



I PRO 346 – Fall 2006
Design of Coal Desulfurization Processes to Improve the
Environment
Midterm Report

1.0 Revised Objectives

The objective of this IPRO is to choose an appropriate method (or combination of multiple methods) for desulfurizing coal. Three types of methods have been researched in order to find the best way to desulfurize coal- chemical, physical and biological. We have decided that two chemical methods seem promising, molten caustic leaching and oxydesulfurization. There is also a physical method involving froth flotation and magnetic separation that has advantages of its own. However at the moment we have not been able to decide which method is most feasible, economically feasible, and conceptually sound. Consequently we are calculating a rough cost estimate and conducting further research on the above-mentioned methods to decide between them. After this imminent decision the group will move forward and design the process equipment; later a more in depth economic assessment will be done to cost the equipment. All of the group's goals will be completed within this semester.

2.0 Results to Date

- A. The majority of the research that needs to be done to fulfill our project goals has been completed. At the moment we are at a decision making step where we have to choose a method to focus on. Economic research and further analysis of the data we have collected are being used to aid us in the decision making process.
- B. In order to better understand coal and how it is implemented into the energy making process, the group began this project by researching coal, coke produced from coal, different types of sulfur found in coal, and the process of removing sulfur from coal. A few weeks were spent on this part of the project, giving us a firm background knowledge. The following sections outline areas we researched:

1. Information on Coal

What is Coal?

Coal, generally known as a major resource to power generation field, is a very unique compound due to its large yield of energy. Coal formation begins when plants die and undergo incomplete decomposition due to an anaerobic environment, such as the bottom level of a swamp. Over time, the swamp drains and new layers of land form on top of the plant matter. The pressure caused by the new layers forces almost all of the moisture out of the decomposing plants, leaving mainly the organic matter to rest. This then fossilizes into coal.

Coal is composed of four general resources: Carbon (75-84%), Oxygen (5-13.5 %), Hydrogen (5-6%), and Sulfur (0.7-5%). In addition, coal contains a variety of trace elements, such as arsenic, boron, beryllium, cadmium, chlorine, cobalt, chromium, copper, fluorine, mercury, lithium, manganese, molybdenum, nickel, phosphorus, lead, sulfur, tin, selenium, thorium, uranium, vanadium, and zinc, (Source: "Coal Geology of Illinois", ISGS). Illinois coals unlike other coals within the United States are generally known for their higher calorific value and high sulfur content. The two main Illinois seams, the Springfield seam and the Herrin seam, have between one and four percent sulfur and calorific values between 9,700 -12,700 BTU/lb¹. These coals will be discussed more extensively however later in the report.

¹ Russell Jacobson, "Coal Geology of Illinois" 2003

Most of Illinois rests on a very wide bed of coal known as the Illinois basin, which also extends under parts of Indiana, and eastern Kentucky. The only areas of Illinois not underlain by coal are in the northern fourth of the state and narrow strips beside major waterways.² The beds of coal with the lowest sulfur content in Illinois are all in the southern and central portions of the state, causing a general focus of mining to be concentrated within that area.³

Fuel Type	Yield	Efficiency
Bituminous Coal	30.2 MJ/kg	590.20 MJ/Dollar
Sub-bituminous Coal	23.2 MJ/kg	852.78 MJ/Dollar
Crude Oil	38.5 MJ/L	87.947 MJ/Dollar
Liquid Natural Gas	25.2 MJ/L	-----
Natural Gas	38.4 MJ/m3	120.56 MJ/Dollar

Prices used and sources: Bituminous Coal – \$46.42/short ton, (www.answers.com/topic/bituminouscoal_and_lignite_surface_mining), Note: 2002 price, slightly low but coal prices haven't changed dramatically in recent years.; Sub-Bituminous coal - \$24.68/short ton, Ibid, also 2002 price; Crude Oil \$69.60/barrel (158.99L), (www.nyse.com); Natural Gas \$330.60/(10⁷ kcal), (www.eia.doe.gov/emeu/international/ngasprie.html); No price was found for Liquid Natural Gas

As noted in the table above, all units of energy have a relatively large yield per unit measure, but coal give the most cost-efficient yield of any the fossil fuels. Coal allows nearly a five to ten fold efficiency on the dollar to any of the other fossil fuels. This however, can still be outweighed by the amount of harmful emissions created by the coal burning process.

Because of its relatively high burning potential, coal is the fossil fuel of choice for a large percentage of power plants within the world. Another advantage of coal is that the resource is widely available, and when dealing with power generation, it does not depend on specific weather conditions like its counterparts in solar or wind power. Coal can also be easily stored after mining. Lastly, coal is also portable, allowing power plants to be built in areas where alternative forms of power generation, such as hydroelectric dams, may not be feasible.

Unfortunately, when coal is burned the sulfur it contains is released into the air as sulfur dioxide as well as other emissions, which increases haziness, irritates the lungs, and is a major component of acid rain.⁴ Efforts by watchdog groups such as the EPA to reduce pollution have led to an increased interest in methods to remove sulfur compounds from coal emissions. More on the emission factors of coal will be examined later in this report.

Types of Coal

Coal is classified into four major types, or “ranks.” Based mainly on the select age and depth of each coal member, the carbon content and energy yields vary for each. The general names of each rank are Lignite, Sub-bituminous, Bituminous, and Anthracite.

Lignite, often referred to as “brown coal”, is the softest of the four types of coal. It ranks the lowest in carbon content and is the youngest form of all coals. The moisture content of lignite coal, based on composition, is the highest mainly due to its young age⁵. According to

² "Subsurface Geology and Coal Resources of the Pennsylvanian system in Clark and Edgar Counties, Illinois., ISGS <http://www.isgs.uiuc.edu/coalsec/coal/pubsfolder/c380/c380.pdf>

³ http://www.isgs.uiuc.edu/coalsec/coal/trace_elements.htm

⁴ http://en.wikipedia.org/wiki/Sulfur_Dioxide

⁵ Coal resource, 4

American Coal Foundation, the majority of lignite coal is mined in Texas, but large deposits are also found in Montana, North Dakota, and some Gulf Coast states. It is primarily used for steam-electric power generation, while the heating content of this coal ranges between 4,000 and 8,000 BTUs-per-pound (British thermal units per pound) with a carbon content of 25%-35%.

Sub-bituminous is a medium soft coal which contains lower moisture content than its counterpart lignite coal. Sub-bituminous is mined mainly in a half-dozen Western states and Alaska. Like lignite, it is mainly used as fuel for steam-electric power generation. The heating content of this coal lies between 8,000 and 13,000 BTUs-per-pound while its carbon content is 35%-45%. According to American Coal Foundation, sub-bituminous has lower sulfur content than other types, which makes it attractive for major power generation because it is clean burning potential.

Bituminous coal is the first of the "hard coals". The moisture content in this coal is again very low due to its increased age. This coal is the most abundant form in the United States and it is mined primarily in the Eastern and Midwestern region of the US. It is used primarily for power generation and manufacturing coke for the steel industry. The heating content of bituminous is between 10,500 and 15,500 BTUs-per-pound with a relative carbon content of 45%-85%.

Anthracite is the highest rank and the hardest of the all types of coal. It is mined mostly in the eastern Pennsylvania region. It is used for residential and commercial space heating, municipal water purification, and treatment plants⁶. The heating content of anthracite coal tends to be over 15,000 BTUs-per-pound mainly since its carbon content ranges between 85%-95%. The American Coal Foundation notes that anthracite coal is not a very prevalent coal within the U.S. coal market.

In the state of Illinois, Bituminous coal is the only class of coal present. As stated earlier, Bituminous coal is generally used for power generation and within the steel industry for the generation of coke. However, within the coal in Illinois lie seven distinct subgroups of coal. Each of these groups is named for the various locations in which they were found within the state, and also by the select depth of the coal field under the surface of the earth. The six major groups are as follows: Rock Island (#1), Colchester (#2), Sumnum (#4), Springfield (#5), Herrin (#6), and Danville (#7). Out of these select groups, the most predominantly used types are the Springfield and Herrin coal seams. Both are known for a relatively high energy output and a rather low sulfur percentage within the coal structure.

Springfield coal, mainly found in mid-central and southern Illinois, is Illinois's highest energy coal. The coal, which is usually surfaced mined, yields a calorific value of 12.4-12.7k BTU/lb when at its peak. However, since the burning potential is higher than other coals in the region, Springfield coal also has a moderate sulfur percentage which lies between 3-4% of the coal. The ash percentage also tracks in at 3-4%, which factors in during the burning process of this particular type.

Herrin coal, known for its generally low sulfur content, is Illinois's highest mined coal and is located in the southern areas of the state. The advantage of using this coal for power production lies within the general sulfur content of the coal, which ranges from .5-2.5%. Although this coal does not produce as much energy as Springfield coal, approximately 10.4-11.1k BTU/lb, it is more widely incorporated into power generation. The ash content of this coal however, is very high, ranging from 8-12%.

⁶ Coal resource, 4

Coal Sources

Another important fact when determining a particular coal to mine is whether one wants to gather their coal from surface or underground mines. Surface mining is a relatively cheap process, but yields less energy coal than the underground counterparts, mainly since the coal has a younger age. However, due to the increasing risk of underground mining, the surface mining industry within Illinois has flourished greatly.

Coal Emissions and Harmful Compounds

Coal emissions are a very strong enemy of its use within the world as a predominant energy source. Mainly, coal has three harmful products which it creates both pre- and post-combustion: sulfur dioxide, sulfur oxide, and nitrous oxide. Sulfur dioxide is a harmful gas that is notorious for depletion of the ozone layer. After combustion, the sulfur that exists within the coal, converts mainly to this harmful substance, which exits with all the excess coal fume gases. The most effective way to lower the amount of sulfur dioxide in the emissions is to either utilize a scrubbing of the gases upon exit, or rather to deplete the sulfur from the coal before combustion by a use of scrubbing or other various methods created. The EPA regulates the emissions on coal at 2.5 pounds of SO₂/mmBtu (million British thermal units)⁷, which is stagnantly based on heat input. Generally, if you get the sulfur out of the coal prior to combustion, then the sulfur dioxide output will be kept at a general low.

Another sulfur compound that formed in coal is sulfur oxide. This form is generally present in the coal bed prior to mining. The most efficient way to eliminate this compound is to inject lime or dolomite into the coal bed. This process will then eliminate the sulfur oxide at a relatively fast rate, and could also be used during the combustion stage of the coal use.

The last harmful compound created from coal is nitrous oxide. This is not originally part of the coal, however, when the coal is scrubbed in order to eliminate the select sulfur compounds, this molecule forms due to the formations and oxidations of hydrogen cyanide. It has been found that by using a triple combustion chamber technique to burn the coal has greatly reduced this emission, since it has not been able to form under these conditions. However, this select emissions is not as harmful as the other two stated above, since it is not as prevalent.

Overall it is evident that the use of Springfield and Herrin coal are very beneficial to the Illinois power industry and abroad. However, it is crucial that the implementation of desulfurization coal be used in order to lower its potential to harm the environment.

Coal Selection for this Project

In order to realistically model our process, one type of coal needed to be chosen. Our group decided to remain local and choose a coal found in Illinois. Our decision was Illinois #6, or Herrin coal. This type of coal was chosen because it has a relatively low sulfur content and also has an even distribution of both pyritic and organic sulfur. The following tables display the amounts of various compounds found in Illinois #6 coal.

⁷ www.EPA.gov

Sample Number	Ultimate Analysis ⁸				
	Hydrogen %	Carbon %	Nitrogen %	Oxygen %	Sulfur %
Illinois #6	5.07	66.15	1.40	12.46	3.40
Illinois #6	5.01	64.80	1.28	12.85	4.21
<i>Average</i>	<i>5.04</i>	<i>65.475</i>	<i>1.34</i>	<i>12.655</i>	<i>3.805</i>

Table 1: Composition of Illinois #6 Coal

Sample Number	Heat of Combustion ¹		Forms of Sulfur ¹		
	Kcal/kg	Btu/lb	Sulfate %	Pyritic %	Organic %
Illinois #6	6588.96	1872	0.08	1.34	1.98
Illinois #6	6473.52	1664	0.27	2.31	1.63
<i>Average</i>	<i>6531.24</i>	<i>1768</i>	<i>0.175</i>	<i>1.825</i>	<i>1.805</i>

Table 2: Head of Combustion and Sulfur Amounts of Illinois #6 Coal

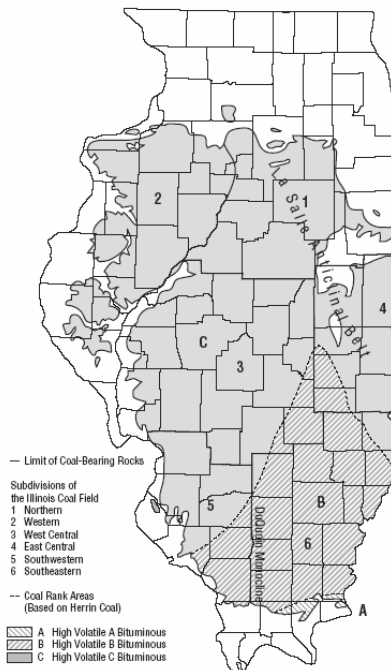


Figure 1: Subdivisions of the Illinois Coalfield. Areas of high volatile A, B, C bituminous rank coals.⁹

⁸ National Coal Resources Data System, "US Coal Quality Database" <http://energy.er.usgs.gov/products/databases/coalqual/index.htm>

⁹ Russell Jacobson, "Coal Geology of Illinois" 2003

Illinois #6 coal is mined extensively in the state and accounts for 40% of the total coal mined. This type of coal is found to be in the best quality and most abundant in the Jefferson-Franklin-Williamson counties. This area is known as the “Quality Circle,” covering 250 square miles. The sulfur content is an average of 1.5% in this area.

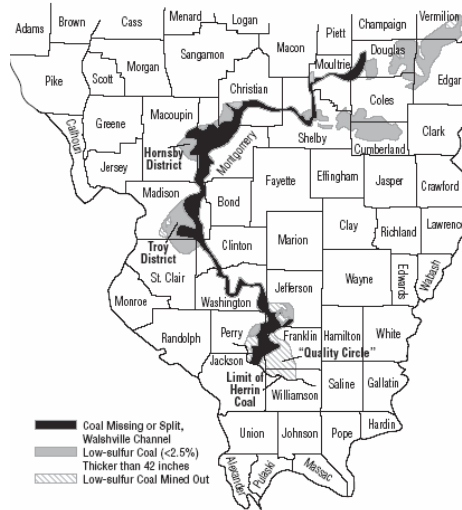


Figure 2: Illinois #6 and the Quality Circle⁹

2. Information on Coke

What is Coke?

When coal is heated to temperatures up to 1100°C in an anaerobic environment, it is stripped of many of its components including tar, ammonia, water, light oils, a gas known as coke oven gas (which is in return reused to heat the furnace), and sulfur compounds. This process is known as carbonization. The leftover substance, referred to as coke, is composed of many crystallographic forms of coal along with ash-like remains containing many of the minerals that survived the carbonization. Also present after carbonization are bits of sulfur that were not completely removed during combustion with the rest of the sulfuric compounds.¹⁰ The following is a table listing the amounts of the different components found in coke, adapted from a table found on the American Iron and Steel Institute’s website:

Physical Components of Coke	Composition % by Weight
Ash	8.0 - 9.0 %
Moisture	2.5 – 5.0 %
Sulfur	0.65 – 0.82 %
Volatile Matter	0.5 – 1.5 %
Alkali (K ₂ O+ Na ₂ O)	0.25 – 0.40 %
Phosphorus	0.02 – 0.33%

Table 1: Coke Physical Composition¹¹

¹⁰ Kroschwitz, Jacqueline, ed. “Coal Conversion Processes.” *Kirk-Othmer Encyclopedia of Chemical Technology*. 4th ed. Vol. 6. pp. 489-510.

¹¹ “Coke Production for Blast Furnace Ironmaking.” American Iron and Steel Institute. 17 Sept. 2006. <<http://www.steel.org/AM/Template.cfm?Section=Home&template=/CM/HTMLDisplay.cfm&ContentID=12304>>

History of Coke

The production of coke was first thought of by Sir Henry Platt in 1603. At that time, England was having problems producing iron because they relied heavily on using wood, which was becoming both limited and expensive. Knowing that burning coal gave off unwanted smoky fumes, Platt suggested that coke be charred in a way similar to how charcoal is made from wood. It took 39 years for the process to actually be used, as it was in Derbyshire to roast malt to prepare it for brewing beer.¹² In 1709 a former apprentice from a malt mill named Abraham Darby produced coke in a blast furnace and used it to produce cast iron; however, this technique remained expensive until the introduction of steam power. The resulting fall in the price of iron production helped lead Europe into the Industrial Revolution.¹³

Worldwide Yearly Production of Blast Furnace Coke

The Kirk-Othmer Encyclopedia of Chemical Technology compiled the following table listing various countries and their yearly production of coke using a blast furnace from 1970 through 1990. Analyzing this table shows that North American and Western European production fell in the twenty years while the rest of the countries increased their amount. One reason for this is because the majority of coke plants in these areas are over 25 years old; as plants age, they become less efficient in producing coke and so less is produced. These numbers are assumed to continue decreasing unless new plants are constructed.¹⁴

Production of Blast Furnace Coke, tons x 10 ⁶							
Country	1970	1980	1985	1987	1988	1989	1990
North America	69.7	47.2	30.7	30.0	30.3	34.7	30.9
Western Europe	98.6	78.1	70.7	63.5	62.6	60.1	58.5
Japan	36.4	54.4	51.7	46.4	50.6	51.6	53.0
Others*	10.1	9.6	5.9	7.5	8.4	8.5	8.5
Total Industrial Countries	214.8	189.3	159.0	147.4	151.9	154.9	150.9
Latin America	4.4	7.7	10.6	9.8	11.7	11.6	11.4
Asia	8.9	17.0	19.9	21.5	23.2	23.6	25.0
Africa and Middle East	0.6	2.2	2.2	2.1	2.1	2.2	2.2
Total developing countries	13.9	26.9	32.7	33.4	37.0	37.4	38.6
Total Western World	228.7	216.2	191.7	180.8	188.9	192.3	189.5
China, etc	25.5	46.4	51.4	61.4	64.6	69.7	76.7
Russia and Eastern Europe	102.8	122.5	119.5	120.9	120.8	115.2	111.7
Total Eastern Countries	128.3	168.9	170.9	182.3	185.4	184.9	188.4
World Total	357.0	385.1	362.6	363.3	374.3	377.2	377.9

*mainly Australia and South Africa

Table 2: Production of Blast Furnace Coke¹⁵

¹² "Coke (fuel)." Wikipedia – The Free Encyclopedia. 17 Sept. 2006. <[http://en.wikipedia.org/wiki/Coke_\(fuel\)](http://en.wikipedia.org/wiki/Coke_(fuel))>

¹³ Goucher, C., LeGuin, C., and Walton, L. *In the Balance: Themes In Global History*. Chapter 15 - "Crucibles of Change: Landscapes, Material Culture, and Social Life after 1500." Boston: McGraw-Hill, 1998.

¹⁴ Kroschwitz, Jacqueline, ed. "Coal Conversion Processes." *Kirk-Othmer Encyclopedia of Chemical Technology*. 4th ed. Vol. 6. pp. 489-510.

¹⁵ Kroschwitz, Jacqueline, ed. "Coal Conversion Processes." *Kirk-Othmer Encyclopedia of Chemical Technology*. 4th ed. Vol. 6. pp. 489-510.

Coking Mechanism

The importance of pre-combustion coal desulfurization can be best realized by studying the mechanism used to produce coke for blast furnaces. Coal is baked in a sealed, airtight oven at temperatures that go up to 1473 K in a process that purifies the carbon by removing water, radicals and other volatile components to fuse the pure coal particles together. The preliminary requirements for the coking process to be undertaken are a constant heat supply that is normally provided by gas burning flues within the oven and contact between the coal particles throughout the carbonization process. The latter is achieved by filling the coal oven vertically through the dropping of pulverized coal particles from a height.

As the coal is heated, radicals and light volatile molecules that have lower molecular weights than coal are liquefied or turned to gas products. While most of the gases escape, the surface tension of the liquids causes the coal particles to adhere to each other and aids in the fusing process that follows.

With the heat source on the oven walls, the layers of coal closest to the walls are the first to completely stabilize by loss of volatile components and start to soften. The partially fused coal gains plastic-like properties and binds to form an envelope that moves inwards as the coking process continues. Coal closer to the centre of the oven is then heated and volatile particles are driven off in gases as the carbon crystal structure purifies. The coking process is completed once all volatiles have been removed from the coal, and the envelope of plastic-like coal has converged at the centre of the oven, leaving behind pure coke.

The mechanism is a time consuming one; taking 18 hours or more at temperatures of 1473 K (1200°C). This inefficiency can be exacerbated by large amounts of impurities in the coal; in particular sulfur, the removal of which requires added time and heat in order to purify the coke produced. Efficient desulfurization of the coal before coking allows the coking process to proceed at faster rates with lower energy expenditure.¹⁵

3. Forms of Sulfur

Forms of Sulfur in Coal

Sulfur in coal can be classified into two main types: Inorganic and Organic Sulfur. These types can be further subdivided. Inorganic forms of sulfur include: Pyritic Sulfur having the general formula FeS_2 , which takes on two crystalline forms Pyrite (cubic) and Marcasite (orthorhombic); and Sulfate Sulfur, or gypsum, which is formed through the oxidation of Pyritic forms and is generally of the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Organic forms of sulfur are actual bonded to the structure of the coal and can be found in the form of: Mercaptans or Thiols (RSH); Sulfides or Thio-ethers (RSR'); Disulfides (RSSR'); or Aromatic Systems containing a thiopene ring (Wheelock).

As mentioned before our research to date has been in three different fields of coal desulfurization, chemical, physical and biological. The specific methods that we found and researched are listed by category.

1. Biological Methods

Microbial desulfurization of coal, or the use of sulfur-eating bacteria to extract sulfur from coal products, has been a field that has shown great growth within the past years. By using

select bacterium, generally thermophiles known for their susceptibility to live at extreme temperatures, coal could be selected degraded of both organic and inorganic sulfur compounds which exist within the fossil fuel.

Out of the many choices of organisms to use for these processes, some have shown more use than others when specializing on a select organic or inorganic type of sulfur present within coal. *Thiobacillus ferrooxidans* and *Sulfolobus acidocaldarius* are used for the removal of inorganic pyritic sulfur within coal, while *Sulfolobus brierleyi* and *Sulfolobus solfataricus* focus primarily on the removal of organic sulfur.

Specific requirements for desulfurization have to be closely monitored though, when dealing with these select organisms. Bacteria in general, are very selective in the environment surrounding them. These particular organisms require a high temperature, around 45-70 degrees Celsius, a highly acidic pH, and a relatively low salt concentration within the environment.¹⁶ Also, in order for an effective amount of coal to be desulfurized, the coal particles need to be subjected to the bacteria in rather small particles to ensure that the organism can extract the maximum out. Fluctuations in the conditions above can lower the desulfurization process, and possibly kill off the bacterium if the conditions are too harsh.

One of the more known bio-desulfurization procedures for coal was committed using the bacterium *Sulfolobus acidocaldarius*. Within the experiment, coal was ground into a slurry mixture and subjected to this bacterium for a series of days. Present within the coal slurry, were also vital yeast and glucose members to help stabilize the exponential growth of the bacterium above. After ten days of exposure at optimal conditions for the bacterium, the coal was removed by filtering out the bacteria from the solution and using HCl to extract sulfate particles from the remaining coal to determine its select sulfur content. The results showed that 96% of the inorganic sulfur present within the coal was removed, yielding 50% total sulfur removal¹⁷.

Overall, there are various advantages and disadvantages of using microorganisms as coal desulfurizing agent. Pre-combustion bio-desulfurization has notable advantages over physical and chemical methods. First, lower capital is needed for startup and operating costs are generally kept at a low. Second, lower energy loss is portrayed within the coal, because specific elements of combustion are not extracted from the coal as shown in the other processes. Third, it is less energy intensive than chemical processes because it operates at lower temperatures and pressures than competing chemical desulfurizing processes¹⁸. Lastly, the inorganic sulfur removal rates of these organisms are very high, although a problem can be established from the lower yield of total sulfur degradation. In conclusion, bio-desulfurization processes of coal are very useful when dealing with the inorganic products of the sulfur compounds present in the system, but extended time and low sulfur yield make this area undesirable. Hopefully, within the future, more emphasis will be set on this field to improve the processes and provide a cheap and effective way to remove all types of sulfur from coal.

¹⁶ Jorjani, E., Rezai, B., Vossoughi, M., Osanloo, M. "Biodesulfurization of the Tabas Deposit Coal by Microorganisms." Journal of Mining Science 40.3 (2004): 310-319.

¹⁷ Kargi, F., Robinson J., "Removal of Sulfur Compounds from Coal by the Thermophilic Organism *Sulfolobus acidocaldarius*" Applied and Environmental Microbiology Oct. (1982): 878-883.

¹⁸ Durusoy, T., Ozbas, T., Tanyolac, T., Yurum, T. "Biodesulfurization of Some Turkish Lignites by *Sulfolobus solfataricus*." Energy & Fuels 6 (1992): 804-808.

Microbial Desulfurization of Coal

There are several types of microorganisms that are used in the coal desulfurization process. *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, & *Thiobacillus acidophilus* are used for the removal of pyritic sulfur from coal¹⁹. *Sulfolobus acidocaldarius* are used for the removal of some of the organic sulfur as well as inorganic pyrite from coal. In addition, *Sulfolobus brierleyi* & *Sulfolobus solfataricus* are primarily used for the removal of organic sulfur and the later one has higher rates and higher percentages removal of organic sulfur in the coal desulfurization process¹⁹.

Effective biodesulfurization of coal depends upon several conditions. They are pH, coal particle size, pulp density, temperature, and mixing rate²⁰. The desulfurization of coal decreased as pH increased from acid to basic. Small coal particles are more effective for removal of sulfur by biodesulfurization process. In addition, the desulfurization of coal decreased as pulp density and temperature increased. According to the "Journal of Mining Science", the maximal sulfur removal conditions are pulp density 5%, coal particle size 350 micrometer, pH-2, incubation 11 days, temperature 30 °C, and the mixing rate 150 rpm (313-316).

Overall, there are several advantages and disadvantages of using microorganisms in coal desulfurization process. Precombustion biodesulfurization has notable advantages over physical and chemical methods. First, it has lower capital and operating costs¹⁹. Second, it has lower energy loss or coal refuse¹⁹. Third, it is less energy intensive than chemical processes because it operates at low temperature (25-75 °C) and low pressure¹⁹. Finally, the total sulfur reductions are 50-60% and organic sulfur reductions are 80-90%^{19,20}. On the other hand, the disadvantages of are low removal percentages in large scale and removal rates have been too low to make the process economically attractive¹⁹.

2. Chemical Methods

IGT Hydrodesulfurization

IGT hydrodesulfurization is a two step process for coal desulfurization that uses a combination of oxydesulfurization and hydrogenation treatments. This technology was developed by The Institute of Gas Technology (IGT), and uses two of the treatments already known. Pulverized coal is contacted with air in a fluidized bed reactor. After this first reaction, coal is reacted with hydrogen in a second fluidized bed reactor. Reactor conditions are: 400C for first reactor, 800C for second reactor²¹. Both operate at atmospheric pressure. For bituminous coal, it is known that this process desulfurizes 25-30% of sulfure in the first fluidized bed reactor. The second fluidized bed reactor removes sulfure as H₂S. The overall efficiency of the *IGT hydrodesulfurization* process is 83% of total BTU if all products are recovered (including steam). An inconvenience from this process is that the step of oxidation destroys the tendency of coal to make coke upon heating.

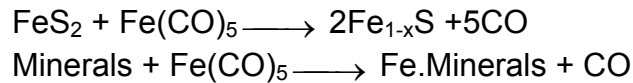
¹⁹ Durusoy, T., Ozbas, T., Tanyolac, T., Yurum, T. "Biodesulfurization of Some Turkish Lignites by *Sulfolobus solfataricus*." *Energy & Fuels* 6 (1992): 804-808.

²⁰ Jorjani, E., Rezai, B., Vossoughi, M., Osanloo, M. "Biodesulfurization of the Tabas Deposit Coal by Microorganisms." *Journal of Mining Science* 40.3 (2004): 310-319.

²¹ S. Komar Kawatra, Timothy C. Eisele, "Coal Desulfurization, High-Efficiency Preparation Methods". Page 332.

Magnex Process

Magnex process uses a chemical reaction to convert weakly magnetic pyrite and nonmagnetic mineral into paramagnetic material. Magnex desulfurization method uses two different reactions to decompose and react with the pyrite and other minerals. This property is used to removal of sulfur and minerals by a low intensity magnet.



The magnetic property is created when metallic iron converts the surface of the pyrite particles into pyrrhotite, which is strongly magnetic. Coal has to be heated and grinded to less than 1.41mm at 170C, therefore this process needs a grinder, a low temperature heater, a reactor, and a magnetic separator. This technology is very simple to use and allows removal of: volatile compounds, elemental sulfur, and pyritic sulfur. This technology has been used in pilot plant scale with bituminous coal. *Magnex* process removes up to 92% of pyritic sulfur, and BTU recoveries range from 86% to 96%.²²

Chemical Comminution

Chemical comminution provides a unique way of crushing coal for mineral liberation. Coal is treated with ammonia solution resulting in selective breakage. As coal size decreases, amount of mineral matter liberated increase, unfortunately cost also increases. Chemical Comminution can liberate more of the pyritic sulfur without grinding to small sizes. Chemically comminuted product after cleaning will contain 80-90% less pyritic sulfur and 50-60% less ash. Ammonia (gas) and methanol are compounds that appear to have the greatest effect in comminution.²² These two compounds fall in the category of chemicals containing a nonbonding pair of electrons. The total capital and operating cost for the chemical treatment using ammonia vapor, under conditions is technically feasible in the laboratory, and vary from \$1.00 to \$1.50 (1970s) per ton of coal product. Using inexpensive density separation technique, the total cost for producing clean coal is around \$2.50 to \$3.00 per ton of product.²³

Laboratory Extraction

Our research showed that laboratory sulfur extraction methods are at their most useful when applied to small scale models. A number of the desulfurization methods studied were highly effective due to the degree to which pyritic and organic sulfur were removed, but would be financially ineffective upon a larger scale due to the high reagent costs involved, or other chemical residues that would be left behind and add on further removal costs.

Methods of using potassium permanganate, sodium hypochlorite or another chlorinated solvent as oxidizing agents were considered, but the usage of sodium hypochlorite is ineffective in the removal of pyritic sulfur and leaves behind deposits of 2-2.7% chlorine within the coal that would require additional cleaning prior to combustion. Potassium permanganate

²² S. Komar Kawatra, Timothy C. Eisele, "Coal Desulfurization, High-Efficiency Preparation Methods". Page 333.

²³ Philip Howard, Rabinder Datta, "Chemical Comminution: A Process for liberating the mineral Matter from Coal" Pages 58-69

is more effective, but costs also outweigh effectiveness with the usage of additional chemicals - 1,1,1-trichloroethane as a pre-cleaning fluid and HCl for a post-filtration wash - making it an increasingly expensive procedure on a large scale.

Supercritical fluid extraction and the Hydride reduction method with SET (Single electron transfer method) and BASE (Lochmann's base reactive mixture) were also considered, but the constant high pressures and heat levels needed for supercritical fluid extraction would make it an inconvenient procedure to apply to several hundred tons of coal each day. The Hydride reduction with SET and BASE, while less expensive, is more time consuming with the combination of the three methods reducing sulfur levels to below 1% but requiring over 54 hours for the desulfurization process to complete. As all these processes involve high costs for the chemical reagents in large quantities, with others also requiring additional heat and temperature controls, or involving slow reaction times, it was decided that the chemical laboratory desulfurization processes would be unviable for application to medium or small sized power plants.

Potassium permanganate

Desulfurization by potassium permanganate requires preliminary pre-cleaning of the coal by heavy media separation using 1,1,1-trichloroethane. The coal is then ground and enters a cycle of oxidation by 6% potassium permanganate solution, followed by filtration and a wash in hydrochloric acid and then hot water. The procedure is repeated thrice, with total sulfur levels being reduced by up to 63%. The process is most effective in the removal of pyritic sulfur, 97% of which is removed²⁴.

Sodium hypochlorite

Sodium hypochlorite is among the least effective chemical desulfurization methods due to the low degree of pyritic sulfur reduction. The process uses treatment of coal with sodium hypochlorite solution and then a wash in sodium carbonate solution, which is repeated twice to reduce overall sulfur by up to 49.5%. However, the usage of sodium hypochlorite causes residual chlorine to be left in the coal (between 2-2.7%), which produces another pre-combustion cleaning requirement²⁵.

Supercritical fluid extraction

Carbon dioxide is used here under supercritical conditions of 54.72 MPa and 755K to remove sulfur from coal in a chromatographic column. This is among the most effective chemical desulfurization methods, removing other volatile materials within the coal as well, but the high pressure and temperature conditions lead to highly prohibitive costs at anything larger than a very small laboratory scale. In addition, the requirement for proper disposal of the solvents would increase costs further²⁶.

²⁴ <http://www.osti.gov/bridge/servlets/purl/10188072-wUqAeu/10188072.PDF>

²⁵ http://pubs.acs.org/cgi-bin/abstract.cgi/enfuem/1989/3/i04/f-pdf/f_ef00016a009.pdf?sessid=600613

²⁶ http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&list_uids=9487670&dopt=Abstract

Hydride reduction, SET and BASE

A series of reactions using lithium aluminium hydride for 24 hours to reduce pyritic sulfur levels, then treating with potassium naphthalene in tetrahydrofuran and finally adding the coal substrate to n-butyl-lithium and potassium t-butoxide at heat in order to remove organic sulfur. The combination of the three methods can leave below 1% total sulfur within the coal, however the slow reaction times (the complete cycle takes at least 54 hours in total) and reagent costs make the method ineffective at industrial levels.

Peroxyacetic Acid

This chemical desulfurization method is intended for laboratory use. This method is not expected to be practical on a large scale due to the multiple reagents used in this method; cost is expected to be higher than most of methods used in industry. Peroxyacetic Acid is two stage process consisted of coal dispersal in glacial acetic acid (CH_3COOH) at 21-104C. Then coal is mixed with 30% hydrogen peroxide (H_2O_2). Finally, coal is filtrated and reacted with sodium bicarbonate in methanol at 350-450C. As a result sulfur compounds are converted into forms that are more amenable to other desulfurization processes. If this method is used in conjunction with a base in an inorganic solvent, peroxyacetic acid removes 85-95% of sulfur. The total yield is expected to be about 80%.²⁷

Oxidative Treatments

Oxidative treatment offers a number of promising chemical methods in regard to Coal Desulphurization. Effectively all the methods result in the removal of both pyritic and organic sulfur by attaching oxygen or similar electronegative element to sulfur.

Metallic Salts

This category includes the Meyers process and a method involving Ferric Chloride. Both of these methods show promise because they integrate well with certain physical methods (magnetic and froth flotation) and operate at atmospheric pressure. However we decided not to pursue developing models using these reactants since they are prohibitively expensive. The reactants necessary for these reactions include NaOH and/or a group I or group II metallic salt. Considering a coal to treating solution (.5M ~ 1M) ratio of 1 / 5 to 1 / 20 (Grant, Coal Desulfurization, US Patent #4167397) we discovered this process to not be economically viable in comparison to alternatives. To further support our conclusion, this method was discovered to only remove about 20% of total sulfur content from Illinois #6 coal.

Chlorinolysis

This method was also found to be prohibitively expensive due to reactant and operating costs. In addition to an expensive reagent, this method also calls for high temperature conditions. Additionally dechlorinating the remaining coal requires the addition of Nitrogen or Hydrogen gas and an even higher temperature. The addition of Nitrogen gas to the coal stream also results in increased NOx emissions (another controlled emission) while Hydrogen gas is expensive. This method does result in extremely good sulfur removal yields peaking at

²⁷ S. Komar Kawatra, Timothy C. Eisele, "Coal Desulfurization, High-Efficiency Preparation Methods". Page 334.

81% total sulfur removal (Ravindram et al, Fluidized Bed Desulfurization, US Patent # 4511362).

Oxydesulfurization

This is the method that we are currently developing. While it does have relatively high operating costs in comparison to some of the other methods we have researched the reagent cost is extremely low. Other than coal the only necessary reagents are water and air. The method operates under high temperature and pressure to fix atmospheric oxygen to both organic and pyritic coal resulting in sulfur removal yields in excess of 90%. Additionally this method, despite its somewhat extreme operating conditions still translates to less than \$8/ton of coal (Diver, Fluidized Oxydesulfurization of Coal, US Patent # 5529587)

Caustic treatments of coal are another possibility for removing sulfur. Strong alkalis can be used to remove both organic and inorganic sulfur, so a few different known methods were looked into in search of a feasible method. These methods include aqueous base leaching, microwave desulfurization, and molten caustic leaching.

Battelle Hydrothermal Coal Process

To understand aqueous base leaching, the Battelle Hydrothermal Coal Process was analyzed. This process involves breaking up the coal in a grinding mill and mixing it in with an aqueous solution of 10% NaOH and 2-3% Ca(OH)₂. This mixture is then heated in an autoclave for 10-30 minutes at temperatures between 250-350°C and pressures up to 2500 psi. Next, the leachant is removed and the clean coal is left to dry; the leachant is reused after treatment with CO₂ and lime to remove sulfur as H₂S and convert the sodium carbonate to sodium hydroxide, respectively²⁸. This method can reduce the ash content of coal from 98% to 0.7%²⁹ and can remove between 90-99% of pyrite and up to 70% of organic sulfur with a heating value loss of 10%²⁸; however, corrosion is a big problem when using the alkaline solution at such high temperatures. It is also quite expensive since the coal must be broken into small particles and heated in an autoclave, so for economical reasons this method was not further explored.

Microwave desulfurization

Microwave desulfurization has the ability of raising the temperature of the coal very quickly so that heat can rapidly raise the temperature of the regions of coal with high sulfur contents to a point at which they will react with NaOH. With this process, coal is ground to fine particles (as small as 600 µm) and blended into an aqueous solution of sodium hydroxide and water. The coal is then microwaved for a few minutes with a 1:1 ratio of coal to NaOH at a

²⁸ Kawatra, S. and Eisele, T. *Coal Desulfurization- High Efficiency Preparation Methods*. Taylor and Francis, New York. 2001.
Norton, G.A., Bluhm, D.D., Markuszewski, R., and Chriswell, C.D. "Application of Microwave Energy to Caustic Cleaning of Coal." *Processing and Utilization of High-Sulfur Coals IV*. Elsevier, Amsterdam, pp. 425-438. 1991.

²⁹ Balaz, P., LaCount, R.B., Kern, D.G., and Turcaniova, L. "Chemical Treatment of Coal by Grinding and Aqueous Caustic Leaching." *Fuel*. Elsevier, Amsterdam, pp. 665-671. 2001.
Meyers, R.A. *Coal Desulfurization*. Marcel Dekker, New York. 1977.

power level of 1.5kW. Norton et. al. experimented with Illinois No. 6 coal, treating it three times total, and found an 83% reduction in the sulfur content of the coal, along with an ash reduction of 87%²⁸. Using microwave desulfurization is a potential method for this project, however it is expensive per unit of energy and may be better off combined with another method so that the coal does not have to be microwaved many times to reach an effective desulfurization percentage.

Molten caustic leaching (MCL), a method using a strong base alone at high temperatures, seems to be a very effective way of removing sulfur from coal. According to Meyers, MCL is one of two chemical methods that has been useful enough to be brought up to pilot-scale processes. Using molten NaOH at 150°C releases pyritic sulfur, and at over 200°C organic sulfur is released. Balaz reports that leaching coal with molten NaOH and KOH for 60-180 minutes at 370-400°C removes 90-95% pyritic sulfur, 70-90% organic sulfur, and 90-99% of ash. MCL has different variations, a few of which were looked into. The first method uses a mixture of molten KOH and NaOH as alkalis to remove the sulfur. In the early 1990s at the Ames Laboratory in Iowa, medium-rank coals were found to have sulfur effectively removed at temperatures below 350° when leached with both KOH and NaOH. Above this temperature, it was more effective to use NaOH alone. High-rank coals were also looked at; with these coals it was better to combine KOH with NaOH, no matter the temperature³⁰. The next method is known as the Gravimelt process. This method heats 2.5 parts anhydrous NaOH with 1 part pulverized dry coal at 400°C for 1-2 hours. Next, the coal and NaOH is rinsed with 2-10 parts water in a counter-current flow. Last the coal is flushed with H₂SO₄ and again rinsed with water, then dried. This method removes over 90% of ash and both organic and inorganic sulfur from bituminous and brown coals. Another method involves washing the coal in boiling water for one hour and then using a float/sink separation in a 50% solution of NaOH. The coal/NaOH mixture is then heated for 15 minutes at 390°C. With this method a 1:1 ratio of NaOH to coal can be used that gives results similar to methods with a larger amount of NaOH²⁹.

Molten Caustic Leaching causes changes in the structure of coal and volatiles to be produced. These volatiles can be taken away and used as fuels themselves because of their high percentage of combustible materials. This loss of volatile materials does make the MCL coal harder to ignite, however when it is burned it does burn in a way that is comparable to the pre-treated coal. The differences in the structure of the coal after leaching (e.g. a higher Na₂O content) could cause slagging or fouling, but the importance of the low amount of ash leftover in the coal and amount of sulfur removed prevails over these possibilities.

Pyrolysis

Pyrolysis is an anaerobic way of breaking down coal that involves heating the coal to a large enough temperature that the majority of the coal is decomposed itself rather than just the sulfur and ash components. Much of the coal is converted to coal gases and char. Experiments have shown that as the rank of the coal increases, the amount of sulfur removed using pyrolysis decreases. This decrease may be due to the higher amount of thiophenic

³⁰ *Processing and Utilization of High-Sulfur Coals IV*. Elsevier, Amsterdam, pp. 425-438. 1991.

Balaz, P., LaCount, R.B., Kern, D.G., and Turcaniova, L. "Chemical Treatment of Coal by Grinding and Aqueous Caustic Leaching." *Fuel*. Elsevier, Amsterdam, pp. 665-671. 2001.

Meyers, R.A. *Coal Desulfurization*. Marcel Dekker, New York. 1977.

sulfur in high-rank coals, which resists the pyrolysis method. With this technique, pyrite must be removed before pyrolyzing the coal; otherwise the decomposing pyrite can be acquired by the coal char as organic sulfur rather than being able to be removed from the coal. Mild pyrolysis (475°C) has been proven to remove 33% of the total sulfur in coal³⁰. This method does not appear to be efficient enough at low enough temperatures to be used in this project.

3. Physical Methods

There are numerous physical methods by which coal can be desulfurized prior to combustion. While physical methods act exclusively on inorganic forms of sulfur in coal, they tend to be far more economical than their chemical or biological counterparts. Physical methods researched primarily in this paper include: Oil Agglomeration, Froth Flotation, High Gradient Magnetic Separation, Jigs & Air Classifiers, Gravity Separation, and certain combinations of the previously mentioned methods. In the review of these particular methods special attention needs to be paid to weight yield, pyrite removal, ash removal, as well as economic factors such as equipment and utility costs.

Jigs/Air Classifiers

Jigs and air classifiers are perhaps the most economic of physical methods as they use, in most cases, only air/water and compressors/pumps. They also have the added advantage of a high processing capacity of up to 1000 tons per hour. Air classifiers first use bursts of air to separate coarse from more finely ground particles. A float-sink analysis can then be performed on the coarse section to remove pyrite from coal. Tests conducted by the EPA showed the reduction of pyritic sulfur to be in the range of 20.1-51.7% for BCR-Majac unit of air classifier, and 16.6-33.1% for the Alpine Zigzag air classifier. It is important to note that data for the Majac unit was conducted over 10 different types of coal while the Zigzag was used on only one type. (Eliot)

Jigs such as the Baum, Pan-American Placer, and Batac are in commercial use and with considerable results. Jigs use a fluid such as air or water in a pulsating, typically sinusoidal, pattern in an effort to stratify and separate coal and pyrite based on density differences. The Baum and Batac Jigs use primarily air in their process, as opposed to the Pan-American Jig that uses water. While structurally similar, the main discerning factor that separates the Baum Jig from the Pan-American Jig is that the Baum Jig emphasizes the pulsing stroke whereas in the Pan-American Jig, the suction stroke is equally important. The Batac Jig, in tests performed by Hoke in 1976, showed distinct advantages over the Baum Jig. It not only has the capability of handling smaller particle sizes, but also yielded a better recovery for combustible material (95.7-97.0% vs 83.7-88.0%). In terms of coal cleaning abilities, the Baum Jig showed pyrite removal in the 53.2-68.2% and ash removal in the 88.0-91.0% range, while the Batac ranged in the 56.6-61.3 % and 67.6-79.8%, respectively. Combinations of Baum and Batac Jigs would increase particle size range, one such installment approximated pyrite removal in the 40-89% range. (Kawatra & Eisele)

While Jigs have the advantage of being an economical choice, their ability to remove sulfur from coal is fairly limited. That is to say, there are other choices that work better. They could potentially be used in conjunction with other methods, however due to the larger particle size necessary for the use of Jigs, an intermediate pulverizing stage would be necessary for other methods to process.

Gravity Separation

The dry method of gravity separation is primarily known as the dry table. It uses an oscillating incline to separate pyrite from coal by gravity. Much like the Jig systems, dry tables use larger particle sizes and produce limited results.

The wet method of gravity separation is a sink-float test conducted in a heavy liquid with specific gravities near 1.4-1.6. These are typically chlorinated or brominated hydrocarbons, though zinc chloride water has also been used. While the effectiveness of gravity separations is widely available in literature, it is not a recommended method. Brominated and chlorinated liquids are not only far too costly materials to be used on a large scale, they can also contaminate groundwater, air, and even alter the coking properties of coal. For these reasons, gravity separation will not be used as part of the design for this project. (Wheelock)

Oil Agglomeration

Oil agglomeration is the method of adding fuel oils to coal slurry. Addition of fuel oil causes the coal particles in solution to agglomerate and float to the top, while impurities such as pyrite and ash remain in solution. While literature has cited oil agglomeration as a useful method for the desulfurization of coal, the added costs of large amounts of fuel oils for a large scale process would be economically unfeasible. The fact that all literature found regarding this process were bench-scale lends credence to that theory. (Eliot)

Froth Flotation

Flotation and Froth Flotation are a couple of the more standard processes used in industry. Flotation exploits the density of coal and pyrite relative to water. Coal is less dense than water and floats to the top, while ash and pyrite sink to the bottom. Froth Flotation, on the other hand, uses a chemical treatment to create a hydrophobic & hydrophilic relationship between coal & pyrite. Hydrophobic coal in the presence of a frothing agent and gas bubbling causes adherence, and hence coal floats to the top. Hydrophilic pyrite and ash become heavy and sink. Flotation and Froth Flotation require raw coal be ground finely for best results. However, finely ground pyrite might also float to the top. As a result, a two-stage process patented by the Mining Bureau uses the typical method of froth flotation for the first stage, where coal is the top product and pyrite the bottom. In the second stage, the top of the first stage are concentrated, fresh water is added, and a flotation suppressant added; resulting in the coal becoming the bottom product of the second stage. Testing of flotation, froth flotation, and two stage froth flotation show it to be effective in eliminating significant portions of both pyrite and ash content in coal with reasonable recovery of flammable materials. This is a possible method in consideration for use. (Wheelock) (Eliot)

High Gradient Magnetic Separation

Magnetic separation is a technique previously used for the purification of kaolin clay. It has recently been applied to coal desulfurization, based on the differing magnetic properties of coal and pyrite. A finely ground coal slurry solution is run through a magnet wrapped in steel or stainless steel wool. Pyrite and ash are attracted to the steel wool while coal is allowed to pass through. Treatment with steam was originally thought to enhance the magnetic properties of coal; more recent studies show the use of chemical treatments to be more effective. When treated, coal particles will be repelled by magnets, while ash and pyrite are

strongly attracted. Studies show high gradient magnetic separation to be effective at eliminating up to 90% of pyritic sulfur with up to 95% recovery of flammable materials. One of the main disadvantages of the magnetic method is the necessary downtime to backwash the magnets to prevent pyrite build-up. However, more recent technology has created a rotating carousel magnetic that can be used continuously. This leaves the only major disadvantage of magnetic separation to be the cost of electricity necessary to power the magnets, which relative to other methods, is more than reasonable. High Gradient Magnetic Separation is a method strongly considered for our design. (Wheelock)

Heavy Media Vessels

Heavy media processes take advantage of the fact that coal has a lower specific gravity than its impurities. If a liquid which has a specific gravity between that of coal and that of the impurities (a so-called 'heavy-liquid') is added to ground coal, the lighter coal particles will float, while the heavier impurities will sink. Performing the process in a cyclone gives better cleaning efficiency than an agitated pool. In full scale plant (Kawatra et al., 1995), a heavy media bath gave a pyritic sulfur removal of 68%. (Kawatra and Eisele)

Heavy Media Cyclones

The advantage to performing heavy media separations in cyclones is that the rotation of cyclones creates an extra force in addition to the gravitational force, increasing the separation efficiencies. In addition, due to their design, they can process a much finer particle size than other separators. The most commonly used media in heavy media cyclone are standard magnetic media, true heavy liquids, micronized magnetite, magnetic fluids, and water only. (Kawatra and Eisele)

Standard Magnetic Media

The advantage to magnetic media is that it is easily recovered by magnetic separation, reducing operating cost. In a full scale plant (Kawatra et al., 1995), a heavy media cyclone using standard magnetic media gave a sulfur removal of 55.6% with a recovery of 56.32 weight %. One drawback is that the magnetite is also removed by the centrifugal force of the cyclone, reducing separation efficiency. (Kawatra and Eisele)

True Heavy Liquids: The advantage to true heavy liquids such as perchloroethylene, carbon tetrachloride, broomcorn, and tetrabromoethane is that, unlike all the other media discussed, they will not settle out of the solution with time. This means that it is not necessary to constantly agitate them to prevent settling. Their disadvantage is that they are for the most part very expensive and highly toxic. (Kawatra and Eisele)

Micronized Magnetite: Grinding magnetite to a very fine particle size (90% finer than 7 micrometers) has two main advantages over standard magnetic media: It makes the solution less likely to settle over time, and as a result, smaller diameter cyclones can be used. (Kawatra and Eisele, p. 84) Its separating efficiency for very fine particles is similar to that of standard magnetic media cyclones for coarser particles.

Magnetic Fluids: “Units using the magnetic fluid principle in combination with centrifugal forces have been marketed both on a laboratory and a pilot plant scale, but the equipment needed for a full-scale plant installation is still under development.” Once such a unit has been developed, its separating efficiency should be at least as good as true heavy liquid separators of the past. (Kawatra and Eisele, p. 85)

Water-Only: The advantages to water-only cyclones are that they are simple and cheap to install and operate. They don’t produce as high separation efficiencies as other process though, so they are best used as a precleaning stage for another separation process. At an industrial-scale, a water only cyclone gave a separation efficiency of 70-80% for particles greater than 600 by 150 micrometers, with corresponding decreases in separation as particle size decreased. (Kawatra and Eisele, p. 86)

Decanter Centrifuge: The advantage to a decanter centrifuge is that it can produce greater centrifugal forces than conventional cyclones. For this reason, it can use heavy liquids that are more viscous than are practical in conventional cyclones. Since these are generally less toxic than the true heavy liquids used in conventional cyclones, cleanup after an accident would cost significantly less. The disadvantage to a decanter centrifuge is its high operating cost compared to other cyclones. (Kawatra and Eisele, p. 88)

Flowing Film Concentrators

Flowing film concentrators use a flowing film moving across a surface to separate out impurities. Since coal is less dense than its impurities, it is less affected by gravity and more affected by the velocity of the fluid. Conversely, the denser impurities are more affected by gravity and therefore less affected by the velocity of the fluid. As a result, the less coal particles are generally displaced to the outside of the film, while the impurities remain mostly undisplaced. Since the method relies on the strength of gravitational forces, larger (and therefore heavier) coal particles will end up in the same place as much smaller (and lighter) particles of impurities. For this reason, flowing film concentrators work best if the feed has been prescreened for size.

Tables: Jets of water are streamed across a table which is being shaken laterally. Denser particles are more affected by the shaking of the table, while less dense particles are more affected by the flow of the water. Efficiencies of 99% sulfur removal have been claimed, but they began with a sample containing 17.51% sulfur. (Kawatra and Eisele, p. 100)

Spirals: A stream of water is run down a spiraling chute. Fluid forces cause the less dense coal particles to move to the outside of the chute, while the more dense particles remain near the inside. Some advantages of spirals are that they are easy and cheap to install, operate, and maintain, and that they take up relatively little floorspace for a given capacity. On a test scale, the sulfur removal of a spiral was found to be 85%.(Kawtra and Eisele, p. 104)

Hindered Bed Separators

Hindered bed separators use an upward flowing fluid to separate coal from its impurities. As in flowing film concentrators, fluid forces affect the less dense coal particles more strongly than the more dense impurities. The less dense particles remain at the top of the fluid and are carried off by the overflow, while the more dense particles sink to the bottom where they are carried off as reject product. The advantages to hindered bed separators are low cost and simple operation. It has also been shown that they have slightly better separation efficiency than spirals at certain ranges of particle size. (Kawatra and Eisele, p. 107)

Packed and Baffled Columns

Column flotation, in which hydrophobic coal attaches to froth bubbles to rise to the top of the liquid, can be improved by adding packing or baffling to the column.

Packing: Adding corrugated plates with only very small spaces between the packing greatly reduces the size of the bubbles, thus increasing the total surface area. The disadvantage to adding packing to the column is that if particles larger than the channels between the packing are present, they can abrade and plug the packing. Additionally, the froth at the top of the machine can dry out and plug the column, making constant wetting of the froth necessary. On a laboratory scale, a packed column was found to have 57.3% sulfur removal.

Baffling: Adding baffles to the column gives many of the advantages of adding packing while avoiding the accompanying problems. Baffles reduce the bubble size, giving more surface area for coal, while still allowing for coarse particles to travel short distances, avoiding the plugging problem. Additionally, if baffles are installed below the feed inlet, they can increase the mean residence time in the column, increasing separation efficiency. One of the largest advantages of baffles is that they are cheap and can be retrofitted onto existing froth flotation columns. On an industrial scale, baffled columns provided between 51.7% (for 85.26% energy recovery) to 94.6% (for 18.19 % energy recovery) pyritic sulfur removal. (Kawatra and Eisele, p. 203)

Selective Agglomeration

Like froth flotation, selective agglomeration takes advantage of coal's hydrophobic nature to produce separation. The main difference is that instead of bubbles, the coal particles attach to immiscible oils upon agitation. Some agglomerants that have been suggested are fuel oils, n-chain hydrocarbons, liquid carbon dioxide, and chlorofluorocarbons. The main disadvantage to the process is that the high usage of agglomerant results in relatively high operating costs. Since selective agglomeration's efficiency is no better than froth flotation's (50-80 % pyritic sulfur removal), separating efficiency doesn't justify the extra cost. However, if a high energy yield fuel is used as the agglomerant, it can be left in and burned along with the clean coal, eliminating the need to dry the coal after cleaning. (Kawatra and Eisele, p. 237)

Wheelock, Thomas D. Coal Desulfurization: Chemical and Physical Methods. American Chemical Society: 1977

Demirbaş, A. & Balat, M. "Coal Desulfurization Via Different Methods". *Energy Sources*, 26: p.541-550. Taylor & Francis, Inc. 2004

Sutcu, Hale. "Coal Desulfurization Using Natural Ca-Based Sorbents". *Coal Preparation*, 24: p.249-259. Taylor & Francis, Inc. 2004

Eliot, Robert C. Coal Desulfurization Prior to Combustion. Noyes Data Corporation: 1978

- C. The results of our research will present, what is in our understanding the most effective method of removing sulfur from coal. If this method can be economically employed prior to combustion, then a method of energy production known as coal gasification can be utilized – resulting in more electricity being generated per unit mass of coal. Additionally since such a large quantity of Illinois coal is of such poor quality (relatively high sulfur content) an effective and cheap method to clean coal could result in the use to coal veins that are currently being ignored in favor of lower coal veins with a lower sulfur content.
- D. Define current or potential outputs produced through the execution of the assigned tasks.
No sabemos.
- E. A deliverable we have completed at the moment is an excel document that contains data on all of the methods we have researched. The excel document contains data on sulfur removal yields, reagents, operating parameters (temperature and pressure), and electrical load. Effectively the document is a condensed summary of our research to date and can help a third party decide which method would be favorable for their purposes based on a significant number of parameters that we have documented. A few selected methods are also being modeled in Hysys, ChemCad and Aspen, which will give us some estimates of the cost and scale involved with each of these methods.
- F. The potential customer for the product of this research currently doesn't have any problems with the way things work with post-combustion coal, so pre-combustion methods are not being implemented. However, as the amount of available low-sulfur content coal decreases and an increased desire for plant efficiency starts to influence the consumer, there will be a need for this research.
- G. The three methods we have chosen, molten caustic leaching, oxydesulfurization, and a combination of froth flotation with magnetic separation, are all going to be examined and the best possible method(s) will be chosen. The method(s) chosen will be based on the research we have already completed. The concept chosen is going to be implemented into our ultimate desulfurization design.

3.0. Revised Task / Event Schedule

- A. Please See attached PDF document (Project Plan).
There have been few changes to our project tasks. The main change was the addition of a new task (task ID #14). After researching for the different methods for desulfurization of coal, the group has been discussing the possibility of the addition of a post-combustion desulfurization method in order to decrease the final price/ton of desulfurized coal. This task will take 11 days (as stated in project plan) and involves all team members. The length of 11 days is due to new considerations, research for post-combustion processes. A final decision will be done on October 25th, if a post-combustion method is used in combination with a pre-combustion method further project plan changes will be expected.
Most of the project plan changes have been due dates, the reasons are explained under Barriers and Obstacles.

- B. Please See attached PDF document (Project Plan). Maroon color font shows changes from our original project plan
- C. Please See attached PDF document (Project Plan). Maroon color font shows changes from our original project plan.
- D. Please See attached PDF document (Project Plan). Maroon color font shows changes from our original project plan.
- E. The time line has changed due the delay in the decision making for choosing a desulfurization method. This task (ID 13) has been delayed almost two weeks forcing us to delay the design section (ID 23-28). When the project plan was designed we knew little about the numerous desulfurization processes available. After research was done the process of picking methods was difficult because of the results we want to achieve (final percentage of sulfur in coal) and the many processes that allow us to achieve it. We considered costs, techniques, feasibility, difficulty, industry experience, and environmental risks as some of the most important reasons (all reasons are stated under . Finally, we decided to extend the date for (ID 13) because it could be the main task in our project since the future trajectory of the project is dependent on the method we pick for desulfurization.
- F. Subtasks completed include finishing initial research on backgrounds of coal, coke, and desulfurization. After this task we completed our second goal of researching various methods of desulfurization. Both of these completed tasks have helped further our knowledge of coal and desulfurization, helping us to reach our decision making step of choosing our desulfurization method. This very important milestone in our project will lead us into the second half of our IPRO, allowing us to design our process.

4.0. Updated Task Assignments and Designation of Roles

Our original project plan of designing a pre-combustion coal desulfurization process has not changed. Minor changes were made to the project plan, including due dates, role assignments, and new sub-groups. We also inserted a decision-making period into our schedule to account for the length of time needed to choose an appropriate method from our research. Changes are listed below and in the project schedule.

- A. Rather than have a couple of main subgroups, IPRO 346's method for getting the entire group involved in as much of the IPRO as possible involves having many small groups with different goals to be completed throughout the semester. These groups become a main focus for a week or two, each with deadlines that must be met; after the goals of the group are accomplished, the members move on to the next step and continue building and growing towards our main goal of designing a pre-combustion desulfurization process. The description of the groups is described in the schedule.
- B. Sub-Group Designations are listed below:

Coal Research Group

Tony Doellman
Greg Kisiel
Myint Toe

Desulfurization and Coal Analysis Group

Andrew Keen
James Maratt
Adejoke Ogunride

Chemical Methods Group

Salil Benegal
James Maratt
Amy McDowell
Oscar Olmos

Process Design Group

Amy McDowell
James Maratt
Oscar Olmos
Andrew Keen

Safety Group

Adejoke Ogunride
Greggory Kisiel
Myint Toe

Coke Research Group

Salil Benegal
Amy McDowell
Oscar Olmos

Physical Methods Group

Tony Doellman
Andrew Keen
Adejoke Ogunride

Biological Methods Group

Greg Kisiel
Myint Toe

Costing and Profitability Analysis Group

Adejoke Ogunride
Andrew Keen
James Maratt
Tony Doellman
Myint Toe

Unit Operations Description Group

Andrew Keen
Oscar Olmos
Andrew Keen

- C. Assignments have also been given for some of the particulars of this IPRO:
- Project Plan – Team Leader in collaboration with members and advisor
 - Research – All Team Members
 - Oral Presentation – All Team Members
 - Midterm Progress Report – Team Leader in collaboration with members and advisor
 - Team Minutes - Adejoke Ogunride
 - Team Poster – Oscar Olmos, Greggory Kisiel
 - Final Report/Abstract – Team Leader in collaboration with members and advisor
 - Collection and Summary of Weekly Time Sheets – James Maratt
 - Weekly Tasks – Oscar Olmos
 - iKnow/ iGroups Coordinator- Amy McDowell
- D. Our team organization has not changed since the submittal of our project plan.
- E. Please see attached Schedule

5.0. Barriers and Obstacles

So far we have encountered only a few problems with this project. The decision making process for choosing a desulfurization method has taken a little longer than expected. Our work has been delayed due to team members' other obligations with other classes and work. While deadlines set were reasonable, some of them overlapped with other priorities as well, such as midterm exams and term papers. Correspondence between group members has been slow, and putting this report together has been taken longer than expected due to a lack of standardization across team members' writing styles. To remedy this problem, guidelines should be set for group members for report writing, and deadlines for final reports should again be set in advance of final exams, perhaps even further ahead of time.