To the Graduate Council:

I am submitting herewith a thesis written by Glenn M. Lawson entitled "A Selective Agglomeration Method To Beneficiate Coal." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

George C. Frazier

George C. Frazier, Major Professor

We have read this dissertation and recommend its acceptance:

Owen L. Culberson

H. W. Hsu

Accepted for the Council:

L. Evans Goff

Vice Chancellor
Graduate Studies and Research

A SELECTIVE AGGLOMERATION METHOD TO BENEFICIATE COAL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Glenn M. Lawson

June 1981

ACKNOWLEDGMENTS

First, I would like to express my appreciation to the Department of Chemical, Metallurgical, and Polymer Engineering for the vital financial support provided by them during this study. There are also a number of individuals without whose assistance this thesis would not have been possible. To them and especially to my advisor, Dr. George C. Frazier, and my good friend, Mr. R. Nick Fowlkes, I would like to express my appreciation for their contributions.

I am very appreciative of the opportunity given to me by the University of Tennessee, the opportunity to make my personal transition at this time of my life smoothly and productively.

Glenn M. Lawson

ABSTRACT

A physical process requiring a range of 10 to 30 weight percent water was investigated for the separation of mineral sulfur (pyritic) from coal. This method was based upon differences in the wettability of coal organic and mineral particles. Spray solutions containing chemicals to enhance this difference were sprayed into coal particles tumbling in a cylinder; selective pelletization of the minerals was the result. Coal particles in the size range of -80, +170 mesh containing approximately 0.86 wt.% organic sulfur and 1.16 wt. % pyritic sulfur were used.

The solutions used contained either a surface active agent (surfactant) alone or one combined with a "depressant" chemical. Anionic surfactants tested included sodium palmitate, sodium dodecyl sulfate, and ethyl xanthic acid, potassium salt. The cationic surfactant tested was hexadecyl trimethyl ammonium bromide. Depressant chemicals used were ferric sulfate and ferric chloride. In addition, the effect of varying the solution's pH was investigated over the range of 2.00 to 10.00.

Approximately 15 weight percent pellets and 85 weight percent cake was consistently produced in experimental runs regardless of the spray solution used. Cationic surfactants solutions gave results opposite of the expected. The concentration of the added chemicals, the amount of pellets produced, and the amount of spray solution added were all

varied to investigate their effects on the selectivity of the sulfur in the pellets produced. The results of tests using anionic surfactants consistently showed a higher sulfur weight percent in the pellets than in the cake. However, this separation was too small under the conditions tested to be of economical significance. Also, better separation was effected at the low pHs.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

LIST OF SYMBOLS

CA = cake amount (grams)

CSP = cake sulfur percent

BA = pellet amount (grams)

BSP = pellet sulfur percent

TSP = total sulfur percent of coal

FR3 = normalized number indicating the transfer of the sulfur to the pellets

FR4 = normalized number indicating the transfer of the sulfur from the cake

G = Gibbs free energy

H = enthalpy

CHAPTER I

INTRODUCTION

Around 1950 the United States became a net importer of energy supplies and since that time our energy demands have increasingly outstripped our domestic energy production. Due to this situation, there has been a growing reliance and dependence upon imported energy in the form of foreign crude oil. Although we actually have plenty of total long-term energy reserves made up of oil reserves, natural gas reserves, coal reserves, and uranium reserves, their individual amounts and availabilities do not satisfy today's demands. While we have huge coal reserves, the demand for coal is low, but the demand for crude oil and natural gas, our relatively small energy reserves, is increasing. The result is a significant shortage in our immediate domestic energy supply that is leading to an increasing amount of our energy needs being met by foreign sources (Power and Energy Committee of the California Intersocieties Legislative Advisory Commission, 1974). Figure I-1 shows the amounts of the United States' oil production, oil consumption, and oil imports.

The disadvantages of our growing reliance upon foreign energy sources were non-existent for the American public until the initial impact of our present energy crisis struck in the latter part of 1973. It was at that time that our

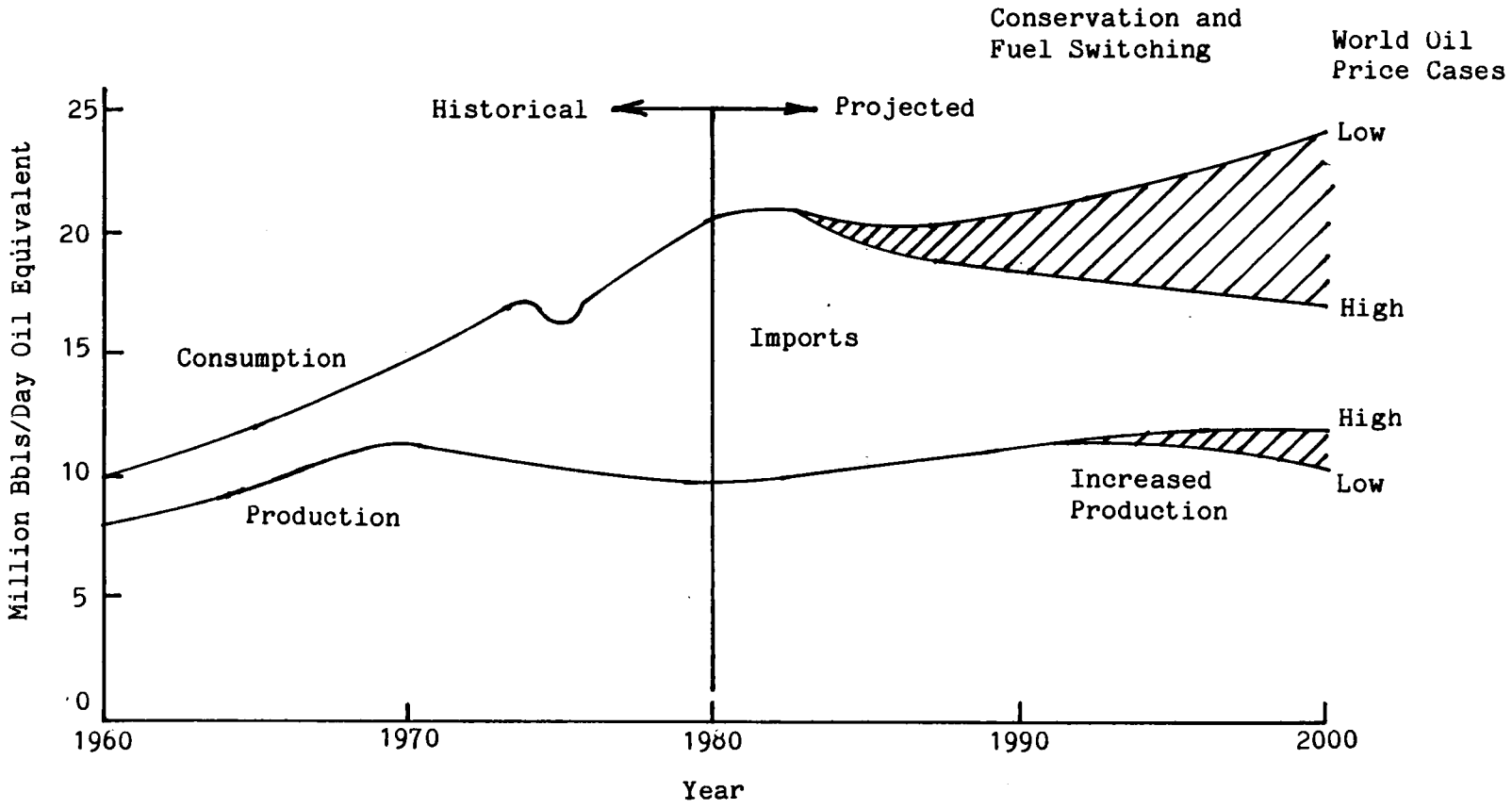


Figure I-1. U.S. Oil Production and Consumption

strong alliance with and support of Israel brought on the "Arab" oil embargo. Since that time, it has become increasingly obvious that we are no longer in a position where we can take our much needed supplies of energy for granted. The effects of this vulnerability have been significant and far reaching. We have had to make gradual political policy changes to insure a continuous supply of Arabian crude oil, and we have had to watch helplessly as the oil cartel, the oil producing and exporting countries (OPEC), periodically increased the price of their oil between 1973 and 1980. The deficit existing between our demand and production of crude oil has been made up by foreign sources, but at the price they dictate and periodically increase. We paid $ 4 billion for imported oil in 1971, $ 8 billion in 1973, $ 45 billion in 1977, and $ 42 billion in 1978 (U.S. Department of Energy, National Energy Plan II, 1979). Figure I-2 graphically shows a relationship between the United States' trade balance and oil import bill. Our economy must have this imported oil in order to survive. A halt in our oil supplies, as in the oil embargo of 1973, led to a $ 60 billion drop in the gross national product (U.S. Department of Energy, National Energy Plan II, 1979). Table I-1 shows the effects of the 1973/1974 oil price increases on the United States' economy. To improve this problem by the turn of the century, we must start working now on both elements of the problem, our gluttonous

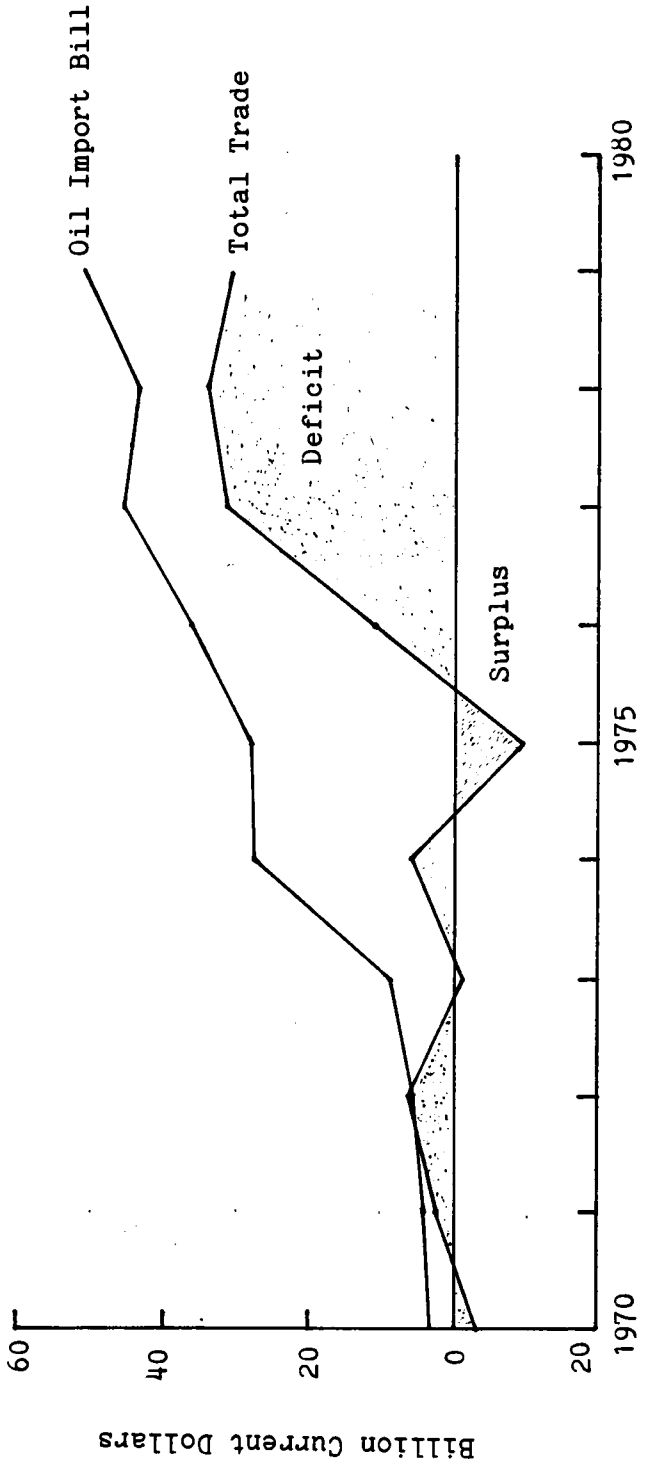


Figure I-2. U.S. Trade Balance and Oil Import Bill

TABLE I-1

EFFECTS OF THE 1973-1974 OIL PRICE INCREASES ON THE U.S. ECONOMY

	1973	1974	1975	1976	1977
Loss of Economic Output (GNP Loss in Billion 1972 Dollars)	--	38	63	41	40
(Percent Reduction)	--	3.1	5.2	3.2	3.0
Increased Rate of Inflation (Change in Consumer Price Index)	0.3	2.5	1.7	0.2	--
Increased Rate of Unemployment	0.1	0.7	1.7	0.5	--
Loss of Employment (thousand jobs)	84	600	1,450	500	--

and somewhat wasteful demand and our inadequate domestic supply.

The United States' current energy crisis can be attributed to the rapid energy demand growth for a non-abundant domestic energy source, crude oil, and to restraints upon the conservation, utilization, and development of all of our available domestic energy sources, including our very abundant energy source, coal. Today's United States energy needs are supplied by crude oil, natural gas, coal, hydroelectric power, nuclear power, and miscellaneous sources. Together, crude oil and natural gas, our non-abundant energy sources, provide 74% of the total demand. We must decrease the amount of our energy that is supplied by crude oil and natural gas and increase the amount of energy supplied by other sources.

Technologies utilizing nuclear fission and fossil fuel energy are expected to play a major role in the American energy scene for the next twenty to thirty years. Regardless of how nuclear fission's role as an energy source develops, fossil fuels will continue to be a major source of our energy. The fossil fuels are oil, natural gas, and coal. They have three outstanding virtues as an energy source: (1) they are a natural storage system; (2) their energy is stored in a high density; and (3) their energy can be released at a high temperature, which means in a thermodynamic sense that they have a high capacity to

produce work. In addition to these virtues, they also have two drawbacks: (1) their supply is limited and in the case of oil and natural gas is being rapidly depleted in this country; and (2) a not so small number of enviromental problems are associated with their development and use (Scott, C.B., 1976). Our dwindling supplies of oil and natural gas mean that coal and nuclear fission power are our only abundant medium-term, 1985-2000, domestic fuels. One or both of them must be counted upon heavily to supply our energy demands to the turn of the century.

Of the three fossil fuels, coal is by far the most abundant in the world, particularly in the United States. On a bright note, it is said that the United States has many times more energy in coal than the Arabs have in their oil resources (Brennan, J.P. and others, 1977). Solid fuels such as coal have a simpler geology than oil and natural gas because solid fuels are usually deposited in relatively large continuous masses (Hartnett, J.P., 1976). For this reason, coal's deposits and amounts are better known than crude oil and natural gas. These amounts are estimated by the United States Geological Survey to be approximately 3,968 billion tons. If all of this could be mined, this is a 5000 year supply at our present consumption rate (Hawley, M.E., 1976). Table I-2 gives the estimated coal resources of the Unites States as of January 1, 1974. The United States Bureau of Mines estimates that of these total coal

TABLE I-2

ESTIMATED REMAINING COAL RESOURCES
OF THE U.S., JANUARY 1, 1974

Category	Billions (10^9) of Short Tons
1. Identified resources:	
A. Reserve base	424
B. Additional identified resources	1,307
C. Total identified resources	1,731
2. Hypothetical resources:	
A. 0-3,000 ft overburden	1,849
B. 3,000-6,000 ft overburden	388
C. Total hypothetical resources	2,237
3. Total remaining resources	3,968

resources, 437 billion tons are proven resources that can be profitably utilized using today's technology to recover them and today's prices to sell them. Since new mining technology is being developed to increase the efficiency in recovering these resources and since all indications are that the market price of energy will increase, the amount of proven coal resources will also increase. See Figure I-3 for a graphical representation of our total and proven coal resources. To bring the amount of the United States' coal resources into perspective, one should know that it is estimated that coal constitutes 69% of our total estimated recoverable fossil fuel resources. Crude oil and natural gas together only constitute 7%, while oil in oil shale makes up the remaining 24% (Hawley, M.E., 1976).

These factors call for an increased usage of our coal resources. Before this can happen, restraints on coal's usage will have to be overcome. The biggest problem is the air pollution resulting from its combustion- specifically, the amount of sulfur dioxide emissions it produces. A method to help eliminate this problem is the topic of my research.

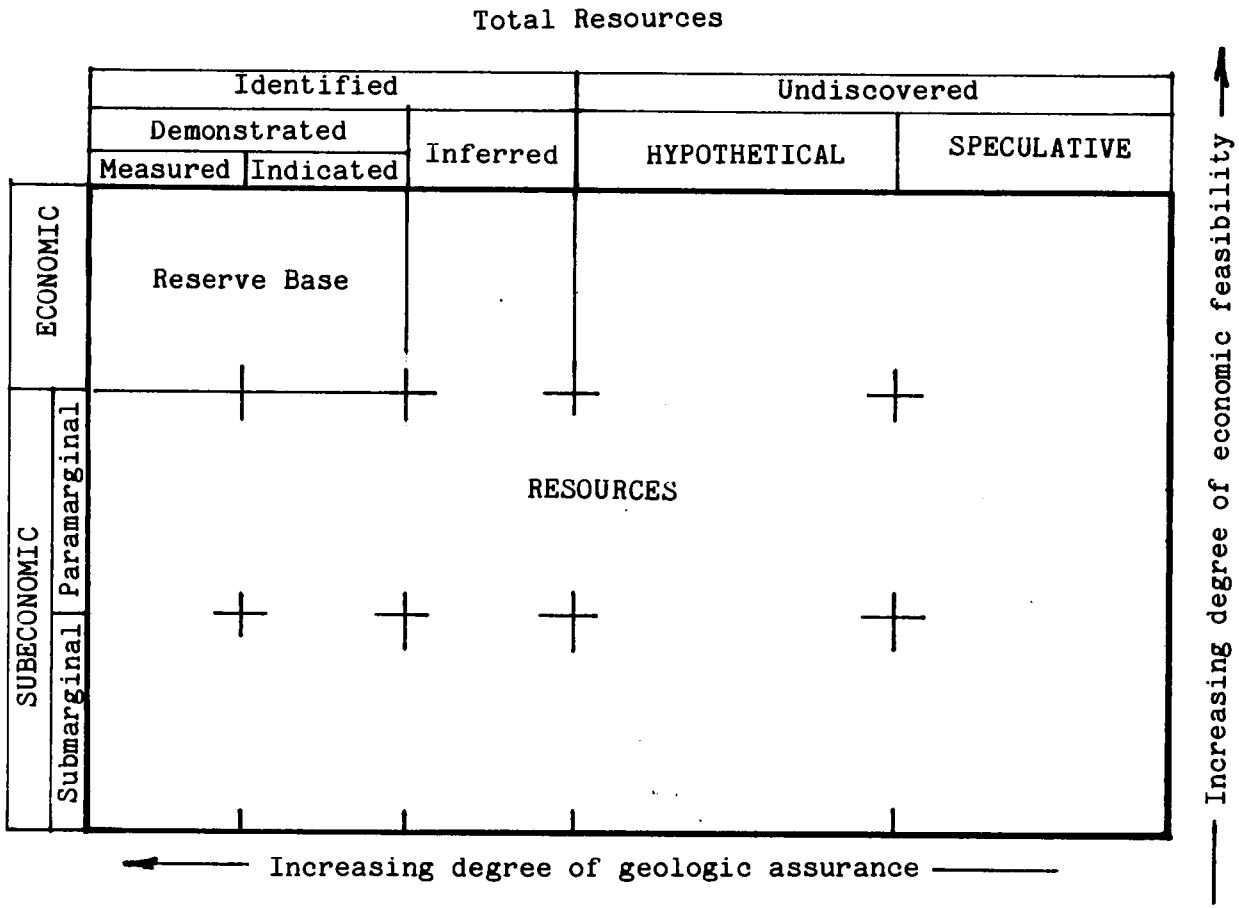


Figure I-3. The U.S. Coal Reserves and Resources

CHAPTER II

BACKGROUND

1. Demands and Restraints on Coal's Usage

President Carter presented a National Energy Plan in April, 1977, that calls for a doubling of our coal use by 1985. In 1977 21.6 quads (21.6×10^{12}BTUs) of fuel resource energy were devoted to electric power generation in the United States. Of this, 10.0 quads were supplied by coal, 3.7 quads by oil, 3.1 quads by natural gas, 2.6 quads by nuclear power, 2.2 quads by hydroelectric power, and 0.04 quads by other sources (Hibbard, W.R., Jr., 1979). Recently, legislation has been enacted that is intended to increase the amount of energy supplied in this sector by coal. Coal use is required in all new electric utilities and new major fuel burning installations and in all existing capable coal combustion facilities by the Powerplant and Industrial Fuel Use Act (PIFUA) that is also known as the Coal Conversion Act. High priority federal funds will be awarded to private programs that convert oil burning electric utility plants to coal (United States Department of Energy, National Energy Plan II, 1979). The result should be that most, if not all, new electric utility plants will be either nuclear or coal powered and that many existing electric utility plants will be converted from oil to coal. The demand by electric utility plants for nuclear and coal

power, two alternatives to oil for electric power generation, should grow steadily in the coming years.

The principal uses of coal today are as a utility boiler fuel to generate electricity, as a coking fuel in the iron industry, and as an industrial steam boiler fuel. Due to the reasons cited above, demands for coal by the electric utility industry are projected to rise steadily from 660 million tons in 1978 to 1 billion tons in 1985, a 6% annual increase (Scallon, T.R. and others, 1977). Since oil would probably have to make up any deficit, any restrainment of this projected growth rate could cause the amount of oil we must import to increase.

Restraints on increasing coal use could come from the safety and enviromental problems that are associated with its production and combustion. Between 1960 and 1965, coal production increased by 23%, productivity due to new mining technology increased by 56% , and the average F.O.B. mine price decreased by 5% (Scallon, T.R. and others, 1977). These developments led to considerable optimism in the coal industry, but other developments followed that reversed the situation. A sudden upsurge in orders for nuclear plants in 1966/1967, the virtual freezing of all restrictions on imported residual oil in 1966, the implementation of restrictive air pollution regulations in 1970, and the enactment of strict health and safety legislation for the mining industry late in 1969 reversed the demand growth for

coal. However, today's crude oil crisis has revived a feeling of optimism in the coal industry. The National Coal Association predicted in 1978 that 713 million tons of coal would be produced in 1979, a 10.4% increase over 1978's 646 million ton production (Wilkinson, J.F., The 79 Outlook: Optimistic But, 1979).

Compliance with today's enviromental standards in general poses the greatest potential restraint upon the increased direct use of coal. Coal's utilization causes the destruction of land surface in strip mining, water pollution coming from mining and coal washing, ash waste problems in power plants, and air pollution coming from its combustion. Air pollution is the major problem and in fact some of the water pollution and solids wastes problems come from techniques used to reduce air emissions. Air pollutants coming from coal combustion are sulfur oxides, particulate matter, carbon dioxide, nitrogen oxides, and small amounts of carbon monoxide and hydrocarbons. Sulfur is the worst pollutant and most of the coal burned in the United States is the high sulfur bituminous coal mined east of the Mississippi River (Lynn, D.A., 1976). Figure II-1 gives the estimated remaining coal resources classified by sulfur content of all ranks in states east of the Mississippi River. Since the use of this coal is predominant in our east-central states, it has a higher detrimental impact upon the enviroment there (United States EPA, Report of the

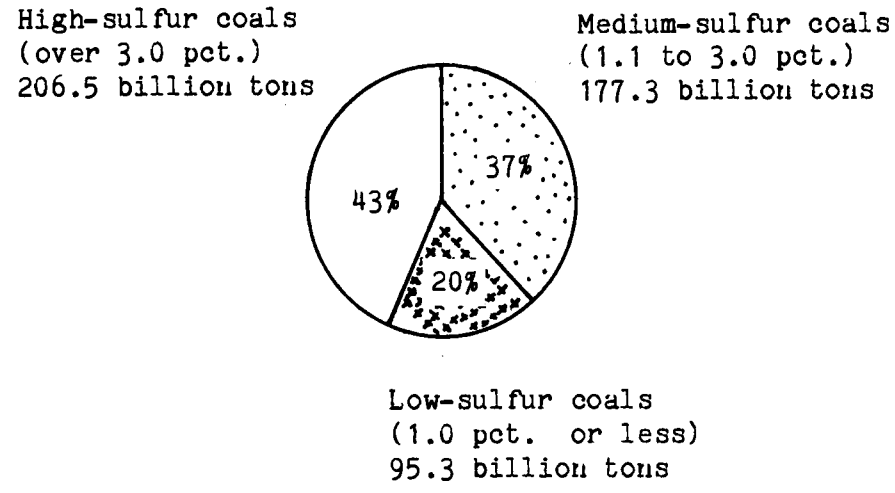


Figure II-1. Estimated Remaining Coal Resources of all Ranks, by Sulfur Content, in Eastern U.S.

Hearing Panel, National Public Hearings on Power Plant Compliance with Sulfur Oxide Pollution Regulations, 1974).

2. The Sulfur Dioxide-Particulate Complex Air Pollutant

Prior to the Industrial Revolution wood was the world's primary energy source. The displacement of its use by coal was one of the many changes that took place when parts of the world industrialized (Lynn, D.A., 1976). Advances in the forms of increased industrialization in the coal industry increased the production and availability of coal, which in turn fueled the growth of industrialization. The recorded history of air pollution began as air pollution coming from coal combustion became prevalent in the world's large industrialized cities, and the annual cost of air pollution today on health, vegetation, and properties has been estimated at over $16 billion (Ruedisili, L.C., 1978).

The six major air pollutant classifications are particulate matter, sulfur oxides, carbon monoxide, nitrogen oxides, hydrocarbons, and photochemical oxidants. Coal combustion produces relatively small amounts of carbon monoxide and hydrocarbons and significant amounts of particulate matter, nitrogen oxides, carbon dioxide, and sulfur oxides. The particulate matter emissions are comprised of ash particles (fly ash) that can be effectively removed prior to atmospheric release by expensive electrostatic precipitators. Sulfur oxide, usually 97 to

99% sulfur dioxide and 1 to 3% sulfur trioxide, is the most prominent of the gaseous pollutants because of its notariety as a respiratory irritant. It is a colorless gas with a pungent odor that reacts with oxygen, ammonia, water, and other compounds in the atmosphere to form sulfuric acid mist and other sulfates. These acid aerosols and particulate sulfates, which also come from sources other than coal combustion, are estimated to comprise about 10% of the total suspended particulate matter that is manifested to us as haze (Lynn, D.A., 1976).

In the atmosphere, excessive amounts of sulfur dioxide and its reaction products are harmful to human and animal health, plant life, aquatic ecosystems, and man-made materials. Damage to human health can be an acute dramatic short-term reaction or a chronic cumulative long-term effect. Inhaled sulfur dioxide gas alone is not usually a potent pulmonary irritant because, unless the levels are abnormally high, it is nearly completely adsorbed in the upper airways and does not reach the lung lining. It becomes much more potent when it is combined with particulate matter, a combination invariably found in the emissions coming from coal combustion. Due to the widespread use of coal during the last century, this mixture became a common combination of pollutants found in the world's industrialized cities, and for this reason there exists an extensive backlog of experience with it. It is

the prime suspect in the "killer smogs" of London and the Muese River valley. Prolonged exposure to sulfur dioxide at levels greater than 1.0 ppm causes progressive damage to the lungs, but sulfur dioxide combined with particulates has an even greater effect at levels less than or equal to 1.0 ppm (Lynn, D.A., 1976).

All vegetation and especially leafy plants are even more sensitive to sulfur dioxide pollution than human health. Sulfuric acid in the atmosphere causes visible damage to the leaf structure when it occurs in levels higher than the normal (no man-made contribution) background level of 4 μg per cubic meter. Sulfuric acid damage to vegetation can also occur through the plants' root systems. Sulfur dioxide in the atmosphere is converted to sulfuric acid which is readily washed out of the atmosphere as "acid rain". Since a portion of this "acid rain" soaks into the soil, it lowers the regional water table's pH. If it becomes too acidic, all the region's vegetation, including valuable farm crops, will be either diminished or destroyed.

"Acid rain" that doesn't soak into the soil leaves as runoff drainage and eventually ends up in streams and lakes that support delicate aquatic ecosystems. Berner (1971) and Friend (1973) estimate that the sulfur content of the average river in this country has increased by 40 to 60% due to sulfur dioxide pollution (Nriagu, J.O., 1978). Again the result is a lowered pH of the water that can, if drastic

enough, destroy the entire aquatic ecosystem.

Sulfuric acid through acid-base reactions also has destructive effects on non-living things, including man-made materials. Sulfates, such as the sulfuric acid and sulfites derived from sulfur dioxide, constitute a significant portion of the suspended particulates found in the atmosphere of many urban and industrialized areas. Upon contact, these particulates corrode metals, building materials, paints, textiles, and paper. The total bill due to corrosion damage in the United States in 1970 is estimated to be $6.75 billion. Of this, $20 million is attributed to atmospheric sulfur introduced in air pollution.

.

CHAPTER III

COAL

1. Coal Formation

The science of coal involves geology, biology, and chemistry. In the formation of coal, the vegetable matter of plants is converted into coal in two steps. First is the biological step of converting plants to peat and then comes the physiochemical step of converting peat to coal (Hawley, M.E., 1976). Millions of years ago the earth's warm and humid climate provided conditions such that great swamps and forests covered the earth. Although plant growth far exceeded losses, hugh quantities of plant material fell into stagnant swamps and formed deposits that underwent a partial decay probably resembling the process of humification (Steinhart, C.E., 1974). During humification, gases, chiefly carbon dioxide and methane, were vented from the deposits and left a residue enriched in carbon. These deposits collected to form "peat bogs" that became covered as time passed. As the sediments accumulated, the pressure on the peat bog increased, which, along with an increase in temperature and an anaerobic environment, caused putrification to take place. This "coalification" process is an extremely slow one (a calculated first order rate constant is approximately 1.2×10^{-5}/min) but the result after millions of years is coal.

Coal consists of transformed plant remains along with some earthy matter. Its mineral content is indicative of the earthy matter, and inherited from the plants is a fibrous texture that can be viewed under a microscope (Wheelock, T.D., Coal Desulfurization, 1977). Its structure and composition are both complex and diverse due to the many different materials and processes in its formation and to the extremely long time over which most of the processes took place. Collectively, coals are many different materials that were formed in many ways in many different places and times. Some of the factors that caused varying compositions of different coals are the diversity of species, kinds, and parts of plants originally contributing to peat deposits, the chemical and mechanical condition of the plants at the time of deposition, the type of peat swamp, and the diversity of external conditions in which the transformation took place. The type of plant residue determines the type of coal , while the stage of chemical alteration, metamorphic stage, determines its rank. Although it is not regarded as a type of coal, peat is the precursor of all coals. A coal's rank is determined by the amount of metamorphic alteration that the original peat has undergone. Lignites (approximately 150 million years old) are nearest in composition to peat followed by subbituminous, bituminous (approximately 300 million years old), semianthracite, anthracite (greater than 300 million

years old), and meta-anthracite (Wen and Lee, 1979). See Table III-1 for the classification of coals by rank.

2. Coal Structure

A highly heterogenous material, coal can be considered as a rock structure that is made up of an organic and an inorganic portion and that contains macroscopic and microscopic features. Coal has a large porous volume due to an extensive pore structure that enables it to adsorb gases, vapors, and liquids. All coals contain moisture in varying amounts; by weight, bituminous is 1 to 5% water, subbituminous 20% water, and lignite up to 45% water (Wen and Lee, 1979).

The organic portion, macerals, comprise most of the coal's weight and consist mainly of carbon, hydrogen, oxygen, nitrogen, and sulfur. Chemically, the organic portion can be viewed as a substance containing the classical functional groups, mainly carbonyl and hydroxyl, aromatic and heterocyclic ring units, and aliphatic bridges (Myers, R.A., 1977). It is a crosslinked polymer, the major feature being the bonding of aromatic nuclei by two methylene linkages. This polymer formed from the cellulosic polymer present in plant material is essentially insoluble and nonvolatile , in the absence of degradation. (Myers, R.A., 1977). Figure III-1 gives a model of the organic coal matrix that is based on spectroscopic and carbon/ hydrogen

TABLE III-1

CLASSIFICATION OF COALS BY RANK

Class	Group	Fixed Carbon Limits % (dry, mineral matter-free basis)		Volatile Matter Limits % (dry, mineral matter-free basis)		Calorific Value Limits BTU/lb (moist[b] mineral matter-free basis		Agglomerating Character
		Equal to or Greater Than	Less Than	Greater Than	Equal to or Less Than	Equal to or Greater Than	Less Than	
I. Anthracitic	1. Met-anthracite	98			2			
	2. Anthracite	92	98	2	8			
	3. Semianthracite	86	92	8	14			Nonagglomerating[c]
II. Bituminous	1. Low volatile Bituminous Coal	78	86	14	22			
	2. Med volatile Bituminous Coal	69	78	22	31			
	3. High volatile A Bituminous Coal		69	31		14,000[d]		Commonly agglomerating[e]
	4. High valatile B Bituminous Coal					13,000[d] 11,500	14,000 13,000	
	5. High volatile C Bituminous Coal					10,500	11,500	Agglomerating
III. Subbituminous	1. Subbituminous A Coal					10,500	11,500	Nonagglomerating
	2. Subbituminous B Coal					9,500	10,500	
	3. Subbituminous C Coal					8,300	9,500	
IV. Lignitic	1. Lignite A					6,300	8,300	
	2. Lignite B						6,300	

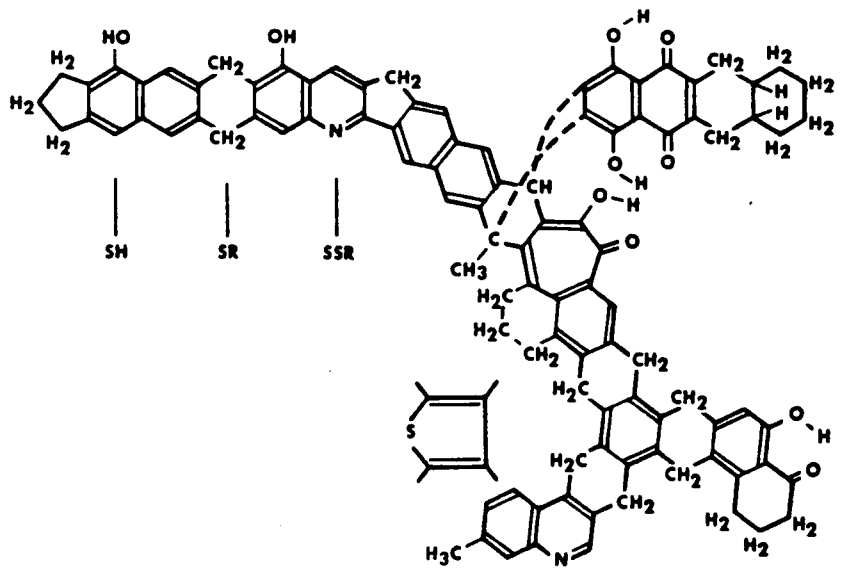


Figure III-1. Model of Organic Coal Matrix

ratio data as well as a knowledge of the chemical reactions of coal with bromine and oxygen. A complete determination is unlikely since its structure is highly variable among various coals.

Coal also contains an inorganic mineral portion distributed throughout the macerals. It is believed that some of the minerals were introduced during the biochemical peat stage and some during the metamorphic stage (Wen and Lee, 1979). Earlier work used the ash residue produced by coal combustion to determine the composition of its mineral matter. Table III-2 gives a typical mineral matter composition for a bituminous coal. Silicon oxide is the most abundant mineral followed by the oxides of alumina, iron, and calcium. Sulfur containing compounds like pyrite also make up some of the mineral matter.

All coals contain some sulfur in each of three forms: as an integral part of the organic coal matrix, organic sulfur; combined with iron as pyrite or marcasite, pyritic sulfur; and combined as calcium and iron sulfates, sulfate sulfur. Pyritic and sulfate sulfur are contained in the coal's inorganic portion. The sulfur distribution among these forms varies but is estimated by weight in certain coals to be organic sulfur, 0.3 to 2.0%, pyritic sulfur, 0.1 to 4.0%, and sulfate sulfur, 0.00 to 0.05%, giving a total sulfur content of 0.4 to 6.05%.

The organosulfur compounds range in structure from

TABLE III-2.

MINERALS ASSOCIATED WITH BITUMINOUS COALS

Group	Species	Formula
Shale	Muscovite Hydromuscobite Illite Bravaisite Montmorillonite	$(K, Na, H_3OCa)_2(Al, Mg, Fe, Ti)_4$ $(Al, Si)_8O_{20}(OH, F)_4$
Kalin	Kaolinite Livesite Metahalloysite	$Al_2(Si_2O_5)(OH)_4$
Sulfide	Pyrite Marcasite	FeS_2
Carbonate	Ankerite Ankeritic calcite Ankeritic dolomite Ankeritic chalybite	$(Ca, Mg, Fe, Mn)CO_3$
Chloride	Sylvine Halite	KCl NaCl

thioethers and mercaptans in the aliphatic series to thiophenes and complex aromatic structures. In these compounds, the sulfur atoms are an integral part of the hydrocarbon molecular structure and must be removed by chemical reactions rather than physical methods that utilize differences in physical properties.

Inorganic sulfur occurs in the form of sulfates, pyrite, and marcasite with pyrite by far being the predominant form. Chemically, pyrite and marcasite are both iron di-sulfide, but pyrite is cubic in crystalline structure and marcasite is orthorhombic. Pyrite is dispersed throughout the organic and inorganic portions in macroscopic forms that can be seen with the naked eye. They appear as thin and film-like veins, as lenses, as nodules or balls, and as pyritized plant tissue. The microscopic forms are finely distributed, making it very difficult to remove them by physical methods. The macroscopic forms of pyrite can be removed by a number of physical methods where the size and distribution of the pyrites in the coal to be cleaned are the primary criteria for method selection.

Sulfate sulfur in the form of iron sulfates, malantrite, calcium sulfate, and jarosite is usually found in small amounts, generally less than 0.05% (Wen and Lee, 1979). Its solubility in water also allows it to be easily removed during water washing. For this reason, sulfate sulfur is usually not a factor in influencing whether or not

a coal is utilized.

3. Coal Classification by Sulfur Content

Since a coal's sulfur content is more a function of the precise coal bed it came from rather than its rank, it can also be classified by its sulfur content. The distribution of a coal's sulfur between organic and inorganic forms is highly variable and is a function of what coal basin it came from, the seams that exist within the basin, and the petrographic and geological location within the particular seam. Figure III-2 gives a typical distribution of pyrite in coal.

The EPA first established performance standard limits for fossil fuel fired steam generators in the Clean Air Act Ammendments of 1977 (Public Law 95-95). The particulate and sulfur dioxide limits are:

(1) particulate emissions - less than or equal to 0.1 pounds per 1 million BTUs.

(3) sulfur dioxide - less than or equal to 0.8 pounds per 1 million BTUs for liquid fuels and less than or equal to 1.2 pounds per 1 million BTUs for solid fuels.

In May of 1979 the EPA adopted revised air pollution standards that require electric utilities burning coal to limit the sulfur dioxide emissions by using what the regulation calls the best available control technology. The revised standards are as follows:

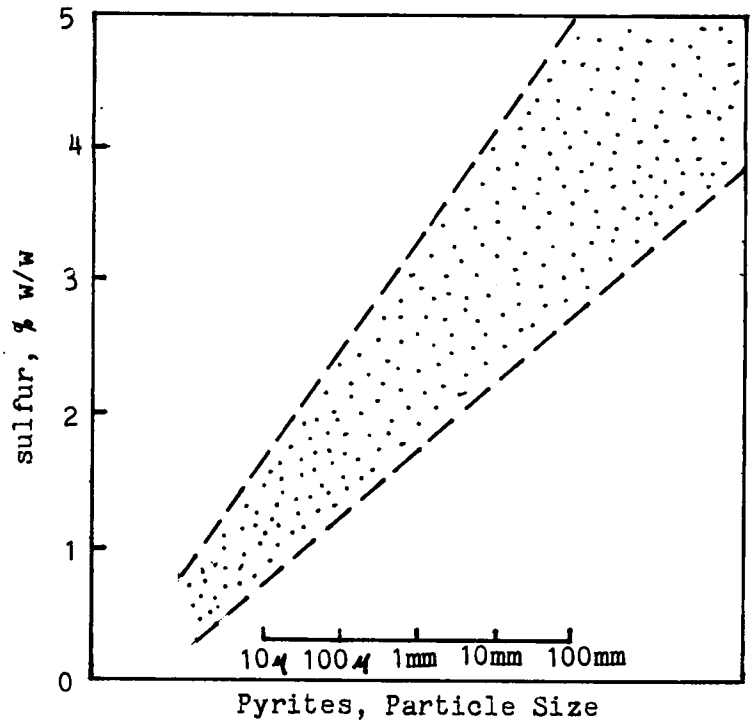


Figure III-2. A Typical Distribution of Pyrite in Coal

Category 1 - All coals with sulfur dioxide levels less than or equal to 2.0 pounds per 1 million BTUs must have 70% of their sulfur dioxide emissions removed.

Category 2 - All coals with sulfur dioxide levels greater than 2.0 pounds per 1 million BTUs but less than 6.0 pounds per 1 million BTUs must have their sulfur dioxide emissions reduced to 0.6 pounds per 1 million BTUs.

Category 3 - All coals with sulfur dioxide levels greater than 6.0 pounds per 1 million BTUs but less than 12.0 pounds per 1 million BTUs must have 90% of their sulfur dioxide emissions removed.

A coal classification system based on the EPA standards for sulfur dioxide emissions has been developed. With regard to the revised EPA standards of 1979, the total sulfur content, S_t, of the coal burned must be less than or equal to $6 \times 10^{-6} \times H$ where H is the calorific value, BTU/pound, of the coal as burned. Coals classified as low total sulfur (LTS) coals meet this requirement as received or after commercial washing techniques (Wen and Lee, 1979). Low organic sulfur (LOS) coals' organic sulfur content meets this requirement but their total sulfur content, organic plus pyritic, does not. Therefore, if their pyritic sulfur content can be sufficiently reduced, they will satisfy the EPA's requirements. For this reason, the development of physical cleaning technology is particularly relevant to their utilization. Other coal classifications are medium

organic sulfur (MOS) coals and high organic sulfur (HOS) coals. These must have some of their organic and inorganic sulfur content reduced before they will meet the EPA's requirements. To do this, either new physical and chemical cleaning processes must be developed or existing ones that are technically and economically feasible must be refined.

4. The Need For Sulfur Removal From Coal

The exclusive combustion of LTS coals is the easiest, cheapest, and most immediate solution to the air pollution problems coming from coal combustion. However, LTS coal supplies are limited. The EPA standard of 1.2 pounds of sulfur dioxide per 1 million BTUs is equal to an approximate 0.8 weight percent sulfur content in coals coming from the eastern Appalachian coal basin. Coals coming from this region supply over 60% of the current United States production, but only 10 to 15% of those now mined can meet the EPA standard. Table III-3, which gives the amount of coal reserves in the eastern United States as classified by sulfur form and content, indicates that the removal of their pyritic sulfur will reduce the sulfur content of a large amount of them to less than 1.0 weight percent total sulfur. If so, the percentage of eastern coals that will meet the EPA standards will triple (Wen and Lee, 1979). The western United States has more tonnage and a greater percentage of LTS coals than the east. Estimates are that approximately

TABLE III-3.

RESERVE BASE (MILLION SHORT TONS) OF BITUMINOUS COAL IN THE EASTERN STATES BY TOTAL SULFUR AND ORGANIC SULFUR CONTENT

State	LTS	LOS	MOS	HOS	Total
Alabama	800	1,030	120	---	1,950
Illinois	1,970	11,820	9,850	42,030	65,670
Indiana	850	2,020	1,810	5,950	10,630
Kentucky	6,900	4,600	1,530	12,520	25,550
Maryland	120	580	350	---	1,050
Ohio	120	5,150	5,690	10,120	21,080
Pennsylvania	1,190	17,430	4,540	720	23,880
Tennessee	390	290	230	80	990
Virginia	2,420	1,020	30	40	3,510
West Virginia	9,900	11,880	7,120	10,690	39,590
Total	24,660	55,820	31,270	82,150	193,900
	(12.7%)	(28.8%)	(16.1%)	(42.4%)	(100%)

90% of all our LTS coal is in the west. Table III-4 gives the coal reserve base figures in the western United States as classified by sulfur forms and content.

At current usage rates, eastern LTS coal should be depleted in 15 to 25 years. When this happens, several alternatives will be available. The EPA standards can be relaxed, western coal can be mined and transported to eastern power plants, or LOS, MOS, and HOS eastern coals can be cleaned to meet the EPA standards. Relaxation of enviromental standards is unlikely; in fact, current trends indicate that the standards will be tightened. The use of western coal is limited by transporting capacity, the required modification of eastern boilers to burn the western coal, and social outcry from the westerners who do not want to supply eastern coal needs at the expense of their ecology. Processing dirty coal to clean coal appears to be the most feasible alternative.

TABLE III-4.

RESERVE BASE (MILLION SHORT TONS) OF BITUMINOUS COAL WESTERN STATES BY TOTAL SULFUR AND ORGANIC SULFUR CONTENT

State	LTS	LOS	MOS	HOS	Total
Alaska	11,070	580	---	---	11,650
Colorado	10,970	3,320	580	---	14,870
Iowa	---	---	550	2,330	2,880
Missouri	---	270	270	8,950	9,490
Montana	30,340	46,330	26,330	5,400	108,400
New Mexico	3,320	820	250	---	4,390
North Dakota	7,330	2,670	4,670	1,330	16,000
Oklahoma	460	510	210	110	1,290
Texas	---	2,450	820	---	3,270
Utah	3,030	510	190	310	4,040
Washington	1,580	270	100	---	1,950
Wyoming	26,280	18,710	8,350	---	53,340
Total	94,380	76,440	42,320	18,430	231,570
	(41%)	(33%)	(18%)	(8%)	(100%)

CHAPTER IV

COAL CLEANING

Much of the coal now mined is not used because its sulfur and ash contents are so high that it is uneconomical or impossible to clean sufficiently for commercial use. Using today's coal cleaning technology, only 32% of our coal reserve can be economically cleaned (Wilkinson, J.F., The 79 Outlook: Optimistic, But, 1979). New technologies that permit cleaner and more convenient ways to use coal would make our huge deposits of bituminous and subbituminous coals available as an energy source in an acceptable enviromental form.

Although coal combustion produces sulfur dioxide, carbon dioxide, carbon monoxide, nitrous oxides, and particulate matter, the focus here is on the sulfur dioxide problem. Sulfur can be removed from the coal after combustion as in flue gas desulfurization, during combustion as in fluidized bed combustion, or before combustion in coal beneficiation processes.

1. Flue Gas Desulfurization (FGD)

The best sulfur dioxide control technology available today is some form of FGD. A scrubber, located between the combustor and the smoke stack, removes sulfur dioxide from the combustion gases. Both wet and dry processes have been

developed and are in use. The scrubber is the most important component in a wet FGD system. There are many different scrubber designs such as spray tower scrubbers, tray scrubbers, packed bed scrubbers, and venturi scrubbers, but all of them are similar in that the absorbent liquid or slurry is brought into contact with the flue gas. The sulfur dioxide in the flue gas is absorbed in the passing liquid and the cleaned flue gas exits to the stack. All scrubbers' cleaning capabilities are limited by the absorption process.

Scrubber costs will vary, depending on the type of system used, the percent emission reduction required, and the volume of emissions being treated. However, all scrubber systems have high capital investment and high running costs. Coal-produced electricity coming from power plants equipped with scrubber systems is up to 4% higher in cost than that coming from plants without them and could be even more expensive than nuclear fission produced electricity (Allen, Z. and Kaslow, D.A., 1979). Perhaps its worst problem, though, is the disposal of the sulfates formed in the process. Although these drawbacks make it less attractive as a desulfurization method, it is the only practical way now to make large power plants emit clean gas.

2. Fluidized Bed Combustion (FBC)

The virtual elimination of sulfur and nitrous oxide

emissions can be accomplished during the coal's combustion in a fluidized bed combustion system. The fluidized bed consists of granular particles, probably residual ash from previously burned coal and an adsorbent, such as graded limestone, supported on a non-sifting grid. A stream of air is passed through the grid with enough velocity to fluidized the bed of particles. As the air velocity is increased, the fluidized bed becomes turbulent, providing excellent conditions for heat transfer. Oil burners supply ignition heat, and when the bed temperature reaches 850° C, a small amount of coal is injected into the bed (approximately 1 part coal to 200 parts bed particles) and ignites there.

During combustion, the released sulfur oxide is adsorbed in part by the limestone and then reacts chemically with the calcium in the limestone to form calcium sulfate. The sulfur is carried away with the ashes instead of being released to the atmosphere. Experts say that sulfur emissions can be reduced by over 90% in this type of system (Sullivan, A.M., 1979). Because of the excellent heat transfer properties of the fluidized bed, the bed temperature is maintained at about 850° C. At this low temperature the formation of nitrous oxides is minimized.

Two types of FBC systems are being developed. One operates at atmospheric pressure and the other is pressurized. It is believed that a pressurized system will further reduce sulfur and nitrous oxide emissions and would

decrease the capital costs of the combustor because it would be smaller. Another advantage of a FBC system is that the waste by-products can be used as agricultural lime, road base material, and during waste water treatment. Operating costs are projected to be less than a conventional coal-fired system equipped with a scrubber. A FBC utility pilot plant is being built by TVA and is scheduled for completion in 1981.

3. Coal Beneficiation

The objective of coal beneficiation is quality improvement of the coal through the reduction of its sulfur and ash content while maximizing its BTU recovery. All beneficiation methods separate the raw uncleaned coal into fractions. By means of the separation, some of the fractions are upgraded in quality to a high carbon, low sulfur and ash content, and some of the fractions are downgraded in quality to a low carbon, high sulfur and ash content. Table IV-1 gives a listing of some beneficiation processes and their developers.

Coal beneficiation has recently been recognized as a possible route to enviromentally acceptable fuel at a reasonable cost. Specialists at Bechtel have concluded that there is ample evidence to indicate that beneficiation methods have the potential for making significant reductions in the total sulfur content of the difficult to clean

TABLE IV-1

COAL BENEFICIATION PROCESSES

Process	Developer
Physical Processes	
CFRI oil-agglomeration process. . . .	Central Fuel Research Institute, Dhanbad, India
Multi-stream coal cleaning system . .	General Public Utilities Corp.
Two-stage froth flotation	U.S. Bureau of Mines
Electrophoretic separation.	U.S. Bureau of Mines
Magnetic separation	Aquafine Corp. Brunswick, GA (two projects)
Magnetic separation	Hazan Research, Golden, Colorado Inex Resources Denver, Colorado
Ilok process.	Ilok Powder Co., Inc. Washington, D.C.
Chemical Processes	
Battelle hydrothermal process	Battelle Memorial Inst. Columbus, Ohio
Meyers process.	TRW, Inc., Redondo Beach, CA
Ledgemont oxygen leaching	Ledgemont Labs (Kennecott Copper) Lexingont, MA.
"Sulfur oxidation".	KVB, Inc., Tustin, CA
Not disclosed	Atlantic Richfield
Chemical comminution.	Syracuse Univ. Research Corp., Syracuse, NY
Chemical cleaning	Otisca Industries Ltd.

eastern coals (Davis, H., 1978). One disadvantage of any beneficiation method is the generation of wastes. Large quantities of water used to clean the coal become "black water" when they leach minerals out of the coal, and then must be cleaned up before being released to the enviroment. The coal fractions containing a low carbon, high sulfur and ash content are solid wastes that must be dealt with.

Both chemical and physical processing methods are used to clean the coal in its beneficiation. Usually, a process chain including physical and chemical methods is used in a preparation plant. In planning a sulfur removal scheme, one should know the proportion of inorganic sulfur versus organic sulfur and the details of the size, shape, orientation, and distribution of the pyrites in the particular coal to be cleaned. The cleanability of a particular coal depends to a large part upon the form in which the sulfur occurs.

Chemical Cleaning

Chemical cleaning methods use a reagent to either leach the mineral sulfur from the coal or to dissolve the organic carbonaceous material from around the sulfur containing parts. They preferentially remove pyritic sulfur but they also remove some of the organic sufur. Since finely disseminated pyrite crystals and the organically bound sulfur cannot be removed by physical methods, chemical methods are required for their removal. Therefore, coals

containing high amounts of organic sulfur and or high amounts of finely disseminated pyrites must be chemically cleaned. A brief description of some of the chemical cleaning methods follows.

The Battelle Hydrothermal Process uses an alkali leachate slurry, either $Ca(OH)_2$ or NaOH, to extract the sulfur containing ash from -200 mesh coal. Approximately 99% of the pyritic sulfur and 70% of the organic sulfur has been extracted in test runs (Stambaugh, E.P. and others, 1977). Disadvantages of this process are the cost of the leachate slurry, the cost of its regeneration, and the disposal of liquid wastes.

Chemical comminution is a chemical "crushing and grinding" method. The coal is treated with a chemical reagent, an ammonium gas or a concentrated aqueous ammonia solution have been the most effective, and the result is a selective breakage of the coal that occurs at the coal's mineral and maceral boundaries. The result is a very effective liberation of the coal's mineral matter from its macerals. It has an edge over the preparation of coal by mechanical crushing and grinding because there is no size reduction of the minerals or macerals. Experiments have proven that over 80% of the pyritic sulfur in certain bituminous coals can be chemically liberated without reducing the coal to below 1/4 inch top-size (Wilkinson, J.F., Will Chemicals Replace Crushing?, 1978). The exact

chemical mechanism is unknown but there appears to be little or no chemical reaction between the coal and the ammonia because tests have shown that the nitrogen content of the coal after comminution is increased only slightly (Wheelock, T.D., Chemical Cleaning, 1977).

A hot aqueous solution containing oxygen will extract pyritic sulfur from coal. The reactions leading to a sulfur reduction are:

(1) $2FeS_2 + 7.5O_2 + 4H_2O = Fe_2O_3 + 2H_2SO_4$

(2) $H_2SO_4 + NaCO_3 = Na_2SO_4 + CO_2 + H_2O$

An aqueous solution of iron salts will also extract pyritic sulfur from coal. The reactions in this case are:

(1) $2Fe(aq) + FeS_2(s) = 3Fe(s) + 2S(s)$

(2) $14Fe(aq) + FeS_2(s) + 8H_2O(1) = 15Fe(aq) + 2HSO_4(aq) + 14H(aq)$.

Other similar processes include nitric acid leaching, leaching with solutions of ferric sulfate, and treatment with nitrogen oxides (Wheelock, T.D., Chemical Cleaning, 1977).

Another chemical cleaning process is hydrodesulfurization. The coal must first be liquefied or gasified by any of several developed processes. Next, the converted coal is brought into contact with hydrogen gas at an elevated pressure and in the presence of a catalyst to cause a reaction. The hydrodesulfurization reaction is of the type:

organic sulfur compound + H_2 (in the presence of a catalyst) = H_2S + desulfurized organic compound.

The catalysts used are alumina supported oxides of cobalt and molybdenum. To date, there has been only very limited success in reducing organosulfur values without either gasification or liquefaction followed by hydrodesulfurization.

Physical Methods

Physical cleaning methods beneficiate coal by utilizing some physical property difference between the coal and refuse particles to separate them into a cleaned product fraction and a waste fraction. Depending upon the relative size of the coal and pyrite particles, pyrite can be efficiently removed using today's conventional physical cleaning processes. Preparation plants that use a chain of these methods are the most highly developed and cost effective coal cleaning processes but can only remove the pyritic sulfur (Wheeler, T.D., Chemical Cleaning, 1977).

The first step in all physical cleaning methods must be the liberation of the pyrite particles from the carbonaceous coal particles so that a separation of the two can later be effected. In fact, the extent of pyrite removal in several of these methods, float-sink for example, can be fairly well predicted from a microscopic analysis that indicates the degree of pyrite liberation because, as the top-size of the coal is reduced, the liberation of the pyrite particles

increases. Coal pyrite usually occurs in roughly spherical globules of diameters from a few microns to 100 microns, with the majority being 25 to 40 microns. Coarse pyrite is irregularly distributed throughout the coal and fine pyrite is more uniformly distributed (McCartney, J.T. and others, 1969). The procedure usually employed to liberate the pyrite particles is the mechanical crushing and grinding of the coal, but chemical comminution, as previously described, can also be used.

After pyrite liberation, a cleaning process follows that uses equipment such as flotation cells, screens, jigs, tables, centrifuges, cyclones, and spirals to upgrade product fractions and downgrade waste fractions. A brief description of some of the methods being used today follows.

Two stage froth flotation is the most widely used fine, -28 mesh (0.595 mm), coal beneficiation method. Separation of the coal's pyrite and other mineral particles from its carbonaceous particles is accomplished by utilizing the difference in density of the two fractions and the difference in their surface chemistry characteristics. The specific gravity of coal's pyrite particles is approximately 3.3 and that of its organic particles approximately 1.8. The difference between the specific gravities of mineral pyrite (5.0) and coal pyrite (3.3) is due to the coal pyrite's porosity (Myers, R.A., 1977). A frothing agent added to the water helps create a surface froth upon

agitation. Other chemicals are added to render the pyrites hydrophilic (water attracting) and the coal particles hydrophobic (water repelling). Coal fines are introduced to the solution's surface where the hydrophobic coal particles tend to attach themselves to the air bubbles and float, while the denser hydrophilic mineral particles tend to sink. The float fraction is sent to a second bank of flotation cells where the process is repeated. Results have had over 90% of the pyrites removed with the weight% sulfur of the coal being reduced from 2.61 to 0.8% (Davis, H., 1978). The problems of coal flotation, non-selectivity, inefficient reagent utilization, and excessive variability of results, can be broadly classified as a lack of predictability (Taylor, S.R., Miller, K.J., and Deurbrouck, A.W., Surface Chemical Problems in Coal Flotation). All of these problems intensify to such a degree at ultra fine sizes that froth flotation is not an effective cleaning method for them.

In the United States it is estimated that per year 10 to 15 million tons of fine coal is beneficiated by flotation and 250 to 300 million tons of coarser wet-cleaned coal is beneficiated by various specific gravity methods. Many of these methods use equipment that accomplish a separation through specific gravity differences. Some of these methods are:

The float sink method is a gravity separation method that uses a dense organic liquid as a medium for the float

and sink separation of the organic particles and denser refuse. Settling of the particles denser than the liquid occurs according to Stoke's Law while the lighter organic particles either float or sink much more slowly. Capacities are usually low because large residence times are required to get a good separation; the time required depends on several factors including particle size, particle density differences, and the specific gravity of the liquid medium.

Dense media cyclones circulate a slurry of crushed coal, water, and magnetite at a very high velocity. The solution's specific gravity is such that when it circulates at a high velocity in the cyclone vessel, the lighter organics rise to the top and are drained off there. The heavier impurities sink and are drained off at the vessel bottom. Since they contain no moving parts, cyclones are the most simple and compact of the processing equipment. Basically, they consist of a cylinder divided into two chambers. One chamber is of a conical shape with an orifice at its apex and the other chamber is of various shapes. A tube concentric with the cylindrical shell and connecting the two chambers is known as the vortex finder. The solution tangentially enters the first chamber opposite the apex orifice. This forced entry along with the equipment's design creates a centrifugal force that separates the particles in the feed.

Spiral Classifiers accomplish separation by a

combination of centrifugal and gravitational forces. A feed slurry of coal and water flows down through a spiral conduit until the centrifugal forces cause the heavier particles to stratify; portals stationed along the conduit progressively remove the heavier particles. The product stream comes off the end of the spiral.

Centrifuges effect a separation by using centrifugal force rather than gravitational force. Since the centrifugal force produced can be much larger than gravitational force, the required residence times in centrifugal methods are much less than those in gravitational methods, a big advantage. A disadvantage is the fact that the centrifuge is much more effective at liquid/solid than solid/solid separations. The cyclone is much better suited for solid/solid separation and it utilizes the same centrifugal concept.

Concentration Tables consist of a flat riffled surface that is slightly inclined from the horizontal. The feed slurry enters the table from one corner and travels along the table's diagonal to the other corner. This motion is caused by the induced oscillatory motion of the inclined table. Wash water flowing perpendicular to the slurry's flow divides and carries the heavier particles to one side as the lighter particles go to the product side. Since good separation is not usually possible in one pass, multistage units have been developed.

Jigs provide agitation in a settling tank with a pulsating, or jigging flow of water. As the water pulsates up and down, a stratification of particles occurs with the less dense ones concentrated at the top. This coal concentrate is the product fraction. Other fractions are the middlings and heavies. The middlings are frequently recycled to increase recovery efficiency and the heavies are removed as waste.

As of 1977, pyrite and other minerals in coal were removed on an industrial scale almost exclusively by gravity separation methods. The increased mechanization of coal preparation plants and the need to grind the coal to liberate the impurities is creating increasing amounts of very fine dirty coal that cannot effectively be cleaned by specific gravity methods (Capes, C.E. and others, Economic Assessment of the Applicability of Oil Agglomeration to Coal Preparation). Recently, the physical beneficiation field has experienced a number of evolutionary and innovative changes, and other methods are being developed to clean these fine coals.

Magnetic methods utilize the difference in the magnetic properties of the coal and pyrite particles by passing fine dirty coal through a powerful magnetic field. The mineral portion is more affected by the field causing a separation between it and the organic portion. As much as 80% of the pyritic sulfur and 45% of the coal ash have been extracted

by magnetic methods (Evans, J.M., 1977). Problems associated with this method are non-reproducable results and the expense involved in producing a powerful magnetic field.

Oil agglomeration is another beneficiation method that can be used to clean fine coal, and results indicate that the finer the grind, the better the separation. Oil and other chemicals are mixed with coal fines and water to make an approximately 10% by weight coal slurry. The oil renders the coal particles more hydrophobic and the chemicals render the mineral particles more hydrophilic. The coal particles are selectively coated by the oil and pellets grow as these oil coated particles collide and agglomerate. The entire mixture is put on a rotating balling disc that produces a pellet fraction and a cake fraction, and then both fractions are screened to complete the separation. Although the mineral content has been reduced by 25 to 40% (Evans, J.M., 1977), two problems are associated with this technique. One is the expense of the oil and the other is the incomplete separation of the coal and its pyrite. The latter problem is believed to exist because the pyrite's surface, like that of the organic coal particle's surface, tends to be hydrophobic, causing some of the two fractions to agglomerate with each other.

If this process or one similar can be perfected, it is likely that it will become important in industrial coal preparation because of its ability to handle very fine

coals. Low quality coals, whose ash and pyrites are extremely finely disseminated throughgout the organic portion, are being increasingly mined. Upgrading them can be accomplished only after fine grinding to liberate these impurities.

CHAPTER V

THEORY

In my experimentation, I attempted to use a "dry" selective agglomeration technique to separate coal into two fractions: a mineral, including the pyrites, fraction; and a carbonaceous fraction. The primary goal, the reduction of the coal's total sulfur content, would then be accomplished by the removal of the mineral fraction. Much of the same theory utilized in the oil agglomeration method of coal beneficiation is applied in this technique. Here, I attempt to utilize differences in surface chemistry between the mineral coal particles and the carbonaceous coal particles to cause them to selectively agglomerate, and then I separate one portion from the other. The removal of some of the inorganic sulfur should lower the coal's total sulfur content.

A sample of crushed and size classified coal particles was sprayed with an aqueous solution while tumbling in a rotating container. The spray solutions used contained substances whose purpose was to chemically enhance the surface chemistry differences between the mineral particles and the carbonaceous particles causing the mineral particles to adsorb the solution while the carbonaceous particles repelled it. The solution's pH was adjusted to various values to see what effect it had on the results. Upon

adsorption of the solution, capillary forces in the pores of the wetted particles in conjunction with the compressing forces of the tumbling action caused their pelletization. Therefore, the theory behind this process can be divided into two sections: the surface chemistry utilized to cause a selective wetting of the mineral particles; and the pelletization process of these wetted particles.

1. Surface Chemistry

Surfactants and a Possible Application

Two terms already used, surfactant and depressant, should be explained in more detail prior to any discussion regarding the utilization of surface chemistry properties. A surfactant is a surface-active agent, a substance that when present at a low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and then altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces. An interface is the boundary between any two immiscible phases and a surface is an interface where one phase is a gas, usually air; in our case the interfaces of interest are the solid/liquid boundaries between the solution and the carbonaceous particle and the solid/liquid boundaries between the solution and the mineral particle.

Surfactants have an amphipathic structure; the surface-active portion of their structural group contains a

lyophobic end that has very little attraction for the solvent and a lyophilic end that has a strong attraction for the solvent. In the case of the ionic solvent water, they have a hydrophobic (water repelling) end and a hydrophilic (water attracting) end. They are classified as: anionic, the surface-active portion bears a negative charge; cationic, the surface-active portion bears a positive charge; zwitterionic, the surface- active portion may bear either a negative or positive charge; and as non-ionic, no apparent ionic charge. One example of a surfactant is any of the soaps and detergents used for cleaning purposes. The effect of their presence in water can be seen at the water/dirt, oil interface.

In the water's interior, the presence of the hydrophobic group causes a distortion of the surrounding water structure, increasing the free energy of the system. This distortion and increasing free energy mean that less work is needed to bring a surfactant molecule to the surface than a water molecule, causing the surfactant molecules to concentrate there. Interfacial free energy is defined as the minimum amount of work required to create or expand an interface per unit area, an example being the interfacial free energy of the air/water interface, the water's surface tension. Since less work is required to bring surfactant molecules to the surface, their presence decreases the amount of work required per unit area to create or expand an

interface as in the case of the reduced surface tension of water. Meanwhile, the hydrophilic end of the surfactant molecule prevents it from being completely expelled from the water as a separate phase. Due to these properties, the surfactant molecule becomes oriented with its hydrophilic end into the water and its hydrophobic end away from the water.

The term depressant is used in the froth flotation industry to describe any substance that selectively attaches itself to one portion of the heterogenous material being cleaned, then renders that porton more hydrophilic, causing it to sink. My interest lies in modifying the properties of the solution/carbonaceous particle interface and the properties of the solution/mineral particle interface in a coal sample. I want to enhance the differences in these two types of particles' hydrophobicity. If a layer of surfactant molecules, adsorbed onto the carbonaceous coal particles, were oriented with their hydrophilic end attached to the solid and their hydrophobic group pointed away, they would enhance these particles' water repelling nature. Meanwhile, a depressant that had selectively adsorbed onto the mineral particles' surface would enhance these particles' water attracting nature. These opposite effects coupled together would result in the solution being preferentially adsorbed by the hydrophilic mineral particles, a condition necessary for their selective

pelletization. Before this can be accomplished, one needs to know something about how the surfactants and depressants are transferred from the solution to the solid, a process known as adsorption.

Adsorption

Essential to my process and a characteristic feature of surfactants is their tendency to adsorb at an interface in a uniformly oriented fashion (Rosen, M.J., 1978). This adsorption process has been extensively studied to determine: (1) the concentration of surfactant at the interface, since this is a measure of how much the interface has been covered and thus changed by the surfactant's adsorption; (2) the orientation of the surfactant at the interface, since this determines how the interface will be affected by the adsorption; whether it will become more hydrophobic or more hydrophilic; and (3) the energy change in the system, ΔG and ΔH resulting from the adsorption, since these quantities provide information on the type and mechanism of any interactions involving the surfactant at the interface and its operation as a surface-active material.

For a solid/liquid interface at a constant temperature, an adsorption isotherm relates the concentration of the surfactant adsorbed at the interface as a function of its concentration in the solution after equilibrium has been reached. Adsorption isotherms can be readily constructed for the solid/liquid interface, but in the case of the

liquid/gas or liquid/liquid interfaces, other properties must be used to study the adsorption process. We are concerned with solid/ liquid interfaces so our adsorption process will be postulated from previous work using adsorption isotherms. In comparing the performance of different surfactants in interfacial phenomena, it is necessary to define: (1) efficiency - the concentration of the surfactant in the liquid phase required to produce a given amount of change in the phenomenon under investigation; and (2) effectiveness - the maximum change in the phenomenon that the surfactant can produce, regardless of the concentration of the surfactant in the liquid phase. The efficiency of adsorption can be related to the various structural groups in the molecules, and the effectiveness of adsorption depends on the structural groupings in the surfactant molecule and its orientation at the interface. In order to understand the electrical aspects of the adsorption of surfactants at interfaces, a phenomenon known as the electrical double layer must be described.

The Electrical Double Layer

At any interface there is always an unequal distribution of electrical charges between the two phases, giving one side a net positive charge and the other side a net negative charge. To maintain electrical neutrality, the

net charge on one side of the interface must be balanced by an exactly equal net charge of the opposite sign on the other side of the interface.

A major area of investigation has been the determination of the exact distribution of the neutralizing charges, the counterions, in the solution surrounding a charged surface, since this distribution determines the rate at which the electrical potential will change with distance from the charged surface. One model, postulated by Stern (1924), divides the double layer into two parts: (1) a layer of strongly held counterions adsorbed close to the charged surface on fixed sites, the Stern layer; and (2) a diffuse layer of counterions (See Figure V-1).

Mechanisms of Adsorption at the Solid/Liquid Interface

Factors that strongly influence the adsorption of surfactants at the solid/liquid interface are: (1) the nature of the structural groups on the solid surface; whether they are highly charged or non-polar groupings, and the nature of the atoms which constitute these structural groups; (2) the molecular structure of the surfactant being adsorbed; whether it is ionic or nonionic, whether the hydrophobic group is long or short, straight chained or branched, aliphatic or aromatic; and (3) the environment of the aqueous phase; its pH, electrolyte content, and its temperature. Together, these factors determine the mechanism by which adsorption takes place.

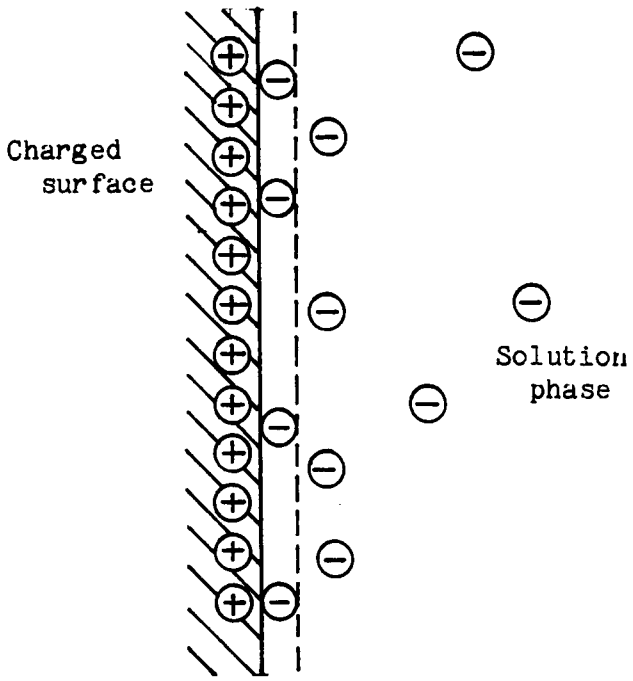


Figure V-1. Stern Model of the Electrical Double Layer

There are a number of mechanisms by which surface-active solutes adsorb onto solid substrates from an aqueous solution. In general, the adsorption of surfactants involves single ions rather than colloid size clusters of surfactants known as miscelles. The mechanisms are:

(1) Ion exchange - involves the replacement of counterions adsorbed onto the substrate (solid surface) from the solution by similarly charged surfactant ions (adsorbate) (Wakamatsu, T., 1968).

(2) Ion pairing - adsorption of surfactant ions from the solution onto oppositely charged sites unoccupied by counterions (Law, J.P., Jr., 1966).

(3) Hydrogen bonding - adsorption by hydrogen bond formation between substrate and adsorbate (Snyder, L.R., 1968).

(4) Adsorption by polarization of pi electrons - occurs when the adsorbate contains electron rich aromatic nuclei and the solid adsorbent has strongly positively charged sites. Attraction between electron-rich aromatic nuclei of the adsorbate and positive sites on the substrate results in adsorption (Snyder, L.R., 1968).

(5) Adsorption by dispersion forces - occurs by van der Waal dispersion forces acting between adsorbent and adsorbate molecules. Adsorption by this mechanism generally increases with increase in the molecular weight of the adsorbate and is important not only as an independent mechanism but also as a supplementary mechanism to all other types (Law, L.R.,

1966).

(6) Hydrophobic bonding - occurs when the combination of the mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an aqueous environment become large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains. Adsorption of surfactant molecules from the liquid phase onto or adjacent to other already adsorbed surfactant molecules may also occur by this mechanism (Wakamatsu, T., 1968). Ion exchange and ion pairing are represented in Figure V-2.

Adsorption Isotherms

At any solid/liquid interface we are interested in determining: (1) the amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent, i.e., the surface concentration of the surfactant at a given temperature, since this is a measure of how much of the surface of the adsorbent has been covered and changed by the adsorption; (2) the equilibrium concentration of surfactant in the liquid phase required to produce a given surface concentration of surfactant at a given temperature, since this measures the efficiency with which the surfactant is adsorbed; (3) the concentration of surfactant at surface saturation at a given temperature, since this determines the effectiveness with which the surfactant is adsorbed; (4) the orientation of the adsorbed surfactant plus any other

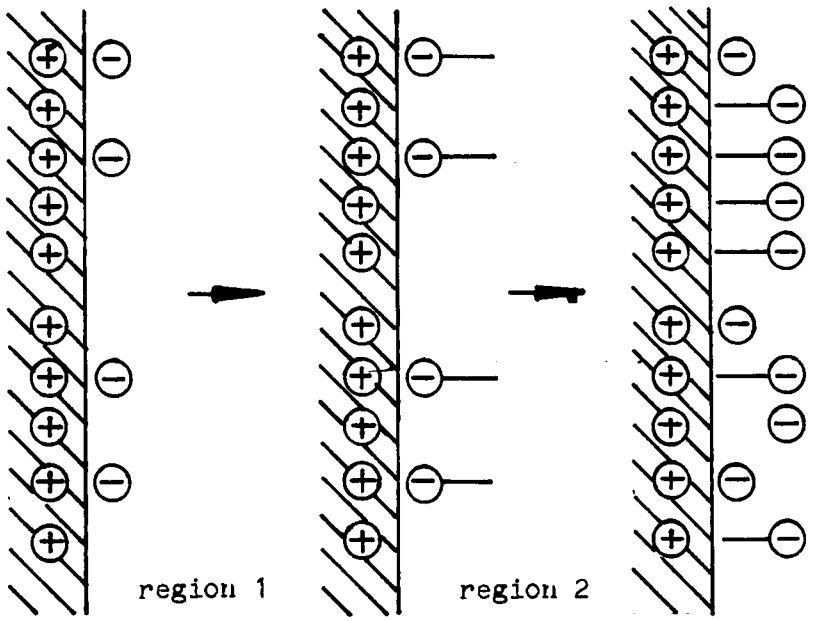


Figure V-2. Adsorption of an Ionic Surfactant Onto an Oppositely Charged Substrate by Ion Exchange (Region 1) and Ion Pairing (Region 2)

parameters that may shed light on the mechanism by means of which the surfactant is adsorbed, since a knowledge of the mechanism allows us to predict how a surfactant with a given molecular structure will adsorb at the interface; and (5) the effect of adsorption on other properties of the adsorbent. Since most of these are directly determinable from the adsorption isotherm, the isotherm is the usual method of describing adsorption at the liquid/solid interface.

Several models have been developed to describe the adsorption isotherm. One model is the Langmuir Adsorption Isotherm:

$$C_2^s = \frac{C_m^s C_2}{C_2 + a}$$

where:

C_2^s = the surface concentration of the surfactant, in moles/cm

C_m^s = the surface concentration of the surfactant, in moles/cm, at monolayer adsorption.

C_2 = the concentration of the surfactant in the liquid phase at adsorption equilibrium, in moles/liter.

a = a constant, $55^{G/RT}$, in moles/liter, at a given temperature T, where G is the energy of adsorption at infinite dilution.

This along with other models is used to study and describe adsorption processes at solid/liquid interfaces; they are

an invaluable tool in determining what mechanisms of adsorption are at work in a specific case.

My specific case involves the adsorption of a surfactant onto a carbonaceous coal particle to enhance its hydrophobicity. In looking at Figure III-1, page 23, a model of the organic coal structure , one sees many O and OH groups that are not part of the ring structure. These sites are ionic in nature, so the carbonaceous coal particles' surface can be characterized as an adsorbent with strongly charged sites.

Adsorption from Aqueous Solution onto Adsorbents with Strongly Charged Sites

Adsorption onto a surface of this type is a complex process during which adsorption of the solute may occur successively by ion exchange, ion pairing, and hydrophobic bonding mechanisms. Figure V-3 is an adsorption isotherm for an ionic surfactant onto an oppositely charged substrate. Its shape is attributed to three distinct mechanisms of adsorption. Ion exchange is the adsorption mechanism in region 1; thus the charge density at the interface remains almost constant. In region 2 the increased slope of the isotherm indicates an increase in adsorption believed to be due to interaction of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactants and with themselves. As the oppositely charged surfactant ions are adsorbed onto the

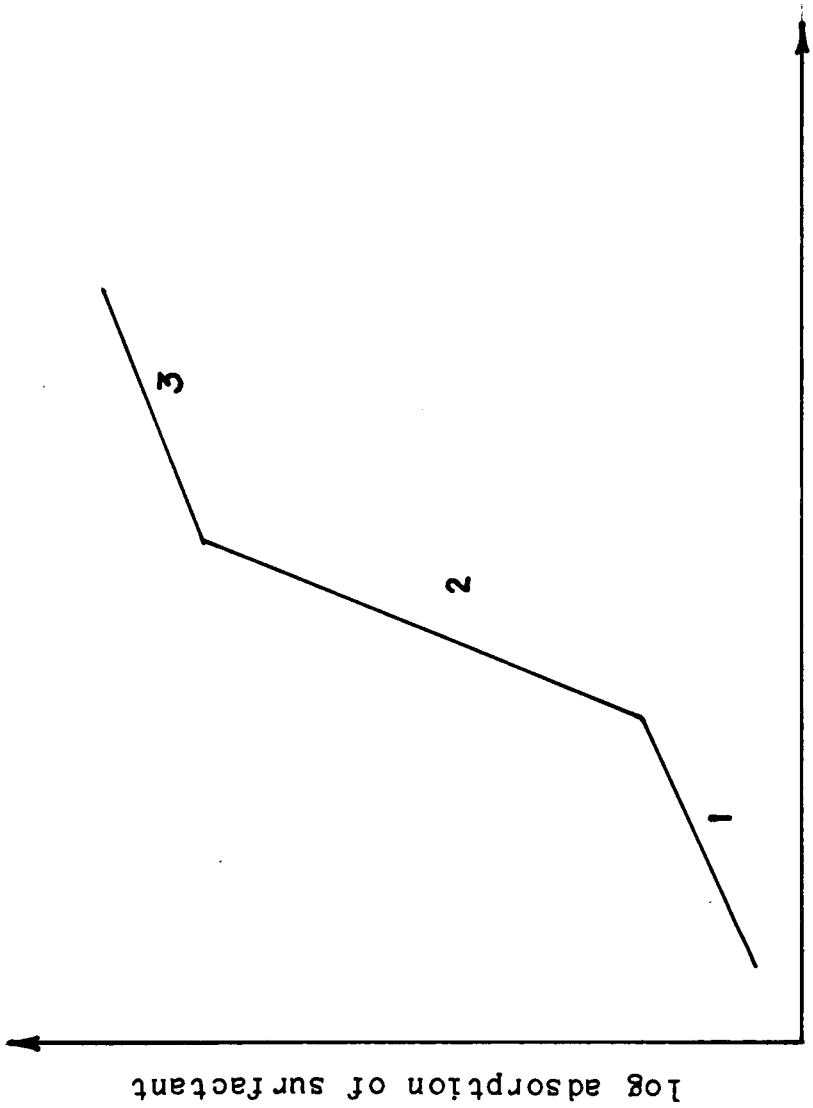


Figure V-3. Adsorption Isotherm of an Ionic Surfactant onto an Oppositely Charged Surface

solid, the charge is first neutralized and then reversed. A decreased slope in region 3, indicating a decrease in the rate of adsorption, is because the adsorption process must overcome electrostatic repulsion between the oncoming ions and the now similarly charged solid. Adsorption in these cases is usually complete when the surface is covered with a monolayer of the surfactant (Robb, D.J.M., 1967).

An increase in the length of the hydrophobic group increases the efficiency of adsorption because the free energy decrease associated with both the removal of the hydrophobic chain from contact with the water and with the tendency to aggregate or adsorb by dispersion forces increases with increase in the length of the chain. In addition, an increase in the size of the hydrophilic group also appears to increase the efficiency of adsorption by ion exchange or ion pairing.

Depending upon the orientation of the adsorbed surfactant molecule, the amount of it adsorbed at surface saturation, i.e., the effectiveness, may increase, decrease, or show no change with an increase in the length of the hydrophobic group. If adsorption is perpendicular and close-packed, an increase in the length of the hydrophobic chain should not affect the cross-sectional area occupied by the chain; an increase in length of the hydrophobic chain will cause no significant change in the effectiveness (Tamamushi, B., 1957). An increase in effectiveness could

occur if the arrangement is not close-packed or if it is slightly tilted from the perpendicular, because of greater van der Waals attractions and the resulting closer packing of longer chains.

A decrease in effectiveness occurs with an increase in the length of the hydrophobic chain when the surfactant is oriented parallel to the interface. In this case, an increase in chain length increases the cross-sectional area of the molecule on the surface, and saturation will be accomplished by a smaller number of molecules.

Another factor to be considered is what effect a change in the pH of the aqueous phase will have on the adsorption process. It usually causes marked changes in the adsorption of ionic surfactants onto charged solid substrates. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative, due to the adsorption onto charged sites of protons from the solution resulting in an increased adsorption of anionic surfactants and a decreased adsorption of cationic surfactants (Connor, 1971). Opposite effects result from raising the aqueous phase's pH.

Changes in the pH can also affect adsorption by changing the characteristics of the surfactant molecules; ionic surfactants can be converted into neutral molecules capable of adsorption only through hydrogen bonding and dispersion forces, and neutral molecules can be converted

into ionic groupings.

Since adsorption by an ion exchange or ion-pairing mechanism results in an orientation of the adsorbed surfactant with its hydrophobic group toward the aqueous phase, the adsorption causes the surface to become increasingly more hydrophobic (Robb, D.J.M., 1967). Negatively charged surfaces show this effect when treated with cationic surfactants, becoming more difficult to wet with water and easier to wet by nonpolar compounds (McCaffery, F.G., 1970). If the adsorption of the surfactant ions onto the adsorbent is continued beyond the point of neutral charge, the charge at the Stern layer of the interface is reversed and the substrate acquires a charge of the same sign as the adsorbate ion. Then, the orientation of the adsorbed surfactant ion is with the hydrophilic end toward the aqueous phase, and as adsorption continues beyond this point, the substrate becomes more hydrophilic in character.

Adsorption from Aqueous Solution onto Nonpolar, Hydrophobic Adsorbents

Although the carbonaceous coal particles have charged sites on their surface, they are characterized as hydrophobic by literature sources (Tayor, S.R., Miller, K.J., and Duerbrouck, A.W.). According to adsorption isotherms, adsorption onto this type of substrate is mainly by dispersion forces with the adsorbate oriented perpendicular to the substrate. However, in this case the

hydrophobic end lies close to the solid's surface and the hydrophilic end is in the aqueous phase, an orientation that is the reverse of the desired one. This adsorption increases the hydrophilicity of the adsorbent, and in the case of ionic surfactants, increases the surface charge density, which also makes it more wettable by the aqueous phase.

Although carbonaceous coal particles are classified as hydrophobic, they do contain polar groups on their surface; for this reason I believe they are better described as adsorbents with strongly charged sites.

Depressants

In the froth flotation process, regardless of the material being processed, a depressant is defined as a wetting agent, and a collector is defined as an anti-wetting agent. I have already discussed collectors or as I choose to call them, surfactants.

A depressant is a modifier that intensifies the selectivity of the surfactant's action, usually achieving this by increasing or decreasing the hydrophobicity of a specific surface. In my experiments, I intend to decrease the hydrophobicity, thus increasing the hydrophilicity, of the mineral particles . The depressant competes with the surfactant for position on the mineral particles' surface but not on the carbonaceous particles' surface. The end

result is the adsorption of the depressant on the mineral particle and the adsorption of the surfactant on the carbonaceous particle. The adsorbed depressant renders the mineral particles more hydrophilic, and the adsorbed surfactant renders the carbonaceous particle more hydrophobic. In summary, the desired combination of surfactant and depressant is one where the depressant preferentially adsorbs to the mineral particles, excludes the surfactant from them, and heightens or maintains their hydrophilic nature. The surfactant preferentially adsorbs to the organic particles and heightens their hydrophobic nature. The result is an increased tendency for the aqueous solution to be adsorbed exclusively by the mineral particles.

2. Pelletization

The Importance of Moisture Content

The first pelletization process was developed in the United States to treat ultra-fine particles produced in the upgrading of Mesabi iron ore. It was discovered that balls (pellets) produced by rolling moistened iron ores in a drum developed densities that could only be obtained in powder compacting through the application of very high pressures, the order of several thousand pounds per square inch (Firth, C.V., 1944). Firth believed that the pressures needed to develop these densities were generated at the ball surface

where a few elements of the ball's surface area supported its entire weight. He considered contact area to be the most important factor in the balling process.

However, in 1950 Tigerschiold and Ilmoni rejected the concept that contact area was the sole means of the development of ball strength. Although they agreed that the rolling action has a high compressing effect on the balls , they considered a more important factor to be the surface tension of the added water also acting as a compressing force. They supported this contention by noting that dry powders will not form balls upon rolling and that already formed balls, when immersed in water, disintegrate rapidly.

How then does the water's surface tension help form balls in a pelletization process? If you take a capillary tube and dip it in water, the water level in the tube will rise above that of the exterior water's surface because the water's surface tension sets up a capillary suction at the water/air interface. In addition, it causes an equivalent positive force to be exerted on the tube's walls. Tigerschiold and Ilmoni proposed that the same phenomena occurs in the formation of a "green" ball of iron ore when the water fills the pores to form a many branched capillary system. At the ball's surface, where many of the capillaries end, capillary suction forces caused by the water's surface tension exert an equal positive force on the grains between the capillary openings causing compression.

This compression force spread over the ball's surface is the most important factor in the balling process.

Because the water's surface tension is of paramount importance in providing the cohesive forces necessary for ball formation, the moisture content is a critical factor in the balling process. The optimum moisture content is defined as that at which water menesci are formed at every surface pore (capillary). An insufficient moisture content will result in air inclusions in the ball that reduce the capillary effect, while excess moisture will coat the ball with a coherent film of water that neutralizes the capillary forces. Other factors that are important in ball formation are the porosity, surface area, and density of the feed material. Another essential requirement is an effective balling technique and its associated equipment.

By paying particular attention to the water/particle systems that occur during a ball formation process, three states of the water/ particle system have been identified: (1) the pendular state, when water is present at points of grain contact only and surface tension holds the particles together; (2) the funicular state, when some pores are fully occupied by water; and (3) the capillary state, when all the pores are filled but the surface is not covered by a coherent water film disruptive to the capillary forces (Newitt, D.M., 1958). Other investigations to determine the contributions to the ball's tensile strength by

electrostatic forces, van der Waal's forces, and adsorbed water films have shown them to be insignificant. Investigations are continuing to determine the bonding forces affecting ball formation, but it is considered unlikely that the views expressed earlier, that the strength of the balls results primarily from capillary forces and the mechanical consolidation effected by rolling, will have to be modified.

The Mechanism of Ball Formation

Ball agglomerates are produced by a process that uses balling drums, balling discs, and other specialized equipment to mechanically roll and tumble the feed material. Earlier investigations into the mechanism of ball formation have proven the extreme dependence of ball formation on moisture content. There exists, depending on the material and its size range, a critical moisture range within which strong balls are formed; within this range small changes in the moisture content can have a marked effect on the rate of ball growth. At the lower end of the range, the rate of ball growth is slow and the balls produced tend to be brittle. At the upper end of the range, the growth rate is much quicker, but the balls produced tend to be plastic and easily deformable. A moisture content of the feed within the critical moisture range is essential to the formation of nuclei or seeds, the beginning of the balling process. Previous tests have shown that the balling process proceeds

by a different mechanism in each of three defined growth regions: (1) the nuclei growth region; (2) the transition stage region; and (3) the ball growth region (Kapur, P.C., 1964).

Feed material with the correct moisture content, when charged to equipment designed for ball formation, has a potential for the formation of nuclei (seeds) that is due to the surface energy associated initially with a thin film of water surrounding the particles. When these particles come into contact with each other, the liquid layers coalesce to form pendular bonds at the point of contact, thus reducing the water/air interface and the surface energy of the system. Upon rolling, highly porous, loosely held aggregates and crumbs are formed in which the particles are held together by pendular bonds, discrete lens-shaped rings of liquid at the points of contact between the particles. After a short induction period in which rearrangement and particle packing of the particles occur, these aggregates and crumbs form small, spherical , stable nuclei. This nucleation period is a pre-requisite to the balling process, since the balls grow from the nuclei. The nuclei formed are in a small size range, are quite porous, and, as a result, consist of three phases: (1) water; (2) entrapped air; and (3) solid particles. Upon further rolling, these nuclei are compacted and the interstitial void volume due to the entrapped air decreases continuously as the capillaries fill

with water. Capillary forces then cause the particles to be pulled together and this, along with mechanical consolidation due to the rolling action, cause the nuclei to densify rapidly.

As the water is segregated into the capillaries, the growth mechanism changes. Now, apart from the decreasing pockets of trapped air, the granule's center consists of two phases, solid and liquid, and its shell of densified material is still highly plastic. Ball growth by the coalesence of a number of these granules can easily take place. In this transition stage, the size range of the granules and balls becomes much wider.

In the ball growth region, the balls and granules are considered to consist of a tightly packed interior surrounded by a thin wet shell. Two growth mechanisms in this growth region have been defined through previous investigations: (1) growth by assimilation that occurs when balling is proceeding without the addition of fresh feed material; and (2) growth by layering that occurs when balling is carried out with the addition of fresh feed material.

CHAPTER VI

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Experimentation was done to determine if a "dry" selective agglomeration technique could be used to beneficiate coal by reducing its pyritic sulfur content. The purpose of the selective agglomeration was to divide the raw coal into two fractions that could be physically separated and individually analyzed for weight % sulfur content. Beneficiation was to be accomplished by an enrichment of the carbonaceous product fraction when the pyrite concentrated waste fraction was removed from it.

The coal used in this study was a high sulfur coal obtained from The Clear Creek Coal Company's Mine Number 2 in the Wilder Seam near Monterey, Tennessee (Putnam County). This coal contained nominally 2.7% total sulfur of which 0.9% was organic, 1.1% was pyritic, and 0.7% was sulfate. The experimental procedure can be divided into three major areas: (1) liberation of the pyrites by mechanical crushing and grinding; (2) the selective agglomeration process; and (3) weight % sulfur analyses.

1. Crushing, Pulverizing, and Screen Sizing

Liberation of the pyrite material from the carbonaceous material is a pre-requisite for any physical beneficiation process designed to separate the two. Various sizes of

untreated coal "rocks" were crushed in a Holmes Model 201 hammermill crusher using a 3/16" screen. This crushed coal was further reduced in size by a Holmes Model 501 pulverizer using a 1/16" screen. Next, a Tyler Ro-Tap sieve shaker and Tyler sieve screens separated the crushed coal particles into specific size ranges by shaking and screening them for approximately 45 minutes; the individual coal fractions were then bottled and labeled. The size fractions used in the experiments were -80, +100 (80/100) mesh, 80/115 mesh, 115/170 mesh, and 170/270 mesh. All of the above equipment is located in Room M-16, Dougherty Engineering Building, University of Tennessee (U.T.).

2. Selective Agglomeration

In this experimentation, I used a "dry" agglomeration technique, as opposed to the already developed "wet" oil agglomeration technique. All of the equipment used for this agglomeration technique was constructed in the machine shop of the U.T. Department of Chemical and Metallurgical Engineering.

Equipment and Materials

(1) Coal sample container - Two models of a container for the tumbling crushed coal particles were made. The first (see Figure VI-1) is an acrylic cylinder with annular plexiglass caps on each end. The holes in the caps allow a solution, sprayed through the front cap, to travel along the

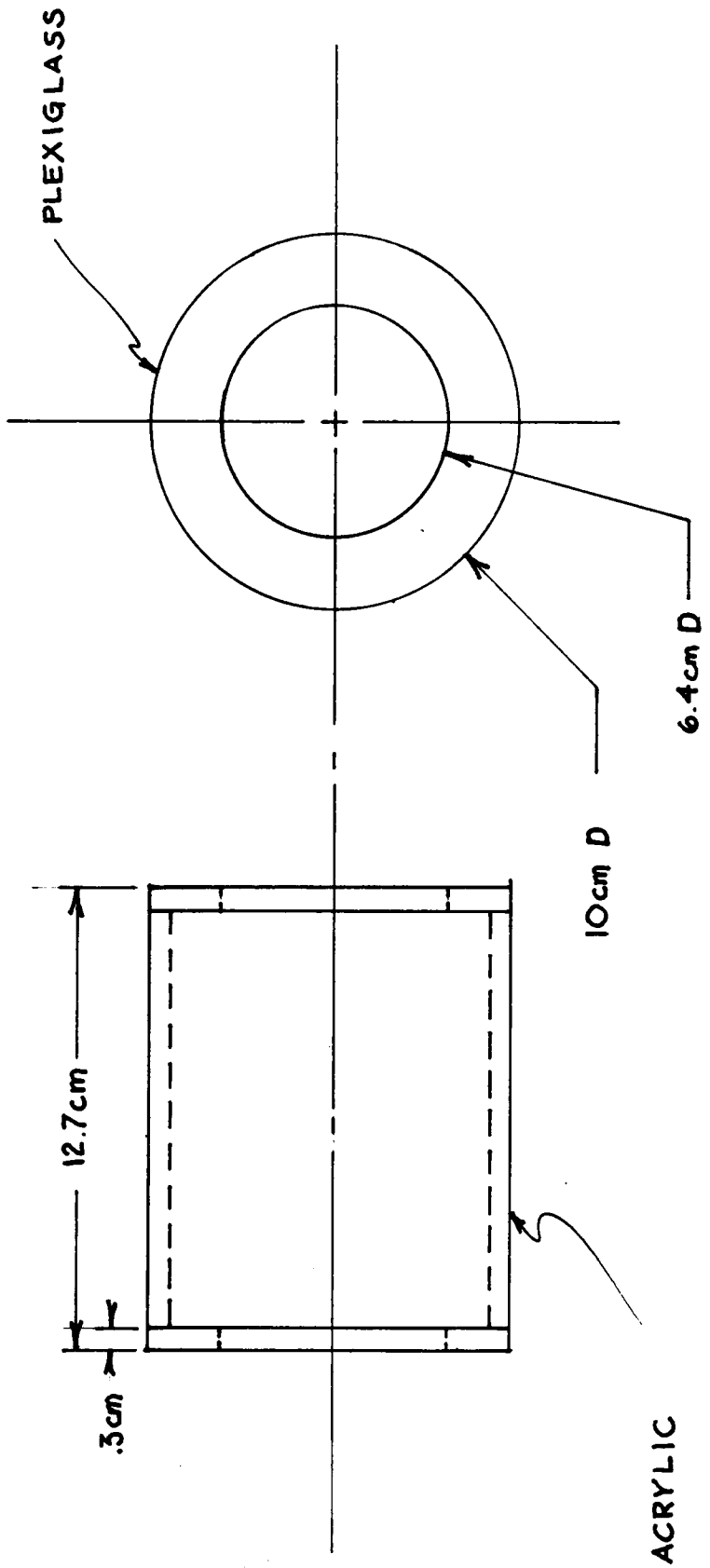


Figure VI-1. Sample Container 1

container's center-line and out through the rear cap. During this passage, most of the solution spray contacts the container's tumbling coal particles. However, this direct uninterrupted path allowed the force of the solution spray to carry significant amounts of the tumbling coal particles through the rear cap and out of the container. To alleviate this problem, modifications were made on the container (see Figure VI-2). A circular plexiglass disc to cover the hole in the rear cap was recessed into the container so that the spray could exit from the container by going around the disc's outer radius and then out the hole in the rear cap. Most of the coal particles that were entrained in the spray stream encountered this disc and fell back into the tumbling coal particles. Although this modification was not 100% effective, the amount of lost coal particles became tolerable.

(2) "Ball Mill" - A laboratory scale "ball mill", also constructed in the machine shop, tumbled the coal particles by rotating the container. The speeds used ranged from 20 RPM (approximately 18.5 ft/min. surface velocity) to 45 RPM (40.8 ft/min. surface velocity). It consists of a continuously variable speed motor that simultaneously drives two parallel rollers upon which the container was placed. The motor speed was controlled by a Gerald K. Heller Co. C-25 Motor Controller. This "ball mill" and its accompanying equipment are located in Dougherty, 321.

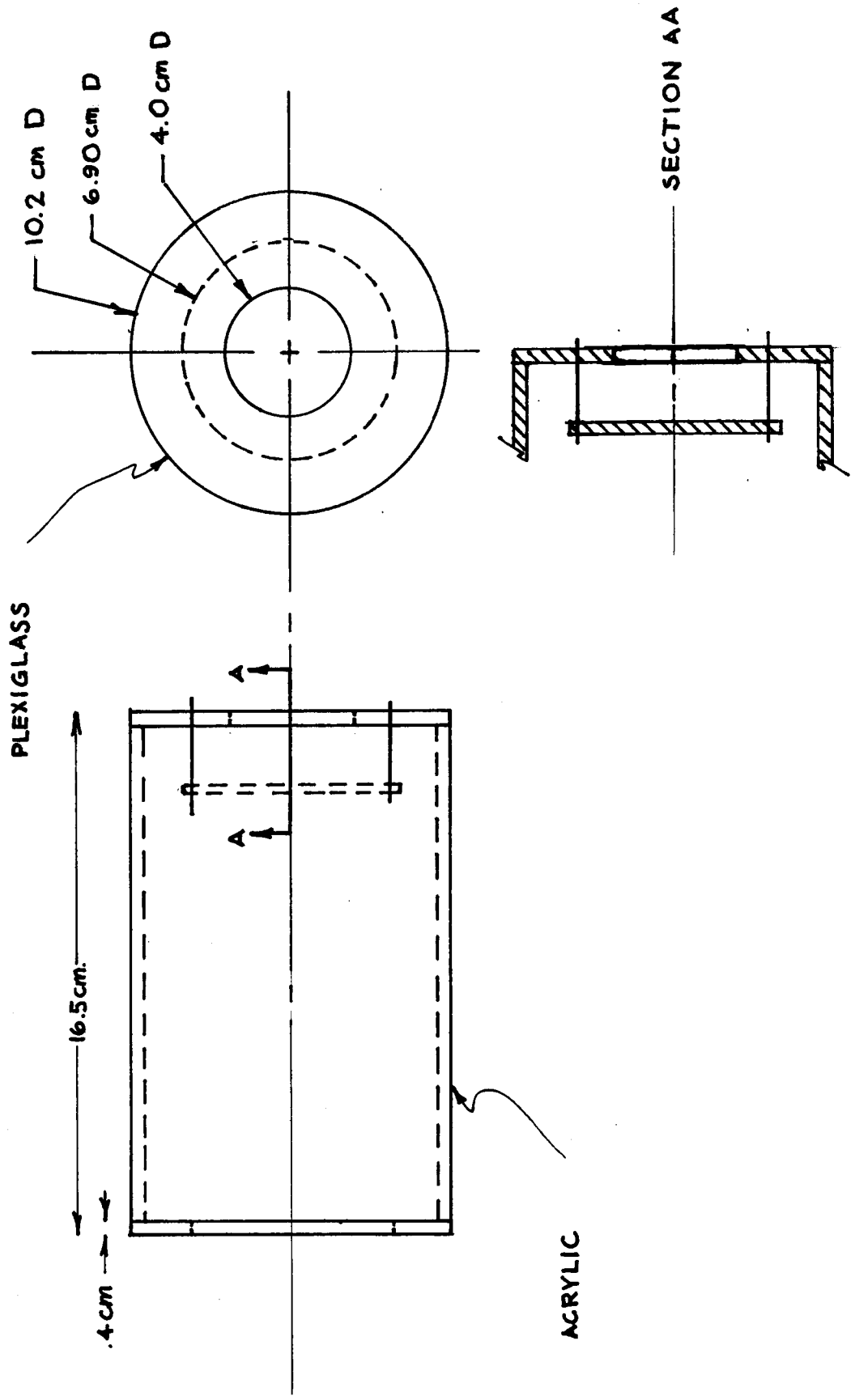


Figure VI-2. Sample Container 2

(3) Solution sprayer - The machine shop modified a "perfume bottle" type spray apparatus that was used to spray solutions into the container and its tumbling coal particles. A compressed air stream passing through the spray nozzle pulls the solution from its receptacle and upon mixing they exit as a spray stream. The delivery air is filtered and regulated prior to the spray nozzle, subsequently regulating the force and amount of the spray stream leaving the nozzle. Figure VI-3 characterizes the solution sprayer.

(4) Spray solution - Different spray solutions were tested in an attempt to isolate an optimum one. Parameters that were varied in making different solutions were the surfactant selection and its concentration, the depressant selection and its concentration, and the pH of the solution. The solution's pH was adjusted by the addition of either 1M sodium hydroxide solution or 1M potassium hydrogen phthiolate solution.

(5) Drying oven - A Precision Scientific Model 625 drying oven, located in Dougherty 316, was used to dry the coal samples.

Experimental Procedure

Between 8 and 12 grams of raw crushed coal particles in one of the size ranges used were placed in the acrylic container. This sample was tumbled by the "ball mill" which longitudinally rotated the cylindrical container along its

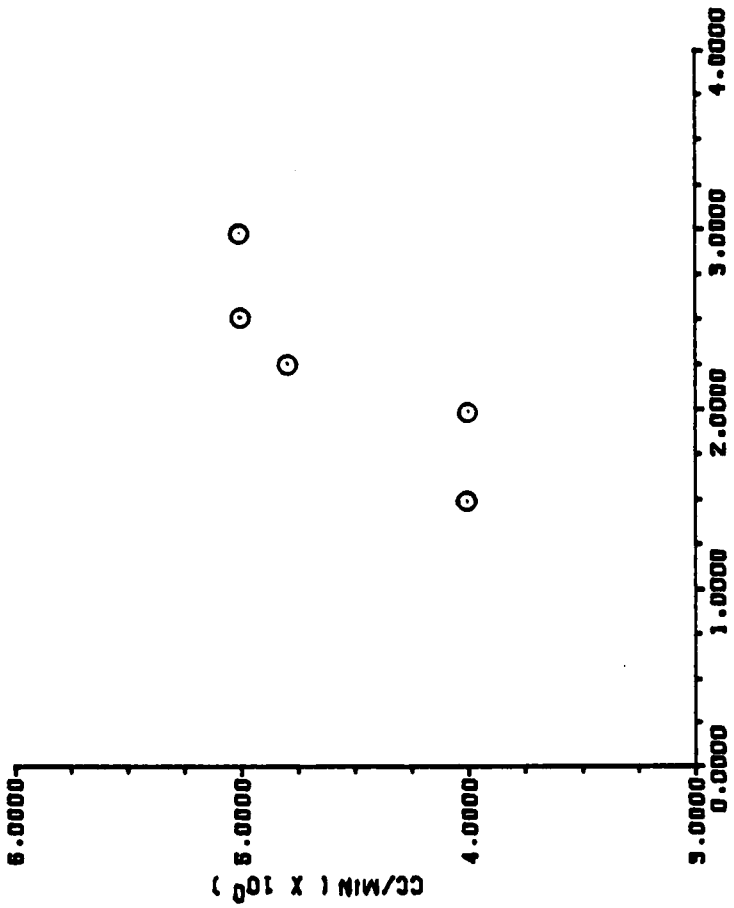


Figure VI-3. Sprayer Characterization

outer radius. The solution was intermittently sprayed into the container and through the tumbling coal particles. Normal procedure was to spray for approximately 30 seconds, wait 1 minute, then repeat, stopping only after significant pelletization had taken place. As the particles adsorbed the solution, capillary forces in conjunction with the tumbling action, caused pelletization to take place. When the pelletization process was complete (appeared to be at steady state), the container was removed from the "ball mill". A flat smooth inclined surface was used to separate the pellets from the cake. Each fraction was weighed (to get a wet weight) and then dryed in the oven at 105°C for approximately two hours. The dried samples were weighed (to get a dry weight) , and the percent moisture prior to drying was calculated. Parameters that could be varied during the selective agglomeration run were the rotation speed of the container (tumbling speed), sample size, spray rate, whether the spray was continuous or intermittent, and the total time of tumbling. The results of these variations are discussed in the Results and Interpretation chapter of this report.

3. Sulfur Analysis

Sulfur analyses to determine weight % sulfur were made on samples of the pellet fraction, the cake fraction, and the untreated coal to determine if any reduction in sulfur was accomplished by the selective agglomeration process.

Equipment and Materials

A Leco Sulfur Analyzer Model No. 534-500 was used to make the sulfur analysis. It consists of a high temperature resistance furnace, a titration apparatus, and other auxiliary equipment and materials (see Figure VI-4).

The auxiliary equipment required are:

(1) Sodium hydroxide solution - Use a 0.1 normal solution. To determine the exact normality of the solution used, I standardized it using reagent grade potassium hydrogen phthiolate.

(2) Hydrogen peroxide solution - Dilute 50 ml of 30% hydrogen peroxide to 1 liter.

(3) Methyl purple indicator and an eye dropper for dispensing - By its color in the solution, the indicator tells you when the solution is acidic, neutral, or basic.

(4) Solution bottles for the above solutions.

(5) Analytical balance to weigh the coal samples.

(6) Tank of oxygen with a two-stage regulator and rubber hose nipple - The oxygen sweeps the combustion gases into the hydrogen peroxide solution.

(7) An ascarite filled tube to keep carbon dioxide from entering the sodium hydroxide solution.

Experimental Procedure

The furnace should be set to provide a constant 2400^{O} F temperature. The needle valve on the oxygen purifying train was adjusted to give an oxygen flow through the combustion

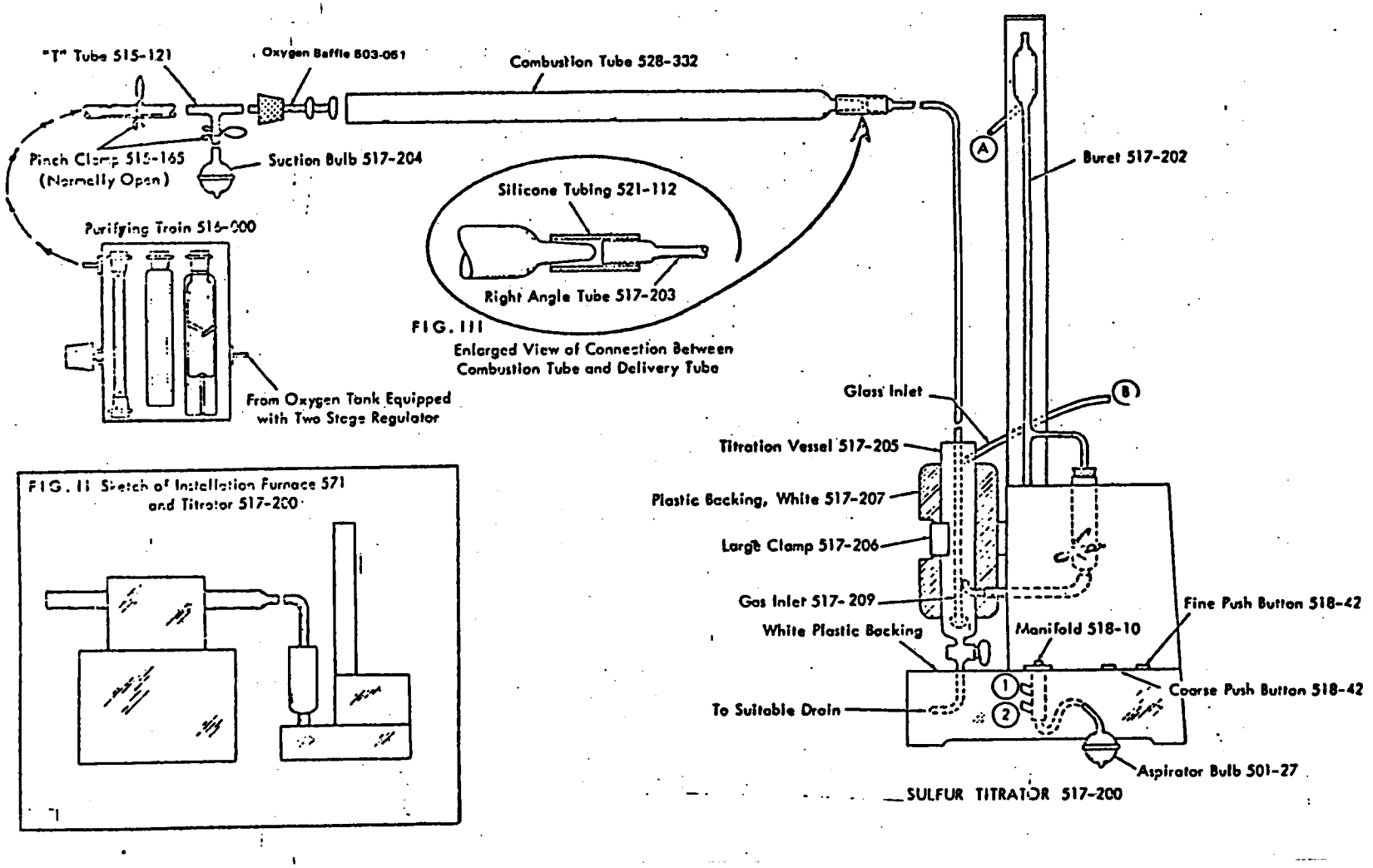


Figure VI-4. Titration Apparatus

tube and out into the hydrogen peroxide solution of approximately 1.5 liters per minute. The titration buret was filled to the zero point with sodium hydroxide solution, and the titration vessel was filled with about 200 ml of the hydrogen peroxide solution. Methyl purple indicator was added (5 to 6 drops) to the hydrogen peroxide solution in the titration vessel. At this point, the solution was purple in color due to the presence of a small amount of acid in the hydrogen peroxide. With the oxygen flowing into this solution, sodium hydroxide was added by means of the titrator's dispensing buttons until a green color just appeared. It was preceeded by a gray color which served as a warning signal that neutralization was about to take place. The sodium hydroxide buret was refilled to the zero point.

The ceramic combustion tube was filled with oxygen prior to inserting the ceramic boat and its sample. The oxygen was allowed to flow through the tube for 1/2 to 1 minute before putting the boat in the tube. With the oxygen still flowing, a boat and its weighed sample were placed directly in the hot zone of the combustion tube. The oxygen baffle, with oxygen flowing through it, was immediately placed in the end of the combustion tube. The sulfur gases from the combusting sample combined with the oxygen and were swept into the titration vessel. As these sulfur gases entered the titration vessel, the solution color changed

from green, indicating a basic solution, to purple, indicating an acidic solution. After about four minutes, the delivery tube was backwashed several times to remove any sulfur trapped within it. Then the solution was titrated. To calculate the weight % sulfur:

% sulfur = (buret reading in %)x(normality of sodium hydroxide)x 10/weight of sample in grams.

CHAPTER VII

RESULTS AND INTERPRETATION

1. Pelletization

Several spray solutions containing different combinations of surfactants and depressants and at different pHs were tested in an attempt to isolate optimum conditions and solutions. The solutions' pHs were adjusted by the addition of either sodium hydroxide or potassium hydrogen pthiolate. Table VII-1 gives the compositions and pHs of the solutions used.

In my experimental setup, the variables (excluding the spray solution makeup) that affect the pelletization process are the coal container's tumbling speed (RPM), the time of tumbling , and the amount of the spray solution adsorbed by the tumbling coal particles. Trial agglomeration runs, where these parameters were varied, were made to determine the optimum values for good quality pellet formation. The optimum values appeared to be equal, regardless of the coal particles size (in a size range of 270 to 80 mesh) or the type of spray solution used.

A container tumbling speed of approximately 32 RPM (approximately 29 ft/min surface velocity) is the best speed for good quality pellet formation in the containers used. Tumbling speeds faster or slower than this hindered the tumbling and mixing action of the coal particles; instead

TABLE VII-1

SPRAY SOLUTION COMPOSITIONS AND pHs.*

Spray Solution #	Solution Composition (g/l)	pH
1A	Sodium Palmitate 0.055 Dextrin - 1.0	6.03
1B	Sodium Palmitate - 0.055 Dextrin - 1.5	6.10
1C	Sodium Palmitate - 0.055 Dextrin - 2.0	5.95
2A	Dextrin - 2.0	6.00
3A	Hexadecyl trimethyl ammonium bromide - 5.03	6.09
3B	Hexadecyl trimethyl ammonium bromide - 10.1	6.07
3C	Hexadecyl trimethyl ammonium bromide - 20.4	6.11
4A	Sodium dodecyl sulfate - 0.3116 Ferric sulfate - 0.3026	5.99
4B	Sodium dodecyl sulfate - 0.3116 Ferric sulfate - 0.15	2.85
4C	Sodium dodecyl sulfate - 0.3116 Ferric sulfate - 0.15	10.10
4D	Sodium dodecyl sulfate - 0.3116 Ferric sulfate - 0.15	8.05
4E	Sodium dodecyl sulfate - 0.3116 Ferric sulfate - 0.15	5.05
4F	Sodium dodecyl sulfate - 0.3116 Ferric sulfate - 0.15	6.35
5A	Sodium dodecyl sulfate - 0.4674 Ferric chloride - 0.0081	3.83

TABLE VII-1 (Continued)

Spray Solution #	Solution Composition (g/l)	pH
5B	Sodium dodecyl sulfate - 0.4674 Ferric chloride - 0.0081	9.16
6A	Ethyl xanthic acid, potassium salt - 0.5 Ferric chloride - 0.0081	4.82
6B	Ethyl xanthic acid, potassium salt - 0.5 Ferric chloride - 0.0081	6.95

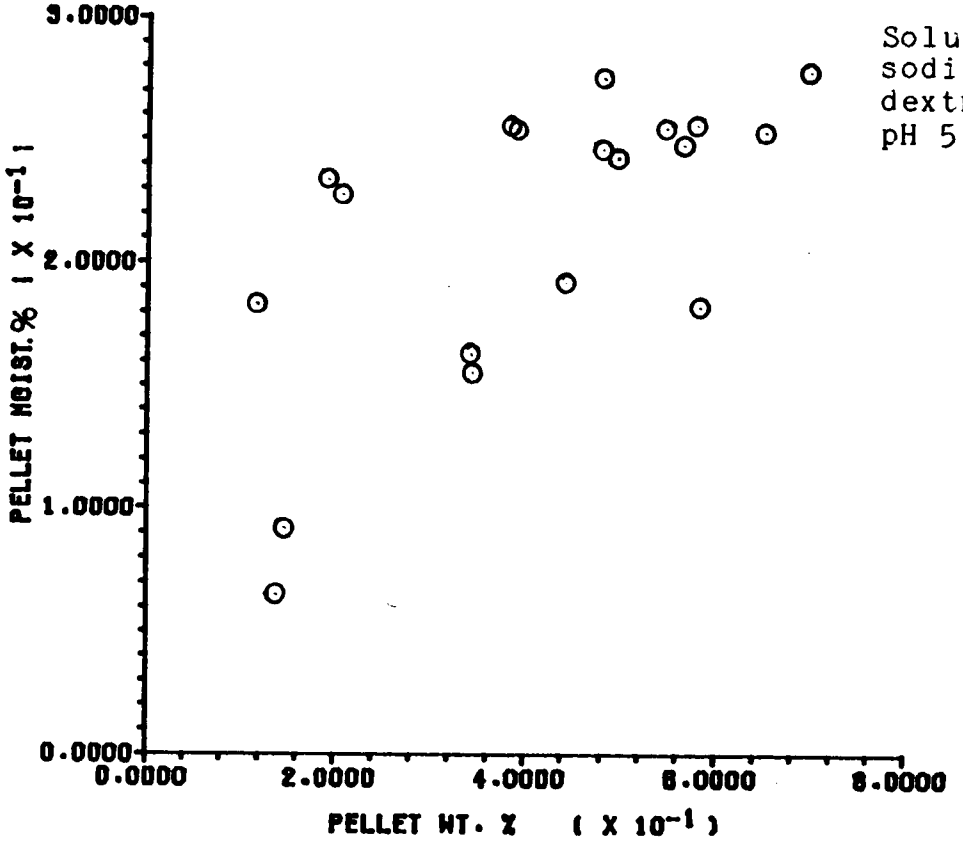
*pH adjustment made by adding either sodium hydroxide or potassium hydrogen pthiolate.

of a tumbling mixture, the particles became one continuous mass that slid in the container and avoided any mixing action. Even at 32 RPM this problem was common and the particles had to be manually mixed by scooping them with a spoon spatula. Forces due to the coal particles' tumbling action were too great at speeds greater than 32 RPM, disintegrating any pellets formed, but at speeds less than 32 RPM they were too small to initiate any significant pelletization. For these reasons, a container tumbling speed of 32 RPM was used in all of the test cases.

In the Theory section, Chapter V, I pointed out that particles must contain moisture in a critical range before good quality pellets would be initiated and propagated by tumbling forces. As one would expect, I discovered that the amount of solution I sprayed into the tumbling coal particles was an important variable in good quality pellet formation. Too much moisture content caused all of the particles to cake together, and to stick to the sides of the rotating container, and any pellets formed were too easily deformed for further handling. Too little a moisture content proved to be insufficient for the initiation of seed pellets and no pelletization occurred. Therefore, a spray amount that gave the particles a moisture content in the critical range, not too high and not too low, had to be sprayed into them before any good quality pellets would form. An intermittent spray procedure was continued until

the critical moisture range, indicated by a significant amount of pellet initiation, was reached. Although a moisture content in the critical moisture range is essential for the formation of pellets, there appears to be only a weak correlation between it and the pellet weight percent of the treated sample, as shown in Figures VII-1, VII-2, and VII-3 for three different spray solutions. The data of these three graphs are plotted together in Figure VII-4. The results of this figure can be classified into three sections: (1) for a pellet moisture percent less than or equal to 5 percent it appears that it is difficult to obtain small amounts of pellets (less than or equal to 10 weight percent) by controlling the pellet moisture percent-i.e., a critical moisture content must be reached before any pelletization will occur; (2) in the pellet moisture percent range of 10 to 20 percent, the pellet weight percent is insensitive to the pellet moisture percent; and (3) in the pellet moisture percent range of 20 to 30 percent, any amount of pellets can be produced depending, it was discovered, upon the time of tumbling. A tumbling time of 8 to 10 minutes following pellet formation limited the pellet weight percent to 20 percent or less.

These optimum parameter values proved to be about the same, regardless of the spray solution used. After the isolation of these optimum values and the determination of methods to overcome the pre-described problems, I was able



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1C:
sodium palmitate 0.055g/l
dextrin 2.0g/l
pH 5.95

Figure VII-1. Pelletization of Coal Using Aqueous Solution 1C: Effect of Pellet Moisture on Fraction of Pellets Produced

Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 3B:
hexadecyl trimethyl-
ammonium bromide 10.1g/l
pH 6.07

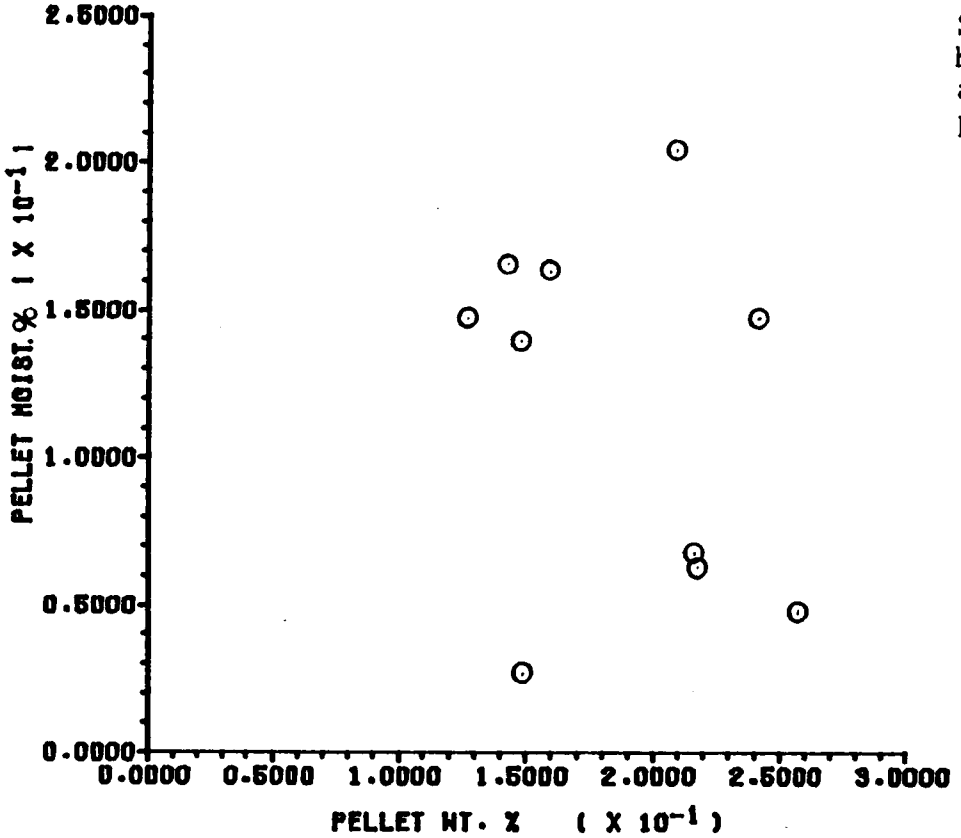


Figure VII-2. Pelletization of Coal Using Aqueous Solution 3B: Effect of Pellet Moisture on Fraction of Pellets Produced

Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 4A:
sodium dodecyl sulfate 0.3116g/l
ferric sulfate 0.3026 g/l pH 5.99

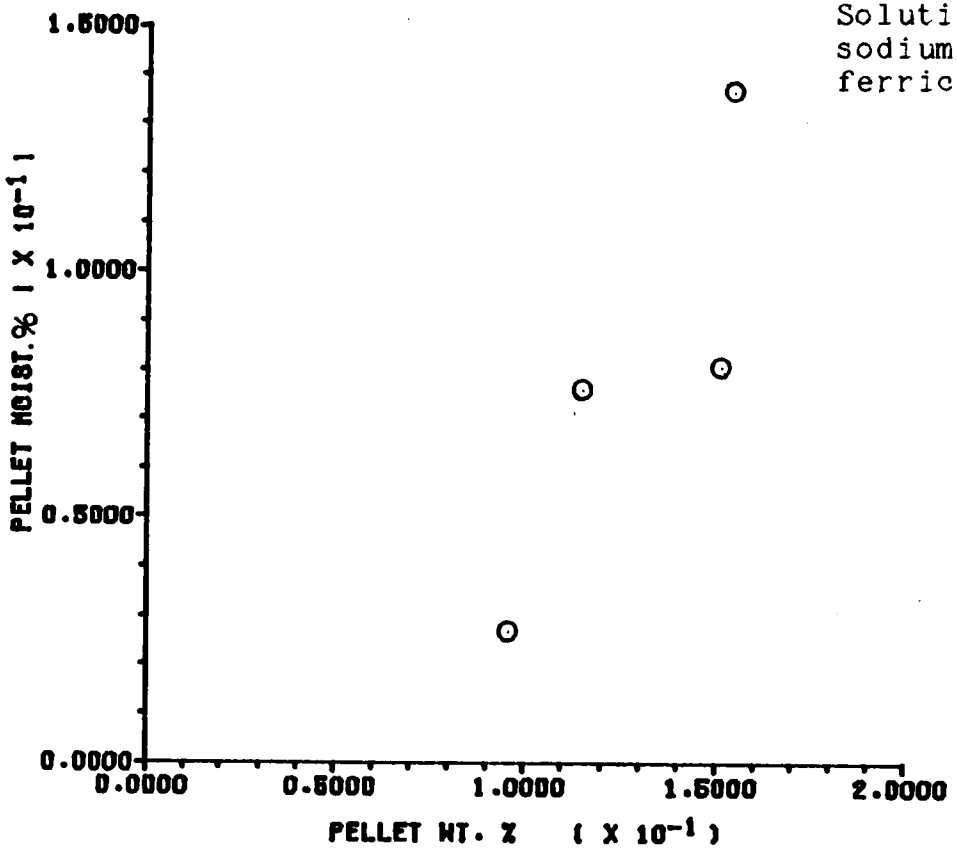
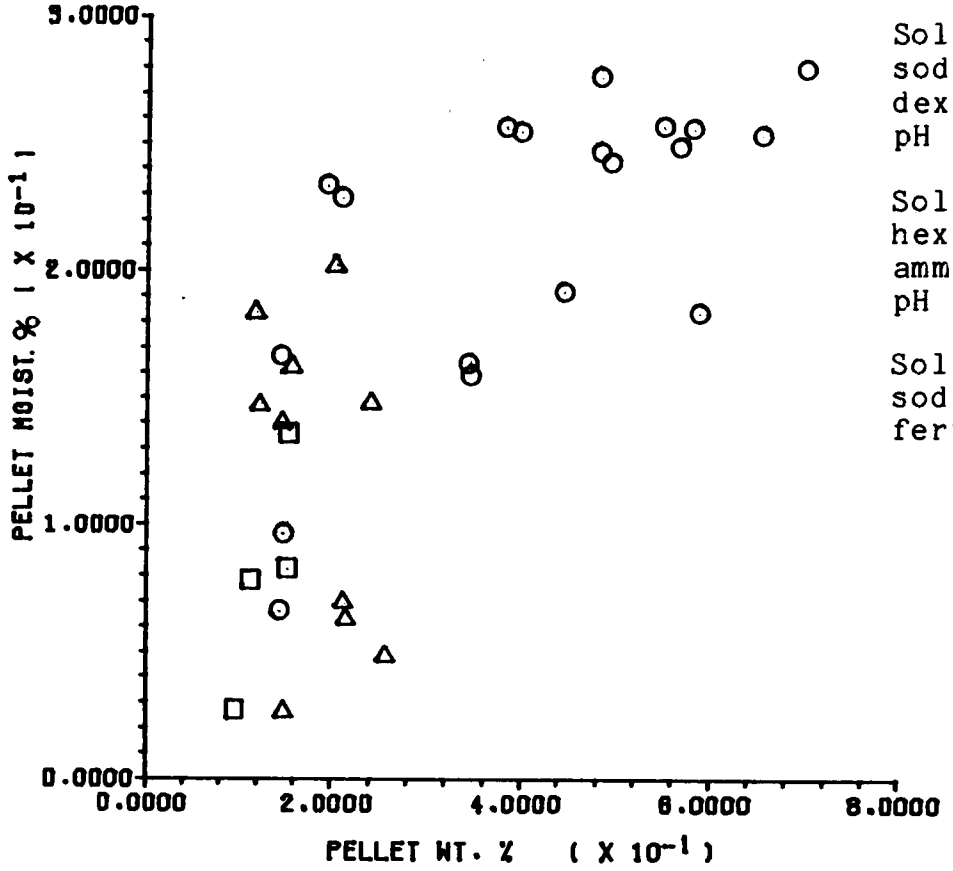


Figure VII-3. Pelletization of Coal Using Aqueous Solution 4A: Effect of Pellet Moisture on Fraction of Pellets Produced



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1C:
sodium palmitate 0.055g/l
dextrin 2.0g/l
pH 5.95

Solution 3B:
hexadecyl trimethyl-
ammonium bromide 10.1g/l
pH 6.07

Soluion 4A:
sodium dodecyl sulfate 0.3116 g/l
ferric sulfate 0.3026 g/l pH 5.99

Figure VII-4. Pelletization of Coal Using Aqueous Solutions 1C, 3B, 4A: Effect of Pellet Moisture on Fraction of Pellets Produced

to consistently make agglomeration runs producing approximately 15 weight percent pellets for all of the spray solutions used.

2. Selectivity

For my experimentation, I want to define the term "selectivity" as the tendency of the pyrites and other minerals to agglomerate together in the pellet fraction of the treated samples. Two numbers calculated for each agglomeration experiment are FR3 and FR4, defined in equations (2) and (3) below. The FR3 number is an indication of the increase in the percent sulfur of the pellet fraction compared to that of the untreated coal sample due to the selective agglomeration of the sample's pyrites and other minerals in the pellet fraction. The FR4 number is an indication of the decrease in the percent sulfur of the cake fraction compared to that of the untreated coal sample due to the same reason.

Extensive tests using spray solutions containing different surfactants at varying concentrations, different pyrite depressants, and different pHs were made in an attempt to force the coal's mineral particles, including its pyrites, to selectively agglomerate together. After each agglomeration process run, an analysis was made on the treated cake and pellet fractions to determine their respective weight percents, their respective moisture

percents, and their respective sulfur weight percents. From these data, FR3 and FR4 were calculated to indicate the distribution of the sulfur between the cake and the pellet. The 3 primary numbers calculated are:

(1) TSP=[(CSP)(CA)+(BSP)(BA)]/(CA+BA)

where:

CSP is the cake sulfur percent.

CSA is the cake amount (grams).

BSP is the pellet sulfur percent.

and BA is the pellet amount (grams)

(2) FR3=(BSP-TSP)/TSP; the normalized number indicating the transfer of the sulfur to the pellets.

(3) FR4=(CSP-TSP)/TSP; a normalized number indicating the departure of the sulfur from the cake.

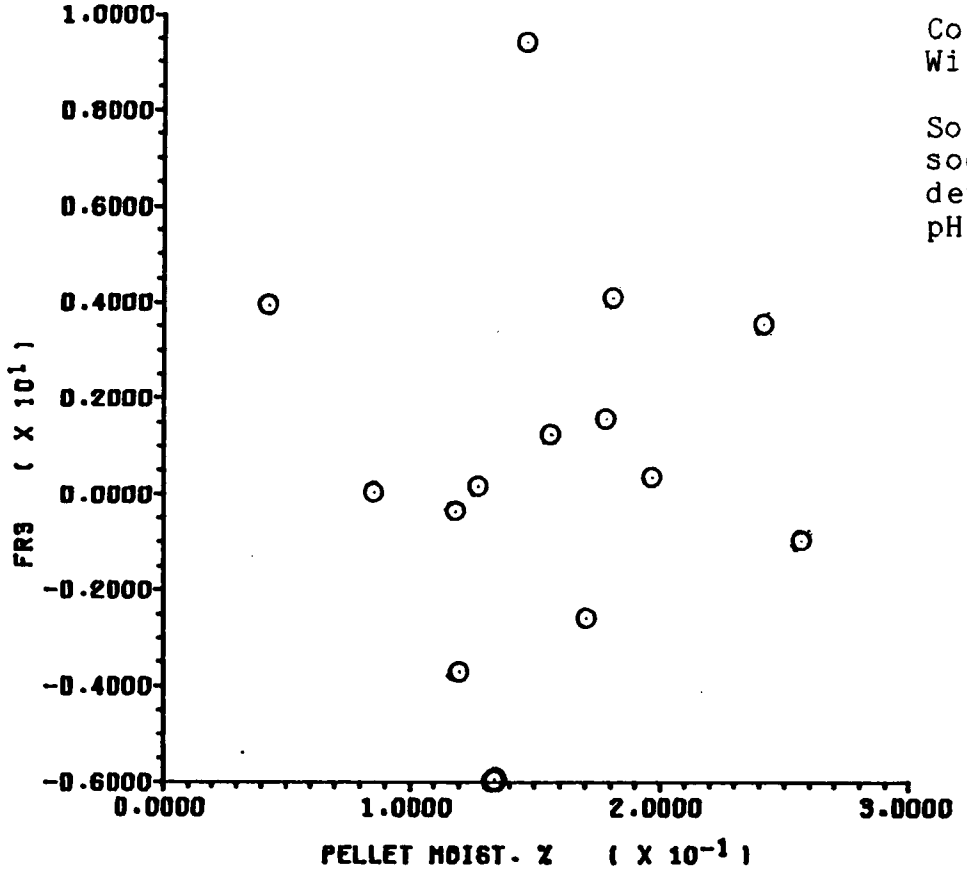
Untreated samples of the coal used were sent to the DOE's Pittsburg Mining Technology Center for analysis. Their results on a moisture free basis indicate the ash content to be approximately 12.0 percent, the pyritic sulfur content to be approximately 1.155 percent, the sulfate sulfur content to be approximately 0.79 percent, and the organic sulfur content to be approximately 0.855 percent. From these numbers one can calculate values of FR3 and FR4 corresponding to a perfect selective agglomeration run, one where all of the ash and none of the organics agglomerated together in the pellets. These theoretical values are: FR3= +4.79; FR4=-0.65.

Spray Solutions of Sodium Palmitate and Dextrin

Three spray solutions, each containing sodium palmitate at a saturated concentration and dextrin at different concentrations, were tested. All three had a pH of approximately 6.00; therefore, any differences in the results of the selective agglomeration process were due to the differing dextrin concentrations.

Solution 1A contained 0.055 g/l of sodium palmitate, a saturated solution. Figures VII-5 through VII-8 and A-1, Appendix, show the results of the experiments using this spray solution. Figure VII-6 shows a decrease in FR3 as the pellet weight percent is increased. Although there is considerable scatter in the data, the selectivity parameter, FR3, shows a value of approximately 0.04 at a pellet weight percent of 10 percent. Figure VII-8 seems to show the reverse behavior of Figure VII-6 as would be expected. There is an increase in FR4 as the pellet weight percent is increased (as the cake weight percent is decreased). Figures VII-5 and VII-7 which show the relationships between FR3 and pellet moisture percent and FR4 and cake moisture percent appear to show no trends. In addition, the average values of FR3 and FR4, 0.0077 and 0.0000 respectively, are not considered to be significant.

Solution 1B contained 0.055 g/l of sodium palmitate, 1.5 g/l of dextrin, and had a pH of 6.10. Figures VII-9 through VII-11 and A-2 and A-3, Appendix, show the results



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1A:
sodium palmitate 0.055g/l
dextrin 1.0g/l
pH 6.03

Figure VII-5. Pellet Selectivity vs. Pellet Moisture % for Solution 1A

Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1A:
sodium palmitate 0.055g/l
dextrin 1.0g/l
pH 6.03

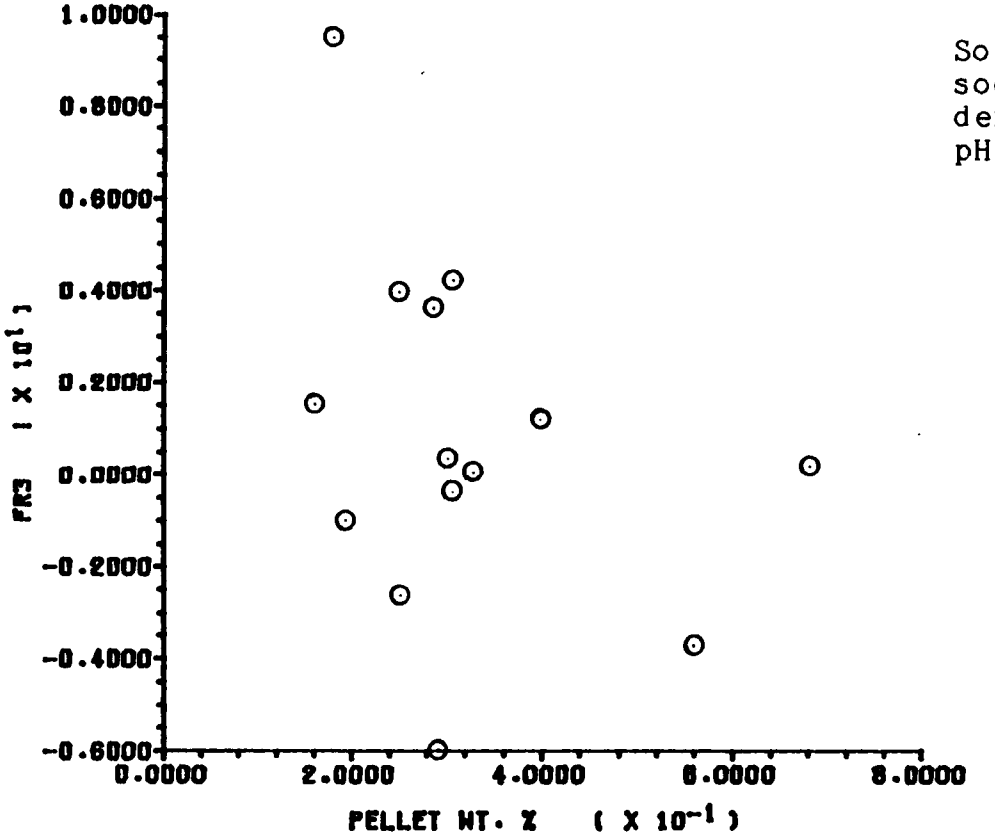
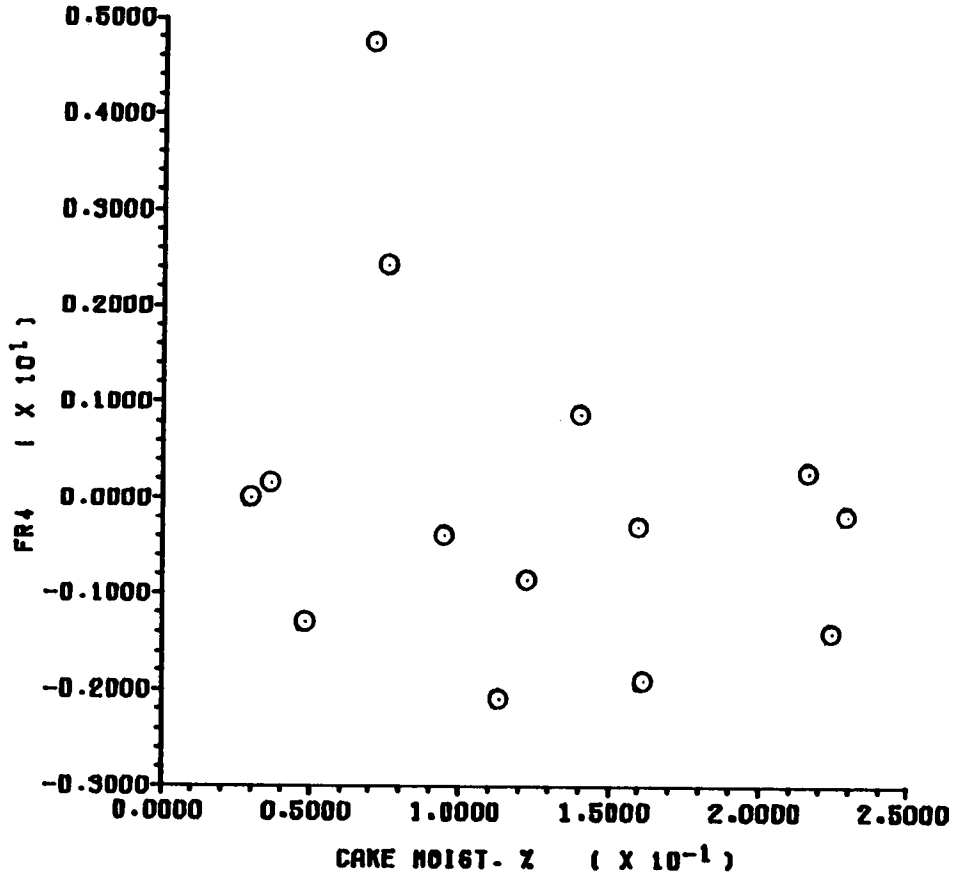


Figure VII-6. Pellet Selectivity vs. Pellet Weight % for Solution 1A



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1A:
sodium palmitate 0.055g/l
dextrin 1.0g/l
pH 6.03

Figure VII-7. Cake Selectivity vs. Cake Moisture % for Solution 1A

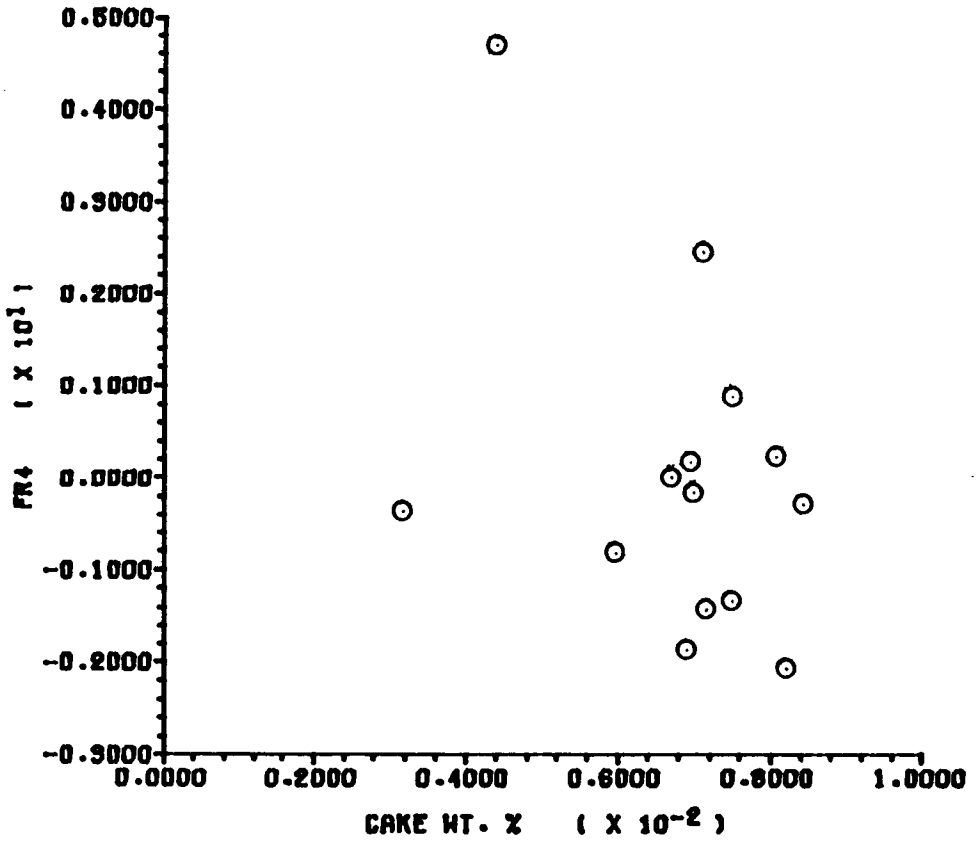


Figure VII-8. Cake Selectivity vs. Cake Weight % for Solution 1A

Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1B:
sodium palmitate 0.055g/l
dextrin 1.5g/l
pH 6.10

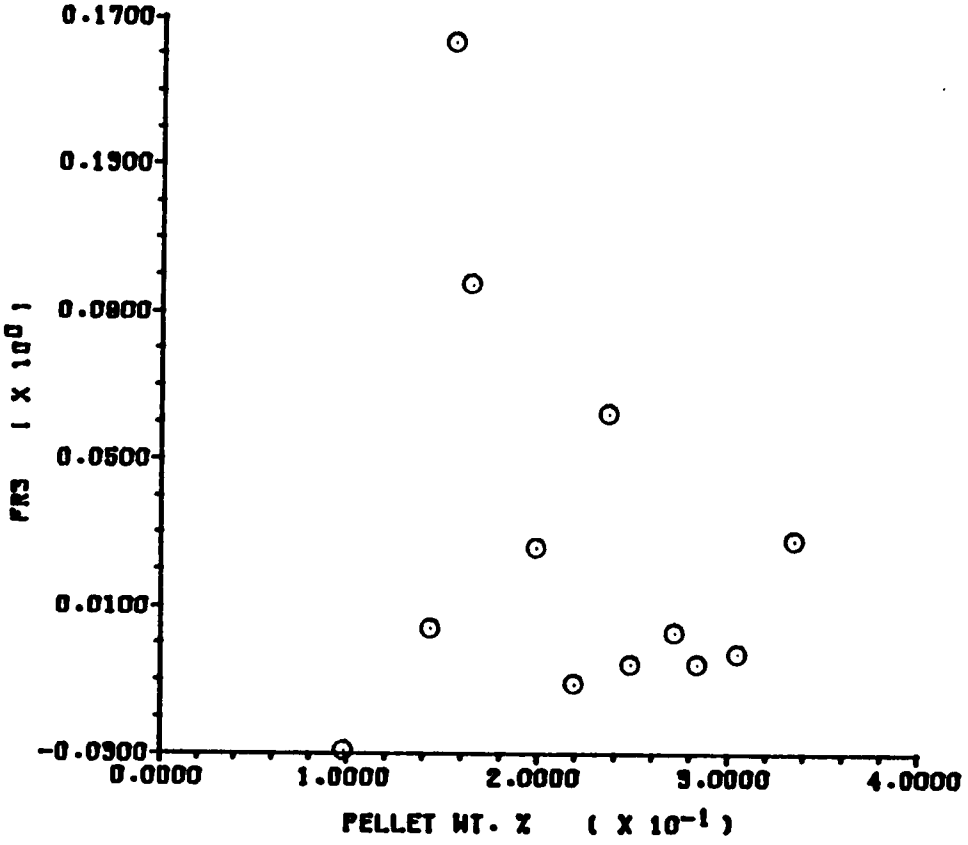
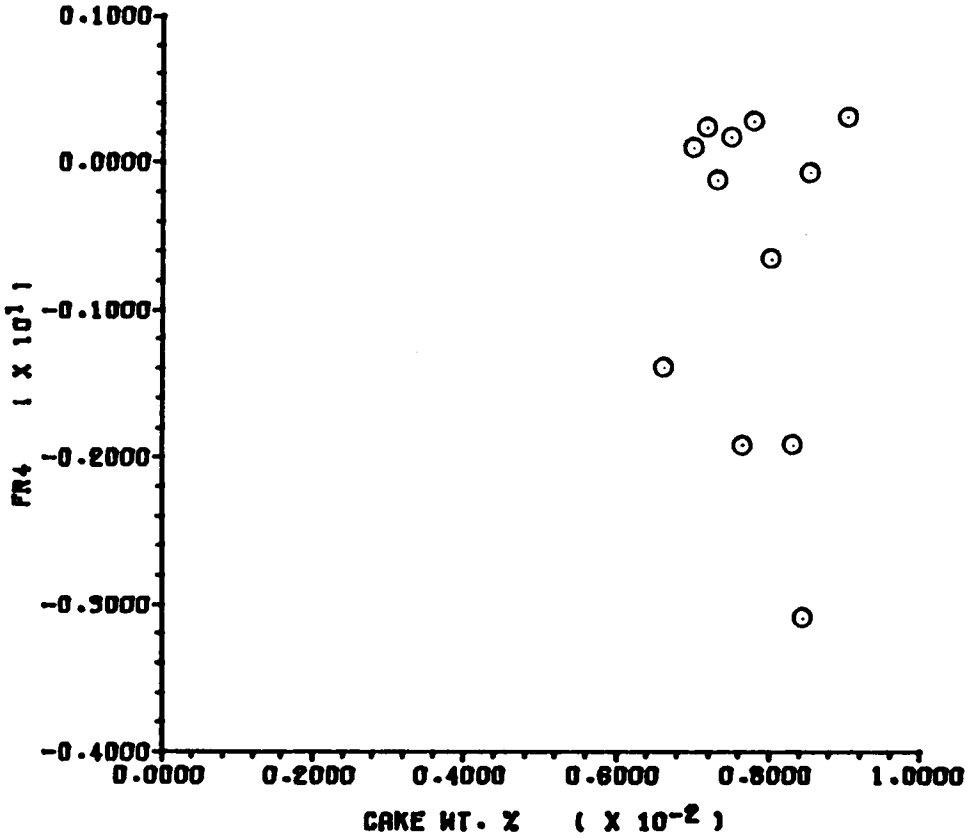


Figure VII-9. Pellet Selectivity vs. Pellet Weight % for Solution 1B

of experiments using these solutions. Figure A-2, Appendix, indicates a trend where the value of FR3 increases as the pellet moisture percent increases up to approximately 13 percent. Since we want to maximize FR3 and minimize FR4 and since the moisture percents of the pellet and cake fractions are approximately equal, the results of Figure VII-7, page 100, and A-2, Appendix, lead me to conclude that there is a maximum value of moisture percent for sulfur reduction through agglomeration. Later tests seem to support this contention. In addition, in this case the values of FR3 are predominately positive (as needed for sulfur reduction by pellet removal) with an average value of FR3 of +0.0279, and the values of FR4 are predominately negative with an average value of -0.0067.

Solution 1C contained 0.055 g/l of sodium palmitate, 2.0 g/l of dextrin, and had a pH of 5.95. The results of experiments using this solution are shown in Figures VII-1, page 91, VII-12 through VII-14, and A-4, Appendix. In this case the values of FR4 are more negative (as desired) than in the case of Solution 1B with an average value of -0.0246. The average value of FR3 is +0.0212, comparable to that of the case of Solution 1B. Figure VII-12 , like Figure VII-7, page 100, indicates a trend where the value of FR4 decreases as the cake moisture percent increases up to approximately 30%. Figure VII-13 shows no particular trend unless it is masked by the scatter, but the selectivity indicated by FR3



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1B:
sodium palmitate 0.055g/l
dextrin 1.5g/l
pH 6.10

Figure VII-10. Cake Selectivity vs. Cake Weight % for Solution 1B

Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1B:
sodium palmitate 0.055g/l
dextrin 1.5g/l
pH 6.10

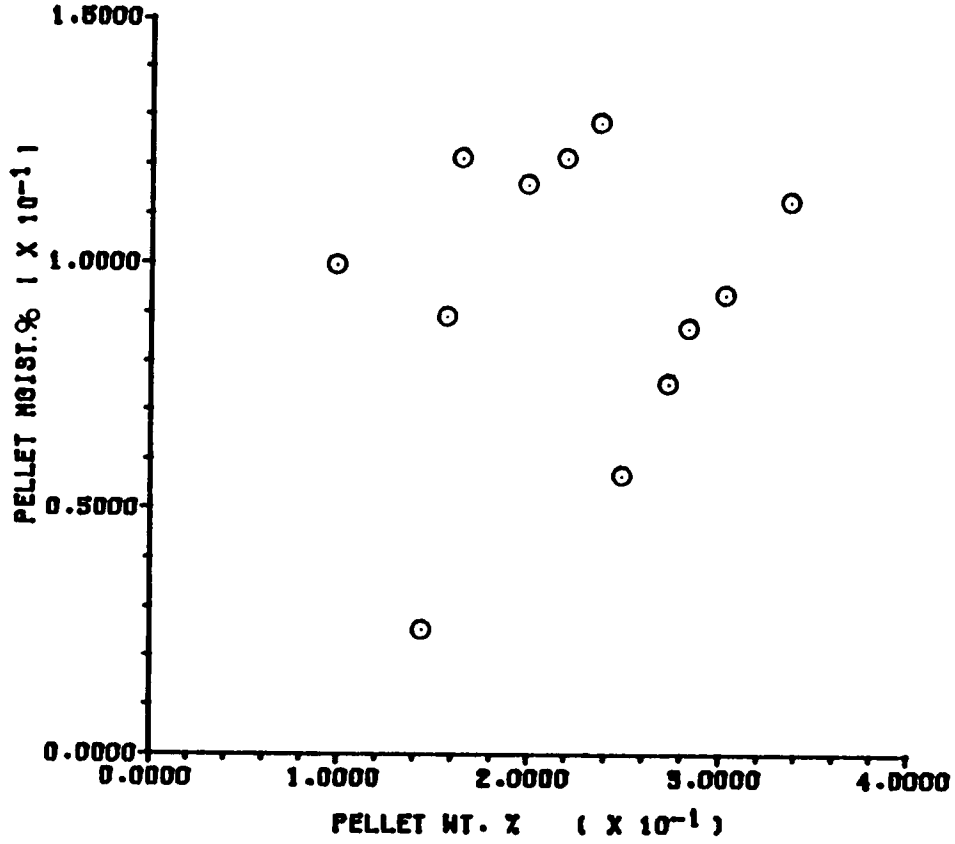
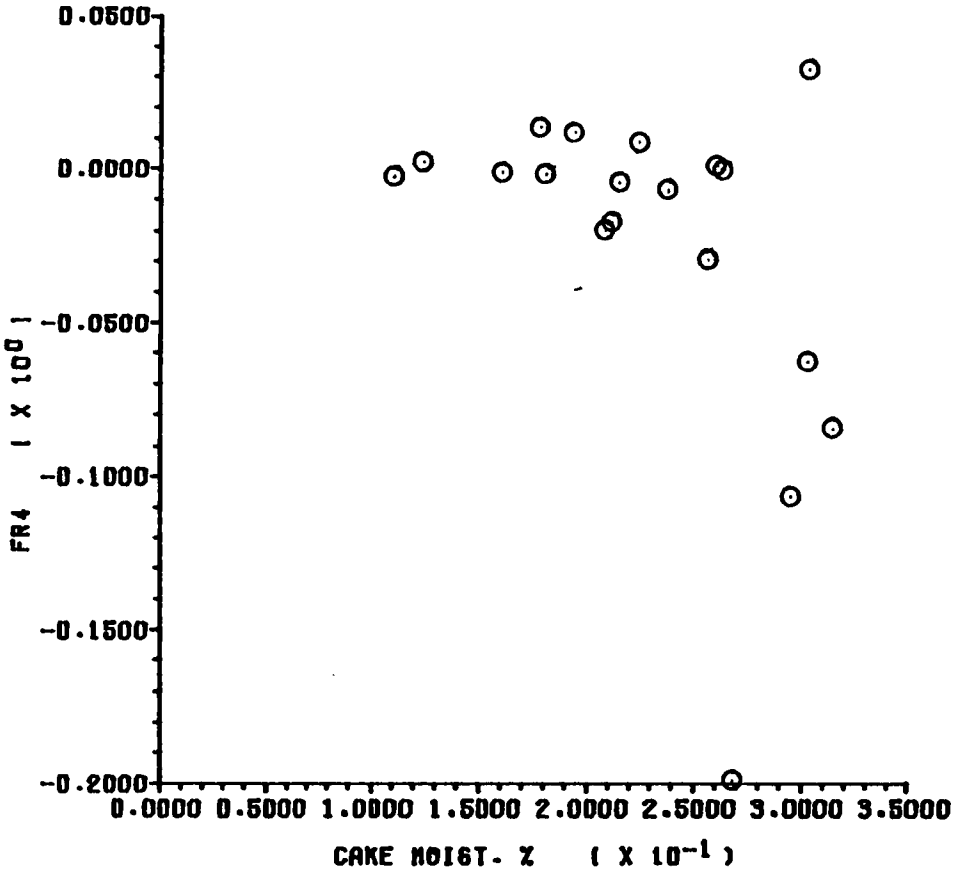


Figure VII-11. Pelletization of Coal Particles Using Aqueous Solution 1B: Effect of Pellet Moisture on Fraction of Pellets Produced



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1C:
sodium palmitate 0.055g/l
dextrin 2.0g/l
pH 5.95

Figure VII-12. Cake Selectivity vs. Cake Moisture % for Solution 1C

Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1C:
sodium palmitate 0.055g/l
dextrin 2.0g/l
pH 5.95

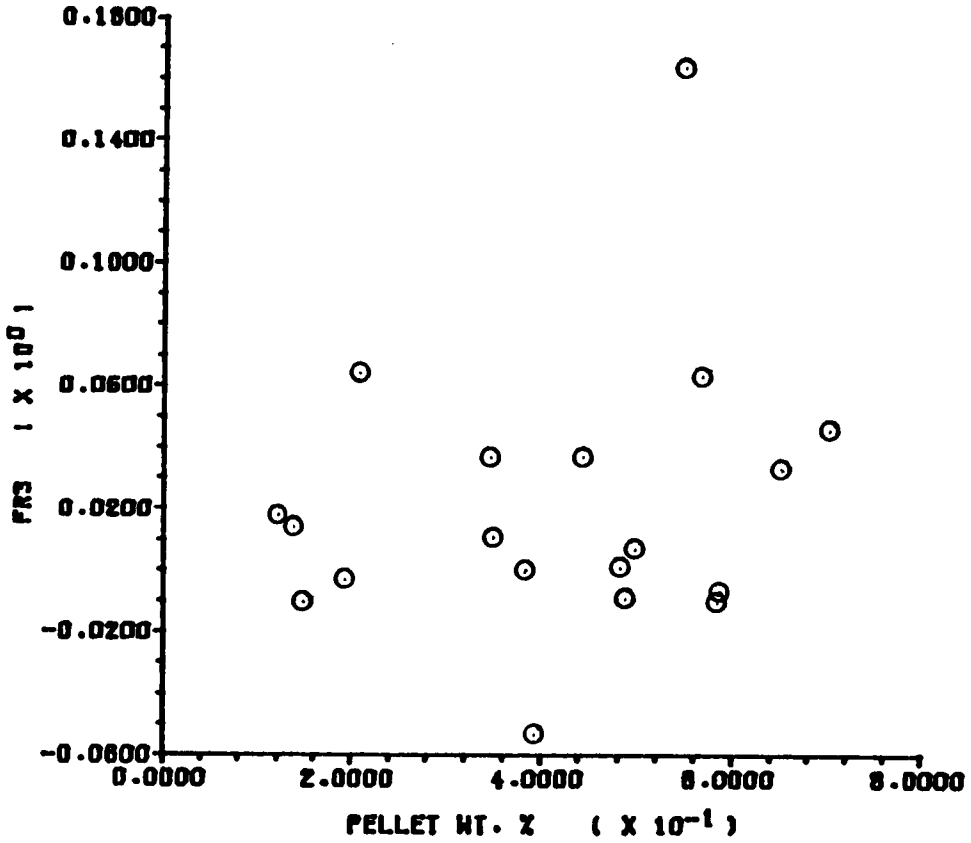
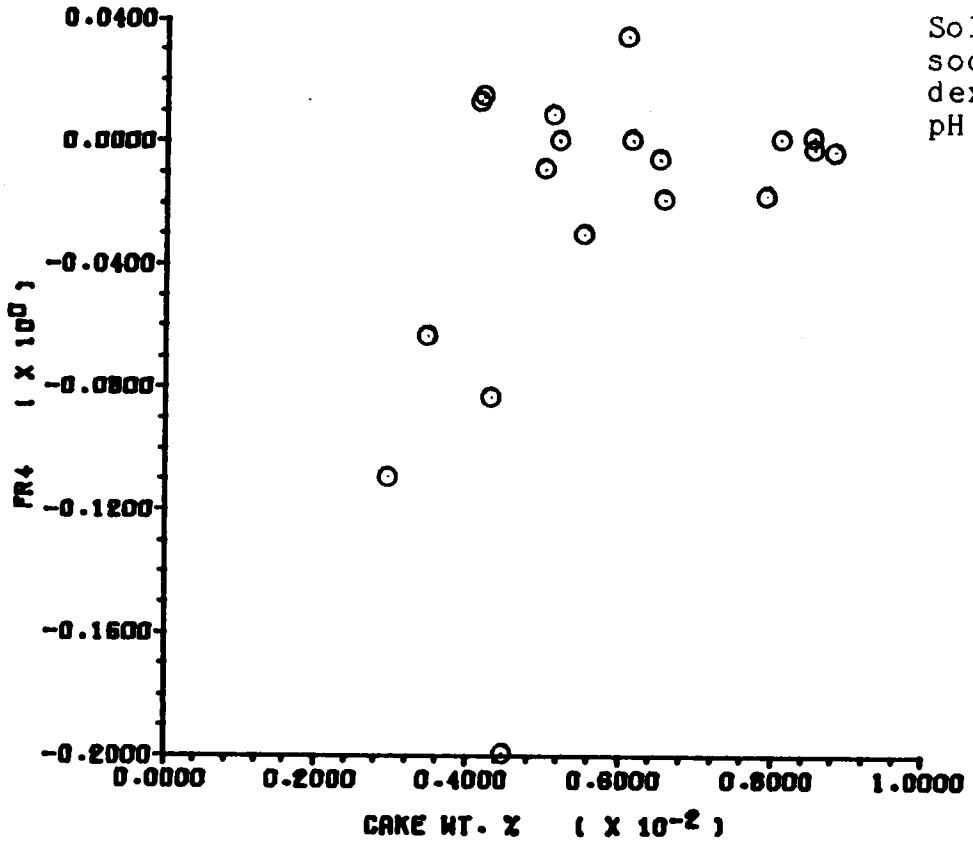


Figure VII-13. Pellet Selectivity vs. Pellet Weight % for Solution 1C



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1C:
sodium palmitate 0.055g/l
dextrin 2.0g/l
pH 5.95

Figure VII-14. Cake Selectivity vs. Cake Weight % for Solution 1C

appears to be greater. Figure VII-14, page 108, shows the trend of an increase in FR4 with increasing cake weight percent.

In these three cases each solution's pH and sodium palmitate concentration were approximately equal, while their dextrin concentrations differed. By varying only the dextrin concentration, I was able to isolate any change in the effects produced by the change in the dextrin concentration. Although the results show an increase in the sulfur percent of the pellets and a decrease in the sulfur percent of the cake, it is such a small amount that any decrease in the coal's weight percent sulfur caused by the removal of the pellets is insignificant in the range of the parameters investigated. See Table VII-2.

Sodium palmitate is a member of the group of surfactants that are classified as sodium and potassium salts of straight chain fatty acids (Rosen, M.J., 1978). Upon dissolution in water, it ionizes to form a positive sodium ion and a negative straight chain carboxylate ion. The straight chain hydrocarbon group, containing a carboxylate ion end group, is the surface active portion of the surfactant molocule. As a group, these surfactants are classified as anionic, containing a negatively charged surface active ion. They also have the common property of being too soluble in an aqueous medium for surface activity if below 10 carbons and too insoluble in an aqueous medium

TABLE VII-2

SELECTIVITY RESULTS OF EXPERIMENTS USING SPRAY SOLUTIONS OF SODIUM PALMITATE AND DEXTRIN

Spray Solution No.	Dextrin Concentration (g/l)	Average FR3	Average FR4
1A	1.0	+0.0077	+0.0000
1B	1.5	+0.0279	-0.0067
1C	2.0	+0.0212	-0.0246

for surface activity if above 20 carbons. In this case there are 16 carbons, but it is still only slightly soluble in water (0.055 g/l for saturation). This leads to a small amount of these ions being in the spray solution, and when one considers their anionic character, it is unlikely that enough of them would selectively adsorb to the carbonaceous coal particles' surface, usually classified as having anionic sites, to deter any wetting by the solution.

These results indicate the effect of varying the solution's dextrin concentration while keeping the solution's pH and sodium palmitate concentration constant; also, and I think for the reasons above, they indicate that the ability of this surfactant in combination with the dextrin to cause the the selective adsorption of the solution by the mineral particles is too small for any significant sulfur reduction of the coal through pelletization.

Spray Solution of Dextrin

Results indicated sodium palmitate as an ineffective or inappropriate surface active agent to render the coal's organic portion more hydrophobic. They also indicated an increased selectivity of pelletization as the dextrin concentration was increased. To check if the presence of the sodium palmitate was hindering the selectivity , I decided to test the effect of using a spray solution containing only dextrin dissolved in water during an

agglomeration run.

Solution 2A contained 2.0 g/l of dextrin dissolved in water and had a pH of 6.11. Again, the possible trend of a decrease of the FR4 value with an increasing cake moisture percent up to approximately 27 percent is indicated in Figure A-5, Appendix. The average values of FR3 and FR4, +0.00488 and -0.0012 respectively, are comparable to, but no more encouraging than those obtained from tests using a solution of sodium palmitate and dextrin. Again, none of the tests show significant reduction of the coal's sulfur content by the removal of the produced pellets.

Spray Solution of Hexadecyl Trimethyl Ammonium Bromide (HTAB)

Upon its dissolution in water, HTAB ionizes to form a negatively charged bromide ion and a positively charged amine ion. Its surface active portion contains 16 straight chain carbons and a positively charged tri-methyl amine end group. This positively charged end group classifies it as a cationic surfactant, one that I thought would be more likely to adsorb to the carbonaceous coal's anionic sites. In addition, HTAB was discovered to be very soluble in water, allowing sufficient quantities of it to be in the solution to allow surface activity effects. To me, these properties gave it good potential to render the carbonaceous particles more hydrophobic; the positive charge would adsorb at the surface and the hydrophobic end would orient itself toward

the solution.

Three spray solutions, each containing a different concentration of HTAB, but each having approximately the same pH, were tested to isolate the effect of the HTAB. Solution 3B contained 10.1 g/l of HTAB dissolved in water and had a pH of 6.07. Ten agglomeration tests were made in an attempt to find the optimum conditions for selective agglomeration. Figure A-6, Appendix, shows the possible trend of an decrease in FR3 with an increase in pellet moisture percent and Figure A-7, Appendix, shows the possible trend of an increase in FR4 with an increase in the cake moisture percent. However, for this solution the average values of FR3 and FR4, -0.0034 and +0.0016 respectively, are the reverse in sign of the results obtained with sodium palmitate and dextrin solutions. Since ten agglomeration runs were made, I think these numbers are representative.

After using this spray, I decided to make spot checks with the HTAB concentration above and below the 10.1 g/l in an attempt to pinpoint any possible effect due to a change in concentration. Solution 3A contained 5.03 g/l of HTAB dissolved in water and had a pH of 6.09. In this case the values of FR3 and FR4, +0.0068 and -0.0031 respectively, had the desired signs but were too small to be significant. Figures A-8 through A-12, Appendix, show the results.

Solution 3C contained 20.4 g/l of HTAB dissolved in

water and had a pH of 6.11. In this case the average values of FR3 and FR4, +0.0035 and -0.0011 respectively, are again too small to be significant. Since concentration at half and double that of 10.1 g/l showed no significant results, I decided to try different solutions. Table VII-3 gives a summary of these results.

Spray Solution of Sodium Dodecyl Sulfate and Ferric Sulfate

In my search for a surfactant to effectively and selectively enhance the hydrophobic nature of the coal's carbonaceous portion, I spent a good deal of time researching the froth flotation industry. Sodium dodecyl sulfate is one of the surfactants and ferric sulfate is one of the depressants used extensively in the froth flotation industry. Because the desired effects of these chemicals on the coal particles in froth flotation are the same effects that I want in my process, I decided to try them.

Sodium dodecyl sulfate is also a member of the group of surfactants classified as long chain fatty acids of sodium or potassium salts. Upon dissolution in water, it produces a positive sodium ion and a negative sulfate ion on the end of a 12 carbon chain. It is classified as anionic, containing a negatively charged polar end (sulfate) and a non-polar hydrophobic end. Although it is in the same group as sodium palmitate, it is much more soluble and for this reason I thought that it would be a much more effective surfactant.

TABLE VII-3

SELECTIVITY RESULTS OF EXPERIMENTS USING SPRAY SOLUTIONS OF HEXADECYL TRIMETHYL AMMONIUM BROMIDE (HTAB)

Spray Solution No.	HTAB Concentration (g/l)	Average FR3	Average FR4
3A	5.03	-0.0034	+0.0016
3B	10.10	+0.0068	-0.0031
3C	20.40	+0.0035	-0.0011

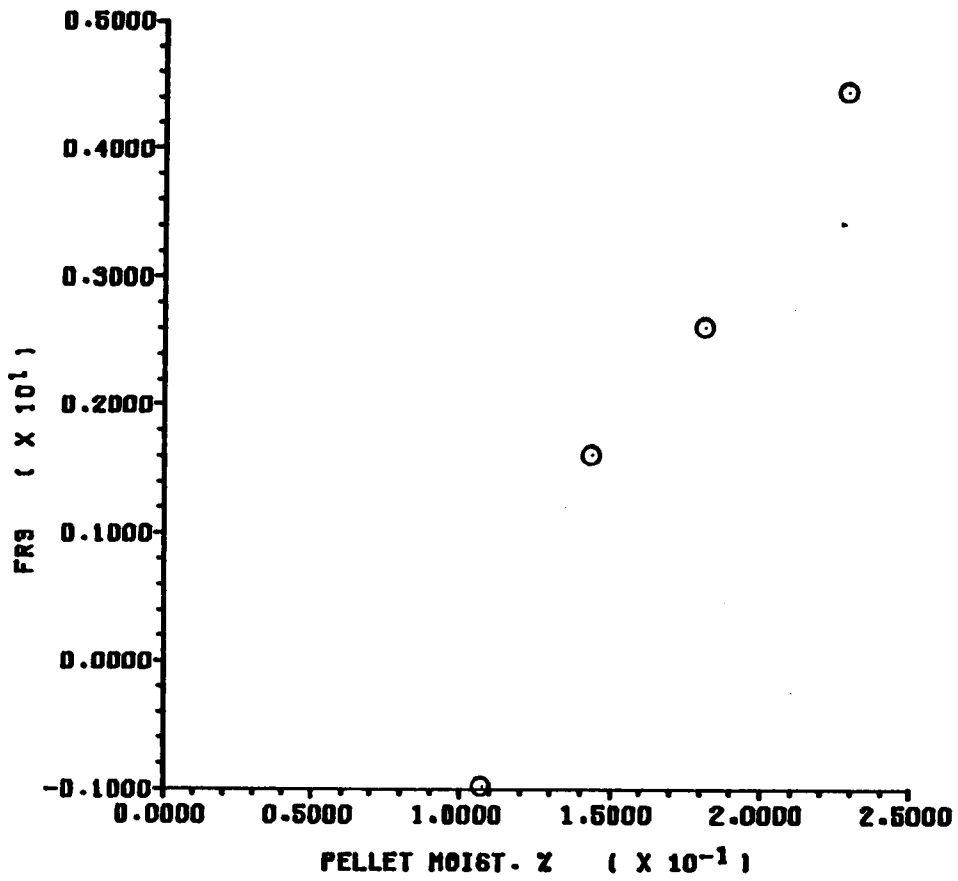
Six solutions (4A,4B,4C,4D,4E, and 4F) were made up, each with sodium dodecyl sulfate at 0.3116 g/l, and each saturated with ferric sulfate at 0.15 g/l. Solution 4A had a pH of 5.99, and after analyzing the agglomeration runs using it, I decided to vary the pHs while keeping the concentrations of sodium dodecyl sulfate and ferric sulfate constant.

Solution 4B had a pH of 2.85. In these cases, again, I was spot checking, looking for any significant results or trends. Figure VII-15 shows an increase in FR3 as the pellet moisture percent increases, while in conjunction, Figure VII-16 shows a decrease in FR4 as the cake moisture percent increases. This trend has been present in previous tests. The average values of FR3 and FR4, +0.0195 and -0.0085 respectively, are again insignificant. Table VII-4 gives the results for all six of these solutions.

From this table, it is apparent that although the value of FR3 increases with decreasing pH, the values are still rather insignificant. There must be a much larger difference in the FR3 and FR4 values in order for any significant amount of sulfur reduction to result from the removal of the pellets. I think that the trends of increasing FR3 and decreasing FR4 with decreasing pH is definite and significant. See Figures VII-17 and VII-18.

Spray Solution of Sodium Dodecyl Sulfate and Ferric Chloride

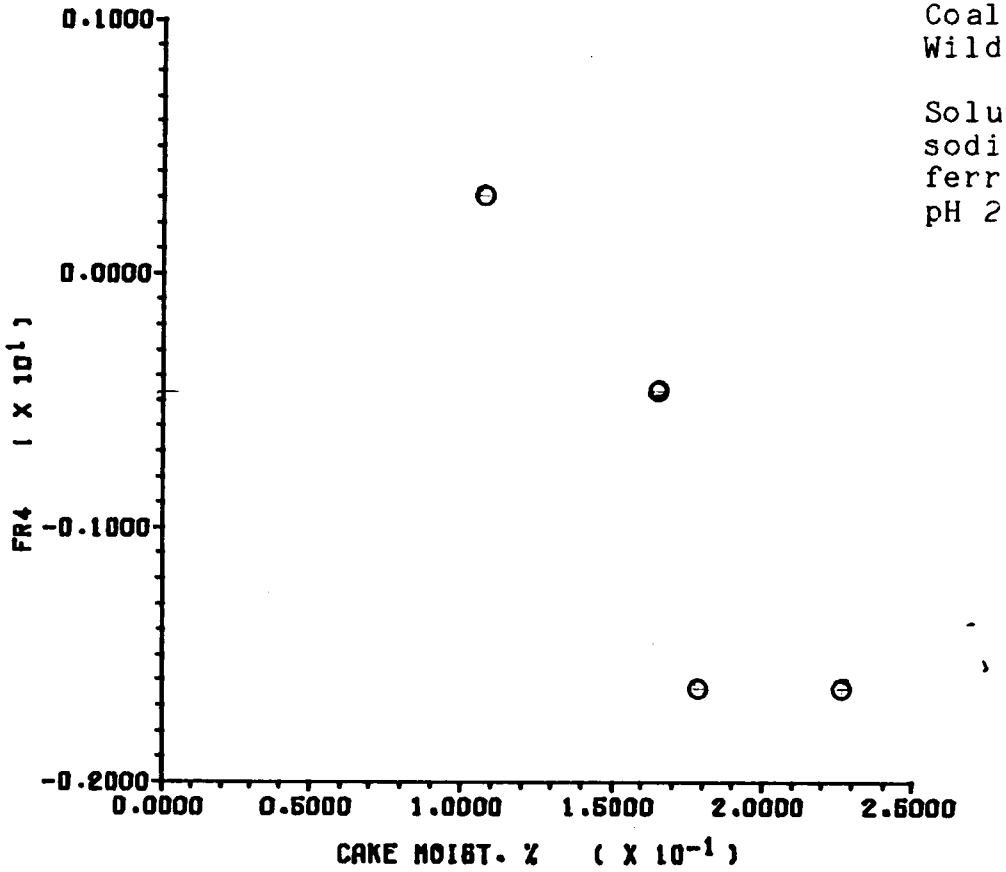
Another pyrite depressant that is commonly referenced



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 4B:
sodium dodecyl sulfate 0.3116g/l
ferric sulfate 0.150g/l
pH 2.85

Figure VII-15. Pellet Selectivity vs. Pellet Moisture % for Solution 4B



Coal Particles:
Wilder Seam, -80 to +170 mesh

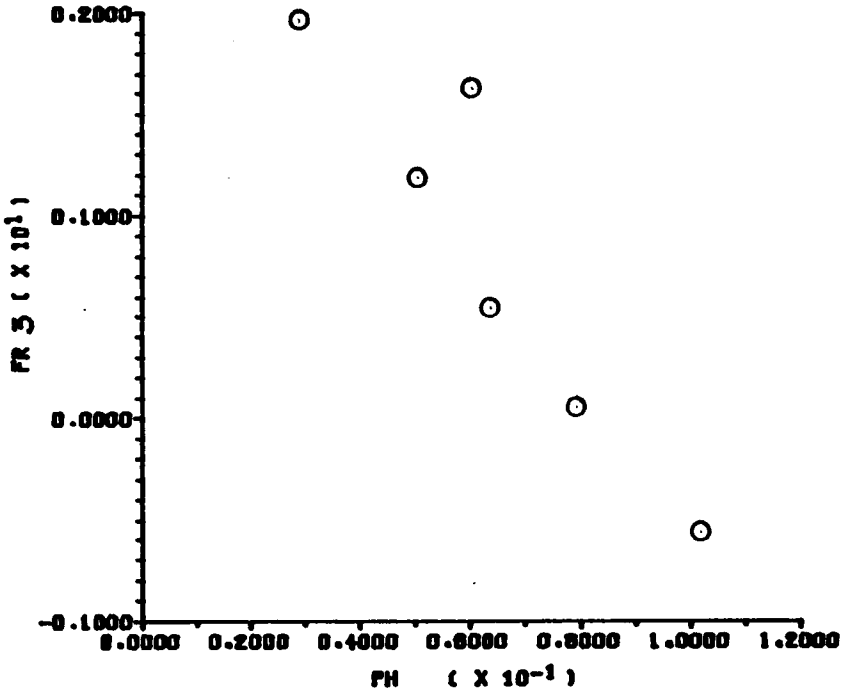
Solution 4B:
sodium dodecyl sulfate 0.3116g/l
ferric sulfate 0.150g/l
pH 2.85

Figure VII-16. Cake Selectivity vs. Cake Moisture % for Solution 4B

TABLE VII-4

SELECTIVITY RESULTS OF EXPERIMENTS USING SPRAY SOLUTIONS OF SODIUM DODECYL SULFATE AND FERRIC SULFATE

Spray Solution No.	pH	Average FR3	Average FR4
4B	2.85	+0.0195	-0.0085
4E	5.05	+0.0117	-0.0036
4A	5.99	+0.0162	-0.0028
4F	6.35	+0.0054	-0.0011
4D	8.05	+0.0001	-0.0022
4C	10.10	-0.0057	+0.0016

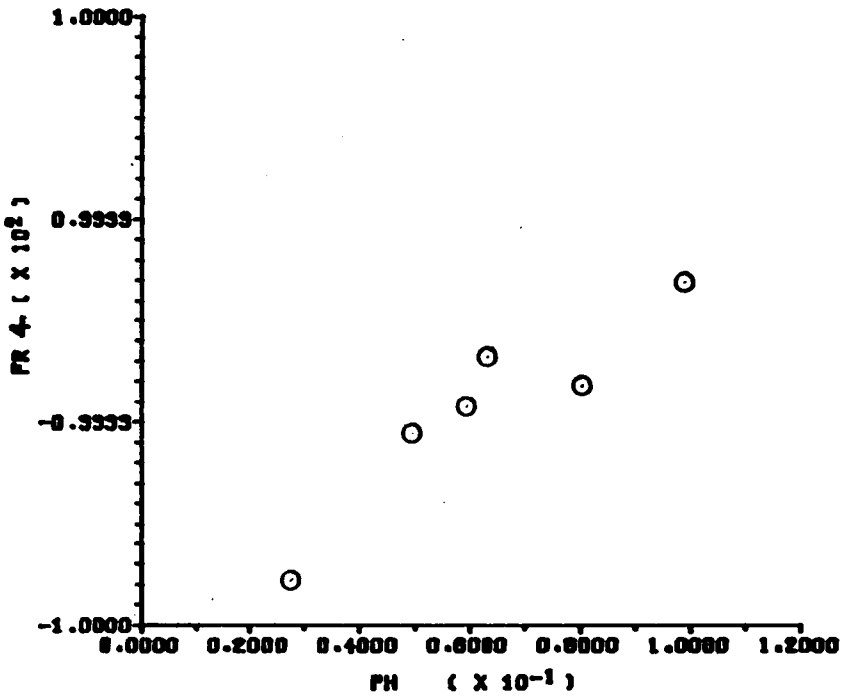


Coal Particles:
Wilder Seam, -80 to +170 mesh

All solutions contain:
sodium dodecyl sulfate 0.3116g/l
ferric sulfate 0.15g/l

Solution pHs:
4A 5.99
4B 2.85
4C 10.10
4D 8.05
4E 5.05
4F 6.35

Figure VII-17. The Effect of Solution pH on Pellet Selectivity



Coal Particles:
Wilder Seam, -80 to +170 mesh

All solutions contain:
sodium dodecyl sulfate 0.3116g/l
ferric sulfate 0.15g/l

Solution pHs:
4A 5.99
4B 2.85
4C 10.10
4D 8.05
4E 5.05
4F 6.35

Figure VII-18. The Effect of Solution pH on Cake Selectivity

in the froth flotation literature is ferric chloride. Spot checks were made on the results of agglomeration runs using spray solutions containing 0.4674 g/l of sodium dodecyl sulfate and the saturated amount of 0.0081 g/l of ferric chloride. Solutions 5A and 5B, both containing the above amounts, were made. Table VII-5 gives the results of these tests.

Spray Solution of Ethyl Xanthic Acid, Potassium Salt

For a final attempt at isolating a solution that effectively causes the coal's mineral particles to agglomerate together, I decided to use another surfactant that is used in the froth flotation industry. Solution 6A and 6B each contained 0.5 g/l of ethyl xanthic acid, potassium salt and 0.0081 g/l of ferric chloride. The solution's pHs were adjusted to 4.82 and 6.95. Then pelletization runs were made to divide the coal particles into a pellet and cake fraction.

Analyses of the cake and pellet fractions obtained from spraying with Solution 6A, pH of 4.82, gave average values for FR3 and FR4 of -0.0042 and +0.0018 respectively. The analyses for Solution 6B, pH of 6.95, resulted in the average values for FR3 and FR4 being +0.0017 and -0.0009 respectively. Again, the results are insignificant; the removal of the pellets resulted in little sulfur reduction in the cake. Table VII-6 gives the results of these tests.

TABLE VII-5

SELECTIVITY RESULTS OF EXPERIMENTS USING SPRAY SOLUTIONS OF SODIUM DODECLY SULFATE AND FERRIC CHLORIDE

Spray Solution No.	pH	Average FR3	Average FR4
5A	3.83	+0.0031	-0.0010
5B	9.16	+0.0117	-0.0021

TABLE VII-6

SELECTIVITY RESULTS OF EXPERIMENTS USING SPRAY SOLUTIONS OF ETHYL XANTHIC ACID, POTASSIUM SALT AND FERRIC CHLORIDE

Spray Solution No.	pH	Average FR3	Average FR4
6A	4.82	-0.0042	+0.0018
6B	6.95	+0.0017	-0.0009

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

1. Pelletization

The critical moisture range required to produce good quality pellets from tumbling Wilder Seam coal particles in the -80, +170 mesh size range is approximately 5 to 30 percent. Once the coal particles' moisture percent is in this range the time of tumbling has the greatest effect upon the weight percent pellets produced. It is difficult to obtain very small amounts of pellets (less than or equal to 5 weight percent) because once the critical moisture content is reached the amount of pellet seeds initiated is greater than 5 weight percent. In the moisture percent range of 5 to 20 percent, the nuclei growth region, the pellet weight percent is insensitive to the pellet moisture percent. In the moisture range of 20 to 30 percent, the ball growth region, the weight percent of the pellets produced depends almost exclusively upon the tumbling time. Greater than 30 moisture percent produces plastic, easily deformable pellets. The coal particles' moisture content, the tumbling process, and the time of tumbling, regardless of the solution's composition or pH, affect the formation and quantity of good quality pellets (agglomeration).

2. Selectivity

Selectivity numbers, FR3 and FR4, were calculated to indicate the amount of transfer of the inorganic sulfur to the pellets and the amount of transfer of the inorganic sulfur from the cake. The effect of the solution's composition and pH on the partitioning of the inorganic sulfur was investigated. Two classes of surfactants, anionic and cationic, were used in the spray solutions. Quantitative conclusions follow.

Cationic Surfactants

Three solutions, each at different concentrations of hexadecyl trimethyl ammonium bromide, were used in selective agglomeration experiments. Numbers indicating the selectivity were either opposite in sign of the expected results or too small to be of signficance; FR3: +0.0068 vs. +4.79 (best theoretical); and FR4: -0.0031 vs. -0.65 (best theoretical). This leads me to conclude that my characterization of the organic coal particles' surface is incorrect- it is not a neutral surface with anionic sites.

Anionic Surfactants

(a) Sodium palmitate along with dextrin was used at different concentrations to make solutions. The selectivity numbers calculated were consistently of the expected sign. However, when compared to the maximum theoretical numbers they are insignificant for each of the solutions tested.

for FR3, the result was +0.0077 and for FR4, the result was 0.0000.

(b) Sodium dodecyl sulfate and ferric sulfate- Same conclusions as in part (a).

(c) Sodium dodecyl sulfate and ferric chloride- Same conclusions as in part(a).

(d) Ethyl xanthic acid, potassium salt- Same conclusions as in part (a).

Qualitative conclusions are: (1) the selectivity decreases with increasing pellet weight percent and decreasing cake weight percent; (2) although no economic studies were conducted to prove this, figures of the results lead me to conclude that there is an optimum economical value of pellet weight percent for sulfur reduction and heating value retention; (3) there is a maximum value of moisture percent for selectivity; and (4) as the pH of the sodium dodecyl sulfate, ferric sulfate solution was decreased from 10.0 to 2.0, selectivity increased.

Recommendations, based upon physical problems encountered during experimentation and upon these conclusions are: (1) a device to continually scrape off any cake sticking to the rotating container's walls during an agglomeration run should be designed, constructed, and used; (2) any further investigation in this area be confined to the use of anionic surfactants at low pHs, that is, below about 6.00; (3) future experimentation should investigate

the selectivity results of the formation of small quantities, 5 to 10 weight percent, of pellets; (4) try different materials for the container. The system set up during this study was actually a solid (coal particles)-liquid (spray solution)-solid (plexiglass container). The effect of the nature of the container surface in this system could be important in affecting particle agglomeration and pyrite partition between the pellets and the cake ; (5) develop a more effective sprayer, one which more uniformly sprays the coal particles; and (6) investigate the selectivity results for zwitterionic surfactants.

LIST OF REFERENCES

LIST OF REFERENCES

Allen, Z., and Kaslow, D.A., Effects of the New Clean Air Regs., Coal Age, Vol. 84, No. 8, McGraw Hill, Inc., 1979.

Brennan, J.P., and others, "Legislative, Institutional, and Financial Factors", Coal Processing Technology, Vol. 2, American Institute of Chemical Engineers, 1977.

Capes, C.E., Smith, A.E., and Puddington, I.E., Economic Assessment of the Application of Oil Agglomeration to Coal Preparation, NRCC No. 14068.

Connor, P., and Otterwell, R.H., J. Colloid Interface Sci., 37, 642, 1971.

Davis, H., "The Changing Scene in Preparation", Coal Age, Vol. 83, No. 1, McGraw Hill, Inc., 1978.

Evans, J.M., "Alternatives to Stack-Gas Scrubbing, Coal Processing Technology", Vol. 3, American Institute of Chemical Engineers, 1977.

Firth, C.V., Proc. AIME Blast Furnace, Coke Oven and Raw Materials Conference, 4, 46-49, 1944.

Hartnett, J.P., (ed.), Alternative Energy Sources, Academic Press, 1976.

Hawley M.E., (ed.), Coal, Part II: Scientific and Technical Aspects, Dowden, Hutchinson, and Ross, Inc., 1976.

Hibbard, W.R., Jr., "Policies and Constraints for Major Expansion of U.S. Coal Production and Utilization", Annual Review of Energy, Vol. 4, Annual Review, Inc., 1979.

Kapur, P.C., and Fuersteneau, D.W., Trans. AIME, 229, 348-355, 1964.

Law, J.P., Jr., and Kunze, G.W., Soil Science Society Am. Proc., 30, 321, 1966.

Lynn, D.A., Air Pollution- Threat and Response, Addison-Wesley Publishing Co., Inc., 1976.

McCaffery, F.G., and Mungan, N., J. Can. Petrol. Technol., 9, 185, 1970.

McCartney, J.T., O'Donnell, H.J., and Ergun, S., "Pyrite Distribution and Coal-Pyrite Particle Association in Steam Coals", U.S. Department of the Interior, Bureau of Mines, Report of Investigations No. 7231, 1969.

Myers, R.A., Coal Desulfurization, Marcel Dekker, Inc., 1977.

Newitt, D.M., and Conway-Jones, J.M., Trans. Instit. Chem. Engrs., 36, 422-442, 1958.

Nriagu, J.O., (ed.), Sulfur in the Enviroment: Part II, Wiley, 1978.

Power and Energy Committee of the California Intersocieties Legislative Advisory Commission, The Energy Problem: A Profile for Solution with Emphasis on Alternatives for California, Institute of Electrical and Electronic Engineers, 1974.

Robb, D.J.M., and Alexander, A.E., Society of Chem. Ind., Monograph No. 25, 292, 1967.

Rosen, M.J., Surfactants and Interfacial Phenomena, John Wiley and Sons, Inc., 1978.

Ruedisili, L.C., (ed.), Perspectives on Energy: Issues, Ideas, and Enviromental Dilemmas, Oxford University Press, 1978.

Scallon, T.R., and others, "Coal Demand and Supply Projections", Coal Processing Technology, Vol. 2, American Institute of Chemical Engineers, 1977.

Scott, C.B., "Enviroment and Energy- Two Discoveries", Energy Sources, Vol. 2, No. 2, Crane, Russak, and Co., 1976.

Snyder, L.R., J. Phys. Chem., 72, 489, 1968.

Stambaugh, E.P., Miller, J.F., Tam, S.S., and Chunham, S.P., "Clean Fuels from Coal", Coal Processing Technology, Vol. 3, American Institute of Chemical Engineers, 1977.

Steinhart, Carol E., Energy, Sources, Use, and Role in Human Affairs, Wadsworth Publishing Co., 1974.

Sullivan, A.M., (assoc. ed.), Dirty Coal Burns Clean in Fluidized Bed, Coal Age, Vol. 84, No. 11, McGraw Hill, Inc., 1979.

Tamamushi, B., and Tamaki, K., 2nd Int. Congr. Surface Activity, III, 449, 1957.

Taylor, S.R., Miller, K.J., and Deurbrouck, A.W., Surface Chemical Problems in Coal Flotation, Coal Preparation Division, U.S. DOE.

U.S. Department of Energy, National Energy Plan II, 1979.

U.S. Enviromental Protection Agency, Report of the Hearing Panel: National Public Hearings on Power Plant Compliance with Sulfur Oxide Pollution Regulations, 1974.

Wakamatsu, T., and Fuersteneau, D.W., Adsorption from Aqueous Solution, American Chemical Society, pp 161-172, 1968.

Wen, C.Y., and Lee, E.S., (eds.), Coal Conversion Technology, Addison-Wesley Publishing Co., Inc., 1979.

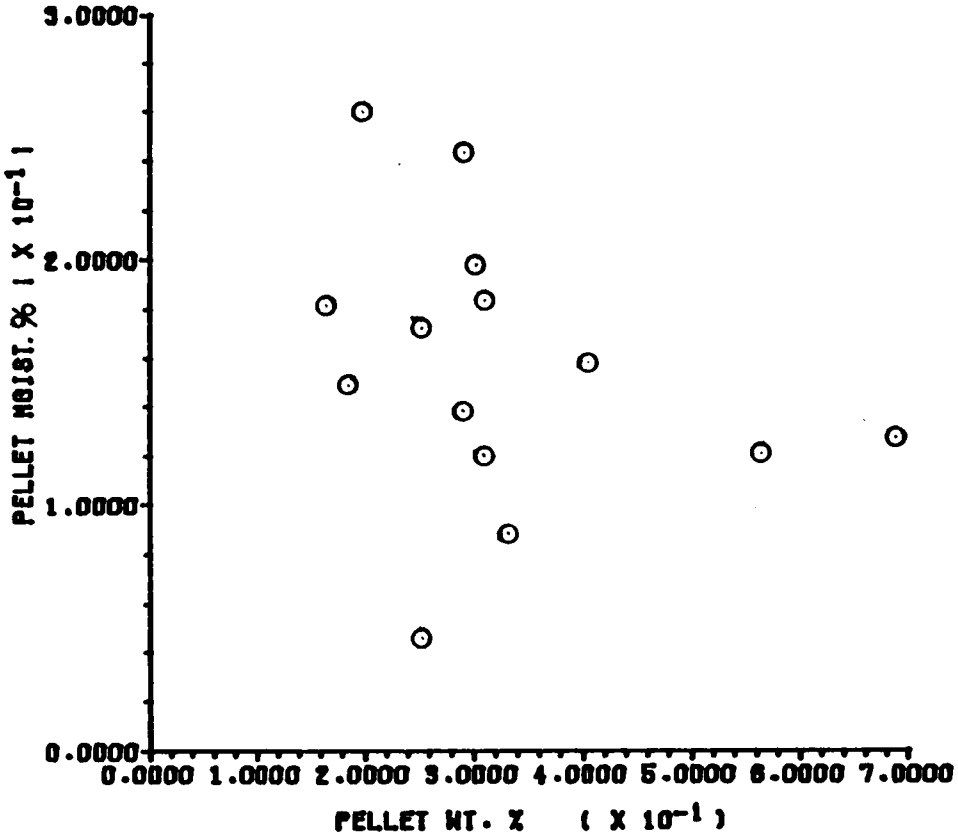
Wheelock, T.D., Coal Desulfurization, American Chemical Society, 1977.

Wheelock, T.D., "Chemical Cleaning", Coal Preparation, The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., 1977.

Wilkinson, J.F., "The 79 Outlook: Optimistic, But", Coal Age, Vol. 84, No. 2, McGraw Hill, Inc., 1979.

Wilkinson, J.F., "Will Chemicals Replace Crushing?", Coal Age, Vol. 83, No. 2, McGraw Hill, Inc., 1978.

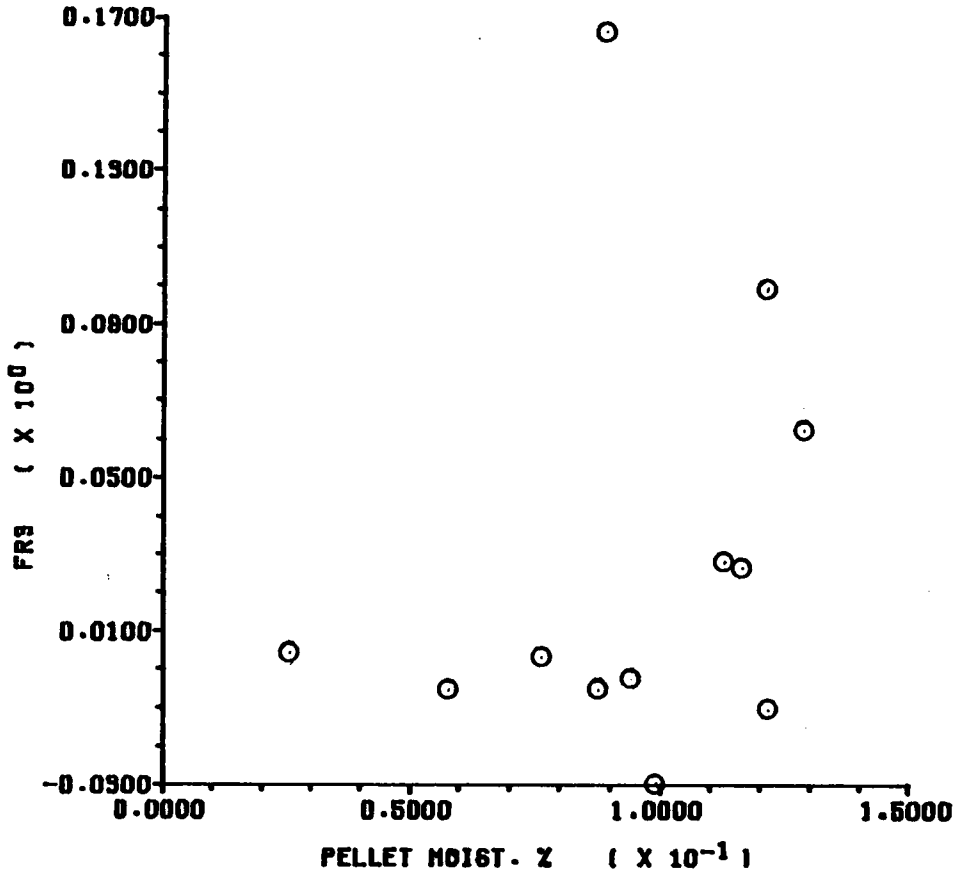
APPENDIX



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1A:
sodium palmitate 0.055g/l
dextrin 1.0g/l
pH 6.03

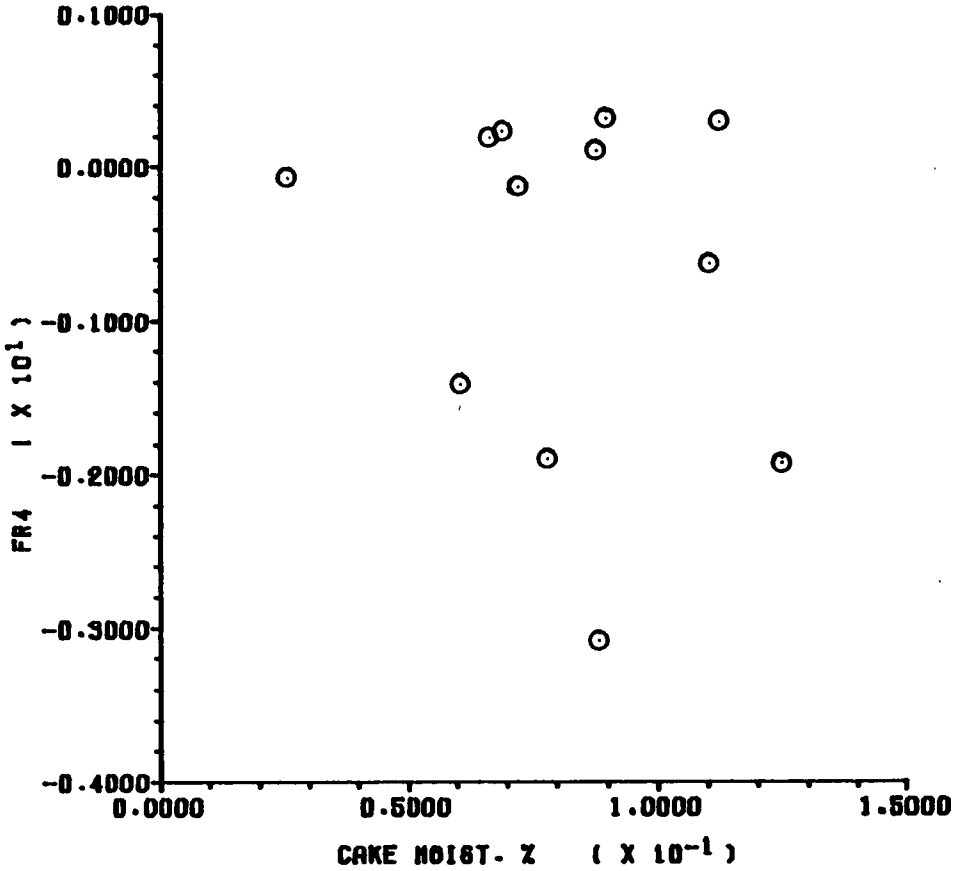
Figure A-1. Pelletization of Coal Particles Using Aqueous Solution 1A: Effect of Pellet Moisture on Fraction of Pellets Produced



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1B:
sodium palmitate 0.055g/l
dextrin 1.5g/l
pH 6.10

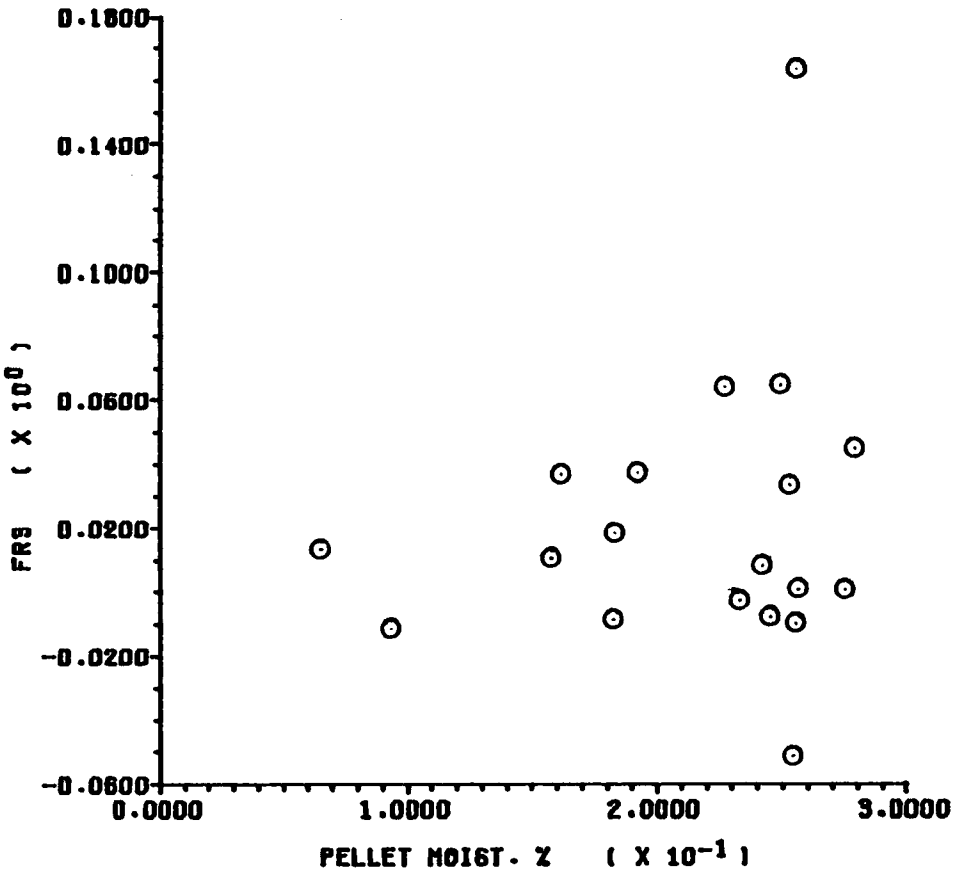
Figure A-2. Pellet Selectivity vs. Pellet Moisture % for Solution 1B



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 1B:
sodium palmitate 0.055g/l
dextrin 1.5g/l
pH 6.10

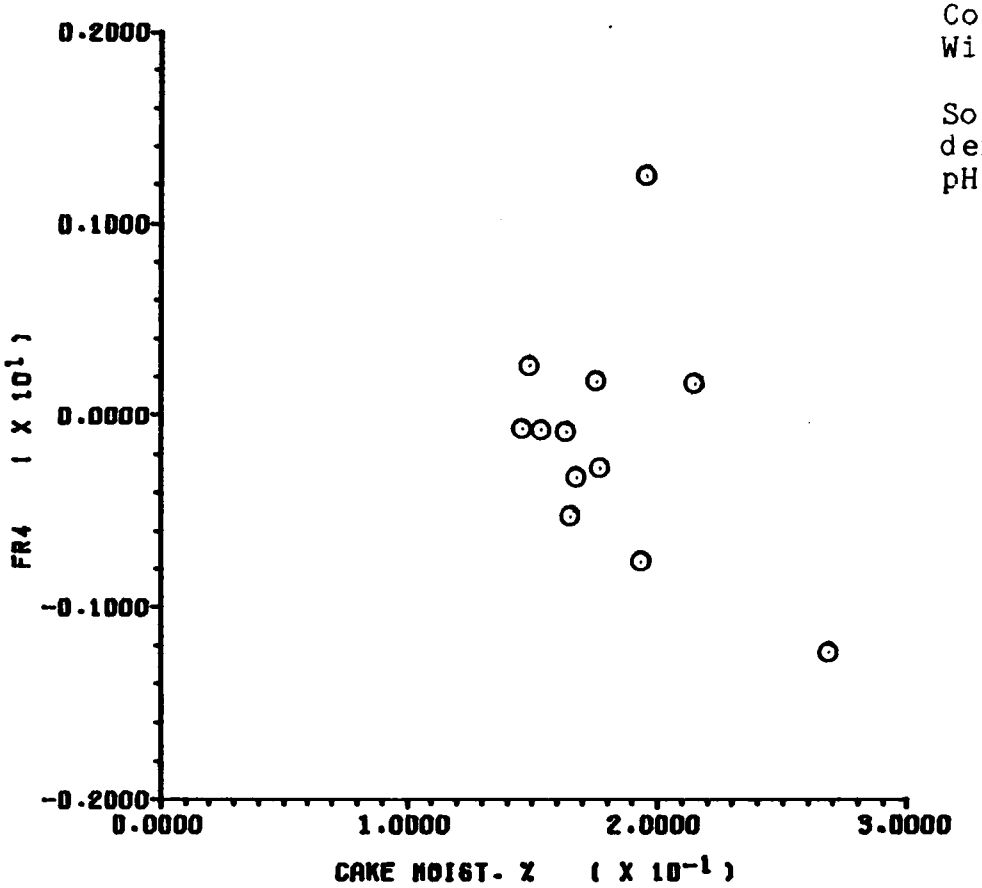
Figure A-3. Cake Selectivity vs. Cake Moisture % for Solution 1B



Wilder Seam, -80 to +170 mesh

Solution 1C:
sodium palmitate 0.055g/l
dextrin 2.0g/l
pH 5.95

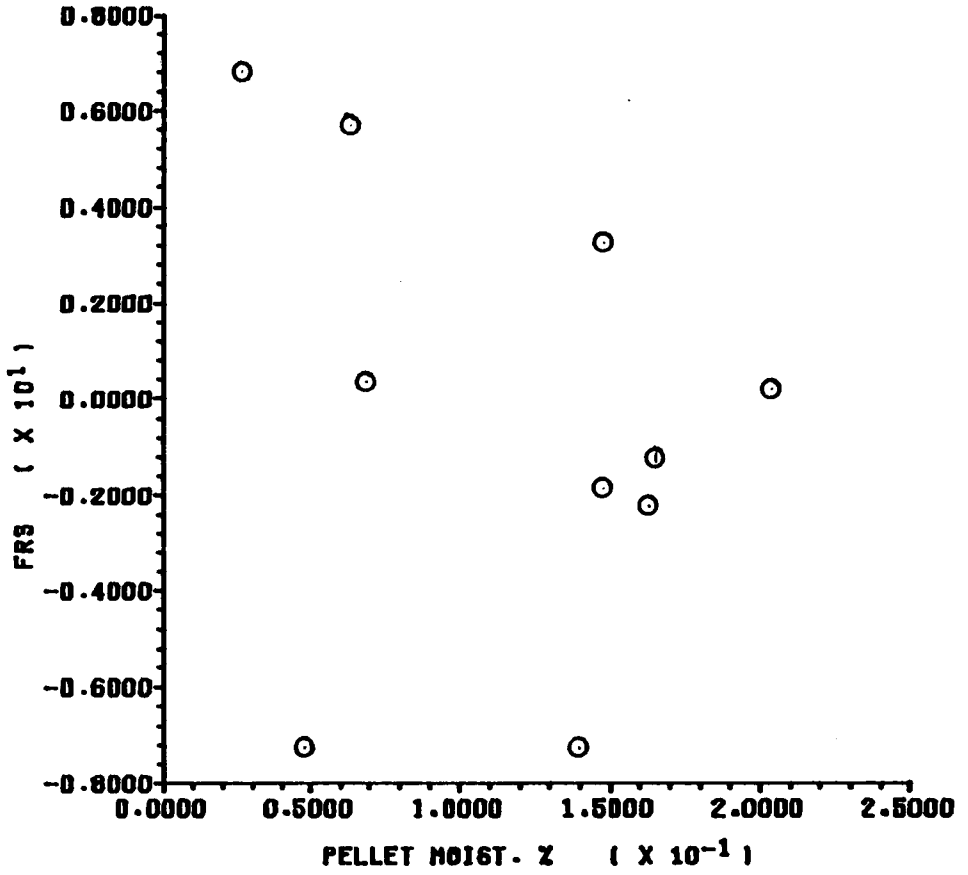
Figure A-4. Pellet Selectivity vs. Pellet Moisture % for Solution 1C



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 2A:
dextrin 2.0g/l
pH 6.11

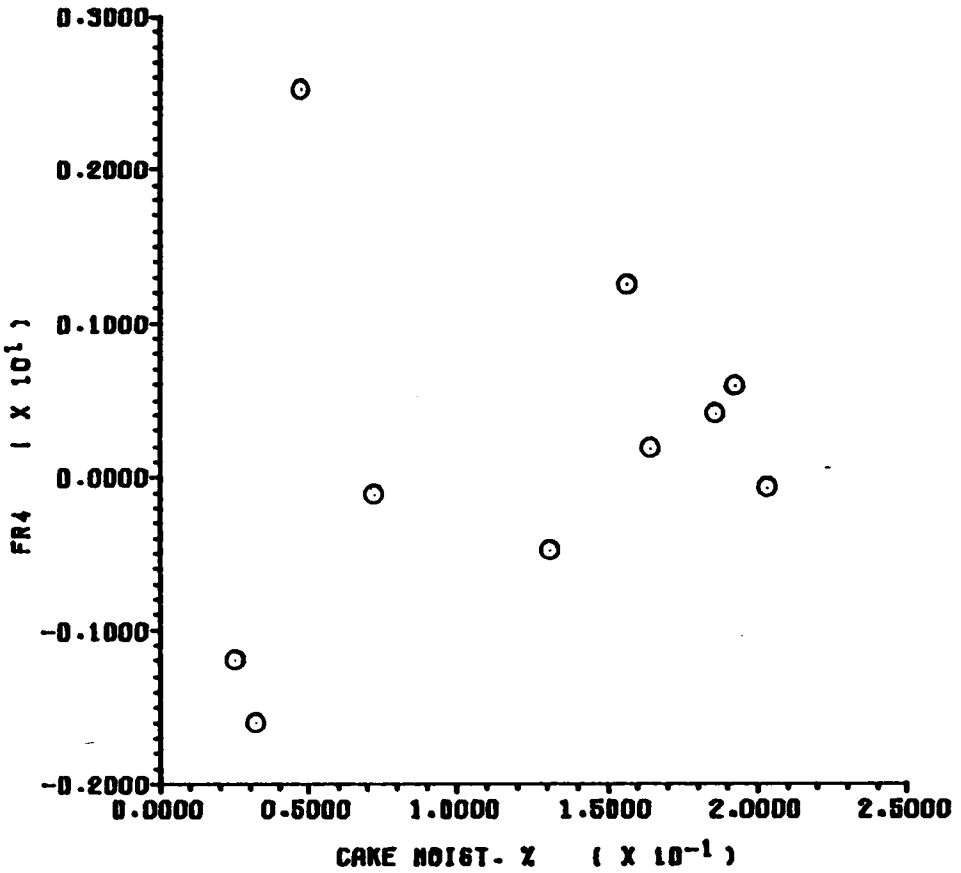
Figure A-5. Cake Selectivity vs. Cake Moisture % for Solution 2A



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 3B:
hexadecyl trimethyl-
ammonium bromide 10.1g/l
pH 6.07

Figure A-6. Pellet Selectivity vs. Pellet Moisture % for Solution 3B



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 3B:
hexadecyl trimethyl-
ammonium bromide 10.1g/l
pH 6.07

Figure A-7. Cake Selectivity vs. Cake Moisture % for Solution 3B

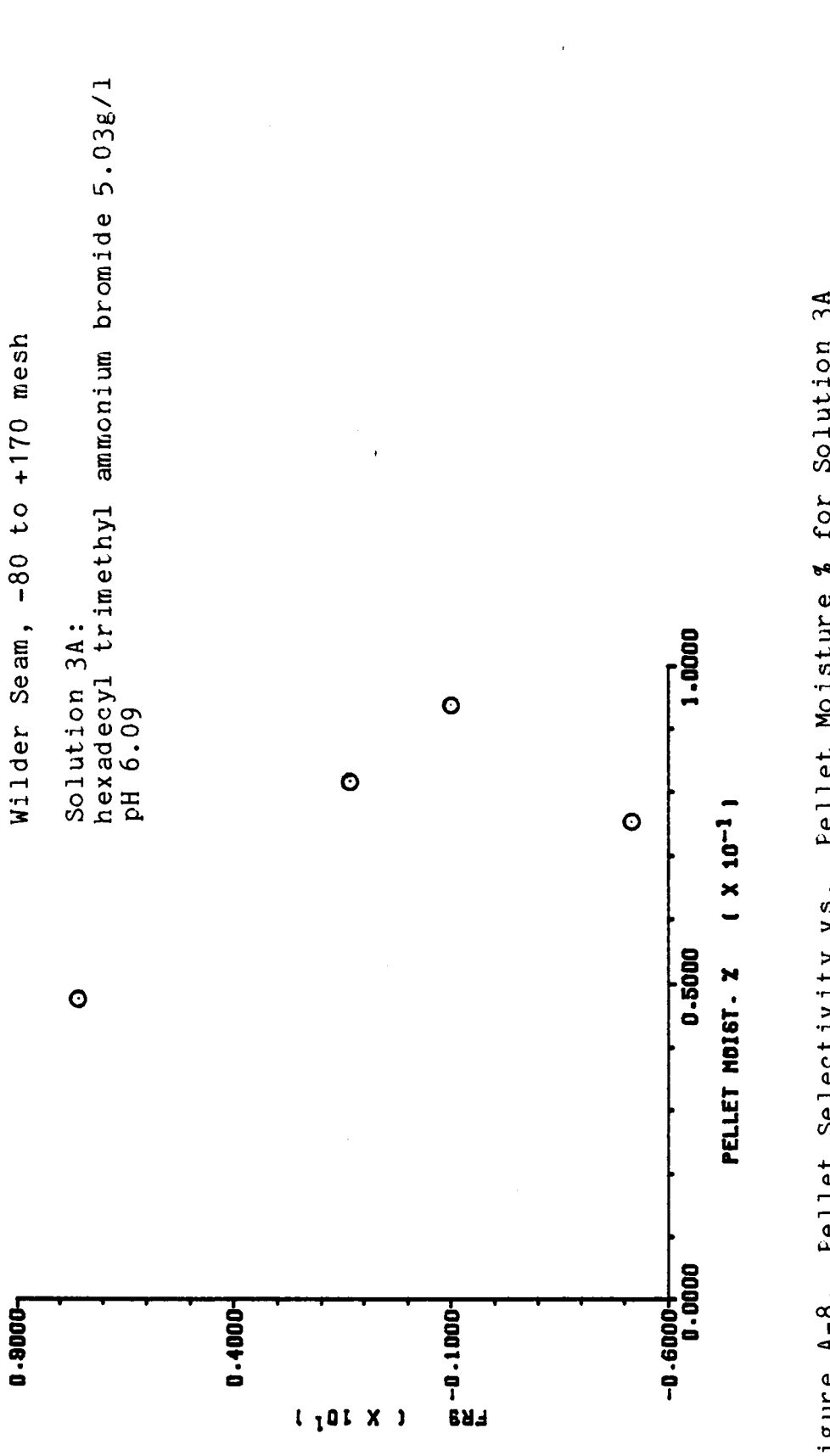


Figure A-8. Pellet Selectivity vs. Pellet Moisture % for Solution 3A

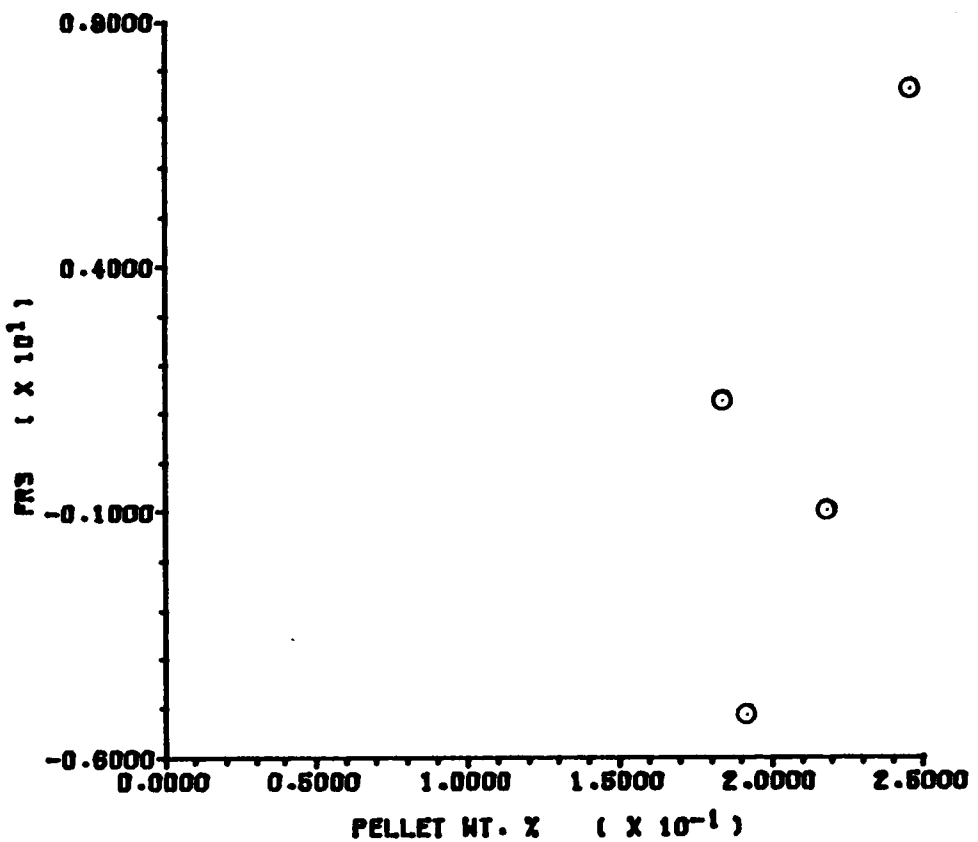
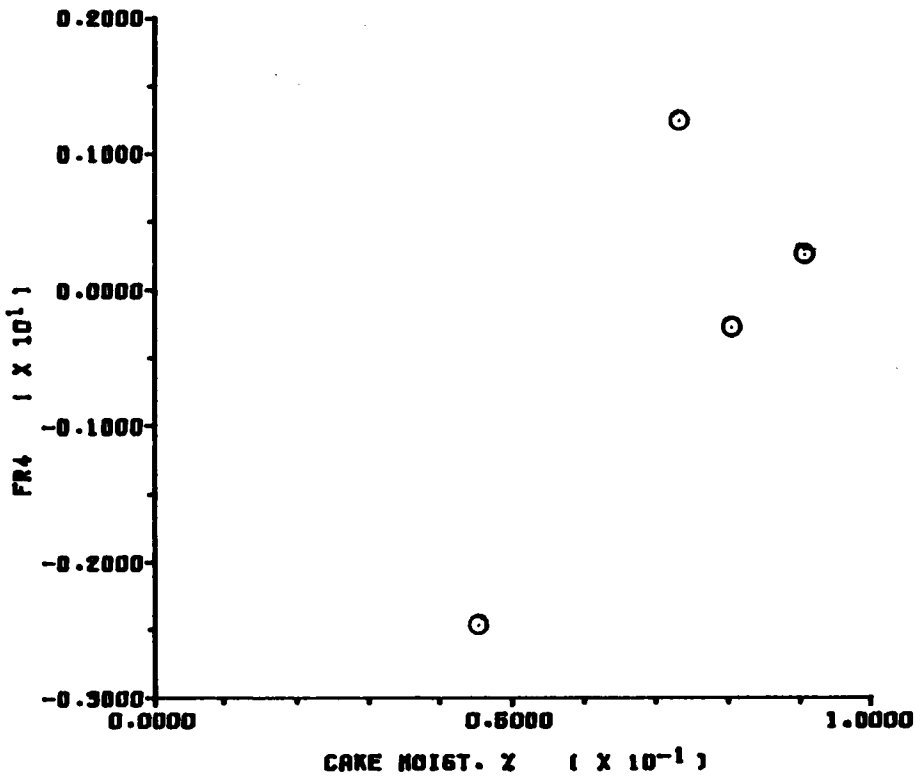


Figure A-9. Pellet Selectivity vs. Pellet Weight % for Solution 3A



Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 3A:
hexadecyl trimethyl-
ammonium bromide 5.03g/l
pH 6.09

Figure A-10. Cake Selectivity vs. Cake Moisture % for Solution 3A

Coal Particles:
Wilder Seam, -80 to +170 mesh

Solution 3A:
hexadecyl trimethyl-
ammonium bromide 5.03g/l
pH 6.09

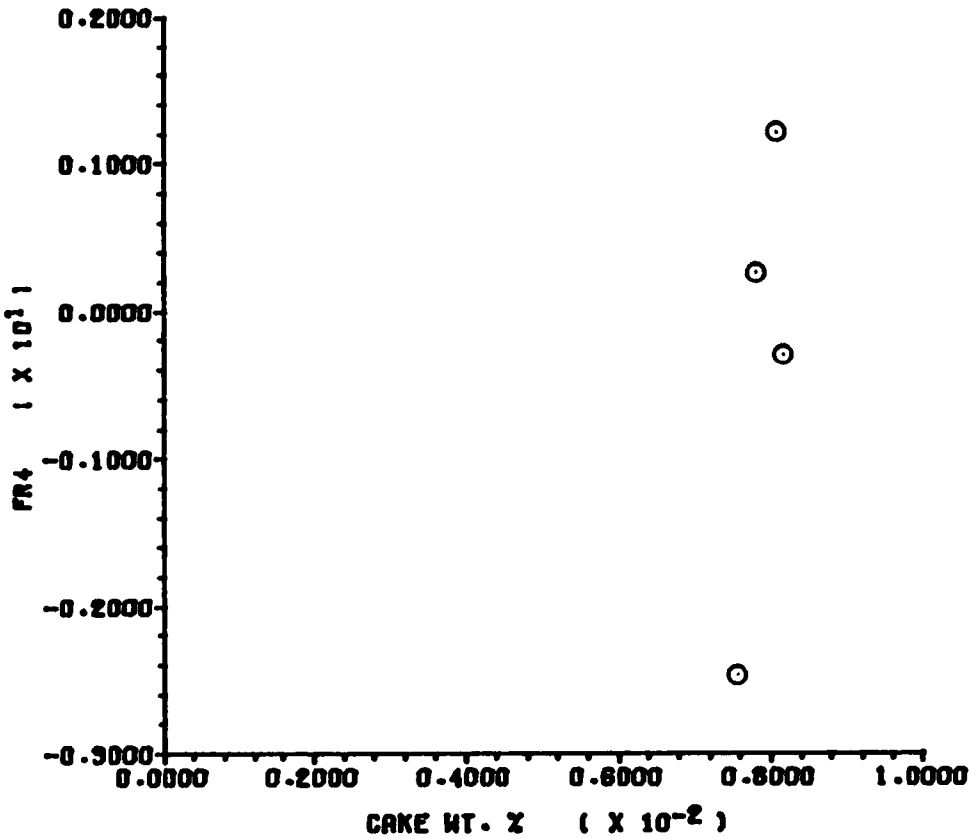


Figure A-11. Cake Selectivity vs. Cake Weight % for Solution 3A

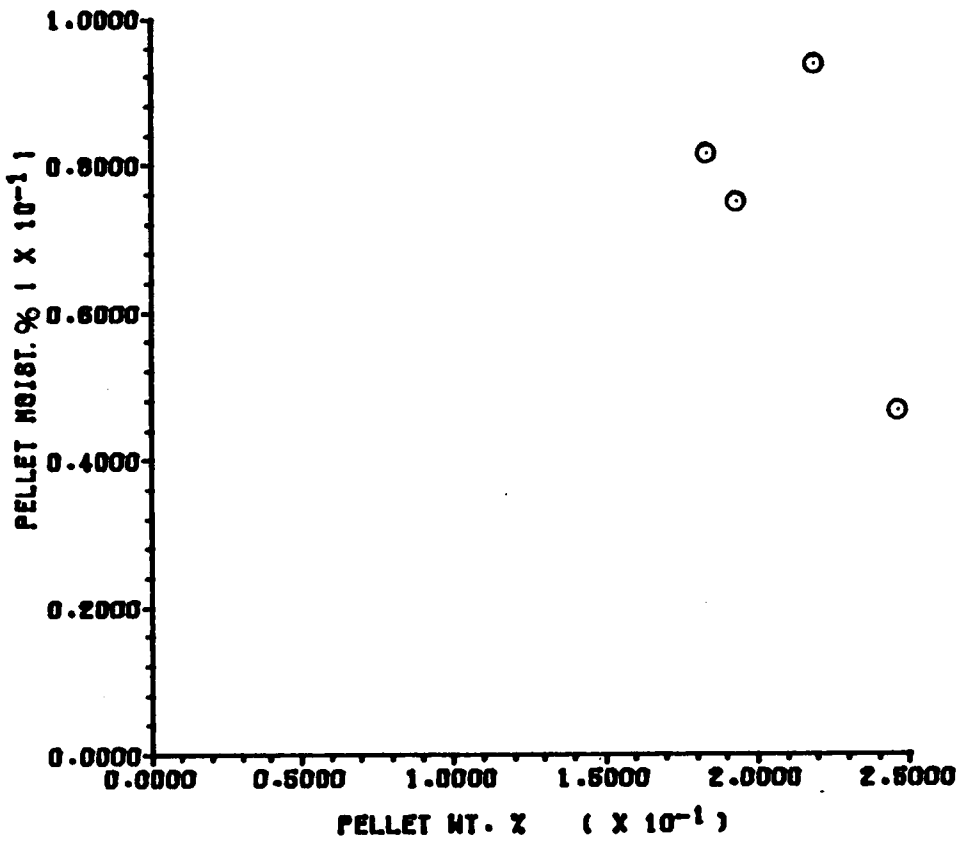


Figure A-12. Pelletization of Coal Particles Using Aqueous Solution 3A: Effect of Pellet Moisture on Fraction of Pellets Produced

VITA

Glenn M. Lawson was born in Atlanta, Georgia on August 31, 1949. He graduated from Oak Ridge High School, Oak Ridge, Tennessee, in 1967, and attended Georgia Tech in Atlanta from 1967 to 1972 where he earned his B.S. degree in Cheical Engineering.

After working for Union Carbide at the Oak Ridge National Laboratory, he entered graduate school at the University of Tennessee to obtain his M.S. degree in Chemical Engineering.