature and atmospheric pressure. Table II.3. lists the sulfur forms and the organic sulfur removal after chemical treatment with 6% each of potassium permanganate $KMnO_4$, sodium hypochlorite NaOCl, hydrogen peroxide H_2O_2, ammonium persulfate $(NH_4)_2S_2O_8$ and potassium perchlorate $KClO_3$. The tests were run with 10% solids content of coal slurry. The oxidized samples were washed with cold water at room temperature for one hour.

TABLE II.3. Comparison of different types of oxidizing reagents for coal desulfurization

Chemical Treatment	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Organic Sulfur Rejection%
None	1.78	1.04	0.02	0.72	----
$KMnO_4$	0.98	0.32	0.32	0.34	52.0
NaOCl	1.51	0.88	0.08	0.55	24.0
H_2O_2	1.03	0.27	0.06	0.70	0.0
$(NH_4)_2S_2O_8$	1.75	----	----	----	0.0
$KClO_3$	1.56	0.94	0.02	0.62	13.4

As an oxidizing agent, sodium hypochlorite (NaOCl) has an oxidation potential of 0.90 Volts. The half reaction [19] is:

$$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-; \qquad E = +0.90 \text{ Volts}$$

Sodium hypochlorite removed about 24% of the organic sulfur, but oxidized only 15.4% of pyritic sulfur. Moreover, the separation of the cleaned coal from sodium hypochlorite reaction solution through filtration proved to be difficult because the very finely oxidized coal seemed to form a stable dispersion in water.

Hydrogen peroxide, in aqueous solution, functions as an oxidizing agent. It oxidizes ferrous salts to ferric, and sulfites and sulfides to sulfates. It oxidized 74% of pyritic sulfur from the coal in the test. The reaction is believed to be as follows [22]:

$$S^{2-} + 4H_2O_2 \text{ ---> } SO_4{}^{2-} + 4H_2O$$

But none of the organic sulfur was oxidized according to the results.

The ammonium persulfate is known as a extremely powerful oxidizing agent, but the reaction is very slow unless silver salts are present [22].

$$S_2O_8{}^{2-} + 2e \text{ ---> } 2SO_4{}^{2-}$$

This might explain why ammonium persulfate was not effective for coal desulfurization at ambient conditions. Potassium perchlorate only oxidized 13.4% of the organic sulfur.

Potassium permanganate is a powerful oxidizing agent in either alkaline or acid media. In alkaline solution, the purple permanganate is quickly reduced to the green manganate, which later deposits brown manganese oxide. The overall half reaction is [22]:

$$MnO_4{}^- + 2H_2O + 3e \text{ ---> } MnO_2 + 4OH^-; \quad E = +1.23 \text{ Volts}$$

In the acid solution, the half reaction is:

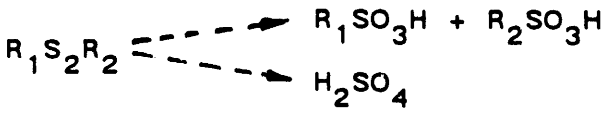
$$MnO_4{}^- + 8H^+ + 5e \text{ ---> } Mn^{2+} + 4H_2O; \quad E = +1.52 \text{ Volts}$$

From Table II.3. both sodium hypochlorite and potassium permanganate can remove organic sulfur, they would therefore oxidize various organic sulfur functionalities such as sulfides, mercaptans and thiophenes in the coal.

The probable oxidation pathways are summarized [19] below:

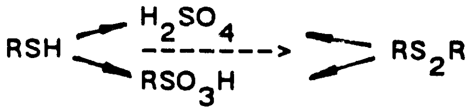
Organic sulfides: $R_1SR_2 \text{-------->} R_1SO_2R_2$

Organic disulfides:



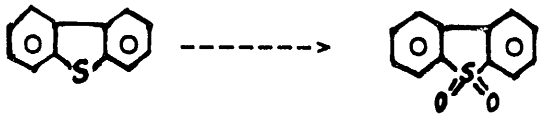
$$R_1S_2R_2 \longrightarrow R_1SO_3H + R_2SO_3H \qquad R_1S_2R_2 \longrightarrow H_2SO_4$$

Mercaptans:



$$RSH \longrightarrow H_2SO_4 \qquad RSH \longrightarrow RSO_3H \qquad \text{-------->} \; RS_2R$$

Thiophenes:



However, the oxidation potential of potassium permanganate is higher than that of sodium hypochlorite, therefore, it is expected to be more effective for removing organic sulfur. The results in Table II.3. showed that potassium permanganate oxidized 37.8% of organic sulfur and 58.7% of pyritic sulfur both to sulfate sulfur, as the oxidation potential of potassium permanganate was higher than the oxidation potential for pyrite.

Effect of Process Parameters on Desulfurization

Since potassium permanganate was more effective for organic sulfur removal than sodium hypochlorite and other oxidizing reagents, it was selected for further investigations on the feasibility of coal desulfurization with a mild chemical process. Important parameters of this process have been investigated and discussed in the following section. These investigations covered the following parameters: concentration of oxidation reagent, reaction time, agitation speed, pH of reaction and the solids content.

Effect of Concentration of Oxidizing Reagents on the organic sulfur removal

Chemical oxidations were conducted with pre-cleaned coal sample #1 using different concentrations of potassium permanganate at room temperature for one hour, then washed by hot water at 80°C for one hour. The solid content of both oxidation and washing step was 10%. The results are shown in Figure II.2 A greater organic sulfur reduction was observed with the increase in the concentration of potassium permanganate. For example, 54.6% of the organic sulfur was removed with 10% of $KMnO_4$, compared with 33.3% removal with 4% $KMnO_4$. Lower concentrations than 4% $KMnO_4$ appeared to have little or no effect.

Figure II.2 reflects the variation of different forms of sulfur in coal with increasing concentration of the potassium permanganate. It appears that total sulfur decreased gradually within the whole range of concentrations, but the pyritic sulfur decreased sharply with the increase in $KMnO_4$ concentration to 4% and then decreased more slowly from 4% to 10%. Correspondingly the sulfate sulfur, increased sharply with the increase of concentration from 0 to 4% and then slowly from 4% to 10%. In contrast, the organic sulfur changed very little at the lower concentrations of potassium permanganate and decreased quickly with increasing the concentration from 4% to 10%. These results indicated that the pyritic sulfur was easier to oxidize than the organic sulfur at the lower $KMnO_4$ concentrations (2-4%), while at higher concentrations (i.e. 6% or more), the organic sulfur was as effectively removed. This might be due to better accessibility of potassium permanganate to pyrite than to organically bound sulfur. It must be pointed out that the trends shown in Figure II.2 might well be exaggerated and somewhat inaccurate, so the sulfur analyses did not account for the precipitation of reaction products which increased the ash content and the final weight of the coal samples.

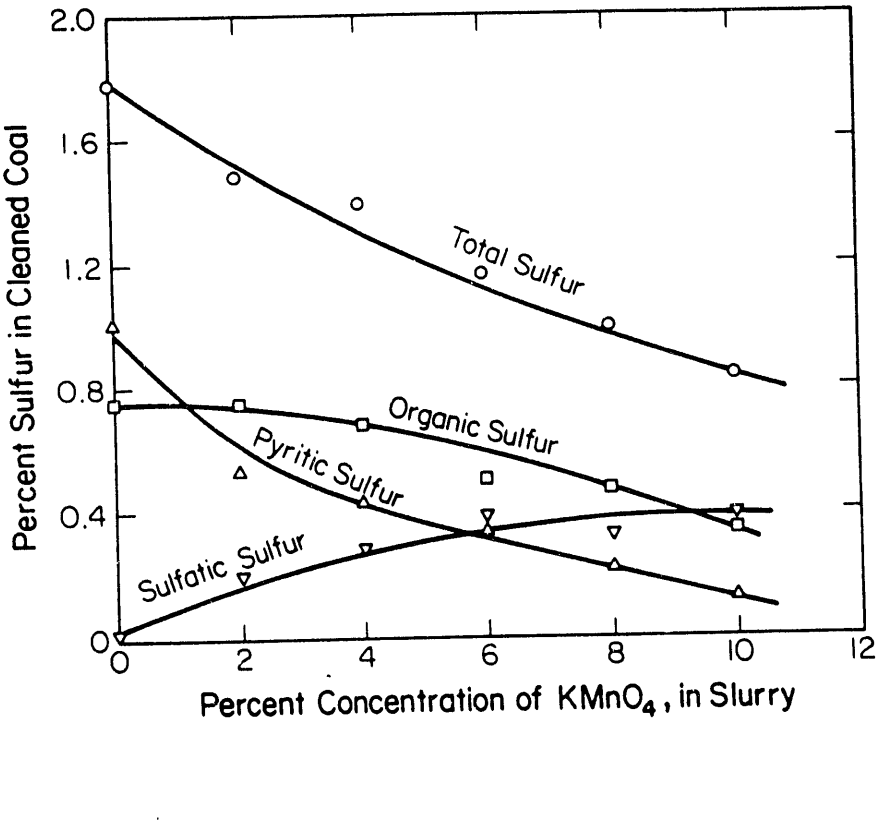


FIG II.2. Effect of concentration of $KMnO_4$ on sulfur content of cleaned coal

Effect of Reaction Time on Organic Sulfur Removal

Table II.4 and Figure II.3 show the results of changing the oxidation time with 10% potassium permanganate on pre-cleaned coal sample #1 at room temperature and atmospheric pressure. The solid content of the slurry was 10%. The reaction time was varied between 0.5 and 2.5 hours. The oxidized samples were washed with cold water at room temperature for one hour. From Table II.4, about 50% of organic sulfur was removed with 1.5 hour chemical treatment. This reaction time of 1.5 hr seems to be the "optimum" for this reaction. The results in Table II.4, in terms of reaction time and percent organic sulfur rejection, are lower

TABLE II-4. Effect of reaction time on chemical oxidation for organic sulfur removal.

Reaction Time, hours	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Organic Sulfur Removal%
0.0	1.79	1.01	0.02	0.76	----
0.5	1.06	0.22	0.35	0.49	35.5
1.0	0.99	0.23	0.31	0.45	40.8
1.5	0.94	0.24	0.32	0.38	50.0
2.0	0.94	0.23	0.33	0.38	51.3
2.5	0.90	0.22	0.31	0.37	50.0

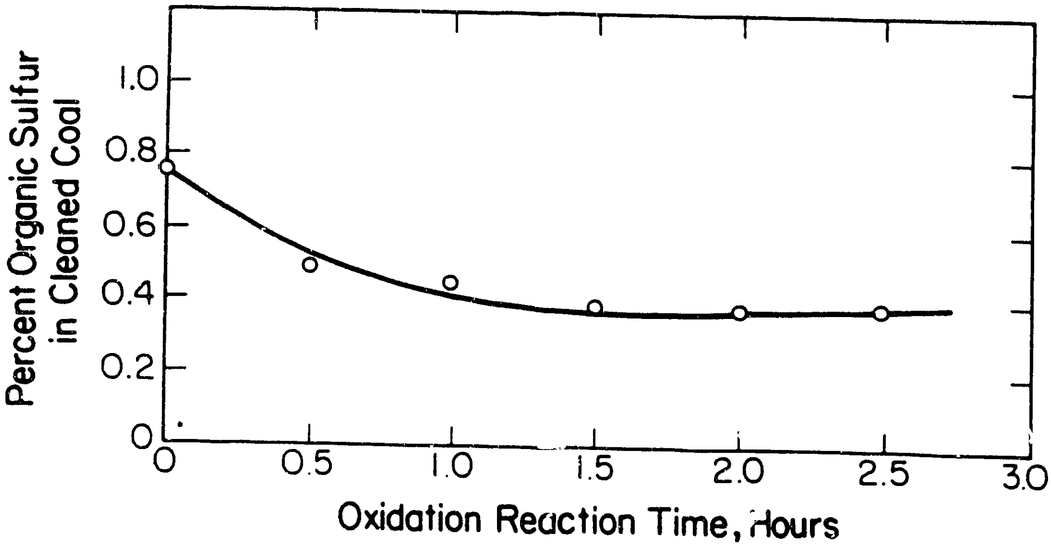


FIG II.3. Effect of reaction time on organic sulfur content in cleaned coal, using cold water in the washing step than those in Table II.5, where hot water was used in the washing step.

Figure II.3 shows that organic sulfur decreased quickly during the first hour, and down to 0.38 (i.e. 50% reduction in organic sulfur) after 1.5 hours, and then tended to be constant as the reaction time was increased. This indicates that the oxidation reaction might have reached a chemical equilibrium state.

Effect of the Agitation Speed on the Sulfur Removal

Table II.5 and Figure II.4 illustrate the effect of agitation speed during the chemical treatment with 10% potassium permanganate and 10% solid content on the efficiency of sulfur removal with pre-cleaned coal sample #1. The chemically treated coal samples were then washed with cold water at room temperature.

These results show that more than half of organic sulfur removal could be expected if the agitation speed was higher than 825 rpm. That indicated the organic sulfur reduction in coal not only depended on the chemical reaction itself, but also on the diffusion factor. Higher rate of transport of the oxidizing agent and the oxidation products to and from the reaction zone was required to enhance the desulfurization process. Hence the idea behind testing various speeds of agitation was to enhance the removal of sulfate sulfur, at higher agitation by attrition. By continuously inhibiting the oxidation products layer from depositing on the coal particle surface through attrition, the leaching process should continue unimpeded. However, the effect of agitation speed on the sulfate sulfur removal appeared to be minimal.

TABLE II.5. Effect of agitation speed on the chemical desulfurization of Pittsburgh No.8 coal, using 10% $KMnO_4$ and cold water washing.

Agitation Speed, rpm.	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Organic Sulfur Removal%
0	1.79	1.01	0.02	0.76	---
625	0.95	0.20	0.30	0.45	40.8
825	0.84	0.20	0.30	0.34	55.3
935	0.84	0.23	0.31	0.30	60.5
1010	0.91	0.23	0.32	0.36	52.6
1100	0.93	0.23	0.34	0.36	52.6

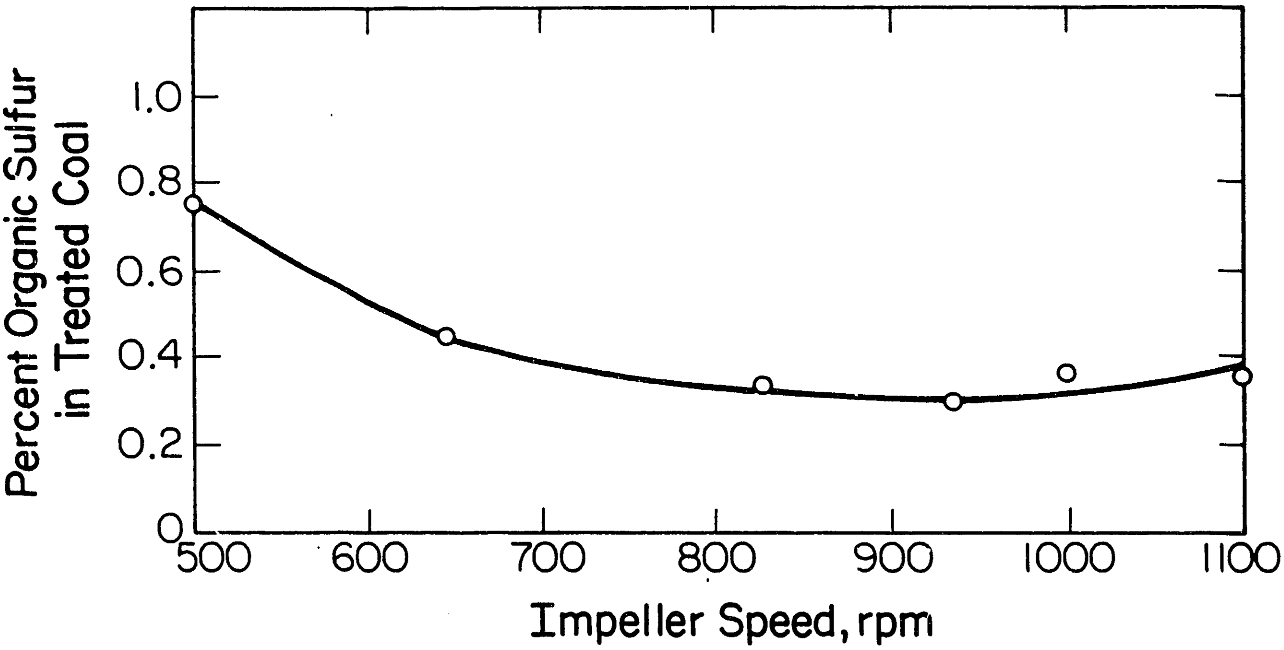


Figure II.4. Effect of agitation speed on the organic sulfur content in treated coal using 10% $KMnO_4$ and cold water wash

Effect of pH of reaction on organic sulfur removal

Chemical oxidation reactions at different pH value were performed. The initial pH of reaction slurry of pre-cleaned coal sample #1 and 8% of potassium permanganate with 10% solids content was 9.2-9.3. It was observed that the final pH at the end of the oxidation step after one hour was about 8.2. The lower and higher initial pH values than 9.2-9.3 were adjusted using 70% HNO_3 and 0.1N KOH. The oxidized samples were washed with cold water at room temperature for one hour. The results are listed in Table II.6.

According to the experiments, the total sulfur was higher at the acid conditions (pH 0.5-4.5) than that at neutral and alkaline conditions. There was very little change in pyritic sulfur and organic sulfur contents from pH 6.5 to 12.8. The sulfate sulfur content was also close at this pH range. These results indicated that sulfur removal was not very sensitive to solution pH during the permanganate desulfurization.

TABLE II.6. Effect of pH on coal desulfurization using potassium permanganate

pH	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	organic Sulfur%
Pre-cleaned Coal	1.78	1.04	0.02	0.72
0.50	1.29	----	----	----
4.50	1.32	----	----	----
6.47	0.99	0.25	0.32	0.42
7.60	1.08	0.26	0.32	0.50
9.17	1.13	0.27	0.33	0.53
10.38	1.10	0.28	0.32	0.40
11.45	1.08	0.31	0.30	0.45
12.80	1.14	0.32	0.32	0.50

Effect of the solid content on chemical cleaning performance

Several tests were conducted to investigate the effect of the solids content in the slurry from 10% to 40% on coal desulfurization with potassium permanganate. Samples of pre-cleaned coal from sample #1 were reacted with 6% $KMnO_4$ at ambient conditions. After filtration, the oxidized samples were washed with cold water at room temperature for one hour. The results shown in Table II.7 indicated that the total sulfur removal appeared to decrease with the increase in the solids content of coal slurry, while the ash content of the oxidized coal decreased and Btu value increased. However, if the increase in ash content was accounted for, the "true" effect of solids content would either be insignificant or cause a slight increase in the sulfur removal at the higher solids content. The suitable solids content for the chemical treatment was considered to be 20% wt.

TABLE II.7. Effect of the solid content on chemical cleaning performance, using 6% of $KMnO_4$

Solids Content wt. %	Total Sulfur%	Ash Content%	Btu/lb	Btu Recovery %
Pre-Cleaned coal	1.78	4.4	13256	100.0
10	1.16	31.5	8572	84.5
20	1.36	21.0	11039	89.9
30	1.50	16.8	11332	91.2
40	1.56	14.3	11593	91.8

REMOVAL OF OXIDATION PRODUCTS DURING THE WASHING STEP

Potassium permanganate is a powerful oxidizing agent,and would be expected to oxidize various organic sulfur functionalities such as sulfides, mercaptans and thiophenes in the coal to related sulfates. In addition to organic sulfur forms, pyrite can also be oxidized by potassium permanganate.

However, during the chemical oxidation with $KMnO_4$, the permanganate is expected to be reduced to the green manganate which later precipites as the brown manganese dioxide. The overall half reaction is [22]:

$$MnO_4^- + 2H_2O + 3e \text{ ---> } MnO_2 + 4OH^-; \quad E = +1.23 \text{ Volts}$$

Another possible precipitate during the oxidation step was jarosite $KFe_3(SO_4)_2(OH)_6$ [23] which is a basic mixed alkali sulfate. This potassium form of jarosite is the easiest to form as the standard free energy of formation of $KFe_3(SO_4)_2(OH)_6$ is the lowest one compared with the other alkali ion jarosites. Potassium appears to be selectively incorporated into jarosite. There is also a possible third type of precipitate which involve the double basic sulfates of manganese.

Among these oxidation products, soluble sulfates are easily removed through filtration, but the precipitates of MnO_2, and jarosite $KFe_3(SO_4)_2(OH)_6$,and possibly Mn-double sulfates were mixed with the cleaned coal particles and increased the ash content. For removing these precipitates from cleaned coal, single or multiple washing step has to be employed following oxidation step. Various of chemicals were investigated as washing reagents in this program. They included hot and cold water, sodium carbonate, complexing reagent, inorganic acids and organic acids. The use of each of these reagents is described in the following sections.

Washing with distilled water

After chemical oxidation, the coal was washed with water for one hour to split off the oxidized sulfur compounds still attached to the hydrocarbon matrix. During the washing step with distilled water, different washing temperatures were tested. Table II.8 and

TABLE II.8. Effect of temperature of washing water on washing step

Temperature of Washing °C	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic. Sulfur%
22	0.99	0.23	0.31	0.45
35	0.97	0.20	0.33	0.44
50	0.96	0.21	0.34	0.41
65	0.89	0.21	0.29	0.39
80	0.87	0.11	0.38	0.34

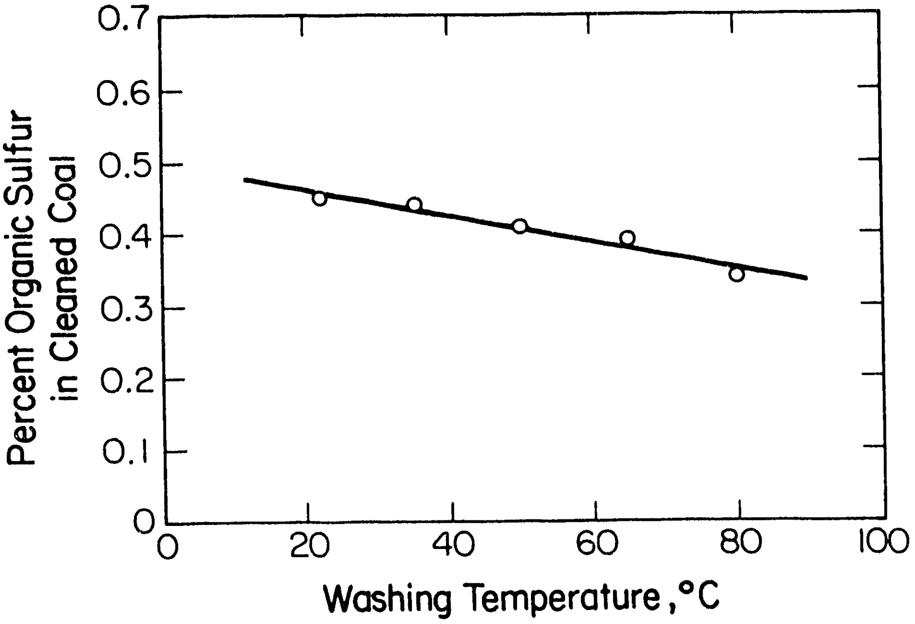


Figure II.5. Effect of temperature of washing water on organic sulfur removal from coal.

Figure II.5 show the effect of washing water temperature on the sulfur content of the coal. The figure shows that the organic sulfur decreased from 0.45% to 0.34%, while the temperature of the washing water was increased from 22°C (room temperature) to 80°C. Thus, the higher washing temperature enhanced organic sulfur removal, but at a low rate. Using cold water to wash oxidized coal is acceptable if a lower energy consumption is desired. However, distilled water was not effective in removing the insoluble precipitates.

Washing with Sodium Carbonate

The washing test with chemically oxidized coal using sodium carbonate was conducted at 80 °C. The results indicated that sodium carbonate was not effective for removing the precipited oxidation products. The sulfate sulfur of the washed coal was 0.3%, which was as high as that of the coal before washing step.

Removal of the Precipitates Using the Complexing Reagent EDTA

The precipitates of MnO_2 and jarosite might be removed using certain complexing reagents which could combine with manganese ions and other metal ions to form water soluble complexes. Table II.9 lists the total sulfur, ash content and Btu values of the cleaned coals which were oxidized by 6% and 10% wt $KMnO_4$ at 40% solids content from pre-cleaned coal sample #1. The oxidation step was followed by multiple washing steps with 5% wt of the complexing reagent EDTA. The results indicated that the ash content of the cleaned coal decreased from 14.3% to 6.9% and from 19.5% to 5.8% as well as Btu recovery reached to 95.7% and 97.0% after two and five step treatments respectively, while total sulfur decreased simultaneously. The manganese content, analyzed by Division of Geological Survey, ODNR, decreased from 7.30% (before washing step) to 0.99% (after washing step), i.e. 87% of the precipitated manganese was removed.

TABLE II.9. Effect of the number of washing steps using 5% EDTA complexing reagent solution on chemical cleaning at 40% solids content

Treatments	Total Sulfur%	Ash Content%	Btu/lb	Btu Recovery%
pre-cleaned Coal Feed	1.78	4.4	13256	100.0
A: Oxidation with 6% KMnO	1.56	14.3	11593	----
1st Washing	1.38	11.0	12026	92.3
2nd Washing*	1.31	6.9	12720	95.7
B: Oxidation with 10% $KMnO_4$	1.48	19.5	11020	----
1st Washing	1.40	16.2	11320	----
2nd Washing	1.35	13.2	11620	----
3rd Washing	1.30	10.6	12040	----
4th Washing	1.26	8.5	12650	----
5th Washing	1.21	5.6	12990	97.0

* characterized by ODNR, manganese content decreased from 7.30% to 0.99%

TABLE II.10. Total sulfur and ash contents of the cleaned coal which was oxidized by 10% $KMnO_4$ at 20% solids content and washed with 14% solution of EDTA complexing reagent

Sample	Total Sulfur,%	Ash Content,%
Pre-cleaned #2	1.98	5.4
Oxidized	1.40	24.8
washed	1.34	15.4
Pre-cleaned #3	2.26	5.8
oxidized	1.49	30.5
Washed	1.50	18.7

Table II.10 lists the results of the tests using 14% wt solution of EDTA complexing reagent during the washing step. The oxidation step was conducted with 10% $KMnO_4$ solution on pre-cleaned coal samples #2 and #3 at 20% solids content. The results indicated that 9-12% of ash was removed from oxidized coal by one step washing with 14% of the complexing reagent. Such high (14%) concentration of the complexing reagent was obtained by heating it in solution until all the solids were desolved. Further removal of precipitates from coal might be possible by repeating the washing step with EDTA, but it was thought that other reagents might be more effective.

Removal of oxidation products from coal with HCl

Washing tests using dilute hydrochloric acid to remove the precipitates of manganese dioxide and jarosite from the oxidized coal were conducted. Table II.11 shows that two different concentration of HCl were used as a washing reagent in the washing step which followed the oxidation step of pre-cleaned coal #2 with 10% $KMnO_4$ at 20% solid content. The results

TABLE II.11. Effect of the concentration of HCl on washing performance

Sample	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Ash Content%	Btu/lb
Pre-cleaned #2	1.98	0.92	0.002	1.06	5.40	13633
Washed with 7% HCl	1.22	0.20	0.10	0.92	12.40	11800
Washed with 14% HCl *	1.02	0.15	0.06	0.81	6.26	12542

* characterized by ODNR, the manganese content decreased from 13.3% to 0.76%.

indicated that the precipitates could successfully be removed by one-step washing with dilute (14%) HCl, and that the ash content approached that of the pre-cleaned coal feed. The Btu recovery reached 92%, and the manganese content decreased from 13.3% to 0.76%, i.e.,94% of the manganese in precipitate was removed.

Two step washings using 14% HCl were tested for the oxidized coals which were treated with different concentrations of $KMnO_4$ from pre-cleaned coal #2, the solids content was 20%. The results shown in Table II.12 indicated that dilute HCl is very effective washing reagent for removing the undesirable precipitates from the oxidized coals which were treated with different concentrations of $KMnO_4$. The ash content of the cleaned coal decreased to the lower value than that of pre-cleaned coal after one washing step. One washing step with 14% of HCl is

TABLE II.12. Effect of the concentration of $KMnO_4$ on chemical cleaning followed by two washing steps with 14% HCl at solids content of 20%

Treatment	Concentration of $KMnO_4$ %	Total Sulfur %	Ash Content %
Pre-cleaned #2		1.98	5.4
Oxidation	6	1.49	22.4
Washing 1		1.35	3.7
Washing 2		1.31	3.8
Oxidation	10	1.30	29.3
Washing 1		1.04	4.8
Washing 2		1.05	3.3
Oxidation	15	1.11	36.9
Washing 1		0.92	4.4
Washing 2		0.96	4.1

therefore considered to be enough. The only problem of using dilute HCl as a washing reagent is the possible increase of the chlorine content in the cleaned coal, which will be discussed later.

Removal of oxidation products from cleaned coal with dilute nitric acid

In order to avoid the possible chlorine adsorption on coal problem, Washing tests were conducted using dilute nitric acid as washing reagent. Table II.13 shows the effect of concentration of nitric acid on washing performance which followed an oxidation step of pre-cleaned coal #2 with 10% of $KMnO_4$. The solids content of coal slurry was 20%. The results shown in Table II.13 indicated that the ash content of the cleaned coal was higher with 8.8% HNO_3 as a washing reagent and decreased to 6.0% and 4.2% with 14% and 20% of HNO_3 respectively. However all forms of sulfur of three cleaned coal washed by HNO_3 were higher than that of the cleaned coal washed by HCl, and the sulfate sulfur was still higher than 0.1%. There probably was some insoluble sulfate

TABLE II.13. Effect of the concentration of nitric acid on chemical washing performance, after coal oxidation using 10% $KMnO_4$

Concentration of HNO_3 %wt	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Ash Content%	Btu/lb
(Pre-cleaned)	1.98	0.92	0.002	1.06	5.4	13633
8.8*	1.42	0.45	0.17	0.80	16.8	11853
14	1.19	0.23	0.15	0.81	6.0	12565
20	1.40	0.44	0.13	0.83	4.2	12583

* characterized by ODNR, the manganese content decreased from 13.3% to 7.65%.

complex still in the washed coal. The manganese content of the cleaned coal washed by 8.8% HNO_3 decreased from 13.3% to 7.65%, i.e., only 42% of the manganese was removed. Table II.14 lists washing tests with 14% of nitric acid for one hour and 16 hours. The total sulfur of the cleaned coal did not show a big difference, but the ash content of the cleaned coal was lower after 16 hrs. washing than that with one hour washing. However, 6% ash content of the washed coal which was obtained in one hour could be acceptable, as it was close to that of the pre-cleaned coal feed.

TABLE II.14. Effect of washing time with 14% of nitric acid on washing performance

Treatment	Washing Time, hr	Total Sulfur, %	Ash Content, %	Btu/lb
pre-cleaned #2		1.98	5.4	13633
Washing	1	1.19	6.0	12565
Washing	16	1.14	4.0	12570

Removal of oxidation products from cleaned coal with dilute sulfuric acid

The dilute sulfuric acid (14% wt). was tested as the washing reagent with the pre-cleaned coal #3. The oxidation step was

TABLE II.15. Washing performance with 14% of sulfuric acid

Treatment	Total Sulfur, %	Ash Content, %
Pre-cleaned #3	2.26	5.8
Oxidation	1.49	30.5
Washing 1	1.66	17.7
Washing 2	1.62	14.0

conducted at the same conditions used for HCl & HNO_3 tests, i.e. 10% $KMnO_4$ solution at 20% solids for one hour. The results listed in Table II.15 shows that ash content decreased from 30.5% to 17.7% after one step of washing with 14% of sulfuric acid, but only 3.7% ash was removed after the second washing step. The ash content of the washed coal was still high. It could therefore be considered that dilute sulfuric acid was not effective for removing insoluble oxidation products. In addition, using sulfuric acid as washing reagent might bring some sulfur to the cleaned coal and cause an increase in the total sulfur.

Investigation of washing step with organic acids

Several organic acids were investigated as washing reagents for removing the oxidation products. Dilute solutions (14% wt.) of ascorbic acid, oxalic acid and citric acid were tested. Table II.16 shows the results of the washing step with 14% ascorbic acid, oxalic acid and citric acid which followed one oxidation step of pre-cleaned coal #3 with 10% of $KMnO_4$ at 20% solids content. The results showed that ascorbic acid and citric acid successfully removed almost all of the added ash during one oxidation step, i.e., from 30.5% to 6.4% and 6.3% respectively, while oxalic acid was not effective. Table II.17 lists the results of the washing step with 14% ascorbic acid and citric acid which followed two oxidation steps. Ascorbic acid removed the added ash after two oxidation steps from 49.5% to 6.2%, citric acid removed the added ash from 49.4% to 17.3%. However, there was very little change in the total sulfur after oxidation and washing steps, and the pyritic sulfur of the washed coal increased from the oxidized coal. The reason might be due to the fact that both ascorbic acid and citric acid are reducing agents. Thus the sulfates produced by the permanganate oxidation of pyritic and organic sulfur, might have been reduced back to insoluble sulfides and/or elemental sulfur during the washing step by these organic acids, and pyritic sulfur increased according the analysis.

TABLE II.16. Washing performance with 14% organic acids following one oxidation step

Washing Reagent	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Ash Content%
(Pre-cleaned)	2.26	0.96	0.04	5.8
Oxidation with $KMnO_4$	1.49	0.43	0.37	30.5
Ascorbic Acid	1.95	0.78	0.013	6.4
Oxalic Acid	1.23	0.49	0.61	21.0
Citric Acid	1.90	0.77	0.013	6.3

TABLE II.17 One-step washing performance with organic acids following two oxidation steps

Washing reagent	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Ash Content%
(Pre-cleaned)	2.26	0.96	0.04	5.8
(Oxidation 1)	1.49	0.43	0.37	30.5
(Oxidation 2)	0.81	----	----	49.5
Ascorbic Acid	1.97	0.81	0.015	6.2
Citric Acid	1.64	0.68	0.13	17.3

Summary of Washing Test Results

Comparison of results of the washing studies using various washing reagents, showed that:

1) Distilled water and sodium carbonate were not effective for removing the oxidation precipitates even at higher

temperatures.

2) Organic acids such as ascorbic acid and citric acid successfully removed almost all of the added ash during oxidation step, i.e., the precipitates, but did not help reduce the total sulfur. It appeared that they reduced the sulfates produced by the permanganate oxidation of pyritic and organic sulfur back to insoluble sulfides and/or elemental sulfur during the washing step.

3) Nitric acid and sulfuric acid could remove part of the precipitation oxidation products formed during oxidation with permanganate after one washing step. They were not as effective as hydrochloric acid with the same concentration. The results showed that all forms of sulfur of the washed coal with dilute nitric acid and sulfuric acid were higher than that of the cleaned coal washed by HCl.

4) 5% solution of the EDTA complexing reagent successfully removed the precipitates of MnO_2 and jarosite but multi-washing steps were needed to achieve that, as only 3 to 4% ash removal was possible by each washing step.

5) Dilute hydrochloric acid was the most effective washing reagent for removing the oxidation products from the permanganate oxidized coal. Almost all the added ash during the oxidation step (i.e. the precipitates products) was removed by only one washing step with 14% of HCl. By combining an oxidation step with 10% $KMnO_4$ and a washing step with 14% HCl, all forms of sulfur can be successfully reduced with acceptable ash content and Btu recovery.

CHARACTERIZATION OF PRE-CLEANED COAL AND CHEMICALLY CLEANED COAL

This study aimed at characterizing certain properties and ash mineralogy of raw coal, pre-cleaned coal, chemically oxidized and chemically washed coal; and at determining the mineralogical characteristics of the materials precipitated during $KMnO_4$ treatment of the coal.

X-ray diffraction, automated image analysis, density determinations, microscopic methods and chemical analysis were used in this study. This characterization study was performed by The Ohio Geological survey [26], Ohio Department of Natural Resources (ODNR), Columbus, Ohio.

The coal products used in this characterization study were prepared and described as follows:

Product number 1 was raw coal from Pittsburgh No. 8 sample #2 from R & F Coal Company. Product number 2 was the pre-cleaned coal #2 which was pre-cleaned by heavy liquid separation using 1,1,1,-Trichloroethane with a specific gravity of 1.33. Most of the coarse pyrite and ash minerals were rejected by this process. Product number 3 was the oxidized coal which has been treated with 10% of $KMnO_4$ from the pre-cleaned coal #2 using a variable speed impeller mixer for one hour. The solids content of the coal slurry of test products 3a and 3b were 40%, and the solids content of test product 3c was 20%. Product number 4 was cleaned coal which has been oxidized as product 3a and 3b, and then washed through three steps with a 5% solution EDTA complexing reagent. Product number 5 was cleaned coal which has been oxidized as product 3c and then washed with 14% HCl (product 5a and 5b) and 7% HCl (product 5c). The washing process was conducted for one hour to remove precipitated materials. The sulfur, ash content and Btu as well as treatment of these products are listed in Table II.18.

TABLE II.18. Sulfur, ash content and Btu of the characterized test products

Product No.	Description of Coal Treatment	T.S. %	P.S. %	S.S. %	O.S. %	Ash %	Btu/lb
1	Raw Coal #2	3.86	2.80	0.02	1.04	15.8	12191
2	Pre-cleaned #2	1.98	0.92	0.002	1.06	5.4	13633
3a	10% $KMnO_4$ at 40% Solid Content	1.48	0.55	0.30	0.63	19.5	11020
3b	10% $KMnO_4$ at 40% Solid Content	1.48	0.55	0.30	0.63	19.5	11020
3c	10% $KMnO_4$ at 20% Solid Content	1.12	0.25	0.32	0.55	29.1	9040
4	10% $KMnO_4$ and 5% Complex	1.21	----	----	----	5.6	12990
5a	10% $KMnO_4$ and 14% HCl	1.02	0.15	0.06	0.81	5.4	12542
5b	10% $KMnO_4$ and 14% HCl	1.02	0.15	0.06	0.81	5.4	12542
5c	10% $KMnO_4$ and 7% HCl	1.22	0.20	0.10	0.92	12.4	11800

Matrix density: The densities of five ground subsamples of Pittsburgh No. 8 coal were determined using methods described by Nuhfer and others [24]. This method utilizes vacuum impregnation of the ground coal with kerosene of known specific gravity. By determining the weight in air and weight in kerosene of the coal sample, the matrix density of the coal can be found to within

manganese and chlorine content for selected products
0.02 g/cc. Densities of the raw coal and subsamples of the cleaned coal subjected to various treatments and washings are shown in Table II.19. The densities of the subsamples generally reflect the changes which occurred when the coal was pre-cleaned, oxidized and washed. The difference in density between the raw coal and the pre-cleaned coal was caused by the removal of ash, specially pyrite, when the coal was pre-cleaned. The high density of product number 3 which was oxidized by $KMnO_4$ from pre-cleaned coal was caused by the precipitation of a substance with higher density than coal. When the oxidized coal was washed with the complexing reagent (product number 4), the density reverted to that of pre-cleaned coal (product number 2), suggesting that most of the precipitated matter was washed out by the complexing reagent. The Chemical analysis of Mn content in products 3 and 4 support this inference.

Three separate subsamples (products 5a, 5b, 5c,) were oxidized with $KMnO_4$ and washed with dilute HCl. Density determinations were made on 5a and 5c and Mn analyses on 5b and 5c. Density and chemical data for 5c suggest that 7% HCl wash was incomplete. The same data for 5a and 5b indicated the 14% HCl wash was as effective as the complexing reagent wash.

Automated image analysis (AIA): Vitrinite reflectance and pyrite size parameters were determined using a Leitz Textural Analysis System. This instrument, commonly referred to as an automated image analysis (AIA) system is capable of reproducing vitrinite reflectance values in oil to within 0.02 percent reflectance.

TABLE II.19. Coal density vitrinite reflectance, and pyrite size data for the raw, cleaned, treated and washed coal samples.

Sample Number Description of Coal	1 Raw	2 1.3 Float	3a Treated $KMnO_4$	3b Treated $KMnO_4$	3c Treated $KMnO_4$	4 $KMnO_4$ and Complex	5a $KMnO_4$ and HCl	5b $KMnO_4$ and HCl	5c $KMnO_4$ and HCl
Coal Top Size (Mesh)	28	200	200	200	200	200	200	200	200
Average Pyrite Size (microns)	12	5	5	-	-	5	3	-	5
Coal Density (g/cc)	1.35	1.30	1.41	-	-	1.28	1.29		1.35
Vitrnite Reflectance	0.64	0.60	0.62			0.61	-		0.62
% Pyrite < 6 microns diameter	22	58	54			52	83		53
% Mn			7.28	7.33	13.25	0.99	-	0.76	2.26
% Cl		0.104						1.34	

In this study average reflectance, Rav was measured. These values were obtained by measuring randomly oriented vitrinite particles without palarized light. The arithmetic mean average reflectance Rav values are shown in Table II.19. Rav values may be converted to mean maximum values by the following formula: Rmax = 1.066 Rav [27].

Geometric mean pyrite size distributions were found by AIA for 5 of the coal subsamples (Table II.19). Pyrite sizes are based on the equivalent circular diameter (ECD) of the cross-sectional areas of the pyrite grains detected by the image analyser on the surface of the polished coal pellet. Geometric means of the pyrite size distributions were found by graphic methods [25].

Vitrinite reflectance values remained essentially unchanged for the samples studied. Hence, coal rank was not affected by the $KMnO_4$ treatment or various washes.

The Geometric mean size of the pyrite decreased significantly (as expected) when the coal was pre-cleaned. In the oxidized and washed samples the average pyrite size differences were insignificant. The percent pyrite less than 6 microns increased when the coal was cleaned but it was fairly constant in the oxidized and washed samples except for 5a. The reason for 5a having excessive amounts of fine pyrite is not clearly understood, although one possible explanation is that this particular sample was not a representative split of parent sample from which all subsamples were drawn.

Mineralogical Characterization

(A) X-ray diffraction: X-ray diffraction analysis of the low temperature ash (LTA) of products #1, 2, 3c, 4, and 5b were performed in an attempt to determine the mineralogical characteristics of the materials precipitated during $KMnO_4$ treatment of the coal, and to compare coal ash mineralogy of the 5 products.

X-ray diffraction analysis of the low temperature ash (LTA) of product number 1 (Figure II.6a.) indicated the presence of the following minerals: Quartz, Kaolinite, pyrite, illite, calcite and possibly goethite and feldspars, although the peaks for the latter two minerals were weak. Product number 2 (Figure II.6b) contained essentially the same mineral suite except for the absence of calcite.

The X-ray diffraction pattern of the LTA of product number 3c (Figure II.6c) had much lower intensities than those for products 1 and 2. Only kaolinite, quartz, and pyrite could be identified with certainty in product 3c (Figure II.6c). Apparently the Mn-rich, precipitated material was amorphous to x-ray diffraction, but caused matrix problems which reduced the mineral peak intensities. As the precipitated material was washed out (products 4 and 5b) mineral peak intensities again become strong (Figure II.6d and 6e).

<u>(B) Microscopic examination</u> Microscopic examination was performed on products 2, 3a, 4 and 5a, using reflected light. A micrograph of product number 2 (Figure II.7a) shows light gray coal macerals embedded in a darker gray epoxy binder. White grains were pyrite, and coal largest maceral in this photo was about 70 microns in length.

A micrograph of product number 3a (Figure II.7b) showed typical coal macerals in epoxy, and also two large aggregates of loosely held together coal (left and upper right sides of photo). The coal in these aggregates rarely exceeded 10 microns and the cementing material was very fine grain, ranging from submicron sizes to 2 or 3 microns. According to the reaction of sulfur in coal and $KMnO_4$ [22], and the high Mn and sulfate content in the oxidized coal (Table II.19), these large aggregates might be MnO_2 and insoluble sulfate complex such as jarosite. X-ray diffraction analysis (Figure II.6c) revealed no unusual mineralogy in product 3, that was because the Mn-rich and jarosite precipitated material were amorphous to X-ray diffraction.

A microscopic examination of product number 4 (Figure II.7c) revealed fewer aggregates than product number 3; it seems that manganese and sulfate precipitates were washed out through the washing steps with the complexing reagent.

From microscopic examination of product number 5b (Figure II.7d), no aggregates were observed, and most of the precipitated materials were washed out through the washing step with dilute HCl.

Summary: According to the results of this characterization of 5 different treated coal products, the following conclusions could be made:

a) From the vitrinite reflectance values, coal rank was not changed by the $KMnO_4$ treatment or the various washes.

b) Through the study of matrix density, X-ray diffraction analysis of the low temperature ashing, microscopic examination and chemical analysis of the manganese content, the precipitated materials formed during $KMnO_4$ treatment were successfully removed after washing with the EDTA complexing reagent or dilute hydrochloric acid.

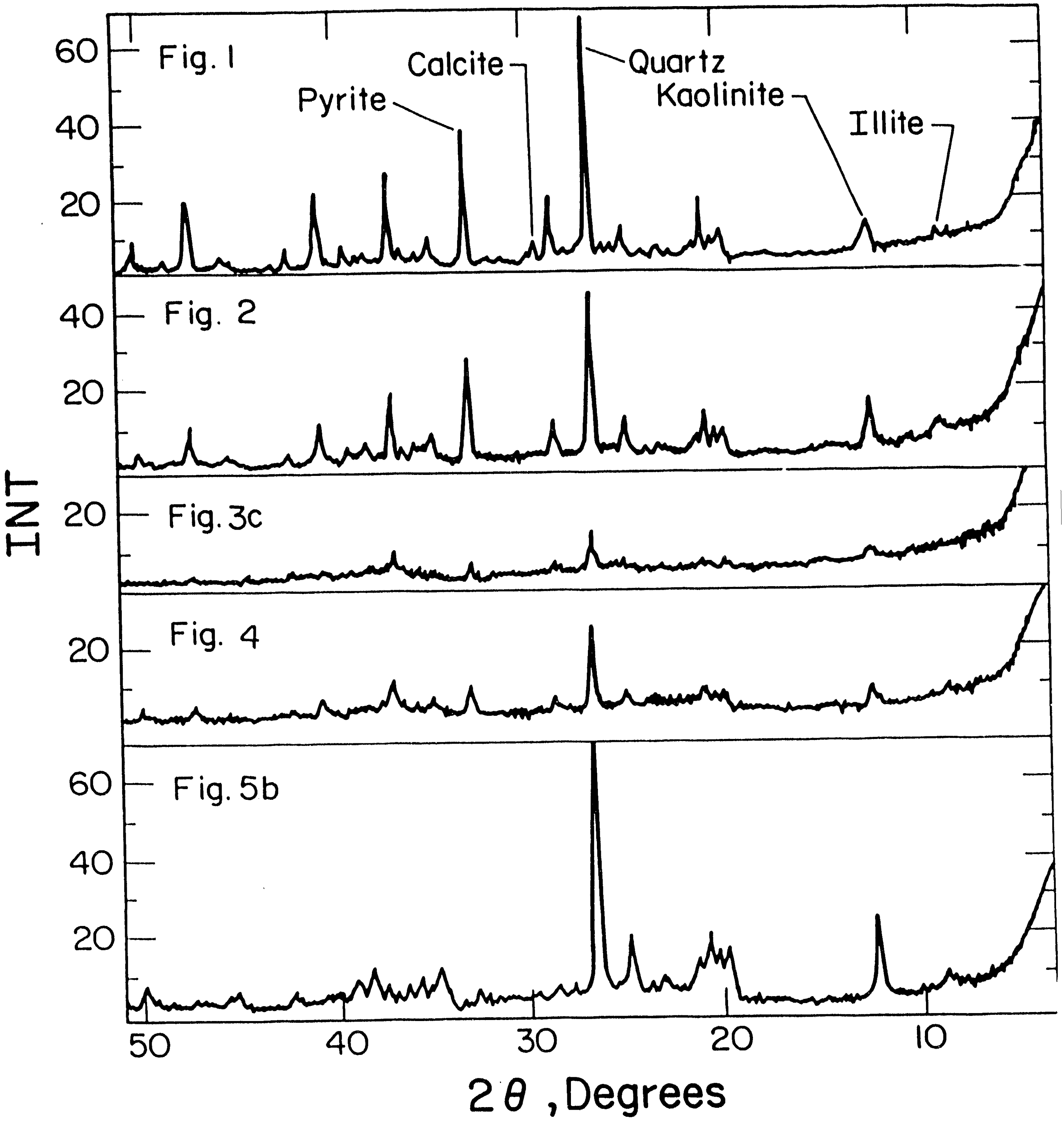


Figure II.6. X-ray diffraction patterns of the low temperature ash for products 1, 2, 3c, 4, and 5b.

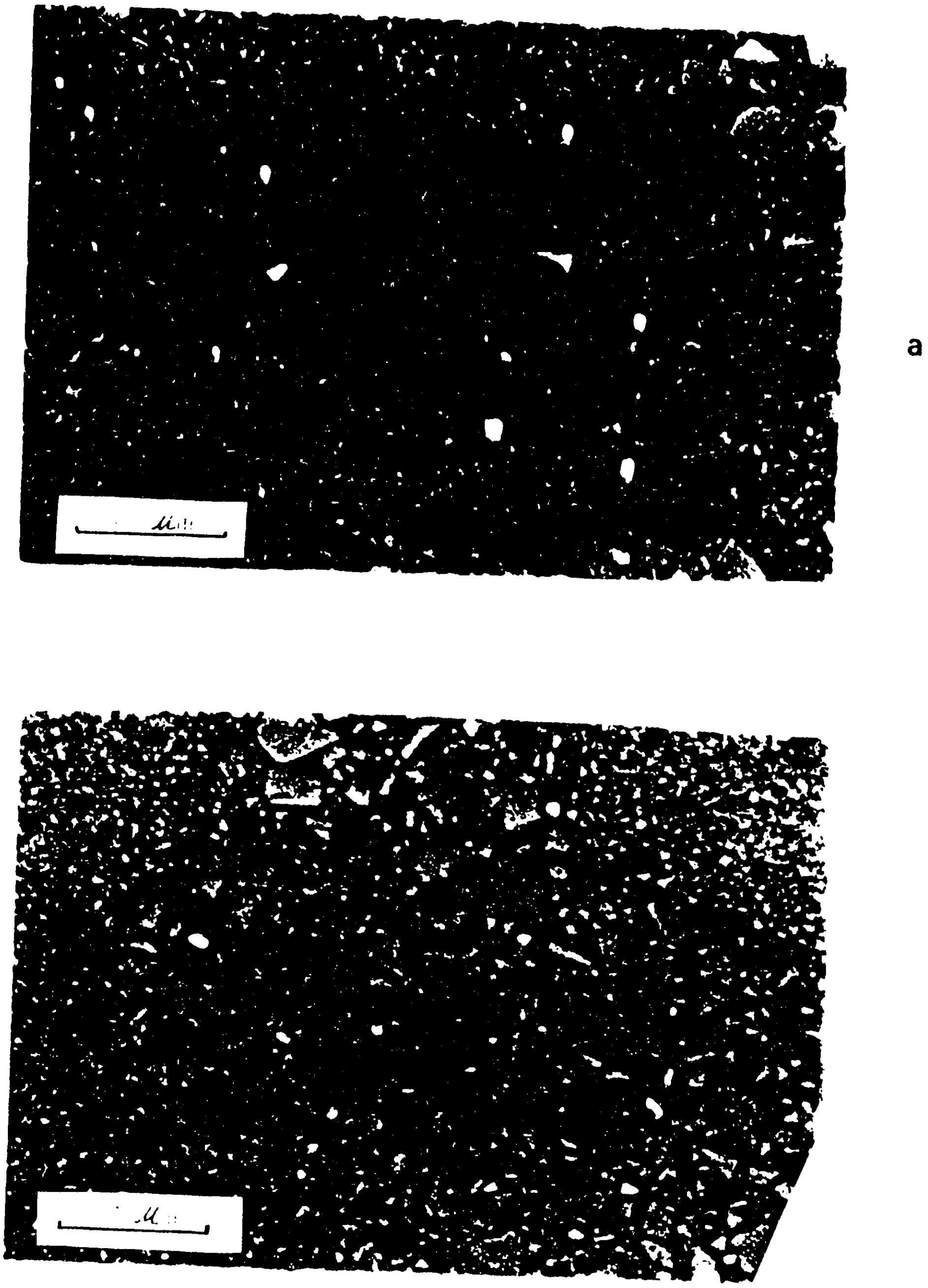


Figure II.7 (a,b). Photomicrographs of the polished surfa coal pellets made from products 2, 3a, 4, and 5a, under r light. Figure II.7a. Photomicrograph of product number 2, represents the float fraction of the pre-cleaned coal. Figure II.8b Photomicrograph[h of the oxidized coal with Large indistinct areas on left and upper right of photo loosely cemented coal aggregates of very fine coal parti

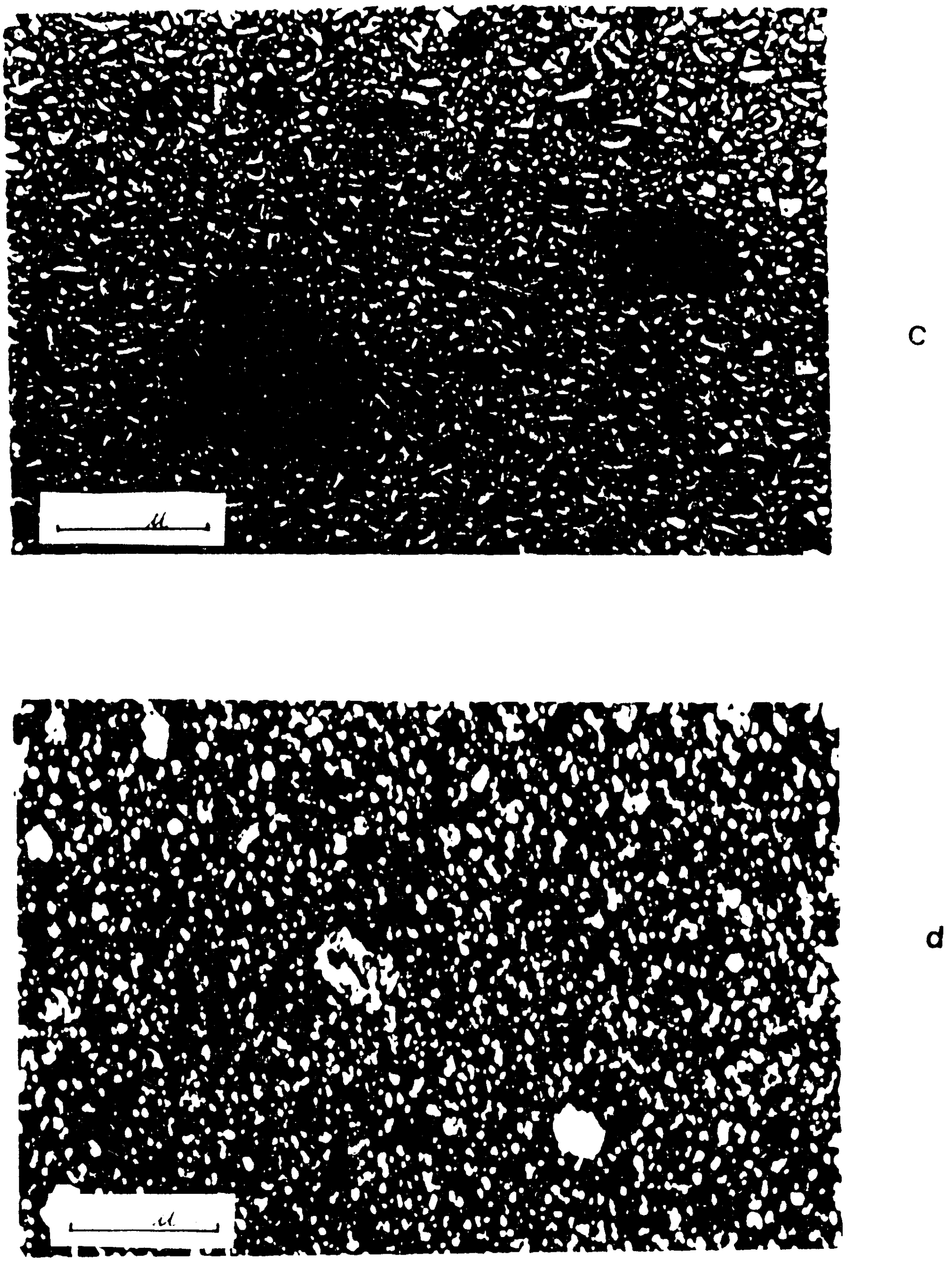


Figure II.7 (c,d). Photomicrographs of the polished surface of coal pellets made from products 2, 3a, 4, and 5a, under reflected light. Figure II.7c. Micrograph of fewer loosely cemented coal aggregates in product number 4. which was washed by complexing reagent. Figure II.7d. no aggregate observed in photomicrograph of product number 5a which was washed by 14% HCl.

MULTI-STEP CHEMICAL OXIDATION AND WASHING

For achieving higher levels of organic sulfur removal, the multi-step chemical oxidation and washing tests were conducted. Studies involved (a) the effect of number of oxidation and washing steps, (b) sequence of oxidation and washing steps, and (c) effect of ultrasonic dispersion during oxidation and washing steps on desulfurization.

Three-step treatment

Three successive steps of treatment with 10% $KMnO_4$ at 20% of solids content and a washing step using 14% HCl following each oxidation step were performed.

TABLE II.20. Three-step oxidation with each step was followed by a washing step

Step	T.S.%	P.S.%	S.S.%	O.S.%	Ash%	Btu	O.S.Removal%
o	1.98	0.92	0.002	1.06	5.4	13633	--
1	1.02	0.15	0.06	0.81	6.2	12542	24
2	0.86	----	----	----	16.7	-----	--
3	0.79	0.10	0.02	0.67	13.4	11201	37

The results shown in Table II.20 indicated that the organic sulfur decreased to 0.67%, and its removal reached 37%, while the total sulfur decreased to 0.8%, and pyritic sulfur removal reached 90% after three steps of treatment.

However, the sulfur removal in the second and the third steps was less than that of the first step, and the ash content was higher than the pre-cleaned coal after three steps of treatment. This could be due to the formation of tightly bound product layer to the coal surface or even inside the pores of the coal particles. Hence, it would be increasingly difficult for the oxidizing reagent (potassium permanganate) to penetrate the coal particles and oxidize the sulfur compounds. In order to remove this product layer and to achieve maximum organic sulfur and ash removal, mechanical or chemical means were employed.

Three steps of treatment employing ultrasonic dispersion

Ultrasonic dispersion was intermittently employed during oxidation and washing steps to break up the product layer.

TABLE II.21. Effect of ultrasonic dispersion on desulfurization and de-ashing using three-step chemical treatment

Step	T.S.%	P.S.%	S.S.%	O.S.%	Ash%	Btu/lb	O.S.Removal%
0	1.98	0.92	0.002	1.06	5.6	13633	--
1	1.02	0.15	0.06	0.81	4 5	12600	24
2	0.86	0.14	0.02	0.70	4.3	12616	34
3	0.76	0.12	0.02	0.62	5.0	11809	42

Each oxidation step was conducted for one hour using 10% $KMnO_4$ at 20% solids content, during which ultrasonic irradiation was intermittently employed for a total of 15 minutes. The oxidation was followed by filtration and a washing step with 14% HCl for one hour. After that the coal slurry was dispersed further in an ultrasonic bath for 20 minutes. The results listed in Table II.21. showed that 34% organic sulfur removal with 4.3% ash content were obtained after two steps of treatment. About 42% organic sulfur removal with 5.0% ash content was obtained after three steps of treatment. The oxidation products were successfully removed with the help of ultrasonic dispersion. Comparison of the results shown in Table II.20 and Table II.21, indicated that the ash content sharply decreased from 13.4% to

5.0% with the ultrasonic dispersion. It could be concluded therefore that ultrasonic dispersion was effective in removing the product layer which covered the coal particle. However, particle size analysis of the coal slurry indicated a sharp decrease in particle size, as shown in Figure II.8. For example, before ultrasonic dispersion, only 30% of the coal particles were below 10 microns, while after ultrasonic dispersion, about 70% of the coal particles were below 10 microns. In other words, the coal was "ground" finer by the ultrasonic treatment, which would produce more fresh surfaces for oxidation.

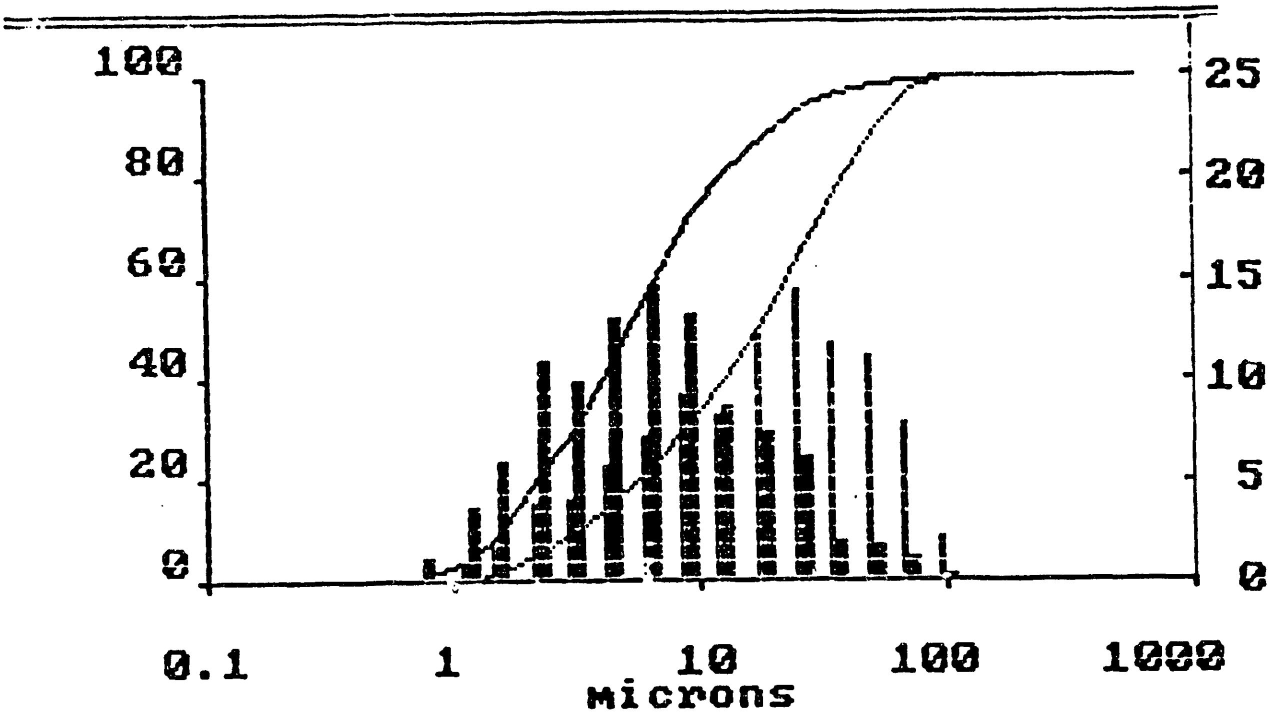


Figure II.8. The change of the particle size of coal after using ultrasonic dispersion

Sequence of multiple oxidation and washing steps

Several tests on the effect of the sequence of oxidation and washing using three step treatments were conducted.

Table II.22 shows the results of a test where three successive oxidation steps with 10% $KMnO_4$ were conducted first, and were then followed by two washing steps with 14% HCl. After each oxidation and washing step, the ultrasonic dispersion was employed for 15 minutes. From the table, it can be seen that the total sulfur of the cleaned coal decreased from about 2.0% to 0.74 %, i.e., 63% of the total sulfur was removed, while the ash content of the cleaned coal was 4.8%, which was lower than that of the pre-cleaned coal feed.

TABLE II.22. Total Sulfur and ash content after three oxidation steps and two washing steps

No. of washing steps	Total Sulfur%	Ash Content%
(Feed coal)	1.98	5.6
1	0.66	9.6
2	0.74	4.8

Two tests of three successive oxidation steps with 6% $KMnO_4$ at 10% solids content, followed by one washing step with 14% HCl were conducted. The results shown in Table II.23 indicated that 46% of organic sulfur removal was achieved, while the ash content of the cleaned coal was lower than that of the pre-cleaned coal feed. The results of the two tests were very close and reproducible.

Table II.24 lists the results of the same procedure conducted with 6% $KMnO_4$ but at 20% solids content. In this case, about 38% of organic sulfur was removed, and the ash content of the cleaned coal was 4.1%. Comparison of results in Table II.22-24 with those in Table II.21 indicated that the procedure of three successive oxidation steps combined with a washing step was a more viable option for removing about 40% of the organic sulfur and the oxidation products.

TABLE II.23. Three successive oxidation steps with 6% $KMnO_4$ and 10% solid content and followed by a washing step with 14% HCl

Test Treatment	T.S.%	P.S.%	S.S.%	O.S.%	O.S.Removal%	Ash
Pre- Cleaned #2	1.98	0.92	0.002	1.06	----	5.6
Oxidation 1	1.18	0.28	0.31	0.59	----	32.6
Oxidation 2	0.70	0.10	0.35	0.25	----	51.6
Oxidation 3	0.53	0.05	0.35	0.13	----	62.7
Washing	0.74	0.10	0.07	0.57	46.2	4.5
Oxidation 1	1.18	0.27	0.34	0.59	----	33.6
Oxidation 2	0.75	0.11	0.35	0.29	----	53.6
Oxidation 3	0.56	0.11	0.32	0.13	----	59.3
Washing	0.76	0.06	0.12	0.58	45.3	4.4

TABLE II.24. Three successive oxidation steps with 6% $KMnO_4$ and 20% solid content and followed by a washing step with 14% HCl

Treatment	T.S.%	P.S.%	S.S.%	O.S.%	O.S.removal%	Ash%
Oxidation 1	1.45	0.44	0.24	0.77	----	21.4
Oxidation 2	1.07	0.21	0.58	0.58	----	34.1
Oxidation 3	0.78	0.13	0.28	0.37	----	47.1
Washing	0.82	0.10	0.05	0.67	38.0	4.1

Two-step treatments

For achieving higher organic sulfur removal with minimum number of steps, two-step treatments were performed. Table II.25 lists the results of several tests which were conducted on pre-cleaned coal sample #2 with 10% $KMnO_4$ at 20% solids content. each oxidation step was followed by a washing step using 14% HCl.

TABLE II.25. Two stage treatments with each oxidation step was followed by a washing step using 14% HCl

Test	Treatment	Total Sulfur,%	Ash Content,%
	(Pre-cleaned)	1.98	5.4
1	Oxidation & Washing 1	0.98	4.1
	Oxidation & Washing 2	0.81	4.9
2	Oxidation & Washing 1	0.99	4.1
	Oxidation & Washing 2	0.88	4.9
3	Oxidation & Washing 1	0.99	4.1
	Oxidation & Washing 2	0.85	4.2

The results indicated that the average total sulfur of these three tests decreased from 1.98% to 0.85%, i.e., 57% of the total sulfur was removed after two oxidation and washing treatments. The average ash content of the cleaned coal was 4.7%.

In order to simplify the procedure, two successive oxidation steps with 10% $KMnO_4$ on coal slurries containing 20% solids, followed by one washing step with 14% HCl were conducted.
The results shown on Table II.26 showed that the total sulfur decreased from 1.98% to 0.88%. This represents more than 80% pyritic sulfur rejection and 34% organic sulfur removal. The ash content of the cleaned coal was 4.6%. Comparison of these results

with the results shown in Table II.24, showed that the total sulfur and the ash content of the cleaned coal were fairly close, but this procedure was more simple, economic and less time consuming.

TABLE II.26. Two successive oxidation steps with 10% $KMnO_4$ followed by a washing step with 14% HCl

Sample	T.S.%	P.S.%	S.S.%	O.S.%	Ash%	Btu/lb
Pre-cleaned #2	1.98	0.92	0.002	1.06	5.6	13633
Cleaned Coal	0.88	0.16	0.02	0.70	4.6	12326

Integration of two oxidation steps using H_2O_2 and $KMnO_4$

The test of integration of two oxidation steps using H_2O_2 for pyrite oxidation and $KMnO_4$ for organic sulfur oxidation was performed. The first oxidation step was conducted with 10% H_2O_2, the second step with 10% $KMnO_4$. The slurry was filtered and later washed with 14% HCl. Hydrogen peroxide was supposed to remove most of pyritic sulfur from the coal (Table II-3), so that only organic sulfur will be available for oxidation with $KMnO_4$. The results listed in Table II.27 indicate very little or no change in the

TABLE II.27. Integration of two oxidation steps using H_2O_2 and $KMnO_4$

Chemical	Total Sulfur,%	Ash Content,%
(pre-cleaned #2)	1.98	5.4
10% H_2O_2	1.13	4.1
10% $KMnO_4$	0.60	21.2
14% HCl	0.87	5.2

total sulfur content of the cleaned coal from the two step chemical cleaning using permanganate only. However, it seems that H_2O_2 removed 92% of the pyritic sulfur based on results and the previous assumption while $KMnO_4$ removed 0.26% organic sulfur.

Summary of multi-step treatments

The main findings from the investigations on multi-step chemical oxidation and washing, can be summarized as follows:

1) Up to 46% organic sulfur removal with three step chemical treatments,and 34% organic sulfur removal with two step chemical treatments can be achieved. The ash content of cleaned coal obtained by both treatments equal to or lower than that of pre-cleaned coal.

2) Ultrasonic dispersion employed during oxidation and washing steps could assist the removal of the oxidation precipitates.

3) Two different multi-step chemical cleaning schemes obtained very similar results. The scheme employing two or three successive oxidation steps followed by one washing step was simpler, and less time consuming than the scheme employing a washing step after each oxidation step.

ENVIRONMENTAL IMPACTS OF CHEMICAL CLEANING

This brief environmental impacts study was based on the following considerations: 1) Chemically cleaned coal is lower in ash and sulfur within EPA compliance limit of 0.6S/10^6 Btu, but washing with HCl may produce contamination of coal with Chlorine. 2) Disposal of waste from chemical cleaning process.

Chlorine determination and removal from chemically cleaned coal

We have discussed the integration of oxidation step and washing step which enable the removal of both organic and pyritic sulfur as well as the undesirable precipitates.

In the tests, it was found that dilute hydrochloric acid is a very effective washing reagent; it could remove more than 80% of the added ash during the oxidation step through only one step washing. However, the chlorine content in the cleaned coal could be increased. It was 1.34% in the cleaned coal as determined by ODNR.

For removing the excess chlorine from the cleaned coal, preliminary experiments and determination of the chlorine content of the cleaned coal were conducted. One step washing of the cleaned coal with hot water at 98-100°C at different solids content and with different leaching time were tested. Table II.29 lists the results of the leaching tests with hot water for 3 hours and with 5% and 10% solids content respectively. Table II.30 lists the results of the leaching tests with hot water and 5% solids content for 3 and 6 hours respectively. The results indicate that 40% of the chlorine could be removed by washing the coal with hot water. The chlorine content of the hot water-washed coal was slightly lower with lower solid content and longer washing time. However, the chlorine content of the washed coal was quite close regardless of the washing time or the solids content in the range of variation used in this study.

TABLE II.29. Effect of solids content on removal of chlorine with hot water washing

Sample	Solids Content %	Washing Time hr	Chlorine Content %
Before Leaching with Water			1.34
After Leaching with Water	5	3	0.75
After Leaching with Water	10	3	0.80

TABLE II.30. Effect of washing time on removal of chlorine with hot water washing

Sample	Washing Time hr	Solid Content %	Chlorine Content %
Before Leaching with Water			1.34
After Leaching with Water	3	5	0.75
After Leaching with Water	6	5	0.75

One alternative technique to avoid the problem of chlorine removal from cleaned coal would be to use dilute nitric acid solutions in the washing step instead of hydrochloric acid. Even though nitric acid is somewhat less effective than hydrochloric acid, the cost of chlorine removal might offset the benefit from the extra sulfur removal with HCl.

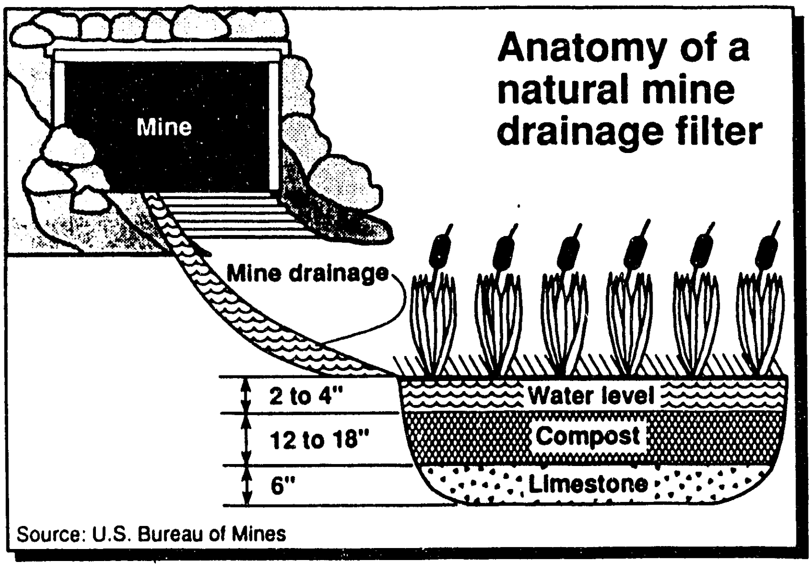
Discussion on Waste Disposals Methods

The produced waste in this permanganate oxidation might be composed of various sulfates, such as potassium sulfate, ferrous sulfate, ferric sulfate, manganese sulfate and other sulfate complexes, iron oxides, and excess acid in the depleted filtrate from the washing step.

In order to solve this problem to meet the environmental requirement, the following disposal systems are recommended:

1. Wetland Techniques: USBM & AEP reported recently [28], that this approach could successfully clean mine acid water. Figure II.9 shows the schematic of the wetland method.

Minerals in the waste water flowing through the ponds are filtered by the cattails. The plants absorb some of the soluble



Source: U.S. Bureau of Mines

Figure II.9. The wetland method

metals, but most is reduced to solid metallic or metal sulfide particles and are deposited in a layer at the bottom of the pond. The pond is lined with several inches of crushed limestone and nearly 2 feet of manure compost. Cattails are planted in clumps about 6 feet apart. Water leaving the ponds is free of discoloration. The AEP test showed that the iron content drops from 114 mg/liter to 3.4 mg/liter and even to 0.5 of a milligrams at the final testing point. The allowable content is 7 milligrams per liter. The level of manganese went from 2 mg/liter, which is considered acceptable, to 0.4 mg/l at the final testing point.

2. ProMac System: ProMac Systems are being used on mined-out land with lots of coal refuse in the soil [29]. This method could be considered for use in the disposal of pyrite from the physical cleaning plant to produce pre-cleaned coal feed for the chemical cleaning plant. It uses liquid spray and controlled-release pellets containing chemical bactericides to control acid formation. According the manufacturer [29] the chemicals wash away the greasy film on the bacteria that allows them to survive in the acid. The bacteria would then die and would not cause acid generation. At the same time, the chemicals feed other types of bacteria needed for healthy vegetation. The products are applied by spraying and scattering time-release pellets that will keep the bactericide working two to seven years. As reported, the product is 95% effective in controlling acid formation.

3. Waste Containment: The waste water could be stored in the mined area which would be well sealed by the impermeable layer.

The impermeable layer would be constructed with plastic sheets, compacted clays and cement.

4. Neutralization and precipitation: Lime could be used to precipitate various sulfates and react with excess acids.

5. Waste Utilization: These wastes might be utilized, for example, to produce fertilizer such as ammonium sulfate.

Systematic research including characterization of wastes, identification of types and amounts of species present, and investigation of possible environmental acceptable disposal methods of these wastes to select the effective method should be conducted before commercialization could proceed.

It can be concluded, therefore, that commercial utilization of the mild chemical cleaning process should not present any significant adverse environmental problem. The process appears to be environmentally sound.

PRELIMINARY ECONOMIC ASSESSMENT OF THE CHEMICAL CLEANING PROCESS

An economic assessment of the process based upon the batch experiments and preliminary process flowsheet was attempted. To establish reproducibility of the chemical cleaning process, three hundred grams of cleaned coal were prepared in several batches by combining one oxidation step with 10% $KMnO_4$ and one washing step with 14%. Table II.30 shows the results of these tests, which demonstrated that up to 50% total sulfur removal and 92% Btu recovery were achieved and that the process performance was largely reproducible.

TABLE II.30. The ash content and total sulfur of pre-cleaned coal and cleaned coal with one step oxidation and one step washing

Sample Number	Chemical Cleaned Coal Ash %	Chemical Cleaned Coal Total Sulfur %	Feed Coal Total Sulfur %	Total Sulfur Removal %
1	6.2	1.05	1.95	44.1
2	3.4	1.08	1.96	44.9
3	8.4	1.03	1.96	47.4
4	8.8	1.02	1.96	48.0
5	3.5	1.06	2.07	48.8
6	7.2	1.10	2.04	48.0
7	4.5	1.15	2.04	43.6
8	6.0	1.09	2.02	46.0
9	5.6	1.10	2.02	45.5
10	7.9	1.08	2.02	46.5

The preliminary process flowsheet proposed for commercial production is shown in Figure II.10. Counter current decantation leaching will be conducted in two stages of both oxidation and washing steps in this process. Continuous vacuum drum filter will be used for solid-liquid separation after both oxidation and washing steps. Potassium permanganate will be regenerated from

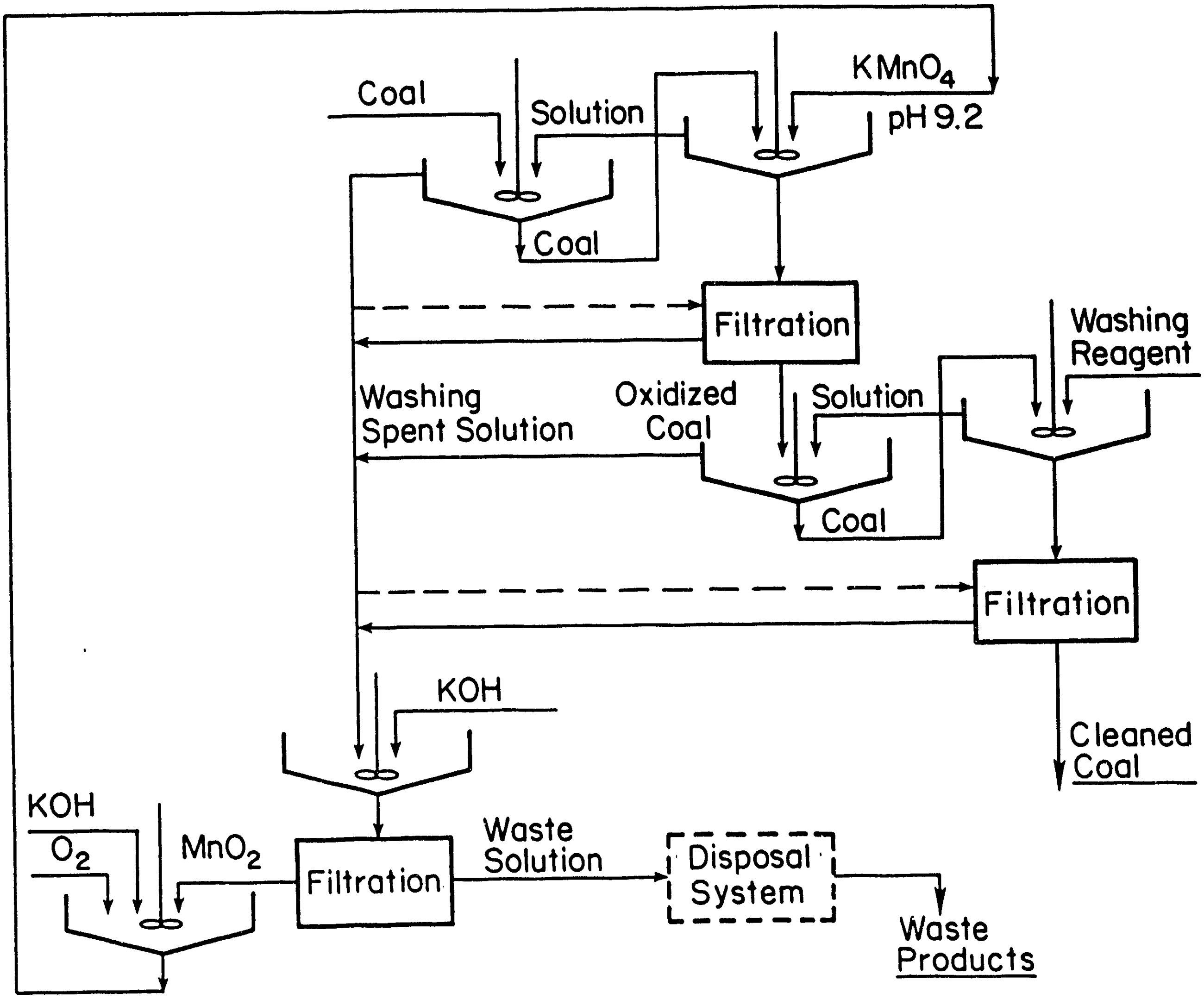


Figure II.10. Chemical cleaning circuit using counter current Decantation spent solution by reacting it with potassium hydroxide and oxygen. Possible methods for regeneration of $KMnO_4$ are outlined in the Appendix II 2.

Cost Estimation of Chemical Process for 1 Million Ton/yr Plant

It is not possible to obtain an accurate figure on the reagents (KOH, HCl) consumption/ton coal treated without running a pilot operation. For example it is not known at this time, how many oxidation cycles can be achieved with same $KMnO_4$ solution. In our conceptual flowsheet we indicated that the solution would be used only twice. But this could well be under utilization of the primary solution. The same argument could be said for HCl. At this time it can only be inferred that the reagents consumption could be estimated as follows. According to the results obtained in our Lab, total sulfur was removed from 2% to 1% through one step oxidation and washing step. Removing 1% sulfur from 1 ton physically cleaned coal, KOH consumption should be 12.5 kg and HCl consumption should be 11.25 kg. Assuming that the commercial price for KOH is \$0.50/kg and for HCl is \$0.07/kg, the cost of KOH and HCl would be \$6.25/ton coal and \$0.79/ton coal respectively. The total chemical cost would be \$7.04/ton coal. Other operating cost might be estimated at \$4/ton coal. Therefore, the total operating cost would be \$11.04/ton coal.

The capital cost of the chemical plant is estimated at \$4m based on the conceptual flowsheet and the knowledge supplied by the handbook [30]. Assuming that plant life is 20 years, the capital cost would be \$0.2/ton coal. Thus the total (capital+operating) cost would be \$11.24/ton coal.

As shown in Part III of this report, the total cost of the integrated physical and chemical cleaning processes including the cost of raw coal is estimated at $40.5/ton of clean coal. The price of the coal produced by this type of plant is expected to be around $45/ton or higher, which allows for about $4.5/ton gross profit. In addition to the profits, this mild chemical process would open up wide markets for Ohio coal, thus increasing the coal's marketability.

Thus if the mild chemical cleaning process is integrated with an existing conventional or advanced coal cleaning plant, production of compliance coal would be technically and economically feasible.

CONCLUSIONS AND RECOMMENDATIONS

This study presented a promising chemical coal cleaning approach for removing the organic and inorganic sulfur in Ohio coal which has a high commercial potential. From the previous results and discussion, the following conclusions can be made:

1. This permanganate oxidation technique is successful in removing organic and pyritic sulfur at ambient conditions.

2. Increasing the concentration of the oxidizing reagent ($KMnO_4$), the number of treatment steps, and the intensity of agitation, will enhance the organic sulfur removal.

3. Removal of the precipitation of manganese dioxide and jarosite from the chemically cleaned coal is now possible using a complexing reagent or dilute acid. The integrated approach of chemical oxidation and chemical washing can remove substantial amounts of both pyritic and organic sulfur from coal. More than 90% pyritic sulfur rejection and up to 50% organic sulfur removal has been achieved. The ash content of the cleaned coal is less than 5%, and Btu recovery is over 90%.

4. From the characterization study, coal rank was not changed by the $KMnO_4$ treatment or the various washes. The precipitated material formed during $KMnO_4$ treatment were proved to be removable after washing the EDTA complexing reagent or dilute hydrochloric acid through this study.

5. The combined approach of pre-cleaning the raw coal with gravity separation, followed by one oxidation step and one washing step, reduced the total sulfur from 3.5% to 0.9%, the

pyritic sulfur from 2.8% to 0.15%, and the organic sulfur from 1.0% to 0.7%. Thus a premium quality coal could be produced from a low-value high sulfur coal by this approach.

6. preliminary economic and environmental assessments showed that this process should be economically viable and environmentally sound.

ACKNOWLEDGEMENT

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PART III

COMBINED PHYSICAL AND CHEMICAL CLEANING AND DESULFURIZATION FOR OHIO COAL

III.1 COBMINED PHYSICAL AND CHEMICAL PROCESSES

In this study, integration of the combined physical and chemical desulfurization processes described in Parts I and II was considered. Two sets of experiments were performed using Pittsburgh no.8 seam coal with and without heavy liquid separation before selective flocculation.

In the first set, samples of coal were crushed and sieved. The -28 and +48 mesh portion of the coal was cleaned by heavy liquid separation using specific gravity of 1.6. The float was then collected and washed with acetone. The clean coal was dried and then ground in a ball mill to -500 mesh. This slurry was used in the selective flocculation process. The experimental conditions were: pH = 10.3, 200 ppm PAAX, 50 ppm FR-7A, single step froth flotation.

The concentrate from the physical cleaning was used as the feed for chemical cleaning process. Three experiments were performed to find the effect of three different chemical cleaning treatments. The first experiment was performed with one step washing with 10% potasium permanganate followed by one step washing with 14% hydrochloric acid. The second test was one step oxidation with 10% potasium permangnate followed by 14% nitric acid washing step. The third experiment was performed with two-step oxidation with 10% potasium permanganate followed by one washing step with 14% hydrochloric acid . Table III.1 shows the results of this set of experiments. The results indicate that after heavy liquid separation at 1.6 specific gravity, the total sulfur was reduced from 3.97% to 3.29% and the ash content decreased from 16.14% to 9.68%. During the selective flocculation process, 72% of the pyritic sulfur was rejected and over 40% rejection of the ash was achieved. The best results of the chemical cleaning process yielded a 33% rejection of organic sulfur. The pyritic sulfur after chemical cleaning was nearly zero.

In the second set of experiments, the heavy medium separation process was eliminated. The flocculation and subsequent chemical cleaning steps were performed in a similar fashion. The results of this experiments are shown in Table III.2. The results indicate that the total sulfur level essentially stayed close to the results obtained in the previous experiments. However, the ash content of the concentrate from the selective flocculation process was doubled. Clearly the two step oxidization with potasium permangnate resulted in the lowest sulfur content in both sets.

From these results, it can be concluded that:

1) the heavy liquid separation process can reduce the ash content of the final product by about 50%.

2) using the optimum operating parameters for selective flocculation, 1.9-2% total sulfur and 3.55% mineral matters contents can be obtained with 84% coal recovery.

Table III-1 Experimental results of the combination process for cleaning the Pittsburgh No. 8 coal after heavy liquid separation

	Btu/lb	Ash (%)	Tot.S (%)	Org.S (%)	Coal Rec. (%)
Feed	12,700	16.14	3.97	1.25	--
Feed after HLS	13,979	9.68	3.29	1.25	92.0
SF/FF	13,246	3.55	1.91	1.25	89.5
10% $KMnO_4$ +14% HCl	12,821	2.40	1.17	0.84	97.0
10% $KMnO_4$ +14% HNO_3	12,506	2.67	1.36	0.89	98.0
2-step with $KMnO_4$ + 14%HCl	12,012	3.83	0.91	0.76	96.0

* SF - selective flocculation, FF - froth flotation
HLS - heavy liquid separation

Table III-2 Experimental results of the combination process for cleaning the Pittsburgh No. 8 raw coal

	Btu/lb	Ash (%)	Tot.S (%)	Org.S (%)	Coal Rec. (%)
Feed	12,700	15.54	3.61	1.25	--
SF/FF	13,016	7.30	2.04	1.25	80.6
10% $KMnO_4$ +14% HCl	12,428	5.29	1.18	0.84	97.0
10% $KMnO_4$ +14% HNO_3	12,306	7.57	1.13	0.90	98.0
2-step with $KMnO_4$ + 14%HCl	11,484	7.63	1.01	0.74	96.0

3) the washing step with hydrochloric acid consistently gave lower level of ash and total sulfur in the chemical cleanig process.

4) the two step oxidization with potasium permanganate experiment resulted in super clean coal products.

Based on these conclusions the combined flow diagram of this process is illustrated in Figure III.1. The heavy medium process is required only if lower level of ash content (below 4%) is required. Note that the total sulfur of the final coal will be about 1% with about 12,500 Btu/lb heating value.

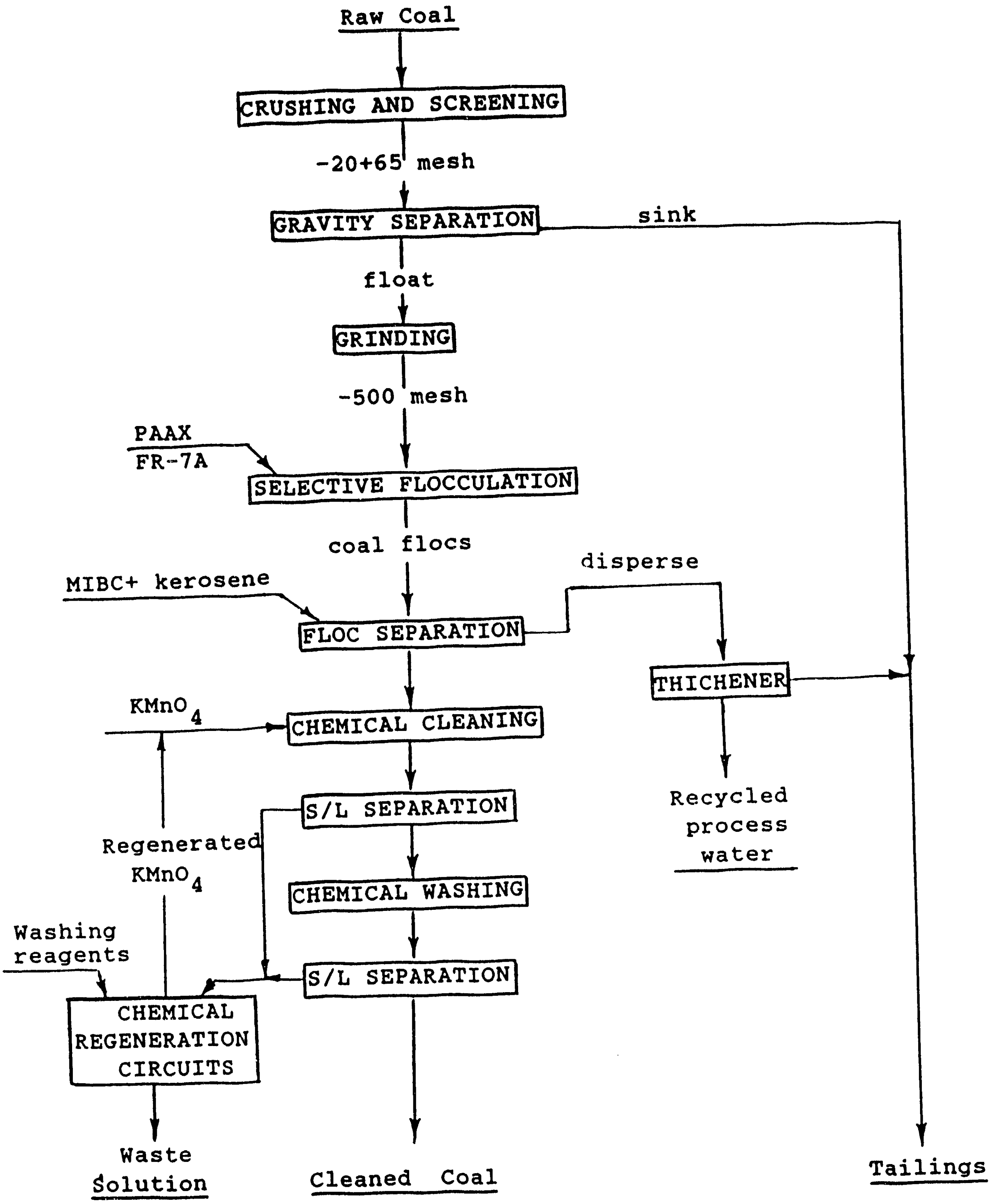

Figure III.1 Schematic Diagram for the Combined Physical and Chemical Process.

III.2 ECONOMICAL ASSESSMENT FOR THE COMBINED PROCESSES

In part I and part II, the technical and economical feasibilities of the individual processes were reported. It was shown that each process individually can be successful and profitable. However, in order to obtain the level of cleaning and desulfurization which can meet the EPA's SO_2 emission requirment for combustion usages of Ohio coal both processes must be integrated. In this section the econonmic feasibility of this process is considered. Of course, the capital cost and the operating cost for this integrated process will be higher than conventional cleaning plants, but cleaner coal with considerably lower levels of sulfur (less than 1%) and mineral matters (less than 4%) can be obtained. Consequently, the prices of the final clean coal will be significantly higher. Furthermore, there are indirect benefits for the final coal users in terms of reduction in their capital and operating costs and lower depreciation. On the other hand, the coal mining industry in the Ohio can potentially benefit from the improved marketability of Ohio Coals.

In order to evaluate the economical viability of the combined process, it was assumed that the chemical cleaning process would be after the selective flocculation process. Although there might be some integration of the auxiliary and waste treatment operations, it was assumed that essentially both processes are independent of each other. In other words, they can be operated in parallel although in this scheme they are in series.

From the section I.5 (i.e; the economic assessment for selective flocculation process) the total capital and operating costs was calculated to be $ 15.8 / ton of clean coal. Similarly, for the chemical cleaning process, the total cost excluding the comminution costs, was $ 11.4 / ton of clean coal. Therefore, the total cost of the combined process is approximately $ 27 / ton of clean coal. This total operating and capital cost does not include the cost of raw coal at 4.% total sulfur and 16% mineral matters contents.

The total cost presented here is based on the tonage of the clean coal product. As was reported earlier (see Table I.14), production of one ton of clean coal by selective flocculation required 1.27 tons of raw coal. Similarly, to produce one ton of chemically clean coal, 1.04 ton of raw coal was required. Therefore, in the combined process approximately 1.33 ton of raw coal is needed for every ton of clean coal (1.27 x 1.04).

The summary of the economical assessments of the combined process are presented in Table III.3. From these results, it is evident that the combined process is still profitable despite the considerably higher capital and operating costs. Note that the price of the final clean coal product (less than 0.8% total sulfur, 4% ash, with 12,500. Btu/lb) is estimated conservatively at $ 45 / ton.

Table III.3 Summary of the Economical Assessment of the Combined Physical and Chemical Processes for Cleaning and Desulfurization of Ohio Coal.

Cleaning Process	Flotation	S. Flocculation/ Flotation	Combined Process
Coal Composition	2.6% T.S 16% ash	1.8% T.S. 7% ash	0.8% T.S. 4% ash
Total cost	$13.8/ton	$15.8/ton	$27.2/ton
Price of raw coal required/ton clean coal	$12.2/ton	$12.7/ton	$13.3/ton
Final cost/ton of clean coal	$26/ton	$28.5/ton	$40.5/ton
Market Price	$30/ton	$35/ton	$45/ton
Net Profit	$4/ton	$6.5/ton	$4.5/ton

III.3 CONCLUSIONS AND RECOMMENDATIONS

From the results obtained form the combined physical and chemical cleaning processes, following conclusions can be made:

1) the integration of physical and chemical desulfurization processes are technically feasible. The final coal product has less than 1% total sulfur and about 4% mineral matters contents with 12,500. Btu/lb heating value. The overall coal recovery of the process is approximately 81%,

2) one step chemical cleaning is sufficient for the production of the clean coal product if the coal is processed first by the physical process.

3) the economical assessment of the combined process indicated of a net profit of $ 4.5 / ton of clean coal.

It is recommended that:

1) further research should be devoted to implementation of the suggested combined process in a pilot scale operation.

2) further study should be conducted on the possible means of recycling the chemical reagents and the waste treatment processes.

APPENDICES

Table A-I.1
Feed: Synthetic slurry (Pittshurgh No.8 precleaned coal + pyrite + shale) + SMP + NaOH
Grinding Time: Attrition for 25 minutes

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%) Ash	Coal	Tot. S
1) 2-step SED, pH 7.5, FR-7A (10 + 5ppm)						
Conc.	51.09	10.17	4.26	23.14	59.18	46.80
Disp. 1	33.65	40.89	5.03	61.29	25.65	36.40
Disp. 2	15.26	22.91	5.15	15.57	15.17	16.90
Feed	100.00	22.45	4.65	100.00	100.00	100.00
2) 2-step SED, pH 7.5, FR-7A (10 + 5ppm)						
Conc.	52.62	12.56	4.51	28.69	59.78	50.49
Disp. 1	35.01	38.24	4.76	58.15	28.09	35.46
Disp. 2	12.37	24.50	5.30	13.16	12.13	13.95
Feed	100.00	23.03	4.70	100.00	100.00	100.00
3) SED + FF, pH 7.5, FR-7A (10 + 5ppm)						
Conc.	10.58	12.14	4.33	5.38	12.21	8.97
Disp. 1	52.56	32.14	5.37	70.75	46.86	55.25
Disp. 2	36.86	15.46	4.96	23.87	40.93	35.78
Feed	100.00	23.87	5.11	100.00	100.00	100.00
4) FF, pH 7.5, FR-7A (10 ppm), 0.2 ml MIBC						
Conc.	73.91	10.64	3.98	32.62	87.02	59.90
Disp. 1	26.09	62.23	7.55	67.38	12.98	40.10
Feed	100.00	24.10	4.91	100.00	100.00	100.00
5) FF, pH 7.5, FR-7A (10 ppm), 2.0-5.0 ml MIBC						
Conc.	33.21	13.24	4.55	10.32	50.24	31.62
Disp. 1	41.53	77.97	5.17	75.90	15.96	44.92
Disp. 2	25.26	23.28	4.44	13.78	33.80	23.46
Feed	100.00	42.66	4.78	100.00	100.00	100.00
6) 2 SED, pH 7.5, FR-7 (10+5 ppm)						
Conc.	35.56	10.73	4.25	16.42	41.35	31.42
Disp. 1	42.86	37.00	5.29	68.28	35.17	47.14
Disp. 2	21.58	16.47	4.79	15.30	23.48	21.44
Feed	100.00	23.23	4.81	100.00	100.00	100.00
7) 2 SED, pH 7.5, FR-7 (10+10 ppm)						
Conc.	76.10	11.27	3.96	35.03	89.41	61.20
Disp.	23.90	66.52	7.99	64.97	10.59	38.80
Feed	100.00	24.47	4.92	100.00	100.00	100.00
8) FF, pH 7.5						
Conc.	54.35	8.79	5.14	21.54	63.70	60.36
Disp. 1	20.17	71.04	3.55	64.60	7.51	15.39
Disp. 2	25.48	12.07	4.41	13.86	28.79	24.25
Feed	100.00	22.18	4.63	100.00	100.00	100.00

Table A- I.1 (Continued)

Product	Weight	Ash	Total S	Total Distribution (%)		
	(%)	(%)	(%)	Ash	Coal	Tot. S
9) SED, pH 10.5, F1029-J (7 + 10 ppm)						
Conc.	48.09	10.83	5.30	22.91	55.50	54.25
Disp. 1	19.82	69.28	3.67	60.41	7.88	15.48
Disp. 2	32.09	11.83	4.43	16.70	36.62	30.27
Feed	100.00	22.73	4.70	100.00	100.00	100.00
10) SED, pH 10.5, F1029-J (10 ppm)						
Conc.	75.78	10.03	4.24	32.62	88.88	65.84
Disp.	24.22	64.79	6.88	67.38	11.12	34.16
Feed	100.00	23.29	4.88	100.00	100.00	100.00
11) SED, pH 10.5, F1029-J (10 ppm), PAAX (350 ppm)						
Conc.	54.97	12.83	5.35	33.98	60.47	56.99
Disp.	45.03	30.43	4.93	66.02	39.53	43.01
Feed	100.00	20.75	5.16	100.00	100.00	100.00
12) SED + FF, pH 10.5, F1029-J (10 + 0 ppm)						
Conc.	69.37	7.00	4.91	20.67	84.31	70.65
Disp. 1	18.04	70.44	3.33	54.10	6.98	12.45
Disp. 2	12.59	47.05	6.47	25.23	8.71	16.90
Feed	100.00	23.48	4.82	100.00	100.00	100.00
13) 2-SED, pH 10, F1029-D (5 + 10 ppm)						
Conc.	38.77	19.76	6.26	34.37	40.03	47.35
Disp. 1	13.01	53.97	1.91	31.48	7.71	4.86
Disp. 2	48.22	15.79	5.08	34.15	52.26	47.79
Feed	100.00	22.30	5.13	100.00	100.00	100.00
14) 2-SED, pH 10.5/7.5, F1029-D (5 + 10 ppm), FR-7A (0 + 10 ppm)						
Conc.	63.07	17.36	6.03	45.92	68.43	76.76
Disp. 1	22.64	45.72	2.50	43.43	16.13	11.42
Disp. 2	14.30	17.76	4.10	10.65	15.44	11.82
Feed	100.00	23.84	4.95	100.00	100.00	100.00
15) FF, pH 10.5, F1029-D (10 ppm)						
Conc.	74.62	13.04	4.93	41.82	84.57	75.08
Disp.	25.38	53.36	4.83	58.18	15.43	25.02
Feed	100.00	23.28	4.90	100.00	100.00	100.00

Table A-I.2

Feed: Synthetic slurry (Pittshurgh No.8 precleaned coal + pyrite
+ shale) + SMP + NaOH
Grinding Time: Ball mill for 8 hours

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%)		
				Ash	Coal	Tot. S
1) SED + FF, pH 7.5/10.0, FR-7 (10 + 10 ppm), PAAX (0 +100 ppm)						
Conc.	61.09	8.15	2.60	17.29	78.81	42.13
Disp. 1	28.46	62.62	5.00	61.88	14.94	37.75
Disp. 2	10.45	57.37	7.27	20.82	6.26	20.12
Feed	100.00	28.80	3.77	100.00	100.00	100.00
2) SED + FF, pH 7.5, FR-7 (10 + 10 ppm)						
Conc.	64.03	7.62	2.49	16.90	83.15	43.06
Disp. 1	26.19	65.94	5.03	59.84	12.54	35.60
Disp. 2	9.78	68.61	8.11	23.26	4.31	21.34
Feed	100.00	28.86	3.70	100.00	100.00	100.00
3) SED + FF, pH 7.5, FR-7A (10 + 10 ppm), PAAX (130 ppm)						
Conc.	62.34	6.86	2.30	15.36	80.47	39.15
Disp. 1	23.70	64.16	4.87	54.63	11.76	31.52
Disp. 2	13.96	59.83	7.69	30.01	7.77	29.33
Feed	100.00	27.83	3.66	100.00	100.00	100.00
4) SED + FF, pH 7.5, FR-7 (10 + 10 ppm)						
Conc.	60.55	7.56	2.41	15.68	79.05	38.83
Disp. 1	27.62	62.65	4.86	59.28	14.57	35.80
Disp. 2	11.82	61.80	8.03	25.02	6.38	25.31
Feed	100.00	29.19	3.75	100.00	100.00	100.00
5) SED + FF, pH 7.5/10.5, F1029-J (5 + 2 ppm), PAAX (0 + 100 ppm)						
Conc.	68.18	15.15	4.07	34.38	82.69	74.00
Disp. 1	10.98	82.21	1.44	30.05	2.79	4.22
Disp. 2	20.84	51.30	3.94	35.57	14.52	21.78
Feed	100.00	30.04	3.75	100.00	100.00	100.00
6) SED + FF, pH 7.5/10.0, F1029-J (5 + 2 ppm)						
Conc.	70.43	10.50	4.15	26.58	87.34	76.90
Disp. 1	14.96	76.68	1.47	41.22	4.83	5.79
Disp. 2	14.61	61.30	4.51	32.20	7.82	17.31
Feed	100.00	27.83	3.80	100.00	100.00	100.00
7) SED + FF, pH 10.0, F-1029-J (5 + 2 ppm), PAAX (0 +100 ppm)						
Conc.	72.44	11.12	4.17	28.08	90.28	78.26
Disp. 1	14.58	83.65	1.52	42.53	3.34	5.74
Disp. 2	12.98	64.94	4.73	29.39	6.38	15.91
Feed	100.00	28.68	3.86	100.00	100.00	100.00

Table A-I.2 (Continued)

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%) Ash	Coal	Tot. S
8) FF, pH 10.5, PAAX (100ppm)						
Conc.	68.29	9.64	2.30	22.61	87.07	43.39
Disp.	31.71	71.10	6.47	77.39	12.93	56.68
Feed	100.00	29.13	3.62	100.00	100.00	100.00
9) FF, pH 10, PAAX (130ppm)						
Conc.	70.27	13.06	2.65	32.09	86.69	49.53
Disp.	29.73	68.46	6.40	68.92	13.31	50.47
Feed	100.00	29.53	3.76	100.00	100.00	100.00

Table A-I.3

Feed: Synthetic slurry (Pittshurgh No.8 precleaned coal + pyrite + shale) + SMP + NaOH

Grinding Time: Ball mill for 18 hours

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%) Ash	Coal	Tot. S
1) SED + FF, pH 7.5, FR-7A (10 + 20 ppm)						
Conc.	35.56	5.52	2.61	10.46	41.33	27.32
Disp. 1	59.46	23.29	3.07	73.69	56.17	53.69
Disp. 2	4.98	59.80	12.90	15.85	2.47	18.89
Feed	100.00	18.79	3.40	100.00	100.00	100.00
2) SED + FF, pH 7.5, FR-7A (10 + 20 ppm)						
Conc.	34.54	5.52	2.41	10.11	40.20	24.94
Disp. 1	59.30	23.87	3.21	75.14	55.62	56.99
Disp. 2	6.16	44.99	9.77	14.75	4.18	18.07
Feed	100.00	18.84	3.34	100.00	100.00	100.00
3) SED + FF, pH 7.5/11.0, FR-7 (30 + 50 ppm), PAAX (200 ppm)						
Conc.	41.85	5.31	2.20	13.10	47.73	27.65
Disp. 1	49.97	23.67	3.30	69.67	45.94	49.52
Disp. 2	8.18	35.78	9.25	17.24	6.33	22.73
Feed	100.00	16.98	3.33	100.00	100.00	100.00
4) SED + FF, pH 7.5/11.0, FR-7 (30 + 50 ppm), PAAX (200 ppm)						
Conc.	41.30	5.82	2.29	12.71	47.97	28.02
Disp. 1	50.58	27.29	3.50	72.96	45.36	52.38
Disp. 2	8.12	33.35	8.16	14.33	6.67	19.60
Feed	100.00	18.92	3.38	100.00	100.00	100.00

Table A-1.3 (Continued)

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%)		
				Ash	Coal	Tot. S
5) 2-FF, pH 11.0, FR-7A (5 + 5 ppm), PAAX (200 + 100 ppm)						
Conc.	48.24	4.44	2.02	8.17	62.46	27.37
Disp. 1	43.48	51.31	4.93	85.18	28.68	60.21
Disp. 2	8.28	21.07	5.35	6.65	8.86	12.42
Feed	100.00	26.19	3.56	100.00	100.00	100.00
6) FF, pH 11, PAAX (100 ppm)						
Conc.	58.16	6.77	2.23	21.22	66.58	39.30
Disp.	41.84	34.95	4.79	78.78	33.42	60.70
Feed	100.00	18.56	3.30	100.00	100.00	100.00
7) FF, pH 11, PAAX (200 ppm)						
Conc.	49.31	5.82	2.07	15.27	57.20	29.16
Disp.	50.69	31.44	4.89	84.73	42.80	70.84
Feed	100.00	18.81	3.50	100.00	100.00	100.00
8) FF, pH 10, PAAX (130 ppm)						
Conc.	63.86	6.25	2.12	21.15	73.79	39.36
Disp.	36.14	41.16	5.77	78.85	26.21	60.64
Feed	100.00	18.87	3.44	100.00	100.00	100.00
9) FF, pH 10, PAAX (400 ppm)						
Conc.	50.70	6.78	2.25	18.08	58.36	30.75
Disp.	49.30	31.61	5.21	81.92	41.64	69.25
Feed	100.00	19.02	3.71	100.00	100.00	100.00
10) 2-SED + FF, pH 11.0, FR-7A (40+10+0ppm), PAAX (200+100+100ppm)						
Conc.	53.77	5.12	2.60	14.80	62.67	38.94
Disp. 1	30.12	37.26	4.01	60.38	23.21	33.64
Disp. 2	14.54	25.44	5.02	19.90	13.32	20.34
Disp. 3	1.57	58.47	16.20	4.92	0.80	7.08
Feed	100.00	18.59	3.59	100.00	100.00	100.00
11) FF, pH 11.0, FR-7A (10 ppm), PAAX (200 ppm)						
Conc.	47.69	6.89	2.40	10.87	63.64	23.82
Disp.	52.31	51.49	6.71	89.13	36.36	76.18
Feed	100.00	30.22	4.61	100.00	100.00	100.00
12) FF, pH 11.0, FR-7A (10 ppm), PAAX (200 ppm)						
Conc.	75.55	7.97	2.05	30.62	86.55	47.20
Disp.	24.45	55.81	7.09	69.38	13.45	52.80
Feed	100.00	19.67	3.28	100.00	100.00	100.00
13) FF, pH 11.0, FR-7A (10 ppm), PAAX (200 ppm)						
Conc.	74.61	7.16	1.87	26.80	86.51	43.28
Disp.	25.39	57.47	7.20	73.20	13.49	56.72
Feed	100.00	19.93	3.22	100.00	100.00	100.00

Table A-1.4
Feed: Pittsburgh No. 8 coal after heavy liguid separation
with 1.6 sp.gr. liquid
Grinding Time: Ball mill for 18 hours

Product	Weight	Ash	Total S	Total Distribution (%)		
	(%)	(%)	(%)	Ash	Coal	Tot. S
1) SED + FF, pH 10.3, FR-7A (50 + 50 ppm), PAAX (50 + 50 ppm)						
Conc.	51.03	3.70	2.39	28.40	52.64	43.67
Disp. 1	42.14	6.57	2.10	41.72	42.17	31.72
Disp. 2	6.83	29.05	10.10	29.88	5.19	24.71
Feed	100.00	6.64	2.79	100.00	100.00	100.00
2) SED + FF, pH 10.3, FR-7A (50 + 50 ppm), PAAX (100 + 100 ppm)						
Conc.	55.37	3.55	2.23	26.82	57.63	42.18
Disp. 1	39.46	8.45	2.62	45.56	38.98	35.39
Disp. 2	5.17	39.14	12.70	27.62	3.39	22.45
Feed	100.00	7.32	2.93	100.00	100.00	100.00
3) SED + FF, pH 10.3, FR-7A (50 + 50 ppm), PAAX (150 + 150 ppm)						
Conc.	56.06	4.74	2.58	38.09	57.41	46.36
Disp. 1	36.58	5.22	2.10	27.37	37.27	24.68
Disp. 2	7.36	32.77	12.25	34.54	5.32	28.96
Feed	100.00	6.98	3.12	100.00	100.00	100.00
4) SED + FF, pH 10.3, FR-7A (50 + 50 ppm), PAAX (200 + 200 ppm)						
Conc.	55.25	3.72	2.32	21.26	58.89	42.44
Disp. 1	27.72	9.17	2.68	26.24	27.88	24.68
Disp. 2	17.03	29.84	5.83	52.50	13.23	32.88
Feed	100.00	9.68	3.02	100.00	100.00	100.00
5) FF, pH 10.3, FR-7A (50 ppm), PAAX (100 ppm)						
Conc.	82.71	3.89	2.00	43.56	85.83	50.27
Disp.	17.29	24.09	2.74	56.44	14.17	49.73
Feed	100.00	7.38	3,29	100.00	100.00	100.00
6) FF, pH 10.3, FR-7A (50 ppm), PAAX (200 ppm)						
Conc.	86.41	3.55	1.91	44.90	89.45	50.16
Disp.	13.59	27.66	9.99	55.10	10.55	49.84
Feed	100.00	6.82	3.01	100.00	100.00	100.00
7) FF, pH 10.3, FR-7A (50 ppm), PAAX (300 ppm)						
Conc.	82.07	4.20	2.04	46.30	84.95	50.88
Disp.	17.93	22.33	8.52	53.70	15.05	49.12
Feed	100.00	7.45	3.29	100.00	100.00	100.00
8) FF, pH 10.3, FR-7A (50 ppm), PAAX (400 ppm)						
Conc.	77.86	3.96	2.23	42.69	80.60	52.77
Disp.	22.14	18.70	6.66	57.26	19.40	47.23
Feed	100.00	7.23	3.29	100.00	100.00	100.00

Table A-1.4 (Continued)

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%)		
				Ash	Coal	Tot. S
9) FF, pH 10.3, FAAX (200 ppm)						
Conc.	67.88	3.02	1.91	28.99	70.84	39.40
Disp.	32.12	15.64	5.76	71.01	29.16	60.60
Feed	100.00	7.08	3.29	100.00	100.00	100.00
10) FF, pH 10.0, FR-7A (50 ppm)						
Conc.	79.99	4.11	2.06	46.71	82.51	50.08
Disp.	20.01	18.72	5.15	53.29	17.49	49.92
Feed	100.00	7.03	3.29	100.00	100.00	100.00
11) SED + FF, pH 10.3, FR-7A (60 + 40 ppm), PAAX (40 + 100)						
Conc.	64.61	5.84	2.19	39.58	67.25	43.01
Disp. 1	22.14	16.96	5.73	39.39	20.33	38.59
Disp. 2	13.25	15.15	4.55	21.03	12.42	18.40
Feed	100.00	9.54	3.29	100.00	100.00	100.00
12) 2-SED+FF, pH 10.3, FR-7A (80+20+0 ppm), PAAX (300+150+50 ppm)						
Conc.	57.31	3.43	2.36	23.98	60.29	42.00
Disp. 1	29.80	12.02	3.15	43.68	28.56	29.15
Disp. 2	8.59	17.19	4.31	18.01	7.75	11.50
Disp. 3	4.30	27.30	12.90	14.33	3.40	17.35
Feed	100.00	8.20	3.22	100.00	100.00	100.00

Table A-1.5
Feed: Pittsburgh No. 8 coal
Grinding Time: Ball mill for 18 hours

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%)		
				Ash	Coal	Tot. S
1) FF, pH 10.0, FR-7A (60 ppm), PAAX (200 ppm)						
Conc.	74.53	21.36	2.34	68.19	76.46	43.94
Disp.	25.47	29.14	6.91	31.80	23.54	56.06
Feed	100.00	23.34	3.97	100.00	100.00	100.00
2) FF, pH 10.0, FR-7A (50 ppm), PAAX (200 ppm)						
Conc.	76.50	11.06	1.99	52.80	80.60	38.35
Disp.	23.50	30.29	6.97	47.20	19.40	61.65
Feed	100.00	16.14	3.97	100.00	100.00	100.00
3) FF, pH 10.0, FR-7A (40 ppm), PAAX (200 ppm)						
Conc.	62.57	9.64	2.44	38.91	66.92	38.46
Disp.	37.43	25.33	5.54	61.09	33.02	61.54
Feed	100.00	15.52	3.97	100.00	100.00	100.00

Table A-I.5 (Continued)

Product	Weight	Ash	Total S	Total Distribution (%)		
	(%)	(%)	(%)	Ash	Coal	Tot. S
4) FF, pH 10.0, FR-7A (30 ppm), PAAX (200 ppm)						
Conc.	62.92	9.60	2.52	38.59	67.44	39.89
Disp.	37.08	25.96	5.55	61.41	32.56	60.11
Feed	100.00	15.67	3.64	100.00	100.00	100.00
5) FF, pH 10.0, FR-7A (20 ppm), PAAX (200 ppm)						
Conc.	68.94	9.60	2.47	42.58	73.80	42.89
Disp.	31.06	28.77	6.54	57.42	26.20	57.11
Feed	100.00	15.56	3.73	100.00	100.00	100.00
6) FF, pH 10.0, FR-7A (10 ppm), PAAX (200 ppm)						
Conc.	71.23	9.92	2.40	46.56	75.64	42.97
Disp.	28.77	28.16	6.73	53.44	24.36	57.03
Feed	100.00	15.17	3.64	100.00	100.00	100.00
7) FF, pH 10.0, FR-7A (5 ppm), PAAX (200 ppm)						
Conc.	66.22	9.17	1.95	38.69	71.34	32.52
Disp.	33.78	28.47	6.43	61.31	28.66	67.48
Feed	100.00	15.69	3.46	100.00	100.00	100.00
8) FF, pH 10.0, PAAX (200 ppm)						
Conc.	67.82	10.81	2.48	46.60	71.78	42.36
Disp.	32.18	26.13	5.77	53.40	28.22	57.64
Feed	100.00	15.74	3.54	100.00	100.00	100.00
9) 2-FF, pH 10.0, FR-7A (50 + 20 ppm), PAAX (200 + 200 ppm)						
Conc.	62.25	7.30	2.02	28.92	68.47	33.20
Disp. 1	23.42	31.18	6.56	46.45	19.12	40.64
Disp. 2	14.33	27.03	6.93	24.63	12.41	26.26
Feed	100.00	15.72	3.78	100.00	100.00	100.00
10) FF, pH 5.0, FR-7A (50 ppm), PAAX (200 ppm)						
Conc.	77.37	9.71	2.62	46.32	82.53	51.06
Disp.	22.63	34.63	6.40	53.68	17.47	48.94
Feed	100.00	16.14	3.48	100.00	100.00	100.00
11) FF, pH 7.0, FR-7A (50 ppm), PAAX (200 ppm)						
Conc.	77.58	9.62	2.81	45.92	82.69	54.91
Disp.	22.42	34.53	6.75	54.08	17.31	45.09
Feed	100.00	16.14	3.69	100.00	100.00	100.00
12) FF, pH 9.0, FR-7A (50 ppm), PAAX (200 ppm)						
Conc.	72.21	9.43	2.51	41.70	77.49	45.65
Disp.	27.79	31.63	6.58	58.30	22.51	54.15
Feed	100.00	16.14	3.64	100.00	100.00	100.00

Table A-I.5 (Continued)

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%) Ash	Coal	Tot. S
13) FF, pH 11.0, FR-7A (50 ppm), PAAX (200 ppm)						
Conc.	58.47	12.16	2.54	44.04	61.25	37.41
Disp.	41.53	21.74	5.00	55.96	38.75	62.59
Feed	100.00	16.14	3.56	100.00	100.00	100.00

Table A-I.6
Feed: Pittsburgh No.8 raw coal, different griding time

Product	Weight (%)	Ash (%)	Total S (%)	Total Distribution (%) Ash	Coal	Tot. S
1) FF, pH 10, grinding 1 hr., FR-7A (20 ppm), PAAX (200 ppm)						
Conc.	95.94	7.53	1.99	72.45	98.54	86.23
Disp.	4.06	67.78	8.18	27.55	1.46	14.77
Feed	100.00	9.97	3.00	100.00	100.00	100.00
2) FF, pH 10, grinding 2 hr., FR-7A (20 ppm), PAAX (200 ppm)						
Conc.	82.42	6.92	2.08	46.56	87.43	62.80
Disp.	17.58	37.21	5.77	53.44	12.57	37.20
Feed	100.00	12.25	3.00	100.00	100.00	100.00
3) FF, pH 10, grinding 3 hr., FR-7A (20 ppm), PAAX (200 ppm)						
Conc.	76.45	6.83	1.66	39.86	81.97	48.00
Disp.	23.55	33.46	5.84	60.14	18.03	52.00
Feed	100.00	13.10	3.00	100.00	100.00	100.00
4) FF, pH 10, grinding 4 hr., FR-7A (20 ppm), PAAX (200 ppm)						
Conc.	78.73	6.56	1.93	42.81	83.66	55.86
Disp.	21.27	32.46	5.63	57.19	16.34	44.14
Feed	100.00	13.10	3.00	100.00	100.00	100.00
5) FF, pH 10, grinding 18 hr., FR-7A (20 ppm), PAAX (200 ppm)						
Conc.	75.90	9.39	1.89	45.85	81.44	52.60
Disp.	24.10	34.99	5.60	54.25	18.56	48.40
Feed	100.00	15.57	3.00	100.00	100.00	100.00

Table A-1.7
Feed: Pittsburgh No. 8 coal
Grinding Time: Ball mill for 18 hours

Product	Weight (%)	Ash (%)	Total Distribution (%)	
			Ash	Coal
1) FF, pH 10.0, FR-7A (100 ppm), PAAX (200 ppm)				
Conc.	93.20	7.17	67.98	95.39
Disp.	6.80	38.49	32.02	4.61
Feed	100.00	10.58	100.00	100.00
2) FF, pH 10.0, FR-7A (80 ppm), PAAX (200 ppm)				
Conc.	92.21	7.62	68.79	94.66
Disp.	7.79	38.28	31.21	5.34
Feed	100.00	10.58	100.00	100.00
3) FF, pH 10.0, FR-7A (60 ppm), PAAX (200 ppm)				
Conc.	83.70	6.66	53.26	86.73
Disp.	16.30	26.67	46.74	13.27
Feed	100.00	10.58	100.00	100.00
4) FF, pH 10.0, FR-7A (40 ppm), PAAX (200 ppm)				
Conc.	85.04	6.92	56.55	87.90
Disp.	14.96	27.12	43.45	12.11
Feed	100.00	10.58	100.00	100.00
5) FF, pH 10.0, FR-7A (20 ppm), PAAX (200 ppm)				
Conc.	82.90	6.01	48.71	85.06
Disp.	17.10	20.00	51.29	14.94
Feed	100.00	10.58	100.00	100.00
6) FF, pH 10.0, FR-7A (10 ppm), PAAX (200 ppm)				
Conc.	80.72	6.40	49.14	83.52
Disp.	19.28	22.69	50.86	18.75
Feed	100.00	10.58	100.00	100.00
7) FF, pH 10.0, FR-7A (5 ppm), PAAX (200 ppm)				
Conc.	77.99	6.00	43.53	81.25
Disp.	22.01	23.15	56.47	18.75
Feed	100.00	10.58	100.00	100.00
8) FF, pH 10.0, PAAX (200 ppm)				
Conc.	79.22	6.79	51.50	81.72
Disp.	20.78	20.50	48.50	18.28
Feed	100.00	10.58	100.00	100.00

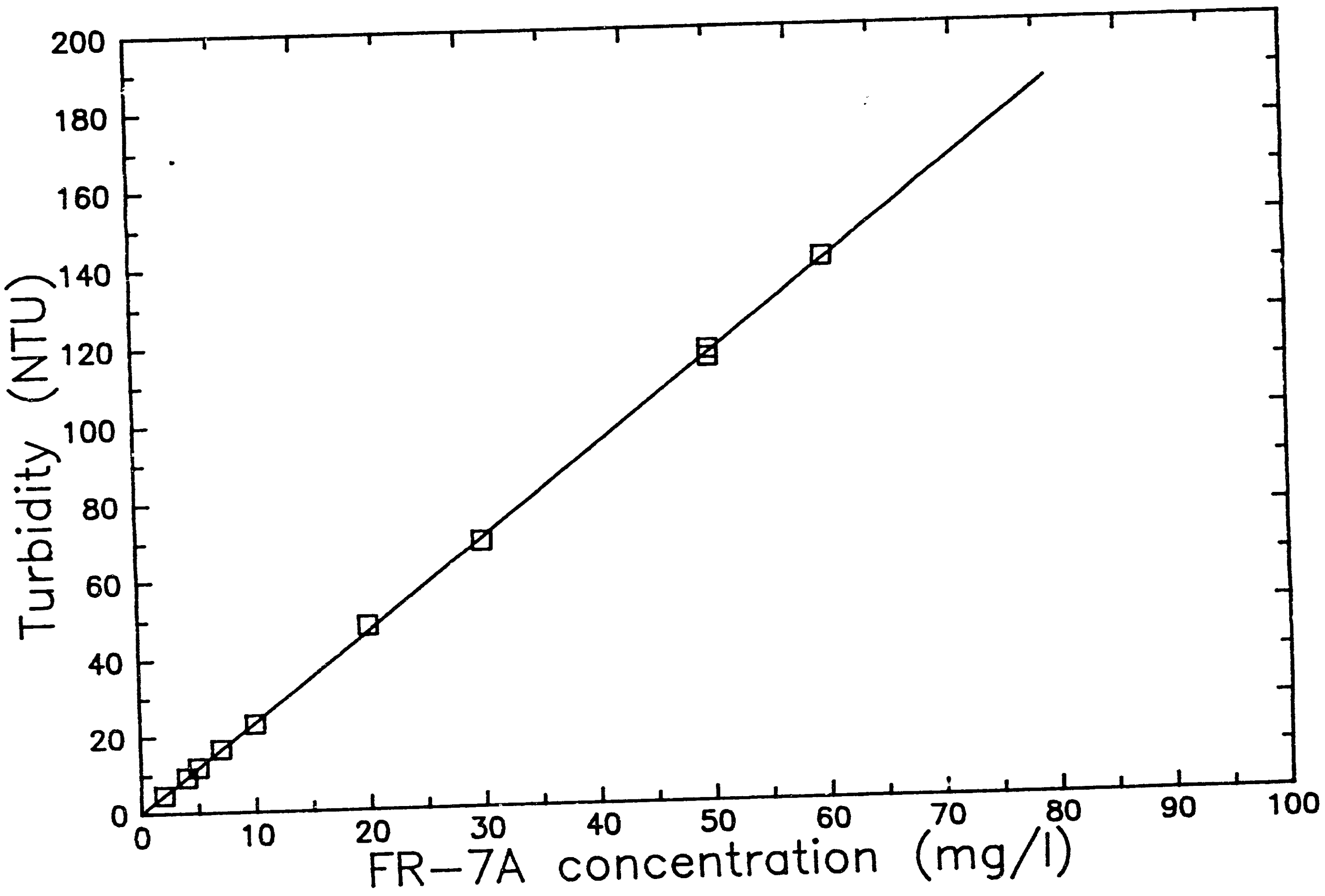

Figure B.I.1 Calibration Curve for FR-7A versus Turbidity of the Solution.

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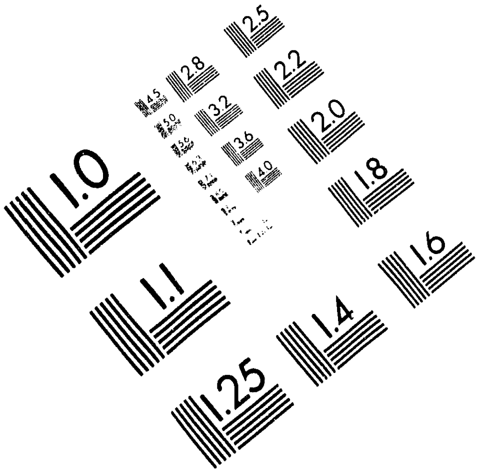

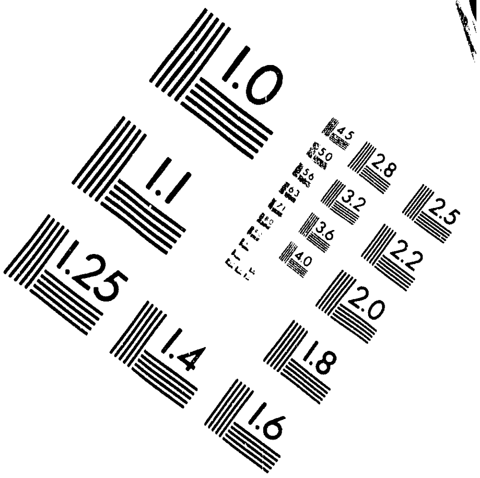

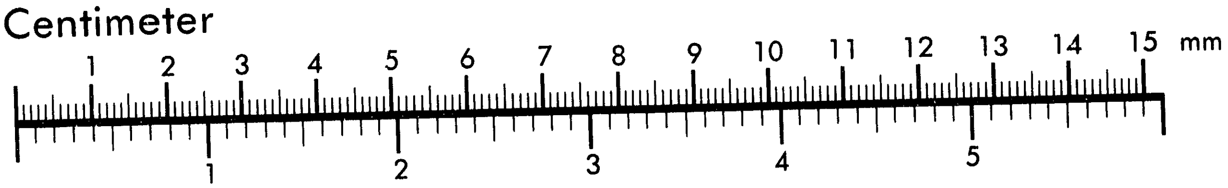

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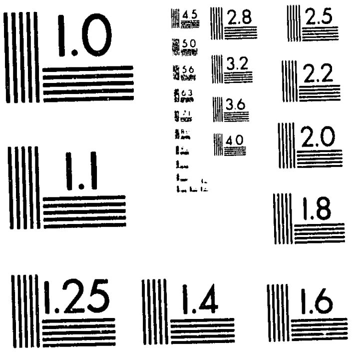

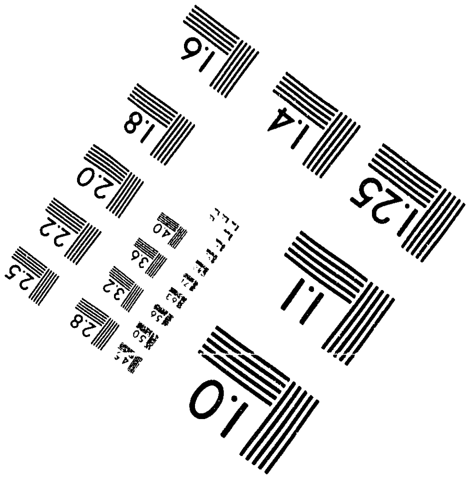

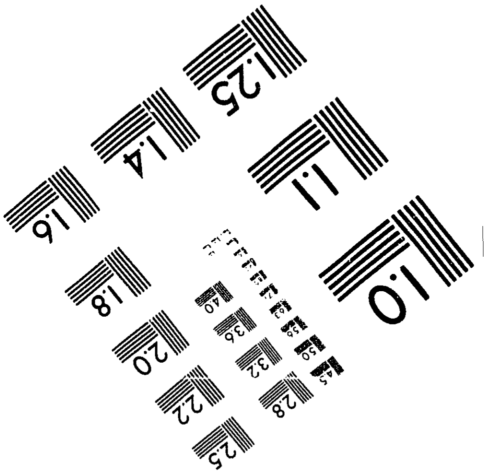

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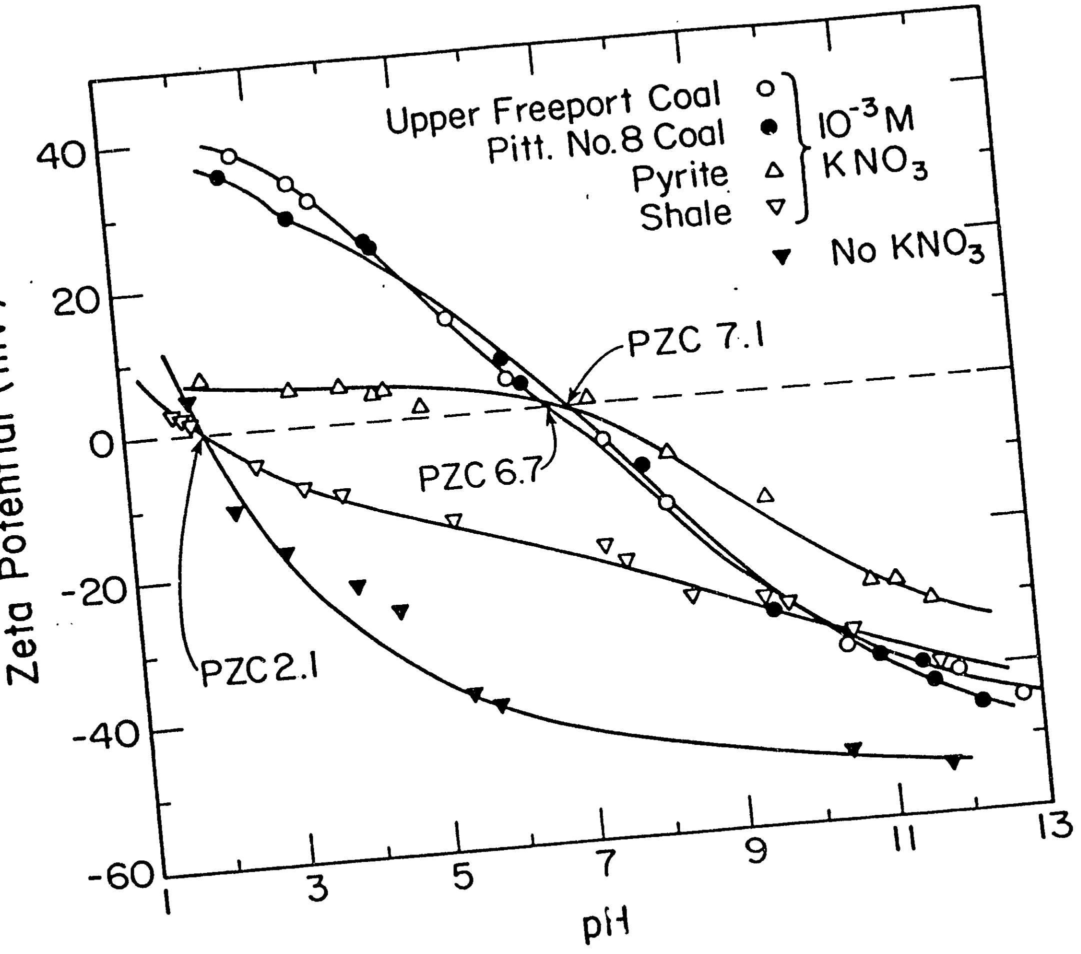

Figure B.I.2 Zeta-Potential Characteristics of Different coals and Minerals use in the Experiments.

C.I Published Paper on Selective Flocculation:

Y.A. Attia, F. Bavarian and K.H. Driscoll, Use of Polyxanthate Dispersant for Ultrafine Pyrite Removal from High Sulfur Coal by Selective Flocculation, <u>Coal Preparation</u>, 1988, vol.6, pp 35-51.

USE OF POLYXANTHATE DISPERSANT FOR ULTRAFINE PYRITE REMOVAL FROM HIGH SULFUR COAL BY SELECTIVE FLOCCULATION

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ABSTRACT

The technical feasibility of removing ultrafine pyrite from high sulfur coals by selective flocculation using poly acrylate-acrylodithiocarbonate xanthate dispersant (PAAX) has been investigated. The key element in this study was to develop and utilize an xanthate containing dispersant to enhance the dispersion pyrite. The preparation and stability of the polyxanthate dispersant (PAAX) was investigated to optimize the production and purification of the dispersant.

The sulfur removal efficiency of the PAAX was tested on coal samples of the Pittsburgh No. 8 seam. The coal samples were first pre-cleaned by heavy liquid separation ($\rho_\ell = 1.6$ gm/cc) and then were ground to -25 μm size. A co-dispersant, sodium metaphosphate, was also added in proportional amount to 5. wt.% coal slurry to make a 500 ppm solution.

The flocculant used throughout the research was FR-7, a totally hydrophobic flocculant obtained form Calgon Corporation. The coal flocs were separated either by sedimentation followed by decantation or by dissolved-air flotation. Single and multiple stage flocculation tests were performed.

The results indicated significant reduction in sulfur level of high sulfur coal by this process. Using a two step selective flocculation process, after heavy liquid pre-cleaning, the total sulfur was reduced from 3.6% to 0.9% while the pyritic sulfur was reduced from 1.94% to less than 0.25%. The ash content was also reduced from 13.8% to about 2.5%, while the coal (Btu) recovery was over 90% by selective flocculation.

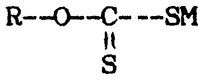
Although a more detailed study of the process using PAAX is required, the results showed great promise for the use of PAAX as selective dispersant for pyrite, and for possible production of super-clean coal from high sulfur coals.

INTRODUCTION

Selective flocculation is a feasible process for super-cleaning (less than 3% ash and 1% sulfur) of ultrafine coal slurries for coal-water fuels (Attia et al., 1977). The process uses differences in surface chemical properties of the particles to effect separation. In this process, a polymeric flocculant selectively adsorbs on the material to flocculated, leaving all other materials suspended in the slurry. The flocculated particles are the separated from the slurry by differential gravitational settling, or some other appropriate technique.

In order to enhance the dispersion of pyrite and other ash minerals, dispersing agents are used. The use of a selective dispersant such as poly arylate-acrylodithiocarbonate xanthate can improve the dispersion of non-coal particles which also enhances the selective flocculation process.

Xanthates are widely used chemicals as mineral collectors and flotation reagents for sulfide minerals. The basic structure of xanthates is:



$$R\text{--}O\text{--}\underset{\underset{S}{\parallel}}{C}\text{---}SM$$

where R can be an alkyl hydrocarbon group and M is a monovalent metal such as sodium or potassium (Rao, 1971).

High molecular xanthates such as cellulose xanthates have been use as flocculants for processing of sulfide minerals. Attia (1974) extensively studied the production and characterization of cellulose xanthate for selective flocculation of copper minerals. The use of cellulose xanthate have been also extended to selective flocculation of pyrite and coal-cleaning processes.

However, the use of xanthate-containing polymeric dispersants has been recently reported to enhance the dispersion process of ultrafine pyrite particles in coal desulfurization process using selective flocculation method (Attia and Fuerstenau, 1982; Attia, 1984). The xanthated reagent is used as a selective dispersion agent to enhance the selectivity of the flocculation process. Possible structure of PAAX has been reported by Attia (1985) as shown in Figure 1. Attia (1985) reported that the procedure for preparation of PAAX. The xanthation process is a reversible reaction, therefore, seldom does the reaction goes to completion which means that not all the carboxylic acid groups are xanthated. The degree of xanthation for a molecule is called "d" which refers to the number of xanthate groups in a polymeric chain as indicated in Figure 1.

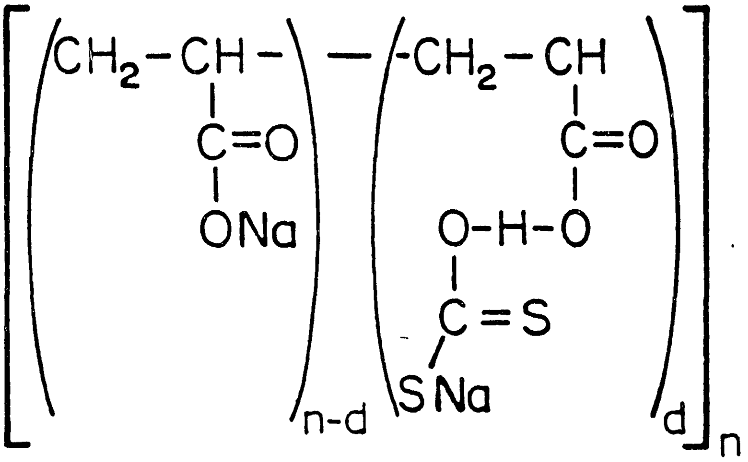


Figure 1. Postulated Structure of PAAX Dispersant (Attia, 1985).

The dispersion process involves chemical adsorption of short chain xanthate-containing polymer molecules on the active sites of the pyrite particles which deactivates the surface chemical reactivity of the pyrite. Therefore, during the flocculation step the pyrite particles have no affinity toward the flocculant molecule and stay dispersed in the slurry while the coal particles agglomerate and settle at the bottom of the beaker. Nevertheless, a mechanistic picture of the exact surface chemistry of the dispersion process is yet to be developed.

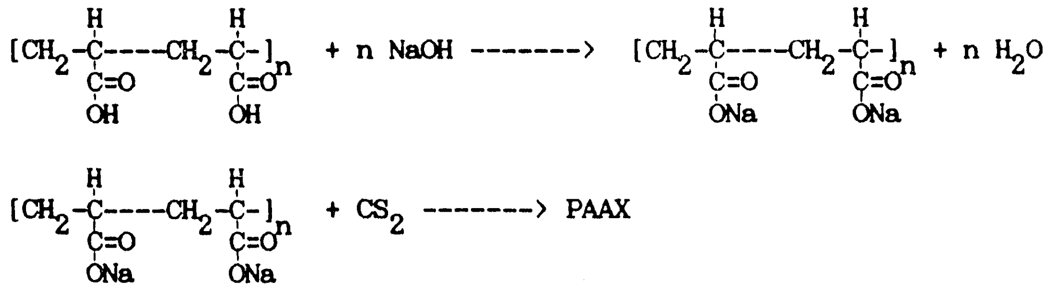
The development of any mechanistic approach is strongly dependent upon the basic understanding of the physieo-chemical properties of the xanthates which are inherently unstable and susceptible to heat and neutral or acidic environments. Therefore, one of the objectives of this research was to develop an optimum way of production, purification and storage of the PAAX dispersant. This, of course, required a full characterization of the PAAX compound which involved identification of the important parameters influencing the stability of the product.

The other objective of this work was to study the sulfur removal efficiency of the PAAX selective dispersant together with the selective flocculation process. Several parameters were studied in the selective flocculation such as the pH, and the effects of multiple cleaning stages.

EXPERIMENTAL TECHNIQUES

I. Preparation and Purification of PAAX

Preparation of PAAX: The sodium salt of poly acrylate-acrylodithiocarbonate xanthate, or in short PAAX, is formed by reacting carbon disulfide (CS_2) with sodium poly acrylate as shown below:



$$[CH_2-\overset{H}{\underset{\substack{C=O\\ OH}}{C}}----CH_2-\overset{H}{\underset{\substack{C=O\\ OH}}{C}}-]_n + n\ NaOH \text{-------}> [CH_2-\overset{H}{\underset{\substack{C=O\\ ONa}}{C}}----CH_2-\overset{H}{\underset{\substack{C=O\\ ONa}}{C}}-]_n + n\ H_2O$$

$$[CH_2-\overset{H}{\underset{\substack{C=O\\ ONa}}{C}}----CH_2-\overset{H}{\underset{\substack{C=O\\ ONa}}{C}}-]_n + CS_2 \text{-------}> PAAX$$

Unfortunately, the above reaction sequence is complicated by the formation of by-products such as mono- and tri-sodium thiocarbonate and dixantogens. Moreover, being an unstable compound at low pH and room temperature, xanthate group easily decomposes to CS_2 and its initial sodium salt. Consequently, the reaction conditions such as temperature and stochiometric ratio of the reactants must be optimized for the production of PAAX. The experimental range of different parameters are listed in Table 1.

Table 1. The Ranges of Variables for the Reaction Parameters investigated.

Temperature: 15-50 °C
Stochiometric ratio: 1.5: 1.: 0.15 to 8.: 1.: 17. wt. ratio of NaOH: PAA: CS_2
Reaction Time: 1 to 5 hours
pH: 11 to 12.5
1% to 15% polyacrylic acid solution

Table 2 list the optimum conditions for production of PAAX. The PAAX was prepared by reacting NaOH, polyacrlic acid (PAA) with average molecular weight of 5000, and CS_2 in 1.5:1.0:4.0 weight ratio respectively.

PAAX Preparation Procedure: At first 1.5 gm of polyacrylic acid with average molecular weight of 5,000. supplied by Polysciences, Inc., Warrington, PA, was dissolved in 10 ml of distilled water and then 2.2 gm of NaOH was added to the polyacrylic acid solution. The mixture was then stirred until all of NaOH was dissolved which resulted in a clear and colorless solution. This solution was cooled down to 15 °C in a constant temperature water bath shaker using ice cubes, and 5.6 gm of CS_2 was slowly added to the solution. A reflux condenser was placed at the top of the reaction vessel to condense and reflux any CS_2 vapor. In approximately 30 minutes the clear solution changed to a pale yellow mixture. As the reaction time increased, the color of the mixture became darker and eventually the color turned orange. After about 5 hours, the reaction was stopped and the excess CS_2 was removed by decantation. However, most of the CS_2 can be evaporated by merely leaving the crude product at the room temperature under a ventilated hood since CS_2 has a low boiling temperature and is immiscible in water.

Table 2. The "Optimum" Reaction Parameters for Production of PAAX.

Temperature: 15 °C
Stochiometric Ratio: 1.5: 1.0: 4.0 wt. ratio of NaOH: PAA: CS_2
Reaction Time: 5 hours
pH 12.5
15% polyacrylic acid solution

Purification of PAAX: The purification of the product of the low temperature reactions (less 20 °C) involved basically only one single step. Simply, 100 ml of ethanol was added to the reaction mixture upon which the mixture separated into two yellow and orange liquid layers. The yellow liquid layer contained most of the ethanol-soluble compounds which also included some of the low molecular weight xanthates and also most of the water. The immiscible orange layer contained most of the high molecular xanthates. The mixture was then separated by decantation or through separatory funnel. The purity of each layer was tested by UV-spectroscopy where no observable indication of the by products (no absorbance peak) was detected, whereas for the products of high temperature reaction (more than 25 °C) formation of by products was clearly detected through the UV-sepctroscopy analysis.

Storage of PAAX: Since xanthate compounds are not stable at room temperature and susceptible to thermal decomposition, both liquid layers were kept under refrigeration to reduced thermal decomposition of the products. Nevertheless, it was observed that upon the dilution of the alcohol insoluble layer (the orange liquid layer) in water the orange color of the solution gradually changed to pure yellow even at the refrigeration condition within approximately three weeks period. Similarly, the ethanol soluble layer (the yellow liquid) was gradually faded and became pale yellow within the same time interval. The change in the color of the solutions directly correlated with the reduction in the UV-absorbance level which indicates the gradual decomposition of the PAAX.

However, it was observed that when the alcohol insoluble part was not diluted and maintained refrigerated at its original concentration after purification step, the color did not change or fade. The UV-absorbance level of diluted solution also indicated that the concentration of the PAAX did not change significantly when it was stored at high concentration and under refrigeration.

Characterization of PAAX

Characterization of each liquid layer for its composition and concentration was made by using UV-Visible Spectroscopy technique. The spectrophotometer system used in the experiments was a Bausch&Lomb Spectronic model 2000.

Selective Flocculation Experiments

Chemicals: The flocculant used throughout the research was FR-7, a totally hydrophobic flocculant obtained from Calgon Corp, Pittsburgh, Pennsylvania. This polymer is an oil in water emulsion, and-therefore is easily dispersed in water, and has a molecular weight of less than one million. Two dispersants were used. Sodium metaphosphate (SMP) was used at a 500 ppm concentration as a general dispersant to produce a stable suspension and to disperse the ash forming minerals. The SMP was obtained from Fisher Scientific. The slurry pH was adjusted using sodium hydroxide and hydrochloric acid. The second dispersant used was the purified PAAX solution at various concentration for 50-300 ppm.

Minerals: The coal used in this study was Pittsburgh Number 8 coal seam, obtained from the R&F Coal Company, Cadiz, Ohio. The coal was first pre-cleaned using a heavy liquid separation (tetrachlorethylene, s.g. 1.6). The properties of the raw coal and the pre-cleaned coal are listed in Table 3.

Table 3. Characterization of the coal samples used from the Pittsburgh No. 8 seam.

	Ash%	Total Sulfur%	Pyritic Sulfur%	Organic Sulfur%
Raw Coal	13.8	3.58	2.82	0.74
Pre-cleaned by H-L, S.G. 1.6	7.66	2.66	1.94	0.72

The coal slurry was prepared from one kilogram of coal and two kilograms of distilled water which had a pH of approximately 10, and 3000 mg/ℓ SMP. The high SMP concentration was used so that when the slurry was diluted to 5% solids, the SMP concentration would be 500 mg/ℓ. The coal was ground to minus 500 mesh (25 micron) in an attrition mill supplied by the Fort Pitt Mine Machine Co., Pittsburgh, Pennsylvania.

Standard Selective Flocculation Procedures: Figure 2 shows the basic steps in the flocculation experiments. After heavy liquid separation, the coal particles were ground and a 5 wt% slurry mixture was prepared. The coal slurry was first agitated for five minutes at a shear rate of 425

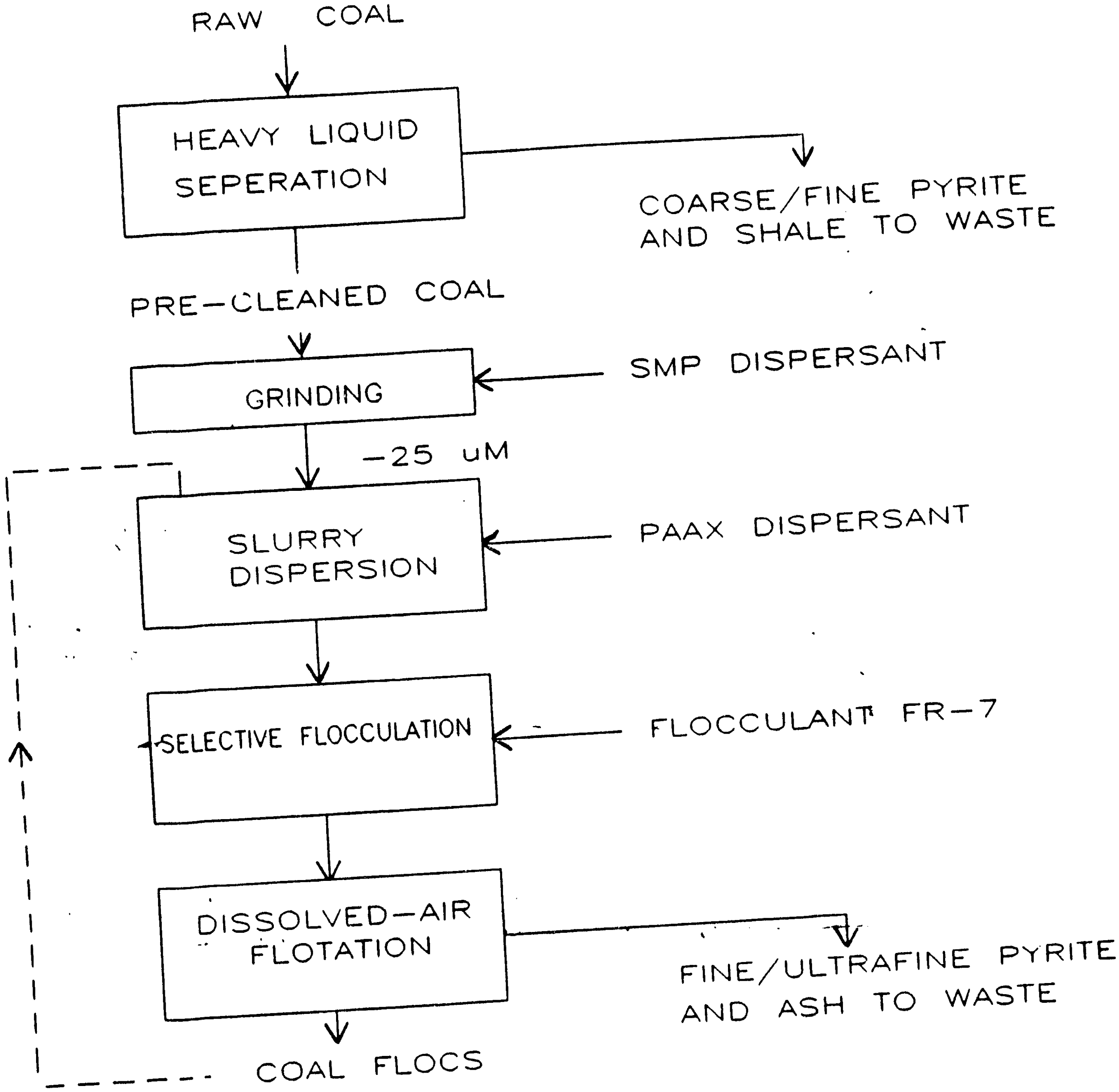


Figure 2. Scheme of Selective Flocculation of Coal Slurries.

sec^{-1}, and the pH was adjusted to the desired value. When the experiment involved the use of PAAX, it was added at this time, and was allowed to disperse for an additional five minutes. A 5 ppm concentration of the flocculant was then added over a one minute interval, and was allowed to disperse for one minute. The shear rate was then reduced to 170 sec^{-1}, and the flocs were allowed to condition for three minutes. The flocculated slurry was then allowed to settle for five minutes, and the dispersed and flocculated fractions were separated by decantation or by dissolved air flotation. The two fractions were dried, weighed, and the ash , total sulfur, and pyritic sulfur contents were determined using the ASTM recommended procedures.

Parametric Studies: Of the four parameters investigated, two dealt with the slurry conditions during flocculation. These were the alcohol soluble PAAX concentration, and the slurry pH. The alcohol soluble PAAX concentration was studied by varying the concentration during flocculation from 50 ppm to 300 ppm. These experiments were conducted at two different pH levels, pH 8.0 and pH 9.5, to determine the effect of pH on the process.

During the PAAX purification studies, it was discovered that PAAX existed in both the alcohol soluble and the alcohol insoluble fractions of the crude reaction product. To determine which fraction was better able to disperse the pyrite, dispersion tests were done using pure pyrite. Pyrite was ground to -140 mesh and suspended in 100 ml of distilled water with 500 ppm SMP. The PAAX concentration in the slurry was adjusted to 100 and 200 ppm, and then agitated for five minutes. The dispersed and settled fractions were separated by decantation. These two fractions were dried and weighed, and the pyrite distribution was calculated.

Finally, multiple cleaning stages were tested by performing one and two step selective flocculation tests. For this set of experiments, the flocs from the first cleaning stage were re-dispersed, and then re-flocculated. With this set of tests, the flocculant concentrations were 7 ppm and 3 ppm in the first and second steps, respectively. In these tests, the flocs were separated by dissolved air flotation. In this process, the flocs do not settle, so the pyrite which is not dispersed by the PAAX will not report with the flocculated fraction.

RESULTS AND DISCUSSION

Stability Analysis of PAAX

UV-Spectrophotometry of PAAX: The analysis of the alcohol soluble layer showed a distinct peak at 301 nm and for the alcohol insoluble layer the peak was at 302 nm. The UV-spectroscopy of the both liquid layers also indicated a lower absorbance peak at about 227 nm. Figure 3 shows the UV characteristic absorbance for the both solution. These results were compared with the UV analysis of pure sodium isopropyl and potassium amyl xanthates which showed sharp absorbance peaks at 301.3 and 300.3 nm, respectively. The pure xanthate compounds and the purified alcohol insoluble PAAX were also used to caliberate the absorbance of UV light for the concentration and the decomposition rate.

Effect of Reaction Temperature: Analysis of the reaction products whose reaction temperatures were maintained above 25 °C showed a strange behavior on the alcohol insoluble product. The UV-analysis of these reaction products exhibited consistently an initial peak at 318 nm which

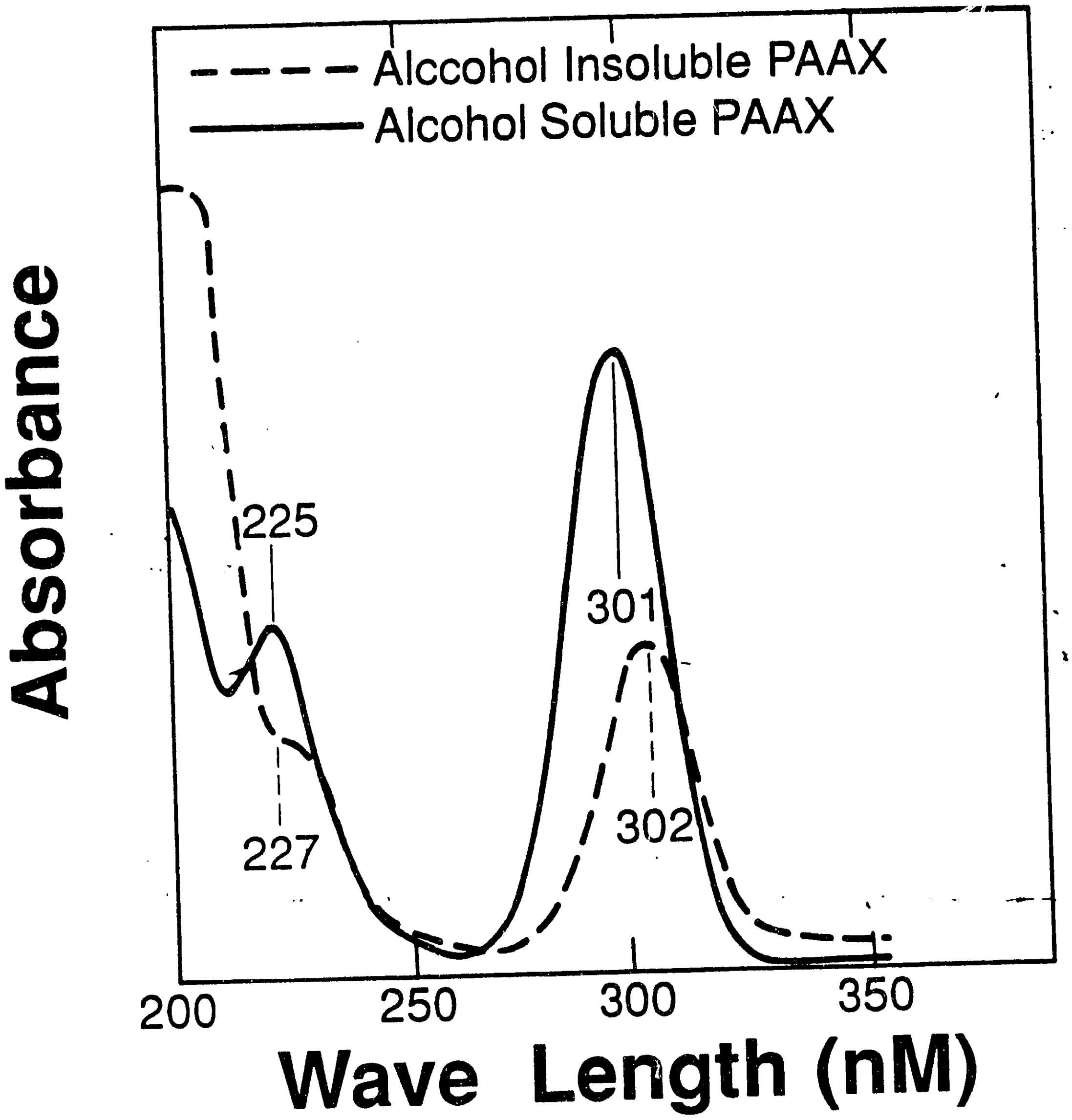


Figure 3. Characterization of PAAX by UV-absorption Spectroscopy.

gradually leveled off to 307 nm as shown in Figure 4. Similarly, the UV-absorbance level also decreased with the the drifting wavelength as shown in Figure 5. It should be noted that this behavior was observed at low concentrations of the reaction solutions (approximately 5 to 10 ppm of the crude PAAX), however the pH of the solution was maintained above 10. Markedly, the alcohol insoluble product of the low temperature reaction showed considerably more stable behavior and higher absorbance which means a higher degree of xanthation.

In addition, at higher temperature, the characteristic peak for tri-sodium thiocarbonate compound was also observed at 332 nm, whereas the low temperature products did not indicate the formation of tri-sodium thiocarbonate.

Effect of CS_2 Dosage: Figure 6 shows the effect of initial dosage of CS_2. As was expected, the higher dosage of CS_2 resulted in a higher degree of xanthation. However, excessive dosage of CS_2 is not recommended since after a certain amount of CS_2 dosage, the xanthate concentration did not increase significantly and further addition of CS_2 would merely prolong the purification process. It should be noted that the optimum amount of CS_2 dosage is a function of the reaction temperature and the reaction time. Therefore, the results of one set of reaction conditions could not be employed to predict the dosage for a different reaction condition.

Attia (1974) reported similar findings for the xanthation of cellulose. The comparison of 40 wt% initial $CS_2$to cellulose dosage with 400 wt% CS_2 dosage indicated a significantly higher xanthate content and

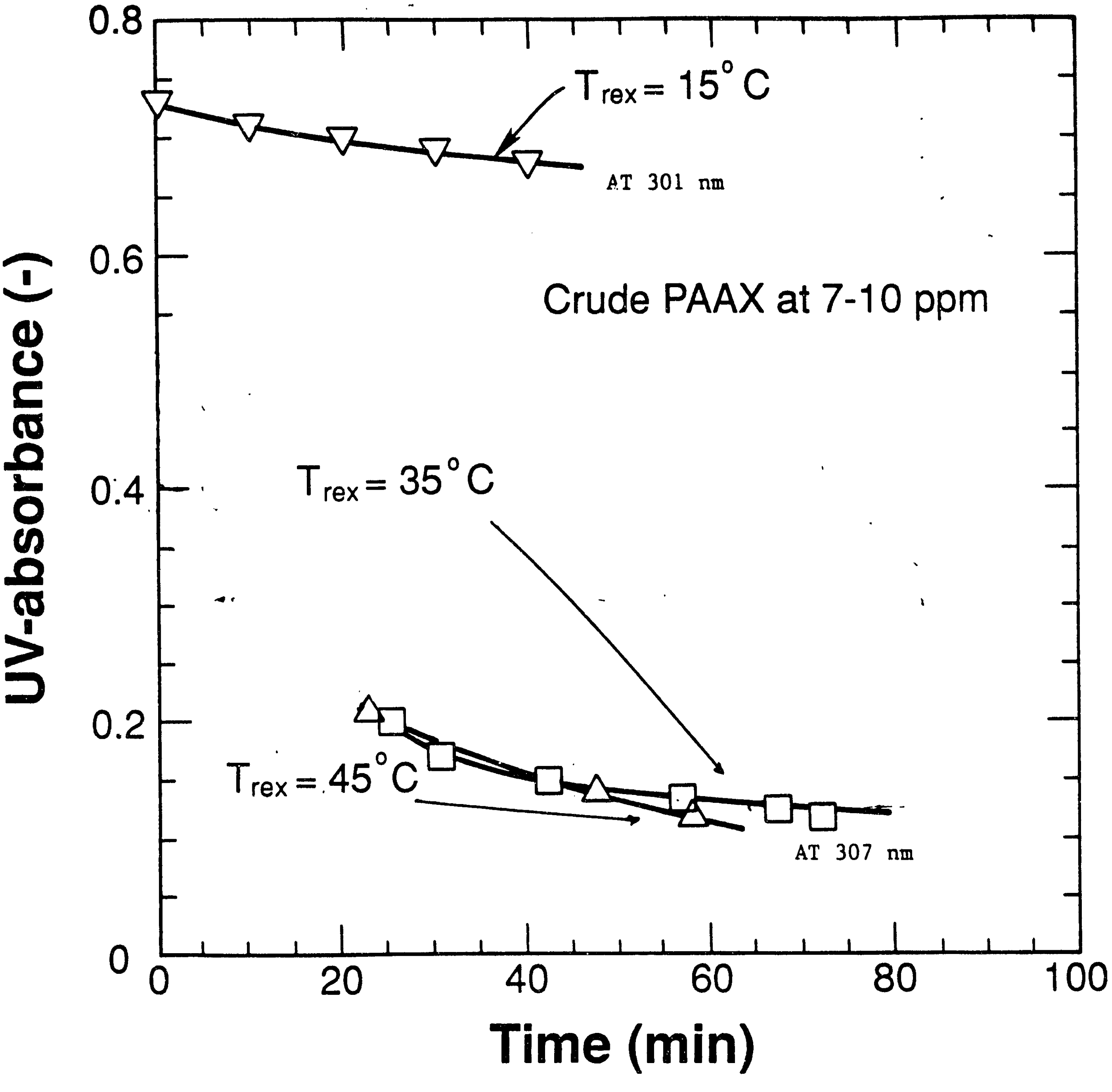


Figure 4. Effect of Recation Temperature and Room Temperature Storage After Dilution on the Decomposition of PAAX products for: 15 °C at 301 nm, and 35 °C and 45 °C at 307 nm.

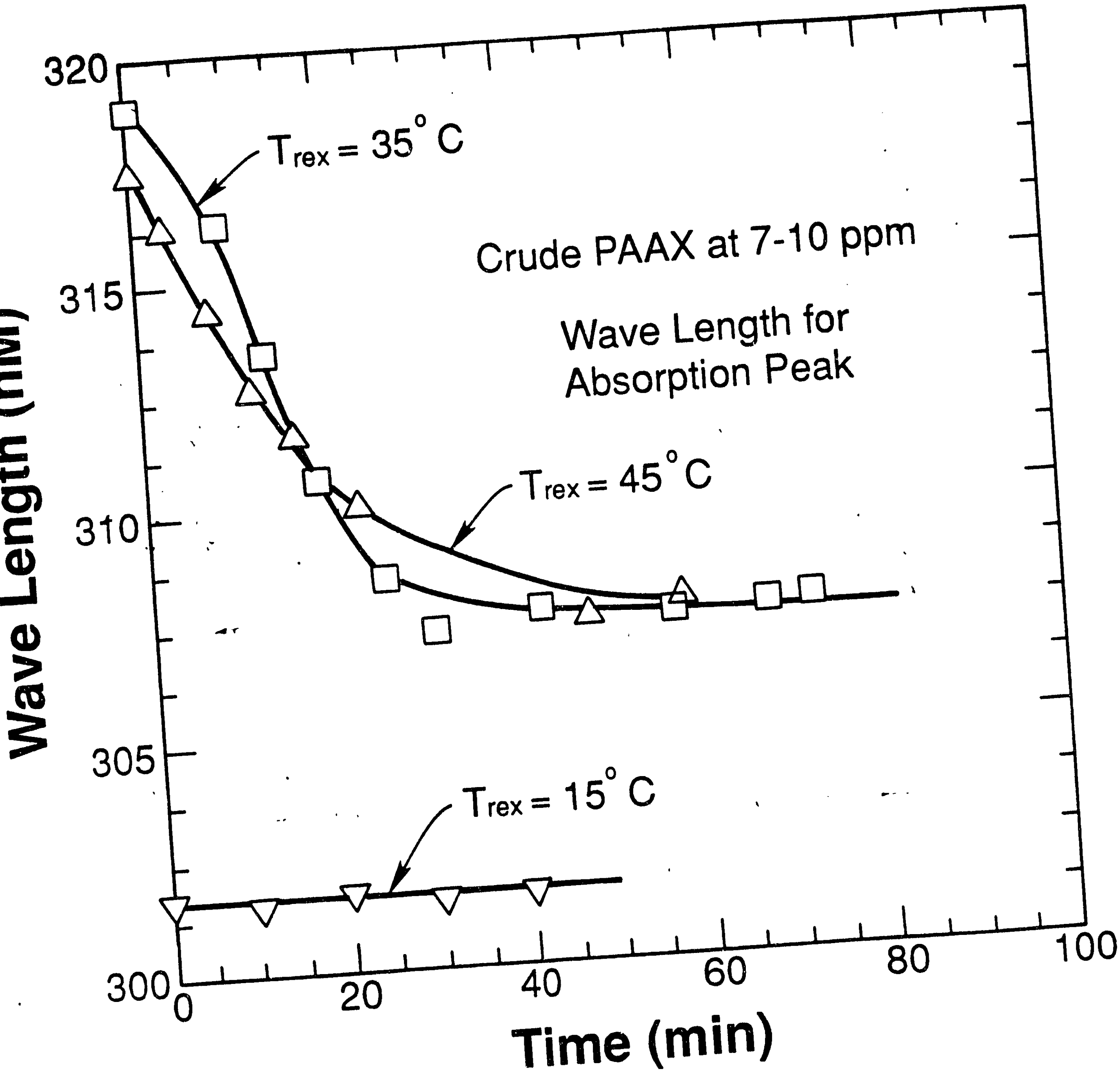


Figure 5. Effect of Reaction Temperature and Room Temperature Storage After Dilution on the stability of the UV-absorption Wave Length for PAAX Products. Recation time was: 5 hours for 15 °C, 2 hours for 35 °C and 2 hours for 45 °C Reaction Temperatures.

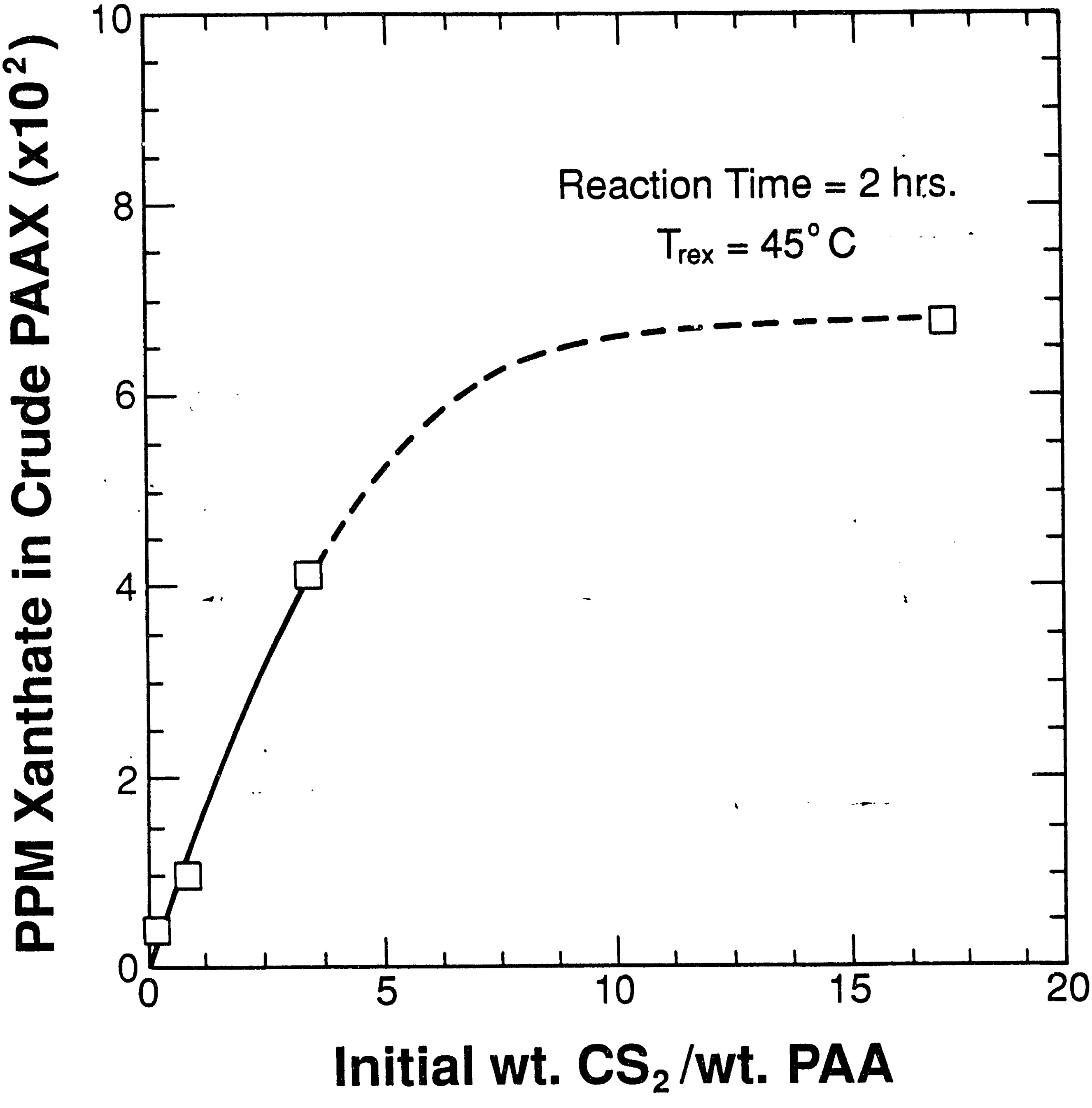


Figure 6. Effect of Initial CS_2 Dosage on Xanthation.

also more uniform substitution of xanthate group. The reported results are compatible with the data obtained in these experiments. As shown in Fig. 6, the xanthate concentration increased approximately by a factor of four when the initial CS_2 / PAA wt. ratio increased from 1. to 4. Nevertheless, as discussed before, excessive dosage of CS_2 is not recommended since it can complicate the purification step.

Flocculation Results

Flocculation and Dispersion with Alcohol Soluble and Insoluble PAAX:

The effect of the alcohol soluble PAAX concentration on the process is shown in Figure 7, which is a plot of the recovery and upgrading as a function of the PAAX concentration, and in Figure 8, which shows the pyritic sulfur content of the flocs as a function of the PAAX concentration. The recovery was seen to decrease and the upgrading increased as the alcohol soluble PAAX concentration increased. This is believed to be the result of the non-xanthatated portion of the polyacrylic acid acting as a general dispersant for the coal as well. This causes the flocs to form in smaller sizes which also leads to a higher upgrading and lower recovery. In figure 8, the pyritic sulfur in the flocs can be seen to drop initially, and then showed no further reduction after approximately 100 ppm PAAX.

Table 4 shows the results of the dispersion experiments which compared the dispersion ability of the alcohol soluble and the alcohol insoluble PAAX. From these results it can be seen that the alcohol insoluble PAAX was able to disperse almost twice as much pyrite as SMP alone, and over three times as much pyrite as the alcohol soluble PAAX. Interestingly, the alcohol soluble PAAX seemed to actually reduce the

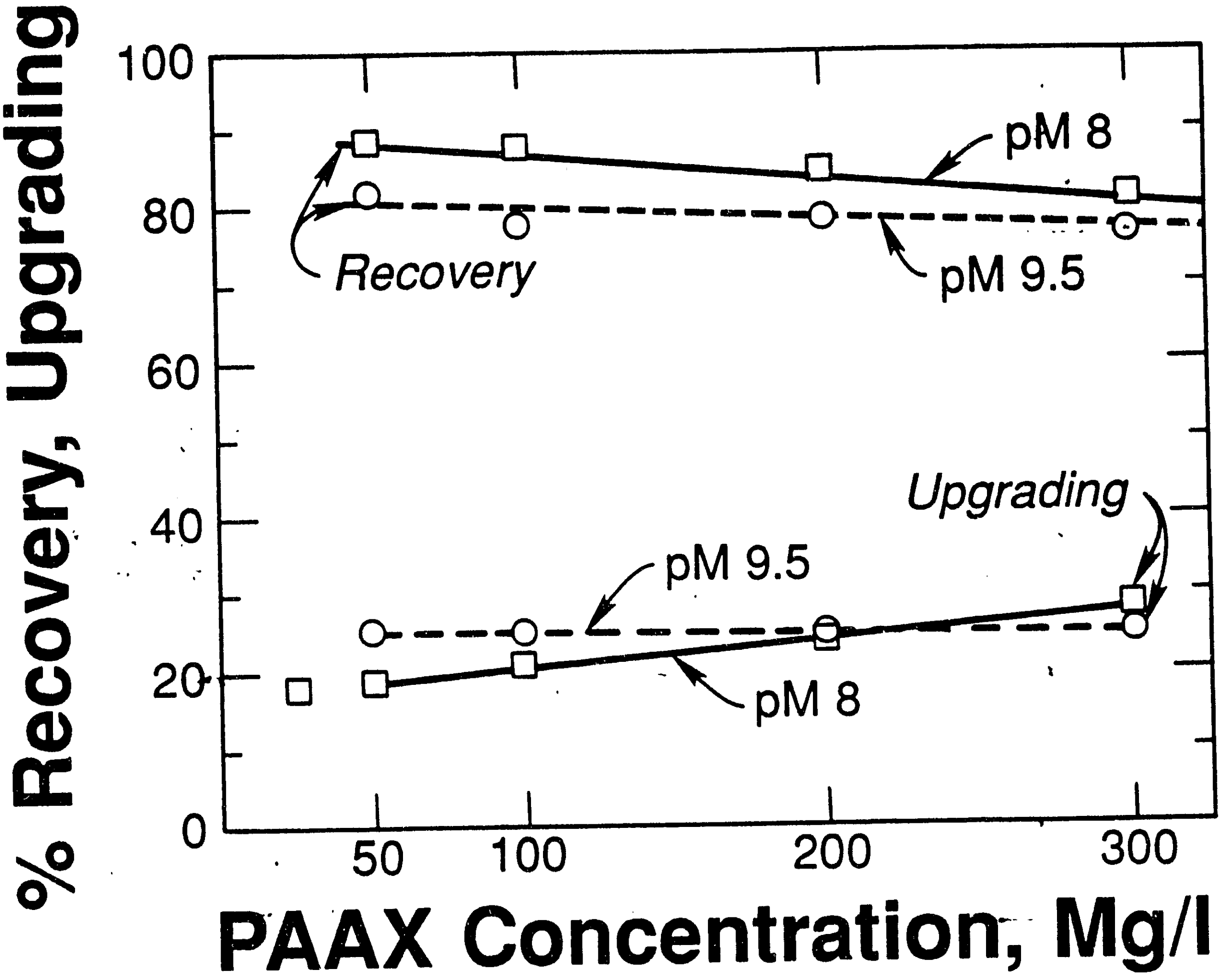


Figure 7. Effect of Acohol Soluble PAAX Concentration on Recovery and Upgrading.

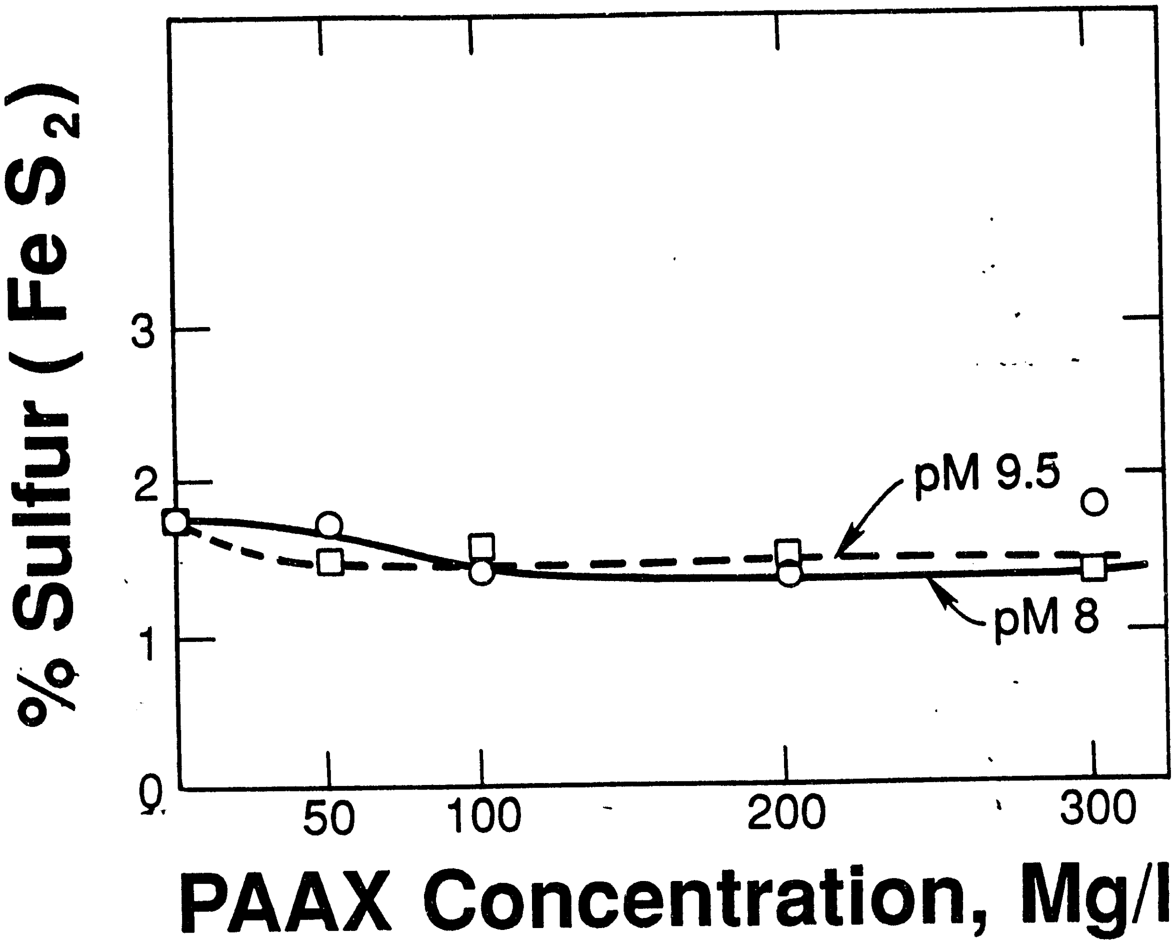


Figure 8. Effect of the Acohol Soluble PAAX Concentration on the Pyritic Sulfur Removal Process.

dispersion of pyrite. However, it should be noted that the pyrite size was approximately -140 mesh in size, whereas the coal for the selective flocculation tests was ground to 25 µm. Clearly, the smaller size particles can form a more stable dispersion.

Table 4. Dispersion ability of alcohol soluble and alcohol insoluble PAAX.

PAAX concentration	Product	Weight (g)	Weight %	PAAX type
100 ppm	Dispersed	0.0487	3.42	alcohol
	Settled	1.3752	96.58	soluble
	Feed	1.4239	100.00	
200 ppm	Dispersed	0.0650	4.81	alcohol
	Settled	1.2858	95.19	soluble
	Feed	1.3508	100.00	
100 ppm	Dispersed	0.1362	10.90	alcohol
	Settled	1.1138	89.10	insoluble
	Feed	1.2500	100.00	
200 ppm	Dispersed	0.1489	11.61	alcohol
	Settled	1.1331	88.39	insoluble
	Feed	1.2820	100.00	
0 ppm	Dispersed	0.0784	7.57	no PAAX
	Settled	0.9568	92.43	used
	Feed	1.0352	100.00	

<u>Selective Flocculation of pre-cleaned pittsburg No. 8 Coal:</u> Tables 5 and 6 show the results of the one and two step selective flocculation when 200 ppm of the alcohol insoluble PAAX was used in conjunction with dissolved air flotation as the floc separation technique. It can be seen that using a single step selective flocculation, the total sulfur content was reduced from approximately 2.6% to 1.6% and the pyritic sulfur was reduced from 1.9% to 0.95%. The ash content of the pre-cleaned coal was reduced to 3.9% with a coal recovery of 93% . This is very close to the

super-clean coal level. The use of the second of the selective flocculation produced a clean coal that had a total sulfur content of 0.95%, and pyritic sulfur content of 0.2% , i.e. about 90% removal of the ultrafine pyrite was achieved. The ash content of the cleaned coal in these tests was 2.5%, while the recovery was still above 90% .

Table 5. Selective Flocculation - Dissolved-Air Flotation Cleaning of Pre-cleaned Pittsburgh No. 8 Coal Using One Step Flocculation.

	ANALYSIS%				DISTRIBUTION%		
Product	Weight	Ash	Coal	Total Sulfur	Ash	Coal	Total Sulfur
Flocs	91.8	4.74	95.26	1.67	56.8	94.7	57.5
Dispersed	8.2	40.52	59.48	13.81	43.2	5.3	42.5
Feed	100.0	7.66	92.34	2.66	100.0	100.0	100.0
Flocs	91.4	3.48	96.52	1.64	40.5	95.7	54.3
Dispersed	8.6	54.66	45.66	14.65	59.5	4.3	45.7
Feed	100.0	7.65	92.35	2.76	100.0	100.0	100.0
Flocs	88.8	3.79	96.21	1.73	44.0	92.5	52.2
Dispersed	11.2	38.24	61.76	12.25	56.0	7.5	47.8
Feed	100.0	7.65	92.35	2.91	100.0	100.0	100.0

Table 6. Selective Flocculation - Dissolved-Air Flotation Cleaning of Pre-cleaned Pittsburgh No. 8 Coal Using Two Steps Flocculation.

	ANALYSIS%				DISTRIBUTION%		
Product	Weight	Ash	Coal	Total Sulfur	Ash	Coal	Total Sulfur
Flocs	85.5	2.83	97.17	0.94	30.5	90.3	29.3
Dispersed 1	6.9	42.52	57.48	13.48	36.6	4.3	33.9
Dispersed 2	7.6	34.23	65.77	13.27	32.9	5.4	36.8
Feed	100.0	7.94	92.06	2.74	100.0	100.0	100.0
Flocs	88.1	2.40	97.60	0.97	30.1	92.4	30.3
Dispersed 1	5.8	56.90	43.10	14.77	47.2	2.7	30.4
Dispersed 2	6.1	26.01	73.99	18.17	22.7	4.9	39.3
Feed	100.0	7.03	92.97	2.83	100.0	100.0	100.0
Flocs	86.2	2.25	97.75	0.87	25.7	91.2	26.6
Dispersed 1	6.0	45.88	54.12	13.30	36.1	3.5	28.4
Dispersed 2	7.8	37.07	62.93	16.21	38.2	5.3	45.0
Feed	100.0	7.57	92.43	2.81	100.0	100.0	100.0

CONCLUSIONS

Optimum conditions for the preparation of the polyxanthate dispersant (PAAX) are identified and were listed in table 2. The low temperature reaction products showed both higher degree of xanthation and stability. In addition, the purification of the reaction product was substantially simplified since at lower temperature the formation of by-products was significantly reduced.

The use of the PAAX as a selective dispersant for pyrite is feasible, and indeed, can reduce the sulfur level of high sulfur coal by significant amount. Using the alcohol insoluble PAAX at a pH 8.0 and a concentration of 200 ppm, the sulfur content of Ohio No. 8 coal was reduced from 3.6% to

0.95%, with the pyritic sulfur being reduced from 1.94% to less than 0.25% when a two stage selective flocculation cleaning process is employed after a pre-cleaning step with heavy liquid separation of 1.6 specific gravity. Further research is needed to develop this process into commercially viable technique for the super-cleaning and desulfurization of high sulfur coals.

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APPENDIX II

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1. Published Paper:

   Y.A. Attia and W. Lei, Removal of Organic Sulfur from High Sulfur Coals by Mild Chemical Oxidation Using Potassium Permanganate, in "Processing and Utilization of High Sulfur Coals", Elsevier, Eds. Y.P. Chugh and R.D. Caudle, 1987.

2. Possible Method for Regeneration of Potassium Permanganate for Spent Solutions

REMOVAL OF ORGANIC SULFUR FROM HIGH SULFUR COALS BY MILD CHEMICAL OXIDATION USING POTASSIUM PERMANGANATE

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ABSTRACT

This study was aimed at the removal of organic sulfur from an Ohio coal, Pittsburgh No. 8, by chemical cleaning using mild, inexpensive oxidizing reagents such as sodium hypochlorite and potassium permanganate under ambient conditions.

In the tests, the coal sample was pre-cleaned by heavy liquid separation at a specific gravity of 1.33 to reject coarsely sized pyritic sulfur and ash minerals, and was wet ground to -200 mesh (-75 microns). The oxidation process was conducted at room temperature and atmospheric pressure with either sodium hypochlorite, or potassium permanganate, followed by a washing step with warm or cold water.

Experimental results indicated that chemical oxidation was effective for removing organic sulfur. A high level of removal of organic sulfur from coal, more than 50%, was achieved with potassium permanganate. It also oxidized most of the pyritic sulfur in coal to sulfate sulfur at the same time. To our knowledge, this is the first time that potassium permanganate was used for coal desulfurization.

Process parameters such as concentration of oxidizing reagents, reaction time, agitation intensity, number of washing steps and temperature of washing solutions are reported and discussed in this paper. Approximately, 76% of total sulfur, 90% of pyritic sulfur and 87% of organic sulfur removal were achieved after three steps of treatment with 6% potassium permanganate. Thus a premium quality coal could be produced from low-value, high sulfur coal by this approach. This process approach is simple, easy to control and has high technical and commercial potentials.

INTRODUCTION

The high sulfur content of Ohio coals imposes severe limitation on their utilization, since the level of sulfur oxide gases emitted from the combustion of these coals are higher than that recommended by the U.S. Environmental Protection Agency and are blamed for the acid precipitation problem. Removal of sulfur from Ohio coals before combustion would therefore help greatly to eliminate this problem.

Physical coal cleaning methods are very efficient in removing the pyritic sulfur but are incapable of removing organic sulfur. The organic sulfur is chemically bonded into the coal structure. It can only be removed by chemical treatments that selectively destroy the sulfur compounds present in the coal matrix and render the sulfur amenable to extraction by leaching [1].

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Several chemical cleaning processes for coals have been reported such as Battelle, Ames, PETC, LOL processes [2-5]. Most of these processes were successful in achieving more than 90% pyritic sulfur rejection and up to 50% organic sulfur removal. Some of the chemical processes have been developed to pre-pilot plant scale or pilot plant scale [1,5]. However, these methods are not universally applicable, but are rather suitable for special applications, because these processes are mostly conducted at high temperature and pressure and tend to be more complex and very costly. In addition, the high temperature treatment alters the properties of the coal itself and destroys the caking tendency of coal [4]. Recently, Boron and Taylor [6] and Brubaker and Stoicos [7] developed an oxidation process for the removal of organic sulfur from the coal matrix through mild chemical oxidation using sodium hypochlorite. Sodium hypochlorite, as an oxidizing agent with an oxidation potential of 0.9 Volts, was used for removing sulfur from crude oil and petroleum distillates early in this century [8,9]. It was also used for studying the coal structure [10-12]. Using NaOCl in the oxidative removal of sulfur from coal, appears to be a promising approach compared with other chemical processes, because it can be conducted at room temperature and atmospheric pressure and uses inexpensive commercial oxidizing reagents. However, this process is at an early stage of development and further systematic studies are needed.

In this study, another good commercial oxidizing reagent, potassium permanganate having an oxidation potential of 1.52 Volts, was employed. It was believed to be more effective for removing organic sulfur from coal and had more economic potential than sodium hypochlorite.

The objectives of this study were: 1) to investigate the feasibility of removing organic sulfur from Ohio coal using potassium permanganate and sodium hypochlorite at room temperature and atmospheric pressure; and 2) to investigate the important process parameters and define the conditions for achieving maximum organic sulfur removal from Ohio coal.

EXPERIMENTAL TECHNIQUES

Materials:

Coal Sample Preparation: The coal sample utilized in this study was Pittsburgh No.8 from R & F Coal Company, Lamira Preparation Plant, Warnock, Ohio. The raw coal was crushed and screened to the size range of -6 +100 mesh (-2800 +150 microns) and was pre-cleaned by heavy liquid separation using 1,1,1,-Trichloroethane with a specific gravity of 1.33. To eliminate the effects of the residual 1,1,1,-Trichloroethane on coal surface properties, the float products were washed with acetone and were dried overnight in an oven at 100° C to evaporate the organic solvent. Table 1 shows the ash and sulfur contents of the raw coal and the pre-cleaned coal sample which was used in this study. The pre-cleaned coal

TABLE 1. Ash and sulfur contents of the Pittsburgh No. 8 coal sample before and after heavy liquid separation

Sample	Ash %	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%
Raw coal	13.8	3.58	2.82	0.02	0.74
Pre-cleaned by heavy liquid	4.4	1.78	1.04	0.02	0.72

sample was ground to -200 mesh (-74 microns) before use in the chemical oxidation experiments.

Chemical Reagents: The 4%-6% solutions of high purity sodium hypochlorite and crystals of potassium permanganate were obtained from Fisher Scientific Company, Chemical Manufacturing Division, Fairlawn, New Jersey, U.S.A. Solutions of the potassium permanganate were made at the required concentration.

Procedures

Chemical oxidation: Twenty grams of -200 mesh (-74 microns) pre-cleaned coal sample were transferred into a 500 ml flat-bottom flask containing 200ml of 4% to 6% sodium hypochlorite or of the required concentration of potassium permanganate. Mixing of the coal slurry with the reagents was accomplished using a magnetic stirrer for one hour. The pH of the oxidation step was 9.3 using potassium permanganate and was 10.9 using sodium hypochlorite. At the end of the oxidation period of one hour, the reaction mixture was filtered on a Buchner Funnel, and was washed repeatedly with distilled water until the pH of the filtrate was neutral. To investigate the effect of agitation intensity, different agitation speeds were tested, using a variable speed impeller Y-line mixer, model 102, supplied by Sepor Inc. Wilmington, California, U.S.A.

Washing of oxidation products: The filter cake was transferred to a 500 ml flat-bottom flask, equipped with a condenser, where it was re-slurried with 200 ml cold or hot distilled water. The slurry was continuously stirred for one hour while the washing temperature was maintained by a water-bath. The washed slurry was filtered in a Buchner Funnel, dried at 75°C overnight and was analyzed for the different forms of sulfur.

A series of $KMnO_4$ treatment tests was conducted on a pre-cleaned coal sample for evaluating the following variables:
(1) concentration of potassium permanganate (2, 4, 6, 8 and 10%);
(2) oxidation time (0.5, 1.0, 1.5, 2.0 and 2.5 hours);
(3) agitation speed (645, 825, 935, 1010 and 1100 rpm);
(4) number of oxidizing/washing steps (1, 2, and 3);
(5) temperature of the washing step (22, 35, 50, 65 and 80°C).

Analysis

Ash contents were determined in an ashing oven according to the standard ASTM procedure. Total sulfur was determined using a LECO automatic sulfur titrator. Pyritic sulfur and sulfate sulfur were determined according to the recommended ASTM procedures. The sulfate sulfur was analysed using gravimetric method in which the sulfate ion was precipitated and weighed as barium sulfate. Pyrites were extracted quantitatively by dilute nitric acid. The extracted iron was determined by atomic absorption techniques using Perkin-Elmer Model 3030. Organic sulfur was calculated by subtracting the sulfate and pyritic sulfur from the total sulfur in the coal.

RESULTS AND DISCUSSION

Feasibility of Removing Organic Sulfur from Pre-cleaned Coal

The pre-cleaned coal feed samples were oxidized with 6 potassium permanganate or sodium hypochlorite at room temperature and atmospheric pressure for one hour and then washed with warm water at 80°C, also for one hour. The results shown in Table 2, indicate that chemical oxidation was effective for removing organic sulfur from coal. Organic sulfur removal reached 24% with sodium hypochlorite and up to 52% with potassium permanganate. Potassium permanganate also oxidized more than 50 percent of pyritic sulfur to sulfate sulfur at the same time.

TABLE 2. Sulfur analyses of untreated and treated coals with 6% sodium hypochlorite and potassium permanganate

Coal Sample Treatment	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Sulfur Rejection%
Untreated					
Feed	1.78	1.04	0.02	0.72	---
$KMnO_4$	0.98	0.32	0.32	0.34	52
NaOCl	1.51	0.88	0.08	0.55	24

As an oxidizing agent, sodium hypochlorite (NaOCl) has an oxidation potential of 0.90 Volts. The half reaction [7] is:

$$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-; \quad E = +0.90\ V$$

Potassium permanganate is a powerful oxidizing agent in either alkaline or acid media [13]. In alkaline solution, the purple permanganate is quickly reduced to the green manganate, which later deposits brown manganese oxide. The overall half reaction is [13]:

$$MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH^-; \quad E = +1.23V$$

In the acid solution, the half reaction is:

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O; \quad E = +1.52V$$

Both sodium hypochlorite and potassium permanganate should therefore oxidize various organic sulfur functionalities such as sulfides, mercaptans and thiophenes in the coal. However, the oxidation potential of potassium permanganate is higher than that of sodium hypochlorite; therefore, it is expected to be more effective for removing the organic sulfur.

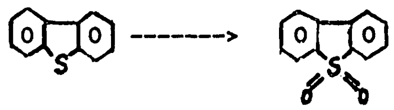
The probable oxidation pathways are summarized [7] below:

Organic sulfides: $R_1SR_2 \longrightarrow R_1SO_2R_2$

Organic disulfides: $R_1S_2R_2 \begin{cases} \dashrightarrow R_1SO_3H + R_2SO_3H \\ \dashrightarrow H_2SO_4 \end{cases}$

Mercaptans: $RSH \xrightarrow[RSO_3H]{H_2SO_4} RS_2R$

Thiophenes:



Potassium permanganate also oxidized part of the pyritic sulfur to sulfate sulfur. This was understandable, as the oxidation potential of potassium permanganate was higher than the oxidation potential for pyrite. The following equation described pyrite oxidation [5]:

$$FeS_2 + 8H_2O \longrightarrow Fe^{+2} + 2SO_4^{-2} + 16H^+ + 14e^-, \; E = -0.362$$

Effect of Concentration of Oxidizing Reagents on the Organic Sulfur Removal

Chemical oxidations of pre-cleaned coal were conducted with different concentrations of potassium permanganate at room temperature for one hour, then washed by hot water at 80°C for one hour. The results are shown in Figure 1. A greater organic sulfur reduction was expected with the increase in the concentration of potassium permanganate, 54.6% of the organic sulfur was removed with 10% of $KMnO_4$, compared with 33.3% removal with 4% $KMnO_4$. Lower concentrations than 4% $KMnO_4$ had little or no effect.

Figure 1 reflects the variation of different forms of sulfur in coal with increasing concentration of the potassium permanganate. It appears that total sulfur decreased gradually within the whole range of concentrations, but the pyritic sulfur decreased sharply with the increase 4% and then decreased more slowly with $KMnO_4$ concentrations from 4% to 10%. The sulfate sulfur, on the other hand, increased sharply with the increase of concentration from 0 to 4% and of concentration from-0% to then slowly from 4% to 10%. In contrast, the organic sulfur changed very little at the lower concentrations of potassium permanganate and decreased quickly with increasing the concentration from 4% to 10%. These results indicate that the pyritic sulfur was easier to oxidize than the organic sulfur at the lower $KMnO_4$ concentrations (2-4%), while at higher concentrations (i.e. 6% or more), the organic sulfur was as effectively removed. This might be due

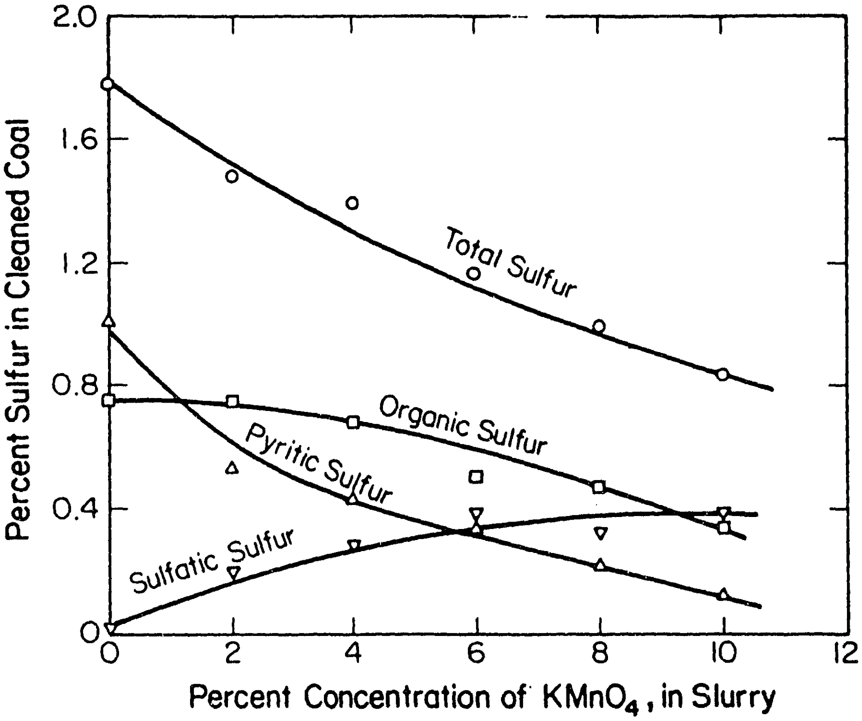


FIG 1. Effect of concentration of $KMnO_4$ on sulfur content of cleaned coal

to better accessibility of potassium permanganate to pyrite than to organically bound sulfur.

Effect of Reaction Time on Organic Sulfur Removal

Table 3 and Figure 2 show the results of changing the oxidation time with 10% potassium permanganate on pre-cleaned coal at room temperature and atmospheric pressure. The reaction time was varied between 0.5 and 2.5 hours. The oxidized samples were washed with cold water at room temperature for one hour. From Table 3, about 50% of organic sulfur was removed with 1.5-hour chemical treatment. This reaction time of 1.5 hr. seems to be the "optimum" for this reaction. The results in Table 3, in terms of reaction time and percent of organic sulfur rejection, are lower than those in Figure 3, where hot water was used in the washing step.

TABLE 3. Effect of reaction time on chemical oxidation for organic sulfur removal

Reaction Time,hours	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Organic Sulfur Removal%
0	1.79	1.01	0.02	0.76	---
0.5	1.06	0.22	0.35	0.49	35.5
1.0	0.99	0.23	0.31	0.45	40.8
1.5	0.94	0.24	0.32	0.38	50.0
2.0	0.94	0.23	0.33	0.38	51.3
2.5	0.90	0.22	0.31	0.37	50.0

Figure 2 shows that organic sulfur decreased quickly during the first hour, and down to 0.38 (i.e. 50% reduction in organic sulfur) after 1.5 hours, and then tended to be constant as the reaction time was increased. This indicates that the oxidation reaction might have reached a chemical equilibrium state.

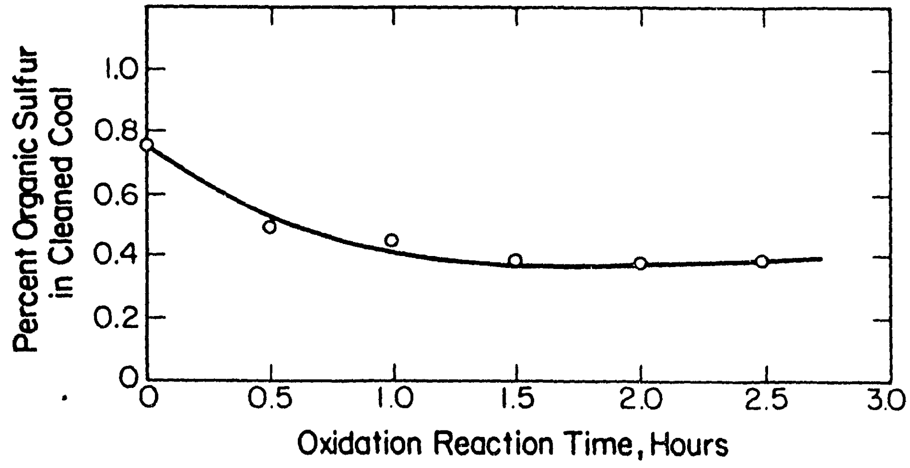


FIG 2. Effect of reaction time on organic sulfur content in cleaned coal, using cold water in the washing step

Effect of the Agitation Speed on the Sulfur Removal

Table 4 and Figure 3 illustrate the effect of agitation speed during the chemical treatment with 10% potassium permanganate on the efficiency of sulfur removal. The chemically treated coal samples were then washed with cold water at room temperature.

TABLE 4. Effect of agitation speed on the chemical desulfurization of Pittsburgh No.8 coal, using 10% $KMnO_4$ and cold water washing

Agitation Speed,rpm.	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Organic Sulfur Removal%
0	1.79	1.01	0.02	0.76	---
625	0.95	0.20	0.30	0.45	40.8
825	0.84	0.20	0.30	0.34	55.3
935	0.84	0.23	0.31	0.30	60.5
1010	0.91	0.23	0.32	0.36	52.6
1100	0.93	0.23	0.34	0.36	52.6

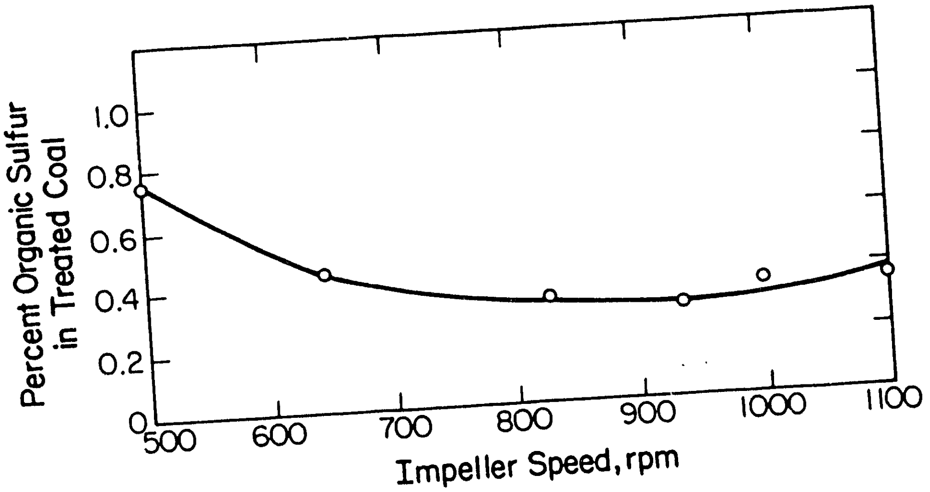


FIG. 3. Effect of agitation speed on the organic sulfur content in treated coal using 10% $KMnO_4$ and cold water wash

These results show that more than half of organic sulfur removal could be expected if the agitation speed was higher than 825 rpm. That indicated the organic sulfur reduction in coal not only depended on the chemical reaction itself, but also on the diffusion factor. Higher rate of transport of the oxidizing agent and the oxidation products to and from the reaction zone was required to enhance the desulfurization process. Hence the idea behind testing various speeds of agitation was to enhance the removal of sulfate sulfur, at higher agitation by attrition. By continuously inhibiting the oxidation products layer from depositing on the coal particle surface through attrition, the leaching process should continue unimpeded. However, the effect of agitation speed on the sulfate sulfur removal appeared to be minimal.

Effect of the Temperature of Washing Water on Sulfur Removal

After chemical oxidation, the coal was washed with water for an hour to split off the oxidized sulfur compounds still attached to the hydrocarbon matrix. Figure 4 shows the effect of washing water temperature on the organic sulfur removal extent. The figure shows that the organic sulfur decreased from 0.45% to 0.34%, while the temperature of the washing water was increased from 22°C (room temperature) to 80°C. Thus, the higher washing temperature enhanced organic sulfur removal, but at a low rate. Using cold water to wash oxidized coal is acceptable if a lower energy consumption is desired. Using cold water in the washing step, about 40% of the organic sulfur could be removed with a magnetic stirrer (Table 3), and 52% to 60% of organic sulfur could be removed using mechanical agitation in one step of treatment (Table 4).

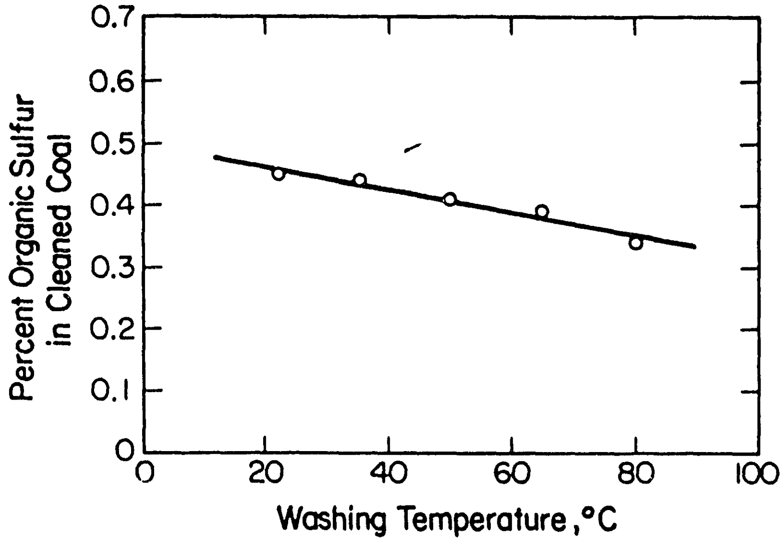


FIG. 4. Effect of temperature of washing water on organic sulfur removal from coal

Effect of the Number of Treatment Steps with 6% $KMnO_4$ on Organic Sulfur Removal

Three successive steps of treatment with 6% $KMnO_4$ were performed. Each treatment step was followed by a washing step with warm water as described earlier, except the third washing step, where cold water (room temperature) was used. After each oxidation and washing step, five grams of treated coal sample were taken for total sulfur, pyrite sulfur and sulfate sulfur analyses. The rest of the treated coal samples went to the next oxidation step. The results are shown in Table 5 and Figure 5. The results show an increased reduction of all sulfur forms in the cleaned coal after three steps of treatment. It appears that the organic sulfur was decreased to 0.1% and it removal reached 87%, while the total sulfur decreased to 0.42%. Pyritic sulfur decreased to 0.10% after three steps of treatment, but the sulfate sulfur remained at 0.22%.

Figure 5 reflects the different reaction behaviors of organic sulfur and pyritic sulfur. About 66% of pyritic sulfur reacted with $KMnO_4$ and was

TABLE 5. Effect of the number of treatment steps on coal desulfurization with 6% $KMnO_4$

Number of Treatments	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Organic Sulfur Removal%
0	1.78	1.01	0.02	0.75	---
1	1.16	0.34	0.32	0.50	33.2
2	0.76	0.12	0.31	0.33	56.0
3	0.42	0.10	0.22	0.10	86.7

removed in the first treatment step, compared with 34% of organic sulfur reduction and removal. However, the reactivity of organic sulfur with $KMnO_4$ increased substantially in the third treatment step, when the removal of 70% of the organic sulfur was achieved, while the pyritic sulfur removal in the third step was only 16.7%. The cumulative organic sulfur removal of the three treatment steps was 86.7%.

One of the problems encountered in the permanganate desulfurization of coal, was the precipitation of manganese dioxide. This is because the reaction was conducted at alkaline conditions (pH 9.3). The brown precipitate was mixed with the cleaned coal powder and introduced some errors in the sulfur analysis. The relative error due to precipitation would

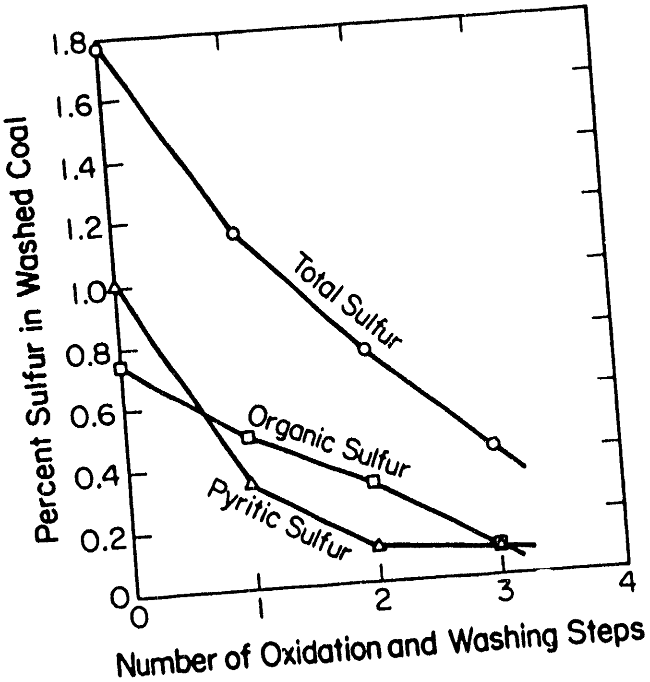


FIG. 5. Effect of number of steps on the sulfur content of chemically cleaned Pittsburgh No. 8 coal

vary depending on the amount of coal in the feed slurry, being lower for the higher coal weight percent in the slurry. To assess the relative error on the results in Table 5, a correction factor was applied. The correction factor was arrived at by determining the coal sample weight before and after the permanganate treatments. For a repeat test of results in Table 5, the total weight of treated coal was 29 grams, while the initial weight of the coal sample feed was 20 grams. The increase in weight, i.e. 9 grams was assumed to be due to the precipitation of MnO_2. Since this experiment was a three-step permanganate treatment. The average MnO_2 precipitation pei one treatment step was 3 grams assuming no major losses in coal due to the chemical treatment, the correction factors for the sulfur analyses were as follows: 23/20 for the first step, 26/20 for the second step and 29/20 for the third step. The corrected sulfur analyses and test results are shown in Table 6. Similar correction factors could presumably be applied to the results of other experiments, but the removal of MnO_2 precipitate would be a better approach.

TABLE 6. Effect of the number of treatment steps on coal desulfurization with 6% $KMnO_4$ using correction factor for the MnO_2 precipitation

Number of Treatments	Total Sulfur%	Pyritic Sulfur%	Sulfate Sulfur%	Organic Sulfur%	Organic Sulfur Sulfur%
0	1.78	1.01	0.02	0.75	----
1	1.33	0.39	0.37	0.58	22.7
2	0.99	0.16	0.40	0.43	43.6
3	0.61	0.15	0.32	0.15	80.0

Removal of MnO_2 precipitate requires mild acid treatment to solubilize it. However, if the permanaganate desulfurization treatment is conducted at acidic conditions, precipitation of the manganese dioxide should not take place. Future experiments in this research program will be conducted at low pH to test this concept and to avoid the precipitation problem.

SUMMARY AND CONCLUSIONS

This paper presents a promising chemical coal cleaning approach for reducing the organic sulfur in Ohio coal which has a high commercial potential. From the previous results and discussion, the following conclusions can be made:

1. Potassium permanganate has a significant effect on the organic sulfur removal through mild chemical oxidation at ambient conditions. A substantial reduction of the organic sulfur, up to 87%, has been achieved.

2. Potassium permanganate, as an oxidizing reagent having higher oxidation potential, is more effective for organic sulfur +removal than sodium hypochlorite.

3. Increasing the concentration of the oxidizing reagent ($KMnO_4$), the number of treatment steps, and the intensity of agitation, will enhance the organic sulfur removal. Most of pyritic sulfur can be oxidized with a lower concentration of $KMnO_4$, or at the first step of oxidation.

4. The chemical oxidation of Ohio coal can be successfully con-

ducted at room temperature and atmospheric pressure using inexpensive commercial oxidizing reagent and followed by a washing step with cold water.

5. The combined approach of pre-cleaning the raw coal with heavy medium separation, followed by three steps of chemical cleaning using 6% $KMnO_4$, reduced the total sulfur from 3.5% to 0.42%, the pyritic sulfur from 2.8% to 0.1%, and the organic sulfur from 0.74 to 0.1%. Thus a premium quality coal could be produced from a low-value high sulfur coal by this approach. This process is simple, easy to control, and is very promising novel technique which has high technical, economic,and commercial potential.

6. The solids recovery, volatile matter and heating value of the cleaned coal as well as the environmental effects will be studied in the future experiments.

ACKNOWLEDGEMENT

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2. POSSIBLE METHOD FOR REGENERATION OF POTASSIUM PERMANGANATE FOR SPENT SOLUTIONS

After the washing step with HCl or HNO_3, the manganese salt solution is obtained.

Alternative 1 Precipitation of MnO_2 and its further oxidation to permanganate

a) $2MnCl_2 + 4KOH = 2Mn(OH)_2 + 4KCl$

b) $2Mn(OH)_2 + O_2$ (atmosphere) $= 2MnO_2 + 2H_2O$

c) $2MnCl_2 + 4KOH + O_2 = 2MnO_2\downarrow + 4KCl + 2H_2O$ (1)

$$4MnO_2 + 3O_2 + 4KOH \underset{\text{fusion}}{\overset{\text{heat}}{=\!=\!=\!=\!=\!=}} 4KMnO_4 + 2H_2O \quad (2)$$

and/or potassium chlorate

Most used route commercially

$$4MnO_2 + 3O_2 \overset{\text{heat}}{=\!=\!=\!=} 2Mn_2O_7;\quad 2Mn_2O_7 + H_2O = \underset{\text{(permanganic acid)}}{2HMnO_4}$$

Alternative 2

Mn^{2+} salt + nitric acid + sodium bismuthate

A two-step reaction:

a) $2Mn^{2+} + 5BiO_3^- + 16H^+ = 2HMnO_4 + 7H_2O + 5Bi^{3+}$

b) $2HMnO_4 + 2KOH = 2KMnO_4 + 2H_2O$

$2Mn^{2+} + 5BiO_3^- + 2KOH + 16H^+ = 2KMnO_4 + 9H_2O + 5Bi^{3+}$ (3)

Other Alternatives

3-Oxidation of MnO_2 or Mn salt by air, Cl_2, persulfate, ozone or other oxidizing agents, or electrolysis.

4-Lead dioxide in concentrated H_2SO_4 or HNO_3 and periodates convert manganous salts directly into permanganate.

Form B

GRANTEE:	Ohio State University	CONTRACT NO. CDO/R-86-78/91	REQUEST NO. 6
AGREEMENT TITLE:	Removal of Organic/Inorganic Sulfur from Ohio Coal	DATE: 06/14/89	
ADDRESS:	2070 Neil Ave. Columbus, Ohio 43210	FEDERAL TAX I.D. NO.: 31-602-5986-W	

Budget Categories	Total Project Budget	Total Expenditures Through Last Invoice* FROM: 12/01/86 TO: 06/30/88	This Period Expenditures Only** FROM: 07/01/88 TO: 05/31/89	TOTAL	Balance	Non-DOD Project Funds Expended to Date	
Personnel (attach time sheets)	73,830.00	45,735.28	31,194.56	76,930	(3,099.84)	50,152.00	50,152
Fringe Benefits	11,505.00	6,990.65	5,160.05	12,151	(645.70)	21,876.68	21,876
Travel (attach receipts)	3,000.00	2,880.94	201.00	3,082	(81.94)	0.00	
Equipment (attach receipts or lease agreement)	9,000.00	8,391.91	0.00	8,342	608.09	0.00	
Supplies (attach documentation)	10,266.00	5,525.29	1,338.73	6,864	3,401.98	462.44	462
Contractual (attach invoices)					0.00	0.00	
Total Direct Charges	107,601.00	69,524.07	37,894.34	107,418	182.59	72,491.12	72,491
Indirect Charges	42,399.00	26,286.82	16,294.77	42,584	(182.59)	31,171.18	31,171
Total	150,000.00	95,810.89	54,189.11	150,000 OCDO	0.00	103,662.30	103,662 OSU

* This includes funds expended from inception of Grant Agreement through the previous monthly reporting date.

** This includes funds expended during the current reporting period only.

*** Graduate student fees are included in "Fringe Benefits".

**** Account Number 529722 ****

Final Nos.

6/21/89

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