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Edward Charles Patterson

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The effect of chemical pretreatment on the desulfurization of coal by selective oil agglomeration

by

Edward Charles Patterson

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ABSTRACT

An experimental investigation was carried out to improve selective oil agglomeration as a method for separating coal and mineral particles. The effectiveness of a special method of chemical pretreatment for enhancing the rejection of inorganic sulfur and ash by subsequent agglomeration was studied. The special treatment used hot alkaline solutions containing dissolved oxygen to oxidize pyrite, reducing its tendency to agglomerate with finely divided coal particles.

Sodium carbonate was found to be a very effective alkali for use in the pretreatment reaction. There appeared to be an optimum sodium carbonate concentration (1 or 2 wt %) for the rejection of inorganic sulfur by oil agglomeration. By pretreating coal containing 4.96% inorganic sulfur and 15.7% ash with a 2.0 wt % sodium carbonate solution at $80^{\circ}C$ for 15 min, 87.9% of the inorganic sulfur and 63.6% of the ash were removed by selective agglomeration with a heavy fuel oil mixture.

Chemical pretreatment was found to be more effective in reducing the inorganic sulfur content of minus 400 mesh coal than of minus 100 mesh coal.

The chemical pretreatment reaction only leaches small portions of the pyrite from the coal and serves mainly to develop a hydrophilic surface on the pyrite particles. The method of chemical pretreatment followed by selective oil agglomeration was found not to be equally effective on all of the kinds of coal tested.

Chemical pretreatment was found to be a very effective method of suppressing the agglomeration of relatively pure, finely divided pyrite.

INTRODUCTION

The nation's requirements for energy are expanding at a tremendous rate. By the year 2000, the total annual energy demands are expected to reach 135 quadrillion Btu, more than doubling the energy consumption for 1970 (13). In view of the recent shortages of petroleum and natural gas, it is evident that the domestic reserves of these fossil fuels will not continue to sustain the demands for energy indefinitely.

Estimates of domestic coal reserves published by the U.S. Geological Survey establish a resource base of 3.2 trillion tons, about half of which is generally considered recoverable (24). Assuming a 5% growth rate in the production of coal, the life of these reserves has been estimated at about 330 years. Due to its abundance and long term availability, coal is destined to emerge as a prominent source of energy.

Each year, coal fired power generating stations emit an estimated 12 million tons of sulfur oxides into the atmosphere (13). This corresponds to about one-half of all sulfur oxides discharged annually from manmade sources. In order to reduce the severe enviornmental costs associated with the emission of sulfur oxides, a variety of pollution control codes have been promulgated. As a result of these air quality regulations, much effort has been made to improve the technology of sulfur oxides emission control. These emissions are presently controlled primarily by: (1) flue gas desulfurization, (2) coal beneficiation, and (3) burning low sulfur coal.

The combustion of low sulfur coal is a very short term solution to the problem. Low concentrations of sulfur oxides present in flue gas and the tremendous gas flow rates encountered in large boilers present a myriad of problems. In view of these difficulties and the often prohibitive costs of stack gas scrubbers, physical and chemical coal beneficiation processes appear more economically promising.

Coal beneficiation involves the removal of some of the ash and sulfur from the coal prior to combustion. The organic sulfur, being molecularly bound to the carbonaceous matrix, cannot be removed by simple mechanical beneficiation methods. The so-called "inorganic sulfur," consisting of the pyritic and sulfate forms can be removed by mechanical separation techniques commonly employed by the mineral industry.

The separation techniques presently used in commercial coal preparation facilities are largely based upon the difference in densities between the carbonaceous and mineral matter. These techniques are generally effective only on relatively coarse coal. Jigs, tables, and many heavy medium processes cannot efficiently clean coal smaller than 35 mesh (22). Unfortunately, many coals contain large amounts of finely disseminated pyrite.

It then follows that large pyrite reductions can be effected only by liberation of the pyrite through fine crushing and subsequent separation of the coal and mineral matter. Currently, hydrocyclones and froth flotation are most often used commercially for cleaning fine sized coal. The hydrocyclone has been found to provide very good pyritic sulfur reductions in the range of sizes from 35 to 150 mesh. In the minus 150 mesh fraction however, the hydrocyclone yields only moderate reductions in pyritic sulfur content (22). Froth flotation is the most important method for cleaning the 35 to 200 mesh fraction. Flotation however, becomes less effective in the minus 200 mesh size range or when there is considerable clay slime present (8).

Another method of recovering and cleaning fine sizes of coal is a process known as selective oil agglomeration. In this process, finely divided coal particles are agglomerated while in aqueous suspension, using oil as a bridging liquid for the coal particles. Ideally, the mineral material is not agglomerated with the coal. The agglomerated product may then be recovered on a sieve, while the fine suspended mineral matter washes through. Since much of the mineral matter has been removed, the agglomerated coal contains less ash and inorganic sulfur than the feed coal. Like froth flotation, the principles of selective oil agglomeration are firmly based upon the surface chemistry of the solid particles involved.

The purpose of this investigation was to develop a good understanding of selective oil agglomeration as a technique for desulfurizing and deashing low grade bituminous coals. As an improvement of the oil agglomeration process, a novel chemical pretreatment for the feed coal was developed. The special pretreatment consisted of treating finely divided coal with a hot oxidizing solution of sodium carbonate through which air was bubbled continuously. In this manner, the surface of the pyrite was oxidized, rendering it hydrophilic. Solids with hydrophilic surfaces are not agglomerated by the oil and remain in suspension. Chemical pretreatment greatly increased the ash and inorganic sulfur reductions that could be achieved by subsequent oil agglomeration. Basically, this investigation took the form of a parametric study of the oil agglomeration and chemical pretreatment processes.

The results presented in the pages to follow indicate that chemical pretreatment followed by selective oil agglomeration is an effective method of recovering and cleaning fine coals. The conclusions drawn from this investigation can be used as a basis for the design of a prototype fine coal beneficiation process.

LITERATURE REVIEW

Selective Oil Agglomeration

Principles of selective oil agglomeration

The selective agglomeration of finely divided solids in liquid suspension is based upon the difference in wettability of solids by different liquids (36). Finely divided solids may be agglomerated by agitating with the suspension a small quantity of an immiscible liquid that wets the solids better than the suspending liquid. The agglomerating liquid causes the solid particles to stick together, forming agglomerates which are substantially larger than the original suspended solids. If some of the particles are not preferentially wetted by the agglomerating liquid, they will remain in suspension. Since the agglomerates are larger than the individual particles, they may be easily retained on sieves. The remaining suspended material is washed through, along with the suspending liquid. With a judicious choice of the agglomerating liquid and agitation conditions, it is possible to effect a fractionation of complex mixtures of minerals (32).

The principles of simultaneously de-ashing and recovering coal fines in aqueous suspension through selective agglomeration with oil were first reported in 1921 by Perrott and Kinney (28,29). In this early investigation, it was reported that vigorous agitation of a slurry of powdered coal, water, and oil resulted in egg shaped granules of a deashed plastic fuel. When oil is introduced into an agitated suspension of coal and water, the hydrophobic coal particles are readily wetted by the dispersed oil droplets. The oil coated coal particles adhere to one another, largely displacing surface moisture to form a mass of small agglomerates. Under proper agitation conditions, larger spherical agglomerates may result (32,36). The agglomerated coal may then be recovered on a sieve, while the tailings containing suspended water-avid mineral matter are washed through. During this process, the coal fines are recovered, desulfurized, and deashed. Many of the problems associated with the handling and transportation of coal fines are eliminated by the size enlargement and reduction in surface moisture which occurs during selective oil agglomeration.

Industrial application of oil agglomeration

Over the years, a number of coal beneficiation processes involving oil agglomeration have been proposed. During the first World War, Walter E. Trent made one of the earliest proposals to use the technique (29). In this proposal, Trent suggested applying selective agglomeration to powdered coal, prior to combustion, in an attempt to reduce slag formation. The developmental work carried out by the Bureau of Standards and later by the Bureau of Mines resulted in the Trent Process. The process required relatively large quantities of oil, ranging from 25 to 40% based upon the weight of coal (28). Although the ash rejection was quite satisfactory, the granular coal product was very plastic and presented great difficulties in handling (23). The Trent Process appears not to have advanced beyond the early experimental stage.

In 1952, details were released concerning the Convertol Process, developed by Bergverksband, a German research organization run by the Coal Operators Association of the Ruhr Valley (23,34). The original process outlined by Muschenborn (27) began by mixing coal, oil, and water in a high-shear agitator. The slurry was then passed through a kneading pump to a dispersion mill and finally to a centrifuge where the agglomerated coal was retained on the screen basket. The tailings were ejected through the perforations in the screen. Later, at the Second Coal Preparation Congress held at Essen, Germany, Lemke (21) described a simplified Convertol Process consisting of only a high-shear agitator and a centrifuge.

Fraser (17) reported that a semicommercial pilot plant for demonstrating the Convertol Process was constructed at the Hanover Colliery near Essen. The plant employed a Pallman dispersion mill for agitation followed by a centrifuge for recovering and dewatering the agglomerated product. The Pallman mill not only provided excellent dispersion of the oil, it also guarded against oversize coal particles. Following the demonstration period, the pilot unit was incorporated into commercial operation. Typically, the plant processed about 4 ton/hr of dry solids in the form of a slurry containing 30 to 50 wt % solids. Using 3 to 10% oil based on the weight of solids, the moisture content of the product ranged from 8 to 10%.

In 1958, Brisse and McMorris (3) presented the results of a similar Convertol pilot plant built by U.S. Steel Corp. near its Alpheus preparation plant in Gary, West Virginia. The plant was designed to clean and recover coal fines produced at the facility and continued to operate for several years. Although the plant produced a relatively low ash, low moisture coking coal, the plant was closed in 1963 due to the economics of the operation (15).

In recent years, several processes involving oil agglomeration have been suggested and are in various stages of development. Bergbau-Forschung GmbH is developing a process known as the Olifloc Process and is currently operating a 3 ton/hr pilot plant near Essen (15). Work done by the National Research Council of Canada has led to the development of the Spherical Agglomeration Process (8,10,32); however, the process is still in the laboratory stage. In India, a 2 ton/hr oil agglomeration unit is being built by Bharat Coking Coal Ltd. for upgrading fine coal slurries produced at its Lodna preparation plant (30).

Shell International Petroleum Co., Ltd. has developed a device specifically for the production of large spherical agglomerates (36). The device, known as the Shell Pelletizing Separator, consists basically of a cylindrical agitator rotating inside a cylindrical shell about twice its diameter. Prototype units have been able to produce low ash coal pellets 3 to 5 mm in diameter from waste coal slurries containing up to 40% ash. In 1972, Mitsui Mining in Japan began operating a 10 ton/hr commercial unit.

Recovery of combustible material

Great interest has been shown by a number of research groups in developing selective agglomeration as a method for recovering the tremendous quantities of coal fines generated by modern preparation plants. The results of their investigations have shown that a number of factors may affect the degree of recovery of combustible material.

The type of oil

Many types of oil may be used in the agglomeration of fine coals; however, all oils are not equally effective. From the results of experiments performed using various oils and other hydrocarbons, Sun and McMorris (34) reported that the extent of recovery of combustible material could be predicted roughly from the specific gravity of the oil. Using a high speed Waring blender for agitation and a 100 mesh screen for recovering the agglomerated product, it was found that the most effective materials had specific gravities in the range from 0.702 to 0.850. The use of hydrocarbons and oils with specific gravities outside of this range resulted in moderate to poor yields of combustible material. It was thought that the extremely heavy oils were too viscous to be sufficiently dispersed in the pulp, while the very light hydrocarbons were not sufficiently hydrophobic. Similarly, Perrott and Kinney (29) felt that high recovery would be expected from oils which do not readily form emulsions with water.

Min (25) performed similar experiments using oils with specific gravities ranging from 0.807 to 0.946. All of the oils tested, including kerosene on the light end and No. 5 heavy fuel oil on the heavy side, were found to be very effective in agglomerating fine coals obtained from various sources. The type of oil seemed to have little effect on the recovery of combustibles.

Capes et al. (9) were able to achieve high yields of combustible material with a variety of oils including heavy residual fuel oils such as Bunker C. It was also pointed out that the inability of Sun and McMorris (34) to agglomerate coal fines with heavy fuel oils was largely due to hydrodynamic problems. Sun and McMorris used very short agitation periods of about 1 min for all oils. The experiments done by Capes et al. as well as those done by Min used periods of agitation as long as 10 min.

The amount of oil   A preliminary economic assessment of the oil agglomeration process has shown that it is so sensitive to oil and coal costs that capital and fixed costs would have minimal effect on business decisions (12). The economic viability of the oil agglomeration technique is thus heavily dependent upon achieving a high recovery of combustible material using a minimum amount of oil.

In order to study the effect of the amount of oil on the recovery of clean agglomerated coal, Min (25) performed several experiments using heater oil (sp gr 0.811). In these experiments various amounts of heater oil were added to a 4 wt % suspension of minus 100 mesh solids, agitated with a high speed blender. As the oil concentration increased from 1.6 to 14% based on the weight of coal, the yield of combustibles increased monotonically from 25% to about 90%. Work done by Sun and McMorris (34) using kerosene (sp gr 0.801) and coals obtained from several mines yielded similar results. In the range of kerosene concentrations from 2 to 6%, the combustible recovery rose steadily to approximately 95%. As the kerosene concentration increased from 6 to 10%, only a slight increase in recovery resulted.

Slurry concentration The slurry concentration or pulp density does not appear to be a critical factor in recovering fine coals by selective oil agglomeration. In their experiments, Capes et al. (9) were able to successfully agglomerate slurries containing up to 60 wt % solids. Using 8% heater oil (sp gr 0.811), Min (25) was able to obtain high yields of combustible material over the range of pulp density from 2 to 15 wt % solids. The recovery of agglomerated product increased only slightly as the pulp density was increased to 15 wt %. Sun and McMorris (34) reported similar results using kerosene (sp gr 0.801) and No. 2 fuel oil (sp gr 0.848) to agglomerate slurries containing 5 to 40 wt % solids. These results are in stark contrast to pulp densities normally encountered in froth flotation, where slurry concentrations of 3 to 5 wt % solids are recommended (10).

Operational variables A number of operational variables such as the degree of agitation, the retention time, and the method of introducing the oil to the slurry appear to affect the recovery of combustible material. Since hydrocarbons do not spread spontaneously on wet coal surfaces, the distribution of the oil is highly dependent on the agitation conditions (5).

Min (25) conducted several experiments using a kerosene-No. 5 heavy fuel oil mixture (sp gr 0.830) and a variable speed agitator. When the oil mixture was added directly to the agitated slurry, it was found that the yield of agglomerated coal increased from approximately 40% to about 90% as the agitation speed increased from 350 to 1150 rpm. It should also be noted that the use of emulsified oil resulted in essentially instantaneous agglomeration of fine coal. With an agitation speed of 1050 rpm, the yield of agglomerated coal remained relatively constant at 85% for retention times ranging from 30 sec to 30 min. When straight oil was introduced to the slurry under identical agglomeration conditions, the yield rose from 35% at 30 sec to 85% at 3 min of agitation.

Size enlargement and moisture reduction

The form of the agglomerated product is highly dependent upon the amount of oil used and on the degree and type of agitation employed (32). Small quantities of oil generally lead to the formation of lightly textured flocks of coal particles (7). As the amount of oil is increased to some critical value, the flocks collapse to form discrete spherical agglomerates. With the addition of still larger quantities of oil, a more or less fluid mixture of coal particles in oil is formed. Spherical agglomerates represent by far the most desirable form for the agglomerated product.

Although nearly any agitation system can be used for agglomeration, not all agitators lead to the formation of spherical agglomerates. Sirianni et al. (32) have used devices such as high speed blenders, colloid mills, and reciprocating shakers to agglomerate finely divided solids. In their work, it was reported that high speed blenders and colloid mills provided excellent dispersion of the oil; however, the high shear form of agitation led to the formation of very small, irregular agglomerates, generally much smaller than 1 mm in diameter. Using a reciprocating shaker operating in the range of 150 to 600 strokes/min, highly spherical agglomerates as large as 2 mm in diameter were produced. Agitators with a motion similar to that of a paint shaker also produced excellent spherical shapes. Using an agitator similar to the Shell Pelletizing Separator, Min (25) was able to produce coal agglomerates up to 1 cm in diameter. Other than the general lack of success found in using high shear agitation, there is little information available on which to base the design of an agitator for producing large spherical agglomerates.

Besides alleviating many of the problems associated with handling coal fines, the resultant size enlargement also aids in reducing the moisture content of the product. Capes et al. (10) demonstrated the ease of dewatering coal fines following selective agglomeration in experiments involving minus 28 mesh coal and 3% diesel oil. A filter cake of the original suspended coal prior to agglomeration was found to contain about 24% moisture. Following agglomeration however, a similar filter cake composed of microagglomerates less than 1 mm in diameter contained only 9 % moisture. Agglomeration of the coal fines also considerably increased the rate of filtration.

The production of large spherical agglomerates or the subsequent pelletization of the microagglomerates could totally eliminate the need for filtration. According to a model described by Capes (7), the volume of surface moisture per volume of agglomerated solids is related inversely to the diameter of the agglomerates. In other words, an increase in the size of the agglomerates would lead to a general reduction in the moisture content of the product. Large spherical agglomerates could then be dewatered by sieving, without the need for thermal drying or filtration.

Desulfurizing and deashing fine coals

At present, most of the interest being shown in selective oil agglomeration is in its application as a beneficiation method for low grade coals and waste coal fines. Considerable work has been done in an attempt to reject most of the ash and sulfur containing constituents from the fine coal. The extent to which mineral impurities may be rejected is dependent mainly upon the physical chemistry of the surfaces involved, the state of subdivision of the particles, and the type of oil or hydrocarbon used in selective agglomeration.

The type of oil

The extent to which ash and sulfur containing minerals can be separated from the coal during selective agglomeration appears to depend upon the type of oil or hydrocarbon used. Starting with coal containing 6.1% total sulfur and 21.1% ash, Capes et al. (8) were able to achieve a 76% reduction in ash and a 58% reduction in total sulfur using Varsol (sp gr 0.778) as the agglomerating oil. The use of other light oils such as kerosene yielded a similar quality of product. However, when a mixture of 50% Bunker C fuel oil and 50% kerosene was employed, reductions of only 34% in ash and 25% in total sulfur were obtained. Agglomeration with light coal tar yielded a product of even poorer quality.

Working with fuel oil blends of constant specific gravity, Min (25) found that the ash and sulfur reductions depended upon the particular heavy fuel oil used in the blend. The use of oil blends containing either light or heavy No. 6 fuel oils resulted in poor rejections of ash and sulfur. Results reported by Sun and McMorris (34) generally agree with those of Capes et al. (8).

The ability of a particular oil or hydrocarbon to reject mineral impurities cannot be predicted easily using physical properties such as viscosity or specific gravity. Most workers agree that the heavy residual fuel oils are not very selective and tend to agglomerate mineral particles along with the coal. Some investigations have shown that the use of hot coal slurries and preheated Bunker C fuel oil does not greatly affect the ash and sulfur contents of the product (8). Thus, a reduction in the viscosity of the fuel oil does not lead to a high quality product. Capes et al. (10) believe that the heavier fuel oils contain functional groups which are able to condition the ash constituents, rendering them hydrophobic and causing them to agglomerate along with the carbonaceous fraction. Although the light hydrocarbons and oils tend to produce low ash and sulfur products, several anomalous results have been reported. As an example, McMorris (23) found that all of the types of gasoline (sp gr 0.712-0.716) tested yielded products of poorer quality than those obtained with light coal tars.

Particle size distribution of the coal   Results of coal microstructure studies by Greer in (38) indicate that a significant portion of the pyrite found in Iowa coals is present as finely disseminated particles as small as submicrometers in diameter. This indicates that much of the pyrite can be removed from the coal only through liberation by fine grinding and subsequent separation of the coal and pyrite particles.

The effect of various comminution methods on the removal of pyritic sulfur from coal by oil agglomeration was investigated by Min and Wheelock (26). In these studies, oil agglomeration was more effective in removing pyrite from coal samples which had been ground in a ball-mill to pass a 400 mesh screen than from samples which had been ground to only minus 35 mesh size in a laboratory hammer-mill. When the samples were both chemically comminuted and mechanically crushed, an even larger portion of the pyrite was removed. Although mechanical crushing to fine sizes liberates a significant portion of the pyrite, some of the pyrite remains attached to the coal particles. During chemical comminution, the coal is soaked in a specific chemical agent such as methanol or anhydrous ammonia which causes the coal to fracture along bedding planes and phase boundaries between the coal and pyrite. In this manner, chemical comminution liberates some of the pyrite that mechanical crushing could not separate from the coal.

Removal of Pyritic Sulfur from Coal

Hydrophobic nature of pyrite

Selective agglomeration of finely divided coal with oil does remove some of the pyritic sulfur from coal; however, most workers generally agree that the removal of pyrite is considerably more difficult than the removal of other minerals such as clay, shale, or calcite. As mentioned earlier, during oil agglomeration hydrophilic mineral particles are not preferentially wetted by oil and remain largely suspended in the aqueous phase. Unfortunately, it has been observed that pyrite has a substantial hydrophobic character and is readily wetted by oil, particularly in fine states of subdivision.

While working on the Trent Process, Perrott and Kinney (29) studied synthetic mixtures of bituminous coal and pyrite in order to determine the percentage of pyrite which could be removed from mixtures in which the pyrite was definitely known to be separated from the coal. Although the compositions of the mixtures were not reported, they found that 60% of the pyrite could be removed from a mixture which was ground to pass a 200 mesh sieve. When the mixture was ground to 600 mesh or finer, essentially none of the pyrite was removed. It was also observed that the pyrite which remained suspended in the aqueous phase retained a considerable amount of oil. In view of these results, Perrott and Kinney concluded that when separation of pyrite from coal occurred, it was primarily due to a mechanical separation based upon the difference in densities between pyrite and coal. In addition to these results, they found that it was possible to agglomerate finely divided pyrite alone, with very little of the pyrite remaining in suspension.

Similar results have been reported by Gaudin (18) in regards to the flotation of pyrite. The mechanistic theory of flotation is based upon the electrokinetic and molecular interactions between the bubbles and mineral particles; however, in practice, froth flotation is generally thought of in terms of the hydrophilic or hydrophobic nature of the particles involved (1,19). In the beneficiation of coal fines, this amounts to ensuring that the coal particles are hydrophobic and the mineral particles are hydrophilic. As a result, in coal flotation the coal particles are collected at the air-water interface of the bubble and the hydrophilic minerals remain suspended in the aqueous phase. The floatability of certain particles may be enhanced by the addition of a reagent known as a collector, which is selectively adsorbed as a monolayer on the particles of interest.

Gaudin (18) reported that clean pyrite could be floated completely with the addition of small quantities of xanthate collectors. The amount of collector introduced was too small to form a complete monolayer even if all of the reagent was adsorbed onto the pyrite. This would indicate that pyrite exhibits some hydrophobic character. Gaudin also reported that the floatability of partially oxidized pyrite particles is greatly reduced.

These findings indicate that the amount of pyrite rejected during selective oil agglomeration could be significantly increased by rendering the pyrite surface hydrophilic. In recent years, a number of research groups have attempted to improve the oil agglomeration technique by altering the pyrite surface through the use of pyrite depressants and chemical reactions. These attempts have been met with varying degrees of success.

The effect of pH and chemical agents on pyrite rejection

In froth flotation, it has long been recognized that certain chemical agents known as depressants reduce the floatability of pyrite by selectively adsorbing onto the pyrite surface (18). Since some collectors can act as depressants over certain pH ranges and conversely, the pH of the slurry can greatly affect the degree to which the flotation of pyrite is inhibited. Although the mechanism of pyrite rejection in oil agglomeration is not the same as that found in froth flotation, the two methods do exploit the surface chemistry of the mineral and coal particles in much the same fashion. In view of this, it would seem that the adsorption of certain chemical agents on pyrite would reduce the extent to which it reports with the coal particles in oil agglomeration.

Capes et al. (11) investigated the effect of several pyrite depressants suggested in froth flotation literature on the rejection of pyritic sulfur from coal during agglomeration. The depressants were added to the slurry at levels corresponding to 1 lb/ton of dry solids. Agglomeration was then carried out in natural, acidic, and basic pH ranges. Of the depressants tested at natural pH levels, only sodium cyanide, potassium ferrocyanide, potassium ferricyanide, and sodium carbonate resulted in increased rejection of sulfur. At basic pH levels, only potassium ferrocyanide and potassium ferricyanide proved effective in rejecting additional sulfur from the agglomerated product. None of the depressants were found to be effective in the acidic pH range. When the most effective depressants were introduced at their optimum pH conditions, only about 50% of the pyrite could be removed from coal which had been crushed to a top size of 50 microns (i.e. about 270 mesh).

In a similar study, Min (25) investigated the effect of sodium carbonate, ferric chloride, and sodium silicate on the rejection of ash and sulfur. Although the experiments were conducted over a wide range of pH levels, the chemical agents did not greatly affect the sulfur or ash contents of the agglomerated product. In separate experiments involving slurry pH alone, Min observed that at high pH the product generally contained less pyritic sulfur than those obtained at the natural pH. As a result of zeta potential measurements, Sankar et al. (31) concluded that at certain pH levels the coal and mineral matter tend to be oppositely charged and remain coagulated during agglomeration.

Bacterial oxidation of pyrite

Several bacteria including ferrobacillus ferrooxidans, ferrobacillus sulphooxidans, and thiobacillus ferrooxidans are characterized by their ability to oxidize ferrous ions rapidly in acidic solution (4). It is not entirely understood whether these bacteria use metal sulfides as their sole source of energy or whether they simply oxidize ferrous ions in solution. Some workers claim that the main effect of the bacteria is to oxidize ferrous to ferric sulfate, while others contend that some of the bacteria are able to directly attack pyrite to form ferric sulfate and excess sulfuric acid.

In work reported by Capes et al. (11), it was observed that selective oil agglomeration removed a much larger fraction of the total sulfur from waste coal fines than from run-of-mine coal containing a similar amount of total sulfur. They attributed this to the larger proportion of sulfate sulfur present in the waste coal fines due to weathering of the pyrite by thiobacillus ferrooxidans. Using this information, Capes et al. developed a novel bacterial pretreatment whereby the coal is treated with an iron oxidizing mixture of thiobacillus-ferrobacillus bacteria prior to agglomeration. The pretreatment involved grinding an aqueous slurry of coal and bacteria in a ball-mill for 19 to 96 hr. Selective agglomeration of the pretreated coal with Varsol typically resulted in rejection of 80 to 90% of the pyrite. It was also noted that very little of the pyrite was actually oxidized to sulfate during the process. As a result, it was concluded that the enhanced rejection of pyrite was not due to the leaching of soluble iron, but rather to the formation of hydrophilic iron compounds at the pyrite-water interface. In other words, the pyrite surface was rendered hydrophilic and was no longer preferentially wetted by the oil.

Chemical pretreatment of coal

It is also possible to oxidize pyrite in basic solutions containing dissolved oxygen (4). Many different alkalis have been studied in hydrometallurgical investigations and a number of reactions have been proposed. Forward and Halpern (16) reported that pyrite is oxidized by solutions of sodium carbonate containing dissolved oxygen in the following fashion:

$$2\ FeS_2 + 7\tfrac{1}{2}\ O_2 + 7\ H_2O = 2\ Fe(OH)_3 + 4\ H_2SO_4 \qquad (1)$$

$$4\ H_2SO_4 + 8\ Na_2CO_3 = 4\ Na_2SO_4 + 8\ NaHCO_3 \qquad (2)$$

When pyrite is oxidized with a sodium hydroxide solution containing dissolved oxygen, Stenhouse and Armstrong (33) reported that the products of the reaction are sulfate ions and iron oxides in the form of Fe_2O_3 and Fe_3O_4. It was also noted that the iron oxides form a stable layer around the pyrite particle. Tai et al. (35) have proposed the following reactions for the oxidation of pyrite in oxygen-bearing caustic solutions:

$$FeS_2 + 15/4\ O_2 + 2\ H_2O = \tfrac{1}{2}\ Fe_2O_3 + 2\ H_2SO_4 \qquad (3)$$

$$2\ H_2SO_4 + 4\ NaOH = 2\ Na_2SO_4 + H_2O \qquad (4)$$

Reactions (1) through (4) seem to indicate that the sole purpose of the alkali is to neutralize the sulfuric acid and force reactions (1) and (3) to the right (35). Since the mechanism of pyrite oxidation in oxygen-bearing solutions is not clearly defined, it is highly likely that the alkali plays other significant roles in the actual oxidation step.

Min (25) used reactions of this type to chemically pretreat coal in an attempt to render the pyrite hydrophilic through oxidation of its surface. Although it has been demonstrated that large amounts of pyrite can be leached from coal using solutions of sodium carbonate or sodium hydroxide under relatively high temperatures and pressures (15,35), Min utilized this chemistry under very mild conditions to achieve only a surface oxidation of the pyrite.

In his experiments, Min chemically pretreated minus 35 mesh coal with alkali solutions containing 0.1 to 0.2 wt % alkali. The pretreatment was carried out in a small chemical reaction flask at atmospheric pressure and 80°C for 5 min. Oxygen was supplied to the reaction by bubbling air through the slurry. Pretreatment with alkalis such as sodium carbonate, sodium hydroxide, calcium oxide, and calcium hydroxide followed by agglomeration of the slurry with a fuel oil mixture (sp gr 0.830) containing kerosene and No. 5 heavy fuel oil resulted in total sulfur reductions ranging from 34 to 42%. The agglomeration of a similar coal slurry containing sodium carbonate, but not pretreated, resulted in a 26% reduction in total sulfur. From this data, it is not apparent exactly how much pyrite was rejected; however, it does indicate that chemical pretreatment does increase the amount of sulfur which is rejected during selective oil agglomeration.

Chemical pretreatment also appears to increase the amount of pyrite rejected during froth flotation of coal fines. Work done by Min (25) using the same pretreatment method described above yielded very similar results when froth flotation was used to recover the coal instead of oil agglomeration. The results of work done by Le (20) on the floatability of pyrite and coal indicate that the chemical pretreatment step greatly reduced the floatability of pyrite, while reducing the floatability of coal only slightly. In this study, Le performed the pretreatment in the same manner as Min (25), but used a residence time of 30 min and a 10 wt % sodium carbonate solution. An examination of untreated and chemically pretreated pyrite particles by scanning electron microscopy indicated that there were no marked differences between the two types of particles (37). As a result, it would appear that chemical pretreatment affected only the surface of the pyrite.

EXPERIMENTAL INVESTIGATION

Materials and Equipment Used

The coals used as feedstock in this investigation were obtained from several different mines. The names and sources of these coals are presented in Table 1. Since the ash and sulfur contents of these coals are quite variable, they are provided in conjunction with the "Experimental Conditions and Results." With the exception of Illinois No. 5 coal, all of the coals were obtained as run-of-mine samples. The Illinois No. 5 feedstock had been washed in a jig type preparation plant.

The pyrite used in the Group II experiments was carefully hand-picked from the Iowa State University coal preparation plant refuse, produced in beneficiating coal from the same seam as Scott coal. Chemical analysis revealed that the samples contained 86.0% pyrite and 2.13% calcium.

Deionized water was used for all experiments in this study. The water was prepared by running Iowa State University tap water through a 0.2 micron Ultipor filter (Pall Corp., Cortland, New York) and then through a high capacity ion exchange column (Model D8901, hose nipple cartridge,

Table 1. Coals used as feedstock for the experiments

Coal	Source
Scott	Iowa State University Demonstration Mine No. 1, Mahaska County, Iowa
Illinois No. 5	Midland Coal Co., Rapatee Mine, Middle Grove, Illinois
Western Kentucky	No. 9 seam, Fies Mine, Hopkins County, Kentucky
Lovilia	Lovilia deep mine, Monroe County, Iowa

Barnstead Sybron, Corp.).

For size reduction, the following equipment was used:

1. A bench scale Double Roll Crusher (Smith Engineering Works, Milwaukee, Wisconsin) was used to crush coal to 1/4 in. top size.
2. A Mikro-Samplmill (Pulverizing Machinery Division, American-Marietta Co., Summit, New Jersey) was used to crush coal to 60 to 100 mesh top size.
3. A 1.5 gal. ceramic jar ball-mill was used to produce minus 400 mesh coal. The charge consisted of either 2000 g of 1/2 in. stainless steel balls or

1900 g of smooth 3/8 in. by 3/8 in. cylindrical aluminum oxide pellets.

Froth flotation was carried out using a laboratory scale froth flotation cell, the Wemco Flotation Machine (Western Machinery Co., San Francisco, California). Two liters of slurry could be agitated at a speed of 1725 rpm and processed by froth flotation using this cell.

All of the oil agglomeration experiments were performed using a 14 speed kitchen blender (Sears Insta-Blend, Model 400). This blender could provide agitation speeds up to 20,000 rpm.

Chemicals

All of the chemicals used in this investigation were of reagent grade with the exceptions of the 4-methyl-2-pentanol (MIBC) used as the frother in froth flotation and the Skelly B (a mixture of hexanes) used to extract the heavy fuel oils from the agglomerated product prior to chemical analysis. The purities of the MIBC (obtained from Union Carbide Corp.) and Skelly B were as received.

Oils for Agglomeration

The fuel oils used in the agglomeration experiments were obtained from Amoco Oil Company, Chicago, Illinois. The oils, along with various physical properties provided by Amoco are given in Table 2.

Table 2. Physical properties of fuel oils used for agglomerating coal

Oil	Spec. Gravity at 60°F	Viscosity, Centistokes	Pour Point, °F
Heater Oil	0.811	---	---
Furnace Oil	0.855	2.08	-20
No. 200 Fuel Oil, LLS	0.916	13.11	-20
No. 5 Light Fuel Oil, LLS	0.934	49.70	-10
No. 5 Heavy Fuel Oil, LLS	0.946	58.89	0
No. 6 Fuel Oil, LLS	0.959	350.43	+30
No. 6 Fuel Oil	0.973	297.17	+30

Chemical Pretreatment Apparatus

The apparatus used for chemical pretreatment is shown in Figure 1. Air was supplied from the compressed air line in the laboratory and was introduced to the slurry via a gas dispersion tube (12EC Pyrex 39533, ASTM 170-220) at a flow rate in the range from 0.3 to 0.5 cu. ft/min. The uncertainty in the flow rate was due to clogging of the glass frit on the gas dispersion tube. During chemical pretreatment, the slurry was agitated by means of the electric stirrer, which was set at a predetermined speed range. Due to heating of the motor during operation, the actual agitation speed was quite variable. The temperature of the slurry during pretreatment could be maintained relatively close to the desired temperature. All of the temperatures reported in this thesis are accurate to within approximately 2°C. The solution was maintained at nearly constant volume using the reflux condenser.

Experimental Procedures

In all of the experiments to follow, the feed coal was obtained in the form of fairly large lumps of about 1.5 in. top size. These lumps were crushed to 1/4 in. top size

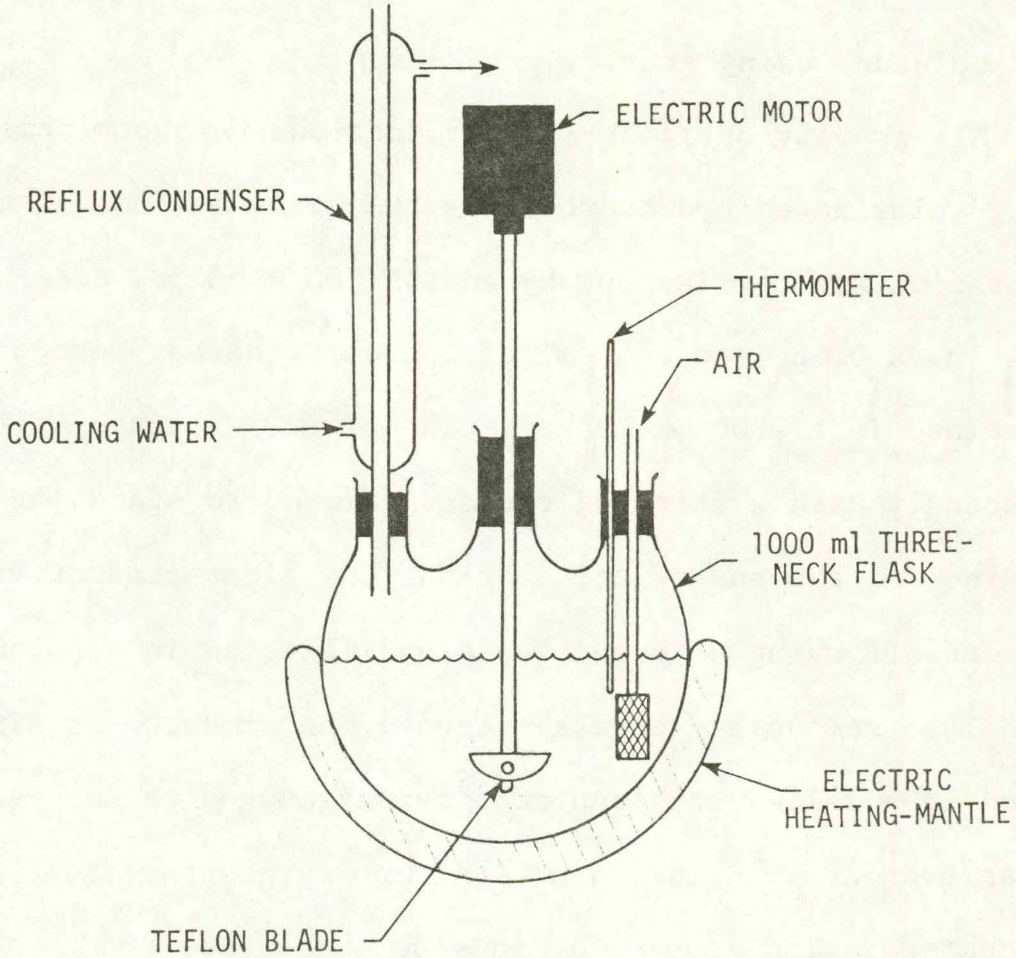

Figure 1. Chemical pretreatment apparatus

using a double roll crusher. This material was then dried in an oven overnight at about 90°C to remove most of the moisture. At this stage of size reduction, the coal was either reduced to 60 mesh top size with the Mikro-Samplmill or precleaned using gravity separation.

All gravity or float-sink separations were performed using chlorinated hydrocarbons as the heavy medium. The separation was carried out by adding 500 g of dry coal (1/4 in. x 0 in.) to 1500 ml of the chlorinated hydrocarbon contained in a 2000 ml beaker. The slurry was then agitated vigorously with a stirring rod and allowed to stand for 30 min. At the end of this period, the float product was skimmed off using a screen ladle and filtered in a Buchner funnel to remove the excess medium. The product was air dried in a well-ventilated hood overnight and then dried in an oven at 90°C for 24 hr. After drying, the float product was also ground to minus 60 mesh size.

Size reduction to minus 400 mesh size was carried out using two different procedures. In the Group I experiments, 100 g of minus 60 mesh coal was placed in the ball-mill along with 1000 ml of deionized water. The ball-mill was then charged with 2000 g of 1/2 in. stainless steel balls and allowed to tumble for 12 hr. In all of the other experiments, 800 g of minus 60 mesh coal was placed in the ball-mill, along with 1500 ml of deionized water. The ball-mill was then charged with 1900 g of aluminum oxide pellets and allowed to tumble for 24 hr. In either case, the fine coal was recovered from the slurry by filtration using a Buchner funnel. The filter cake was dried in an oven at $90^{\circ}C$ for 24 hr. Prior to using the minus 400 mesh coal, the filter cake was ground for a few minutes in a porcelain mortar and pestle. The ball-milled coal was determined to be of minus 400 mesh size by wet screening using a No. 400 U.S. Standard sieve.

Chemical pretreatment was initiated by placing a quantity of the desired coal in the reaction flask of the pretreatment apparatus. About 500 ml of a solution of the desired concentration of alkali was added to the coal. Where largely insoluble alkalis were used in the Group I experiments, 500 ml of deionized water and 10 g of the alkali were added to the coal. The slurry was then agitated at room temperature for a few minutes to ensure complete wetting of all of the coal particles. After obtaining a relatively homogeneous pretreatment suspension, the slurry was heated to the desired reaction temperature whereupon air was bubbled through the slurry. The air was allowed to flow for the desired length of time. At the end of this reaction period, the air flow was discontinued, and the reaction slurry was cooled quickly to room temperature using a cold water bath. The slurry was then agglomerated.

For oil agglomeration, either the chemical pretreatment slurry or a similar suspension of untreated coal and deionized water was placed in the high-speed blender and agitated for 1 min. With agitation continuing, a quantity (10% based on the weight of coal) of some particular fuel oil or fuel oil mixture was added. The agitation was continued for another 5 min at the highest possible speed. The agglomerated coal was poured onto a sieve and allowed to drain. A 60 mesh screen was used to collect agglomerates formed from coarse coals with top sizes of 60 to 100 mesh. Agglomerates formed from minus 400 mesh coal were collected on a 150 mesh screen. The solids were returned to the blender along with 500 ml of fresh deionized water. The suspension was agitated at high speed for 5 min and screened. The solids were filtered in a Buchner funnel to remove excess water and then dried overnight in an oven at 75 to 90°C.

All of the agglomerated products except those obtained through agglomeration with heater or furnace oils were extracted with hexanes (Skelly B) to remove the fuel oil prior to chemical analysis and the calculation of combustible yield data. The extraction was carried out using the standard Soxhlet extraction technique. The dry agglomerated coal was placed in a 43 mm by 123 mm cellulose extraction thimble and was extracted with refluxing hexanes for 2 hr, or until the extract showed no signs of fuel oil. The extracted coal was then dried in an oven overnight at about $90^{o}C$. Volatile matter tests performed on feed coal and agglomerated coal revealed that this procedure removed essentially all of the fuel oil from the coal.

Froth flotation was initiated by placing the pretreatment slurry in the bowl of the froth flotation cell along with an additional 1500 ml of deionized water. In the case of untreated coal, the coal was placed in the cell along with 2000 ml of deionized water. About 1 ml of MIBC was added to the mixture and the slurry was agitated for 5 min. With agitation continuing, the product was floated by introducing air at a rate of about 0.3 cu. ft/min. This was continued until very little coal was seen in the froth.

The product was filtered in a Buchner funnel and dried in an oven overnight at about 90°C.

EXPERIMENTAL CONDITIONS AND RESULTS

In view of the relatively wide variety of experiments performed in this investigation, the experimental program was divided into four groups of experiments. The results of each of these groups of experiments are discussed separately.

Group I consisted of a set of preliminary experiments devised to provide general information about chemical pretreatment and oil agglomeration and to identify certain parameters which might be changed to increase the effectiveness of these techniques. Some of the experiments in this group were aimed at investigating the effects of slurry pH and the type of oil used in oil agglomeration. An attempt was also made to determine the effectiveness of various alkalis for the chemical pretreatment reaction. In order to gather some information concerning the usefulness of chemical pretreatment prior to physical beneficiation, a number of runs were made using various combinations of fine grinding, gravity separation, and chemical pretreatment prior to oil agglomeration or froth flotation.

In Group II, a series of experiments was devised to determine the effect of chemical pretreatment on pyrite alone. Part of the experiments involved oil agglomeration of both untreated and chemically pretreated pyrite. Other experiments were carried out to gather information on the leaching action and surface chemical alterations which affect pyrite during chemical pretreatment.

The objective of the Group III experiments was to study the effects of particle size, alkali concentration, reaction temperature, and residence time used in chemical pretreatment on the amount of ash and inorganic sulfur rejected through oil agglomeration. A very limited study was conducted regarding the use of different oils in agglomeration following chemical pretreatment.

The experiments of Group IV were somewhat similar to those of Group III, but involved the use of different coals as feedstock for the runs. This part of the investigation was devised to determine the applicability of the chemical pretreatment/oil agglomeration technique to the beneficiation of coals from different geographical sources.

Group I Experiments

Effectiveness of different alkalis in chemical pretreatment

Early in this investigation, an attempt was made to determine which of several common alkalis used for chemical pretreatment would prove most effective in rejecting ash and inorganic sulfur from fine coals during oil agglomeration. Besides rejecting large fractions of the ash and inorganic sulfur, an effective alkali should also lead to the recovery of most of the carbonaceous material in the feed coal.

The alkalis chosen in this study were sodium carbonate, magnesium carbonate, calcium hydroxide, sodium phosphate, and potassium hydroxide. Due to the obscure chemistry of the chemical pretreatment reaction and the low solubility of some of the alkalis chosen, it was difficult to arrive at an equitable basis for comparing the various alkalis. As a result, the alkalis were compared on a more or less economic basis and were introduced to the pretreatment apparatus as solutions or suspensions containing about 2.0 wt % alkali.

In all of these experiments, minus 60 mesh run-of-mine Scott coal was used as the starting material. The particle size distribution of this coal is presented in Table 3.

Table 3. Particle size distribution for Scott coal

U.S. Standard screen, No.	Mat'l retained, wt %	Mat'l passing wt %
60	0.00	100.00
100	10.71	89.29
140	29.43	70.57
170	39.21	60.79
200	48.58	51.72
230	53.19	46.81
270	59.81	40.19
325	89.35	10.65
400	91.93	8.07

In each of the experiments, 100 g of Scott coal was pretreated at 50^{o}C for 15 min; the pretreatment period being measured as the length of time air was bubbled through the hot reaction slurry. The coal was agglomerated using 10.0 ml of a fuel oil mixture containing 86.0 vol % heater oil and 14.0 vol % No. 6 fuel oil.

The results of these experiments are presented in Table 4. Throughout this thesis, the reduction in ash, the

Table 4. A comparison of various alkalis used in chemical pretreatment

Treatment	pH_i	pH_f	TIS, %	Ash, %	Reduction in, %		Metal, %	Combust. yield, %
					TIS	Ash		
Feed coal	---	---	4.56	15.72	---	---	0.05 Na 0.17 Ca 0.02 Mg	---
Agglom. only	2.4	2.4	3.93	12.83	18.38	13.82	0.05 Na 0.10 Ca 0.05 Mg	87.36
Na_2CO_3	9.5 9.7	9.4 9.5	1.76 1.99	10.42 9.92	61.40 56.36	33.72 36.89	0.30 Na 0.26 Na	83.65 84.12
$MgCO_3$	6.0 6.3	7.9 8.0	1.54 1.77	11.74 10.68	66.23 61.18	25.32 32.06	0.10 Mg 0.22 Mg	86.60 87.01
$CaCO_3$	5.3 5.2	6.9 6.2	2.33 2.80	11.72 11.00	48.90 38.60	25.44 30.02	0.39 Ca 0.24 Ca	63.37 75.50
$Ca(OH)_2$	12.1 12.2	11.5 11.8	2.04 2.04	11.89 11.18	55.26 55.26	24.36 28.80	0.49 Ca 0.38 Ca	53.42 47.95
Na_3PO_4	7.5 7.7	6.6 6.7	2.48 2.60	11.62 11.78	45.61 42.98	26.08 25.06	0.18 Na 0.24 Na	82.84 81.12
KOH	13.1	13.1	---	---	---	---	---	---

reduction in total inorganic sulfur (TIS), and the combustible yield have been used to measure the effectiveness of the chemical pretreatment/oil agglomeration process. The reduction in ash was calculated using equation (5):

$$\text{reduction in ash (\%)} = \frac{AF - AP}{AF} \times 100 \qquad (5)$$

where AF = ash content of dry feed material

AP = ash content of dry, oil-free product

Similarly, the reduction in total inorganic sulfur was defined as:

$$\begin{array}{l}\text{reduction in total}\\ \text{inorganic sulfur (\%)}\end{array} = \frac{SF - SP}{SF} \times 100 \qquad (6)$$

where SF = total inorganic sulfur content of dry feed material

SP = total inorganic sulfur content of dry, oil-free product

The combustible yield is a measure of the yield of carbonaceous material. It is essentially the yield of dry, oil-free, ash-free coal and was defined as:

$$\text{combustible yield (\%)} = \frac{(WP)(100 - AP)}{(WF)(100 - AF)} \times 100 \qquad (7)$$

where WP = weight of dry, oil-free product

WF = weight of dry feed material

AF, AP = as in equation (5)

Although equation (7) does not take into account mineral weight loss during ashing of the coal due to (1) the oxidation of pyrite, (2) dehydration of minerals, or (3) decomposition of carbonates, it is still a fairly good measure of the recovery of combustible material.

In Table 4, the column marked pH_i lists the pH of the pretreatment slurry after the initial mixing period, prior to heating. The value of pH_f is the pH of the slurry after it was cooled to room temperature following chemical pretreatment. In the case of oil agglomeration alone, these values represent the natural pH of the agglomeration slurry. Duplicated experiments appear as pairs in the table.

Although some of the data presented in Table 4 lacks a high degree of reproducibility, some significant information can be gathered from these results. It can readily be seen for all alkalis that chemical pretreatment significantly increased the amount of total inorganic sulfur rejected through oil agglomeration. At the particular alkali concentration chosen, sodium carbonate and magnesium carbonate, with average reductions in total inorganic sulfur of 58.9% and 63.7% respectively, appear to be most effective in reducing the inorganic sulfur content of the coal.

Chemical pretreatment increased the ash reduction achieved through oil agglomeration; however, the increased reduction was not as pronounced as that found for total inorganic sulfur. Nevertheless, with an average reduction in ash of 35.3%, sodium carbonate appears to reject the largest fraction of ash.

Among the combustible yield data, several interesting results are found. Although chemical pretreatment with calcium hydroxide resulted in significant reductions in ash and total inorganic sulfur, it appeared to have a deleterious effect on the combustible yield. The poor yield of combustibles could be accounted for by a number of factors. One of these factors is the high pH of the slurry prior to oil agglomeration. The average pH value for the agglomeration slurry was about 11.7. Other alkalis providing good yields of combustibles had slurry pH levels in the range from 6.2 to 9.5. The use of potassium hydroxide, however, with a slurry pH of 13.1 resulted in no yield of agglomerated product. Other experiments in this investigation have shown that high yields of agglomerated product can be obtained by lowering the pH of the potassium hydroxide slurry through acidification with dilute hydrochloric acid. Scott coal which had been precleaned was used in these experiments and, as a result, no inorganic sulfur or ash data are available for comparison with the data presented in Table 4. Min (25) also found that the yield of agglomerated coal declined at pH levels higher than 10. In view of these results, relatively strong alkalis such as calcium hydroxide and potassium hydroxide may require acidification prior to oil agglomeration in order to provide a suitable pH. It is also quite possible that these alkalis might provide good inorganic sulfur rejection and high yields of combustible material at a somewhat lower alkali concentration.

The results in Table 4 also seem to indicate that calcium ions may affect the yield of combustible material. Although the average combustible yield (69.4%) resulting from the use of calcium carbonate was not as poor as that found for calcium hydroxide (50.7%), it was still low compared with the yields obtained with the more effective alkalis. In contrast with calcium hydroxide, the calcium carbonate pretreatment slurry always remained slightly acidic. These results do not provide a great insight into the phenomenon of selective oil agglomeration, but they do support the contention that oil agglomeration is dependent upon the surface chemistry and electrokinetic properties of the solid particles and oil droplets involved (31,32).

These preliminary experiments also revealed what may be a major problem in the commercial application of the chemical pretreatment process. In all cases, the coal was found to accumulate the particular metal of the pretreatment reagent. For example in the case of sodium carbonate, the agglomerated product contained about 0.28% sodium, whereas the untreated agglomerated coal contained only 0.05% sodium. The increased metal content of the coal is probably largely due to the accumulation of metal ions within the pore structure of the coal, but may also be caused in part by the inherent ion exchange properties of the coal. If this desulfurized product is to be used as a boiler fuel or feedstock for the production of metallurgical coke, the accumulated metals (particularly the alkali metals) will probably have to be removed by some method.

Use of different fuel oils in the agglomeration of coal

Since most investigators generally agree that the type of fuel oil used in selective oil agglomeration does affect the degree to which inorganic sulfur and ash constituents are rejected from coal fines, a fairly extensive study was made to determine the effects of using various fuel oils to agglomerate untreated and chemically pretreated coals. In these experiments, 50 g of minus 60 mesh Scott coal was used as the starting material for either chemical pretreatment or selective agglomeration. This coal had been precleaned by gravity separation prior to fine grinding, using trichloroethylene (sp gr 1.47) as the heavy medium. Starting with coal (1/4 in. x 0 in.) containing 19.7% ash and 6.5% total inorganic sulfur, the float product recovered in 60.0% yield contained 9.6% ash and 1.7% total inorganic sulfur. The chemical pretreatment step was carried out using a 2.0 wt % sodium carbonate solution in the usual fashion at a temperature of 80°C for 15 min. The untreated and chemically pretreated coals were agglomerated (using 5.0 ml of the particular fuel oil) in the manner described earlier, except that the pH of the agglomeration slurry in the second stage was adjusted to 2.0 by adding a 10.0 wt % solution of hydrochloric acid.

This modification in the agglomeration step was instituted in an attempt to lower the sodium content of the agglomerated product. It was hoped that the acid might drive the sodium ions from the fine pore structure of the coal and also exchange with any sodium ions attached to functional groups associated with the ion exchange properties of the coal.

The results of these experiments are presented in Tables 5 and 6. Each of the experiments was repeated three times to reduce the effect of errors associated with sampling and chemical analysis. Although all of the samples were analyzed for ash and total inorganic sulfur, only one sample in each group was analyzed for sodium. By comparison of the sodium contents given in Tables 5 and 6, it appears that the modified agglomeration technique did succeed in removing a large portion of the accumulated sodium, but the agglomerated pretreated products still contained more sodium than either the feed coal or the agglomerated untreated coal. Even so, the average sodium content of

Table 5. A comparison of different fuel oils used to agglomerate precleaned minus 60 mesh Scott coal

Fuel oil	TIS, %	Ash, %	Avg. reduction in, %		Na, %	Combustible yield, %
			TIS	Ash		
Feed coal	1.71	9.65	---	---	0.027	---
Heater	1.15	8.10	40.15	18.93	0.029	94.39
	0.99	7.64				96.56
	0.93	7.73				96.81
Furnace	0.99	7.93	40.35	17.65	0.026	97.42
	1.08	7.86				99.33
	0.99	8.05				98.11
No. 200, LLS	1.16	7.61	34.70	19.34	0.027	99.56
	1.06	7.62				101.12
	1.13	8.12				99.72
No. 5 heavy, LLS	1.18	8.30	30.02	17.82	0.027	92.83
	1.20	7.67				91.48
	1.21	7.82				90.80
No. 6	1.24	8.94	29.24	14.99	0.026	97.06
	1.26	7.75				99.06
	1.13	7.92				99.94

Table 6. A comparison of different fuel oils used to agglomerate precleaned minus 60 mesh Scott coal which was pretreated with Na_2CO_3

Fuel oil	TIS, %	Ash, %	Avg. reduction in, %		Na, %	Combustible yield, %
			TIS	Ash		
Feed coal	1.71	9.65	---	---	0.027	---
Heater	0.68	7.99	62.96	19.76	0.055	96.54
	0.70	7.62				96.72
	0.52	7.62				97.54
Furnace	0.70	7.54	53.33	21.69	0.061	97.42
	0.76	7.43				98.97
	0.78	7.70				97.46
No. 200, LLS	0.68	7.94	59.26	16.96	0.061	98.02
	0.63	7.88				95.84
	0.78	8.22				96.30
No. 5 heavy, LLS	0.84	7.68	49.71	20.65	0.065	89.70
	0.84	7.58				89.54
	0.90	7.71				88.05
No. 6	0.84	7.90	48.93	19.44	0.066	97.20
	0.87	7.55				97.25
	0.91	7.87				97.12

these agglomerated pretreated samples (0.062% Na) is still a marked improvement over that found in the previous section (0.28% Na).

The results in Table 5 generally agree with results reported by Min (25) and Capes et al. (8); i.e., that the heavier fuel oils are not as selective as the lighter oils in separating the coal and mineral particles. As can be seen, the average reduction in total inorganic sulfur tended to decrease as the specific gravity of the fuel oil increased. While heater oil resulted in an average reduction in inorganic sulfur of 40.2%, the heavier No. 6 fuel oil yielded only a 29.2% reduction in the inorganic sulfur content. A similar trend was observed in Table 6 for chemically pretreated samples.

Omitting the chemical pretreatment step reduced the effectiveness of the separation achieved through oil agglomeration. As can be seen by comparing Tables 5 and 6 in the case of heater oil, pretreatment followed by oil agglomeraation resulted in a 63.0% reduction in inorganic sulfur; omitting pretreatment resulted in only a 40.2% reduction. Pretreatment followed by agglomeration with No. 6 fuel oil led to a 48.9% reduction in inorganic sulfur, but once again, omission of the chemical pretreatment step reduced the effectiveness of the separation and resulted in a 29.2% reduction in total inorganic sulfur. Of all the experiments listed in Tables 5 and 6, pretreatment followed by agglomeration with heater oil led to the greatest rejection of inorganic sulfur. In this case, based on run-of-mine Scott coal, the combined effects of gravity separation, chemical pretreatment, and oil agglomeration yielded an 89.5% overall reduction in total inorganic sulfur.

Very little can actually be said regarding the form of the ash reduction data. Unlike the inorganic sulfur contents of the agglomerated products, the ash contents in neither Table 5 nor 6 follow an easily discernible trend with respect to the specific gravity of the fuel oil. A comparison of Tables 5 and 6 does seem to indicate that chemical pretreatment did slightly increase the degree to which ash constituents were rejected through oil agglomeration.

Chemical pretreatment did not affect the yield of combustible material. The combustible yields achieved by agglomeration of pretreated coals were roughly the same as those found for agglomeration of untreated coals. All of the yields were very good and ranged from 88.0% to essentially 100% recovery of combustibles.

As an extension of this work, minus 400 mesh precleaned Scott coal was also agglomerated with various types of fuel oil. These experiments were performed exactly like those described using minus 60 mesh precleaned Scott coal, except that the feedstock consisted of minus 400 mesh material. The results are presented in Table 7. The trend found for the reduction in inorganic sulfur is not as simple as the trends observed using the minus 60 mesh feedstock. The inorganic sulfur content of the product increased slightly with increasing specific gravity, as the agglomeration oil changed from heater to furnace to No. 200, LLS fuel oil. Using these light fuel oils, the reduction in inorganic sulfur decreased from 47.5% with heater oil to 42.9% with No. 200, LLS fuel oil. Quite unexpectedly, when No. 5 heavy, LLS fuel oil was used to agglomerate the coal, the inorganic sulfur content of the product decreased sharply rather than increasing with respect to the No. 200, LLS product. When No. 6, LLS fuel oil was used, an even cleaner product was obtained.

These results can possibly be explained by examining the character of the agglomerated product obtained using

Table 7. A comparison of different fuel oils used to agglomerate minus 400 mesh Scott coal

Fuel oil	TIS, %	Ash, %	Avg. reduc. in, %		Combust. yield, %
			TIS	Ash	
Feed coal	1.82	9.97	---	---	---
Heater	0.93	8.41	47.52	14.14	78.43
	0.98	8.71			71.18
Furnace	0.99	7.74	45.32	22.22	87.72
	1.00	7.77			88.61
No. 200, LLS	1.05	8.33	42.86	16.30	94.18
	1.03	8.36			93.95
No. 5 heavy, LLS	0.84	8.19	57.14	17.58	97.59
	0.76	8.24			96.11
	0.74	8.22			92.56
No. 6, LLS	0.62	8.21	65.93	17.65	89.72
	---	---			0.00
No. 6	---	---	---	---	0.00

each of the fuel oils. The use of light oils such as heater and furnace oils to agglomerate extremely fine coals (e.g., minus 400 mesh) generally results in the formation of large flocculated structures of coal particles. Although the light fuel oils may tend to be more selective in wetting solid particles, the resultant flocks rapidly clog the openings in the screen used to recover the agglomerated product. This leads to difficulties in dewatering and demineralizing the product since the water and suspended mineral particles cannot easily penetrate the densely matted flocculates. The large flocculated structures are not especially durable and are easily broken apart by the flow of liquid through the screen and by mechanical action such as shaking the screen. This leads to a considerable amount of coal passing through the screen and thus to lower yields of combustible material.

The use of heavier fuel oils such as No. 5 heavy, LLS and No. 6, LLS leads to the formation of a relatively coarse agglomerated product consisting of more or less micro-spherical agglomerates. Upon screening of the slurry, this coarse granular material does not form a dense mat, but rather leaves a multitude of void spaces and channels through which the aqueous medium and suspended mineral particles may pass. As a result, the durable micro-spherical agglomerates dewater rapidly to provide a high yield of combustible material.

The effect of agglomerate character on the recovery of combustible material is borne out in Table 7. Heater oil did not prove especially effective in recovering combustible material and led to an average combustible yield of only 74.8%. The highest yields of combustible material were achieved using No. 5 heavy, LLS fuel oil which resulted in a 95.4% combustible yield. Neither No. 6, LLS nor No. 6 fuel oil proved highly effective in recovering combustible material. As can be seen in Table 7, the use of No. 6, LLS fuel oil did not always lead to the formation of agglomerates. The use of this oil yielded highly inconsistent results ranging from no yield to 89.7% yield of combustibles. In no instance did the use of No. 6 fuel oil result in the agglomeration of the suspended coal particles. Other than hydrodynamic problems associated with the high viscosity of the No. 6 fuel oils, no other theories can be advanced to account for the failure of these oils to agglomerate very fine coals.

In all cases, fine grinding to minus 400 mesh yielded greater reductions in inorganic sulfur than were achieved by grinding to only minus 60 mesh. This can be seen by comparing the results presented in Tables 5 and 7. This was expected since fine grinding would increase the amount of intrinsic mineral matter liberated from the coal. Fine grinding did not appear to have a significant effect on the rejection of ash constituents during agglomeration.

In order to further compare the effectiveness of sodium carbonate and magnesium carbonate as pretreatment alkalis, several experiments were carried out involving chemical pretreatment with magnesium carbonate, followed by oil agglomeration with various fuel oils. The chemical pretreatment was carried out in the usual fashion, under conditions identical to those used earlier in this section for pretreatment with sodium carbonate (i.e., 15 min at 80°C with a 2.0 wt % suspension of alkali). In each experiment the feedstock consisted of 50 g of minus 60 mesh precleaned (at sp gr 1.47) Scott coal. The results are tabulated in Table 8. By comparison with Table 6, it is apparent that for the oils tested, a 2.0 wt % solution of sodium carbonate was more effective than a similar suspension of magnesium carbonate in reducing the inorganic sulfur and ash contents of the agglomerated product. Pretreatment with sodium carbonate followed by agglomeration with heater oil led to reductions of 63.0% in total inorganic sulfur and 19.6% in ash. A similar treatment using magnesium carbonate resulted in reductions of only 46.2% and 13.7% in inorganic sulfur and ash respectively. A similar result was observed in the

Table 8. Chemical pretreatment with $MgCO_3$

Fuel oil	TIS, %	Ash, %	Avg. reduc. in, % TIS	Avg. reduc. in, % Ash	Combust. yield, %
Feed coal	1.71	9.65	---	---	---
Heater	0.91	8.37	46.20	13.68	95.94
	0.97	8.29			96.23
	0.88	8.33			93.95
Furnace	0.91	7.92	43.47	17.86	100.28
	1.01	7.99			99.80
	0.98	7.87			100.13

case of furnace oil. Both alkalis were effective in recovering combustible material, with combustible yields ranging from 93.6% to essentially 100%.

These results, along with those presented earlier, indicate that sodium carbonate is an effective pretreatment alkali. In order to narrow the scope of this investigation, only sodium carbonate was used as the pretreatment alkali in the remaining experiments.

A comparison of various beneficiation schemes

As a result of work completed involving the beneficiation of coal using various combinations of gravity separation, fine grinding, and physical separation, Min (25) found that the greatest rejection of pyritic sulfur occurred using those schemes that employed both gravity separation and fine grinding to minus 400 mesh prior to oil agglomeration. In view of these results, a number of experimental schemes employing various degrees of fine grinding, gravity separation, chemical pretreatment, and physical separation were devised. The main objectives of these experiments were: (1) to determine the extent to which chemical pretreatment enhances the rejection of inorganic sulfur during physical beneficiation following gravity separation and fine grinding to minus 400 mesh and (2) to compare, in much the same fashion as Min (25), several coal beneficiation schemes. The schemes proposed in this section are not intended to be an exhaustive list of all possible combinations.

When the experiments were performed, all fine grinding was carried out in the normal fashion. Gravity separation was performed using tetrachloroethylene (sp gr 1.61) as the heavy medium. In each experiment, 100 g of either run-of-mine Scott coal or Scott coal precleaned by gravity separation was used as feedstock. The coal was chemically pretreated in the standard fashion with a 2.0 wt % sodium carbonate solution for 15 min at 80°C. Froth flotation was also carried out as described earlier.

Oil agglomeration was performed in a somewhat different fashion. Using a mixture of 14 vol % No. 6 fuel oil and 86 vol % heater oil, the slurry was agitated as in the first stage of the standard agglomeration procedure. Instead of screening the agglomerated slurry, it was poured into a 1000 ml separatory funnel and allowed to settle into two layers, with the agglomerated coal on top and a suspension of refuse on the bottom. The refuse was then drained off and 500 ml of fresh deionized water was added to the agglomerated coal. This material was shaken and again allowed to settle into two layers. The refuse material was withdrawn and the agglomerated coal was filtered in a Buchner funnel to remove the excess water. Sample preparation prior to analysis remained the same.

The results of these experiments are given in Table 9. Once again, most experiments were duplicated and appear as pairs in the table. Under the column marked "treatment," a series of letters was used to describe each of the cleaning schemes. Each letter represents one step in the overall cleaning scheme. The steps represented by the

Table 9. A comparison of various cleaning methods

Run no.	Treatment	TIS, %	Ash, %	Reduction in, %		Combustible yield, % based on	
				TIS	Ash	Precleaned coal	Feed coal
1	Feed coal	6.42	19.72	---	---	---	---
2	R-G-P	1.95	11.76	69.93	40.36	100.00	83.37
3	R-P-O	3.98	12.83	38.78	34.94	---	94.74
		3.78	12.69	41.12	35.65	---	92.44
4	R-P-F	3.98	14.00	38.01	29.01	---	90.15
		3.87	14.25	39.72	27.74	---	95.34
5	R-G-P-B-O	1.35	15.49	78.97	21.45	89.45	74.58
		1.25	15.37	80.53	22.06	88.33	73.56
6	R-G-P-B-F	1.34	11.33	79.13	42.55	95.46	79.59
		1.38	11.42	78.50	42.09	93.56	77.99
7	R-G-P-B-C-O	0.52	11.98	91.90	39.25	88.78	74.02
		0.59	11.87	90.81	39.81	90.39	76.60
8	R-G-P-B-C-F	0.89	15.25	86.14	22.67	89.80	74.87
		0.93	15.79	85.51	19.93	88.28	73.59

letters are outlined as follows:

R = size reduction to 1/4 in. top size

G = gravity separation at a specific gravity of 1.61

P = size reduction to minus 60 mesh

B = size reduction to minus 400 mesh

O = oil agglomeration

F = froth flotation

C = chemical pretreatment

The letters are listed in the order in which the operations were applied.

By comparing the results of treatments 2,3, and 4, one can easily see some of the advantages and disadvantages of gravity separation and other physical separation techniques. Simple gravity separation, represented by treatment 2, removed a considerable portion (69.6%) of the inorganic sulfur, but recovered only 83.4% of the combustible material. By comparison, the use of oil agglomeration in treatment 3 produced a 39.9% reduction in inorganic sulfur coupled with a 93.5% yield of combustibles. Although this one-stage oil agglomeration technique did not remove as much inorganic sulfur or ash as gravity separation, the technique did result in a greater yield of combustible material. Froth flotation alone (treatment 4) yielded results which were very similar to those involving oil agglomeration alone (treatment 3). Neither oil agglomeration nor froth flotation alone removed as much ash as gravity separation.

Treatments 5 and 6 show that fine grinding to minus 400 mesh and subsequent physical separation greatly complement gravity separation. In treatment 5, the addition of fine grinding and oil agglomeration to gravity separation resulted in rejection of 79.8% of the inorganic sulfur and recovery of 74.1% of the combustible material present in the feed coal. This represents an additional 10.1% reduction in inorganic sulfur over that obtained by gravity separation alone. Similarly, in treatment 6, the incorporation of fine grinding and froth flotation with gravity separation resulted in rejection of 78.8% of the inorganic sulfur and recovery of 78.8% of the combustibles present in the feed coal. This treatment resulted in an additional 9.2% reduction in the inorganic sulfur content of the gravity separation product. Although the addition of fine grinding and physical separation did increase the amount of inorganic sulfur rejected, the additional steps also lowered the overall yield of combustible material (based on feed coal). Whereas gravity separation alone recovered 83.4% of the combustibles present in the feed coal, the incorporation of fine grinding and physical separation resulted in overall combustible yields of 74.1% for oil agglomeration (treatment 5) and 78.8% for froth flotation (treatment 6). So, the increased rejection of inorganic sulfur is complicated by the decrease in overall yield of combustibles.

Beyond these schemes, a further improvement was made by adding a chemical pretreatment step between fine grinding and physical separation. These two new treatments are represented in Table 9 as treatment 7 for oil agglomeration and treatment 8 for froth flotation. A comparison of treatments 5 and 7 show that chemical pretreatment greatly increased the amount of inorganic sulfur rejected by oil agglomeration of minus 400 mesh, precleaned Scott coal. While agglomeration of precleaned minus 400 mesh coal (treatment 5) resulted in rejection of 79.8% of the inorganic sulfur present in the feed coal, the addition of chemical pretreatment (treatment 7) yielded an even higher quality product by rejecting 91.4% of the inorganic sulfur. The addition of fine grinding, chemical pretreatment, and oil agglomeration to gravity separation produced an increase of 21.7% in the reduction of inorganic sulfur of the feed coal over gravity separation alone. The addition of chemical pretreatment to oil agglomeration did not further reduce the yield of combustibles, but rather increased the yield very slightly to 75.3%.

As can be seen by comparing treatments 6 and 8, the addition of chemical pretreatment also increased the amount of inorganic sulfur rejected by froth flotation. These results, along with those presented above for oil agglomeration, indicate that chemical pretreatment greatly enhances the ability to which physical separation techniques can separate carbonaceous and mineral particles. This is most likely due to surface chemical alterations affecting the mineral particles during chemical pretreatment.

Effect of slurry pH on oil agglomeration

Before continuing with a more intensive investigation of the chemical pretreatment/oil agglomeration process, several experiments were conducted in order to determine the effect of slurry pH on the effectiveness of oil agglomeration. The main objective of these experiments was to determine whether slurry pH had a significant effect on the amount of inorganic sulfur and ash rejected during oil agglomeration.

The feedstock used in these experiments consisted of 50 g of minus 80 mesh Scott coal which had been precleaned by gravity separation using trichloroethylene (sp gr 1.47) as the heavy medium. Oil agglomeration was performed as usual, using 5.0 ml of No. 6 fuel oil as the agglomerating oil. In each stage of agglomeration the slurry pH was adjusted to the desired level by adding the necessary amounts of either a 10.0 wt % solution of sodium hydroxide or a 10.0 vol % solution of hydrochloric acid (prepared on a volumetric basis with concentrated hydrochloric acid). In the case of the natural slurry pH, only deionized water was used in both stages of agglomeration. All samples were prepared as usual for analysis and the calculation of combustible yield data.

The results of these experiments are presented numerically in Table 10 as well as graphically in Figure 2. The recovery of combustible material did not appear to be affected by pH, with combustible yields hovering near 95% over the entire range of pH values from 1.5 to 13.0. The pH was not increased beyond 13, so it is not known

Table 10. Effect of slurry pH on the agglomeration of minus 80 mesh precleaned Scott coal

Slurry pH	TIS, %	Ash, %	Reduction in, % TIS	Reduction in, % Ash	Combust. yield, %
Feed coal	1.50	7.90	---	---	---
1.5	0.72	6.66	52.00	15.70	96.95
	0.73	6.52	51.33	17.47	93.81
	0.73	6.61	51.33	16.33	99.13
2.8	0.82	7.26	45.33	8.10	95.49
	0.87	7.17	42.00	9.24	95.03
	0.91	7.19	39.33	8.99	95.29
4.0	0.79	6.84	47.33	13.42	94.86
	0.88	6.94	41.33	12.15	94.94
	0.84	6.89	44.00	12.78	95.20
7.0	0.80	6.99	46.67	11.52	92.99
	0.80	6.87	46.67	13.04	95.43
	0.76	6.97	49.33	11.77	93.10
10.0	0.77	7.00	48.67	11.39	93.71
	0.70	6.53	53.33	17.34	95.17
	0.70	6.46	53.33	18.23	95.47
13.0	0.58	9.33	61.33	---	92.32
	0.64	7.71	57.33	2.40	96.21
	0.50	9.39	66.67	---	95.69

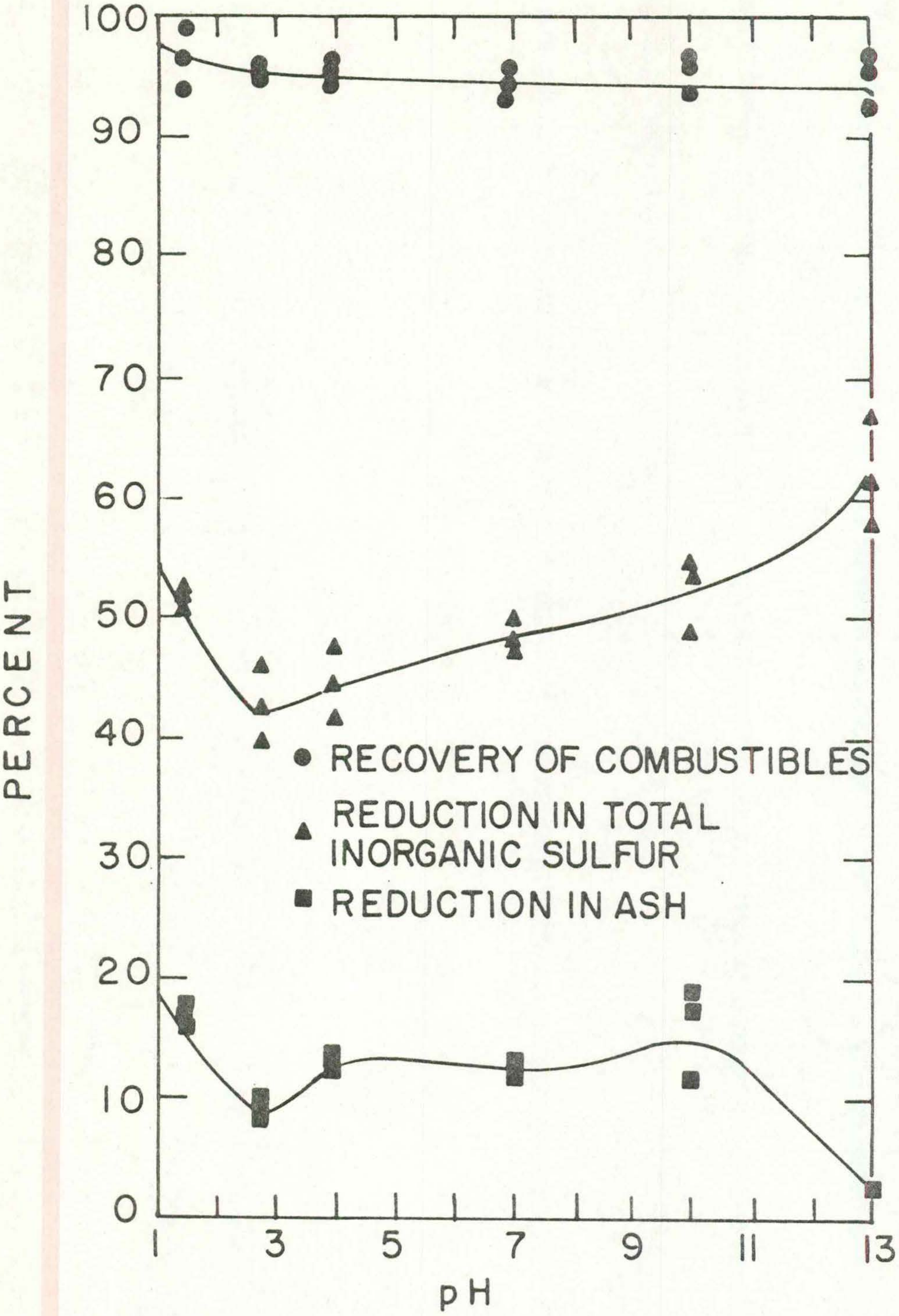

Figure 2. The effect of slurry pH on the agglomeration of minus 80 mesh precleaned Scott coal

whether the combustible yield would have decreased at some higher pH.

The ash contents of the agglomerated products did not appear to follow any easily discernible trend with respect to the slurry pH. It does appear, however, that the amount of ash rejected through oil agglomeration did decrease at a pH level of 13.0. While the amounts of ash rejected over the range of pH values from 1.5 to 10.0 varied from 8.1% to 18.2%, at pH=13.0, a maximum reduction in ash of 2.4% was observed. In the other two runs performed at pH=13.0, the ash content of the product was found to be significantly greater than that of the feed material. The poor ash rejection which resulted may be due to (1) the accumulation of sodium from the sodium hydroxide used to raise the pH and (2) unfavorable electrokinetic properties of the ash and coal particles. These causes are merely suggested and cannot be defended using the data thus far available.

The degree to which inorganic sulfur was rejected by agglomeration appears to be a fairly strong function of the slurry pH. Starting with a minimum at the natural pH of 2.8, the average reduction in total inorganic sulfur increased steadily with pH from 42.2% to 61.8% at pH=13.0.

Once again there is little physical data available on which to base an explanation of the observed minimum. Since air oxidation of pyrite has been observed in both acidic and basic media (4), it seems plausible that a beneficial, hydrophilic layer may be forming about the pyrite at extreme pH levels, either high or low. The presence of the hydrophilic layer would reduce the tendency for the pyrite particles to report with the oil and coal. Thus, these results show that the inorganic sulfur content and perhaps the ash content of the agglomerated product is dependent upon the pH of the agglomeration slurry.

Group II Experiments

The agglomeration of pyrite

While working on the Trent Process, Perrott and Kinney (29) found that through agglomeration with oil, it was possible to form a paste of wet ground pyrite, with little of the pyrite remaining suspended in the water. If the increased rejection of inorganic sulfur observed for the agglomeration of pretreated coal is truly due to surface chemical alterations of the pyrite, then chemical pretreatment of pyrite alone should affect the extent to which the pyrite particles may be agglomerated and recovered from aqueous suspensions. In this part of the present investigation, an attempt was made to determine the effect of chemical pretreatment on the agglomeration of finely ground pyrite, using various fuel oils.

In all of the Group II experiments, the pyrite used as feedstock contained approximately 86% FeS_2. For the experiments performed in this particular section, the feedstock consisted of 50 g of minus 250 mesh pyrite. The samples were agglomerated using either 5.0 ml of straight fuel oil or an emulsion containing 5.0 ml of fuel oil. Due to stratification of the pyrite during agitation (in oil agglomeration) the initial volume of deionized water or pretreatment solution was reduced to 250 ml. Where straight fuel oil was used in agglomeration, the procedure followed was the same as that described earlier, except that only one stage was employed. In other words, the product recovered after the first agitation with oil was not agitated again with fresh water. Where emulsified oil was used, this procedure was again followed, but the oil was added as an emulsion containing 5.0 ml of the oil and 45.0 ml of deionized water. The emulsion was prepared by agitating the mixture with an ultrasonic transducer (Sonifier Cell Disruptor, model W140, from Heat Systems-Ultrasonics, Inc.) until a stable oil/water emulsion was formed. In all cases, the agglomerated pyrite was recovered on a 150 mesh screen. Prior to calculating yield data, the No. 5 light, LLS and No. 200, LLS fuel oils were extracted from the pyrite.

Chemical pretreatment was carried out as usual, except that only 250 ml of a 2.0 wt % sodium carbonate solution was used. In Table 11, pretreatment was carried out for 15 min at 80°C. The pretreatment conditions (except alkali concentration) varied in Table 12 and are presented along with the results.

In Tables 11 and 12, the "pyrite recovered" is based upon the weight of oil-free pyrite recovered and was calculated using equation (8):

$$\text{pyrite recovered, \%} = \frac{\text{wt of dry, oil-free pyrite recovered}}{\text{wt of dry feedstock pyrite}} \times 100 \qquad (8)$$

Table 11. The agglomeration of minus 250 mesh pyrite

Fuel oil	Emulsified/ straight oil	Untreated/ pretreated pyrite	Pyrite recovered, %
Heater	straight	untreated	0.00
	straight	untreated	0.00
Heater	emulsified	untreated	0.00
	emulsified	untreated	0.00
No. 200, LLS	straight	untreated	59.89
	straight	untreated	67.64
No. 200, LLS	emulsified	untreated	89.76
	emulsified	untreated	93.62
No. 200, LLS	emulsified	pretreated	11.29
	emulsified	pretreated	6.33
No. 200, LLS	emulsified	pretreated[a]	82.15
	emulsified	pretreated[a]	86.93
No. 5 light, LLS	straight	untreated	42.58
	straight	untreated	50.21
No. 5 light, LLS	emulsified	untreated	71.47
	emulsified	untreated	78.24
No. 5 light, LLS	emulsified	pretreated	5.73
	emulsified	pretreated	10.21

[a] Pretreated under a blanket of nitrogen instead of air.

Table 12. The effect of pretreatment conditions on the agglomeration of minus 250 mesh pyrite with No. 200, LLS fuel oil

Run no.	Temperature, °C	Residence time, min	Pyrite recovered, %
1	23	15	89.12
	23	15	86.69
2	50	5	8.61
	50	5	10.43
3	50	15	10.77
	50	15	9.38
4	80	15	11.29
	80	15	6.33

In Table 11, a contrast is made between the agglomeration of untreated and chemically pretreated pyrite using various types of fuel oil. In some cases, the fuel oil was introduced as an oil/water emulsion. As can be seen in runs 1 and 2, the pyrite could not be recovered using heater oil as the agglomerating oil. Following agglomeration with either straight or emulsified heater oil, the oil did not appear to float on the surface of the water containing the suspended refuse material. This would seem to indicate that the oil wetted the particles; however, it was not able to sufficiently bind the heavy pyrite particles together to form recoverable agglomerates. This may be the key to the apparent selectivity observed when heater oil is used to agglomerate relatively coarse coal (e.g., minus 60 mesh).

Using No. 200, LLS fuel oil (runs 3 and 4), a substantial portion of the pyrite was recovered through agglomeration. As has been observed with coal (25), the amount of pyrite recovered for a given period of agitation increased when emulsified, rather than straight fuel oil was used in agglomeration. In this case, the use of emulsified No. 200, LLS fuel oil resulted in the recovery of approximately 91.7% of the pyrite. The use of straight fuel oil on the other hand, led to the recovery of only 63.8% of the original pyrite. Evidently, emulsified fuel oils provide the greater dispersion of fuel oil necessary for a high yield of agglomerated particles.

A comparison of runs 4 and 5 illustrates the utility of chemical pretreatment in suppressing the agglomeration of pyrite. While agglomeration of the untreated pyrite with emulsified No. 200, LLS fuel oil led to the recovery of 91.7% of the original pyrite, pretreatment reduced the recovery to an average of only 8.8%. In run 6, the pyrite was chemically pretreated as in run 5, but under a blanket of nitrogen. The absence of oxygen virtually halted the pretreatment reaction, leading to the recovery of 84.5% of the pyrite. This is still somewhat less than that obtained in run 4 (91.7%) for untreated pyrite. This small difference may be due to the presence of sodium carbonate in run 6; i.e., the presence of sodium carbonate may have reduced the degree to which pyrite is agglomerated with No. 200, LLS fuel oil.

Once again, the use of emulsified No. 5 light, LLS fuel oil (run 8) to agglomerate untreated pyrite provided a greater recovery of pyrite than that achieved using straight oil (run 7). Agglomeration with emulsified oil resulted in the recovery of 74.9% of the pyrite; whereas, straight oil recovered only 46.4%. In both cases, some of the oil was retained on the screen and on the walls of the blender jar.

The recovery which resulted from the agglomeration of untreated pyrite with straight No. 5 light, LLS fuel oil (46.4%) was substantially lower than that which resulted using straight No. 200, LLS fuel oil (63.8%). This could be due in part to the greater viscosity of the No. 5 light, LLS oil. The increased viscosity would make it more difficult to achieve adequate dispersion of the oil. Similarly, a lower recovery was achieved with emulsified No. 5 light, LLS oil than with emulsified No. 200, LLS fuel oil and breakage of a No. 5 light, LLS emulsion normally precedes that of a No. 200, LLS emulsion. Since some of the No. 5 light, LLS oil was found to coat the glass of the blender jar, substantial breakage of the emulsion probably occurred during agglomeration. This may have reduced the degree to which the No. 5 light, LLS fuel oil was dispersed in the suspension.

As in the case of No. 200, LLS fuel oil, chemical pretreatment (run 9) greatly reduced the amount of pyrite which was recovered through subsequent agglomeration with emulsified No. 5 light, LLS fuel oil. Whereas agglomeration of untreated pyrite resulted in recovery of 74.9% of the original pyrite, agglomeration of pretreated pyrite led to the recovery of only 8.0% of the feed material. Thus, chemical pretreatment leads consistently to the reduced recovery of pyrite by agglomeration with oil.

In Table 12, the results of similar experiments are presented. These experiments were designed to determine the effect of pretreatment conditions on the recovery of pyrite by agglomeration with emulsified No. 200, LLS fuel oil. The procedures followed were identical to those followed in Table 11. In each case, the pyrite was pretreated using 250 ml of a 2.0 wt % sodium carbonate solution.

Chemical pretreatment for 15 min at 23°C did very little to reduce the extent to which pyrite was agglomerated by the No. 200, LLS fuel oil, resulting in an average recovery of 89.9%. Pretreatment for as little as 5 min at 50°C however, drastically reduced the recovery of pyrite to yield only 9.5% of the original material. More severe pretreatment conditions, such as those in run 4, did not greatly reduce the extent to which pyrite was recovered. When the pyrite was pretreated at 80°C for 15 min, about 8.8% of the feed pyrite was collected on the screen. This recovery is only 0.7% lower than that achieved by pretreatment for 5 min at 50°C. These results seem to indicate that the chemical pretreatment reaction leads to suitable surface chemical conditions fairly rapidly (within 5 min) at temperatures as low as 50°C.

Leaching of pyrite during chemical pretreatment

In this section, an attempt was made to determine to what extent pyrite is chemically leached by means of the pretreatment reaction. As an extension of this work, an attempt was also made to determine the chemical composition of the surface of both untreated and pretreated pyrite samples.

The feedstock for these experiments consisted of minus 60 mesh pyrite. Prior to chemical pretreatment, approximately 500 g of the pyrite feedstock was agitated overnight in 800 ml of 10 vol % hydrochloric acid. This was done to remove most of the acid soluble compounds present on the surface of the pyrite. After this acid washing, the pyrite was filtered in a Buchner funnel and allowed to air dry for 24 hr. At this point, 50 g quantities of the dry feedstock were pretreated with 500 ml of a 2.0 wt % sodium carbonate solution at 80°C for the prescribed length of time. As air was bubbled through the hot pretreatment slurry, the slurry turned more and more toward a rust orange color. This was due to the formation of a gelatinous precipitate believed to be ferric hydroxide. When the pretreatment slurry cooled to room temperature, it was filtered in a fritted glass funnel (Pyrex 55 mm medium fritted glass funnel) so that the fine gelatinous precipitate would pass through, along with the pretreatment liquor. The collected pyrite was then washed in the funnel with 250 ml of deionized water. The pyrite was then air dried overnight in the tared funnel, and the pyrite weight loss was recorded.

Since the increased rejection of inorganic sulfur from pretreated coals by oil agglomeration is believed to be due to the formation of hydrophilic iron oxide or hydroxide layers around the pyrite particles, all of the samples were analyzed for their acid soluble iron contents. This was done by atomic absorption. Five grams of the sample to be analyzed was agitated for 15 min with 50 ml of 10 vol % hydrochloric acid. This material was then filtered in a Buchner funnel and was washed with 25 ml of deionized water. The filtrate was diluted to 100 ml total volume and was analyzed for iron.

The results of these experiments are presented in Table 13. In run 1, the untreated pyrite was initially acid washed exactly like the pretreated samples. One can easily see that the pyrite weight loss increased with increasing pretreatment residence time. This result would

Table 13. Pyrite weight loss due to chemical pretreatment and the amount of acid soluble iron contained in the product

Run no.	Residence time, hr	Pyrite weight loss, g	$\frac{\text{g Fe extracted}}{\text{g Fe in pyrite}}$
1	untreated pyrite	---	5.16×10^{-3}
2	0.25	0.83	5.30×10^{-3}
3	1.00	2.28	5.30×10^{-3}
4	2.00	2.55	5.46×10^{-3}

be expected since further reaction would simply leach more pyrite. The greatest weight loss was recorded in run 4, but even here, the weight loss represents only about 5.1% of the original sample weight. Thus far in this investigation, coal has typically been pretreated with 2.0 wt % sodium carbonate solutions for 15 min at 80°C. In run 2, pyrite was pretreated under these conditions; the weight loss recorded was only 1.7% of the original sample weight.

The acid soluble iron contents of the pretreated samples do not lend themselves to easy interpretation. Although the weight of extracted iron per gram of pretreated sample is larger than that for the untreated sample, it is not clear whether this is indicative of the formation of an iron oxide or hydroxide layer about the pretreated pyrite particle. Nevertheless, the acid soluble iron content for run 2 is 2.7% greater than that found in the untreated sample. A better characterization of the pretreated pyrite surface could probably be achieved by analyzing pyrite particle cross-sections for iron and sulfur using scanning electron microprobe analysis. Analysis of the resultant x-rays would provide quantitative information concerning the composition of the iron compounds present in the outer layer.

The Group II experiments have thus shown that chemical pretreatment results in only a mild oxidation of the pyrite surface rather than a gross decomposition of pyrite particles. This mild oxidation, however, causes changes to occur in the surface chemistry of the pyrite particles, suppressing their tendency to agglomerate with heavy fuel oils. Although the experiments conducted in this section used pyrite which was essentially free of coal, the chemical pretreatment reaction is most likely acting in a similar fashion to suppress the agglomeration of pyrite in finely divided coals.

Group III Experiments

The experiments in this group were devised to determine the effects of several pretreatment parameters on the subsequent separation of coal and mineral particles by selective oil agglomeration. In nearly all experiments, the feedstock consisted of minus 400 mesh run-of-mine Scott coal containing 4.96% total inorganic sulfur, 15.66% ash, and 0.016% sodium. Minus 400 mesh coal was chosen for two reasons: (1) chemical pretreatment and oil agglomeration were shown to be more effective when applied to minus 400 mesh material than to minus 60 mesh material and (2) size reduction in a ball-mill tends to produce very homogeneous samples. It was hoped that more homogeneous coal samples would provide more consistent and reproducible results.

In all experiments the feedstock consisted of 50 g of coal. Pretreatment was carried out in the standard fashion, except that nitrogen was bubbled through the reaction slurry during the initial heating period and again during cooling. This was done to ensure that the coal was oxidized only while air was being bubbled through the heated slurry. The samples were agglomerated in the usual manner with 5.0 ml of an oil mixture consisting of 75 vol % No. 6, LLS fuel oil and 25 vol % No. 200, LLS fuel oil. By cutting the viscous No. 6, LLS fuel oil with the relatively light No. 200, LLS fuel oil, agglomeration of the minus 400 mesh coal was achieved. As mentioned earlier, straight No. 6, LLS fuel oil did not prove effective in agglomerating extremely fine sized coal. Following agglomeration, the product was filtered in a Buchner funnel and washed by pouring 250 ml of 10 vol % hydrochloric acid over the filter cake. This was done in an attempt to remove some of the sodium from the agglomerated product. All samples were dried and extracted as usual.

Effect of pretreatment conditions

In this particular section, an attempt was made to determine the effects of pretreatment residence time, sodium carbonate concentration, and reaction temperature on the subsequent separation of inorganic sulfur and ash from minus 400 mesh coal. The results of these experiments are presented in Figures 3 through 8. The complete set of data for these experiments is tabulated in the Appendix.

The results presented in Figures 3 through 6 are concerned with chemical pretreatment at 80°C where the residence time and sodium carbonate concentration have been

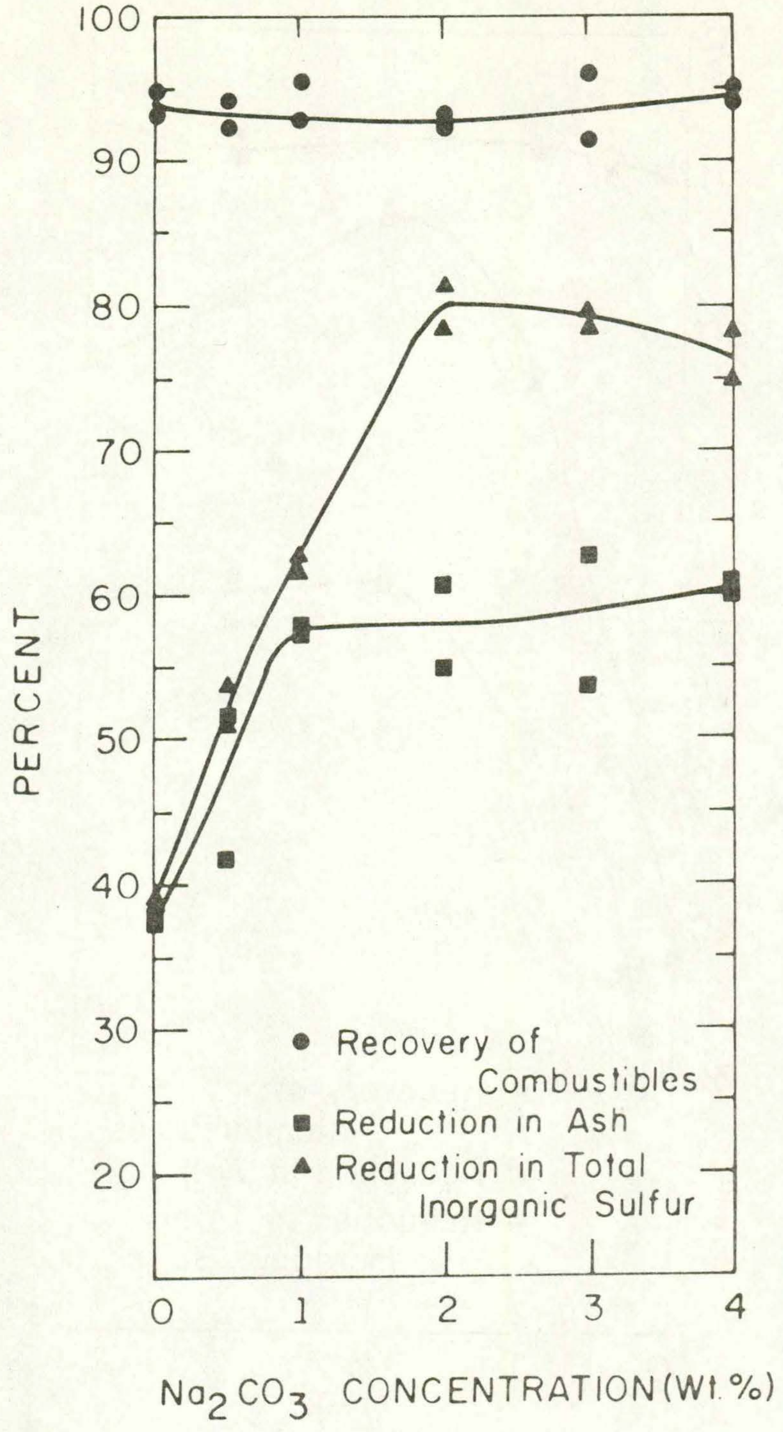

Figure 3. Minus 400 mesh Scott coal, pretreated for 5 min at 80°C and agglomerated with a mixture of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils

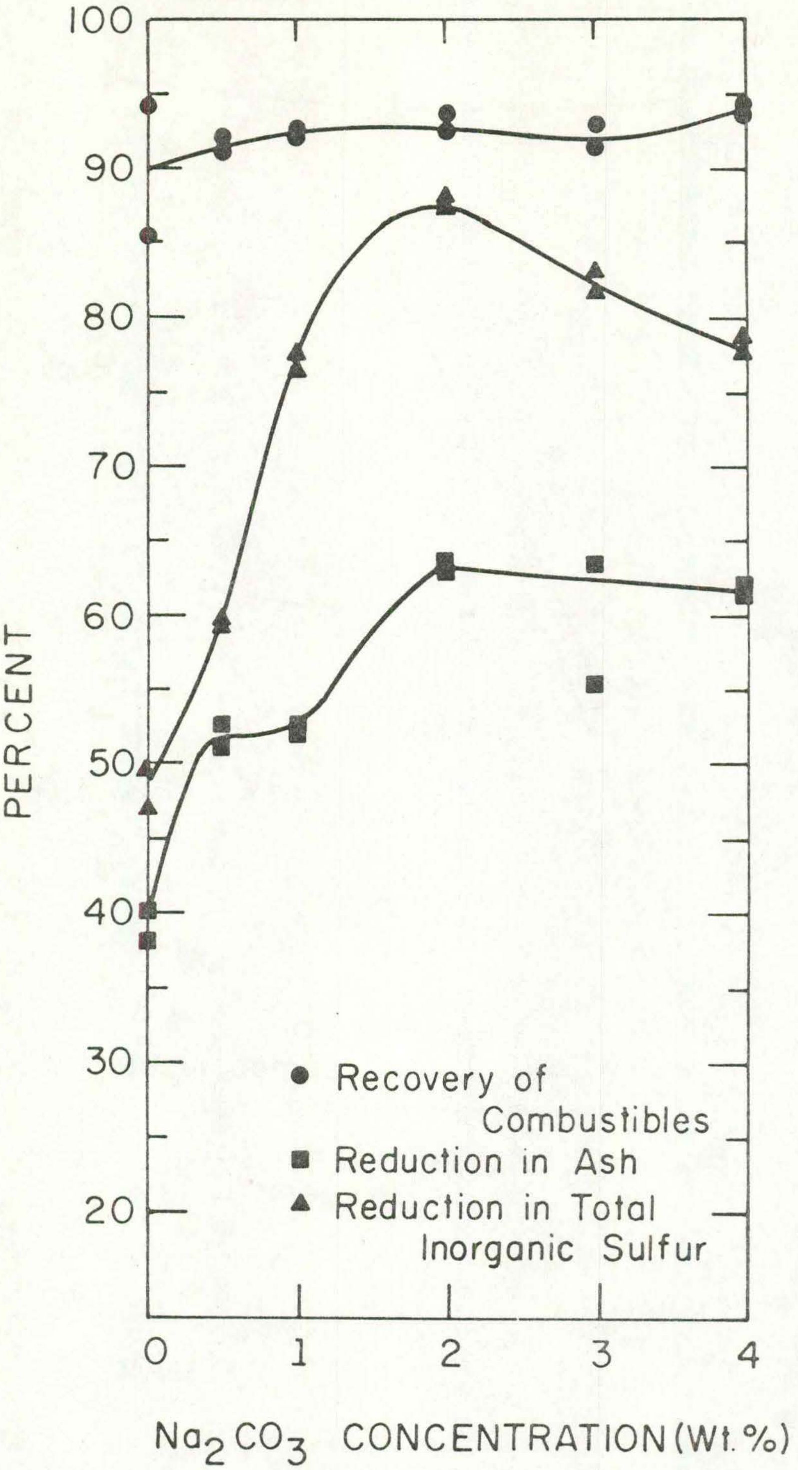

Figure 4. Minus 400 mesh Scott coal, pretreated for 15 min at 80°C and agglomerated with a mixture of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils

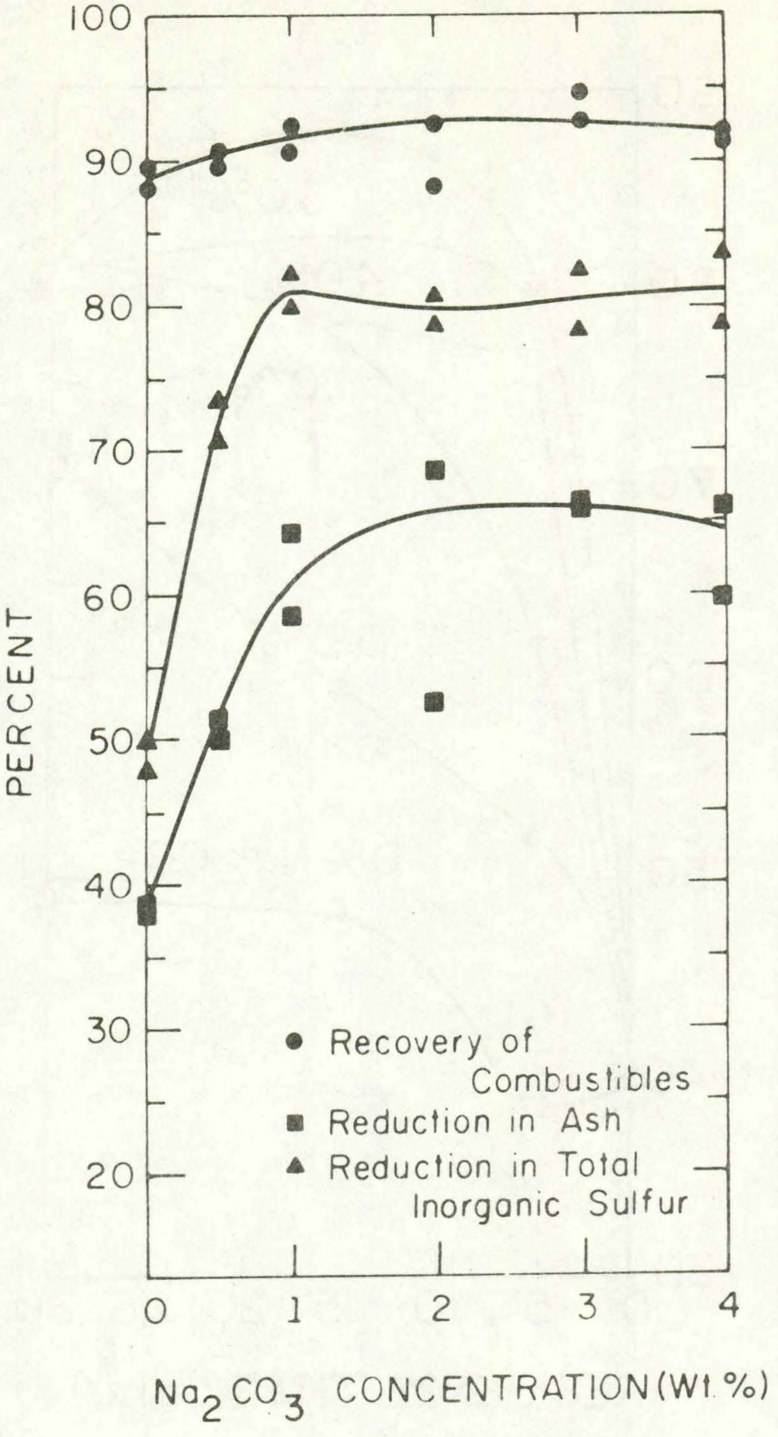

Figure 5. Minus 400 mesh Scott coal, pretreated for 30 min at 80°C and agglomerated with a mixture of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils

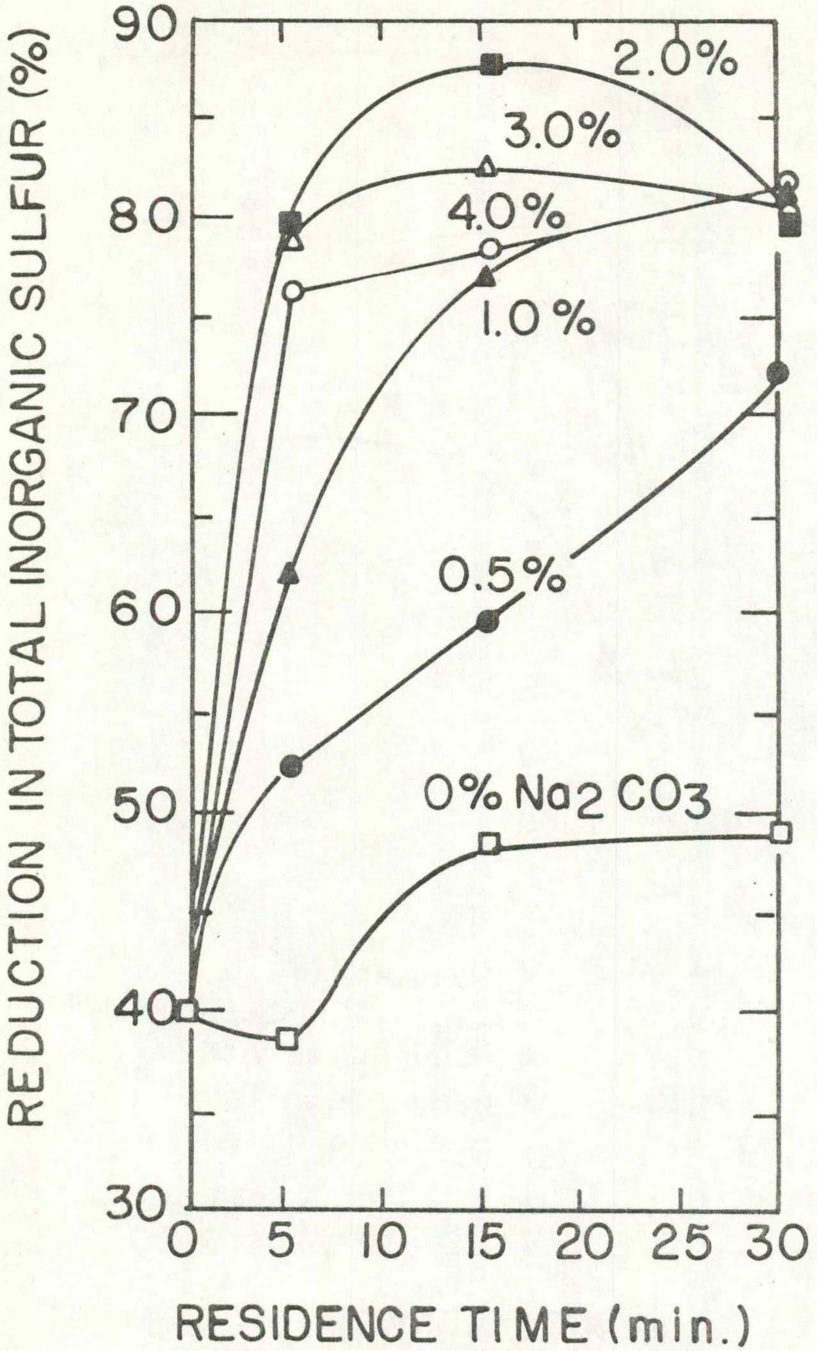

Figure 6. The effect of pretreatment residence time on the reduction in inorganic sulfur, as illustrated by constant sodium carbonate concentration contours

varied. In the first three figures, profiles of the combustible yield, reduction in ash and reduction in inorganic sulfur are presented as functions of the sodium carbonate concentration, for residence times ranging from 5 to 30 min.

Comparing the combustible yield curves in Figures 3 to 5, it is evident that the recovery of combustible material is not significantly affected by either the sodium carbonate concentration or the residence time. The average yield of combustible material for each concentration ranged from 92.7% to 94.4%, 89.6% to 93.3%, and 88.9% to 93.7% for residence times of 5, 15, and 30 minutes respectively. By comparison, oil agglomeration alone, without any sort of pretreatment, resulted in an average combustible yield of 93.6%. These results may indicate that chemical pretreatment decreases slightly the recovery of combustibles normally expected from agglomeration. This slight decrease, however, is probably due to little more than the increased amount of handling required by the addition of the chemical pretreatment step. Thus, while improving the rejection of inorganic sulfur and ash, pretreatment does not significantly alter the effectiveness of selective agglomeration in recovering coal fines.

In comparing Figures 3 through 5, it is clear that the reduction in inorganic sulfur is a strong function of the sodium carbonate concentration. For residence times of 5 and 15 min, there appears to be an optimum concentration for the rejection of inorganic sulfur through subsequent agglomeration. In both cases, the maximum amount of inorganic sulfur was rejected using a sodium carbonate concentration of 2.0 wt %. Over the range of concentrations from 0 to 2.0 wt %, the reduction in inorganic sulfur increased rapidly with sodium carbonate concentration for residence times of both 5 and 15 min. Increasing the concentration beyond 2.0 wt % not only failed to improve the rejection of inorganic sulfur, but caused a significant decrease in the amount rejected, particularly with a residence time of 15 min. With chemical pretreatment for 15 min, an increase in the sodium carbonate concentration from 2.0 to 4.0 wt % led to a corresponding decrease in the reduction in inorganic sulfur from 87.5% to 78.0%. For the 5 min pretreatment the decrease was not as pronounced.

As the residence time was increased to 30 min (Figure 5), there did not appear to be an optimum sodium carbonate concentration. In this case, the reduction in inorganic sulfur increased rapidly from 49.0% with 0 wt % sodium carbonate to 81.0% at a concentration of 1.0 wt %. An increase in the alkali concentration beyond 1.0 wt % did not significantly affect the rejection of inorganic sulfur. The average reductions in inorganic sulfur were found to be 79.5%, 80.4%, and 81.2% for sodium carbonate concentrations of 2.0, 3.0, and 4.0 wt % respectively.

For all three residence times, the increase in sodium carbonate concentration beyond 2.0 wt % was not accompanied by a corresponding increase in the rejection of inorganic sulfur. Why the reduction in inorganic sulfur does not continue to rise beyond the optimum alkali concentration cannot be definitely explained. A similar trend, however, was observed by Burkin and Edwards (6) when pyrite was leached with caustic solutions. In their experiments, they found that the rate of decomposition of pyrite increased rapidly with increasing sodium hydroxide concentration, up to 2 wt %. Increasing the caustic concentration beyond this level had no effect on the reaction rate. The appearance of an optimum caustic concentration was also observed in the leaching of molybdenite (MoS_2) and galena (PbS) (2,14). In both of these cases, the decline in the rate of decomposition with increasing caustic concentration was attributed to the decreased solubility of oxygen with increasing sodium hydroxide concentration.

A possible explanation of this behavior was offered by Dresher et al. (14). At caustic concentrations below the optimum, the solubility of oxygen is large enough to supply a sufficient amount of oxygen to the mineral surface in order to sustain the reaction. In this region, however, the hydroxyl ion does not diffuse to the surface rapidly enough to sustain the reaction. So, the reaction rate increases with increasing hydroxyl ion concentration until the rate of supply of hydroxyl ions equals the rate of formation of active oxidized surface sites. Beyond this concentration, an increase in the level of caustic reduces the solubility of oxygen to such an extent that the reaction rate is hindered by the reduced supply of oxygen to the mineral surface.

Although sodium carbonate was used as the alkali in this investigation, the preceding argument remains a plausible explanation for the decline in the reduction in inorganic sulfur as the alkali concentration was increased beyond the optimum. Even though chemical pretreatment is not strictly concerned with the leaching of pyrite, the necessary surface reactions are probably still governed by the kinetics of the reactions associated with leaching.

In Figure 6, the effect of residence time on the rejection of inorganic sulfur is illustrated for each of the sodium carbonate concentrations. The data points on this graph are averages of the data pairs used in Figures 3 to 5. The data point at zero residence time represents oil agglomeration without any sort of pretreatment. It appears that increasing the residence time to 30 min only improved the rejection of inorganic sulfur for those concentrations which exhibited relatively low reductions in inorganic sulfur with a residence time of 5 min, namely 0.5, 1.0, and 4.0 wt %. In the case of 2.0 or 3.0 wt %, the reduction in inorganic sulfur observed at 30 min was lower than that observed at 15 min. No explanation can be offered to account for this behavior. The increased reduction in inorganic sulfur with increasing residence time observed for pretreatment without sodium carbonate is probably due to the increased dissolution of sulfates and other marginally soluble minerals.

Returning now to the reduction in ash curves presented in Figures 3 through 5, it appears that there is no optimum sodium carbonate concentration for the rejection of ash. Although the ash data are somewhat erratic, for each residence time the reduction in ash seemed to level out at about 1.0 to 2.0 wt % alkali. It appears that the increased residence time marginally improved the rejection of ash; with the 30 min curve lying slightly above the 5 min curve. In view of the lack of information concerning the composition of the ash, not a great deal can be said regarding the improved rejection of ash following chemical pretreatment. The important point in each of these figures is that at those sodium carbonate concentrations where good rejection of inorganic sulfur occurs, good rejection of ash also results.

As an extension of this work, similar experiments were performed at 23°C and 50°C to investigate the effect of reaction temperature. Again, the feedstock consisted of minus 400 mesh run-of-mine Scott coal containing 4.96% inorganic sulfur and 15.66% ash. The results of these experiments are presented in Figures 7 and 8.

In Figure 7, the data were obtained by pretreating each of the samples for 15 min at 50°C using various concentrations of sodium carbonate. The combustible yield

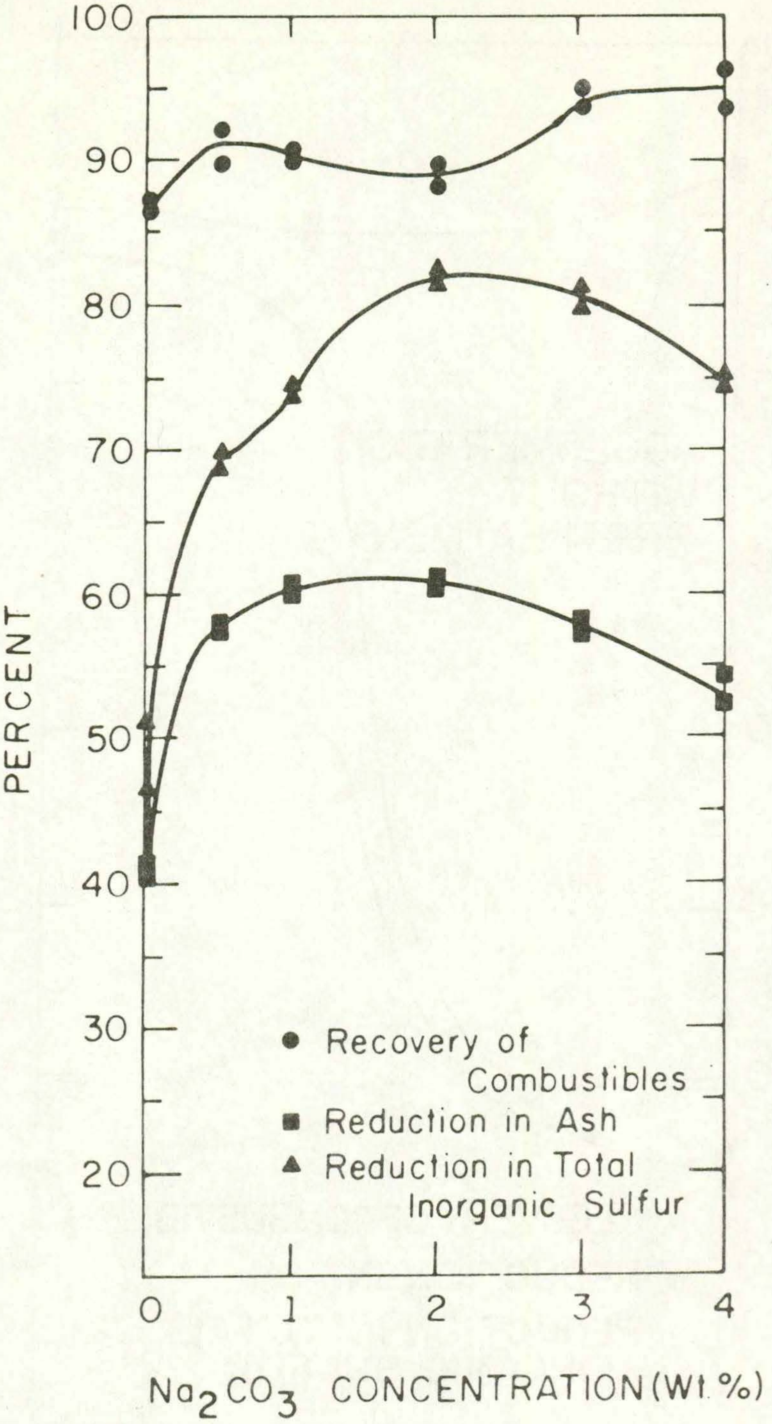

Figure 7. Minus 400 mesh Scott coal, pretreated for 15 min at 50°C and agglomerated with a mixture of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils

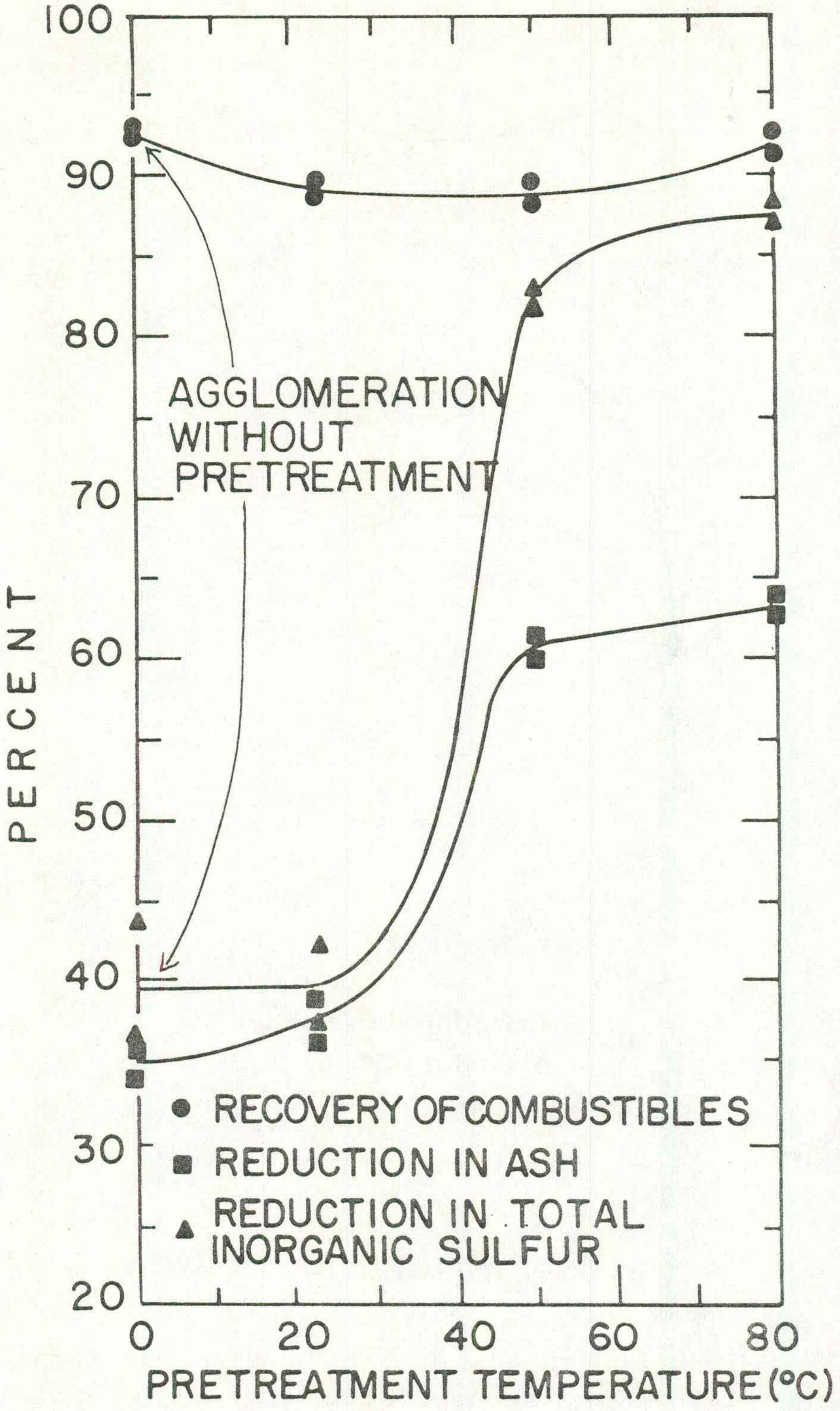

Figure 8. The effect of pretreatment temperature

data seem to indicate that on the whole, the combustible yield obtained at 50°C were slightly lower than that obtained by similar pretreatment at 80°C (Figure 4). This difference is probably not significant and is most likely due to experimental technique. In general the recovery of combustibles was relatively good for all experiments, ranging from 87.1% to 96.0%

Once again, 2.0 wt % sodium carbonate was the optimum concentration for the rejection of inorganic sulfur. While the reductions in inorganic sulfur obtained using 1.0 to 4.0 wt % sodium carbonate at 50°C were slightly lower than those obtained at 80°C, the lower temperature substantially improved the results obtained using 0.5 wt % sodium carbonate. The decrease in pretreatment temperature from 80°C to 50°C caused the average reduction in inorganic sulfur to increase from 59.5% to 69.1% for the treatment with 0.5 wt % sodium carbonate.

The ash data presented in Figure 7 were quite reproducible. In this case, it appears that the optimum sodium carbonate concentration for the rejection of ash falls somewhere between 1.0 and 2.0 wt %. Thus, the optimum concentration for the rejection of ash may correspond with the optimum concentration for the rejection of inorganic sulfur. Although the data in Figure 4 are somewhat erratic, it appears that reducing the pretreatment temperature also somewhat reduced the rejection of ash.

A very limited study was made concerning the effect of residence time on pretreatment at 50°C. In this case, the pretreatment time was reduced to 5 min for the 2.0 wt % concentration. Subsequent agglomeration led to average reductions in ash and inorganic sulfur of 58.8% and 76.2% respectively, and to an average combustible yield of 91.3% (complete data are presented in the Appendix in Table A-4). By comparison, pretreatment for 15 min led to average reductions in ash and inorganic sulfur of 60.4% and 82.0% respectively, and to an average combustible yield of 88.6%. These results seem to indicate that the reduction in residence time caused small decreases in the amounts of inorganic sulfur and ash rejected through agglomeration. The change in combustible yield is probably not significant.

In Figure 8, a graph is presented concerning the effect of reaction temperature on chemical pretreatment for 15 min with 2.0 wt % sodium carbonate. Once again, minus 400 mesh coal was used in the experiments. The data points placed at 0°C represent oil agglomeration alone. The temperatures employed in these experiments included 23°C, 50°C, and 80°C. The combustible yield did not appear to be greatly affected by the pretreatment temperature.

The reductions in ash and inorganic sulfur were strongly affected by the pretreatment temperature, particularly between 23 and 50°C. At 50°C, both the ash and inorganic sulfur contents of the agglomerated products appeared to level off, decreasing slowly between 50 and 80°C. Pretreatment at 23°C did not appear to improve the rejection of inorganic sulfur. It did seem to assist very slightly, however, in the rejection of ash. The sodium carbonate may have aided somewhat in the dispersion of clay (25).

As a summary of the results presented thus far, it seems that pretreatment for 15 min with 2.0 wt % sodium carbonate at 80°C greatly improves the rejection of ash and inorganic sulfur by subsequent oil agglomeration. While still providing excellent rejection of ash and inorganic sulfur, pretreatment schemes employing lower reaction temperatures (50°C) and/or shorter residence times with 2.0 wt % sodium carbonate are somewhat less effective than those using a residence time of 15 minutes and a temperature of 80°C. The shorter residence time may, however, be suitable in commercial preparation facilities.

Effect of particle size in chemical pretreatment

In order to investigate the effect of particle size in chemical pretreatment, experiments similar to those described in Figure 4 were carried out using identical coal ground to minus 100 mesh. In each experiment, the samples were pretreated for 15 min at 80°C and agglomerated with the mixture of No. 6, LLS and No. 200, LLS fuel oils. The results of these experiments are presented in Figure 9. In this figure, a comparison is made between the reductions in ash, reductions in inorganic sulfur, and combustible yields obtained with minus 400 mesh coal and those achieved using identical minus 100 mesh material.

Over the entire concentration range, the combustible yields obtained from the minus 100 mesh coal were significantly greater than those obtained with the minus 400 mesh coal. This is probably a result of the increased size and durability of the agglomerates formed from minus 100 mesh coal. At 2.0 wt % sodium carbonate, essentially 100% recovery of combustibles was achieved using the minus 100 mesh coal.

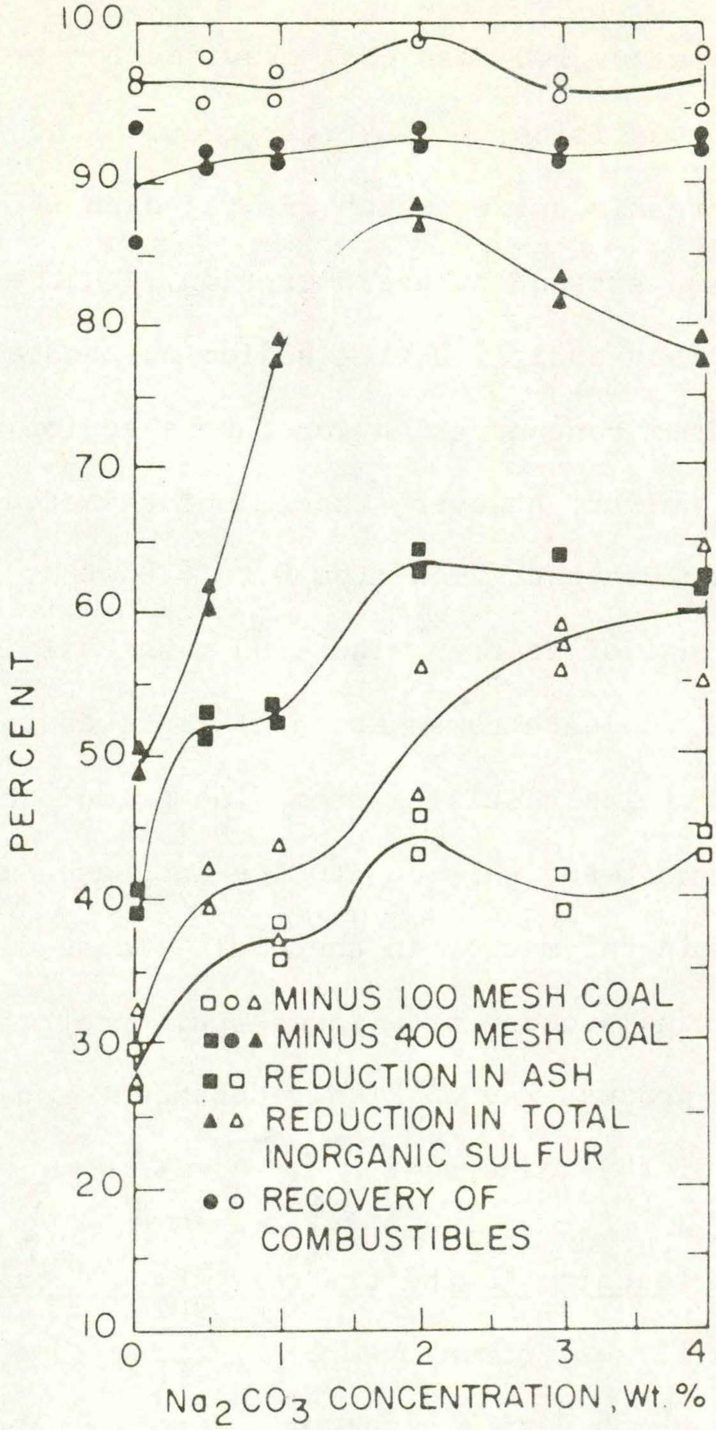

Figure 9. The effect of particle size on chemical pretreatment for 15 min at 80°C and subsequent agglomeration with a mixture of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils

While the minus 100 mesh coal provided for excellent recovery of combustibles, it severely reduced the amount of ash and inorganic sulfur which was rejected by chemical pretreatment and subsequent agglomeration. In the case of the minus 100 mesh coal, 2.0 wt % sodium carbonate appeared to be the optimum concentration for the rejection of ash. For inorganic sulfur, however, the amount rejected increased with increasing concentration from 0 to 4.0 wt %. As was expected, the use of coarser minus 100 mesh coal increased the scatter of the data somewhat. The improved rejection of mineral particles resulting from fine grinding to minus 400 mesh is almost entirely due to the increased liberation of intrinsic mineral matter in the coal. These findings indicate that the success of a large-scale pretreatment/agglomeration process may be highly dependent upon the size distribution of the feedstock.

The effect of leaching in the pretreatment of coal

In Group II, experiments were performed to determine the extent to which pyrite alone was chemically leached during the pretreatment reaction. In this part of the investigation, an attempt was made to determine what part leaching plays in the desulfurization of coal resulting from chemical pretreatment followed by selective oil agglomeration.

To do this, 50 g samples of minus 400 mesh run-of-mine Scott coal were chemically pretreated in the standard fashion, at 80°C using 2.0 wt % sodium carbonate. After cooling, however, the samples were not agglomerated. Instead, they were filtered in a fritted glass funnel (Pyrex 55 mm medium fritted glass funnel). The filter cake was washed with 250 ml of 10 vol % hydrochloric acid, like other pretreated/ agglomerated products. The product was then dried overnight in an oven and analyzed for ash, pyritic sulfur, and sulfate sulfur. The results of these experiments are presented in Table 14. Combustible yields were not determined due to some loss of fine coal through the glass frit.

As can be seen in Table 14, the coal used in this study contained 2.04% sulfate sulfur. This represents 44.0% of the total inorganic sulfur. This coal was chosen as a representative sample of the other Scott coal samples used in the other Group III experiments. Although this coal contained slightly less inorganic sulfur and ash than the coal used thus far, it was stored for the same length of time and should have contained the same relative proportions of pyritic and sulfate sulfur.

Table 14. The effect of leaching in the chemical pretreatment of Scott coal

Residence time, min	Ash, %	Pyritic sulfur, %	Sulfate sulfur, %	Reduction in, %		
				Ash	Pyritic sulfur	Sulfate sulfur
Untreated coal	15.22	2.59	2.04	---	---	---
15	11.50	2.57	0.13	24.44	0.77	93.63
	11.64	2.58	0.21	23.52	0.39	89.70
30	15.53	2.36	0.22	---	8.88	89.22
	14.52	2.34	0.21	4.53	9.65	89.71
60	11.98	1.99	0.17	21.29	23.17	91.67
	11.54	1.97	0.18	24.57	23.94	91.18
90	12.00	1.87	0.16	21.16	27.80	92.16
	11.48	1.59	0.14	24.57	38.61	93.14
120	11.51	1.44	0.15	24.38	44.40	92.65
	12.57	1.50	0.16	17.41	42.08	92.16

One can easily see that the hot oxidizing solution used in chemical pretreatment was very effective in removing most of the sulfate sulfur. When a more or less standard residence time of 15 min was used, an average of 91.7% of the sulfate sulfur was removed. During this same time, however, only an average of 0.58% of the pyritic sulfur was extracted. Much longer pretreatment times were required to remove a significant portion of the pyritic sulfur. In Figure 4, pretreatment of similar coal under these conditions followed by selective agglomeration resulted in a product with an average of only 0.62%. Assuming that the untreated coal contained 2.59% pyritic sulfur and that all of the inorganic sulfur contained in the agglomerated product was present as pyritic sulfur, chemical pretreatment followed by agglomeration resulted in a 76.1% reduction in the pyritic sulfur content. It is highly unlikely that all of the inorganic sulfur contained in the agglomerated product is pyritic. In fact, it seems reasonable to assume that the sulfate sulfur content of the agglomerated product may not differ significantly from those values reported in Table 14. As a result of these findings, it is apparent that mere chemical leaching is not responsible for the rejection of pyritic sulfur. Instead, it appears that certain changes resulting from chemical pretreatment improve the effectiveness of oil agglomeration in separating pyrite and coal particles.

While the ash content of the pretreated samples listed in Table 14 (with the exception of 30 min) was lower than that of the untreated coal, the rejection of ash was not improved by increasing the residence time. This is very peculiar since pretreatment for 120 min extracted nearly all of the sulfate minerals and 40% of the pyrite. If the pretreatment reaction resulted in the formation of a stable layer of iron oxides or hydroxides rather than soluble iron compounds, one would not expect the ash content to decrease. This observation may lend some credence to the notion that the increased effectiveness of oil agglomeration following pretreatment is due to the formation of a hydrophilic surface around the otherwise hydrophobic pyrite paricles.

The use of a light fuel oil in agglomeration

Once again, the effect of the type of oil used in agglomeration was studied. In this part of the investigation, the experiments presented in Figure 4 were repeated using heater oil rather than the mixture of No. 6, LLS and No. 200, LLS fuel oils to agglomerate the pretreated slurry. To review, the samples were pretreated for 15 min at 80°C using sodium carbonate solutions ranging from 0 to 4.0 wt %. Since heater oil is fairly volatile, the agglomerated samples were dried, but not extracted with hexanes. The coal samples were split from the same coal used in Figures 3 through 9 and thus contained 4.96% inorganic sulfur and 15.66% ash. The results of these experiments are presented in Figure 10.

By comparison with Figure 4, it appears that the combustible yield obtained using heater oil was slightly lower than that achieved using the mixture of No. 6, LLS and No. 200, LLS fuel oils. It should be noted that the use of heater oil once again resulted in the formation of very small agglomerates which were extremely difficult to dewater. The use of the heavy fuel oil mixture on the other hand resulted in the formation of larger agglomerates which were dewatered very easily.

Although chemical pretreatment did improve the rejection of ash and inorganic sulfur, the rejections obtained through agglomeration with heater oil were very poor compared with the results obtained using the heavy fuel oil mixture.

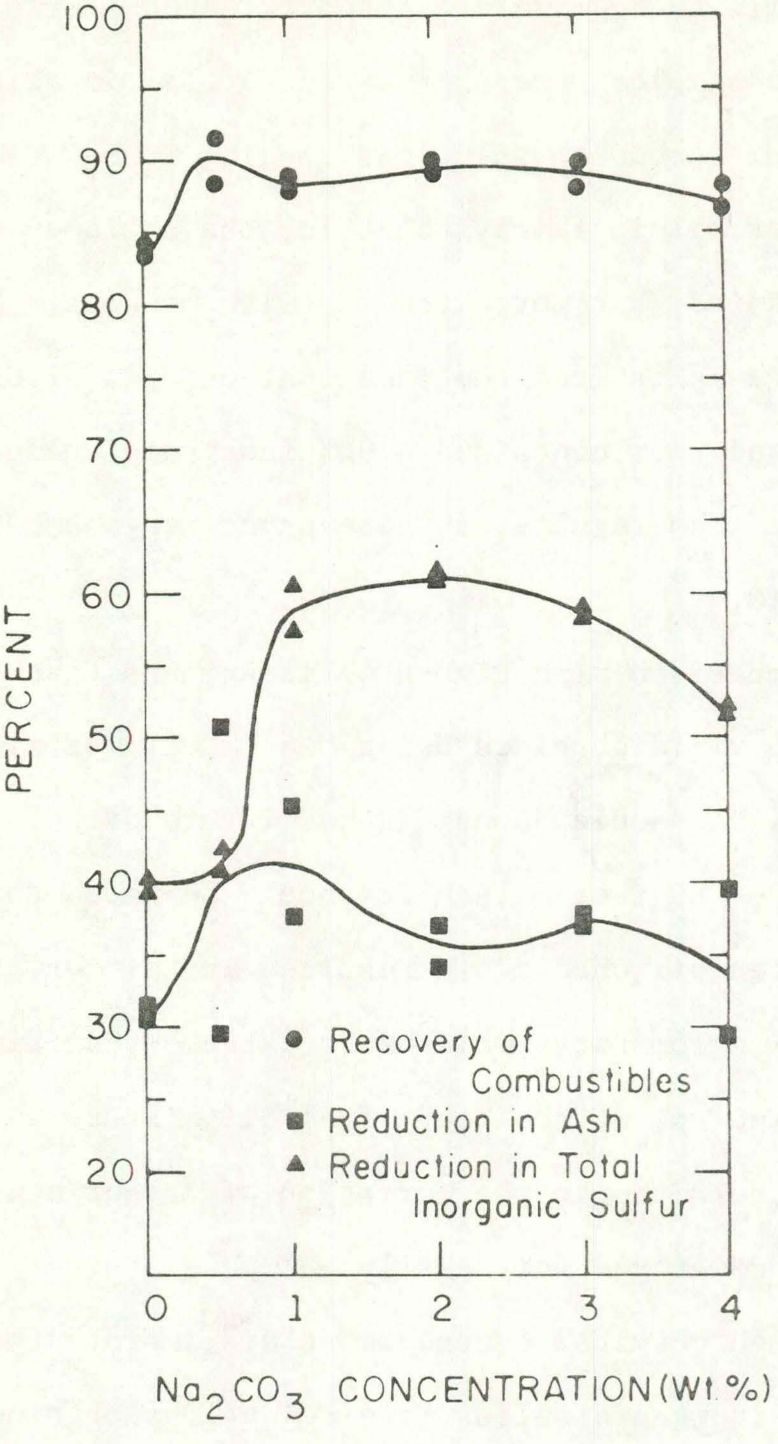

Figure 10. Minus 400 mesh run-of-mine Scott coal pretreated for 15 min at 80°C using various concentrations of sodium carbonate and agglomerated using heater oil

These results are consistent with those reported in the Group I experiments. Once again, with heater oil it appears that 2.0 wt % sodium carbonate may be the optimum concentration for the rejection of inorganic sulfur by oil agglomeration. The ash data were quite scattered which may have been due to problems with dewatering. This may have led to the retention of substantial quantities of colloidal clays. As a result of these findings, it seems (very fortunately) that the greatest rejections of ash and inorganic sulfur from minus 400 mesh coal are obtained using the less expensive heavy fuel oils.

Effect of removing pretreatment liquor prior to agglomeration

While attempting to develop a suitable pretreatment procedure, it was discovered that replacing the pretreatment liquor with fresh deionized water prior to agglomeration drastically reduced the amount of inorganic sulfur and ash which were rejected. This was observed when minus 400 mesh run-of-mine Scott coal was pretreated in exactly the same manner as that used in Figure 4. In other words, the coal was pretreated for 15 min at 80°C using various concentrations of sodium carbonate. Following pretreatment, the hot suspension was filtered and the recovered coal was placed in the blender along with 500 ml of deionized water. The suspension was agglomerated using 5.0 ml of the mixture of No. 6, LLS and No. 200, LLS fuel oils as in Figure 4. The feedstock contained 4.77% inorganic sulfur and 15.16% ash.

The results of these experiments are presented graphically in Figure 11 and are tabulated in full in Table A-7 in the Appendix. On comparison of Figures 4 and and 11, it can be seen that the addition of the filtration step resulted in a marked deterioration in the effectiveness of the combined pretreatment/agglomeration process. Although the maximum rejection of inorganic sulfur in Figure 11 (54.4%) was substantially lower than that in Figure 4 (87.5%), this comparison may be slightly biased. Oil agglomeration of the feedstock in Figure 11 without any sort of pretreatment rejected 28.1% of the inorganic sulfur and 31.6% of the ash. For Figure 4, similar agglomeration of the feed material led to reductions of 40.0% and 35.3% in inorganic sulfur and ash respectively. Even though there appears to be a small difference in the amount of mineral matter which can be rejected from the two slightly different coals, it is unlikely that this can account for the complete dissimilarity between Figures 4 and 11.

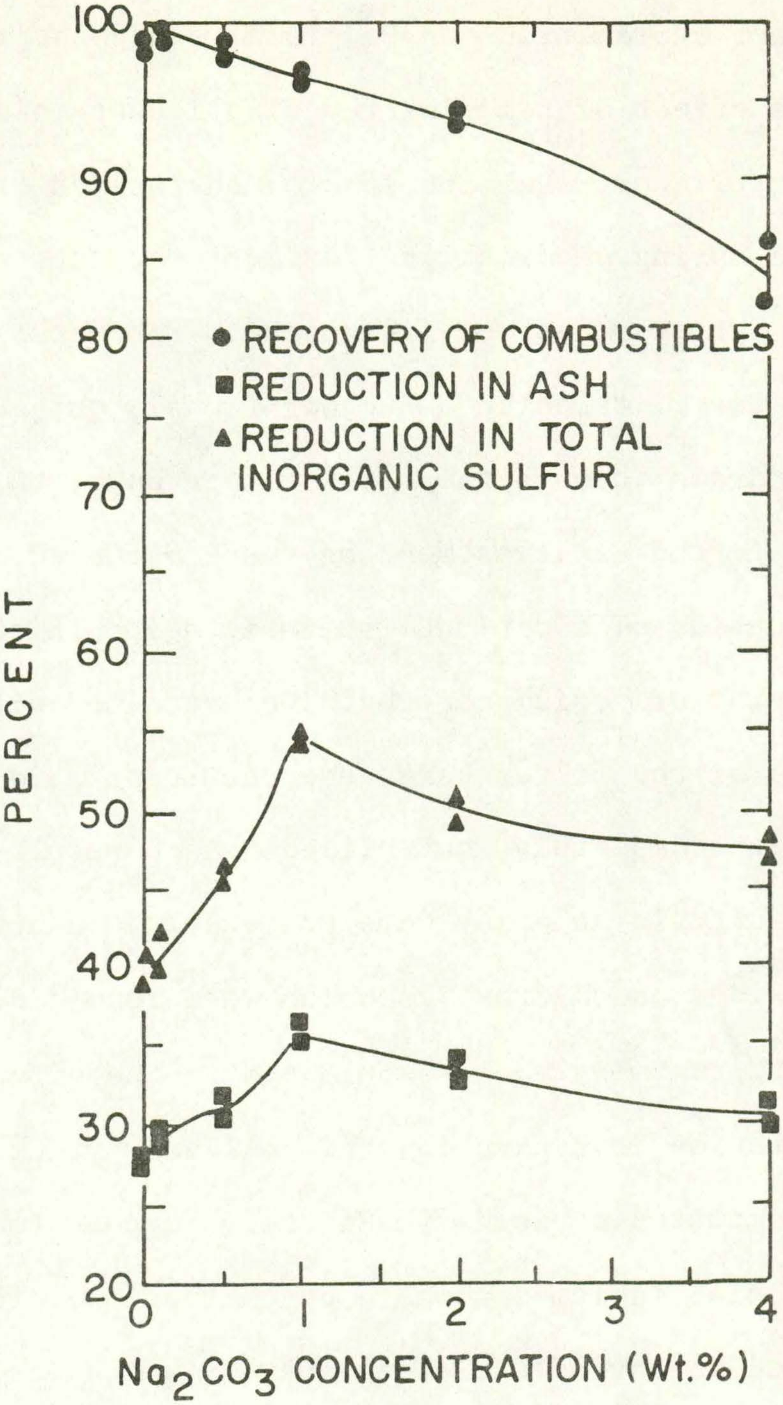

Figure 11. The effect of removing the pretreatment liquor prior to agglomeration

No exact explanation can be given to account for the deleterious effect of removing the alkali containing pretreatment liquor. Perhaps some of the oxides or hydroxides formed during chemical pretreatment were destroyed during the latter stages of filtration. Since the hot suspension was filtered in a Buchner funnel, quite a lot of air was drawn through the moist filter cake. During this time, further pretreatment may have occurred, resulting in the formation of additional sulfuric acid. Since a minimal amount of sodium carbonate was retained within the void spaces of the filter cake, the resultant acid may not have been completely neutralized. As a result, the remaining sulfuric acid may have proceeded to neutralized the iron oxides and hydroxides which were formed during chemical pretreatment. This would reduce the effectiveness of agglomeration in separating the coal and pyrite particles.

The combustible yields in Figure 11 appear to decrease with increasing sodium carbonate concentration. This was not observed in any of the other systems which were studied. No explanation can be offered to account for this trend.

In summary, the addition of a filtration step between chemical pretreatment and oil agglomeration appears to impair the separation of carbonaceous and mineral constituents. Thus, a better separation of coal and mineral particles results using the simpler scheme of chemical pretreatment followed by agglomeration of the alkaline suspension.

Group IV Experiments

In order to supply some logical end to this study, a very limited study was made to determine the applicability of chemical pretreatment and subsequent agglomeration to the beneficiation of other coals. The experiments performed in this group were identical to those described for Figure 4.

Staring with 50 g of minus 400 mesh Western Kentucky, Lovilia, or Illinois No. 5 coal, the samples were pretreated for 15 min at 80°C, using from 0 to 4.0 wt % sodium carbonate solutions. As in the Group III experiments, a blanket of nitrogen was maintained during pretreatment, except for the 15 min aeration period. The cooled alkaline suspension was agglomerated as in the preceding group of experiments, using 5.0 ml of a fuel oil mixture. For the Western Kentucky and Illinois No. 5 coals, the agglomerating oil consisted of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils. In order to agglomerate the suspensions of Lovilia coal, it was necessary to use an even less viscous mixture consisting of 50 vol % No. 6, LLS and 50 vol % No. 200, LLS fuel oils. Drying and extraction of the agglomerated products were done as usual.

The results of these experiments are presented in Figures 12 through 14. The complete set of data for each figure may be found in the Appendix in Tables A-8 to A-10. In Table 15, the ash and inorganic sulfur contents of each of the coals are summarized.

Table 15. Ash and inorganic sulfur contents of coals used

Coal	Ash, %	Inorganic Sulfur, %
Western Kentucky	20.55	1.77
Lovilia	15.21	2.99
Illinois No. 5	13.15	1.39

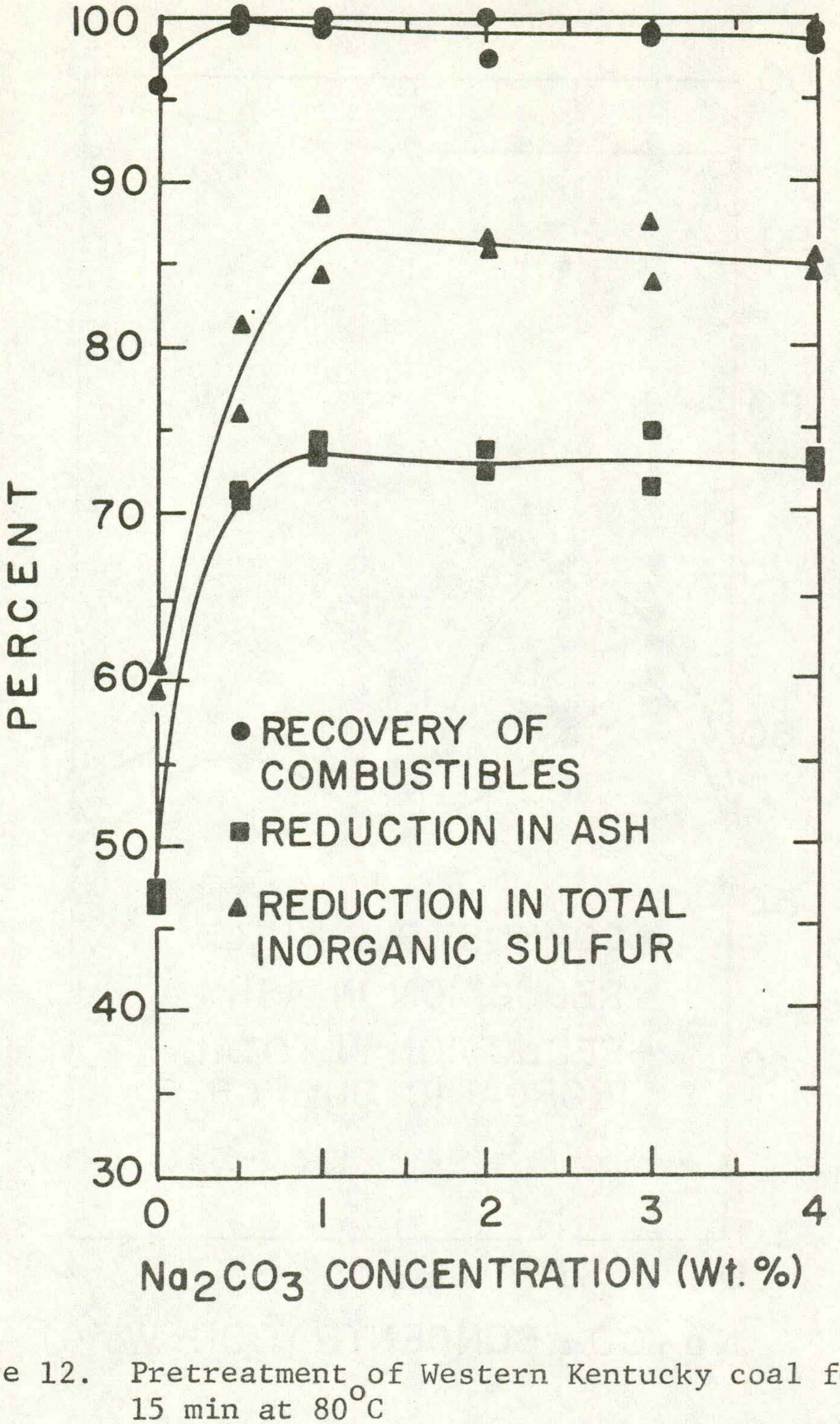

Figure 12. Pretreatment of Western Kentucky coal for 15 min at 80°C

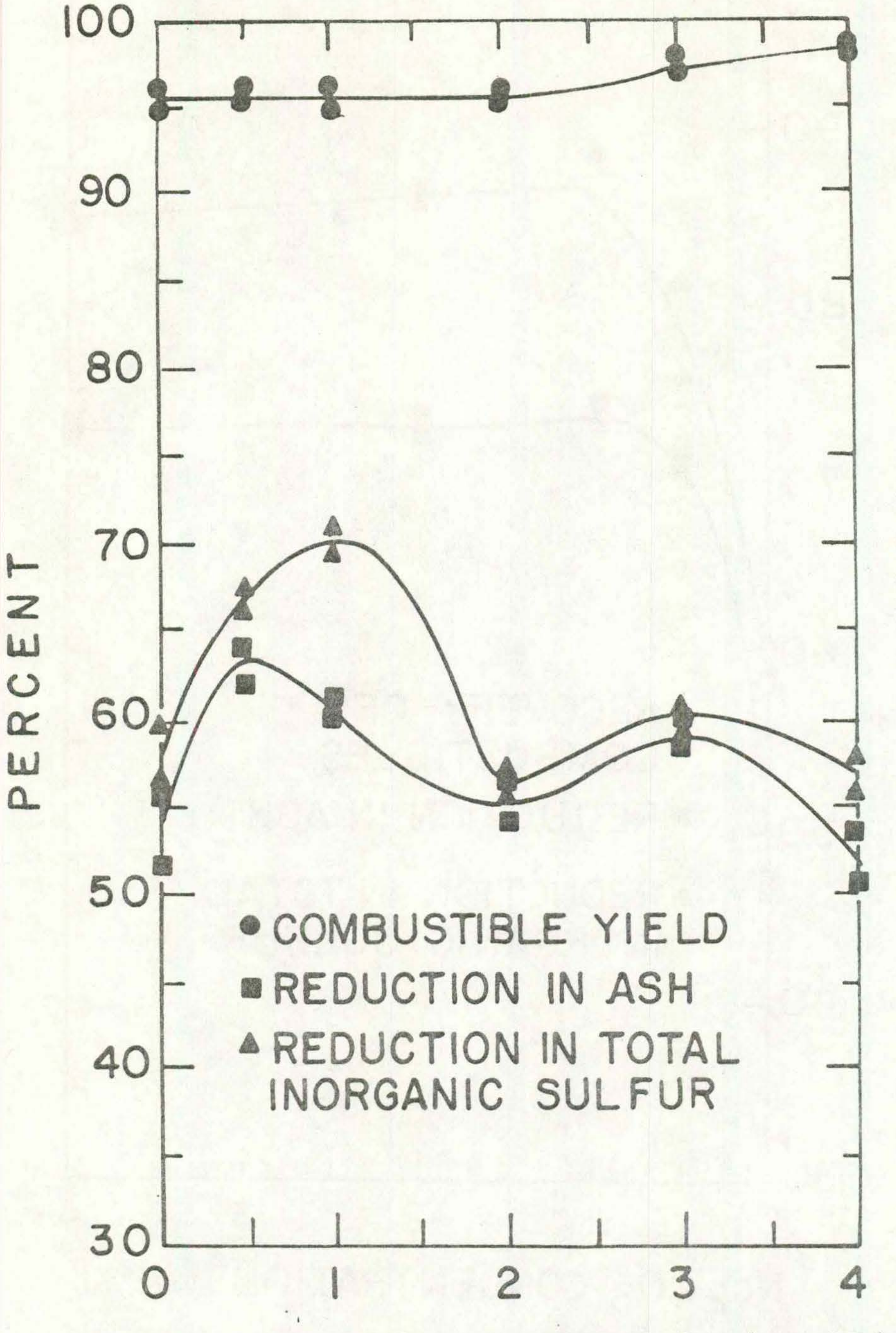

Figure 13. Pretreatment of Lovilia coal for 15 min at 80°C

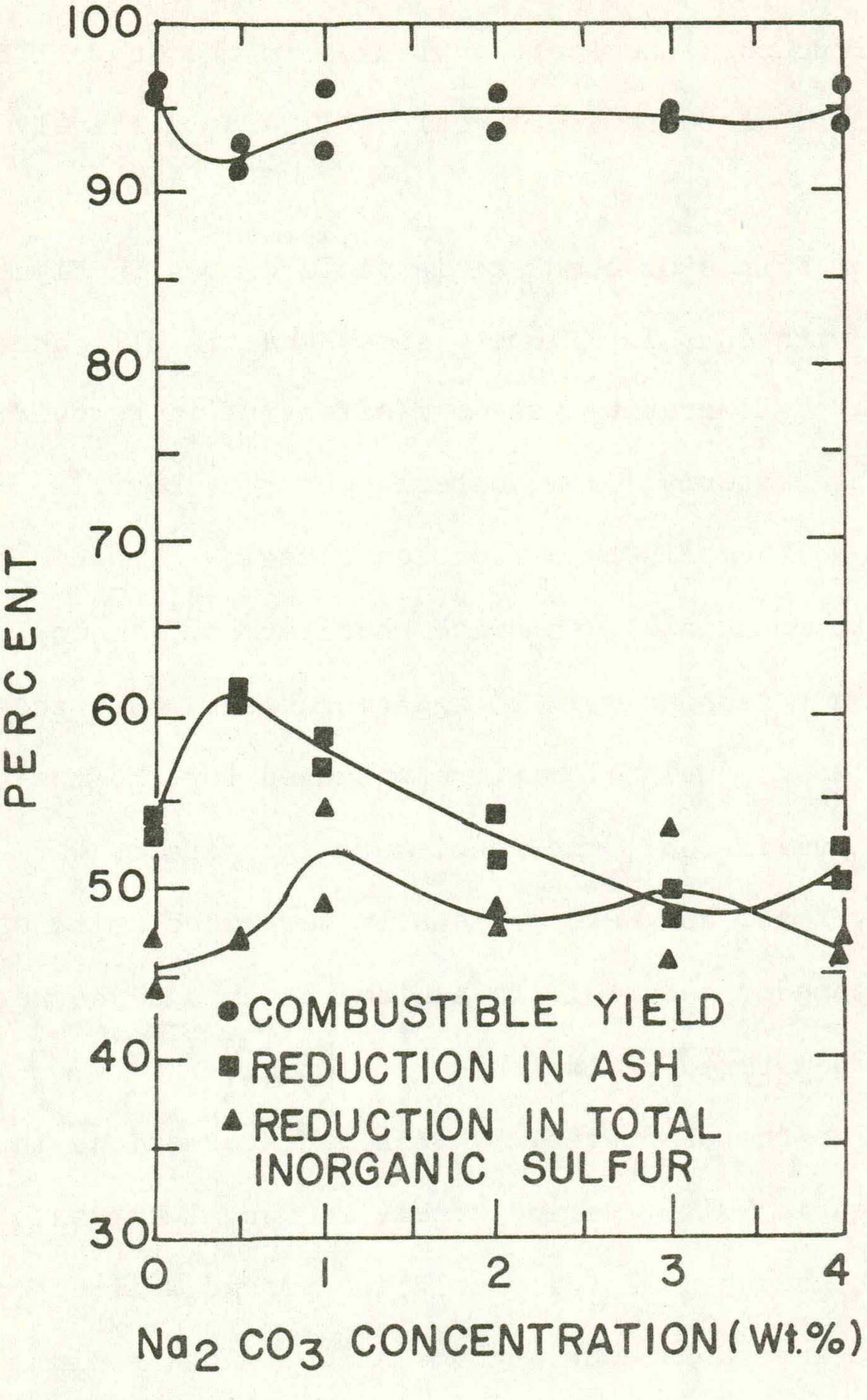

Figure 14. Pretreatment of Illinois No. 5 coal for 15 min at 80°C

All of these coals contained substantially less inorganic sulfur than the Scott coal used in the Group III experiments. As with Scott coal, all were relatively high in ash.

A comparison of combustible yield curves in Figures 12 to 14 with that in Figure 4 shows that in all cases selective agglomeration was more effective in recovering combustible material from Western Kentucky, Lovilia, and Illinois No. 5 coals than from Scott coal. Although the yield of combustibles was quite good for Lovilia coal, the coal did not respond well to agglomeration. Even though a less viscous fuel oil mixture was used for the agglomeration of Lovilia coal, the resultant agglomerates were extremely small and were not easily dewatered. The other coals responded very well to agglomeration and the resultant products dewatered rapidly upon screening.

Unlike the combustible yields, the reductions in ash and inorganic sulfur varied widely from coal to coal. Western Kentucky coal (Figure 12) responded well to pretreatment and subsequent agglomeration. At a sodium carbonate concentration of 1.0 wt %, maximum amounts of both ash and inorganic sulfur were rejected. As the concentration was increased beyond this optimum, the reductions in ash and inorganic sulfur decreased slightly. Using oil agglomeration alone, without any pretreatment, resulted in reductions of 46.2% and 54.2% in ash and inorganic sulfur respectively. At the optimum concentration however, reductions of 73.6% and 86.4% in ash and inorganic sulfur respectively, were achieved. In view of these results, it appears that chemical pretreatment followed by selective agglomeration would be a very effective means of upgrading fines associated with Western Kentucky coal.

As can be seen in Figure 13, chemical pretreatment of Lovilia coal did improve the rejection of ash and inorganic sulfur, but not to the degree seen for Western Kentucky and Scott coals. As with Western Kentucky coal, the optimum sodium carbonate concentration for the rejection of ash and inorganic sulfur appears to be around 1.0 wt %. While oil agglomeration alone without pretreatment resulted in reductions of 47.0% in ash and 57.2% in inorganic sulfur, pretreatment with 1.0 wt % sodium carbonate increased the reductions to only 60.3% and 70.1% in ash and inorganic sulfur respectively. Depending upon economic factors, the relatively small improvement in the rejection of ash and inorganic sulfur may not justify the use of chemical pretreatment prior to agglomeration of Lovilia coal.

As with Lovilia coal, Figure 14 shows that chemical pretreatment of Illinois No. 5 coal did not greatly improve the ash and inorganic sulfur contents of the agglomerated product. Whereas oil agglomeration alone led to a reduction of 47.5% in inorganic sulfur, the largest average reduction in inorganic sulfur achieved following chemical pretreatment was 51.8%, which occurred using 1.0 wt % sodium carbonate. The optimum concentration for the rejection of ash appeared to be 0.5 wt %, where a reduction of 60.9% was achieved. By comparison, oil agglomeration alone rejected 51.4% of the ash.

In summary, these results show that chemical pretreatment using the conditions chosen was not equally effective for all coals, in improving the rejection of ash and inorganic sulfur by subsequent agglomeration. Of the four kinds of coal studied, chemical pretreatment improved the separation of carbonaceous and mineral constituents in only two cases. In these two coals, however, the improvement was tremendous.

It is very likely that the effectiveness of chemical pretreatment in improving the rejection of inorganic sulfur and ash by selective oil agglomeration is dependent upon the structure of the coal and on the composition of the mineral constituents. A correlation between the microstructure of the coal and the effectiveness of chemical pretreatment would play an important role in identifying potential improvements in both the chemical pretreatment and selective oil agglomeration techniques.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Group I experiments

A preliminary investigation of chemical pretreatment and selective oil agglomeration led to the following conclusions:

1. The heavier fuel oils are not as selective in separating mineral and carbonaceous particles when used to agglomerate fairly coarse coal (minus 60 mesh).
2. The use of heavy fuel oils to agglomerate extremely fine coal (minus 400 mesh) aids in rejecting mineral matter; however, good yield of product is not guaranteed.
3. Size reduction from minus 60 mesh to minus 400 mesh increases the amount of inorganic sulfur which may be rejected through agglomeration.
4. Chemical pretreatment prior to oil agglomeration results in increased rejection of inorganic sulfur during agglomeration.
5. For the pretreatment conditions examined, sodium carbonate appears to be the most effective of the

common alkalis for use in chemical pretreatment.

6. Chemical pretreatment also increases the amount of inorganic sulfur which may be rejected by froth flotation.
7. Extreme slurry pH levels, either high or low appear to increase the rejection of inorganic sulfur by oil agglomeration. In some cases however, high pH levels may reduce the yield of agglomerated product.
8. Chemical pretreatment followed by oil agglomeration or froth flotation effectively complements other beneficiation methods such as gravity separation.

<u>Group II experiments</u>

By performing experiments involving chemical pretreatment and oil agglomeration of various pyrite samples, the following conclusions were drawn:

1. Heater oil, a light fuel oil, is not effective in agglomerating finely divided pyrite in aqueous suspension.
2. Heavy fuel oils can agglomerate substantial portions of the suspended pyrite; however, chemical pretreatment is an effective means of suppressing such

agglomeration.

3. Larger portions of the pyrite may be agglomerated during a given period of agitation using emulsified rather than straight fuel oil.
4. Using pretreatment conditions similar to those applied to coal, only a small portion (less than 2%) of the pyrite was lost due to chemical leaching.

Group III experiments

An investigation of various chemical pretreatment and oil agglomeration parameters led to the following conclusions concerning Scott coal:

1. In chemical pretreatment of minus 400 mesh coal, there appeared to be an optimum sodium carbonate concentration (1 or 2 wt %) for the rejection of inorganic sulfur. To a limited extent this was also true for the rejection of ash.
2. While chemical pretreatment at room temperature was shown to be essentially non-effective, pretreatment for 15 min at 50°C and higher temperatures was very effective in rejecting ash and inorganic sulfur from minus 400 mesh coal.

3. Chemical pretreatment and subsequent agglomeration was shown to be substantially more effective in reducing the ash and sulfur contents of minus 400 mesh samples than of minus 100 mesh samples.
4. Replacing the chemical pretreatment liquor with deionized water prior to agglomeration reduced the amount of ash and inorganic sulfur which was rejected.
5. The agglomeration of pretreated suspensions with heavy fuel oil mixtures resulted in the rejection of more inorganic sulfur and ash than agglomeration with light oils.

Group IV experiments

As a result of experiments involving the chemical pretreatment and agglomeration of coals from different geographical sources, the following conclusion was drawn:

1. For the conditions and methods used in these experiments, chemical pretreatment and subsequent oil agglomeration was shown to be very effective in the case of Scott coal and Western Kentucky coal. The method of pretreatment was not nearly as effec-

tive when applied to coals from the Lovilia mine or the Illinois No. 5 seam.

Recommendations

1. A more thorough investigation should be made concerning the use of other alkalis in chemical pretreatment. Experiments should be performed using several alkali concentrations, particularly in the case of soluble alkalis.
2. Some work should be done to determine the effect of other operational variables on the combined chemical pretreatment/oil agglomeration process. These variables might include the concentration of solids used in the pretreatment reaction and the use of oxygen rather than air in the oxidation reaction.
3. A better understanding of the chemistry of chemical pretreatment and the associated changes in surface chemistry might allow a more systematic approach to improving the process.
4. Since chemical pretreatment appears not to be equally effective on all types of coal, a correlation between the structure of the coal and the

effectiveness of chemical pretreatment would be helpful in improving the technique.

5. Since selective oil agglomeration is largely responsible for the separation of coal and mineral particles and for the recovery of clean coal, much work should be done to improve the rejection of mineral matter and the character of the agglomerated product.
6. The operation of a large-scale process development unit incorporating both chemical pretreatment and selective oil agglomeration would provide valuable information concerning the use of these techniques in commercial coal beneficiation. This type of operation would yield a more realistic picture of the techniques and the problems which must be solved.

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APPENDIX: SUPPLEMENTAL DATA FOR THE GROUP III AND GROUP IV EXPERIMENTS

Table A-1. Minus 400 mesh run-of-mine Scott coal was pretreated for 5 min at 80°C using sodium carbonate solutions of various concentrations. The samples were agglomerated using an oil mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	Na, %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
				TIS	Ash	
Feed coal	0.016	4.96	15.66	---	---	---
0.0	0.019	3.06	9.73	38.31	37.87	93.05
	0.017	3.05	9.84	38.51	37.16	94.91
0.5	0.120	2.31	7.58	53.42	51.60	94.17
	0.150	2.45	9.15	50.60	41.57	92.01
1.0	0.170	1.93	6.68	61.09	57.34	95.36
	0.240	1.86	6.68	62.50	57.34	92.72
2.0	0.320	1.08	7.09	78.22	54.72	93.20
	0.280	0.94	6.18	81.05	60.54	92.17
3.0	0.260	1.08	5.93	78.22	62.13	91.17
	0.320	1.02	6.42	79.44	53.00	95.75
4.0	0.260	1.26	6.27	74.60	59.96	93.84
	0.240	1.09	6.18	78.02	60.54	94.93

Table A-2. Minus 400 mesh run-of-mine Scott coal was pretreated for 15 min at 80°C using sodium carbonate solutions of various concentrations. The samples were agglomerated using an oil mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	Na, %	TIS, %	Ash, %	Reduction in, % TIS	Reduction in, % Ash	Combust. yield, %
Feed coal	0.016	4.96	15.66	---	---	---
0.0	0.016	2.50	9.38	49.60	40.10	85.33
	0.016	2.63	9.68	46.98	38.19	93.79
0.5	0.082	1.99	7.43	59.88	52.55	91.98
	0.108	2.08	7.67	59.07	51.02	90.99
1.0	0.180	1.11	7.54	77.62	51.85	92.52
	0.160	1.18	7.42	76.21	52.62	92.29
2.0	0.150	0.64	5.70	87.10	63.60	93.49
	0.150	0.60	5.82	87.90	62.84	92.24
3.0	0.160	0.92	7.02	81.45	55.17	91.17
	0.160	0.84	5.70	83.06	63.60	92.67
4.0	0.230	1.06	6.10	78.63	61.05	93.21
	0.270	1.12	6.02	77.42	61.56	93.38

Table A-3. Minus 400 mesh run-of-mine Scott coal was pretreated for 30 min at 80^{o}C using sodium carbonate solutions of various concentrations. The samples were agglomerated using an oil mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	Na, %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
				TIS	Ash	
Feed coal	0.016	4.96	15.66	---	---	---
0.0	0.017	2.48	9.71	50.00	37.99	89.72
	0.016	2.58	9.63	47.98	38.50	88.03
0.5	0.128	1.46	7.83	70.56	50.00	89.63
	0.131	1.31	7.60	73.59	51.47	90.89
1.0	0.128	0.89	5.62	82.06	64.11	90.40
	0.148	1.00	6.52	79.84	58.36	92.37
2.0	0.220	1.07	7.43	78.43	52.55	88.29
	0.140	0.96	4.92	80.64	68.58	92.49
3.0	0.160	1.08	5.37	82.66	65.71	94.54
	0.150	0.86	5.31	82.66	66.09	92.78
4.0	0.150	0.81	5.42	83.67	65.39	91.84
	0.140	1.06	6.36	78.63	59.39	91.24

Table A-4. Minus 400 mesh run-of-mine Scott coal was pretreated under various conditions and agglomerated with an oil mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	Res. time, min	Temp., ^oC	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
					TIS	Ash	
Feed coal	--	--	4.96	15.66	---	---	---
0.0	15	50	2.44	9.20	50.80	41.25	87.10
	15	50	2.66	9.34	46.37	40.36	86.70
0.5	15	50	1.56	6.67	68.55	57.41	91.82
	15	50	1.51	6.66	69.56	57.47	89.53
1.0	15	50	1.26	6.30	74.60	59.77	90.52
	15	50	1.31	6.21	73.59	60.34	89.94
2.0	15	50	0.88	6.15	82.26	60.73	89.31
	15	50	0.91	6.24	81.65	60.15	87.89
2.0	5	50	1.20	6.55	75.81	58.17	90.59
	5	50	1.16	6.34	76.61	59.51	91.93
2.0	15	23	2.88	9.34	41.94	38.04	95.54
	15	23	3.11	9.67	37.30	36.46	94.57

Table A-4. (continued)

Conc. of Na_2CO_3, wt %	Res. time, min	Temp., °C	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
					TIS	Ash	
3.0	15	50	1.02	6.59	79.44	57.92	93.23
	15	50	0.94	6.74	81.05	56.96	94.79
4.0	15	50	1.28	7.25	74.19	53.76	93.26
	15	50	1.26	7.53	74.60	51.92	95.96

Table A-5. Minus 100 mesh run-of-mine Scott coal was pretreated for 15 min at 80°C using sodium carbonate solutions of various concentrations. The samples were agglomerated using an oil mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
			TIS	Ash	
Feed coal	4.96	15.66	---	---	---
Agg. only	4.17	12.89	15.93	17.69	95.79
	3.72	11.32	25.00	27.71	96.08
0.0	3.38	10.98	31.85	29.88	96.39
	3.63	11.58	26.81	26.05	97.12
0.5	3.00	9.44	39.52	39.72	98.70
	2.88	10.49	41.93	33.01	95.64
1.0	3.14	10.14	36.69	35.25	95.78
	2.81	9.92	43.35	36.65	97.58
2.0	2.20	8.57	55.64	45.27	100.32
	2.64	8.98	46.77	42.66	100.97
3.0	2.07	9.30	58.27	40.61	95.84
	2.11	9.61	57.46	38.63	96.58

Table A-5. (continued)

Conc. of Na_2CO_3, wt %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
			TIS	Ash	
4.0	2.28	9.06	54.03	42.14	94.71
	1.77	8.89	64.31	43.23	98.58

Table A-6. Minus 400 mesh run-of-mine Scott coal pretreated for 15 min at 80°C using sodium carbonate solutions of various concentrations. The samples were agglomerated using heater oil.

Conc. of Na_2CO_3, wt %	TIS, %	Ash, %	Reduction in, % TIS	Reduction in, % Ash	Combust. yield
Feed coal	4.96	15.66	---	---	---
Agg. only	3.03	10.03	38.91	35.95	88.62
	2.94	10.59	40.72	32.37	81.20
0.0	2.99	10.86	39.72	30.65	84.49
	2.96	10.84	40.32	30.78	83.92
0.5	2.94	10.98	40.72	29.88	87.54
	2.84	7.68	42.74	50.96	91.62
1.0	2.11	8.59	57.46	45.15	88.14
	1.95	9.80	60.68	37.42	88.42
2.0	1.91	10.33	61.49	34.03	89.33
	1.94	9.84	60.89	37.16	89.60
3.0	2.06	9.81	58.47	37.36	88.09
	2.06	9.85	58.47	37.10	89.94
4.0	2.37	9.46	52.22	39.59	86.57
	2.38	11.10	52.02	29.12	88.14

Table A-7. Minus 400 mesh run-of-mine Scott coal was pretreated for 15 min at 80^{o}C using sodium carbonate solutions of various concentrations, but the alkaline solution was removed prior to agglomeration. The samples were agglomerated using an oil mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	Na, %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
				TIS	Ash	
Feed coal	0.029	4.77	15.16	---	---	---
Agg. only	0.026	3.24	10.84	28.50	32.07	97.36
	0.022	3.28	10.96	27.70	31.23	96.78
0.0	0.025	2.92	11.01	38.78	27.37	98.90
	0.027	2.84	10.97	40.46	27.64	98.65
0.1	0.065	2.77	10.70	41.93	29.42	99.28
	0.056	2.89	10.80	39.41	28.76	99.52
0.5	0.051	2.57	10.38	46.12	31.53	98.51
	0.059	2.60	10.59	45.49	30.14	98.20
1.0	0.060	2.19	9.69	54.09	36.08	96.88
	0.049	2.16	9.75	54.72	35.69	96.78
2.0	0.064	2.42	10.21	49.27	32.65	93.58
	0.062	2.36	10.05	50.52	33.71	94.04

Table A-7. (continued)

Conc. of Na_2CO_3, wt %	Na, %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
				TIS	Ash	
2.0 (w/N_2)	0.021	2.92	10.90	38.78	28.10	98.38
	0.023	3.06	10.64	35.85	29.82	100.52
2.0 (w/o air)	0.061	2.33	10.41	51.15	31.33	98.82
	0.062	2.23	10.34	53.25	31.79	98.60
4.0	0.057	2.49	10.62	47.80	29.95	81.83
	0.057	2.54	10.46	46.75	31.00	85.85

Table A-8. Minus 400 mesh run-of-mine Western Kentucky coal was pretreated for 15 min at 80°C and agglomerated with a mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Concen. of Na_2CO_3, wt %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
			TIS	Ash	
Feed coal	1.77	20.55	---	---	---
Agg. only	0.78	11.10	55.93	45.98	96.87
	0.84	11.03	52.54	46.33	97.47
0.0	0.70	11.05	60.45	46.23	95.90
	0.72	11.01	59.32	46.42	98.59
0.5	0.33	5.93	81.36	71.14	100.46
	0.43	5.98	75.71	70.90	99.91
1.0	0.20	5.49	88.70	73.28	99.03
	0.28	5.34	84.18	74.01	99.59
2.0	0.25	5.42	85.88	73.62	97.28
	0.24	5.64	86.44	72.55	100.01
3.0	0.29	5.83	83.62	71.63	98.42
	0.22	5.22	87.57	74.60	98.90
4.0	0.26	5.71	85.31	72.21	98.86
	0.28	5.57	84.18	72.90	98.28

Table A-9. Minus 400 mesh run-of-mine Lovilia coal was pretreated for 15 min at 80 °C using sodium carbonate solutions of various concentrations. The samples were agglomerated with an oil mixture consisting of 50 vol % No. 6, LLS and 50 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
			TIS	Ash	
Feed coal	2.99	15.21	---	---	---
Agg. only	1.28	8.15	57.19	46.42	96.16
	1.28	7.96	57.19	47.67	96.87
0.0	1.21	6.64	59.53	56.34	96.16
	1.30	7.21	56.52	52.60	94.94
0.5	0.97	5.50	67.56	63.84	95.39
	1.01	5.76	66.22	62.13	95.65
1.0	0.91	6.07	69.56	60.09	96.20
	0.88	6.02	70.57	60.42	94.84
2.0	1.32	6.99	55.85	54.04	95.81
	1.29	6.61	56.87	56.54	95.71
3.0	1.21	6.34	59.53	58.32	97.08
	1.19	6.15	60.20	59.57	97.81
4.0	1.32	7.03	55.85	53.78	97.62
	1.26	7.57	57.86	50.23	97.71

Table A-10. Minus 400 mesh Illinois No. 5 coal was pretreated for 15 min at 80°C using sodium carbonate solutions of various concentrations. The samples were agglomerated using an oil mixture consisting of 75 vol % No. 6, LLS and 25 vol % No. 200, LLS fuel oils.

Conc. of Na_2CO_3, wt %	TIS, %	Ash, %	Reduction in, %		Combust. yield, %
			TIS	Ash	
Feed coal	1.39	13.15	---	---	---
Agg. only	0.73	6.57	47.48	50.04	93.67
	0.73	6.21	47.48	52.78	96.82
0.0	0.74	6.19	46.76	52.93	95.73
	0.78	6.08	43.88	53.76	95.84
0.5	0.74	5.10	46.76	61.22	91.45
	0.74	5.19	46.76	60.53	92.91
1.0	0.71	5.44	48.92	58.63	92.58
	0.63	5.62	54.68	57.26	96.41
2.0	0.73	6.02	47.48	54.22	95.94
	0.72	6.37	48.20	51.56	93.73
3.0	0.76	6.68	45.32	49.20	94.94
	0.65	6.86	53.24	47.83	94.22
4.0	0.75	6.57	46.04	50.03	96.30
	0.74	6.35	46.76	51.71	94.06