

FORMATION OF OXIDES OF NITROGEN IN PULVERIZED COAL COMBUSTION

By

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ABSTRACT

Nitrogen oxides are a potential atmospheric pollutant. Their formation and decomposition were studied in an experimental pulverized furnace. The concentration of nitrogen oxides (NO_x) was a maximum in the combustion zone and decreased as the combustion gas cooled. At a coal burning rate of 2 lbs an hour and 22 percent excess air, reduction of nitrogen oxides was obtained by selective secondary-air distribution. With 105 percent of the stoichiometric air fed to the coal-combustion zone and 17-percent additional air fed just beyond the flame front, 62-percent reduction of NO_x occurred with good combustion efficiency. Lowering the quantity of excess air lowered the NO_x concentration, but at the expense of combustion efficiency. At 22-percent excess air fed to the primary combustion zone, NO_x concentration in the effluent was 550 ppm and

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carbon in the fly ash 2.0 percent. At 5-percent excess air, the NO_x concentration fell to 210 ppm and carbon in the fly ash rose to 13.8 percent. At stoichiometric combustion the NO_x was 105 ppm a reduction of 81 percent, and the carbon 42.3 percent. Recirculation of combustion gas was not an effective means of lowering NO_x formation.

INTRODUCTION

Any combustion process that produces high temperatures in the presence of atmospheric nitrogen and oxygen will yield nitrogen oxides as a product. At the high temperatures obtained in internal combustion engines and in thermal power stations, boilers, and space heaters appreciable amounts of nitrogen oxides are formed. Although nitric oxide (NO) is the predominant oxide formed during combustion, once emitted to the atmosphere and hastened by sunlight conversion to the dioxide (NO_2) occurs. Nitrogen dioxide has not been considered a major air pollutant. Although average maximum concentrations as high as 0.45 ppm have been reported in the atmosphere of major U.S. cities (13)⁴, it is well below the threshold level of 5 ppm suggested by the American Conference of Governmental

4

Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Industrial Hygienists (1). Nitrogen dioxide, however, has been indicted as a precursor of smog by reacting photochemically with hydrocarbons in the atmosphere (9,15). Recently it has been shown that individuals suffering from cardiovascular dysfunction are impaired by breathing smog-laden air (7). The California Department of Public Health is currently evaluating the data on oxides of nitrogen and their role in air pollution to determine whether air quality and motor vehicle emission standards should be adopted regarding them (11).

Changes in automotive-engine design and operation are only slightly effective in reducing emissions of oxides of nitrogen. On the other hand the most promising methods at present for reducing auto exhaust hydrocarbons have the effect of increasing nitrogen oxides slightly (8).

Barnhard and Diehl (5) showed that with a 2-stage combustion, reduction of nitrogen oxides occurred in gas- and oil-fired boilers. With 95 percent of theoretical air through the burners and 15 percent through the auxiliary air ports, nitrogen oxides concentration for both gas and oil firing was reduced from 525 to 385 ppm--a 27 percent reduction. On oil firing with 90 percent of theoretical air through the burners and the balance through the air ports, the NO_x content was reduced from 580 to 305 ppm--a reduction of 47 percent. Burners for new stations of the Southern California Edison Company were designed for two-stage combustion (3) and existing ones converted when outages could be arranged (4).

Sensenbaugh and Jonakin (14) showed that tangential firing gave consistently lower NO_x concentrations than horizontal firing for both oil- and gas-fired furnaces. Because two-stage combustion introduces additional control problems they recommended standard tangential firing rather than two-stage combustion with horizontal firing as a preferred technique in reducing nitrogen oxides formation.

There has been no work reported in lowering nitrogen oxide formation in coal-fired furnaces despite the large role that coal plays in the energy picture--accounting for 66 percent of the utility fuel market. Projection of coal used in power generation indicates a large gain from the 225 million tons in 1964 to 550 million tons in 1980 (12).

Because of the importance of coal combustion in the production of nitrogen oxides and the pollution potential of those oxides, an experimental program was undertaken in cooperation with the U.S. Public Health Service to evaluate the factors in their formation.

EXPERIMENTAL APPARATUS

Furnace

This study was conducted in a pulverized-coal-fired furnace capable of burning 1 to 4 lbs of coal per hour (10). The furnace is fired vertically downward into the primary combustion chamber. The combustion gases pass under an arch in the first chamber, over a baffle into a larger secondary chamber, and then under a second arch into the furnace breech and out the stack. Figure 1 shows a cross-section of the furnace. The combustion air is metered and divided into three streams. The primary-air stream transports the pulverized coal from the coal-feeder outlet. The secondary- and tertiary-air streams control the flame pattern and maintain ignition stability. The secondary air enters the furnace through the burner in a tube concentric with that carrying the primary air-coal mixture and mixes with that stream at the burner tip. The tertiary air enters through two tubes as shown in figure 1. The tertiary air emerges horizontally from a hole near the bottom of each tube tangentially to the flame.

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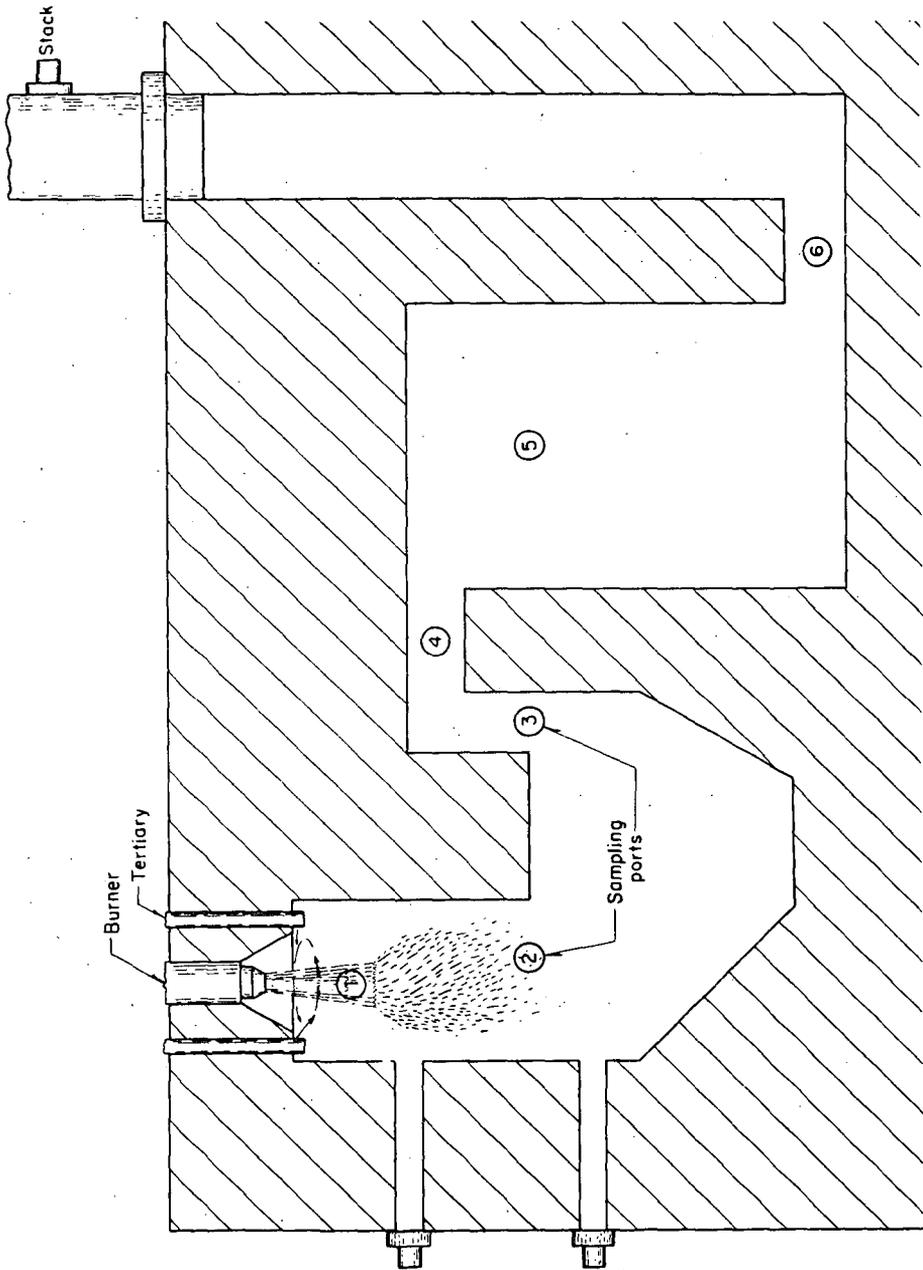


Figure 1.- Cross-section of experimental furnace with location of sample ports.

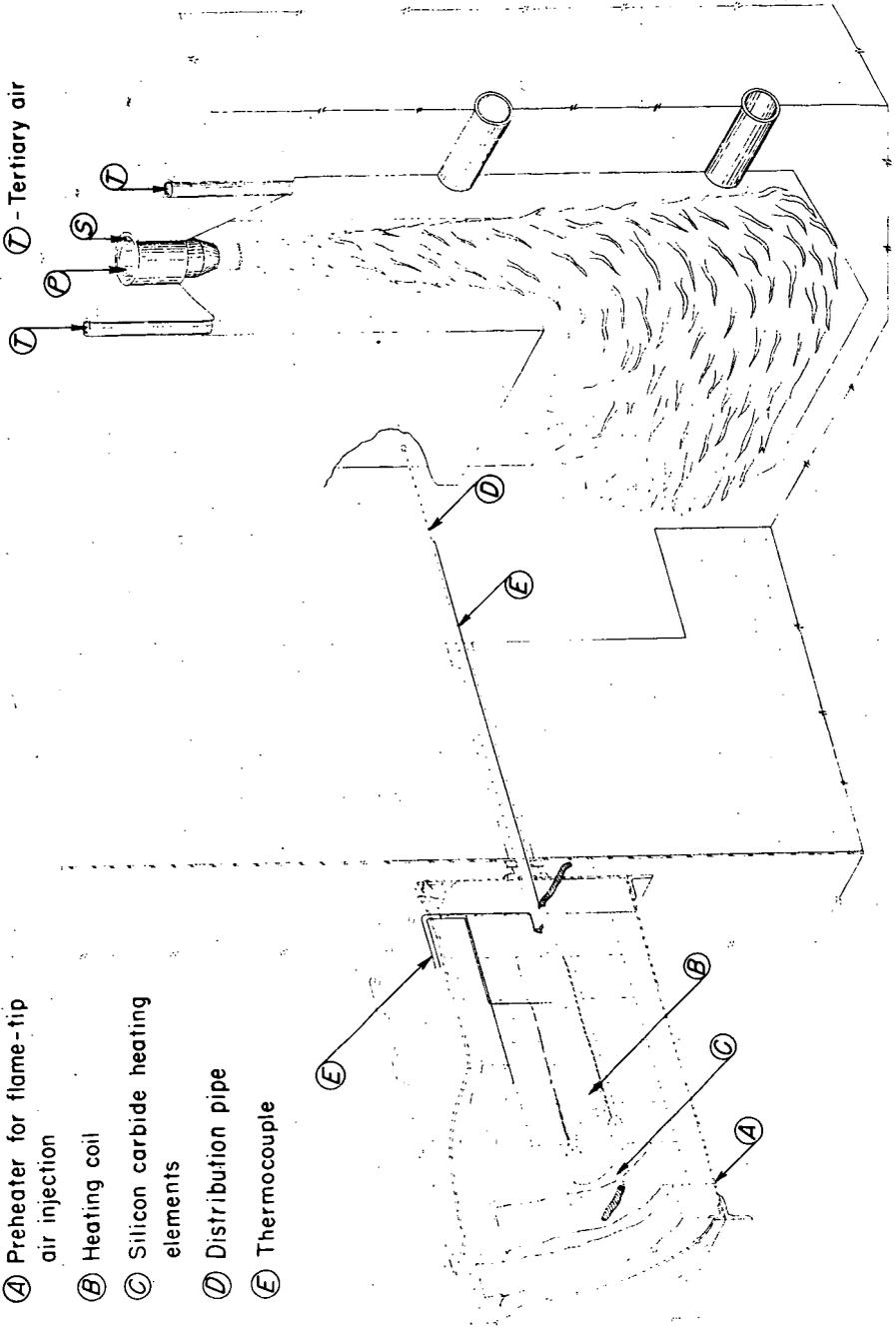
Nine access ports are available for observation and sampling. Any of these ports may be fitted with a sight glass or a flange to admit a sampling probe. The ports in figure 1, numbered 1 through 4 and stack, were used for sampling. Ports 2 and 3 were also adapted for air injection during two-stage combustion. In the air-injection system part of the combustion air was preheated to approximately 1,900° F and dispersed across the path of the combustion gases just beyond the flame front. Figure 2 is a sectional view of the air-injection system in position at port 3. When air injection was used at a port that location could not be sampled.

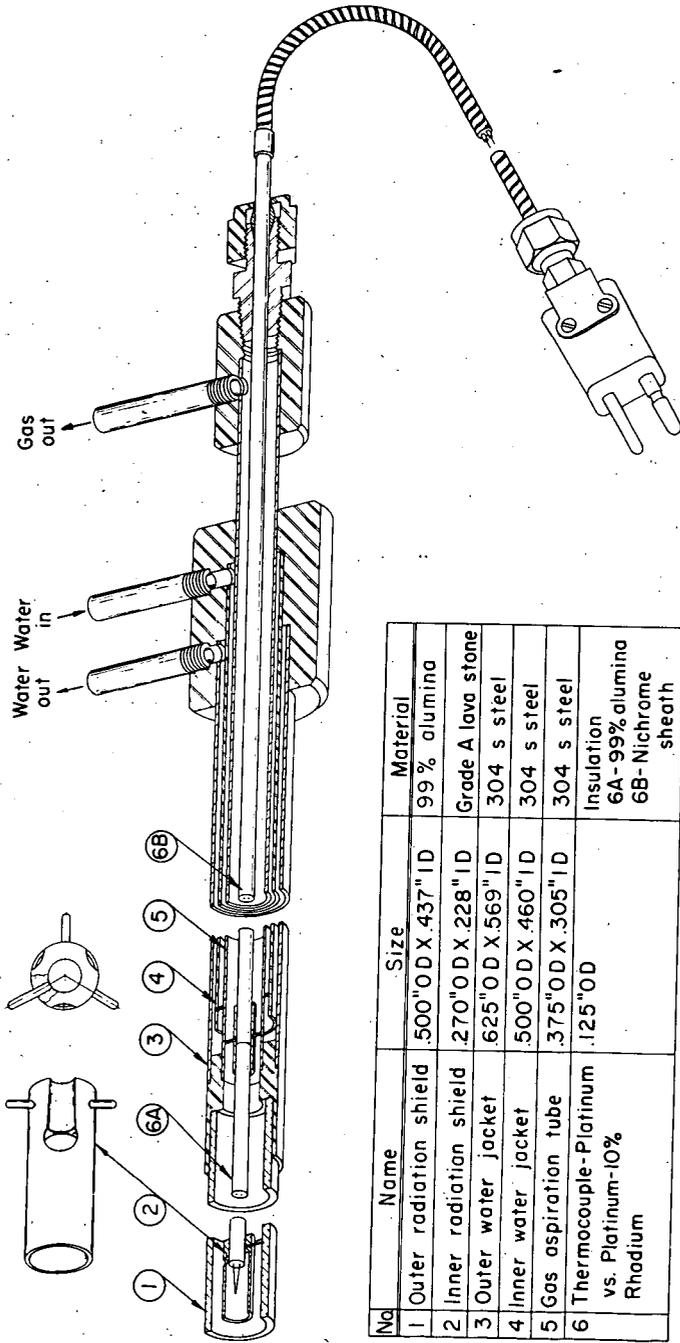
Probe

Gas samples were drawn from the furnace and temperatures measured with a shielded aspirating probe, shown in figure 3. These probes were built smaller in diameter than commercially available equipment because of the limited volume of gas available for aspiration in the experimental furnace. The probes carried Pt/Pt-10 percent Rh thermocouples to measure temperatures at the point from which the samples were taken. The thermocouple is protected from errors in temperature measurement by two concentric radiation shields. The base is tapered outward at each of its three gas ports to allow a gradual change of direction for the combustion gas minimizing fly ash deposition. The probe is water-cooled to the base of the

- Ⓐ - Primary air
- Ⓑ - Secondary air
- Ⓒ - Tertiary air

- Ⓐ Preheater for flame-tip air injection
- Ⓑ Heating coil
- Ⓒ Silicon carbide heating elements
- Ⓓ Distribution pipe
- Ⓔ Thermocouple





No	Name	Size	Material
1	Outer radiation shield	.500"OD X .437" ID	99% alumina
2	Inner radiation shield	.270"OD X .228" ID	Grade A lava stone
3	Outer water jacket	.625"OD X .569" ID	304 s steel
4	Inner water jacket	.500"OD X .460" ID	304 s steel
5	Gas aspiration tube	.375"OD X .305" ID	304 s steel
6	Thermocouple-Platinum vs. Platinum-10% Rhodium	.125"OD	Insulation 6A-99% alumina 6B-Nichrome sheath

Figure 3.- Aspirating, water-cooled probe.

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radiation shielding. Gas is aspirated through the radiation shielding to minimize the loss of heat by radiation from the thermocouple. The effect of aspirating gas upon temperature measurement is shown in figure 4. With no aspiration the temperature indicated was 2,125° F. The indicated temperature increased with increasing volume of aspirating gas until a maximum temperature of 2,600° F was reached at 55 SCFH. Additional aspiration did not cause further temperature increase. Moving at a velocity of 100 ft/sec the gas in the probe is quenched from >2,000° F to 120° F in 0.02 second. High chilling rates are necessary to prevent significant dissociation of the nitric oxide.

Sampling System

The sampling system including the probe is shown in figure 5. The system is mobile and is shown in position on the furnace in figure 6. One pump is high volume, low vacuum and serves as the aspirator. The second pump is low volume, high vacuum and is used to evacuate sample flask and tubing. Nitrogen oxides and combustion gas are sampled simultaneously. The nitrogen oxides were analyzed by the phenoldisulfonic acid method (2,6) and the remaining components in the combustion gas were determined by

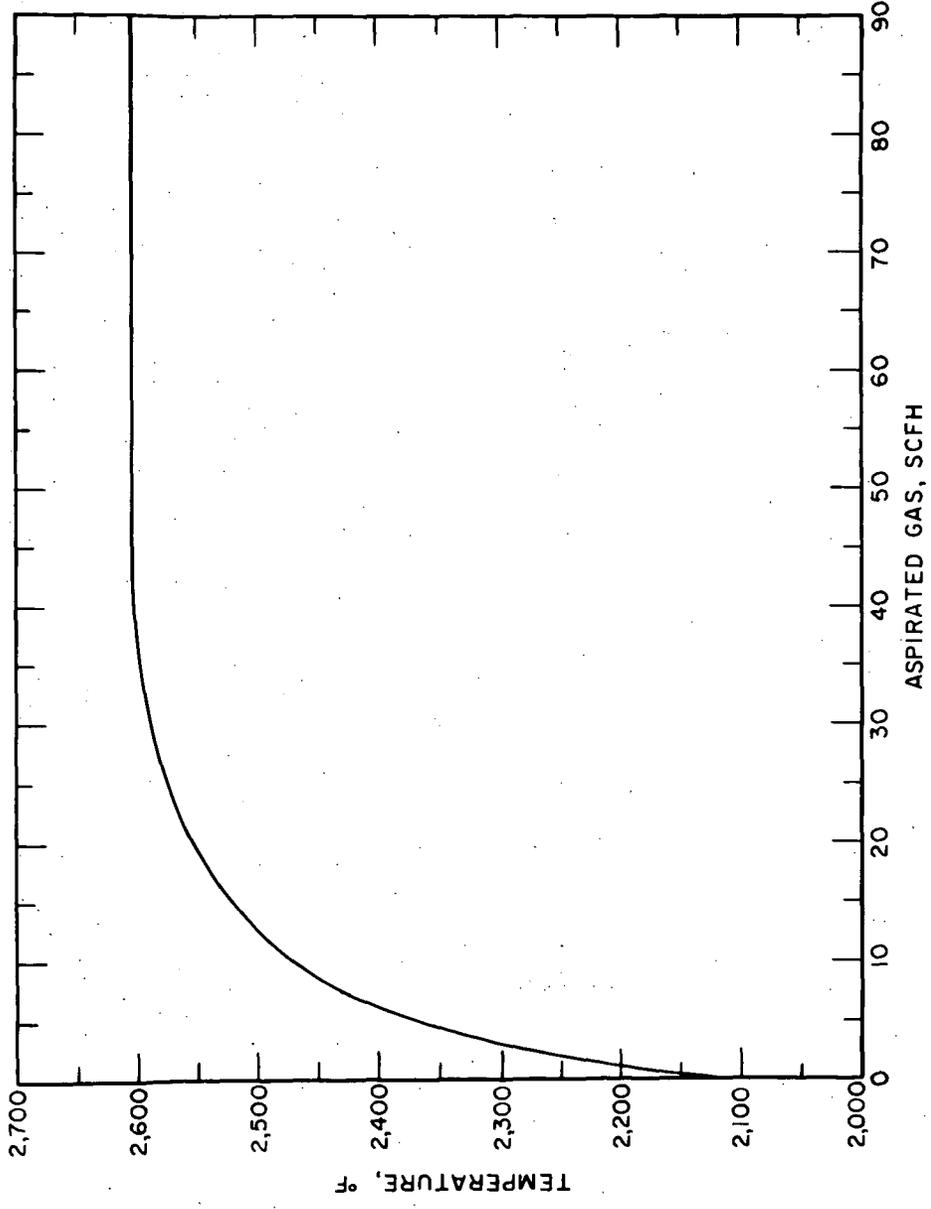


Figure 4.- Temperature indication with aspirating thermocouple as a function of volume of gas drawn.

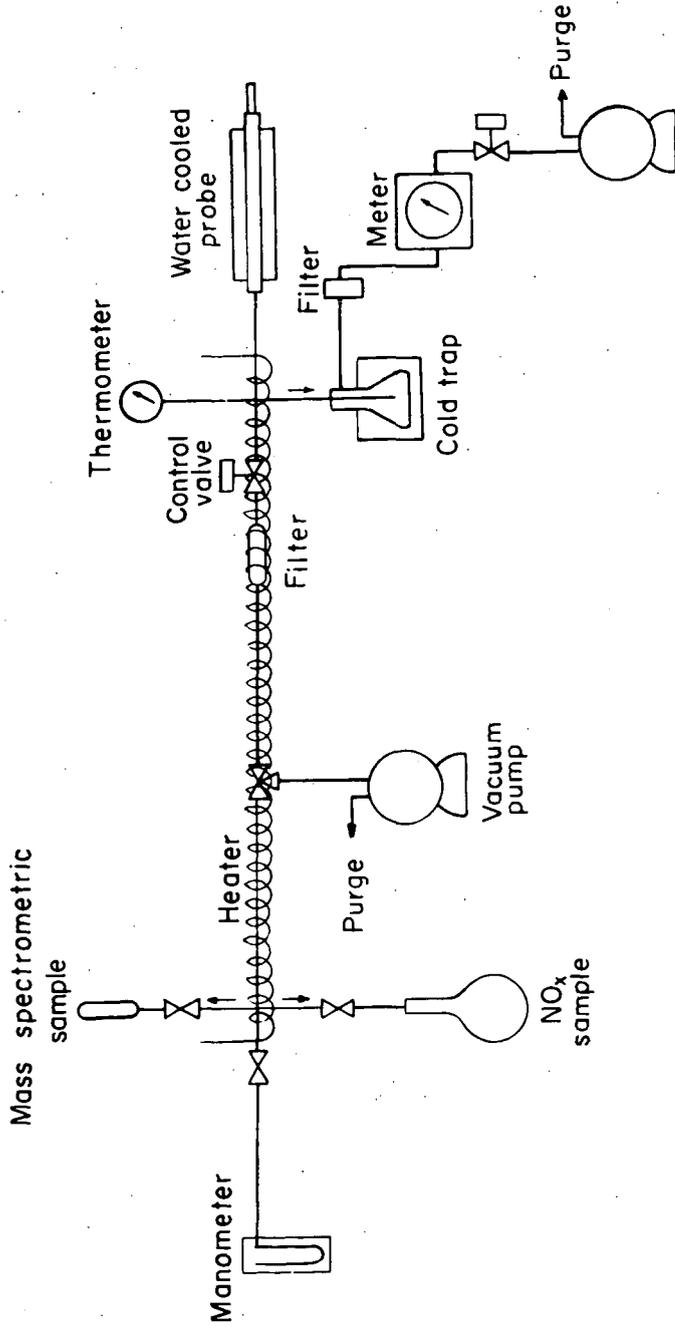


Figure 5.- Aspirating thermocouple for sampling gases in pulverized-coal combustion

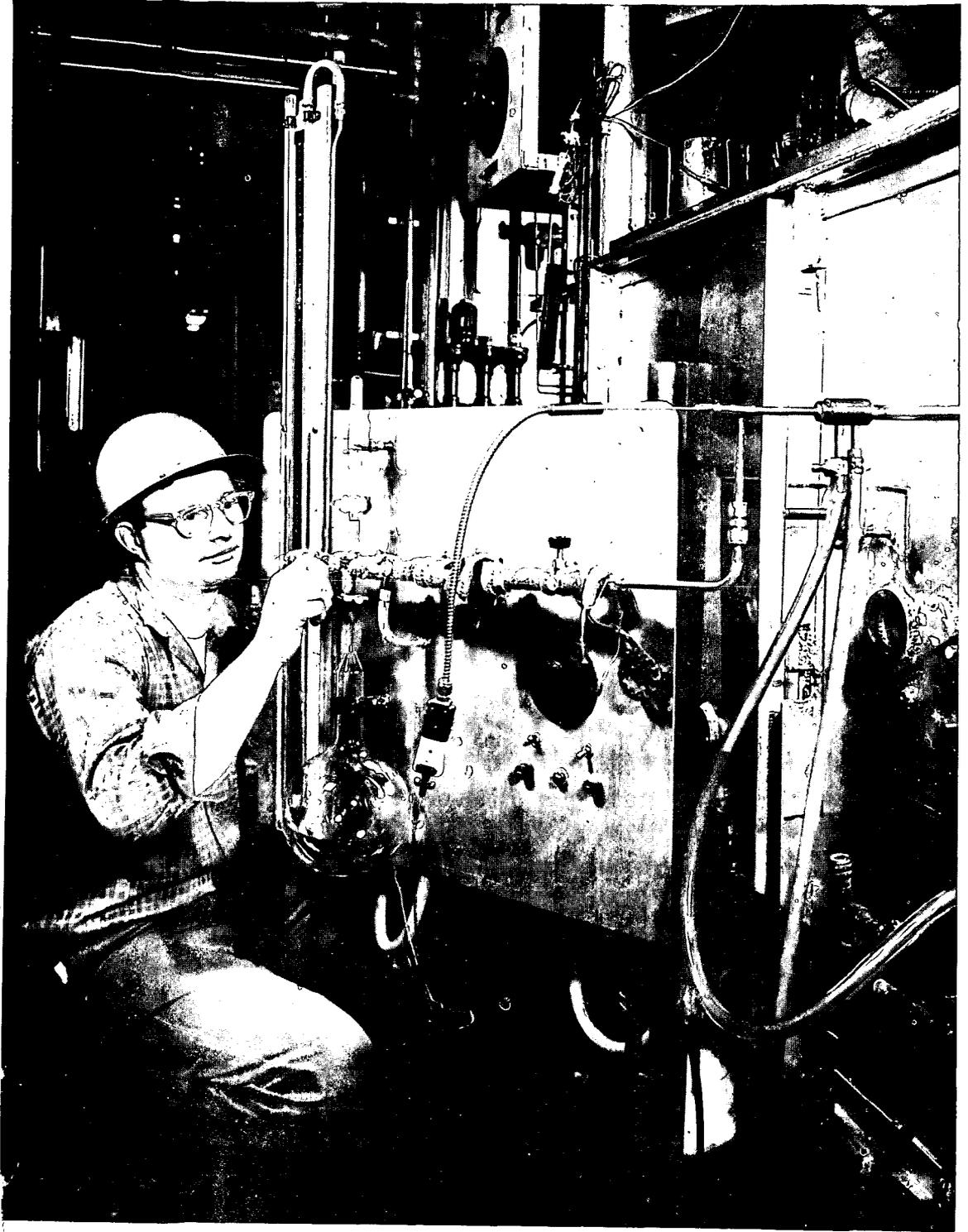


Figure 6.- Sampling combustion gases from experimental pulverized-coal-fired furnace.

mass spectrometry. The values of nitrogen oxides reported here include NO plus NO₂. No attempt was made to determine these oxides separately. For the nitrogen oxides determination a 1,600 cc sample was taken. Light transmission in the treated sample was measured on a Bausch and Lomb⁵ "Spectronic 20" spectrophotometer at a wavelength of 410 mμ.

Fly ash was sampled isokinetically from the stack during these tests and analyzed for carbon content to determine the efficiency of combustion.

Coal

The coal used in these tests was a high-volatile B bituminous. The analysis is given in table 1. This particular coal was chosen for its high ash-fusion temperature to eliminate plugging of the probe caused by molten ash. The coal was ground so that 95 percent of it would pass through a 325-mesh screen before being placed in the feeder. The feeder is a vibrated screw of commercial design driven by a variable speed drive. The screw discharges on to an inclined plane so as to eliminate pulsations in the coal feed due to the double-lead screw. The coal is picked up by the primary combustion air as it drops from the inclined plane.

5

Reference to specific makes or models of equipment is made to facilitate understanding and does not imply endorsement of such devices by the Bureau of Mines.

TABLE 1.- Analysis of coalProximate, weight percent

Moisture -----	0.3
Volatile matter -----	36.3
Fixed carbon -----	54.9
Ash -----	8.5

Ultimate, weight percent

Hydrogen -----	5.3
Carbon -----	77.1
Nitrogen -----	1.3
Oxygen -----	6.9
Sulfur -----	0.9
Ash -----	8.5
Heating value -----	13,670 Btu/lb
Ash fusibility - initial deformation temperature-	> 2,910° F

EXPERIMENTAL RESULTS

Effect of Air-to-Coal Ratio

As a base case, coal was burned at 2 lbs an hour with combustion air supplied at 22 percent in excess of stoichiometric requirements. The total combustion air was distributed as follows: 22 percent primary, 5 percent secondary, and 73 percent tertiary. Oxides of nitrogen reached a maximum concentration of 780 ppm at the point of highest measured temperature of the flame, 2,440° F, and decreased to 550 ppm at the stack as the combustion gas cooled. As the gas cools nitric oxide dissociates into N₂ and O₂, however the rate of dissociation decreases rapidly with falling temperature. Although the temperature of the combustion gas leaving the stack in this experimental unit is 500°-600° F higher than the gas leaving the stack from a power plant, this additional cooling would have very little effect on the NO_x concentration. An NO_x concentration of 550 ppm at 4.0 percent oxygen is the equilibrium concentration at 2,230° F. Carbon content in the fly ash was 2.0 percent indicative of a carbon combustion efficiency of 99.8 percent.

On lowering the quantity of combustion air to 105 percent of stoichiometric the NO_x concentration at the stack was lowered to 210 ppm, a reduction of 62 percent relative to the base case. The carbon content in the fly ash rose to 13.8 percent--a carbon combustion efficiency of 98 percent. Further lowering of the combustion air to stoichiometric decreased the NO_x content to 105 ppm--a reduction of 81 percent. However the carbon content of the fly ash rose to 42.3 percent. These results are plotted as curves 1, 2, and 4 in figure 7 and tabulated in table 2.

Two-stage Combustion

As industry prefers to operate its pulverized-coal-fired furnaces at excess air levels of approximately 20 percent because of considerations of heat transfer and combustion efficiency, it was decided to maintain about 20 percent excess air and at the same time take advantage of the effect of reduced air flow in the flame on NO_x formation. This was accomplished by supplying 5 percent excess air in the primary combustion zone and injecting additional air for secondary combustion just beyond the flame front, as shown in figure 2, to bring the total excess air to 22 percent. The injected air was heated to $1,940^\circ \text{F}$, the combustion gas temperature at point of admittance in port 3, and dispersed in front of the

TABLE 2.- Furnace operating conditions with variations in percentage of excess air

Excess air, %	Port No 1		Port No 2		Port No 3		Port No 4		Stack			
	NO _x , ppm	Temp, °F	O ₂ , %	Carbon in ash, %								
0	630	2480	320	2190	265	2120	0.4	255	1850	800	0.2	42.3
5	600	2375	440	2275	340	2070	2.2	300	1900	975	1.1	13.8
22	690	2335	780	2440	590	2090	4.3	590	1950	975	4.0	2.0

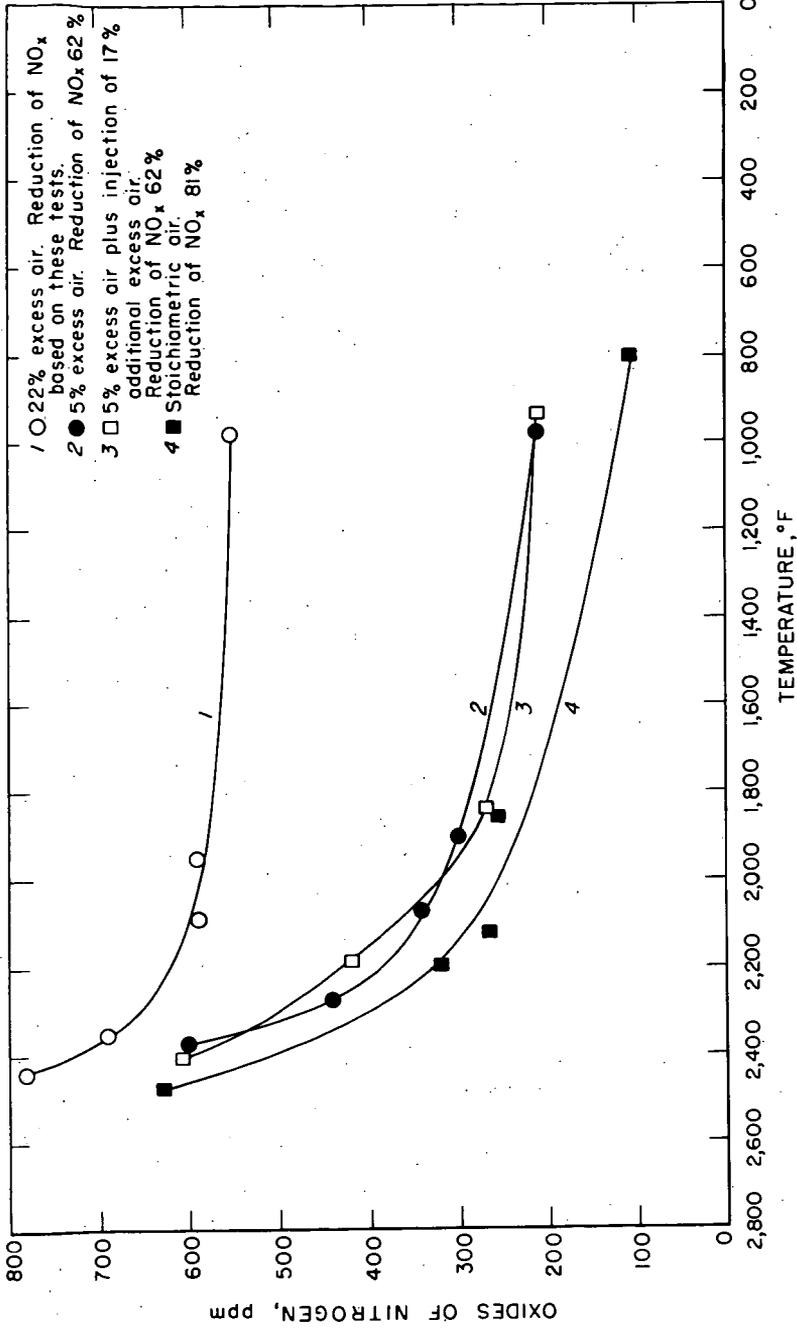


Figure 7.—NO_x concentration as a function of excess combustion air.

flame zone through a series 1/32-inch apertures. This high preheat was necessary to prevent quenching in this small unit and would not be necessary in a commercial installation. The concentration of NO_x at the stack was 210 ppm, a reduction of 62 percent compared to the base case, and equal to that obtained in the earlier test using a total of 105 percent of the stoichiometric air requirement. With the above 2-stage operation the carbon in the fly ash was 6.6 percent--a carbon combustion efficiency of 99.2 percent. Comparison of the 2-stage operation with single stage operation of 5 and 22 percent excess air is shown in figure 7. By injecting the 17 percent additional air into port 2 rather than port 3, the air entered in the tip of the flame rather than downstream of the flame. As shown in table 3 the NO_x concentration at the stack was 320 ppm, a reduction of 42 percent, and the carbon in the fly ash was approximately the same, 7.3 percent. For another comparison a stoichiometric amount of air was admitted in the primary combustion zone with 22 percent additional in port 3. The NO_x concentration at the stack was 265 ppm and the carbon in the fly ash 14.6 percent.

TABLE 3.- Furnace operating conditions with 2-stage injection of combustion air

Excess air to primary zone, %	Port No 1		Port No 2		Port No 3		Port No 4		Stack					
	NO _x , ppm	Temp, °F	NO _x , ppm	Temp, °F	NO _x , ppm	Temp, °F	NO _x , ppm	Temp, °F	NO _x , ppm	Temp, °F	O ₂ , %	O ₂ , %	Carbon in ash, %	
0	610	2510	0.9	405	2270	1.4	22% air injection	285	1800	3.8	265	870	4.0	14.6
5	670	2510	1.8	420	2185	1.4	17% air injection	270	1840	5.0	210	930	3.9	6.6
5	610	2400	1.4	17% air injection	395	2040	5.3	385	1870	4.7	320	840	3.9	7.3

Gas Recirculation

Recirculation of flue gas is used in boiler operation to maintain thermal efficiency under reduced load. As recirculation lowers the flame temperature it could result in lowering the nitrogen oxide concentration. To test this hypothesis, flue gas was taken from the stack at 900° F mixed with the tertiary combustion air, and returned to the furnace through the tertiary-air inlet tubes. A sketch of the recycle system is shown in figure 8. The volume of recirculated gas ranged from 0 to 22 percent of the total combustion air. Flue gas addition in the larger volumes decreased the stability of the flame. The oxygen content in the combustion zone increased and the flame temperature decreased with gas recirculation. These two effects counteracted each other in the formation of nitrogen oxides. Without gas recirculation the NO_x concentration in the stack was 490 ppm. With 10 and 15 percent recirculation there was no decrease in the NO_x content although the flame temperature decreased from 2,580° to 2,490° F. At 20 percent recirculation the NO_x content dropped to 420 ppm a decrease of 14 percent. The flame temperature at this higher rate of gas recirculation was still lower, 2,380° F. This small decrease in NO_x is not considered sufficient to warrant use of gas recirculation as a means of reducing nitrogen oxide pollution. These results are given in table 4.

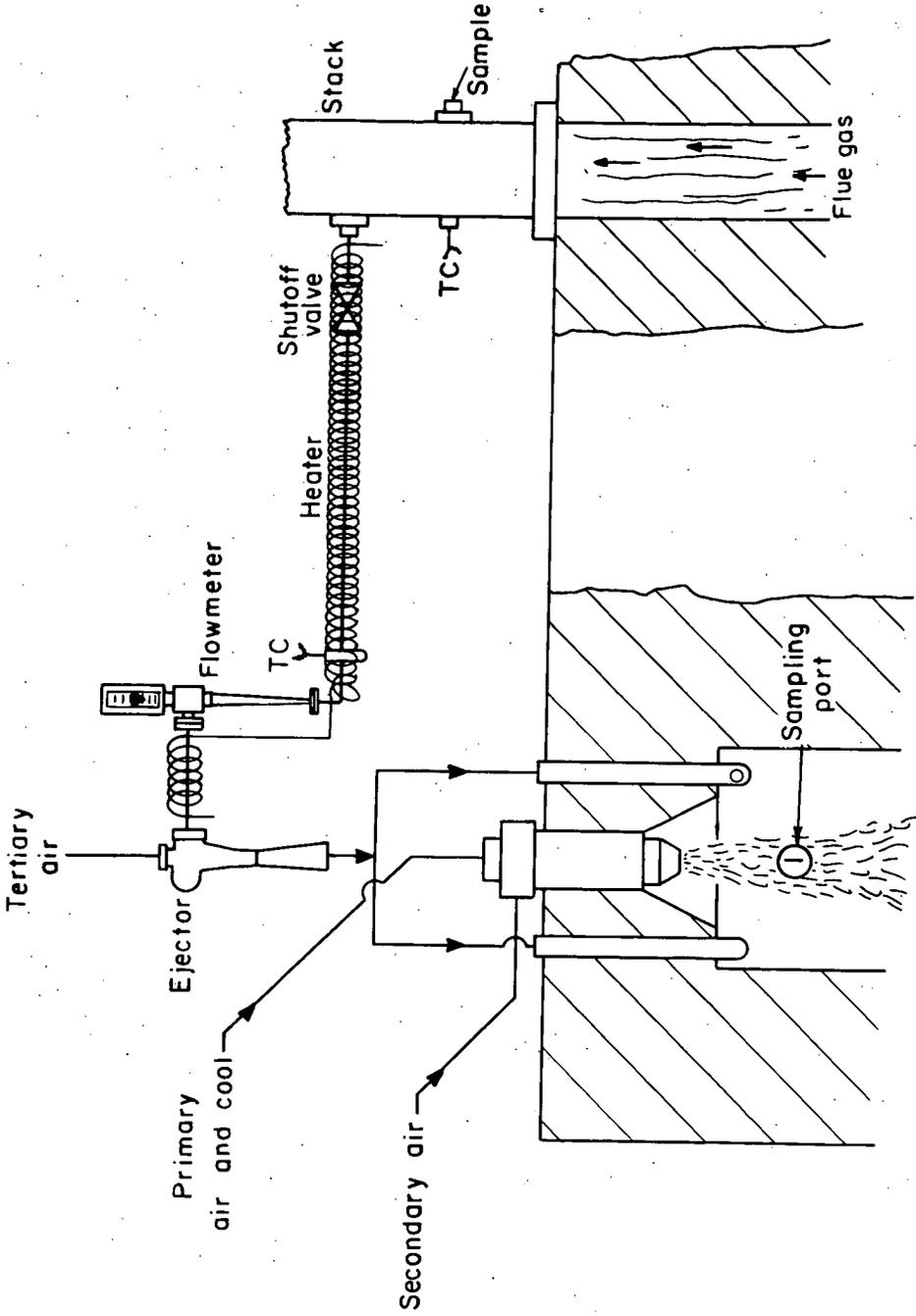


Figure 8.- Recirculation of flue gases in nitric oxide study.

TABLE 4.- Furnace operating conditions using gas recirculation

Ratio of recirculated gas to com- bustion air	Port No 1		Port No 2		Port No 3		Port No 4		Stack	
	NO _x , ppm	Temp, °F								
0	700	2580	560	2210	540	2020	510	1820	490	920
0.10	720	2520	740	2280	610	1980	600	1860	500	940
.15	760	2490	500	2100	530	2040	510	1820	500	950
.22	720	2380	450	2140	460	2010	460	1850	420	910

Combustion Temperature

The effect of flame temperature in the primary combustion zone upon nitrogen oxide formation was investigated. The flame temperature was varied by adjusting the coal feed rate from 1 to 4 lbs of pulverized coal an hour. At these coal rates the heat flux ranged from 18,000 to 72,000 Btu/hr ft³. The heat flux in a commercial pulverized-coal-fired furnace may range from 50,000 to 100,000 Btu/hr ft³. The combustion air was maintained at 122 percent of stoichiometric requirements. Flame temperatures measured in the center of the primary combustion zone were 2,280, 2,440, and 2,800° F burning coal at 1, 2 and 4 lb an hour. NO_x concentrations varied with the coal burning rate and the temperatures in the furnace--a maximum concentration of 830 ppm was obtained at the maximum coal rate. NO_x concentrations dropped as the combustion gas was cooled flowing through the furnace. Stack concentrations of NO_x were 320, 550, and 745 ppm, respectively. At 1 lb of coal an hour combustion gas temperatures dropped rather rapidly in the system resulting in the higher carbon content in the ash of 13.3 percent. These results are given in table 5 and plotted in figure 9. Although increasing the coal burning rate increases the temperature of combustion, other secondary effects such as gas residence time and intensity of radiation may also play a role in nitrogen oxides formation.

TABLE 5.- Furnace operating conditions with variations in coal-fed rate

Combustion rate, lb/hr	Port No 1			Port No 2			Port No 3			Port No 4			Stack			
	NO _x , ppm	Temp, °F	O ₂ , %	NO _x , ppm	Temp, °F	O ₂ , %	NO _x , ppm	Temp, °F	O ₂ , %	NO _x , ppm	Temp, °F	O ₂ , %	NO _x , ppm	Temp, °F	O ₂ , %	Carbon in ash, %
1	660	2280	3.2	415	1860	4.0	360	1725	3.9	355	1580	5.0	320	635	4.2	13.3
2	690	2335	3.5	780	2440	2.0	590	2090	4.3	590	1950	4.0	550	975	4.0	2.0
4	815	2800	0.5	830	2670	2.5	750	2385	4.0	685	2215	3.8	745	1255	4.3	1.1

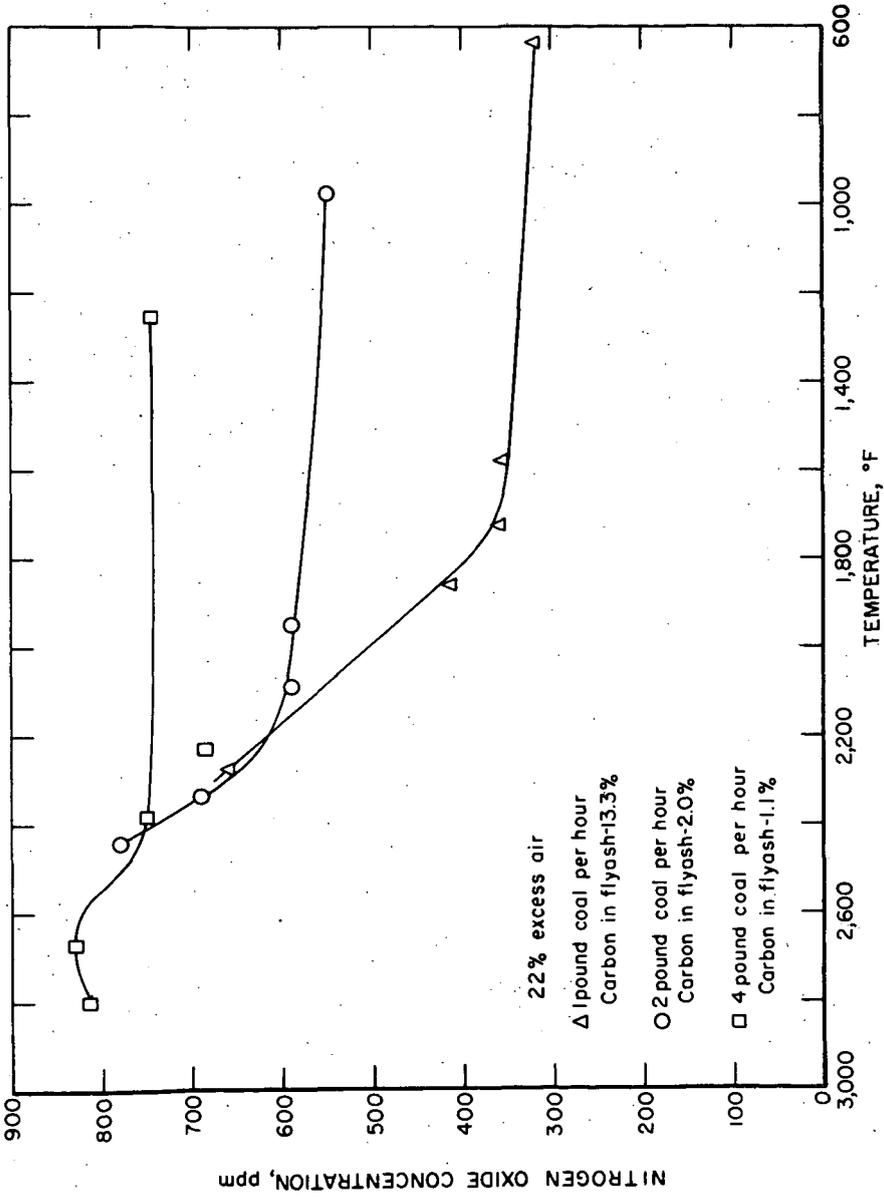


Figure 9.- NO_x concentration as a function of combustion temperature obtained in varying coal burning rate.

CONCLUSIONS

1. In pulverized-coal combustion the concentration of nitrogen oxides in the stack varies directly with excess air and the flame temperature. Although the NO_x concentration in the furnace effluent fell as the amount of excess air was lowered, the combustion efficiency was adversely affected and very likely in a commercial installation the rate of heat transfer across heat-absorbing surfaces would be similarly affected. At 5-percent excess air fed to the primary combustion zone compared with 22 percent, a 62-percent reduction of NO_x was obtained at carbon combustion efficiencies of 98 percent.

2. By supplying 5-percent excess air to the primary combustion zone and an additional 17 percent injected just beyond the flame front the same reduction in NO_x was obtained as by operating at a total of only 105 percent of stoichiometric air. In addition the carbon combustion efficiency was improved--achieving 99.2 percent. With this injection technique not only is a substantial reduction in nitrogen oxides obtained but as the same amount of air is used as in conventional coal-burning plants no significant change in equipment is required and the same rate of heat transfer is expected.

3. Gas recirculation was not effective as a means of lowering nitrogen oxides formation. No sizeable reduction was obtained with gas recirculation rates as high as 22 percent of the combustion air rates.

LITERATURE CITED

- (1) American Conference of Governmental Industrial Hygienists,
1014 Broadway, Cincinnati, Ohio 45202.
- (2) ASTM Standards D1608-60. Standard Method of Test for Oxides
of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic
Acid Procedure).
- (3) Austin, H.C., and Chadwick, N.L. Control of Air Pollution from
Oil-Burning Power Plants. Mech. Engineering, v. 82, 1960, pp.
63-66.
- (4) Austin, H.C., and Sedor, P. Combustion Scheme Cuts Power Plant
Smog Components. Electrical World, v. 157, 1962, pp. 51-53.
- (5) Barnhart, D.H., and Diehl, E.K. Control of Nitrogen Oxides in
Boiler Flue Gases by Two-Stage Combustion. J. Air Poll. Control
Assoc., v. 10, 1960, pp. 397-406.
- (6) Beatty, R.L., Berger, L.B., and Schrenk, H.H. Determination of
the Oxides of Nitrogen by the Phenoldisulfonic Acid Method.
Bureau of Mines Rept. Invest. 3687, 1943.
- (7) Brant, J.W.A. Human Cardiovascular Diseases and Atmospheric
Air Pollution in Los Angeles, Calif. Internat. J. Air and
Water Poll., v. 9, 1965, pp. 219-231.
- (8) Engdahl, R.B. Trends in Technology and Economics of Energy from
Fuels. II. Heating, Transportation, and Air Pollution. Presented
at A.S.M.E. Annual Meeting, Nov. 7-11, 1965, Chicago, Ill. Paper
65-WA/FU-6.

- (9) Haagen-Smit, A.J., Bradley, C.E., and Fox, M.M. Ozone Formation in Photochemical Oxidation of Organic Substances. *Ind. Eng. Chem.*, v. 45, 1953, pp. 2086-2089.
- (10) Kurtzrock, R.C., Bienstock, D., and Field, J.H. A Laboratory-Scale Furnace Fired with Pulverized Coal. *J. Inst. Fuel*, v. 36, 1963, pp. 55-61.
- (11) Maga, J.A. Considerations in Setting Standards for Oxides of Nitrogen. *J. Air Poll. Control Assoc.*, v. 15, 1965, pp. 561-564.
- (12) Nelson, H.W. Trends in Technology and Economics of Energy from Fuels. I. Fuel Availability, Transport of Energy, Gasification and Carbonization. Presented at A.S.M.E. Annual Meeting, Nov. 7-11, 1965, Chicago, Ill.
- (13) Report of the Surgeon General to the U.S. Congress. Motor Vehicles, Air Pollution, and Health. 87th Congress, 2nd Session, House Document No. 489,427, 1962.
- (14) Sensenbaugh, J.D., and Jonakin, J. Effect of Combustion Conditions in Nitrogen Oxide Formation in Boiler Furnaces. Presented at A.S.M.E. Annual Meeting, Nov. 27-Dec. 2, 1960, New York, N.Y. Paper 60-WA-334.
- (15) Stephens, E.R., Hanst, P.L., Doerr, R.C., and Scott, W.E. Reactions of Nitrogen Dioxide and Organic Compounds in Air. *Ind. Eng. Chem.*, v. 48, 1956, pp. 1498-1504.

CONTROL OF CONTAMINANT EMISSIONS
FROM FOSSIL FUEL-FIRED BOILERS *

by

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INTRODUCTION

There are at least three basic environmental elements which must be considered when examining the needs and the future of mankind. These are land, water and air. For the most part, land and water have been recognized as limited resources and society has been fairly astute in developing methods for their conservation and improvement. Society has not been so discerning, however, with regard to the third element, without which we would cease to exist. The air we breathe has traditionally been regarded as a free and inexhaustible commodity. For years it has been used as an aerial dumping ground for noxious, odorous, and toxic vapors and gases and other contaminating materials. Because of its vastness, it is often difficult to conceive that man's activities could seriously affect its quality. Only recently have all segments of this country become aware that there are real and observable limits to the extent to which man can continue to contaminate this precious resource. We have come to realize that we can no longer encroach upon the air we breathe and that something must be done to prevent its further deterioration.

In terms of need, the air we breathe is of paramount importance. In terms of the actual volumes inspired, our needs are comparatively small, however, when contrasted with the tremendous volumes of air consumed in combustion processes. It has been estimated that each person in the world has about sixty billion cubic feet of air at his disposal. Since the average daily personal intake for breathing is only about three to four hundred cubic

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feet, the air supply would seem to be almost inexhaustible. Population densities, meteorological conditions and topographic factors, however, impose restrictions in some areas on the available supply. For example, in the Los Angeles Basin, when the inversion base is at one thousand feet, there is available roughly five million cubic feet of air per person. On a day of severe smog, the inversion base may be as low as 100 feet, so that the air available is only one-tenth as much or about five hundred thousand cubic feet per person. This is about the same volume of air that the air conditioning industry has estimated is required by a person for his comfort. Air required for the combustion of fuels in the Los Angeles Basin approximates five to six thousand cubic feet per person per day. In terms of actual weight, more air than fuel is used in all combustion processes, including the burning of gasoline in motor vehicles or the burning of fuel oil and coal in steam-electric generating power plants. These combustion processes deplete the natural supply of oxygen in the air and replace it with potentially harmful air contaminants. Thus, the available supply of air is diminished as the demands placed on it become greater.

An eminent scientist and international expert on air pollution recently warned that, "the world's atmosphere will grow more and more polluted until a century from now it will be too poisonous to allow human life to survive--". This statement may seem rather dramatic, but others have also expressed a similar concern about air pollution. The late President Kennedy underlined this concern in his 1962 health message to Congress when he said, "Fresh air cannot be piped into the cities nor can it be stored for future use. Our only protection is to prevent pollution". President Johnson in his message last year to the Congress pointed out that air pollution is no longer confined to isolated places and referred to the health hazard present as a result of air pollution, along with loss of efficiency, reduction in property values, and added costs to the nation. He referred to motor vehicle pollution and to many other sources, particularly the contribution of stationary combustion sources and to the extent that sulfur dioxide and other contaminants were being added to the atmosphere from the burning of fossil fuels.

The effects of air pollution are many and varied and all are objectionable and undesirable. Polluted air is harmful to our health, it damages vegetation and property, offends our senses and lessens our enjoyment of life. Without a doubt, the most serious problem in air pollution today is that which results from the combustion of fuels.

AIR POLLUTION FROM COMBUSTION SOURCES

The extent of an air pollution problem may be measured in a variety of ways--in terms of quantities of contaminants emitted, atmospheric concentrations, and in terms of effects such as health, damage to vegetation, reduction in visibility, rubber cracking, or just plain dirt. The acute

effects of air pollution on health are well documented by disasters in England and in the United States. We know from these incidents that prolonged periods of atmospheric stagnation can result in a build-up of contaminant concentrations which can be lethal. The effects on health from continued exposure to lesser concentrations of air contaminants are not so well documented but are nevertheless recognized by the medical profession. It is noteworthy that high atmospheric concentrations of sulfur compounds have been associated with each of the disaster incidents. For the purpose of this discussion we will examine the air pollution problem from combustion sources in terms of emissions.

Nationally, the air pollution sources requiring the highest priority of attention are motor vehicles and fuel burning, principally for steam-electric power generation. The importance of fuels combustion processes was brought into sharp focus recently in a staff report on air pollution to the Committee on Public Works of the United States Senate ^{1/}, in which it was stated, "These processes replace usable air with potentially harmful pollutants, and the capability of the atmosphere to disperse and dilute these pollutants--especially in urban areas where people, vehicles, and industries congregate in even greater numbers--is strictly limited."

The burning of fossil fuels generates a variety of air contaminants ranging from visible aerosols to invisible inorganic and organic gases. Aerosols is a generic term used to include all solid and liquid particulate matter, including ash, carbon, and sulfur trioxide. The gaseous combustion contaminants include oxides of nitrogen, sulfur dioxide, hydrocarbons, and carbon monoxide. The combustion products from boilers and heaters are sulfur dioxide and its oxidation products, oxides of nitrogen and particulate matter. Carbon monoxide and hydrocarbons are the products of incomplete combustion. The principle source of carbon monoxide and hydrocarbon emissions to the atmosphere is the motor vehicle. In contrast to motor vehicle emissions, the production of carbon monoxide and hydrocarbons from boilers and heaters is virtually negligible. The overwhelming burden of emissions of sulfur oxides, oxides of nitrogen and particulates in the United States today is that originating from the burning of coal and fuel oil in stationary combustion sources. Thus, combustion has a large influence on the quality of the atmosphere in most urban areas. Some of the contaminants from combustion processes are objectionable in the form in which they are emitted, while others are converted into objectionable products after they enter the atmosphere. The best known example is the reaction involving hydrocarbons and oxides of nitrogen in the presence of sunlight resulting in the production of eye irritating and visibility reducing materials contributing to the characteristic conditions often referred to in Los Angeles County as "smog".

Aerosols and Visible Plumes

For many years visible smoke plumes have been the most obvious manifestation of air pollution from combustion processes. Plumes varying in

color from grey to black are produced by finely divided carbon particles entrained in the effluent. This plume phenomenon usually occurs from the combustion of coal and fuel oil. A black smoke plume is indicative of inefficient utilization of fuel and for the most part is not tolerated in large industrial operations. Fuel economy is not equally important, unfortunately, in the operation of most small industrial, commercial and residential installations; and, as a result, these are chief sources of smoke. The obvious remedy for smoke pollution is proper combustion equipment, improved operation and better fuels.

White or yellowish smoke plumes from oil fired boilers and heaters are due principally to sulfur trioxide present in the stack effluent and, to some extent, to particulates which are microscopic in size, varying from one micron to less than one-half micron in diameter. The light scattering ability of particles in this size range is most pronounced. The quantities of particulates from fuel oil combustion are small when compared with those produced by coal burning. Tests on power plant steam generators show that sulfur trioxide in concentrations of as little as 3 parts per million cause a visible plume. At stack concentrations of 15 ppm of SO_3 , a conspicuous plume was emitted ^{2/}. This kind of a stack plume cannot be eliminated by more efficient combustion methods. Typical stack gas particulate loadings for an oil-fired steam generator without controls vary from 0.02 to 0.03 grain per standard cubic foot. A comparable coal-fired unit will produce stack concentrations of the order of 1.5 to 4 grains per std. cu. ft. Removal of sulfur trioxide and sub-micron particulates by mechanical collection and electrostatic precipitation has proven unsuccessful for plume control.

Sulfur Dioxide

Quantitatively, sulfur dioxide is the most significant combustion contaminant. The role of sulfur dioxide in atmospheric pollution has received a great deal of investigation and public attention in the past and is now recognized as a most important air contaminant. With pulverized coal firing, 95 per cent or more of the sulfur in the coal is converted to SO_2 and discharged in the stack effluent. A small amount of the sulfur in the coal may remain in the ash ^{3/} With fuel oil firing, virtually all of the sulfur is discharged as SO_2 . Approximately 1 to 3 per cent of the total sulfur oxides are discharged as SO_3 .

Oxides of Nitrogen

Oxides of nitrogen are the other important air contaminants produced from the burning of coal and fuel oil; and, to a lesser extent, from natural gas. In all combustion processes, some of the nitrogen in the air required for combustion is fixed as nitric oxide. Boiler furnaces, particularly the water-wall types used in large steam generators, offer extremely favorable conditions for the formation of nitrogen oxides. Flame

temperatures can exceed 3000°F. in these furnaces and both oxygen and nitrogen are present in appropriate concentrations for fixation to occur. The extent of fixation is influenced primarily by flame temperature and length of time that the combustion air is in contact with the high temperature flame zone. Other factors influencing the fixation may be classified generally as fuel variables, operating variables, burner and furnace design variables. Coal usually produces a higher yield of nitrogen oxides than fuel oil, with the least amount being produced by natural gas.

Dimensions of the Problem

The principle sources of emissions of the three major air contaminants-- aerosols, oxides of sulfur and oxides of nitrogen--are the combustion of fuels for heat generation for industrial uses, space heating, thermo-electric power generation and for transportation. These sources may be divided into two broad categories--stationary sources and moving sources. Moving sources encompass trains, ships, aircraft and motor vehicles. For purposes of comparison here, however, we will use only motor vehicles as this is the major contributor. The burning of fuels in stationary combustion sources is the major source of air pollution in the nation today.

Based on the 1965 consumption estimate of 70 billion gallons of gasoline, motor vehicle emissions, as shown in Table I, amounted to approximately 4.75 million tons of nitrogen oxides, 150,000 tons of sulfur oxides and 425,000 tons of particulates. ^{4/}

TABLE I
EMISSIONS OF AIR CONTAMINANTS FROM
MOTOR VEHICLES IN THE UNITED STATES, 1965

CONTAMINANT	THOUSANDS OF TONS PER YEAR
Nitrogen Oxides	4745
Sulfur Oxides	150
Particulates	425
Gasoline Consumption -- 70,000,000 Gallons Per Year	

The burning of coal, fuel oil and natural gas contributes over 6.6 million tons of nitrogen oxides or nearly 2 million tons more than that

produced by motor vehicles. Stationary combustion sources contribute over 99 per cent of the sulfur oxides produced and approximately 95 per cent of the total particulate emissions, as shown in Table II.

TABLE II
COMPARATIVE EMISSIONS OF AIR CONTAMINANTS FROM
MOTOR VEHICLES AND COMBUSTION OF FUELS IN
STATIONARY SOURCES IN THE UNITED STATES, 1965

Source	Contaminant Emissions, In Thousands of Tons/Year		
	Nitrogen Oxides (as NO ₂)	Sulfur Oxides (as SO ₂)	Particulates
Motor Vehicles	4,745 (42%)	150 (1%)	425 (5%)
Stationary Combustion Sources	<u>6,600 (58%)</u>	<u>20,800 (99%)</u>	<u>7,640 (95%)</u>
Totals	11,345 (100%)	20,950 (100%)	8,065 (100%)

In Table III a summary is shown of the approximate quantities of coal, fuel oil and natural gas burned annually in the nation and the annual rate of emissions of nitrogen oxides, sulfur oxides and particulates. The total of these three fuels burned annually approximates over 5 billion equivalent barrels. Of this total, coal and fuel oil, including both distillate and residual fuel oils, supply in nearly equal proportions approximately 50 per cent of the total fuel requirements in the United States. The remaining 50 per cent, or approximately 2.5 billion equivalent barrels, is supplied by natural gas. In the order of their pollution potential, coal burning is uppermost, with fuel oil second in importance and natural gas third. Coal burning in stationary sources produced approximately 3 million tons of nitrogen oxides, or over 45 per cent of the total quantity emitted by all stationary fuel burning sources. Fuel oil burning resulted in emissions of 2.1 million tons and natural gas, 1.5 million tons. The burning of coal is also the major source of sulfur oxides emissions. Combustion of coal produces 16 million tons or 77 per cent of the annual emissions of sulfur oxides. Fuel oil burning results in emissions of about 4.8 million tons or 23 per cent of the total annual emissions of this contaminant. Emissions of sulfur oxides from natural gas are negligible.

TABLE III

ESTIMATED ANNUAL FUEL CONSUMPTION AND EMISSIONS FROM
COMBUSTION OF FUELS IN STATIONARY SOURCES
IN UNITED STATES, 1965

Fuel Type	Contaminant Emissions, Thousands of Tons/Year			
	Millions of Equiv. Bbls. (a)	Nitrogen Oxides (as NO ₂)	Sulfur Oxides (as SO ₂)	Particulates
Coal	1300 (25%)	3,000 (45%)	16,000 (77%)	7,000 (92%)
Fuel Oil	1250 (25%)	2,100 (32%)	4,800 (23%)	540 (7%)
Natural Gas	2500 (50%)	1,500 (23%)	Negligible (b)	100 (1%)
Totals	5,050 (100%)	6,600 (100%)	20,800 (100%)	7,640 (100%)

(a) Fuel Oil Heat Equivalents: 1 Ton of Coal = 4 Bbls. of Fuel Oil = 24,000 Cu. Ft. of Natural Gas

(b) Less Than 3000 Tons Per Year

The Future

We can expect that air pollution effects will increase at least in proportion to increases in emissions. The most dismal outlook for the future is to assume that there will be no changes in control technology and in current control efforts; consequently, future emissions would be calculable by applying factors which represent estimates in the increase in the number and the size of sources accompanying increase in fuel use at some future date. Almost every projection of social and economic activity between now and the year 2000 indicates that fuel use and emissions will multiply many fold. Over a quarter of a million industries in the nation are expected to double their activities every 20 years; pollution from thermal power production is expected to increase at a rate of some 20 per cent each year. Forecasts have been made by some authorities which indicate that, by the year 2000, fifty per cent of the U.S. electric generating capacity will be nuclear; nevertheless, it is expected that fossil-fuel fired steam-electric generating capacity will double by 1980 and redouble by the year 2000. Another appraisal has been made on the assumption of controls at the maximum level that technology will allow. Such estimates show, in the case of SO₂ emissions, a 20 per cent increase by 1980 and a 20 per cent decrease by the year 2000. This means that if everything technically possible is done, pollution will "break even" by the year 2000.

CONTROL OF COMBUSTION CONTAMINANTS

Today, while we still do not know all we would like, we have learned a great deal about air pollution and its control; and there are very few industrial emissions that cannot be controlled. Much technology is available which is not now being used in the control of pollution from combustion sources. Often the reasons for this are not technical but social and economic.

The unit processes of contaminant removal from combustion effluents are particulate removal by filtration, centrifugal separation, electrostatic precipitation, fabric filtration; and gas or vapor removal by absorption, adsorption or scrubbing. Some systems use intermediate steps such as agglomeration to aid particulate removal, the use of additives or chemical reaction to change the character of the gas or vapor to aid in its removal. Sufficient knowledge is available about each of these processes to enable the design of systems for particulate, gas and vapor removal where contaminant concentrations are relatively high. However, at lower concentrations current control methods become increasingly difficult and costly, to the point where, as in the case of removal of sulfur dioxide from combustion effluents, new technology is needed. In such cases, the approach to control must necessarily seek to prevent the formation of the emission.

Heat Generation for Industrial Uses and Space Heating

The technology to reduce air pollution effects from emissions associated with heat generation and space heating includes:

1. Promotion of more efficient combustion of fuels assisted by equipment standards and ordinances.
2. Stringent fuel specifications with respect to ash, sulfur, volatility, etc.
3. Methods to reduce emissions of nitrogen oxides.
4. Restriction of fuel types.
5. Substitution of natural gas for oil or coal.

Generation of Electricity

The technology to reduce air pollution effects from emissions associated with the generation of electricity includes:

1. Increasing plant efficiency so that less fuel is needed to produce a given amount of energy.

2. Increasing the efficiency of power distribution and utilization so that total energy requirements are lessened.
3. Increasing the use of nuclear and hydroelectric generation systems.
4. Reducing the emissions of contaminants produced by fossil-fuel burning power plants by such means as:
 - a. For sulfur oxides emissions,
 - (1) Use of lower sulfur bearing fuels.
 - (2) Use of means for removing sulfur oxides from the effluent.
 - b. For nitrogen oxides emissions,
 - (1) Use of fuels which produce lesser amounts of nitrogen oxides.
 - (2) Use of means for preventing the formation of nitrogen oxides.
 - c. For particulate emissions,
 - (1) Use of fuels which produce lesser amounts of particulates.
 - (2) Use of more efficient particulate collection equipment.

Technology is not too adequate today for controlling the contaminants emitted from fossil-fuel fired steam generators, particularly sulfur oxides and nitrogen oxides emissions. More often than not, the problem of air pollution from the combustion of fuels is only solvable in a relatively straight-forward manner, such as by the substitution of fuels. This has been the approach to control adopted by the Air Pollution Control District of Los Angeles County. A similar but much less stringent effort to control emissions from combustion sources was recently adopted by the City of New York.

LOS ANGELES COUNTY VS. NEW YORK CITY - A CASE STUDY

In New York City, sulfur dioxide is considered one of the major air contaminants. A recent Public Health Service study of more than 40 cities showed that New York has the highest average (0.16 ppm) and also experiences the highest average yearly maximum (0.37 ppm) atmospheric concentrations of sulfur dioxide⁵. The primary source of sulfur dioxide

emissions in the City is the burning of fuel oil and coal in stationary combustion sources. In October 1964, New York City adopted an ordinance limiting the sulfur content of solid fuel and residual fuel oil to 3.0 per cent. This is to be progressively reduced to 2.2 per cent over a period of 5 years. The ordinance also restricts the sulfur content of No. 2 fuel oil to 1 per cent. A recent survey of fuel use showed that No. 6 fuel oil burned in the City currently averages 2.31 per cent. Other fuel oils as well as coal now used in the City already meet or are substantially lower in sulfur content than that ultimately required by the ordinance. In essence, the ordinance restrictions are inadequate to curb emissions of sulfur dioxide. In fact, emissions of this contaminant can be expected to increase many fold just as fuel requirements will increase. No processes or equipment have yet been advanced that will reduce substantially all of the contaminants that result from the combustion of solid and liquid fuels. Some progress has been made, however, in methods for removing some of the sulfur compounds and some of the particulates. In view of this, it has been the official determination of the Los Angeles County Air Pollution Control District that the only practical approach to the control of emissions of these contaminants from stationary combustion sources is to use natural gas as a fuel.

Comparative Statistics for New York City and Los Angeles County

The following analysis of fuel usage in New York City in 1964 is based on the fuel consumption estimates found in the City Council Report M-970 (Low Report) and on data obtained from the Consolidated Edison Company and the Air Pollution Control Department of New York City. To facilitate fuel use comparisons shown in Table IV, the quantities of the various types of fuels used are expressed in terms of equivalent barrels of fuel oil.

New York City has a land area of 320 square miles, or roughly one-twelfth of that in Los Angeles County. It has a population of over 8 million or more than 1 million greater than Los Angeles County. In 1964 the total energy and heating requirements of the City required the burning of nearly 140,000,000 equivalent barrels of fuel oil. This fuel requirement was nearly 25 per cent greater than that of Los Angeles County in the same year. Of greater significance, however, is the manner in which these fuel requirements were met. Approximately 20 per cent of the total of all fuels burned was coal and 60 per cent was fuel oil which, in large part, was a high sulfur bearing residual type of oil. The remaining 20 per cent of the total fuel requirements was supplied by natural gas. Of the total gas consumed, over 32 per cent was burned by Consolidated Edison Company. By contrast, in Los Angeles County, approximately 80 per cent of the total fuel requirements were supplied by natural gas. No coal is burned in Los Angeles County, and for all practical purposes, the only fuel oil burned is that which is burned by power plants and refineries out of necessity when natural gas supplies are curtailed to these consumers during the period from November 16 to April 14.

TABLE IV

COMPARATIVE STATISTICS FOR NEW YORK CITY AND
LOS ANGELES COUNTY, 1964

	<u>Los Angeles County</u>	<u>New York City</u>
Population	6,800,000	8,000,000
Land Area, Sq. Miles	4,083	320
Steam-Electric Utilities		
No. of Plant Locations	11	16
No. of Boilers	60	107
Steam Generation, M lbs/hr	35,000	45,000

Summary of Fuels Consumed--Equivalent Barrels *

	<u>Los Angeles County</u>	<u>New York City</u>
Coal	0 (0%)	27,848,000 (20%)
Fuel Oil	9,574,000 (8%)	82,752,000 (60%)
Natural Gas	89,505,000 (80%)	29,270,000 (20%)
Refinery Make Gas	14,337,000 (12%)	(Unknown)
Totals	113,416,000 (100%)	139,870,000 (100%)

Contaminant Emissions from the Combustion of Fuels, Tons Per Day

	<u>Los Angeles County</u>		<u>New York City</u>	
	Avg. Space Heating Day	Max. Space Heating Day	Avg. Space Heating Day	Max. Space Heating Day
Particulate Matter	20	75	380	725
Nitrogen Oxides (as NO ₂)	195	380	615	1030
Sulfur Oxides (as SO ₂)	15	660	1800	2965

* One ton of coal is the heat equivalent of 4 barrels of fuel oil.

The burning of fuels in stationary combustion sources on an average space heating day in New York, as shown in Table IV, produces 1800 tons of sulfur oxides, over 600 tons of nitrogen oxides and 380 tons of particulates. On a comparable space heating day in Los Angeles County, the burning of fuels produces only 15 tons of sulfur oxides, about 200 tons of nitrogen oxides and 20 tons of particulates. On a maximum space heating day in New York City, fuel burning in 1964 produced nearly 3000 tons of sulfur oxides, over 1000 tons of nitrogen oxides and 725 tons of particulates. In contrast, in Los Angeles County, on a maximum space heating day, fuel burning produced 660 tons of sulfur oxides, 380 tons of nitrogen oxides, and 75 tons of particulates.

Control of Fuel Oil Burning in Los Angeles County

The industrial fuel requirement of Los Angeles County are met in quite a different manner from that of the rest of the country. Together, fuel oil, natural gas and refinery produced fuel gas supply essentially 100 per cent of the County's fuel requirements. In terms of total air contaminants emitted to the atmosphere, fuel oil burning by industry, including a refinery complex which is the third largest in the nation, and particularly by steam-electric generating power plants, is a major contributor. Fuel oil burning is the largest source of sulfur oxides emissions and particulates, and the second largest source of nitrogen oxides. Accompanying the unprecedented population and industrial growth of Los Angeles County has been the growth in demand for electric energy; energy which in this area is produced almost entirely by steam-electric generating power plants.

In the last fifteen years, the population of Los Angeles County has increased more than 60 per cent. In the same period of time, the thermo-electric power requirements have more than quintupled, going from 4.5 billion kilowatt-hours per year in 1950 to nearly 23 billion kilowatt-hours per year in 1964. To produce this amount of electrical energy in 1964, power plants burned the equivalent of nearly 35 million barrels of fuel oil. The total of all fuels burned in 1964 by all industry approximated 73 million equivalent barrels. In Table V a breakdown is shown of the annual consumption of fuels in 1964 by the various major source categories, both for Los Angeles County and New York City. Of particular interest is the pattern of fuel use by the commercial and residential category of consumer. In Los Angeles County, natural gas is used almost exclusively by this category of consumer, while in New York City fuel oil is the predominant fuel.

TABLE V
 COMPARISON OF FUELS CONSUMED IN
 NEW YORK CITY AND LOS ANGELES COUNTY, 1964

Annual Fuel Consumption, in Equivalent Barrels		
	<u>Los Angeles County</u>	<u>New York City</u>
Steam-Electric		
Coal	0	21,928,000
Fuel Oil	7,830,000	13,350,000
Natural Gas	<u>27,020,000</u>	<u>9,500,000</u>
Sub-Total	34,850,000	44,778,000
Industrial		
Coal	0	1,600,000
Fuel Oil	1,744,000	5,992,000
Natural Gas	21,604,000	3,670,000
Refinery Gas	<u>14,337,000</u>	<u>(Unknown)</u>
Sub-Total	37,685,000	11,262,000
Commercial and Residential		
Coal	0	4,320,000
Fuel Oil	Neg.	63,410,000
Natural Gas	<u>40,881,000</u>	<u>16,100,000</u>
Sub-Total	40,881,000	83,830,000
Grand Total	113,416,000	139,870,000

The need for control of pollution from fossil fuel fired boilers must consider the types and quantities of fuels consumed and the nature and magnitude of the contaminants emitted. At the same time, consideration must be given to the expected increase in thermal energy demands resulting from community growth and the air pollution potential of fossil fuels expected to supply this demand.

We have estimated that there are some 4000 boilers and heaters, including 60 large power plant steam generators, now operating in Los Angeles County which are fired either with fuel oil or natural gas or with some combination of these two fuels. The total number of individual stationary combustion sources, including small domestic and commercial units, approximates over 7,000,000. The magnitude of contaminant emissions resulting from the combustion of fuels in these sources is extremely large when compared to the total quantities of such contaminants emitted from all sources. Experience has shown that these contaminant emissions can be reduced greatly by the use of natural gas in lieu of fuel oil, and that reductions already accomplished through partial substitution of natural gas have had a measurable impact upon the air quality of Los Angeles County.

Fuel oil burning in Los Angeles County produces three times as much sulfur oxides as produced by all other sources combined, including motor vehicles; as much particulates as would be emitted by 30 completely uncontrolled open hearth steel furnaces; and as much oxides of nitrogen as one million automobiles. Steam-electric generating power plants produce nearly 90 per cent of the total of sulfur oxides, nitrogen oxides and particulates emissions from fuel oil combustion. As shown in Table VI, the burning of fuel oil in a power plant results in the emission of over seven times as much pollution as does the use of an equivalent amount of natural gas. In addition to achieving substantial reductions in nitrogen oxides, amounting to over 50 per cent, the substitution of natural gas for fuel oil results in almost complete elimination of both sulfur oxides and particulates.

In view of these findings, a responsible public agency could reach only one conclusion--that fuel oil must be replaced by a superior fuel. To curb emissions from fuel oil burning, the Los Angeles County Air Pollution Control District adopted Rules 62 and 62.1, which, in effect, require the use of natural gas in lieu of fuel oil. Total air pollution studies have shown that in 1964 these rules prevented average daily emissions of 330 tons of sulfur oxides, nearly 100 tons of nitrogen oxides and approximately 20 tons of particulates. In addition, the rules have prevented other objectively verifiable problems traceable to fuel oil burning, including the occurrence of esthetically offensive visible plumes which much of the time are also in violation of opacity restrictions, generalized reductions in visibility, damage to property and vegetation, and nuisance to a large number of the residents of Los Angeles County.

TABLE VI

COMPARISON OF AVERAGE EMISSIONS OF AIR CONTAMINANTS FROM
POWER PLANTS BURNING FUEL OIL AND NATURAL GAS AND
REDUCTION OBTAINED BY USE OF NATURAL GAS

Type of Air Contaminant	Comparative Emissions Pounds Per Thousand Equiv. Bbls. (a)		Reduction by Use of Natural Gas	
	Fuel Oil	Natural Gas	Lbs/1000 Bbl.	Percent
Particulate Matter	800	20	780	98
Nitrogen Oxides (as NO ₂)	5,000	2,340	2,660	53
Sulfur Oxides (as SO ₂)	10,930 ^(b)	Negligible	10,930	100
TOTALS	16,730	2,360	14,370	86

(a) 6,000 cubic feet of natural gas is considered equivalent, on a heating basis, to one barrel of fuel oil.

(b) SO₂ emissions from fuel oil based on an average sulfur content of 1.54 percent and an average weight per barrel of 355 pounds.

Reductions in Fuel Oil Use Affected by Rules 62 and 62.1

Under the terms of Rules 62 and 62.1, a blanket prohibition is placed on the use of certain gaseous and liquid fuels during specified periods of the year. Fuel oils containing more than 0.5 per cent sulfur are prohibited together with gaseous fuels containing more than 50 grains of sulfur per 100 cubic feet of gas. Rule 62 is operative from April 15 to November 15 and Rule 62.1 applies during the rest of the year. The basic difference between the rules is that under Rule 62.1 a consumer is allowed to burn fuel oil when natural gas service is "interrupted" by the supplier. Under the existing gas supply situation, interruption or gas curtailment commonly occurs during the winter months due to a shortage of natural gas. Curtailment is the result of increased demand by domestic consumers for space heating requirements.

Since its adoption in 1958, virtually no fuel oil of any kind has been burned during the so-called Rule 62 period of the year, with the result that fuel oil's share of the total market has sharply declined--a condition which has been the cause of quite some considerable anxiety to the oil industry. Examination of the historic fuel use by power plants, shown in Tables VII and VIII, reveals the impact of the Rules on fuel oil usage in Los Angeles County. In terms of power plants, alone, total fuel requirements (gas plus oil) have increased from nearly 107,000,000 equivalent barrels in the five years prior to Rule 62 (1954-58) to about 148,000,000 equivalent barrels in the most recent five-year period (1960-64). This represents an increase in total fuel usage of 38 per cent. Nevertheless, total fuel oil consumption declined from 50 million barrels to about 39 million barrels in the same period, for a reduction of approximately 20 per cent.

The Rule has produced even a more dramatic decline in summertime fuel oil use. In 1957, the summertime use of fuel oil by power plants averaged over 30,000 barrels per day. In contrast, power plant fuel oil usage shrank to an almost immeasurable level in 1959, when Rule 62 became effective... 5,250 barrels for the entire summer, or an average of about 34 barrels per day, and all of this was low-sulfur oil (0.5% sulfur, by wt.). Clearly, the major impact of Rule 62 and 62.1 has been to secure a substitution of natural gas for fuel oil. By contrasting contaminant emissions between natural gas and fuel oil it becomes evident how these Rules have reduced the burden of air contaminants released to the atmosphere of Los Angeles County.

TABLE VII

ANNUAL POWER PLANT FUEL USAGE
1954-58, LOS ANGELES COUNTY

Year	Total Fuel Usage * (Gas & Oil)	Fuel Oil Usage	Percent Oil of Total Fuel Usage	Annual Daily Average (Gas & Oil) **
1954	16,591,260	5,012,510	30.2%	45,700
1955	21,099,674	11,111,785	52.7%	57,800
1956	21,476,030	11,417,635	53.2%	58,000
1957	25,669,723	14,557,321	56.7%	70,300
1958	21,944,076	7,414,083	33.8%	60,100
Totals	106,780,763	49,513,333	46.4%	

* In equivalent barrels.

** Total annual fuel use ÷ 365

TABLE VIII

ANNUAL POWER PLANT FUEL USAGE
1960-64, LOS ANGELES COUNTY

Year	Total Fuel Usage (Gas & Oil)	Fuel Oil Usage	Percent Oil of Total Fuel Usage	Annual Daily Average (Gas & Oil) **
1960	26,673,886	9,274,241	34.8%	73,100
1961	27,809,771	7,976,025	28.7%	76,300
1962	29,015,380	7,327,869	25.3%	79,500
1963	29,813,973	6,571,097	22.0%	81,700
1964	34,847,698	7,830,735	22.5%	95,500
Totals	148,160,708	38,979,987	26.3%	

* In equivalent barrels.

** Total annual fuel use ÷ 365

The magnitude of the reductions obtainable by full implementation of Rules 62 and 62.1 is revealed in Table IX. Substitution of natural gas for fuel oil on the peak day of fuel oil usage in 1964 would have reduced daily emissions of sulfur oxides by 740 tons and particulate emissions by 65 tons.

TABLE IX

REDUCTION OBTAINABLE IN PEAK DAY EMISSIONS OF
AIR CONTAMINANTS FROM THE BURNING OF FUELS IF
NATURAL GAS HAD BEEN SUBSTITUTED FOR
FUEL OIL BURNED IN LOS ANGELES COUNTY

Fuel Use Configuration	Contaminant Emissions, Tons Per Day ^(b)		
	Nitrogen Oxides (as NO ₂)	Sulfur Oxides (as SO ₂)	Particulate Matter
Actual peak day emissions from the burning of liquid and gaseous fuels ^(a)	435	740	90
Peak day emissions which would have resulted if natural gas had been substituted for fuel oil	265	Negligible	25
Reductions in emissions which would have been gained in natural gas had been sub- stituted for fuel oil	170	740	65

(a) Peak day of fuel oil usage by interruptible industrial gas consumers.

(b) Emission figures rounded.

Additional Gas Supplies Needed

Although Rules 62 and 62.1 in effect ban fuel oil burning year-round in Los Angeles County, thus far both public law and policy have been frustrated by the lack of adequate gas supplies to provide for the full wintertime requirements of industry and power plants. During the fall and winter months, when gas supplies are limited, fuel oil burning contributes to a dramatic increase in atmospheric concentrations of pollution. Sulfur dioxide concentrations increase by 50 to 100 per cent; nitrogen oxide and aerosol concentrations increase by 300 to 400 per cent. In fact, nitrogen oxide concentrations have twice exceeded the District's first alert level of 3 ppm.

For over three years hearings have been in progress before the Federal Power Commission on two competing natural gas supply projects which have been specifically designed to commit major gas supplies for year-round power plant use in Los Angeles County. One is the Gulf Pacific Pipeline Company project for which the Southern California Edison Company and the Los Angeles Department of Water and Power have contracted. The other is an alternative proposal by the Transwestern Pipeline Company and the El Paso Natural Gas Company, supported by the Southern California and Southern Counties Gas Companies. The Air Pollution Control District, by order of the Board of Supervisors of Los Angeles County, intervened in these proceedings in the public interest to support certification of the project or projects which would provide the largest volumes of natural gas, at the earliest date, for the greatest number of years and at a reasonable price, to the end that industry and power plants in Los Angeles County will be able to burn natural gas exclusively on a year-round basis. The primary objective of the intervention is to secure cleaner air for Los Angeles County.

Two intervenors in the Federal Power Commission proceeding, the Western Oil and Gas Association, and one of its members, the Standard Oil Company of California, have opposed Rules 62 and 62.1 from the day that the rules were proposed. They have asserted that the burning of fuel oil can safely be ignored and that the air contaminants emitted from such combustion have no effect whatsoever on the air quality of Los Angeles County. Nothing could be further from the truth.

On December 16, 1965, Federal Power Commission Presiding Examiner Alvin A. Kurtz filed an initial decision which would authorize Gulf Pacific Pipeline Company to build a \$314,000,000 pipeline to transport natural gas purchased in Texas by Edison Company and the Department of Water and Power for use as a boiler fuel in their power plants. The examiner at the same time rejected competing applications by Transwestern and El Paso for an alternative project. 6

In his decision, Examiner Kurtz said, "The preponderance of the evidence is against the contentions of Western Oil and Gas Association and in

favor of the benefits to be derived by the people in the Los Angeles Basin by the use of gas under the boilers in the power plants therein. The record here is clear that the public wants the increased level of gas service and is ready to pay for it. The benefits not only relate to the health of the people and their welfare but also to the loss of food and fibre crops in the Los Angeles area which has been estimated to be in excess of \$5,000,000 annually." He added, "The advantages of using natural gas in the power plants instead of fuel oil is that no ash is found in the combustion of natural gas, no oxides of sulfur, nitrogen oxides are less than one-half the amount produced from fuel oil burning and the problem of opacity violating stack plumes is eliminated."

Examiner Kurtz continued, "Public complaint as to air pollution is continuous and wide spread, including complaints directed to the operation of steam-electric generating plants. These complaints include eye irritation and respiratory discomfort. The present atmospheric conditions in the Los Angeles Basin do present a health problem. This is borne out by the testimony of three outstanding doctors of medicine specializing in this field, called by the APCD." He went on to say, "The Los Angeles air pollution problem will not be eliminated by the increased use of gas under boilers but the reduction in tonnage of pollutants in the magnitude here under consideration will affect the concentrations of contaminants and aid in the program of the APCD to reduce air pollution to the benefit of the people in the Los Angeles Basin."

merits of any scientific controversy over the burning of fuel oil, are faced with regulatory prohibitions against the burning of fuel oil, public complaints about such burning and advice from the medical fraternity to its patients to the effect that air pollution is harmful. These facts, alone, impose upon Edison and Department the public duty to minimize, if not eliminate, the burning of fuel oil in their steam-electric generating plants in the Los Angeles Basin." Concerning coal burning, the Examiner said, "The Los Angeles County Air Pollution Control District has made it clear that it will not tolerate coal burning in the Los Angeles Basin." Following oral arguments before the Commission on March 29, 1966, a final decision will be rendered in this case.

In its latest attack on the Rules, the Western Oil and Gas Association filed a lawsuit in Los Angeles County in which it asked the Superior Court to declare Rules 62 and 62.1 unlawful (Superior Court No. 836, 864). The complaint alleged six causes of action. The court rejected five of the six Western Oil and Gas Association charges before trial. In the sixth charge, WOGA challenged the entire rule making power of the District under the Air Pollution Control Act adopted in 1947 by the California Legislature, and further alleged that Rules 62 and 62.1 were arbitrary, capricious and void and are a deprivation of the equal protection of the law and a deprivation of property without due process of law. On January 26, 1966, after nearly a year of litigation, the court ruled against

WOGA on the remaining charge. In his decision the judge ruled that, "The power to control the release of air contaminants clearly encompasses the power to regulate the burning of fuels since no fuel can be burned that does not emit or result in the release in the atmosphere of some kind and quantity of contaminants." He went on to say that, "Neither Rule 62 nor Rule 62.1 varies or enlarges the terms of the Act. They are consistent and not in conflict with it." Also that, "The argument that said rules are beyond the rule-making power delegated to the Board falls before the terms of the Act and the facts of this case." The judge further said, "The wisdom, propriety or necessity for Rule 62 or 62.1 is the primary function of the Board of the District and not the judiciary. If there is any rational connection between the adopted rules and the legislative purpose, the rules are impervious to attack." He added, "It is plain that there is a rational factual connection between the prohibition of fuel burning and the release of contaminants into the air. The objective of the Act was the control and suppression of air pollution. The prohibition of fuel burning unquestionably serves that end."

The air pollution evidence presented by the Western Oil and Gas Association in this Superior Court case showed its position there to be as lacking in merit as that before the Federal Power Commission.

POWER PLANT POLLUTION CONTROL IN LOS ANGELES COUNTY

Any discussion of control equipment per se to reduce air pollution from fossil fuel-fired boilers must necessarily be limited to power plant steam generators or other combustion equipment of comparable size. Attempts to reduce emissions from smaller units have mainly been concerned with the relatively heavy particulate concentrations emitted during soot blowing. Emissions are definitely influenced by burner and furnace design and configuration and some improvement can be achieved in this area, but the best approach to control of smaller units is to use cleaner fuels, such as natural gas.

The electric utility industry in Los Angeles County must be commended for its outstanding efforts to resolve its power plant pollution problem. The industry, in cooperation with the Air Pollution Control District, has made significant contributions in the development of means for reducing or controlling pollution from fuels combustion. Beginning in 1956 with the formation of the Joint Research Council on Power Plant Air Pollution Control, the combined talents of the electric utility industry in cooperation with the District were directed to the control of power plant pollution. Notable among the contributions of the industry to power plant pollution control has been the research to control sulfur oxides emissions, the development of two-stage combustion controls to reduce nitrogen oxides emissions, research on plume formation, experimental work on electrostatic precipitators and the bag filter house for particulate removal and, most recently, the vigorous efforts of the Southern California

Edison Company and the Department of Water and Power to obtain a year-round supply of natural gas for their steam generating stations.

Joint Research Council

The Joint Council was organized in March 1956 by the Southern California Edison Company, the Los Angeles Department of Water and Power, and the Los Angeles County Air Pollution Control District. The municipal electric utilities of Glendale, Burbank, and Pasadena joined the Council immediately upon its organization, and a short time later, the Air Pollution Control Districts of the adjacent Counties of Orange, San Bernardino, and Riverside became associate members of the Council. The Council's stated objective is "to arrive at a better understanding of the mutual problem and to develop a program to promote progress in the development of further corrective measures of control of air pollution from fuel burning power plants of electric utilities in the Los Angeles Basin, through cooperative efforts in the development and interpretation of data and free interchange of information related to air pollution; and to keep the membership advised of the activities and progress."

Control of Sulfur Oxides

Control of sulfur oxides has been given major attention by Council member agencies. Removal of the comparatively minute quantities of sulfur trioxide appears practical. Presently available commercial methods of removing sulfur dioxide have been investigated but none appears practical at this time for the low concentrations of this gas in the large volumes discharged from power plant stacks. Investigations of stack gas treatment for removal of sulfur dioxide and of possible methods of treatment of fuel to remove sulfur are being continued by Council members.

Visible Plume Control

Because of the State law on plume opacity, which is violated when fuel oil is burned by steam-electric generating plants in the Los Angeles Basin, a major part of the research efforts of the utility members has been directed toward determining the causes of plume opacity and means of reducing it. At present, some of the principle factors in plume opacity are known, but many others have not been determined as yet. Tests have been made to determine how plume opacity might be eliminated through variation of operating techniques, the use of chemical additives and mechanical and electrical devices. Although a complete solution to the plume opacity problem has not been found, the information which has been derived from these tests has brought the solution much closer. The Edison Company's adaptation of the electrostatic precipitator to fuel oil firing was a step forward in the control of particulate matter, but its effectiveness in controlling plume opacity was unsatisfactory.

Electrostatic Precipitator

The Edison Company initiated a precipitator test program for particulate removal and plume control early in 1955 in cooperation with the APCD. The first phase of this program was designed to investigate precipitator performance on a pilot plant basis. The electrostatic precipitation process was originally selected for pilot plant investigation on the basis of experience developed in coal fired power plants. Edison's pilot plant work demonstrated that major changes in precipitator design were necessary in order to obtain high collection efficiencies on the relatively low particulate load characteristics of oil fired boilers. As the result of nearly three years of intensive investigation, including the services of several consultants and an expenditure of over a half a million dollars, Edison ultimately obtained collection efficiencies of about 95-98 per cent on a pilot unit. Visual evidence also was obtained indicating excellent control of plume formation. Based on these results, Edison installed a full-scale prototype precipitator on its No. 2 unit at its El Segundo steam station in December 1958.

Edison's prototype plant, however, was a failure. Attempts to obtain the efficiency and practicability which had been indicated by the pilot plant investigations were unsuccessful. Although plume control was outstanding on the pilot unit, stack emissions from the full-scale unit did not comply with the District's opacity regulations. In addition, the equipment experienced numerous component failures and continued corrosion problems, which, in one instance, caused a complete boiler shutdown. Although installation and modification of the electrostatic precipitator by Edison has required over one million dollars in expenditures, it was Edison's final judgment that satisfactory performance and reliability could not be achieved with an electrostatic precipitator on oil-fired steam generators.

Two-Stage Combustion Controls

Experimental work by the Joint Council, and particularly by the Southern California Edison Company in cooperation with the Babcock and Wilcox Company over the past five years, has led to the development of burner and equipment modifications on one type of power plant boiler design that reduces the average production of nitrogen oxides by about 40 per cent at full load operation. These modifications, which have been termed "two-stage combustion", are effective in reducing the formation of nitrogen oxides when either oil or natural gas is used as a fuel. In its present stage of technical development, two-stage combustion, as a control method, is applicable only to large front-fired power plant boilers. Theoretically, at least, two-stage combustion modifications are applicable to all power plant boilers; however, the adoption of this method would necessarily be preceded by a period of experimentation on each type of unit to be modified. In two-stage combustion, approximately 90 per cent

of the air required for combustion is introduced at the burner tip. The remainder of combustion air is introduced through auxiliary airports installed above the burners. Major furnace modifications are required on existing boilers to permit the use of this type control. However, if incorporated in the original design, the modifications are comparatively minor.

Bag Filter House

Extensive research work and pilot plant studies by the Southern California Edison Company has led to the development of a full-scale prototype bag filter house as a means for controlling particulate emissions from fuel oil combustion. In the past, the bag filter house has been considered impractical for power plant application because of such inherent filter fabric limitations as temperature, pressure drop and fabric deterioration. Results of full-scale tests indicate that these limitations can be largely overcome by selection of suitable bag material and by the addition of alkaline additives to the gases entering the filter house. In operation, the bag filters are pre-coated with dolomite before startup. The additive is continually injected into the gas stream at two to three times the stoichiometric equivalent of the sulfur trioxide content of the flue gases. Sulfur trioxide reacts in the gas stream and on the surface of the bags to form calcium sulfate, a collectible solid. This control device removes only sulfur trioxide and particulates. It has no effect on sulfur dioxide or nitrogen oxides.

Edison's prototype bag filter house has been operated intermittently since February 15, 1965. Many equipment and operating difficulties have been encountered over the past year. Fabric deterioration and failure have required replacement of all 1200 filter bags at a cost in excess of \$30,000. Other technical difficulties encountered with the baghouse have included:

1. Gas leakage into the bag compartments when baghouse is out of service resulting in condensation and corrosion problems.
2. Unequal distribution of stack gases in the baghouse.
3. Excessive pressure drop and accompanying high power requirements.
4. Fabric damage caused by filter bag clamps and mechanical problems with bag suspension systems.
5. Failure to obtain uniform distribution and deposition of powdered dolomite additive.

6. Caking of material on filter bags due to moisture.
7. Problems with reverse-flow bag cleaning operation.
8. Major difficulties with conveying and disposal of collected material.

Edison's expenditures for research, pilot plant studies and installation and testing of the full-scale prototype bag filter house have already exceeded \$1,200,000. Experimentation and tests on the baghouse by Edison are expected to continue for at least another year. In view of Edison's experience with the electrostatic precipitator and the current status of their bag filter house, the APCD has concluded that there is presently no completely satisfactory method available for controlling contaminant emissions from fossil fuel burning power plants, other than to use natural gas.

Conclusions

Almost every projection of social and economic activity between 1960 and the year 2000 indicates that pollution from fossil fuels combustion will multiply many fold. 7/ 8/ A few key indicators are:

1. United States population will double.
2. Electric power production in the U. S. will increase from 850 billion kilowatt-hours per year to over 2800 billion kilowatt-hours in 1980 and to about 3700 billion kilowatt-hours in the year 2000.
3. In 1980, nearly two-thirds of the total electrical power requirements will be provided by fossil fuels and, in 2000, from 40 to 50 per cent will be provided by fossil fuels.

These estimates of national growth suggest that if we are concerned with the deterioration of our air environment now, we will have much more cause for anxiety in the next four decades. It is too often concluded that more effective technology must be developed or that more research must be done. Indeed, further research is needed, but there is a great deal which can be done right now. It is impossible to predict the point in time when critical concentration of pollutants in the atmosphere may be reached. Past experience has been that air pollution is virtually ignored until levels are reached where detrimental effects are observed. Control of pollution from fossil fuels combustion is one of the most compelling problems in air pollution today. Steps to reduce pollution from this source which are scientifically and technically possible must be taken now. To wait any longer is to wait too long.

REFERENCES

1. A Study of Pollution--Air, A Staff Report to the Committee on Public Works, United States Senate, 88th Congress, 1st Session, September 1963, U.S. Government Printing Office, Washington: 1963.
2. H.C. Austin and W. L. Chadwick, Control of Air Pollution From Oil Burning Power Plants, presented at the annual meeting of the American Society of Mechanical Engineers, Atlantic City, New Jersey, November 29 to December 4, 1959.
3. S. T. Cuffe and R. W. Gerstle, Emissions from Coal-Fired Power Plants; A comprehensive summary, presented at the American Industrial Hygiene Association meeting, Houston, Texas, May 1965.
4. A Regional Look at U.S. Gasoline Markets, Oil and Gas Journal, Vol. 64, No. 2, P. 32, January 10, 1965.
5. Air Pollution in New York City, Council of the City of New York, M-970 An Interim Technical Report of the Special Committee to Investigate Air Pollution, June 22, 1965.
6. Presiding Examiner's Initial Decision upon Applications for Certificates of Public Convenience and Necessity under the Natural Gas Act. Docket Nos. CP63-204 et. al., United States Federal Power Commission, December 16, 1965.
7. A. N. Heller and D. F. Walters, Impact of Changing Patterns of Energy Use on Community Air Quality, A.P.C.A. Journal, Vol. 15, No: 9, September 1965.
8. National Power Survey, A Report by the United States Federal Power Commission, 1964, U.S. Government Printing Office, October 1964.

OBJECTIVE MEASUREMENT OF SMOKE FROM COMBUSTION SOURCES

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INTRODUCTION

Interest in fine particle pollution began a long time ago. In England, the Owens Pollution Recorder has been used for many years to determine atmospheric concentrations of smoke. Early in the 1950's Hemeon developed the AISI automatic smoke sampler and demonstrated the logic of drawing a relatively small sample of air through a white filter paper strip with automatic indexing and evaluating the residue retained on the paper by optical means. (1). The unit of measurement of the resultant sample suggested by Hemeon is called the Coh Unit and is defined as that quantity of light scattering solids producing an optical density of 0.01 when measured by light transmission.

The City of Cincinnati, Division of Air Pollution Control, early recognized the value of making continuous measurements of the non-settling particulates in the general atmosphere and has maintained several such monitoring stations since 1952. (2) It has considered that the soiling of light-colored surfaces is of particular interest and that the evaluation of the stain by light reflectance is preferable to transmission. In order to differentiate the results obtained by reflectance, the unit of soil was christened the Rud (Reflectance Unit of Dirt), the Rud value being that quantity of light scattering solids producing an optical density of 0.01 when measured by light reflectance.

Rud or Coh values are further standardized to a unit volume of air filtered through a unit area of filter. The resultant values have become known as the Soiling Index (3) of the atmosphere, and are generally reported as Ruds or Cohs per 1000 linear feet of air, equivalent to filtering 1000 cubic feet of air through one square foot of filter area.

NEED FOR A METHOD OF QUANTITATING SMOKE EMISSION

The smoke plume from the incomplete combustion of the volatile matter in fossil fuels is an important source of fine particles in many urban atmospheres. Most black smoke plumes from combustion sources contain only an infinitesimal weight of particulate matter even though at times such plumes appear to be solid black. The opacity is due to the presence in the smoke plume of a tremendous number of sub-micron carbon particles which have a highly effective light scattering effect but contribute little to the mass of the emission. Therefore, quantification in mass emission units or light concentration is not a practical measurement and authorities rely almost universally on subjective evaluation such as the Ringelmann Chart.

THE SOILING POTENTIAL METHOD APPLIED TO SMOKE PLUME MEASUREMENT

In view of the success in quantitating the build-up of fine particles in community atmospheres by the soiling index method it appears only logical that this same method

could be applied to evaluating the source strength of smoke plumes in objective units. Such objective units could then be used in the development of emission inventories, in cause and effect studies, and in setting objective performance criteria for combustion equipment.

The analogy between weight units and optical units is illustrated in Table I. It can be seen that for every mass unit there is a corresponding optical unit.

TABLE I COMPARISON BETWEEN COMMON WEIGHT UNITS AND OPTICAL SOILING UNITS (4)

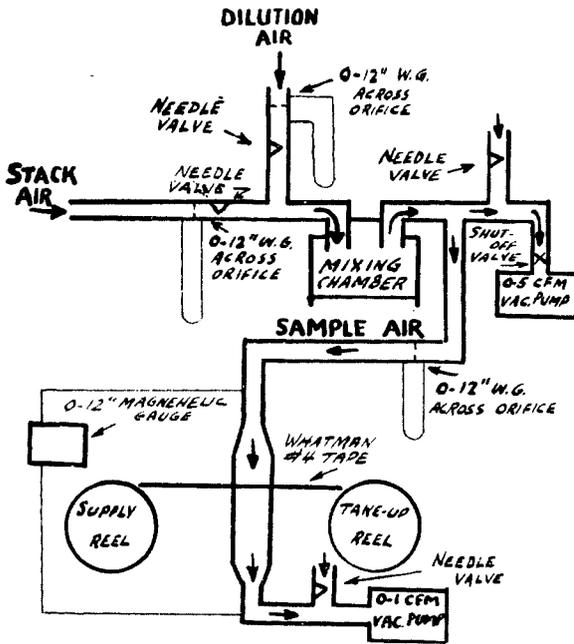
Quantity	Weight Units		Optical Units	
	Metric	English	By Trans.	By Ref.
	Gms	Pounds	Coh-ft ²	Rud-ft ²
Concentration	gms/cc	lbs/1000# gas grains/scf	Coh-ft ² /ft ³ Also: Coh-ft ² /1000 ft ³ (Coh/1000 ft)	Rud-ft ² Also: Rud-ft ² /1000 ft ³ Rud/1000 ft)
Rate (time)	gms/l.in.	lbs/min.	Coh-ft ² /min.	Rud-ft ² /min.
Rate (fuel)	gms/kg coal	lbs/# coal	Coh-ft ² /# coal	Rud-ft ² /# coal

THE SOILING POTENTIAL SAMPLER

In 1953, Hemeon (1) applied the automatic tape sampler to a stoker-fired coal burning boiler plant and reported the smoke emissions in terms of Coh-ft²/min. When such information is obtained, it is necessary to know only the total gas flow and by simple arithmetic calculation the total quantity of smoke in Coh-ft²/unit of time can be obtained.

In 1964, the authors, using a sampling train similar to that arranged by Hemeon, constructed the Soiling Potential Sampler (SOPOS). Figure 1 shows the sampling train and Figure 2 is a photograph of SOPOS, Model 4. Essentially the instrument is arranged to draw a variable sample of the combustion gases from the breeching either directly through the filter tape or through a circuit which first dilutes the sample from the source. From the direct extraction or from the diluted sample, a portion is taken through the filter tape at a rate of approximately 1/4 cfm. Isokinetic sampling is not considered necessary because of the sub-micron size of the smoke particles. Sampling time must be adjusted according to the concentration of the smoke in the source so that a combination of sampling rate and time will produce a spot having a reflectance of greater than 50%. The spots are moved, or indexed, manually as they are completed. Data are recorded on a log sheet as the test progresses. The spots are evaluated by means of a reflectance meter, and the soiling potential in terms of Rud-ft²/cu.ft. of gas sampled is calculated.

A sample calculation is shown in Appendix 1.



SCHEMATIC DIAGRAM OF
SOILING POTENTIAL SAMPLER
 (MODEL #4)

Figure 1

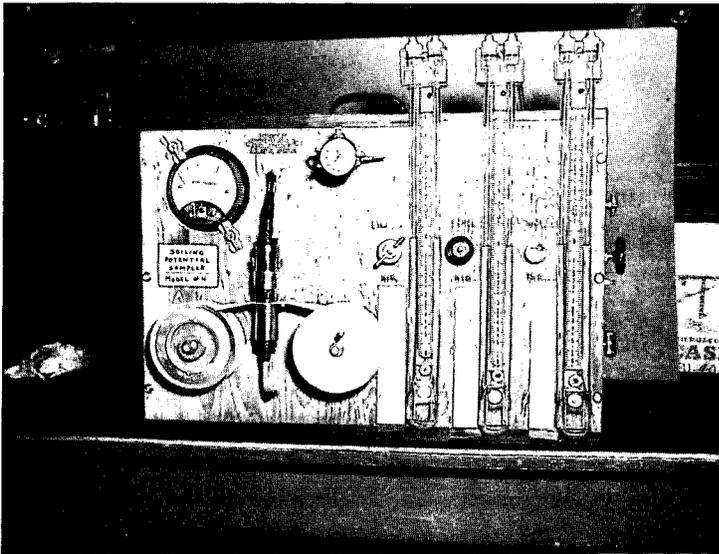


Figure 2

FIELD TESTING

To date 17 tests have been made on 9 different plants ranging from a small 70 H.P. steel fire tube boiler, fired by a single retort underfeed stoker, serving a school heating load to a 225,000 lb. water tube boiler, fired by pulverized fuel burner, serving an industrial steam processing load. One test on one plant taken during start-up of a newly installed boiler was discarded because the operating conditions were not considered typical.

The average value of soiling potential per cubic foot of stack gas for 16 tests was 1.10 Ruds-ft²/cu.ft. with a maximum of 7.4 and a minimum of .05. The soiling potential per pound of coal burned was an average of 134 with 1250 maximum and 9 minimum. Figure 3 shows the average soiling potential for the 9 different plants tested while Table II summarizes the results of the 16 tests.

SOILING POTENTIAL VS VISIBLE SMOKE

There appears to be good correlation between the soiling potential and opacity of plume for any one plant.

Plant No. 9 contains a newly installed 85,000 lb. steam/hr. water tube boiler fired by a traveling grate spreader stoker. The plant is equipped with a moderate draft loss collector with decanting re-injection and a good over-fire-air smoke consuming system. The combustion controls include a Bailey recording smoke meter.

During the test 300 samples were taken one each minute or less for 4½ hours. Readings were made from the smoke meter chart once each minute and periodic observations of the visible plume were made and recorded as Ringelmann Numbers.

Figure 4 shows a plot soiling potential values in Rud-ft²/cu.ft. of stack gas versus time. Directly above is the plot of the smoke recorder values as percent of chart. The individual observations are indicated by circles. Visual comparison shows excellent and sensitive correlation while statistical analysis shows a correlation coefficient of .90 (5).

Another type of test was run on Plant 4. A city air pollution inspector made smoke observations from a post about 1/4 mile from the stack. Using conventional procedures he recorded the opacity of the plume in Ringelmann numbers on 1/4 minute intervals. The observed smoke is plotted against SOFO values in Rud-ft²/cu.ft. in Figure 5 and again it can be seen that a general correlation between soiling potential and observed opacity exists for this one plant.

SOILING POTENTIAL FOR EMISSION INVENTORY FOR COMBUSTION SMOKE PLUMES

Soiling potential per pound of fuel burned will lend itself readily to an emission inventory of smoke particles from incomplete combustion of the volatiles in the fuel burned in any given area. It is only necessary to make sufficient numbers of tests of representative equipment under all operating conditions to obtain a statistical average. Then, by knowing the total fuel burned in any significant unit of time the total contribution of incomplete combustion of this fuel to the dark particle soiling index of the general atmosphere can be calculated.

The Cincinnati Division of Air Pollution Control in cooperation with the Meteorological Section of PHS, Division of Air Pollution at Taft Center in Cincinnati, explored this procedure which produced encouraging results. A rather accurate estimate was made of

Figure 3
SOILING POTENTIAL OF NINE BOILER PLANTS

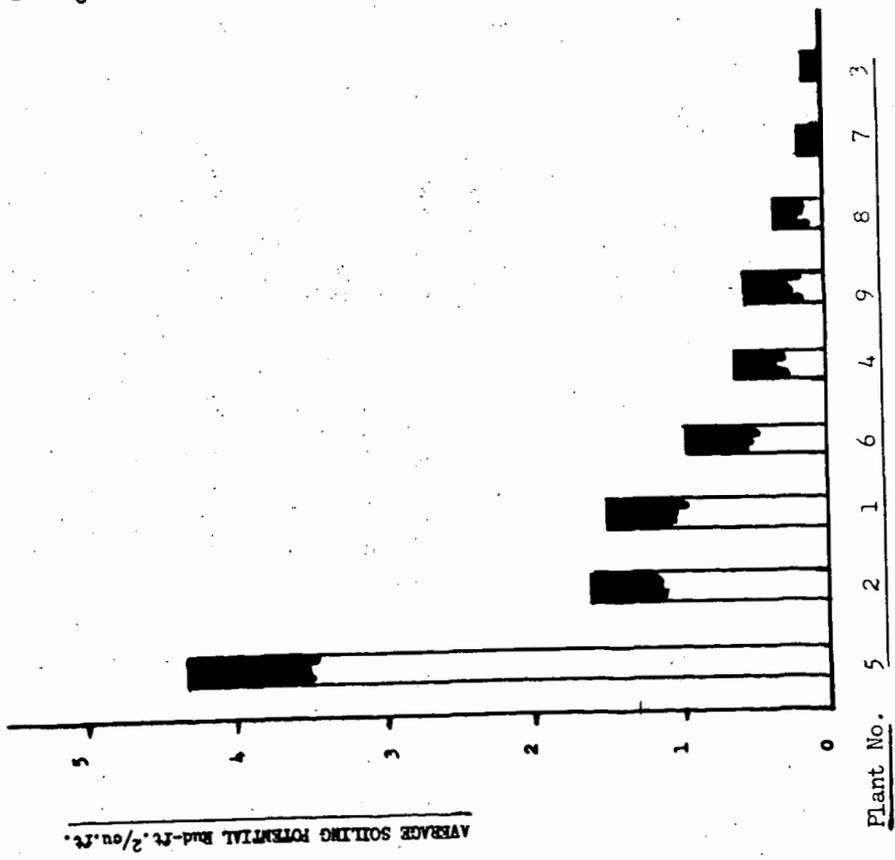


FIGURE 4
SOILING POTENTIAL VS. RECORDED AND OBSERVED SMOKE

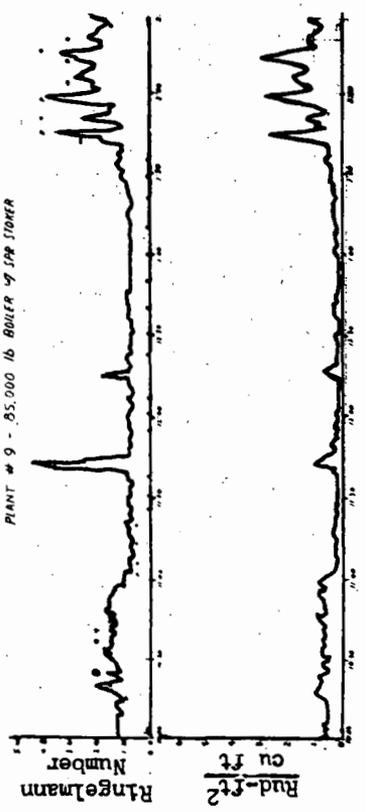


FIGURE 5
SOILING POTENTIAL VS OBSERVED SMOKE

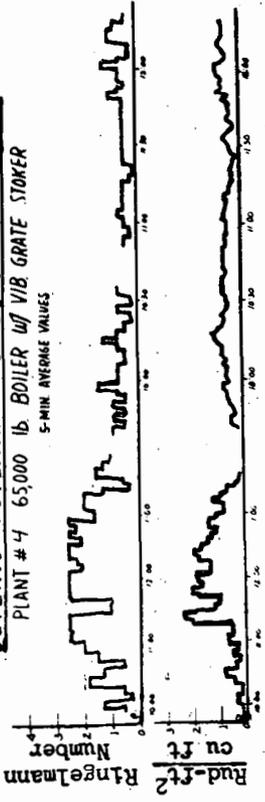


TABLE II

PLANT	BOILER	METHOD OF FIRING	NO. OF TESTS	SOILING POTENTIAL		
				RUD-FT2/CU.FT. STACK GAS AV.	RUD-FT2/# COAL Max. Min.	RUD-FT2/# COAL AV. Max. Min.
1.	38,000# W. T.	Spreader Sta. Grate	3	1.43	4.6	.11
2.	189 H.P. St. F.B.	U.F. Stoker Single Retort	3	1.53	7.4	.06
3.	200,000# W. T.	Pulv. Fuel	1	.07	.09	.05
4.	65,000# W. T.	Vibrating Grate	4	.60	2.54	.06
5.	71.5 H.P. St. F.B.	U.F. Stoker Single Retort	1	4.3	5.6	2.9
6.	26,800# W. T.	U.F. Stoker Single Retort	1	.9	1.9	.19
7.	225,000# W. T.	Pulv. Fuel	1	.20	.28	.14
8.	65,000# W. T.	7 Retort Underfeed	1	.32	.82	.12
9.	85,000# W. T.	Spreader Trav. Grate	1	.57	2.88	.15
SUMMATION OF ALL TESTS				1.10	7.4	.05
					134	1,250
						9

coal consumed in one segment of the city between 8:00 and 9:00 a.m. on a cold day. A DFO value of 500 Rud-ft²/lb. coal burned was used and the total emission in Rud-ft² between 8:00 and 9:00 a.m. from all coal burning sources was calculated. Then using the working equation reported by Clarke (6) in his development of a simple diffusion model for calculating point concentrations from multiple sources, the expected smoke particle concentration (Soiling Index) in the general atmosphere was determined.

The calculated values of soiling index for the Downtown Cincinnati Station with light W winds and slightly stable atmosphere was 1.4 Rud-ft²/1000 cu.ft. (Rud/1000 ft) and for moderate WNW winds with neutral condition was .4 Rud-ft²/1000 cu.ft. Those familiar with soiling index measurements in the general atmosphere will recognize such values as being representative of levels measured in many communities.

SUMMARY - USES & ADVANTAGES OF THE SOPO METHOD OF SMOKE MEASUREMENT

In summary there is strong indication that the soiling potential method of quantitating smoke plume values will produce reliable information which can be used in a number of different fields related to the soiling of light colored surfaces by dark colored sub-micron smoke particles.

It produces sensitive, reproducible, objective quantity measurements of smoke particles resulting from incomplete combustion of the volatile matter in fossil fuels.

The resultant measurements are in terms of concentration: soiling potential per cubic foot of combustion gas (Rud-ft²/cu.ft.) or rate soiling potential per unit of fuel input (Rud-ft²/lb. coal).

The resulting value of soiling potential per unit of fuel lends itself to quantitating the emission per unit of time from single or multiple sources within an area by simple arithmetic calculations. The summation of source strengths, in the same terms as the measurement of the resultant soiling index of the atmosphere, provides a ready means of estimating the contribution of various combustion sources to the total build-up of fine particles in the atmosphere. Such information is invaluable in estimating the corrective action within an area in order to reduce the fine particle pollution in any air pollution control effort.

REFERENCES

- Hemeon, W. C. L. Determination of Haze and Smoke Concentration by Filter Paper Sampler. Air Repair 3, No. 1, August, 1953.
- Gruber, C. W. The Automatic Filter Paper Sampler in an Air Pollution Measurement Program. Air Repair, November, 1954.
- Schumann, C. E. and Gruber, C. W. A Recommended Method for Soiling Index Surveys by Automatic Filter Paper Sampler. J. of APCA. December, 1960.
- Hemeon, W. C. L. Personal conversation.
- Linear Regression Analysis by Technical Assistance Branch, Div. of A.O., USPHS, Taft Sanitary Engineering Center, Cincinnati. April, 1965.
- Clarke, J. F. A Simple Diffusion Model for Calculating Point Concentrations from Multiple Sources, J. of APCA 14, No. 9, September, 1964.

APPENDIX 1CALCULATING SOILING POTENTIAL VALUES - EXAMPLE

<u>SAMPLE DATA:</u>	Duration of Sample	<u>Air Flow Data</u>		Dilution Air	% CO ₂	Density of Spot, % Reflectance
		Sample Air	Stack Air			
	5 min.	.23 cfm	.11 cfm	3.1 cfm	11.5	80

CALCULATING VOLUME OF STACK GASES SAMPLED:

$$\text{Dilution Ratio: } \frac{.11}{.11 + 3.1} = \frac{.11}{3.21} = .034$$

$$\text{Volume of stack gases sampled: } .23 \text{ cfm} \times 5 \text{ min.} \times .034 = .039 \text{ cu.ft. (Q)}$$

CALCULATING SOILING POTENTIAL:

$$\text{Rud-ft}^2/\text{ft}^3 = \frac{\text{O.D.} \times 100}{Q/A} \quad A = .0054 \text{ sq.ft. (area of spot)}$$

$$\text{O.D.} = \log_{10} \frac{100}{\% R} = \log_{10} \frac{100}{80} = .097$$

$$\text{Rud-ft}^2/\text{ft}^3 = \frac{.097 \times 100}{7.2} = \frac{9.7}{7.2} = 1.3$$

CALCULATING Rud-ft²/lb. of COAL BURNED:

Theoretical: 143 cu.ft. of air required to burn 1 pound of coal.
(for coal at 14,550 Btu/lb.)

$$11.5 \% \text{ CO}_2 = 58\% \text{ Excess Air} = 83 \text{ cu.ft. of Excess Air}$$

$$\text{Total air per pound of coal} = 143 + 83 = 226 \text{ cu.ft.}$$

$$\text{Then, } 1.3 \text{ Rud-ft}^2/\text{ft}^3 \times 226 \text{ cu.ft.} = 294 \text{ Rud-ft}^2/\text{lb. of coal}$$

Gaseous and Particulate Emissions from Shale Oil Operations

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World-wide and domestic demands for hydrocarbons tend to seek the most economical and convenient sources for potential exploitation. It has been said that the oil shale deposits of the world constitute many times the total of the world's reserves of liquid petroleum. The oil shale beds of some 16,000 square miles in the states of Colorado, Utah, and Wyoming constitute the world's greatest reserve of hydrocarbons.¹ It is only a question of time until these sources will be used.

President Johnson, in his state of the union message of January 4, 1965, made this pertinent remark, "... we will seek power to prevent pollution of our air and water before it happens...", a statement that emphasizes the national feeling at this time. None of the recent, comprehensive papers^{2,3,4,5,6,7} on shale oil technology mentions or alludes to air pollution. In a paper delivered to the Second Symposium on Oil Shale at Golden, Colorado, on April 22, 1965, Frank J. Barry, Solicitor, U. S. Department of the Interior, mentions air pollution as one of the factors to be considered in a national policy for oil shale.⁸

The deposits in the Piceance Basin of Colorado, being the most economically attractive in the United States, will likely be the location of the first commercial oil shale plant. The major patented oil shale mining claims owned by some 25 companies, where the shale industry will likely begin, lie mostly on the southern part of the Piceance Basin and cover an area of approximately 800 square miles. The shale oil reserves in this area, containing 25 gallons of oil per ton of shale or more, contain approximately 55,000 million bbls.

The Piceance Basin lies between the Colorado and White Rivers, which are approximately 50 miles apart. Both rivers flow in a generally western direction. The elevation of the Colorado River at this point is approximately 5000 ft., and of the White River, approximately 6000 ft. Between the two rivers the land forms a plateau (see Figure 1) having an elevation of 7500 to 8500 ft.; this plateau is cut by numerous gulches running generally north and south.

The so-called "mahogany" ledge or rich oil shale strata on the southern part of the Piceance Basin varies from 50 to 100 ft. in thickness, generally has 500 to 1000 ft. of overburden, and lies from 1500 to 2000 ft. above the Colorado River valley. To minimize transportation costs, the crushing and retorting plants probably will be located near the mine portals and near the mahogany ledge, with waste dumped into the gulches.

Precipitation in the area is only 10 to 15 inches of water per year, with over half of the moisture falling as snow. Mean daily air temperatures on the plateau vary from approximately 0°F to 70°F, with an average relative humidity of about 20%. The prevailing winds in western Colorado are from the southwest and would tend to carry any pollutants from a shale industry up out of the valleys toward the Rocky Mountains; the topography of the area indicates that temperature inversions probably occur during certain times of the year. These, of course would be conducive to pollution of the air at the processing sites.

Properties of Shale and Oil

The inorganic matrix of Colorado oil shale is a laminated marlstone intimately mixed or "cemented" together with kerogen, a high-molecular-weight waxy material. When retorted at temperatures in the range of 900°F, oil and gases are given off in the vapor phase. Recent studies⁹ have shown the following average individual particle-size distributions of the inorganic matrix: less than 0.3 wt %, 200-2000 microns; 8.3 wt %, 20-200 microns; 75.8 wt %, 2-20 microns; and 15.8 wt % less than 2 microns. The retorted shale, of course, does not disintegrate into this size distribution, since it still has a certain amount of mechanical strength. Depending upon the retorting process, the retorted shale ash may or may not be partially fused.

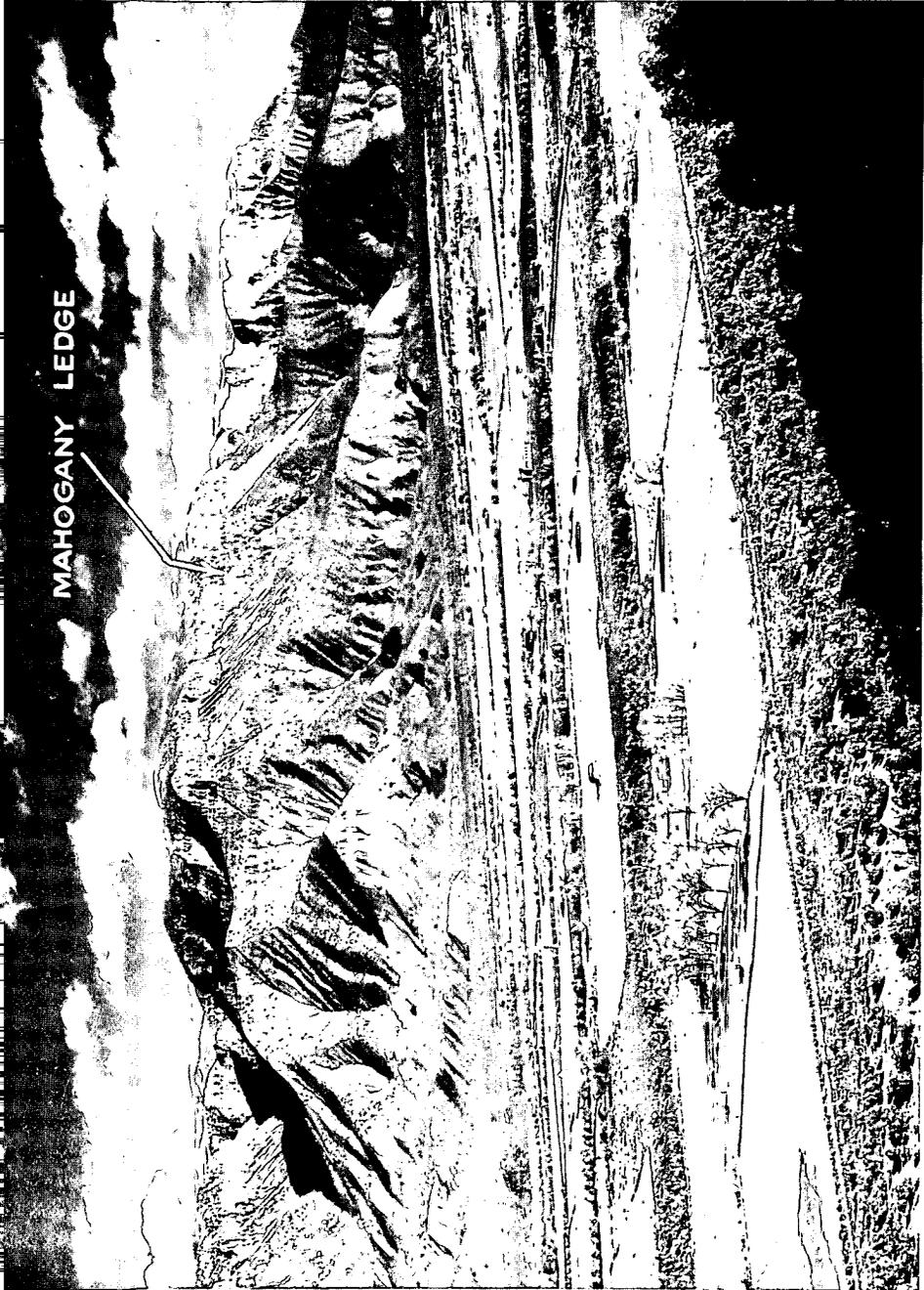


Figure 1. Photograph of the southern part of the Piceance Basin oil shale cliffs with the Colorado River Valley in the foreground.

The average ash analysis of the inorganic matrix in Colorado shale is shown in Table I. Depending upon the retorting process and the

Table I

	<u>Wt %</u>
SiO ₂	42.1
CaO	23.8
MgO	12.5
Al ₂ O ₃	10.0
Fe ₂ O ₃	4.3
Na ₂ O	3.1
K ₂ O	2.3
SO ₃	2.0

temperatures involved, the retorted shale ash will contain carbon up to a maximum of approximately 4%, and a part or all of the calcium and magnesium oxides may be in the form of calcite or dolomite.

Table II shows the approximate composition, on an air-free basis, of a retort gas produced from a shale yielding 30 gal/ton. The volume of gas produced will be approximately 500 ft.³/ton of shale, depending upon retorting conditions.

Table II

	<u>Volume %</u>
Methane	17.5
Ethane	7.0
Propane	3.4
N- and Iso-butane	1.7
Pentanes	0.7
Hexanes	0.3
Ethylene	2.2
Propylene	2.6
Butenes	1.9
Pentenes	1.1
Hexenes	.9
Heptenes	.2
Carbon Dioxide	30.3
Carbon Monoxide	2.0
Nitrogen	2.0
Hydrogen	23.9
Hydrogen Sulfide	2.3

If the hydrocarbons contained in the kerogen of the shale were accompanied by amounts of impurities similar to those of liquid petroleum, there would be no occasion for extra interest or concern with respect to air pollution.

The detailed chemical structures of shale oil are largely unknown. In general, however, it is an oil of approximately 20° API gravity with a pour point of 80-90° F, containing 1.6 to 2.2 % nitrogen, 0.6 to 0.8 % sulfur, and 1.5 to 2.0 % oxygen.¹⁰ Cady and Seelig¹¹ have shown that shale oil consists of 39% hydrocarbons (many of which are unsaturated) and 61% non-hydrocarbons; of these non-hydrocarbons, 60% are nitrogen compounds, 30% are oxygen compounds, and 10% are sulfur compounds.

The recovery of useful hydrocarbons from oil shale could result in air pollution from five main operations: (a) mining and crushing, (b) retorting, (c) disposal of spent shale, (d) refining, and (e) power generation.

Mining

The shale must first be mined and crushed to proper size for the retorts. One need only be reminded that for a 25,000 bbl./day operation approximately 35,000 tons of 30 gal./ton shale must be mined and crushed each day.¹² Such operations as drilling, blasting, conveying, and crushing all produce dust. With modern mining techniques and proper precautions the dust problems can be controlled.

Retorting

More than 2000 patents have been issued for various shale oil recovery methods.¹³ The only industrially successful ones to date involve the destructive pyrolysis of the crushed oil shale at atmospheric pressure and at temperatures of about 900°F. The severity of air pollution from the retorting operation will naturally depend upon the type of retorting process used. Any type of retorting operation could result in emissions of complex compounds of nitrogen, sulfur, oxygen, hydrogen, and carbon and inorganic dust. It is unlikely that the low-molecular-weight retort gases (shown in Table II) would be vented or flared to the atmosphere, since economics will dictate that they be either recovered or used for process heat or power generation. Since the retorting operations will

be confined to the immediate vicinity of the mines, without proper design and precautions large quantities of vapors could concentrate in the deep valleys and canyons rather than dispersing harmlessly at the higher altitudes. The area could also be subject to severe temperature inversions conducive to the accumulation of pollutants.

Although several companies are actively working on in-situ recovery of shale oil, essentially nothing has been published on the subject. The problems of in-situ recovery of shale oil are formidable, and it is most probable that a U. S. oil shale industry will begin with the more advanced above-ground retorting processes. In any case, air pollution problems in connection with in-situ recovery of shale oil would likely be akin to those associated with in-situ recovery of crude petroleum.

Disposal of Spent Shale

Since processing 35,000 tons/day of raw shale will require disposal of approximately 28,000 tons/day of spent shale ash, more than a small problem in materials handling will be involved. The canyons and dry gulches of the shale region should provide adequate space for disposal of shale ash. It is also conceivable that the waste could be returned to the mine from which it was originally removed. This procedure, of course, would preclude mining of lower levels in the future. Depending upon the particle size of the shale ash, the temperature of disposal, and the carbon content, the problems of dusting could vary widely. If shale ash containing appreciable amounts of carbon were dumped at an elevated temperature, a severe problem might arise if combustion started; the subsequent production of hot spots might release SO_2 from the small amount of pyrites in the shale. On the other hand, a well-burned shale ash will contain considerable amounts of calcium and magnesium oxide, which will recarbonate and hydrate over a period of time and stabilize the spent shale ash. In some cases, soil stabilization techniques may be required. Also, vegetation such as sagebrush and native grasses can be planted on the abandoned dump areas to minimize dusting.

Refining

The oil as recovered from most retorts "is a waxy, intermediate gravity, high nitrogen, and intermediate sulfur crude."¹⁴ The decision whether this oil is to be transported to more populated areas and refined or is to be refined near the retorts may determine the nature of the refining techniques. Generally, these oils must first be made wax-free or cracked to lighter fractions before transmission through pipelines. The fractionation, cracking, and refining of these oils present problems different from those of processing normal petroleum crudes. At this stage the processes can be engineered to recover much of the sulfur as elemental sulfur and most of the nitrogen as ammonia. Also, sophisticated techniques can be used to produce useful chemicals containing nitrogen or sulfur. In any event, the opportunities for air pollution are always present and will offer a challenge to the chemical or petroleum engineer. The economic disposal of these products could be of great interest; their release to the atmosphere would be out of question.

Power Generation

Considerable quantities of power will naturally be required for any sizeable oil shale industry. Depending upon the economics, this power will probably be produced at or near the shale industry sites. The pollution problems will be typical of those in the power industry and will depend upon the fuel used, i.e., retort gases, refinery gases, fuel oil, or other fuel.

The vast shale oil industry is nearly upon us as the problems of finding new economical sources of liquid petroleum are becoming more acute. The next 5 or 10 years could see the emergence of shale oil industry producing a million or more barrels a day in this small area of the Rocky Mountains. Any ripples of unfavorable prices on imported crude or finished products could cause abrupt waves of decision as to the time of arrival of this industry. It is hoped that all operations involving a future shale oil and industry will take cognizance of the potential air pollution problem. To disregard air pollution at the early stages of development may require later intensive and extensive engineering at a much higher cost.

REFERENCES

1. Jaffe, Felix C., Colorado School of Mines Mineral Industries, Bulletin 5 No. 2, March, 1962
2. Prien, Charles H., Ind. and Engr. Chem. 56 No. 9, 32, 1964
3. Editors, Oil and Gas J., 62 No. 10, 65, 1964
4. Benson, H. E. and Tegros, C. L., Hydrocarbon Proc., 44 No. 9, 191, 1965
5. Cane, R. F., Hydrocarbon Proc., 44 No. 9, 185, 1965
6. Chem. Engrg. Symposium Series, "Hydrocarbons from Oil Shale, Oil Sand and Coal," 54 No. 61, 1961
7. Thorne, H. M., Stanfield, K. E., Dinneen, G. O., Murphy, W. I. R., "Oil Shale Technology: A Review", Bureau of Mines Information Circular 8216, 1964
8. Barry, Frank C., Quarterly of the Colorado School of Mines. Second Symposium on Oil Shale, 60 No. 3, 104, 1965
9. Tisot, P. R., Murphy, W. I. R., J. Chem. Engr. Prog. Symposium Series 54 November 25, 1965
10. Thorne, H. M., Quarterly of the Colorado School of Mines First Symposium on Oil Shale, 59 No. 3, 77, 1964
11. Cady, W. E. and Seelig, H. S., Ind. Engr. Chem. 44, 2636, 1952
12. East, John H., Jr., Quarterly of the Colorado School of Mines, 59 No. 3, 105, 1964
13. Williamson, D. R., Colorado School of Mines Mineral Industries Bulletin, 8 No. 2, March, 1965
14. Carver, Harold E., Quarterly of the Colorado School of Mines, 59 No. 3, 25, 1964

TECHNIQUES FOR THE UTILIZATION OF FLY ASH

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Since the introduction of pulverized-coal boilers in the 1920-1930 decade, the problem of fly ash collection and disposal has been a major problem to the electric utility industry. The quantity of fly ash produced and which is not collected is becoming an increasingly greater air pollution problem, subject to control by municipalities, states and the Federal Government. Every emphasis is therefore being made to reduce the amount of fly ash escaping to the atmosphere by the installation of fly ash collecting equipment, where it does not exist, and by increasing the collection efficiency of equipment where it is already installed. This reduction in air pollution, however, aggravates the already difficult problem of disposal of the collected fly ash. At Duquesne Light Company there are twenty pulverized-coal boilers, and in 1964 they produced nearly 500,000 tons of fly ash. In the United States in 1962, more than eleven million tons of fly ash were collected; and it is estimated that by 1980, there will be twenty-five million tons produced annually. At Duquesne Light Company the fly ash produced was collected by mechanical collectors and electrostatic precipitators, sometimes in combination. The collected fly ash is generally handled in two ways. One method is to transport it from the collection hoppers to a silo in a dry state and, after passing through a wetting pug mill, it is loaded on trucks and hauled to the ash disposal area. A second method is to remove the fly ash from the hoppers, mix it with water and sluice it to an ash pond. When the pond becomes full and has been de-watered by drainage and evaporation, it is dug with power equipment and hauled to the ash disposal area.

Duquesne has been disposing of fly ash in these ways for more than twenty years and has found that they are wasteful and represent a continuing expense, from which no benefits can be realized. The dump areas, at best, are unsightly and are a source of secondary fly ash entrainment. The unsightliness and the dust source of the dump areas are an annoyance to the nearby populace, and in some locations this annoyance has caused a considerable amount of ill feeling toward the Company. There have been acts of harassment by the public and legislative action by certain municipalities to prevent the dumping of fly ash. For these reasons, it has been increasingly difficult to locate and obtain new dumping areas which are located at reasonable distances from a generating station. All practical and reasonable methods to find solutions to these problems, and thereby placate the neighbors, have been tried by Duquesne, but mostly without too much success. This is especially true if the dump area is still being used. For dumps no longer in use, a method which has been used successfully to eliminate secondary fly ash entrainment has been to cover the dump area with topsoil and plant with grass seed. In many locations, these areas have been made useful to municipalities for recreational activities. However, it is not possible to use these filled areas for heavy buildings because fly ash will not support heavy loads, the inherent tendency being to "flow" when subjected to great pressures or excessive moisture. Taking all facts into consideration, it can be concluded that the present procedure of dumping is a very undesirable method of disposing of fly ash.

Confronted with these conditions, the Duquesne Light Company has been actively engaged, for more than fifteen years, in searching for other methods for the disposal of fly ash in an economic manner. Duquesne has financed, both privately and jointly with other companies, research projects to determine the feasibility of new methods for the utilization of fly ash. In addition, it has

worked closely with national organizations such as the Edison Electric Institute which, of course, also recognizes that with the increase in pulverized-coal boilers, the disposal of fly ash is becoming a more acute problem.

Several worthwhile uses have been found for fly ash, one of which is in the construction of asphalt roadways. Fly ash has proven to be very effective as a "choking" material for the large, heavy slag base courses, because of its fluidity, and as a replacement for limestone dust in the surface course. In 1953, working in conjunction with Bituminous Coal Research, Inc., Duquesne Light Company constructed a special asphalt roadway at its Phillips Power Station near Aliquippa, Pennsylvania, for the purpose of determining the effect on the durability of this type of roadway when fly ash is substituted for other materials. The road is approximately 170 feet long and runs from a passing highway to the station coal truck scale. The road, over which all of the station trucked coal passes, is considered to be a very heavy one and handles an average of 160 trucks per day for a five-day week at an average loaded weight of at least 25 tons. Various combinations of standard and fly-ash-containing surfaces and bases were installed to compare the different types of construction. The road, as constructed, consists of a 1-inch sand base, two 6-inch large slag bases, a 2-inch binder course and a 1-inch surface course. Fly ash was used for filling ("choking") between the large slag of the bases and as a substitute for limestone dust in the surface course. The road is still in use and did not require repair until May 1965, when very minor repairs were made. The results of the test indicate that those portions of the road which were constructed using fly ash, as previously described, have performed as well, if not better, than the portions using regular construction materials with respect to surface wear and general road upkeep. It was due mostly to the results of this test road that the Pennsylvania State Highway Department accepted fly ash as a suitable material in their asphalt road specifications. With the prospect of having a market for its fly ash, the Duquesne Light Company installed fly ash bagging facilities at its Phillips Station. The fly ash is marketed by a local contractor under the name of "Durosil". There has, however, never been any real demand for the product in this area.

Although subsequently there have been roads in other areas similarly constructed, there has not been any real wide-spread use of fly ash for this purpose. Electric utilities, whose primary interest is generating electric power, have, perhaps, not attempted to push greatly the uses of fly ash for road construction. This method of utilization also would not nearly approach the total amount of fly ash produced each year by the electric industry, and its seasonal demand would produce problems of storage or intermittent disposal.

Due to its pozzolanic properties, another use for fly ash is as a concrete additive substituted for cement. Although fly ash cannot be wholly substituted for cement, it has been shown to be effective when used as a replacement in quantities up to 25-30 per cent of the cement used in bulk concrete and concrete block. Much research has been done by the electric utility industry, as well as many other interested organizations, to determine the effects of substituting fly ash for cement in the preparation of concrete. The Battelle Memorial Institute has been engaged for several years in research for the Edison Electric Institute for the purpose of determining cementitious characteristics of fly ash and the effect of variations in chemical composition of different ashes. As long ago as 1952, Duquesne Light Company engaged the Pittsburgh Testing Laboratory to perform tests on concrete containing fly ash. Using basic 1:2:3 and 1:2:4 concrete mixes, fly ash was substituted for cement in amounts of 10, 20 and 30 per cent. The concrete samples were then used to conduct compressive and fracture tests. In 1954 Duquesne Light Company, when installing a new concrete road at its Elrama Station, used fly ash in 10, 20 and 25 per cent quantities in certain test sections of the road. Concrete samples taken at that time were also tested by Pittsburgh Testing Laboratory.

The results of these tests, as well as tests by many other organizations, indicate that fly ash can be substituted successfully for cement in concrete up to 25-30 per cent replacement and still produce a concrete which exceeds the minimum compressive strength. The following table shows the compressive strength of concrete with various percentages of fly ash substituted for Portland cement. The data was taken from tests performed by the National Ready-Mixed Concrete Association.

Cement Replaced Per Cent	Compressive Strength, psi		
	7 days	28 days	3 months
0	3 320	5 180	6 050
10	2 800	4 690	5 330
20	2 270	4 040	5 380
30	1 900	3 440	4 820
40	1 470	2 740	4 180

It can be seen that as the fly ash percentage increases, the compressive strength of the concrete decreases. However, the strength increases considerably with time until, with a 20 per cent substitution, the fly ash concrete exceeds the regular concrete at about 100 days. The degree of substitution is generally a function of the chemical properties and fineness of the fly ash. The ASTM has set chemical standards for fly ash acceptance; however, many cities and federal agencies have set their own, and sometimes more rigid, standards. The exact effect of the chemical composition is not known in all cases. However, it is known that the greater the percentage of carbon in the fly ash, the weaker will be the concrete. This effect will be partially offset, however, by increased fineness of the material. All of the combinations of circumstances affecting the strength of the concrete, however, are not yet known; and, therefore, considerable research has yet to be done in order to know completely the chemical effects.

The following table shows the physical and chemical properties of Duquesne Light Company fly ash as compared to the ASTM specifications for fly ash to be used in concrete:

Chemical Composition - % by Weight

	ASTM	D.L. Co.
Silica (SiO ₂)		41-51
Aluminum Oxide (Al ₂ O ₃)	70 max.	26-32
Iron Oxide (Fe ₂ O ₃)		9-14
Magnesium Oxide (MgO)	5.0 max.	0.4-1.0
Sulphur Trioxide (SO ₃)	5.0 max.	0.3-0.8
Available Alkalies (Na ₂ O)	1.5 max.	0.5-1.5
Moisture content @ 105°C	3.0 max.	0.1-0.3
Ignition loss @ 750°C	12.0 max.	3-7

Physical Properties

Fineness, Blaine Method, cm ² /g	-	2800-4200
Specific Gravity	-	2.3-2.5
Soundness, per cent	0.5 max.	0.07-0.2
Mean particle size, microns	9.0 max.	6.7-10.0

The cement-water reaction in regular concrete liberates lime in the form of calcium hydroxide. After the concrete hardens and is exposed to water, the calcium hydroxide, which is water soluble, will leach out with time, leaving voids in the concrete. Leaching begins soon after the concrete is placed and continues for its lifetime. The free calcium hydroxide is attacked by various sulfates and

other compounds, increasing the permeability of the concrete and thereby leading to deterioration and decrease in durability. Therefore, concrete should contain a minimum of calcium hydroxide in order to increase its durability and decrease its permeability. By using fly ash in concrete, the fly ash takes advantage of the hydrated lime freed in the cement-water reaction by combining with it. A chemical reaction between the hydrated lime and the silicon and aluminum oxides in the fly ash produces insoluble cementing compounds. These aid the hardened particles in the remaining cement mixture to make fly ash concrete superior to ordinary concrete in strength, durability, watertightness and resistance to various acids, alkalies and sulfates. As would be expected, the fly-ash-containing concrete does not harden as rapidly as regular concrete; however, the fly ash concrete will, in time, become stronger than the regular concrete. It can be seen on Figure 1 that for the particular fly ash-cement combination used (20 per cent fly ash, 80 per cent Portland cement), the fly ash concrete becomes harder after about 100 days.

This same lime-fly ash chemical reaction that takes place in concrete also occurs when mixing fly ash with lime and aggregate—a combination which has been used to build low cost temporary roads, airport runways and parking lots. Actually, the Romans used a similar combination for road building nearly 2,000 years ago, except volcanic ash was used in place of fly ash. It is from this ancient use that the word "pozzolanic" is derived.

To date, a limited amount of fly ash has been used by the bulk concrete users. The largest project to date which utilized fly ash as a substitute for cement was the Hungry Horse Dam in northwest Montana. This dam, which contains 3,086,000 cubic yards of concrete, used 126,000 tons of fly ash with a resultant saving of \$1.5 million. Various other dams and buildings throughout the country, including Duquesne Light Company's Shippingport Atomic Power Station, have been built using fly-ash-containing concrete.

If all the concrete used contained fly ash, there would be no difficulty in disposing of all the fly ash that is currently produced. However, there are several factors which presently tend to limit the marketing of fly ash on that large a scale.

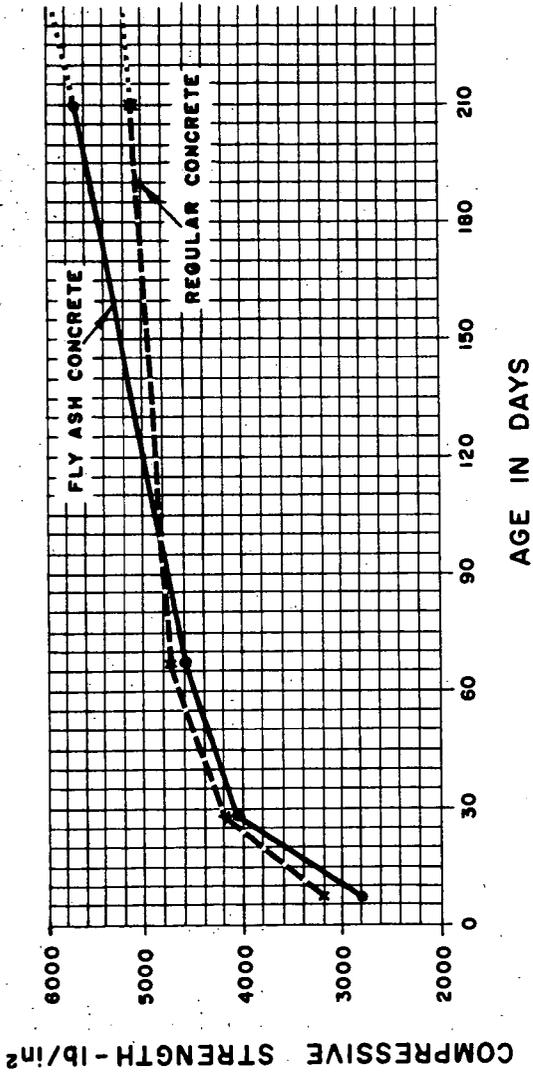
First, some degree of consistency, with respect to the properties of fly ash, is needed before it can be used in concrete. These properties vary from location to location and from time to time, because there is no attempt to control fly ash properties. It must be remembered that fly ash is a by-product of electric power generation and its properties depend, to a large extent, on how that generation is performed and also on the original composition of the coal which is burned. For instance, a station which is base loaded will produce fly ash with a lower carbon content than a station whose electrical output, and therefore coal burning rate, continually fluctuates.

Second, the basic composition of the coal burned may contain excessive amounts of undesirable elements. For instance, fly ash may contain excessive iron and therefore impart an undesirably darker color or may result in staining when incorporated into concrete blocks or other masonry products.

Third, the bulk concrete mixing plants are not always conveniently located to fly ash sources; and, therefore, transportation can be a problem or at least costly enough to eliminate possible savings.

Fourth, the handling and storage of fly ash can be a problem if it is used in large concrete projects like dams and buildings. In construction projects such as these, the need for fly ash is intermittent and storage facilities would therefore be required to meet the demand when needed.

FIGURE - 1
COMPRESSIVE STRENGTH OF FLY ASH
CONCRETE VS. REGULAR CONCRETE



Fifth, the electric utility industry, as a whole, has probably not pushed sufficiently hard to develop a market for the material nor to enlighten concrete users sufficiently. All electric utility companies do not have fly ash disposal problems, since some companies use other fuels and still other companies have not experienced problems with dumping because of geographical location. However, evaluating all factors, it is evident that, at least in certain areas, many problems exist and that much research is still needed if fly ash is to be substituted for Portland cement in any great quantities.

Fly ash has been tried as a substitute material in various processes by many industries. The previous uses discussed are known to be successful; some other processes have been reasonably successful and can use fly ash; while still others have found fly ash to be an unsuitable material for a particular use.

Experimental work has been done on using fly ash as a substitute for core sand for steel and aluminum castings. Although the castings using fly ash molds were smoother, they tended to develop pitting; and also, there was the ever present problem of handling the fly ash.

Fly ash was tested as an extender in paint and as a filler in putty. It proved to be of no value in paint, and particle size was too large for putty.

Some fly ash is being used in asphalt roofing and siding materials, but has been rejected for floor tile because of its dark color.

A building block was tested using lime and fly ash and containing no Portland cement. The blocks had a smooth surface which made them difficult to handle. Also, they were more brittle, tended to chip and spall after installation and were heavier than regular block. They were rejected because they afforded no advantage over the regular block.

An investigation was made into the possibility of using fly ash as a constituent in brick making. It was rejected because when mixed with clay, the material packed too hard, was too abrasive and the bricks were too brittle.

Fly ash was tested for use in a sound deadening plaster, but its color was objectionable.

Fly ash has been tried as an admixture to fertilizer, replacing foundry sand, but was found to be too fine and dusty.

Some agricultural experiments have been conducted on pot plantings of soy beans by adding fly ash to the soil. The fly ash produced a substantial increase in growth and an improvement in color.

Fly ash was tried as a filler for abrasive soap, but was found to be inferior to the pumice which was being used. It was also found to be unsuccessful as a filler material in paper and rubber.

Fly ash was tried as a sound and heat insulator, but was found to pack excessively and absorb moisture when exposed to air.

Insulating cement has been made containing fly ash which results in less shrinkage cracks, and therefore is considered to be superior to other materials used.

Fly ash has been substituted for pumice in buffing compounds and for whiting in tooth paste. It did not produce the desired polished finish when used for buffing, and it was too hard for use in tooth paste.

When fly ash was substituted for clay in ceramic tile, there was no improvement in product quality and it cost more to manufacture. As a substitute for diatomaceous earth in plastics, it resulted in a product of poorer quality.

When tried as a filter for water and oil purification, replacing sand and fuller's earth, fly ash did not produce desired clarification of the water or oil.

The utilization of the individual chemicals of which fly ash is composed may be a possible use in the future. The Bureau of Mines has experimented with removing traces of germanium which have been found in some fly ashes. The extraction of other elements and compounds may be feasible in the future.

It is evident that uses for fly ash have been attempted by many industries, but with only limited success. Those that have found the product useful do not use fly ash in sufficient quantities to consume any great percentage of the yearly production.

To date, the most promising method for utilizing fly ash appears to be as a lightweight aggregate. However, the fly ash must first be sintered and crushed and then it can be used as a substitute for fine or coarse aggregate in concrete, concrete block, roadways and anywhere else where aggregates are required.

The possibility of sintering fly ash came to light in the early 1950's when efforts were made by certain companies to sinter fly ash without first pelletizing. The process was not successful. It was found that pelletizing was necessary and could be accomplished only after adding expensive binders. Experimentation continued to improve pelletizing equipment, mostly in conjunction with iron ore, so that by 1960 pelletizing could be accomplished without binder admixtures. By 1961, pelletizing and sintering tests with fly ash in various pilot plants demonstrated that fly ash sintering plants of a commercial size were now technically and economically feasible. Since that time, three fly ash sintering plants have been installed, one each at Consolidated Edison Company in New York City; Niagara Mohawk Power Company in Buffalo, New York; and at Detroit Edison Company in Detroit, Michigan. All three of these plants utilize the same basic design produced by the McDowell-Wellman Company. The Stirling Sintering Company of Pittsburgh, Pennsylvania, also has installed a small plant near Duquesne Light's Phillips Station. The McDowell-Wellman process and the Stirling process are similar in that pelletizing is achieved by adding water to the fly ash in a rotating drum. Still another process has been developed by the G. & W.H. Corson Company of Plymouth Meeting, Pennsylvania, whereby pelletizing is accomplished through an extrusion process. Both of the processes then feed the pellets into a gas-fired oven at approximately 2000°F, and the carbon in the fly ash is burned while at the same time sintered pellets are formed. These pellets can be crushed to various sizes to give either a fine or coarse aggregate.

The chief advantage of sintered fly ash aggregate is its light weight. When sized to concrete block grade, sintered fly ash weighs 48-50 lbs./cu.ft., while another common block aggregate material, expanded slag, weighs 68-72 lb./cu. ft. This weight differential causes a reduction in block weight from approximately 35 lb. to 25 lb. This reduction can mean a decrease in building structure costs, handling cost and shipping cost. In addition to the reduction in costs realized in using the block, the block containing fly ash aggregate can be produced at a lower cost, since it has been shown that less Portland cement is required to produce a block of comparable strength with fly ash than with regular aggregate. The ASTM specifications for a 28-day cured concrete block having a minimum shell face thickness of 1-1/4" is 1000 psi compressive strength. Tests which have been performed on block made from Duquesne Light Company fly ash and sintered in the Corson Company plant have shown compressive strengths of 1580 to 1920 psi, depending on the quantity of Portland cement used.

Tests have also been performed on bulk concrete made using fly ash as a coarse and fine aggregate. These tests have shown that where the ASTM compressive strength test requires 4000 psi for 28-day cured concrete, the fly-ash-containing concrete was tested to 4910 psi, which surpasses the 4800 psi concrete made using expanded slag as an aggregate. It can readily be seen that concrete and concrete block using fly ash aggregate greatly exceed the minimum established strength requirements. When used in roadway construction, concrete containing fly ash aggregate as an added benefit has been shown to be more skid resistant.

With the advantages previously mentioned, the market for fly ash aggregate appears to be almost unlimited. Present surveys have indicated that a real demand can be established, provided a quality product can consistently be produced by the sintering plant. Because fly ash sintering is a relatively new concept, operational difficulties have been encountered by the three utilities previously mentioned which have fly ash sintering plants; however, all feel that most of the problems that still exist are due to inexperience of operation and newness of equipment design. Duquesne Light Company, at the time of preparation of this paper, is proceeding with the design and will install a fly ash sintering plant at its Elrama Station. With the expectation of being able to turn a costly expense into a profit-making operation, it is anticipated that more companies will likewise investigate the possibilities of sintering fly ash. It is even possible that future designs of pulverized coal burning stations will incorporate fly ash sintering facilities as an integral part of the station design and operation.

The electric utility industry, as a whole, is very enthusiastic over the possibilities of sintered fly ash, feeling that perhaps at last a use has been found that can utilize all of the fly ash that is produced and end once and for all the problems presently encountered in fly ash disposal.

MINE EFFLUENTS

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ABSTRACT

A general discussion of coal mine discharges, either acid or alkaline.

The oxidation of sulfuritic compounds to form acid and subsequent reactions which result in the extreme variation of composition of discharges.

The use of p_H as a means of estimating acidity or alkalinity.

Pollutional constituents and their relation to receiving stream.

A discussion of various suggested methods for control such as neutralization and "Mine Sealing." The possible effectiveness of water handling and control as a means of abatement of pollution.

SOME ECOLOGICAL EFFECTS OF ACID MINE DRAINAGE
IN THE UPPER MONONGAHELA RIVER

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ABSTRACT

Data and interim conclusions are presented as part of a continuing study of fish populations in a thirty-mile reach of the Monongahela River main stem above the West Virginia-Pennsylvania state line. Acid mine water discharged into the Upper Monongahela drainage results in a chemically degraded environmental situation demonstrated by data on pH, acidity, total hardness, and iron. Chemical degradation is ecologically expressed in the limited species composition of bottom fauna and fish communities. Bottom-fauna forms commonly considered to be pollution indicators appear to constitute an adequate food supply for the resident fishes. Elimination of competitive and predator species of fishes by acid conditions is postulated as being of ecological significance in the maintenance of a thriving population of the pollution-tolerant black bullhead. Other species of resident fishes (bluegill, pumpkinseed, and green sunfish) appear to exist under marginal environmental conditions approaching lethal limits of pH and acidity.

KINETICS OF THE SULFIDE-TO-SULFATE REACTION

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A broad-based study of the sulfide-to-sulfate reaction mechanism in relation to the production of acid mine drainage is being made at The Ohio State University. This report concerns one aspect of the program; the attempt to define kinetics of the rate-determining mechanism in a chemical (rather than biological) regime.

This phase of the study was prompted by the numerous and conflicting reports on the quantitative relationship of variables on oxidation rate of pyrite, and to confirm or refute some of the beliefs that have been taken as self-evident or intuitively assumed as fact.

Two obvious items, acknowledged to influence rate of pyrite oxidation, are oxygen and water. In the absence of water and oxygen (or other effective oxidizing agent) the rate is (comparatively) zero. The role of water in the reaction, and the influence of oxygen concentration on oxidation rate have never been satisfactorily explained.

Reports of early laboratory studies (2,4,7,8,9) noted the effect of water and oxygen concentration on oxidation rates. The rate of oxidation was reported to be essentially independent of oxygen concentration (4), to be first order in respect to oxygen concentration (8); and the rate in air to be one-half that in oxygen (7).

More recent work in this laboratory (1,6) indicated that vapor phase oxidation rates varied directly with partial pressure of water and that the rate in air was approximately 35% of that in pure oxygen.

In order to reconcile these differences, an attempt was made to determine the nature of the rate-limiting mechanism and to explain the role of oxygen and water in the kinetics of pyrite oxidation.

EXPERIMENTAL

In addition to standard Warburg equipment and techniques, equipment shown in Figure 1 were used. The apparatus shown in 1A and 1B are similar in concept; 1A recirculating the vapor phase, and 1B the liquid phase, through a bed of pyrite. In each case, oxidation of pyrite was monitored by measuring the quantity of make-up oxygen required to maintain a constant pressure in the vapor space.

This type of equipment was used for several reasons: 1) to establish influence of diffusional resistances and desorption of reaction products on reaction rates, 2) to enable control of concentration of various components in the recirculating fluid, and 3) to permit periodic sampling of streams to follow build-up of reaction products.

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Figure 1C is a modified differential Warburg unit used to determine oxidation over comparatively wide pressure ranges. It consists of two identical flasks on either arm of a manometer. The same quantity of water was added to each flask, then pyrite placed in the right-hand flask. A small amount of manometer fluid was added to the top of the mercury so that when the level was raised, the fluid filled the arms of the manometer to the desired height. To fill the system with vapor, the mercury column was lowered so that the water level was at the right-hand stopcock, the system evacuated, and then the vapor admitted through the vacuum line. The left stopcock was then closed and the mercury leveling bottle raised or lowered depending on the pressure in the system so that the water level rose half-way in the manometer. The entire assembly was agitated during liquid phase runs.

The pyrite sample used for all runs reported in this paper was a "sulfur ball" material collected from the Middle Kittanning No. 6 coal seam in Vinton County, Ohio. Several stages of float-and-sink separation on the crushed coal were used to obtain an 85% FeS_2 material. This was then carefully screened and the 70 to 100 mesh fraction used as the sample.

RESULTS

Data on liquid phase oxidation showed that flow rate of fluid through the bed had no effect on rate of oxidation. Also, the rate remained constant for the duration of the runs (one to two weeks).

Two runs were made with a column of "Amberlite" IRA-120 in series with the reactor to remove all iron from the circulating fluid. With "zero" iron in solution, the rate remained the same.

The relation between increase of iron in solution and oxygen absorbed was frequently checked and found to be approximately 3.5 moles oxygen consumed per mole of soluble iron produced. The relative ferrous-ferric ion concentration was found to vary between 85% and 95% ferrous for runs listed in Table 1.

A series of liquid phase runs were made in which oxygen concentration in the vapor space and temperature were varied. The results of these runs, together with those obtained with the ion-exchange resin in the system, are listed in Table 1.

A similar study was made using the vapor phase apparatus. As in the liquid phase runs, flow rates had no effect on rates. The rate of oxygen absorption remained constant throughout the run period which varied from several days to two weeks. Temperature and humidity of the recycled vapor were varied. The results are listed in Table 2.

Since the other oxidation units were not capable of operating over wide pressure ranges, the equipment shown in Figure 1C was constructed. Runs were made at different oxygen pressures and vapor compositions to study the effect of dissolved oxygen and nitrogen concentrations on oxidation rate. These data are shown in Table 3.

All rate data in Tables 1 and 3 were recalculated to the same reference--100 microgram oxygen per hour per gram of pyrite at 25°C and 76 cm. Hg. oxygen pressure. This was necessary in order to get consistent results from one column packing or washing to the next. The principle problem was the tendency of the sulfur ball particles to break-down during agitation. For one continuous series of runs, the change from run to run was small. But after washing or repacking, a reference run was necessary to obtain comparative rates.

INTERPRETATION OF EXPERIMENTAL RESULTS

Based on the observation that 1) flow rates of the recirculated fluid had no effect on oxygen absorption rates, 2) rates were constant throughout the test period, and 3) removal of iron from solution did not affect rates, it seems evident that reaction rates in the recirculating-type equipment, for the reaction periods used, are not influenced by diffusional resistances nor desorption of oxidation products. This conclusion is substantiated by the value of 14 Kcal. per gram-mole for the activation energy determined from an Arrhenius plot of data presented in Table 1. This value for activation energy is typical of a reaction-controlled mechanism, rather than a physically-controlled rate limiting step.

Role of Water

In studying the role of water, Kim (6) made a series of vapor phase oxidations using the equipment in Figure 1A. Over the limited temperature range studied, he observed that the rate varied linearly with absolute humidity (or partial pressure) of water in the vapor phase, apparently indicating that the rate of oxidation was first order in respect to water and suggesting that water is a reactant.

When this study was extended to cover a wider temperature range, a distinct temperature dependence was observed, as shown in Figure 2. It was also noted that in the temperature range covered by Kim, both the oxidation rate and partial pressure of water vapor (over a saturated salt solution) doubled with a 10°C temperature rise. In other words, the influence on rate observed by Kim may be interpreted as a change caused by temperature at a constant relative humidity. The runs plotted in Figure 2 are replotted as Rate vs. % Relative Humidity in Figure 3. Note that at a given value of relative humidity, the rate nearly doubles with each 10°C increase in temperature, the same as observed in liquid phase oxidation. The curves in Figure 3 are typical Type III adsorption isotherms (according to Brunauer (3), et al.) suggesting that rate may be dependent on quantity of water adsorbed.

When the isotherms of Figure 3 are extrapolated to 100% Relative Humidity and the rates thus obtained plotted together with those from the liquid phase runs (Figure 4), the similarity of temperature effect in both vapor and liquid phase oxidations is apparent.

While it is not possible to describe the role of water in all phases of the reaction, at least for the rate-limiting reaction, water is involved as a reaction medium rather than a reactant. If water were one of the reactants, the rate of reaction would level-off as the partial pressure of water approached saturation pressure (i.e., as water is no longer the limiting reactant). Instead the rate of increase is greater as water concentration nears saturation as seen in Figure 3.

Even in vapor phase oxidation, rates remain constant over long periods of time. This can be explained by products "salting-out" of a condensed liquid phase as the content of dissolved reaction products reaches saturation. This process was qualitatively observed by Birle (1) who presented photomicrographs showing the build-up of salts around the edges of pores or etch marks which contained water.

It is possible that the basic function of water is to provide a means by which the oxidation products are desorbed (dissolved) from the pyrite surface. Normal oxidation, which may occur in the dry state on clean surfaces, could be stopped by build-up of products on the "reactive sites" of pyrite. If the isotherms of Figure 3 are coincident with adsorption isotherms for water, then the rate would be directly related to the quantity of water absorbed. This relationship is now being examined.

Role of Oxygen

Possible kinetic mechanisms by which oxygen enters the rate-limiting reaction are suggested by the data presented in Table 3.

These data give a quantitative relation between oxidation rate and oxygen concentration, and indicate that the concentration of inert gas (nitrogen) affects oxidation rate.

Using procedures and modifications suggested by Hougen and Watson and others (5, 10) rate equations for different assumed mechanisms can be derived. For the type of reaction under study, simplifications can be made. It has been shown that neither desorption of products nor diffusional resistances influence the rate of reaction under the laboratory conditions used in this study. Therefore, the experimental rates can be considered "initial rates" and derivations simplified by eliminating consideration of both product composition and concentration.

It is possible to postulate a mechanism that results in a rate equation which correlates experimental data within limits of experimental error.

This proposed mechanism involves the dissociation of oxygen when adsorbed on "reactive sites" of pyrite (Reaction 2). Simultaneously, inert gas (nitrogen) can be adsorbed (Reaction 1) and compete for these "reactive sites." The rate-limiting step is the decomposition of the activated complex formed by dissociated oxygen (Reaction 3).

This mechanism can be expressed by the following reactions:



where: I = inert gas (nitrogen)

A_2 = oxygen

s = reactive site of FeS_2

As^* = activated complex of dissociated oxygen and reactive site

P = product (or products) of reaction

The rates for the individual reaction are:

$$r_1 = k_{f1} C_I (1 - \theta_A - \theta_I) - k_{r1} \theta_I \quad (4)$$

$$r_2 = k_{f2} C_A (1 - \theta_A - \theta_I)^2 - k_{r2} \theta_A^2 \quad (5)$$

$$r_3 = k_3 \theta_A^2 \quad (6)$$

where: θ_A and θ_I = fraction of total reactive sites occupied by oxygen and inert gas

C_A and C_I = concentration of oxygen and inert gas in aqueous phase

Reaction 3 is the rate-limiting step, so Reactions 1 and 2 are at equilibrium, or r_1 and $r_2 = 0$.

Then the adsorption equilibrium equations can be written:

$$K_I = \frac{k_{f1}}{k_{r1}} = \frac{\theta_I}{C_I (1 - \theta_A - \theta_I)} \quad (7)$$

$$K_A = \frac{k_{f2}}{k_{r2}} = \frac{\theta_A^2}{C_A (1 - \theta_A - \theta_I)^2} \quad (8)$$

Solving for θ_A and θ_I in terms of equilibrium constants, the rate equation may be written:

$$r_4 = \frac{k_4 K_A C_A}{(1 + \sqrt{K_A C_A} + K_I C_I)^2} = \frac{k C_A}{(1 + \sqrt{K_A C_A} + K_I C_I)^2} \quad (9)$$

Another possible mechanism results in a rate equation giving slightly poorer correlation. This assumes the formation of an activated complex by the adsorption of oxygen on single site, i. e.,





The final rate equation for this mechanism is:

$$r_{11} = \frac{kC_A}{1 + K_A C_A + K_I C_I} \quad (12)$$

Using the data for pure oxygen ($C_I = 0$) from Table 3, equations 9 and 12 were solved for "k" and " K_A ."

Plotting the data of Table 3 together with equations 9 and 12 in Figure 5 indicates that the dissociation mechanism (equation 9) is consistent with experimental data. However, it must be emphasized that this does not prove the validity of the mechanism. It merely indicates that the proposed mechanism is possible according to this set of experimental data. The single-site adsorption mechanism (equation 12), although showing greater deviation, can not be eliminated on the basis of these data.

However, other mechanisms that have been suggested can be discarded. For example, the reaction of another molecule of oxygen with the activated complex, i.e.,



is not probable since the rate equation would involve a $(C_A)^2$ term in the numerator.

The same type of analysis can be used to show that neither the physical nor chemical adsorption of oxygen can be the rate-limiting reaction. If this were the case, the initial rate would be proportional to the concentration of oxygen.

The presence of dissolved nitrogen reduces the rate of oxidation slightly as shown in Table 3. The rate data is not so consistent that a reliable value for K_I can be calculated.

Since the adsorption of oxygen occurs in an aqueous medium and since the presence of nitrogen reduces oxidation rate, it is likely that physical rather than chemical adsorption on "reactive sites" is involved. It is unusual for chemisorption to occur from highly polar solvents. Also, if oxygen were chemisorbed, nitrogen would have no effect on rate. At the same time it does not seem likely that nitrogen could compete with oxygen in an aqueous solution for physical adsorption on a relatively non-adsorptive material like pyrite.

A more critical study of the effect of nitrogen on the reaction is needed since the manner in which oxygen is adsorbed is of fundamental importance to inhibition studies. The adsorption of oxygen will have to be determined indirectly since normal procedures used to study adsorption of gases can not be used for the oxygen-water-pyrite system.

TABLE 1
LIQUID PHASE RUNS

Vapor Conc. (% O ₂)	Temp. (°C.)	Oxidation Rate*
100	20	58
100	25	100
100	30	138
100	35	215
10	25	23
26	25	47
54	25	79
79	25	85
100	25	100
100	25	102**
100	35	210**

TABLE 2
VAPOR PHASE RUNS

Temp. (°C.)	Partial Press. of Water (mm. Hg.)	% Rel. Saturation	Oxidation Rate*
25	22.8	96	85
	17.8	75	50
	12.6	53	25
	7.6	32	16
35	40.5	96	168
	31.2	75	90
	21.5	51	57
	13.1	31	33
45	69.	96	400
	53.2	75	152
	33	46	70
	22.3	31	48

**With "Amberlite"

TABLE 3
VARIABLE PRESSURE RUNS AT 25°C

Oxygen Pressure (cm. Hg.)	Nitrogen Pressure (cm. Hg.)	Liquid O ₂ Conc. (ppm.)	Oxidation Rate*
76	0	39.4	100
183	0	95	165
170	0	88	162
170	0	88	156
143	0	74	144
91	0	47	110
48	0	25	68
38	0	19.5	62
28	0	14.5	52
21.5	0	11.2	39.5
20	0	10.4	37
14	0	7.3	34
15	0	7.8	32
10	0	5.2	25
34	128	17.5	47
15	100	7.8	30.5
14	67	7.3	30
15.5	59	8.0	26.5
10	70	5.2	24.5
7.1	27	3.7	19

*Rate = Microgram oxygen, per gm. pyrite, per hour

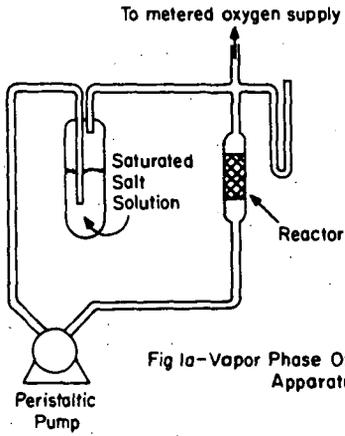


Fig 1a-Vapor Phase Oxidation Apparatus

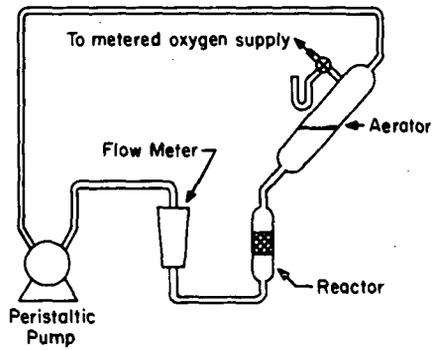


Fig 1b-Liquid Phase Oxidation Apparatus

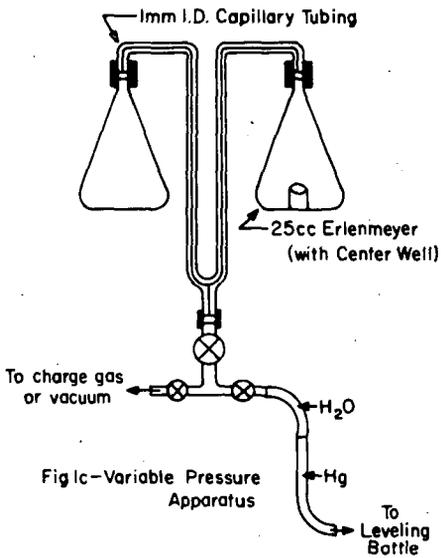


Fig 1c-Variable Pressure Apparatus

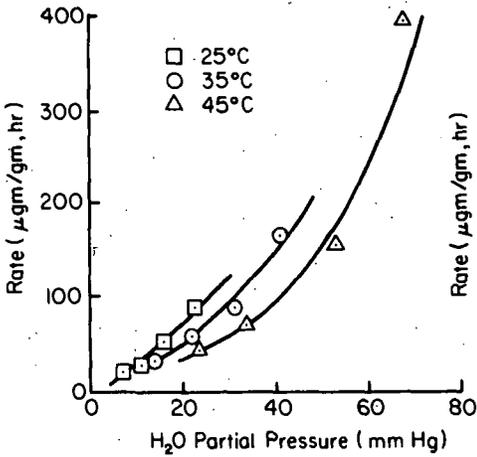


Fig 2 - Oxidation Rate vs. Partial Pressure of Water

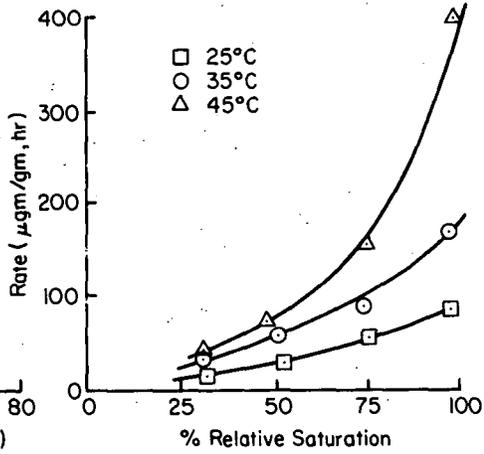


Fig 3 - Oxidation Rate vs. % Relative Saturation

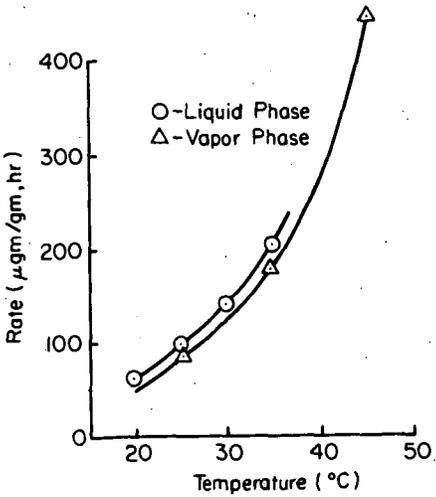


Fig 4 - Oxidation Rate vs. Temperature

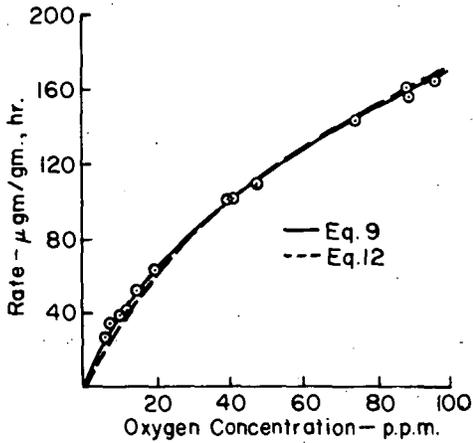


Fig 5 - Oxygen Rate vs. Oxygen Concentration in Aqueous Phase

ACKNOWLEDGMENT

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REFERENCES

- (1) Birle, J. D., "Sulfide to Sulfate Reaction Mechanism in Pyritic Materials" M.S. Thesis Thesis, The Ohio State University (1963)
- (2) Braley, S. A., Summary Report Mellon Institute Fellowship No. 326B, Mellon Inst. of Ind. Research (1954)
- (3) Brunauer, Deming, & Teller, "On a Theory of the Van der Waals Adsorption of Gases" J. A. Chem. Soc. 62 1723 (1940)
- (4) Burke, S. P., Downs, R., "Oxidation of Pyritic Sulfur in Coal Mines" A.I.M.M.E. Transactions 130 425 (1938)
- (5) Hougen, O. A., Watson, K. M., "Chemical Process Principles" Part III, John Wiley & Sons, Inc., New York (1947)
- (6) Kim, H. W., "Vapor Phase Oxidation of Pyrite" M.S. Thesis, The Ohio State University (1964)
- (7) Li, S. H., Parr, S. W., "The Oxidation of Pyrite as a Factor in the Spontaneous Combustion of Coal" I.E.C. 18 1299 (1926)
- (8) McKay, D. R., Halpern, J., "A Kinetic Study of the Oxidation of Pyrite in Aqueous Suspensions" A.I.M.M.E., Transactions 212 301 (1958)
- (9) Nelson, H. W., Snow, R. D., Keyes, D. B., "Oxidation of Pyritic Sulfur in Bituminous Coal," I.E.C. 25 1355 (1933)
- (10) Perry, Chilton, Kirkpatrick, "Chemical Engineers' Handbook" 4th Ed. p. 4-13, McGraw-Hill, New York (1963)

AIR SEALING AS A MEANS OF ABATING ACID MINE DRAINAGE POLLUTION

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ABSTRACT

The oxidation of iron sulfides in a coal mine in the presence of excess moisture results in the formation of free sulfuric acid. The acid may be transported by the mine discharge to streams where it constitutes a major pollutant in several Appalachian States.

Both field and laboratory tests indicate that if oxygen can be excluded from an abandoned coal mine, the oxidation of pyrite will be prevented and acidity of the mine discharge reduced.

The Bureau of Mines has selected a small abandoned mine with a highly acid discharge and plans to seal it to prevent air from entering it. A study of the geologic and hydrologic environment of the mine is expected to serve as a basis for comparing the quality of the mine discharge before and after sealing and to aid in evaluating the effectiveness of mine air sealing.

Certain relationships of dissolved solids and total acidity to the flow rate were determined and explained as dilution or climatological effects. These relationships must be considered in any evaluation of changes in the quality of the mine discharge.

INTRODUCTION

When coal deposits are exposed to natural weathering and erosion, the iron sulfides contained in the coal and adjacent strata oxidize to form new compounds consisting of ferrous sulfate and free sulfuric acid. Oxygen in the atmosphere further oxidizes the ferrous sulfate to ferric sulfate, which then hydrolyzes in an excess of water to insoluble iron hydrates known as "yellow boy," and sulfuric acid. The coal itself is largely unreactive and subject only to mechanical disintegration. Figure 1 summarizes the essential reactions believed to take place during the oxidation of iron sulfides.

Removal of the coalbed by mining exposes large surface areas to oxidation and greatly accelerates an otherwise slow natural process. Mining also may drain ground water from the surrounding strata and this seepage will dissolve the acid salts formed in the mine and transport them to the streams.

So-called sulfur water was recognized several hundred years ago as being common to the coal mining districts in England and first was observed in the United States about 1698, long before commercial mining began. In 1803, a reference was made to sulfurous water issuing from coal outcrop near Pittsburgh, Pa.; by 1890, acid drainage from coal mines in western Pennsylvania was blamed for extensive fish kills in the Youghiogheny River at McKeesport.

A combination of four factors--extensive coal mining, abundant rainfall which produces large quantities of mine water and runoff, a low natural alkalinity of the streams, and the presence of pyrite in the coal--are responsible for the concentration of acid mine drainage problems in the Eastern Mountain States from Pennsylvania to Alabama. Acid drainage from mine sites usually reaches the major rivers via small tributaries.

In a recent special report prepared for the House of Representatives Committee on Government Operations, Subcommittee on Natural Resources and Power, it is claimed that the effects of acid mine drainage pollution are felt by more than 10 million people living in metropolitan and industrial areas of the East.

The problem in the Appalachian Region has become progressively worse in this century because of the large increase in the number of abandoned mines, and because water pollution does not necessarily end when mining is discontinued. The chief offenders are the abandoned above drainage mines from which water may continue to flow indefinitely. However, all such mines do not produce acid water. In many instances the hydrologic and geologic environment is the controlling factor.

In 1924, the U.S. Public Health Service made a study of stream pollution which included an investigation of the possibility of air sealing abandoned deep mines above drainage so as to prevent oxidation and the formation of sulfuric acid.

The basis for mine sealing lies in these two nearly incontestable facts:

1. Exclusion of air from sulfide material prevents its oxidation.^{1/}
2. Reducing the amount of water passing through a mine reduces the acid load put into the streams receiving the effluent.^{2/}

In 1933, the Bureau of Mines issued a report which recommended the air sealing of abandoned mines in ten Eastern States. Consequently, between 1935 and 1938, and again from 1947 to 1950, hundreds of masonry seals were placed in abandoned drift mines by State and Federal organizations. Dry drifts were closed with a simple masonry block air seal, but mine openings through which water was flowing were equipped with a trap which allowed the water to flow out but prevented air from entering.

The sealings were not followed up with a detailed study of the change in water quality; however, general observations showed the results to be favorable, with a substantial initial reduction in the quantity of acid in streams receiving the mine drainage. Some of the seals since have deteriorated, some sealed mines have been reopened, and numerous additional abandoned mines are not presently sealed.

Preliminary results of recent laboratory investigations conducted by the Bureau of Mines seem to offer a positive technical reason for pursuing mine sealing as a means for abatement of acid pollution. Using the Warburg manometric apparatus to determine the effect of oxygen deficiency on the reactivity of pyrite in the presence of water, the atmosphere was varied in the sealed vessel from normal air to 100 per cent nitrogen. After each test, which ranged from 1 to 4 days, the total iron in solution was determined as a measure of the oxidation of pyrite.

After the first day, the amount of iron in solution was directly proportional to the oxygen content of the atmosphere and to the exposure time. With the nitrogen atmosphere, the iron in solution remained constant at a negligible value throughout the test period.

Technical reports on acid mine drainage range over many aspects of the problem but few deal with actual case histories of individual mine sealing and the effectiveness of mine air sealing as a means of abating acid mine water pollution. Clearly what is needed is more data on sealing and the natural environment of the mine.

1/ Braley, S. A. Acid Mine-Drainage VI. Control of Oxidation. Mechanization, v. 18, No. 6, 1954, pp. 105-107.

2/ Pennsylvania, Commonwealth of. Control of Acid Drainage From Coal Mines. Dept. of Health, Sanitary Water Board, 1952, 28 pp.

Early in 1962, the Bureau of Mines and the Coal Industry Advisory Committee to the Ohio River Valley Water Sanitation Commission (ORSANCO) entered into a cooperative agreement to conduct research in acid mine drainage. One of the projects is to evaluate mine sealing as a means of reducing the discharge of acid mine water from abandoned deep coal mines above drainage. As prerequisites to the field study, it was necessary to locate a small abandoned underground mine having a minimum number of openings, isolated from any active workings, and currently discharging acid water. An investigation of possible sites was made and a mine near Kittanning, Armstrong County, Pa., was selected. Cooperative agreements also were signed by the Bureau of Mines, the property owner, and the former operator of the mine, who supplied a map of the underground workings.

This mine affords a good example of the stream pollution which can result from the acid drainage from only one small mine. The total acid load, which is volume times acidity of the mine discharge for 182 days, sampled at random throughout the year of 1964, was equal to 41 tons of sulfuric acid. Therefore, the estimated acid load for the entire year would equal approximately 80 tons, which flows directly into a major tributary of the Allegheny River.

A prefabricated building was erected at the mouth of the mine drainage drift in May 1963 to house equipment for the continuous monitoring of the pH, conductivity, Eh, and flow rate of the mine effluent. An automatic sampler was installed, and all mine water was diverted through a V-notch weir. A continuous record of the quality and quantity of the water has been maintained since September 1963.

In the summer of 1964, a study of the geologic and hydrologic conditions of the mine was initiated so that a better understanding and interpretation of the results of mine sealing might be achieved. In December 1964, a topographic base map of the mine property was prepared from aerial photographs and later a map of the mine workings was superimposed on the topographic map.

In December 1964, four diamond drill holes and two shallow auger holes were drilled to gather additional information on geologic strata, ground water, and mine subsidence. The drill holes also are used, where possible, to collect samples of the mine atmosphere.

The Bureau of Mines plans to air seal the mine this year. The four dry mine openings are to be closed with masonry blocks and mortar, then coated on the outside with urethane foam to assure an airtight seal. The drainage drift seal also is to be of a masonry type structure, provided with a trap, which permits the outflow of water but prevents the inflow of air. Copper tubes are to be placed in all five seals so that samples of mine atmosphere can be collected periodically to test for oxygen depletion. Air samples collected prior to sealing show a normal oxygen content.

GENERAL GEOLOGY

The mine is located in the Allegheny Plateau, a region of virtually horizontal sedimentary strata which have been eroded by streams to form a dissected, hilly topography. The poorly exposed bedrock belongs to the lower part of the Conemaugh series and the upper part of the Allegheny series, both of the Pennsylvanian system. The beds are composed predominately of siltstone and sandstone with minor amounts of claystone, limestone, and coal.

The mine was worked in the Upper Freeport coalbed, which is the top formation in the Allegheny series. It is the only coal of economic importance in the immediate area. It is a bright banded, moderately low sulfur coal, 42 inches thick. The coal seam lies above drainage and was mined from beneath a "peninsula" in the topography. It outcrops on three sides of the hill but to the northeast is under higher topography and deeper cover, which ranges up to 200 feet thick. Structure contours on the

base of the coal seam show a dip of about 1 degree to the south, although at the south end of the property the beds which are exposed in a highwall dip slightly to the north. Mine drainage, therefore, is generally to the southeast.

Surface water is absent from the mine property except during heavy thaw or precipitation. Surface drainage from the hill overlying the mine is by means of small perennial streams in the valley on each side of the hill, which are tributaries to Cowanshannock Creek. The mine effluent of pH 3.1 flows into one of these tributaries. The pH of Cowanshannock Creek above this tributary is 7.2 and below is 6.2. The creek is more than 20 times as great in volume of flow at low level than the stream carrying the mine discharge.

CLIMATE

The climate of the Kittanning area has a direct bearing on the ground water conditions at the mine. Precipitation is distributed fairly evenly throughout the year. June, July, and August are months of maximum evapotranspiration and lowest mine drainage rate, while highest surface runoff and maximum ground water recharge occur during the January to April period when mine drainage rates are highest.

About 46 percent of the land immediately overlying the mine workings is covered by stands of mixed hardwoods which fringe the hill. The remainder of the land is covered by an open grassland growing on the gently sloping hilltop. Figure 2 gives a general view of the setting.

HISTORY OF MINING

Some time prior to 1929, coal was dug from two small drifts on the property; in 1942, one of these drifts was reopened and briefly used as the entry for a small mine.

In 1952, coal was stripped from along the southwest and southeast sides of the hill. The stripping was backfilled but not restored to contour. From later in 1952 until 1958, the coal was deep mined by conventional methods with good roof conditions and relatively little water seepage. Beginning in 1958, the remaining pillars of coal were mined; by 1959, all recoverable coal had been removed. The main entries were sealed in 1962 for safety purposes. The former operators reported a moderate increase in mine water after the pillars were mined.

During and after mining, there was surface subsidence within a small area along the northern limit of the property, but no other evidence of surface subsidence was observed.

SULFUR BURDEN OF ROCKS

It has been well established in the literature that the source of sulfur essential for the formation of acid mine water is in the iron sulfides, which are erratically distributed throughout the coal and adjacent rocks. Organic sulfur compounds associated with coal are not sufficiently reactive to contribute to the formation of acid mine water.

Channel samples of the coal from the mine have an average pyritic sulfur content of 0.35 percent. Low values of 0.17 to 0.36 percent also were determined from samples of roof rock, while gob recovered from the old workings contained an average of 2.00 percent pyritic sulfur. The highest and, also, most erratic values were found in the layer of underclay, just below the coal. These ranged from 0.27 to 17.28 percent. It, therefore, appears that most of the sulfur in the mine occurs in the gob piles and the top layer of underclay.

DIAMOND DRILLING

In order to gather as much information as possible on the environment of the mine, four core holes were drilled into the strata overlying the mine workings and two auger holes were drilled in the spoil banks or backfill from the strip mining.

In brief, the core holes showed the following:

1. Depth to bedrock was 10 to 12 feet.
2. Bedrock was soft or oxidized to a maximum depth of 95 feet.
3. Fracturing due to mine subsidence was not evident.
4. Core recovery was good.
5. Siltstone was the most abundant rock type.
6. Laboratory tests on water permeability of the sandstone showed only 0.01 md.

7. The mine workings were largely filled by caving or heaving of the floor, although conditions varied.

8. Only one of the four holes retained any water above the mine workings.

9. Limestone occurs only below the coal seam and underclay and can have little neutralizing effect on the mine water.

GROUND WATER

The flow rate of the mine discharge ranges from 6 to 632 gpm and is dependent chiefly on the season and quantity of precipitation. The base flow of 6 to 8 gpm persists throughout prolonged dry spells and is derived from ground water storage depletion, while peak flows are associated with late winter and spring precipitation and thaws. The graph shown in figure 3 covers only a 1-year period but is representative of these relationships. The graph also shows that the acid load of the mine effluent, which is a product of acidity times flow rate, is proportional to the flow rate. Similar proportions and seasonal effects on mine flow rates have been reported by S. A. Braley.^{3/}

The graph shows a lag in response of the flow rate to precipitation of from 3 to 5 days, indicative of the time required for water to percolate from the surface to the mine workings.

In calendar year 1964, which was selected for analysis, a total of 41.96 inches of precipitation was recorded. During the same period, total mine effluent was equivalent to 12.84 inches of precipitation for a 92-1/2-acre area. These values suggest that about 30 percent of the precipitation over the area infiltrates downward into the mine; the remaining 70 percent is retained as aquifer recharge or is lost as runoff and evapotranspiration. This is in general agreement with the work of Carpenter and Davidson,^{4/} who found that the quantity of drainage from shallow mines in western Pennsylvania equaled about 25 percent of the precipitation above the mine.

^{3/} Braley, S. A. Acid Mine Drainage IV. Composition and Flow. Mechanization, v. 18, No. 4, 1954, pp. 137-138.

^{4/} Carpenter, L. V. and A. H. Davidson. Development in the Treatment of Acid Mine Drainage. West Virginia Univ. Assoc. Bull. 2, No. 4, 1930, pp. 50 to 57.

The high rate of infiltration occurs chiefly during the dormant season and appears to be facilitated by the gentle slope of the topography, a natural permeability of the soil, and subsidence fractures in the bedrock.

The presence of subsidence fractures may be inferred from the fact that pillars were removed from much of the mine and from the loss of three springs on the property during the course of mining. The relative soil infiltration rate was determined by using the double ring infiltrometer on different soil types above the mine and, for purposes of comparison, on materials of similar or contrasting properties from other localities. Results show that the soil types above the mine may be classified as highly permeable and capable of transmitting relatively large amounts of meteoric water to the subsoil and bedrock.

GEOCHEMISTRY OF GROUND WATER

Drainage from the mine consists of ground water which has derived its chemical composition chiefly while percolating downward through the overburden and passing through the mine workings. It is characterized by high acidity and a high concentration of dissolved solids. The temperature of the water from the mine virtually is constant at 52° F.

Other nearly constant qualities of the mine water are the pH and Eh, which fluctuate within the narrow range of 3.0 to 3.2 and 625 to 825 mv, respectively. Conductivity varies over a moderate range of 1,400 to 2,600 micromho. It correlates closely with the fluctuation in dissolved solids content of which iron sulfate constitutes the major percentage. Total acidity, measured in terms of equivalent CaCO₃, ranged from 180 to 950 ppm and showed a correlation with the total iron content of the mine water since sulfates other than iron contribute very little to the total acidity; the dissolved solids concentration is an approximate index of the total acidity under the current conditions. Figure 4 shows the results of plotting the mine effluent flow rate against 139 total dissolved solids analyses which are separated, according to the time of sampling, into growing and dormant season for the period of October 1963 to October 1964. Two features of the plot are particularly outstanding: The contrast in solute between the dormant and growing season, and the correlation of dormant season solute and flow rate below 300 gpm. High flow rates were not determined. The solute concentration is inversely proportional to the flow rates below 300 gpm reflecting the dilution effect of increased flow. At discharges greater than 300 gpm, the above effect apparently is overcome by a flushing action in the mine whereby higher water levels dissolve an accumulation of highly acid salts which have formed as a result of the oxidation of iron sulfides. In flow rates of less than 150 gpm, there is more solute in the mine water during the dormant season than the growing season. As yet, there is no satisfactory explanation for this relationship. Similar relationships were observed between total acidity and flow rate.

DISCUSSION

We have attempted to determine the environmental conditions of the mine and have collected data on the volume and quality of the mine discharge so that we have a basis for comparing water quality before and after sealing and, therefore, can evaluate the effectiveness of air sealing in reducing the acidity. We have tried to determine the source of the mine water in order to try to divert or seal off surface water and reduce the acid load of the effluent. The high infiltration rate and permeability of the overburden to water suggest that we may not be successful in this direction.

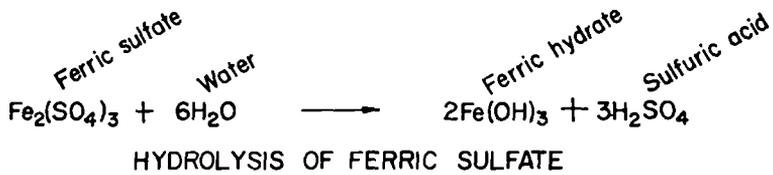
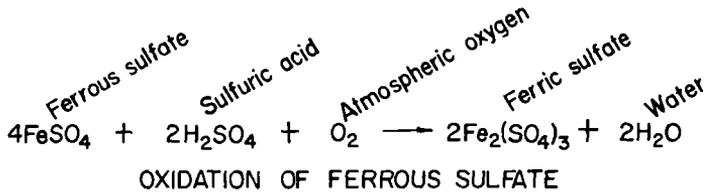
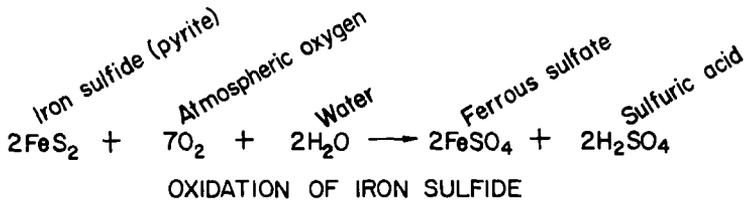


FIGURE 1. - Summary of the Reactions Involved in the Formation of Acid Mine Water



FIGURE 2. - General View of the Mine Property

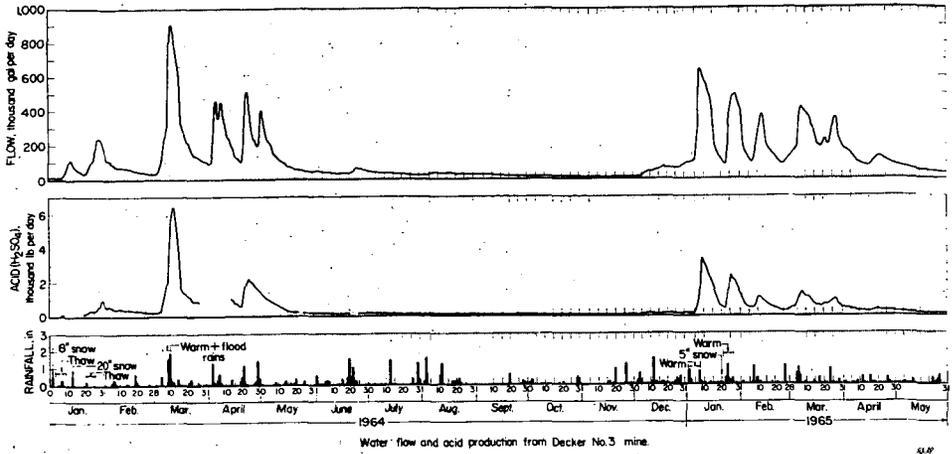


FIGURE 3. - Graph Showing the Relationship of Mine Effluent Flow Rate to Precipitation

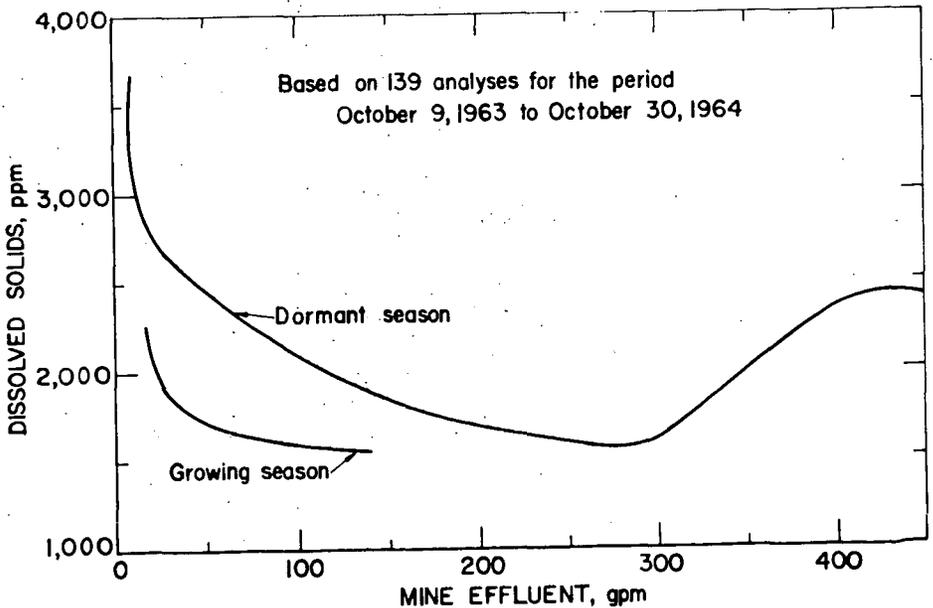


FIGURE 4. - Graph Showing the Relationship of Total Dissolved Solids Concentration to the Mine Effluent Flow Rate

SUBSURFACE DISPOSAL OF ACID MINE WATER

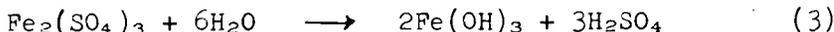
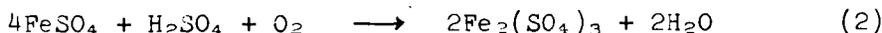
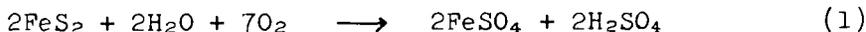
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Introduction

While the mining industry has concerned itself with mine drainage in the past, recent legislation in Pennsylvania has accented the problem. Reclassifying acid mine drainage as an industrial waste and prohibiting its disposal into any stream, clean or polluted, were the two basic changes in the new Clean Streams Bill that caused a re-appraisal of an old and perplexing problem. With millions of gallons of mine water containing sulfuric acid, ferrous sulfate and ferric hydroxide being discharged annually in amounts of acidity varying from 50 to 20,000 ppm, research has been accelerated in an attempt to obtain a solution.

Iron disulfide, FeS_2 , associated in surrounding rock strata as well as in the coal seam itself, undergoes chemical change in the presence of air and water, resulting in acid water formation. While there is some disagreement as to the exact mechanism, the following reactions are generally accepted:



There is no typical acid mine water and it is a more complex solution than the above equations would indicate. Not only does the ferrous to ferric iron ratio vary, but pH is not a true indicator of total acidity. Additional ions such as silica, aluminum, manganese, calcium and magnesium are present, as well as autotrophic bacteria which are thought to accelerate the formation of acid.

While coal associated iron disulfide usually is isolated from oxygen and water in its natural environment in the earth, mining the coal seam removes support from the overlying strata inducing caving. An influx of water and air, together with the exposure of additional acid-producing materials, provide all of the necessary ingredients for the above reactions to occur. Even then, if the water could be removed from the mine immediately, acid water need not be produced. Unfortunately, the caved areas become inaccessible and the overflow is the major contributor of acid mine water. It becomes obvious that any cessation of mining activity would aggravate the problem, since at least in active mines water is pumped regularly and thus exposure time is minimized.

Some people have advocated that sufficient coal be permitted to remain in place to prevent caving. Aside from the economic loss of the coal left behind, other factors must be considered. In many coal fields the systematic pulling of pillars and controlled caving is the only way that excessive rock pressures are relieved and the excavation

can be maintained. Another risk to leaving pillars behind is that spontaneous combustion can lead to a mine fire. With mines going to greater depth because of depletion of shallower deposits, longwall mining will increase. This system more than any other requires controlled caving, thus the problem could become aggravated.

The Coal Research Board of the Commonwealth of Pennsylvania is supporting research projects encompassing a wide variety of studies including: destruction of acid-forming bacteria by phages; economic removal of iron; more efficient neutralization of acid water on a commercial scale; purification of acid water by a distillation process; and the subsurface disposal of acid mine water. This paper is concerned with the last project listed. While better abatement measures will minimize some of the pollution, without doubt there always will be some water that must either be treated or disposed of in a prescribed manner. While the authors make no claim that deep well disposal is a panacea for mine acid problems, nevertheless it deserves close scrutiny as one solution to this problem.

Present Applications of Subsurface Disposal

Subsurface disposal involves removing unwanted materials from their original environment and placing them in isolated subterranean zones. Permanent removal of undesired liquid water generally is accomplished by using injection wells to transport the material to the disposal zone.

The petroleum industry first employed subsurface disposal in the early part of the twentieth century to dispose of oil field brines⁽¹⁾. During the past ten years, other industries have adopted this method to dispose of manufactured wastes. Injection wells are presently being used in the drug, chemical, steel, and paper manufacturing industries⁽²⁾. Radioactive material from nuclear plants also is being injected into disposal wells.

Injection wells are drilled from the surface to the geologic formation selected as the disposal zone. Disposal wells are drilled and completed in the same manner as gas and petroleum wells, and waste travels down the well through a non-corrosive injection tube. Surface facilities associated with injection wells consist of a waste gathering and storage system, filtering equipment, and one or more pumps. Multi-barreled displacement pumps usually are used with injection wells.

The rate at which a disposal well can accept fluid depends upon the fluid properties, rock properties, the size of the well and the pressure gradient in the system. Pumps provide the pressure necessary to push the waste into the disposal zone. The necessary injection pressure may be calculated from the following relationship:

$$P_i = P_f - P_s + P_l \quad (4)$$

where P_i = Injection pressure from pump
 P_f = Well bottom formation pressure
 P_s = Pressure of fluid column in well
 P_l = Friction loss in injection tube

(1) References at end of paper.

Formation pressure (P_f) cannot be measured until the well has reached the disposal zone and, even then, an accurate measurement is not always possible. An estimate of the formation pressure can be made by multiplying the well depth by the geologic pressure gradient. The generally accepted pressure gradient is one pound per square inch pressure per foot of depth. The fluid column pressure (P_s) can be calculated from the well depth and the fluid density. Friction loss (P_1) can be calculated from well depth, injection tube material and size, and the flow rate. Flow rate into the disposal formation is usually not directly proportional to injection pressure. At higher pressures, incremental pressure increases result in a proportionately greater flow rate.

If it becomes desirable to increase flow rate for a given pressure, the formation properties may be altered. Several methods of well stimulation are practiced in the petroleum industry to achieve a more efficient well(3). These practices are hydraulic fracturing, nitro-shooting, well perforating, and acidizing. Hydraulic fracturing is the most popular of these methods.

Despite increased application, disposal wells still are not too numerous. Only six waste injection wells exist in Pennsylvania. This scarcity results from the large financial investment that must be made before the success of the installation can be ascertained. The drilling, casing, and testing of a 2000 feet deep disposal well costs approximately \$70,000. Although an analysis of an injection well's performance cannot be predicted before field trials, some conditions are more favorable to subsurface disposal than others.

Pertinent Geologic Factors

The main factor to be considered when contemplating the establishment of a disposal well is the presence of the proper geologic formations. The disposal formation must have a large enough storage capacity to contain the total volume of fluid that will be injected during the life of the well. This capacity depends upon the area and thickness of the formation and upon the effective porosity of the formation. A disposal formation should also be surrounded by relatively impermeable rocks to prevent migration of the waste away from the disposal zone. The disposal zone, however, should be very permeable to allow rapid flow of the waste away from the well with a minimum expenditure of pumping energy. Finally, a potential disposal zone should not contain usable ground water or any economic fuel or mineral deposit that could be contaminated by the waste.

The bituminous coal fields of central and western Pennsylvania lie in a region of stratified sedimentary formations. Rock types are sandstones, limestones, shales, siltstones and claystones, and all vary in areal extent and thickness. Shales, siltstones, and claystones are very impermeable rocks of low porosity and generally are ruled out. The two remaining rock types, if occurring in large enough bodies, can be considered potential disposal reservoirs.

Many sandstone beds are quite thick, underlie large areas, and often have high values of porosity and permeability. Fluid flow through a sandstone brings the liquid into intimate contact with the rock, causing a maximum amount of contact between the waste and the formation. Sandstones are largely silica, a comparatively non-reactive element.

Limestones generally exhibit lower permeability and porosity than sandstones and are often partially dissolved by ground water, forming a series of subterranean channels. Fluid flow in these channels is similar to flow in an irregular system of pipes. Although formation to fluid contact is minimal, the extent of the fluid migration is difficult to determine. Limestone is calcium carbonate, a more reactive compound than silicon dioxide.

General geologic structural information is available for many of the larger rock units in central and western Pennsylvania. Detailed lithologic information is very limited, however, and any area being considered for an injection well site should be thoroughly evaluated, even to the extent of a core drilling program. Many well driller's logs are available for the above area, but experience has shown that these often do not contain reliable lithologic information.

Waste Properties Vital to Subsurface Disposal

The experience of companies using injection wells has shown that wastes which are to be injected into porous beds ideally should have the following properties:

1. A pH less than the formation water
2. No suspended solids
3. Low viscosity
4. Low metal content
5. High specific gravity
6. No self-polymerizing materials
7. No dissolved gases
8. No bacteria

The waste should also be chemically stable and compatible with the formation rock and fluids. The main concern in injecting wastes into a porous formation is the possibility of plugging the disposal zone with suspended particles carried in the waste or with precipitates resulting from chemical reactions occurring in the disposal zone. Recovery of a plugged well is expensive and time consuming.

Acid mine water, while having a low pH and viscosity and containing no self-polymerizing materials, does not meet the other criteria. Of particular concern are the presence of suspended solids, bacteria, dissolved gases, and concentrations of iron. Acid mine water is not chemically stable and its compatibility with the formation will not be known until samples of the rock and connate water are available. It is felt that these problems, although difficult, are not insurmountable and each can be solved.

Specific Acid Mine Water Disposal Problems

Autotrophic bacteria are present in acid mine water. Research indicates that these bacteria collect on iron particles and form colonies as large as 50 microns in diameter⁽⁴⁾. Particles of this size could easily plug a sandstone face. In other disposal wells bacterial plugging has been eliminated by adding a bactericide to the waste before injection. Addition of an effective bactericide to acid mine water would kill the bacteria and prevent colonization.

Dissolved gases are detrimental because they promote corrosion and provide material for unwanted chemical reactions. Oxygen and hydrogen sulfide which can occur in mine water are particularly undesirable, as both can react with metallic ions to produce precipitates. Large volumes of dissolved gases can lower pump efficiencies. The amount of dissolved gas present in acid mine water can be kept minimal by assuring that the water is collected and stored prior to injection with the least possible exposure to air.

Removal of suspended particles in the waste is also an important consideration, particularly if the disposal formation is a sandstone. Pre-injection filtering should remove particles down to one micron. Coated pressure leaf filters are normally used in this application. If surface filtering facilities are not provided, the disposal formation may act as a filter and become progressively less permeable as it becomes plugged by the suspended particles.

Chemical reactions between acid mine water and the formation water may be prevented by injecting a non-reactive buffer zone between these two liquids. The material selected for the buffer zone, which will physically separate the formation water and the mine water, should be low in cost and chemically inert with respect to the mine water, the formation water, and the rock. After waste injection has commenced, liquid diffusion and dispersion will occur in the formation. This activity will eventually cause the formation water and the waste to contact each other. If a sufficient buffer zone has been injected, this mixing will not occur until near the end of the life of the well. When contact is established, the waste and the formation water will be diluted by the buffer liquid.

The chemical instability of acid mine water may cause intra-formational precipitation. Hopefully, this possibility is reduced by the lack of oxygen in the disposal zone. Possible oxidation of ferrous iron to ferric, and subsequent precipitation of ferric hydroxide is of particular concern as this is a gelatinous material. The oxidation state of iron is a function of pH, therefore, this reaction may be eliminated by lowering the pH of the mine water prior to injection to keep the iron in the ferrous state. Other anti-precipitation agents used in disposal wells are citrates and sodium tripolyphosphate (5).

Conclusions

It is accepted that many variable factors are involved in the installation of a subsurface disposal well. Theoretical solutions are available for many of the foreseeable problems, but several unexpected developments may occur. While past experience with other disposal wells may be used as a guide to developing a new well, it can not be expected to provide answers for all problems that may arise. Each disposal well will have to be approached as an individual engineering problem.

References

1. Anonymous, Subsurface Salt-Water Disposal, American Petroleum Institute; Dallas, Texas, 92 pp, 1960.
2. Donaldson, Erle C., Subsurface Disposal of Industrial Wastes in the United States, Bureau of Mines Information Circular

8212, 34 pp, 1964.

3. Stefanko, R., Vonder Linden, K., and Tilton, J. G., Subsurface Disposal of Acid Mine Water by Injection Wells, Special Research Report SR-52, The Mineral Industries Experiment Station, The Pennsylvania State University, pp 22-28, 1965.
4. Colmer, A. R., Temple, K. L., and Hinkle, M. L., "An Iron-oxidizing Bacterium from the Acid Drainage of Some Bituminous Coal Mines," Journal of Bacteriology, vol. 59, pp 317-328, 1950.
5. Johansen, R. T. and Heemstra, R. J., The Effectiveness of Sodium Tripolyphosphate for Improving Injection Rates of Waterfloods, Bureau of Mines Report of Investigations 6557, 15 pp, 1964.

DESIGN AND ECONOMICS OF AN ACID MINE
DRAINAGE TREATMENT PLANT -
"OPERATION YELLOWBOY"

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INTRODUCTION

With the passing of the Pennsylvania Clean Streams Law a technically sound and economically feasible process for the treatment of acid mine drainage (AMD) is desired. Water standards, set down by the Pennsylvania Sanitary Water Board, prohibit the discharge of mine water that has an iron concentration in excess of seven parts per million. The pH of the mine water discharge must be within a range of 6.0 to 9.0. These standards will require at least 80 percent of the mine discharges within the Commonwealth to resort to an acid mine drainage treatment process.

In an effort to alleviate the problem of acid mine drainage, the general assembly of the Commonwealth of Pennsylvania legislated Act 43A in June, 1964. This act allocated \$100,000 for the payment of cost and expenses incurred in developing, constructing, staffing and operating a mobile pilot plant for the treatment of this vexing pollutant. This appropriation was allocated to the Coal Research Board of the Commonwealth's Department of Mines and Mineral Industries, who awarded Dorr-Oliver, in October, 1964, a research grant to design, fabricate and operate a mobile demonstration plant for the treatment of acid mine water. The objectives of the Dorr-Oliver program are to perform unit operations in a mobile pilot plant at various mine sites throughout the Commonwealth and obtain design and economic data that can be used to evaluate the process under examination.

A four phase research and development program was planned to carry out the objectives of the project.

Phase I - Feasibility Study and Site Selection.

Phase II - Pilot Plant Design and Fabrication.

Phase III - Operation.

Phase IV - Process Evaluation.

The program is currently in Phase III - Operation and to date six mine sites have been tested.

TREATMENT PROCESS

The process chosen for the treatment of the acid mine drainage is the lime-neutralization-aeration-dewatering process. Basically this is a four step process and involves the following steps:

Step 1. Neutralization

This entails the conversion of

- a) sulfuric acid to calcium sulfate

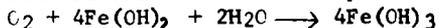
$$\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$$
- b) ferrous sulfate to ferrous hydroxide and calcium sulfate

$$\text{Ca(OH)}_2 + \text{FeSO}_4 \longrightarrow \text{Fe(OH)}_2 + \text{CaSO}_4$$

green ppt.

Step 2. Aeration (oxidation)

The oxidation of ferrous hydroxide to ferric hydroxide



Step 3. Clarification - Thickening

Step 4. Dewatering

The flow sheet of the process is presented in Figure 1. Acid mine drainage is brought into the pilot plant by the means of a self-priming centrifugal pump and is pumped through a flow meter into a flash mixer where hydrated lime is added from a screw feeder to neutralize the mine water. By means of gravity the neutralized mine water and suspended solids, consisting primarily of ferrous hydroxide and gypsum, flow into an aerator. Air is brought into contact with the ferrous hydroxide converting it to ferric hydroxide by the means of a turbine mixer and an air blower. After aeration the slurry, consisting of neutralized mine water and suspended solids, flows by gravity into a thickener. Chemical flocculating agents can be added to this slurry to increase the settling rate of the suspended solids and improve the effluent clarity if desired. The suspended solids in the neutralized mine water slurry settles to the bottom of the thickener while the clear effluent overflows the thickener and is considered treated mine water. The thickened slurry is then pumped to a solid bowl centrifuge for additional dewatering. The centrate, depending on its quality, may be considered treated mine water or, if required it may be returned to the thickener for additional processing. The cake is considered process waste.

PILOT PLANT

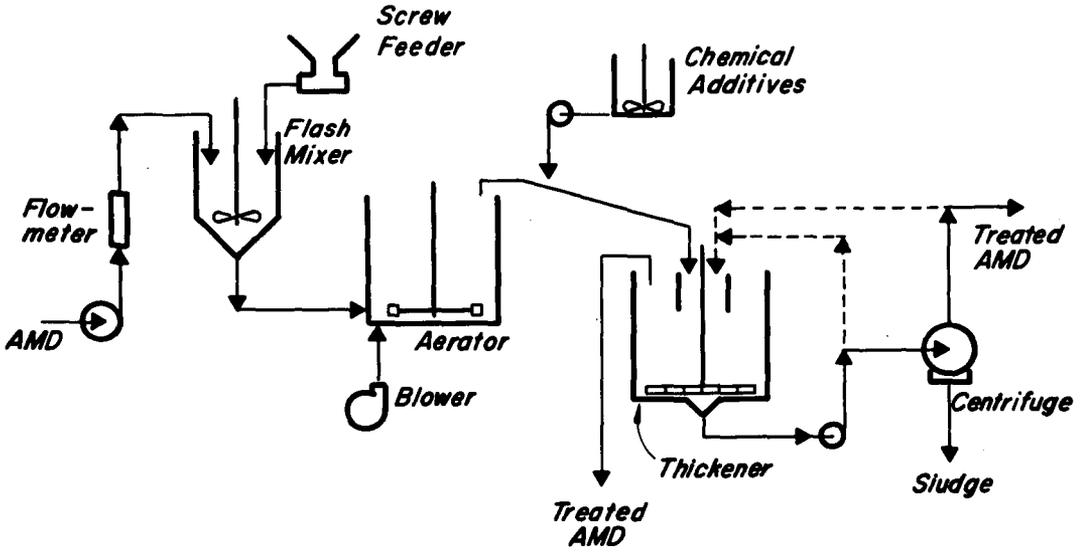
Information derived from Phases I and II led to the hydraulic design of a 50 gallon per minute pilot plant. The pilot plant was erected in a 40 foot long van type trailer that complied with the regulations for use on Pennsylvania roads without special permits. The mobile pilot plant was easily hauled from one site to the next. Figure 2 is a curb side view of the trailer while Figure 3 is a close-up of the pilot plant. The flow of mine water through the plant is from left to right. Pilot units shown in Figure 3 are the aerator, flocculent mixing tank, thickener, solid bowl centrifuge, and the pilot plant's power source - a 25 kw diesel generator.

A laboratory bench located in the forward section provides a work area for performing routine chemical analysis, settling tests, and leaf filtration tests.

TEST SITE

The first test site chosen for field operations by the Coal Research Board and that which forms the basis of the material reported in this paper is The Bethlehem Mines Corporation, Marianna Coal Mine No. 58, located at Marianna in Washington County. This is an operating shaft mine in which 7000 tons per day of Pittsburgh coal is mined. The coal is processed in a cleaning plant where 5000 TPD of clean coal is produced along with 2000 TPD of refuse. Mine water is collected in sumps within the mine and pumped to the surface four times a day at periods up to one hour per pumping. Reaching the surface the water flows by gravity through a conduit into Ten Mile Creek.

The acid mine water processed in the pilot plant was obtained from the Marianna Mine No. 58 bore hole prior to its flowing into Ten Mile Creek. Because of the intermittent pumping schedule a 24 ft. diameter by 4 ft. in height storage pool was filled with mine water each day from the morning pumping to serve as a supply for the duration of the pilot run. The influent was obtained by placing a hose into the storage pool and pumping with a self-priming pump into the flash mixer. The raw acid mine water was metered either by a flowmeter on the discharge side of the feed pump or by



FLWSHEET FOR AMD TREATMENT

FIGURE 1

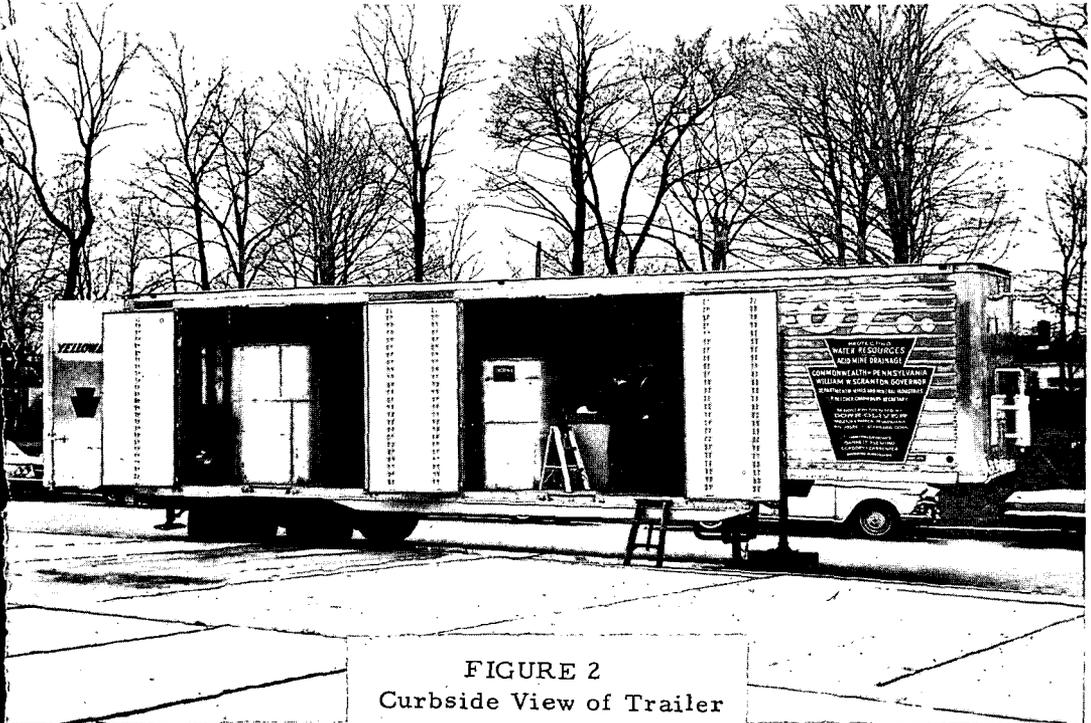


FIGURE 2
Curbside View of Trailer

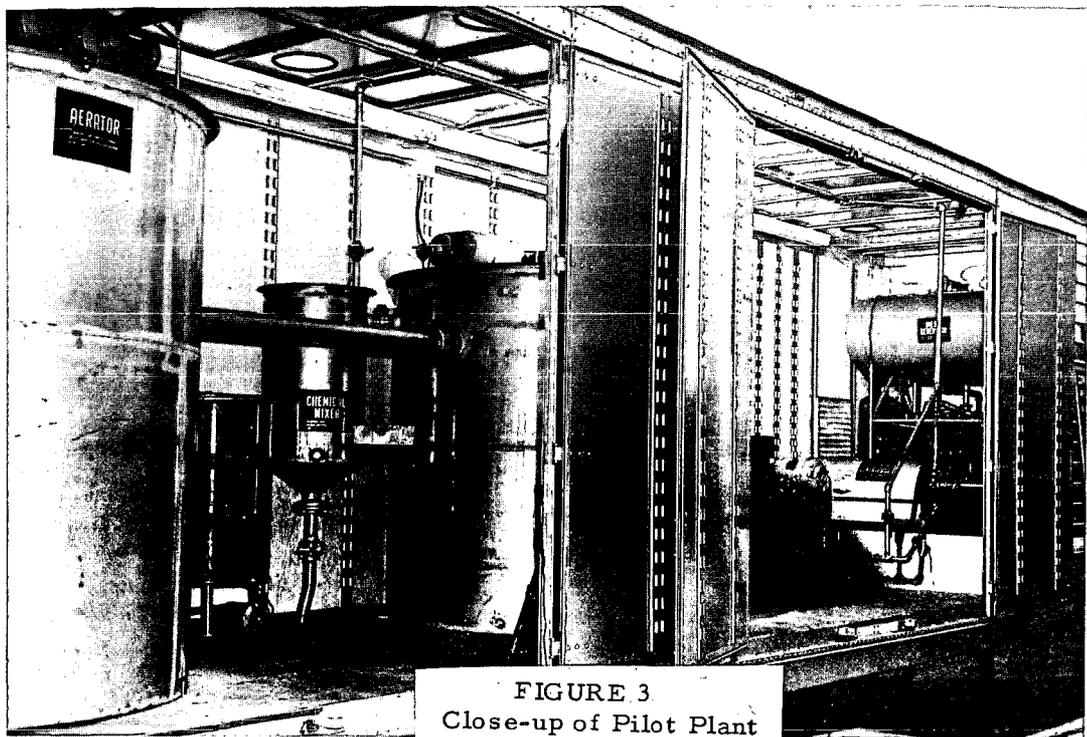


FIGURE 3
Close-up of Pilot Plant

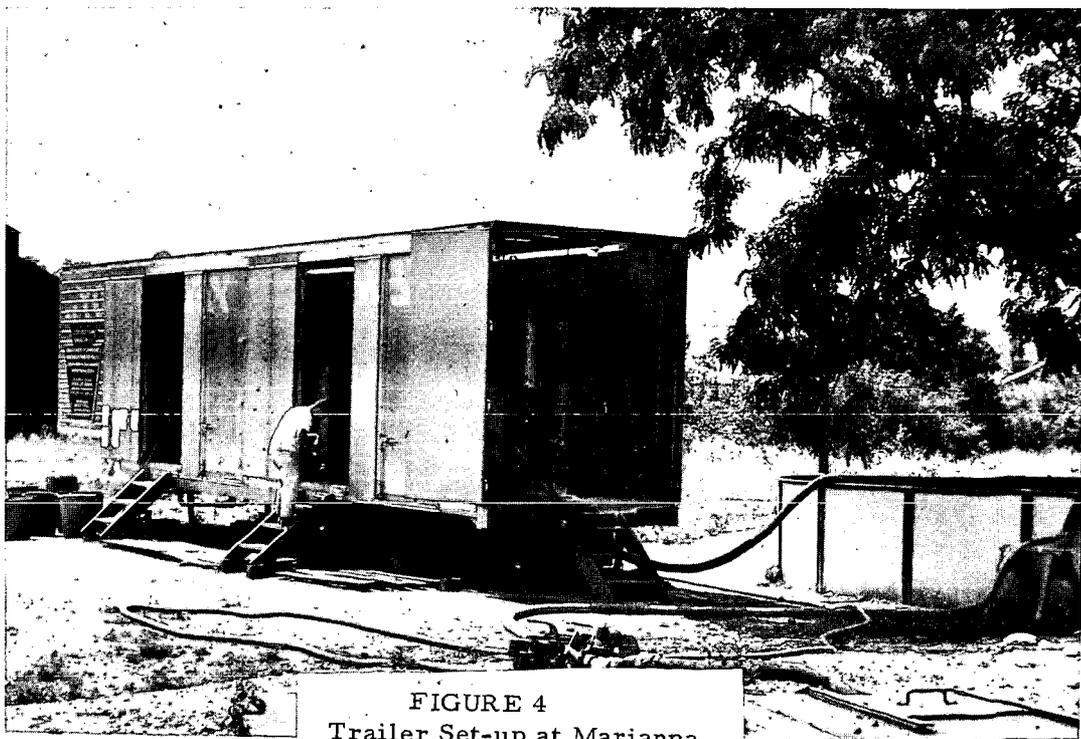


FIGURE 4
Trailer Set-up at Marianna

checking the volume per unit time of thickener overflow which accumulated in a 50 gal. head tank attached to the side of the thickener. After processing, the treated mine water was returned to a man hole where it was discharged into Ten Mile Creek. The resulting yellowish sludge was accumulated in 20 gal. pails. Figure 4 is a photograph showing the set-up at this site.

PILOT PLANT OPERATION

The pilot plant operated at the Marianna Mine No. 58 during May and June of 1965. The first month's operation served as a shakedown period for the pilot plant and its operating crew. This period showed the inconsistency of the mine water chemical analysis in that the iron content and the acidity would fluctuate with each pumping cycle. The reason for this fluctuation, was that the mine water is first collected in sub-sumps and is then pumped to a main sump where it is pumped up the bore hole and permitted to flow to Ten Mile Creek. Acid forming conditions (pyrite, air, and water) varied within different areas of the mine resulting in different strengths of mine water. By using the storage pool, before feeding the acid mine drainage to the pilot plant, the fluctuations were kept to a minimum.

A Mason "N" hydrated lime was used for the neutralization of the mine water. The lime demand of the process proved to be just about Stoichiometric.

After it was felt that the "bugs" had been eliminated from the pilot plant units, a four day continuous test was conducted. This run was well monitored with sampling and laboratory analysis being run every three hours. During this period a close observation was kept on the various unit operations of the pilot plant and necessary design data was recorded.

A composite of the raw and treated acid mine water chemical analyses collected during this continuous test is reported in Table 1. The data demonstrates that the raw acid mine drainage was up-graded from a pH of 2.64 to a pH of 7.6. The total iron in the water which was 815 ppm was reduced to 5.8 ppm. Manganese, silica, and alumina were also reduced with the increase in pH. Silica and alumina had a beneficial effect on sedimentation in that they form large flocs upon reaching their solubility limit and aid the coagulation of the iron hydroxide.

DESIGN DATA

The scaled-up data used for the engineering design was generated during the shakedown period of the operation and confirmed during the continuous test run. Individual unit operations were investigated and the findings are as follows:

A. Flash Mixing

This investigation entailed feeding acid mine water to the flash mixer at different rates. Hydrated lime was mixed with the mine water and pH readings were taken of the neutralized mine water as it flowed on its way to the aerator. Detention times between one and seven minutes were investigated at a constant propeller speed of 350 rpm. During this investigation it was found that the detention time was always sufficient to ensure neutralization ($\text{pH} > 7$). It should be noted that this test was made in May and June and the ambient temperatures at Marianna were in the neighborhood of 80°F. during the day. At colder temperatures longer detention times may be required.

B. Aeration

The pilot plant aerator produced 2 SCFM of air which is the equivalent of 16.9 g. of oxygen per minute. This air supply, assuming 100 percent efficiency, would

oxidize 121 grams per minute of ferrous ion to ferric ion. At this aeration rate satisfactory oxidation always was achieved.

An intensified aeration study was not conducted at Marianna because it was difficult to maintain a uniform supply of ferrous ion to the aerator due to hydrolysis in the storage pool. It was also difficult to supply hydrated lime to obtain neutralization at high through-puts of mine water.

Aeration equipment was designed from basic process data without the need of field testing. The information required was:

- 1) Volume of water per minute
- 2) Oxygen uptake
- 3) Depth of aerator
- 4) Desired dissolved oxygen level

All this information was collected during the test runs.

C. Flocculation Tests

A bench study was conducted to determine flocculating agents that will improve the clarity and settling rates of the aerator overflow during sedimentation. Evaluation was made by comparing the physical behavior of the suspended solids in a freshly obtained sample of aerator overflow before and after the addition of a flocculent.

Reported in Table 2 are some of the favorable flocculents tested and their required dosages to produce a clear effluent. Nalcolyte 670 appeared to be the most prominent flocculent tested from the results of the bench scale tests. However, when Nalcolyte 670 was employed in actual pilot plant operation it did not perform adequately and Nalcolyte 672 was substituted and produced excellent results.

When a flocculent was used on the continuous test run the product water contained less than 1.5 ppm of iron as opposed to an average of 6 ppm in the non-flocculated product water.

It was also discovered during the bench test that some flocculents are apparently more pH sensitive than others which implies that pH control of plant operation must be held to precise control ranges if effective flocculation is to be maintained. It should also be noted that while flocculents increase settling rates they do not necessarily increase the solid concentrations of the thickener underflow. Centrifuge and bench filtration tests demonstrated that within a few hours after the floc had formed and settled it apparently went stale. The original floc formation, when disturbed by pumping, will break up and not reform again to its original well flocculated structure. Because of this effect no real additional benefits can be gained from flocculation in further dewatering steps.

D. Thickening Tests

Bench scale settling tests were performed and the results were checked in the pilot plant thickener during the shakedown period and continuous run. Summarized in Table 3 are the important design criteria that were determined from these tests.

Operation of the pilot thickener was designed so that the feed rate to the thickener would not exceed the unit area of 89 sq. ft. per ton per day. When this rate was followed no difficulty was encountered in maintaining overflow clarity substantiating the bench settling tests.

Centrifuge Tests

Centrifuge tests were conducted using the Merco Z-1-L solid bowl which is an integral unit of the pilot plant. Feed slurry was pumped to the centrifuge from the settled thickener underflow by way of a positive displacement pump. Difficulty was experienced in obtaining and maintaining a clear centrate in the early stages of operation. The slurry is definitely plastic in nature. The unit was operated at solid bowl speeds ranging from 4,620 rpm up to 5,600 rpm with a scroll differential between 23 and 38 rpm's and contained a ring dam with a diameter of 6.5 inches. A ring dam influences the capture and the dryness of the products from the centrifuge. A small inside diameter ring dam causes the depth of the liquid in the bowl to increase, thus improving the capture and increasing the cake moisture. A large inside diameter ring decreases the depth of liquid in the bowl thus reducing the capture and decreasing cake moisture. When it became apparent that the larger ring dam was not producing the desired results a 5.9 inch ring dam was inserted. For the first few days of operation with the small ring dam and a lower bowl speed no effect on the centrate clarity was noticed. At this time a flocculating agent was added to the thickener underflow while it was being fed to the Z-1-L. This immediately cleared the centrate and for a period of time the unit was operated with flocculent until it was discovered that a flocculating agent did not have to be added continuously. A clear centrate was also attained by "slugging" the centrifuge with a flocculating agent whenever the centrate became cloudy. After a good iron hydroxide and gypsum beach had been built up within the unit it was no longer necessary to use flocculents to achieve good consistent clarity.

Although the centrifuge cake consistently averaged 30 percent solids or greater and the suspended solids recovery was approximately 100 percent the desired feed rate to the unit could not be achieved. Power costs also proved to be high. For this reason filters were chosen in place of centrifuges in the final design of the plant.

Filtration Tests

Laboratory filtration tests were conducted on samples of the thickener underflow using a 0.1 sq. ft. test filter leaf at cycles and conditions simulating those of drum and disc filters. For all the tests performed a filtercloth of Nylon 1016 material was used. This is a relatively tight cloth and the use of this cloth has proven superior to other cloths in an earlier laboratory testing program (Phase 1 of the Yellowboy Project). The results demonstrated that only a small benefit can be derived from the filtration of a thickener underflow that had been flocculated.

In all cases tested a quick drum cycle appears to provide the best filtration results. Although the cake thickness is only 1/16 of an inch, the tests demonstrated that a good roll discharge can be attained.

Presented in Table 4 are the important design data derived from the filter tests and used as the basis for filter scale-up.

PLANT DESIGN

Design data generated during the pilot plant operation at Marianna has been used as a basis for the scale-up to a full-size acid mine drainage treatment plant. This plant has been designed to treat a flow of 240,000 gallons per day of mine water.

Presented in Figure 5 is a schematic diagram of the flowsheet recommended for treating all the acid mine water from the Marianna Mine No. 58 bore hole. Basically the flowsheet is the same as that tested in the pilot plant with a few minor modifications to make it adaptable to this location. The raw mine water is pumped to a holding pond, which is already in existence, prior to entering the treatment plant. The process for this is as follows:

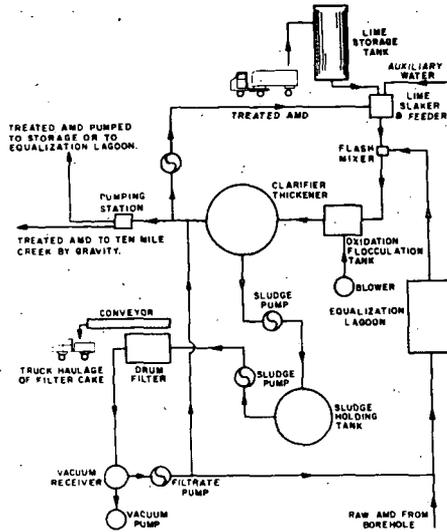


Figure 5

COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF MINES AND MINERAL INDUSTRIES

SCHEMATIC DIAGRAM
OF AMD TREATMENT PROCESS

Bethlehem Steel Company Mine No. 58
Marianna, Pennsylvania

FIGURE 5

FIGURE 6

ACID MINE WATER
TREATMENT PLANT CAPITAL EXPENDITURES

Water Storage and Transportation Facilities	\$ 22,800
Control-Filter Building	223,000
Aeration	6,000
Thickener	45,000
Sludge Holding	9,500
Piping and Site Preparation	<u>40,900</u>
Total Capital	\$347,200

FIGURE 7

ANNUAL COSTS

Amortization (20 yrs @ 4.0%)	\$25,550
Labor	36,500
Power	4,700
Chemicals (Lime)	22,000
Maintenance	<u>6,500</u>
Total Annual Costs	\$95,250

1. A uniform flow will be maintained when pumping from the mine is intermittent.
2. It is anticipated that scaling will be a problem and shut-downs of the plant will be necessary from time to time. In order not to interfere with the pumping from the mine the lagoon will supply ample storage capacity.
3. Hydrolysis will take place resulting in less demand of aeration equipment during the treatment process.

The mine water in the holding lagoon flows by gravity to the treatment plant where it is neutralized by the addition of milk of lime in a flash mixer and then aerated. The slurry then flows to a thickener where the solids settle and the effluent, process product, flows to Ten Mile Creek. The settled solids are then filtered, with the filtrate being blended with the raw mine water or depending on quality, can also be returned to Ten Mile Creek. The filter cake (25% solids) is trucked to a nearby site. The holding lagoon is cleaned periodically by slurring the settled solids and processing at the treatment plant.

COST EVALUATION

Different plans of operating the acid mine drainage treatment plant have been studied and the economics are in favor of continuous treatment of the mine water through the thickening-clarification step. The filters are operated only one shift per day for even days a week.

The scale-up of the pilot plant data to treat a flow of 240,000 gallons per day (167 gpm) would require a capital expenditure of \$347,200. This cost is exclusive of additional treatment of sludge. Annual costs are \$95,250. A breakdown of these costs is shown in Figures 6 and 7.

Based on treating 240,000 gallons per day and marketing 5000 tons of clean coal per day (actually 7000 tons per day of coal is mined; after coal preparation 2000 tons reports to refuse while 5000 tons is marketed) the annual unit costs are \$0.052 per ton of clean coal marketed or \$1.09 per 1000 gallons of acid mine water. These costs exclude expenditures for additional sludge treatment.

CONCLUSION

It is in the scope of this report to present the technical feasibility and economic soundness of treating acid mine water at the Bethlehem Mines Corporation, Marianna Mine No. 58 by the lime-neutralization process. This investigation has produced the following conclusions:

1. Mine water can be treated to produce a product containing less than 6 ppm of iron and a neutral pH without flocculents.
2. With flocculents a product containing less than 2 ppm of iron can be produced at a neutral pH at increased costs.
3. Based on data derived from the pilot plant operation, 1000 gals. of acid mine drainage can be treated for \$1.09. These costs do not include expenditures for additional sludge processing.
4. Scale formation will be an operating problem.
5. Manganese, alumina, and silica are also removed by lime neutralization resulting in a decrease in total hardness.

ACKNOWLEDGMENTS

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TABLE 1

COMPOSITE
CHEMICAL ANALYSES
of
RAW AND TREATED AMD

	<u>Raw AMD</u>	<u>Treated AMD</u>
pH	2.64	7.6
Total Iron, ppm	815.0	5.8
Total Acidity, ppm as H ₂ SO ₄	4040.0	-
Total Alkalinity, ppm as HCO ₃	-	46.0

TABLE 2

FLOCCULENTS PRODUCING A CLEAR EFFLUENT

<u>Flocculent</u>	<u>Dosage (#/Ton of Dry Solids)</u>
Separan NP 10	0.6
Superfloc #84	1.0
Superfloc #16	0.5
Nalcolyte #670	0.4
Nalcolyte #672	0.6

TABLE 3

THICKENER DESIGN DATA

Unit Area, ft ² /T/day	89.0
Time in Compression, hrs	11.4
Capacity, #'s of Solid/ft ² /hr	0.93
Storage, #'s of Pulp/ft ²	192.1
Final Dilution, % Solids	6.7

TABLE 4

FILTER DESIGN DATA

Solids Loading, lbs of Dry Solids/ft ² /hr	10.4
Hydraulic Loading, gal/ft ² /hr	14.9
% Solids of Filter Cake	26.2

Some Interactions Between Coal and Water Which
Change Water Quality

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The investigation (1), of which this discussion is a part, was primarily concerned with the use of coal as a reactant in a potential process to remove soluble pollutants from coal mine drainage. When water and coal come in contact, changes occur in each substance which may have considerable significance. The data developed are conceived to have influence in such coal preparation processes as froth flotation, flocculation and agglomeration as applied to solid-fluid separations, and in the control of water quality in the preparation plant as well as for subsequent discharge. The changes which occur in the coal itself may have some effect upon its utilization in specific instances or upon its handling in cold weather.

It does not seem to be unrealistic to seek an improvement in water quality from such a phenomena despite the occurrence of pyrites in coal strata and the role pyrites play in the origin of pollutants in coal mine drainage. Anthracite coal is successfully used as a filter media and may have characteristics of molecular sieves(2). Sulfonated bituminous coals have ion exchange properties(3). Some coals will react with sulfuric acid under mild conditions(4). Coagulants have been prepared from coal(5) and coal ash(6), which are claimed to be effective in creating flocculation in water treatment processes. Research is currently in progress considering the use of coal for an absorbent-type of response to remove organic contaminants from sewage effluents(7,8,9). Some improvement in water quality is indicated where mine water has been used as makeup water in coal preparation plants(10).

Preliminary studies established that coals will react with coal mine drainage to increase pH, decrease acidity, and remove iron. The extent of the phenomena was found to vary widely, although some response was measured in each of a number of different coals of varying rank and origin which were examined. The data presented in this discussion result from an attempt to explain the nature of this observed response as a base to optimize the effect.

The studies described were carried out on a run-of-mine sample of a Pittsburgh seam, high volatile bituminous coal originating in Southwestern Pennsylvania. The particle size of the coal employed was varied, although most of the studies were made with the minus 200 mesh fraction since it was found to be the most reactive. Limited data were measured using various specific gravity fractions of the coal. The waters considered were: freshly-boiled, distilled water; a municipal tap water; 0.155 N sulfuric acid; two synthetic coal mine drainage solutions containing sulfuric acid - one with ferrous iron, the other with ferric iron; and naturally-occurring coal mine drainage in which all the iron present was in the ferric form.

The basic experimental data were acquired by agitating 10 grams of the coal fraction in 100 ml of a given water for 10 minutes at room temperature. The slurry was filtered. The original water and the filtrate were analyzed for pH, dissolved solids, acidity-alkalinity, calcium, sulfate, and in some cases ferrous and ferric iron. The residue from the dissolved solids determinations as well as the ash of the original and reacted coals, were analyzed for silica, alumina, iron, sodium, and potassium by spectrochemical procedures. The main variables considered were reaction time and coal concentration.

The effluent from distilled water had developed a pH in excess of 8 (Table 1) and acquired substantial concentrations of dissolved solids including calcium, sodium and sulfate. Although there is not a great difference in the level of soluble material between the 150 by 200 mesh fraction and the minus 200 mesh fraction, a much lower solubility existed in the larger size fractions. This is undoubtedly related

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to the more highly liberated mineral particles in the smaller sizes although they did have a higher ash content. The presence of soluble ions in the tap water resulted in a solution which was lower in pH, dissolved solids (including calcium and sulfate concentrations), but higher in alkalinity. A more detailed analyses of the dissolved solids for the minus 200 mesh fractions is described in Table 2 along with the analyses of the ash of the original coal and that of the residual coal ash.

These data show that various soluble minerals are leached from the coal, presumably from the dissolution of calcium sulfate or gypsum. This calcium sulfate leached from the coal represented 58 percent of the total solubles with distilled water. These concentrations indicate the leached liquor to be essentially saturated with respect to calcium sulfate. There is some sulfate ions in excess of that stoichiometrically related to the calcium sulfate present. Since sodium is the only other ion solubilized to any significant extent, at least part of the sodium is assumed to have been associated with the excess sulfate ion. There is, however, insufficient sulfate to relate to the total calcium and sodium ions present. The observed pH suggests these cations are present primarily as salts rather than associated with free hydroxyl ions. There is no significant amount of iron solubilized from the coal. The amount of potassium solubilized is small in respect to the sodium, despite the occurrence in nearly equal amounts in the original coal.

The calcium and sulfate found in solution from the distilled water-minus 200 mesh coal test achieved an overall concentration of 102 parts per million calcium sulfate from each gram of coal. The calcium solubilized corresponds to 29.8 percent of that available in the original coal fraction. The relative amount of sodium from the coal which was solubilized is even higher - 70 percent. It seems probable that most of the remaining calcium in the coal is present as calcium carbonate. The 0.87 percent carbon dioxide present in the original minus 200 mesh coal fraction would correspond to 0.1960 grams of calcium carbonate in the 10 grams coal system studied. The calcium found in the original coal sample but not solubilized, would correspond to 0.1955 grams of calcium carbonate showing a reasonably acceptable balance. The solubilization of calcium and sodium is in agreement with ash analyses of the original and residual coal.

With the 0.0193 N sulfuric acid reaction, rather drastic changes resulted in the water quality as detailed in Table 1. Definite reactions had occurred beyond the leaching of the soluble salts as observed with distilled and with tap water. Here also the level of reactivity was less for the larger sizes although the 1/4-inch by 48 mesh size coal fraction achieved a dissolved solids level of 910 mg/l, almost 500 percent of that observed to be soluble in distilled water. The most significant change in the water quality for the purposes under consideration was the change in pH, going from 2.72 to a value of 6.15. The acidity level of the solution dropped from 705 for the original sulfuric acid to 14 ppm CaCO_3 after the coal reaction.

In comparing the acid reaction with coal solubilities found in distilled water, the dissolved solids increased by 457 mg/l or by 25 percent. The soluble sulfate concentration increased 548 mg/l or nearly 75 percent over the sulfuric acid; however, the sulfate concentration was actually less by 252 ppm than that solubilized by the distilled water plus that contained in the sulfuric acid. The acidity decreased by 691 ppm CaCO_3 or 98.1 percent of that present. If one considers the 43 ppm alkalinity developed in the distilled water test to be related primarily with the solubilized sodium ion, thus in the coal-sulfuric acid reaction 648 ppm CaCO_3 acidity or 94 percent must be related to reaction with calcite or with the coal substance. The calcium found in the effluent increased by 425 ppm (as CaO) or 756 ppm (as CaCO_3) over that solubilized with distilled water. There appears to be distinct evidence that a major change in an acid water quality is related to calcium carbonate minerals in the raw coal and that little if any association can be related to the organic coal phases.

In tests with the synthetic solutions containing iron as well as sulfuric acid, major changes were also observed including an increase in pH, a decrease in acidity, a slight decrease in total dissolved solids, and an increase in the calcium sulfate concentrations in the solutions. In the experiment which dealt predominantly with ferrous ion, only a very small percentage of the iron was oxidized or removed.

TABLE 1
ANALYSES OF THE EFFLUENTS FROM REACTION OF PITTSBURGH SEAM COAL

Coal Size		pH Change		Dissolved Solids	Alkalinity	SO ₄	CaO	Iron		Total
Passed	Retained	Initial	Final	mg/l	ppm CaCO ₃	ppm	ppm	Fe ⁺² ppm	Fe ⁺³ ppm	ppm
				Boiled Distilled Water						
1/4"	48 mesh	7.3	8.50	142.	71.0	41.	15.	-	-	-
150 m	200 m	7.3	8.05	1562.	84.0	583.	350.	-	-	-
200 m	-	7.3	8.10	1818.	42.6	800.	425.	-	-	-
<u>Tap Water - With Minus 200 Mesh Coal</u>										
Original Solution		8.21	-	170 .	195.	119.	90.	-	-	-
Product Effluent		8.21	7.68	1650.	107.	462.	320.	-	-	-
<u>0.0193 N SULFURIC ACID - WITH MINUS 200 MESH COAL</u>										
Original Solution		2.72	-	-	705.*	735.	3.	-	-	-
Product Effluent		2.72	6.15	3010	14.*	1283.	850.	-	-	-
<u>Ferrous Synthetic Solution - With Minus 200 Mesh Coal</u>										
Original Solution		2.92	-	3260.	1690.*	1765.	5.	446.	0.	446.
Product Effluent		2.92	5.05	4170.	820.*	1890.	473.	403.	3.	406.
<u>Ferric Synthetic Solution - With Minus 200 Mesh Coal</u>										
Original Solution		2.91	-	3260.	1690.*	1765.	5.	0.	446.	446.
Product Effluent		2.91	5.65	3500.	423.*	2082.	1060.	14.	2.	16.
Acidity										

TABLE 2
ANALYSES OF SOLID PRODUCTS FROM REACTION OF MINUS 200 MESH PITTSBURGH SEAM COAL

Sample	Weight % Ash	S** %	SiO ₂ %	Al ₂ O ₃ %	MgO %	CaO %	Fe ₂ O ₃ %	Na ₂ O %	K ₂ O %
Original Coal Ash*	23.24	3.88	42.	17.1	1.2	6.5	18.0	2.15	1.73
Residual Coal Ash from dist. water	21.52	3.58	42.	18.1	1.16	5.2	17.6	0.71	1.61
Residual Coal Ash from tap water	22.04	3.76	42.	17.6	1.00	5.1	17.3	0.82	1.68
Dissolved solids in dist. water	-	-	1.2	0.6	0.90	26.2	0.4	21.0	0.36
Coal Ash from Ferrous Soln. Test	21.98	3.83	44.	18.6	1.10	3.7	19.3	0.82	1.68
Coal Ash from Ferric Soln. Test	21.81	3.78	45.	17.9	1.05	2.8	20.8	0.63	1.68

* Original Coal contains 0.87% CO₂
 * Coal analysis, not on ash

However, in the synthetic solution which was all ferric iron, nearly all of the iron was removed. Most of the residual iron in the ferric effluent was present as ferrous ion. It is not obvious whether this small ferrous concentration detected resulted from a solubilization of a ferrous mineral in the coal or a reduction of some ferric iron in solution. Thus, if the iron is to be removed, it must be oxidized to the ferric state prior to or during the coal reaction. It should be noted that the air oxidation of ferrous to ferric iron proceeds rapidly under pH conditions which will allow the precipitation of ferric hydroxide. Thus it is assumed that the almost complete removal of iron from the test solution resulted from the precipitation of ferric hydroxide which remained with the coal upon solid-fluid separation. This is confirmed by the increase in iron content in the residual coal ash.

The results of studies made utilizing a naturally-occurring coal mine drainage sample are shown in Figure 1. The plot illustrates the actual reduction of acidity iron concentrations and increase in pH of the filtrate as a function of time. The reactions obviously occurred very rapidly. The continuing slower reaction can be related to the substantially decreased reactant concentrations and to various physical phenomena which would assist in favoring a continuing reaction. In addition, this drainage sample contained 3700 mg/l dissolved solids, 2130 ppm sulfate, 226 ppm CaO, and 115 ppm MgO. All the iron was present in the ferric state. After reaction for 60 minutes, the dissolved solids had increased to 4480 ppm (26 percent), the sulfate to 2221 ppm (4 percent), and the calcium to 1090 ppm (380 percent). The relative completeness of these reactions and the extent to which they might be expected to proceed is shown in Figure 2 in which the coal sample which had been allowed to react with the coal mine drainage for 60 minutes was filtered, dried in air for 20 hours, and retreated for 10 minutes with another sample of the coal mine drainage. This procedure was repeated three times after which the coal response was negligible. An additional series of tests were carried out in which the coal concentration was varied. The results of these reactions are shown in Figure 3. The data developed from the various gravity fractions of this coal with coal mine drainage established that a much higher level of reactivity resulted from the most dense mineral-containing fraction and that a negligible reaction occurred with the low gravity, low mineral content fractions.

These data show that various soluble minerals are leached from coal including calcium sulfate and some alkaline materials (sodium) with water which can change the water quality. The response found, evaluated and discussed here can result in an improvement in water quality as regards the most serious coal mine drainage pollutants, pH, acidity, and iron contents. It does leave the water with a large dissolved salt contents (primarily calcium and sulfate ions), which can be detrimental in some situations. The reaction found was related primarily to the calcium carbonate content of the raw coal and to its degree of liberation. Consequently any practical application implied from these results will vary with the individual coal and can limit its significance - especially due to the large amounts of coal required to treat a given volume of water. Commercial plant application has been carried out and found to be practical. However, in the course of these studies, other phenomena more related to those originally sought, were observed which show potential of much more significant effects. Further research is being pursued.

Acknowledgement

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References

1. Lovell, H. L. and R. D. Reese, "A Study of the Reactions Between Coal and Coal Mine Drainage," SR No. 54, The Pennsylvania State University and The Pennsylvania Coal Research Board, (1965).

2. "Anthrafilt, Hard Coal Filter Medium," Brochure of Palmer Filter Equipment Company, Erie, Pa. (1965).
3. Broderick, S. J. and D. Bogard, "Carbonaceous Cation Exchangers from Coal and Coal Refuse," Report of Investigations 3559, United States Bureau of Mines, (1941).
4. Thomas M. P. and C. R. Kinney, "Sulfuric Acid in Elucidation of Coal Structure," Industrial Engineering Chemistry 55, 11, 30-34 (1963).
5. Magill, R. P. "Composition For Treating Aqueous Fluids," U. S. Patent No. 2,251, 748, (1941).
6. Ganczarczk, J., "The Preparation of Coagulants from Ashes of Certain Coals," Politech Slaska Zaklad Badan Wodi Kanal Poland Gas, Wodi Tech. Sanit. 27, 292-294, (1953).
7. Lovell, H. L., "The Application of Mineral Preparation Concepts in Water Beneficiation," Mineral Industries 34, 2, 1-8 (November, 1964), The Pennsylvania State Univ.
8. Johnson, G. E., L. M. Kunka and J. H. Field, "Use of Coal and Fly Ash as Absorbents for Removing Organic Contaminants from Secondary Municipal Effluents, American Chemical Society, Division of Water and Waste Chemistry, 148th National Meeting, (1964).
9. Raynes, B. C., "Coal Used in Sewage Treatment," News release of United States Department of Interior, June 28, 1965.
10. Lovell, H. L., Interim Progress Report No 16, The Pennsylvania Coal Research Board by The Pennsylvania State University, (January 1965).

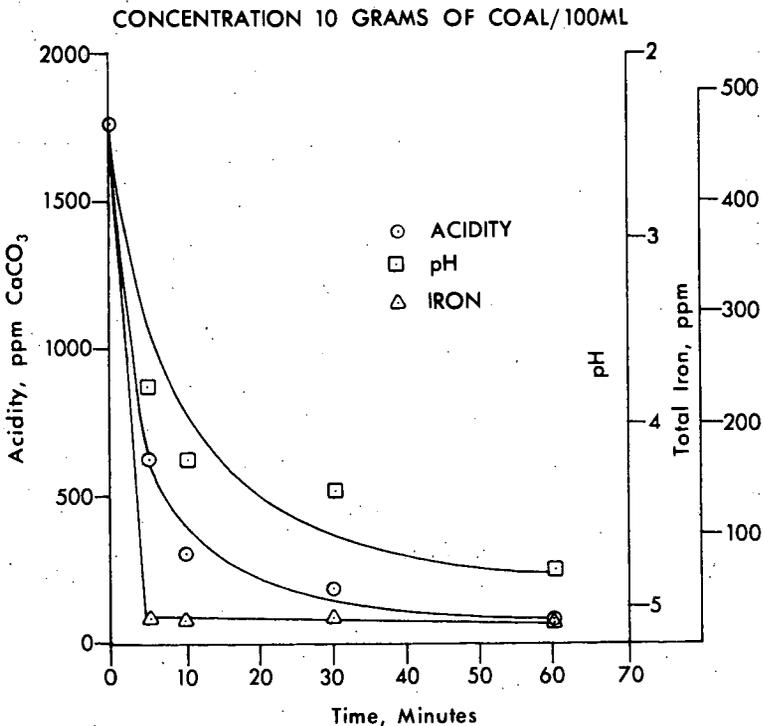


Figure 1
CHANGE OF WATER QUALITY WITH TIME

Minus 200 Mesh Pittsburgh Seam Coal - Coal Mine Drainage

CONCENTRATION 10 GRAMS OF COAL/100ML

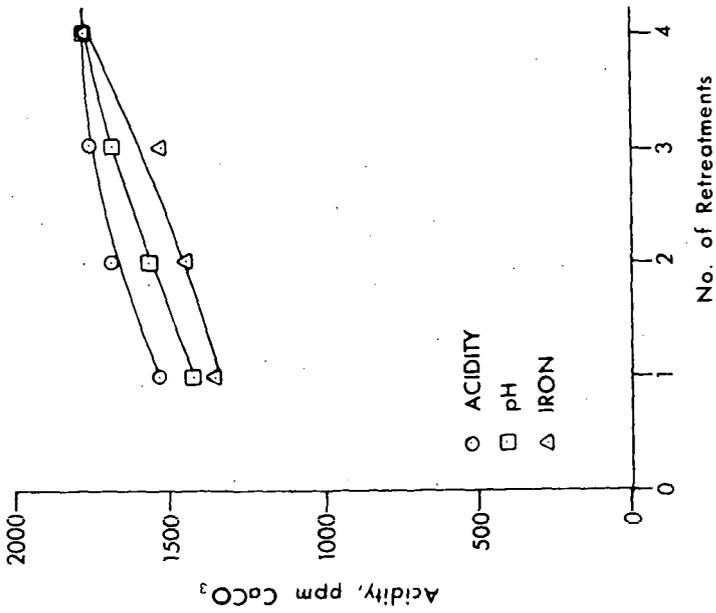


Figure 2

WATER QUALITY VARIATION WITH RETREATMENT OF SAME COAL SAMPLE

Minus 200 Mesh Pittsburgh Seam Coal - Coal Mine Drainage

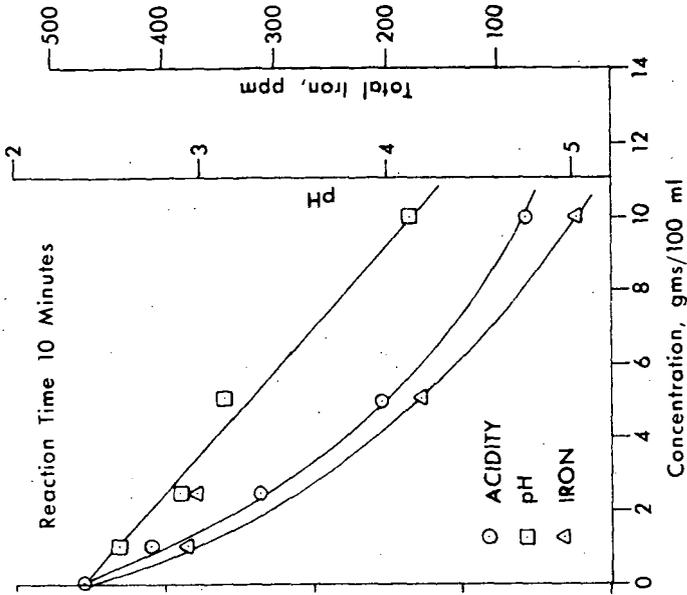


Figure 3

WATER QUALITY VARIATIONS WITH COAL CONCENTRATIONS

Minus 200 Mesh Pittsburgh Seam Coal - Coal Mine Drainage

A NEW ROTATING-ARC HEATER FOR CHEMICAL PROCESSING

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A number of hot cathode plasma processes of the Gerdien type have been proposed for chemical synthesis on the basis of laboratory experiments.¹ Most of these processes, however, are generally limited in their application since the hydrocarbon or air cannot be directly heated by the arc because of their deleterious effects on the electrode. The reactant gases are generally introduced into the plasma downstream from the electrode. Although excellent yields of acetylene, for example, have been obtained, the commercial application appears impractical because of scale-up problems, and the necessity to utilize either inert or reducing-gas plasmas.

The commercial application of electric-arc gas heaters have been realized, however, in the Hüels type of arc by Chemische Werke Hüels AG, in Germany², and by DuPont in the United States.³ Both of these processes are of the long-arc, direct-current type. Although the details of the DuPont process have not been disclosed, it is known from the patents issued that electrical rotation of the arc is utilized. The arc rotation in the Hüels process is obtained by introducing the gas into the arc-chamber in a swirl.

Some of the important technical details of both these processes are that 1) 4.5-6.0 kilowatt-hour of electrical energy are required to produce one pound of acetylene from methane; 2) that the residence time of the gas at ~1500°C in the plenum chamber is 1-3 milliseconds; 3) the product acetylene concentration is about 15 and 20 volume per cent, respectively, in the Hüels and the DuPont processes.

This paper describes the design and application of a rotating arc device of the short arc type which has recently been developed for gas heating. The short arc necessitates high current application, at relatively low voltage. The electrodes, therefore, must be capable of carrying this high current (and heat flux) without failure. Some of the advantages which may be expected from this device are: 1) relatively more uniform temperature profile as compared to the long arc device; 2) better control of arc with both direct and alternating current power; 3) longer electrode life; 4) improved mixing of the reactant gases in the heater.

Thermodynamics

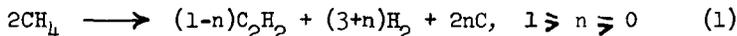
In the application of any high temperature device to a particular chemical reaction, the thermodynamics of the system is first considered. If the reaction is carried out under equilibrium conditions, the products are then clearly defined. The $C + 2H_2$ system, for example, has been studied by a number of workers under equilibrium conditions, and the products agree quite well with the equilibrium calculations based on available thermodynamic data.⁴ Similar studies with methane, as it will be shown, also apply in the arc heater under certain conditions. Some of the economically practical reactions, however, will require high flow conditions at which non-equilibrium conditions prevail. In such instances one needs detailed kinetic information to predict the path of the reactions, and the product compositions thereof. Unfortunately, dependable high-temperature kinetic data for the

cracking of methane are sparse; in particular, such data for flow-reaction conditions approaching those in the arc-heater are practically non-existent.

When the methane passes through the electrode gap of the heater, that volume which sees the arc is perhaps heated to temperatures in excess of 7000°K. This volume of gas is therefore completely dissociated. Part of the gas will not be arced, the proportion depending on the rate of arc rotation and on the gas flow velocity, but will mix with the hot arced-gas in the plenum chamber. Herein lies the critical period of the chemical process. At low gas velocities and high rotation, the gas mixture may easily attain equilibrium conditions. At high gas velocities the residence time of the mixture in the hot zone may be too short to reach equilibrium. The average temperature of the mixture at high flow will also be lower at a given power input. It will be shown that these latter conditions prevail in methane processing, and may be important economical factors.

Figure 1 shows the equilibrium for the $C + 2H_2$ system at a total pressure of one atmosphere. Since our studies are at approximately one atmosphere, this consideration applies. The computation is based on data reported in the JANAF Tables⁵ and programmed by Chambers and Tuba.⁶ Note that solid carbon is an important constituent up to 3400°K, but disappears at 3700°K. At the latter temperature the gaseous species of carbon become important. The maximum acetylene concentration of $x = 9$ appears at 3600°K, and decreases rapidly above 3700° and below 3400°K. Also note that CH_4 and C_2H_4 are quite unstable at these high temperatures. If the gas at 3600° is quenched at a rate of about 10^5 degrees/sec, the acetylene will be essentially frozen, and there will be precipitation of carbon and recombination of H and the other radicals. The composition of the gas phase, then, may contain ~15 mole % C_2H_2 ; the remainder being H_2 , C_2H_4 and C_4H_2 . It is noteworthy that the kinetics of formation of acetylene is much faster than its decomposition, so that essentially all of the acetylene may be quenched. Earlier work⁴ has shown that agreement between theory and experiment is excellent. The amount of solid carbon frozen from an equilibrium mixture, therefore, is about 40% of the total carbon.

In the production of acetylene from methane, we may consider the reaction



Ideally, the reaction should proceed with $n = 0$, with a heat of reaction of approximately 90 kcals. The free energy change for this reaction is approximately $\Delta F_T = 95.4 - 0.0680T$. In engineering units, the heat requirement is equivalent to 5000 Btu/lb CH_4 just for the heat of reaction. Additional sensible heat needs to be added to heat the methane to the reaction temperature. For instance, 2100 Btu/lb are required to heat the gas to 1500°K. The free energy for the reaction also becomes negative at ~1500°K. For the reaction as shown in equation (1), the heat of reaction is $\Delta H_T = \Delta(\Delta E_0)_i + \Delta(H_T - E_0)_i$, where the symbols have their usual thermodynamic designations. Note that the last term is the sensible heat at T. As carbon precipitates, therefore, the heat of reaction decreases at 1500° since it's $\Delta E_0 = 0$.

From the equilibrium computation, the enthalpy-temperature relationship is obtained as shown in Figure 2. This curve conveniently allows the average temperature determination for equilibrium systems since the enthalpy is usually known in an experiment. This does not apply, however, to non-equilibrium systems.

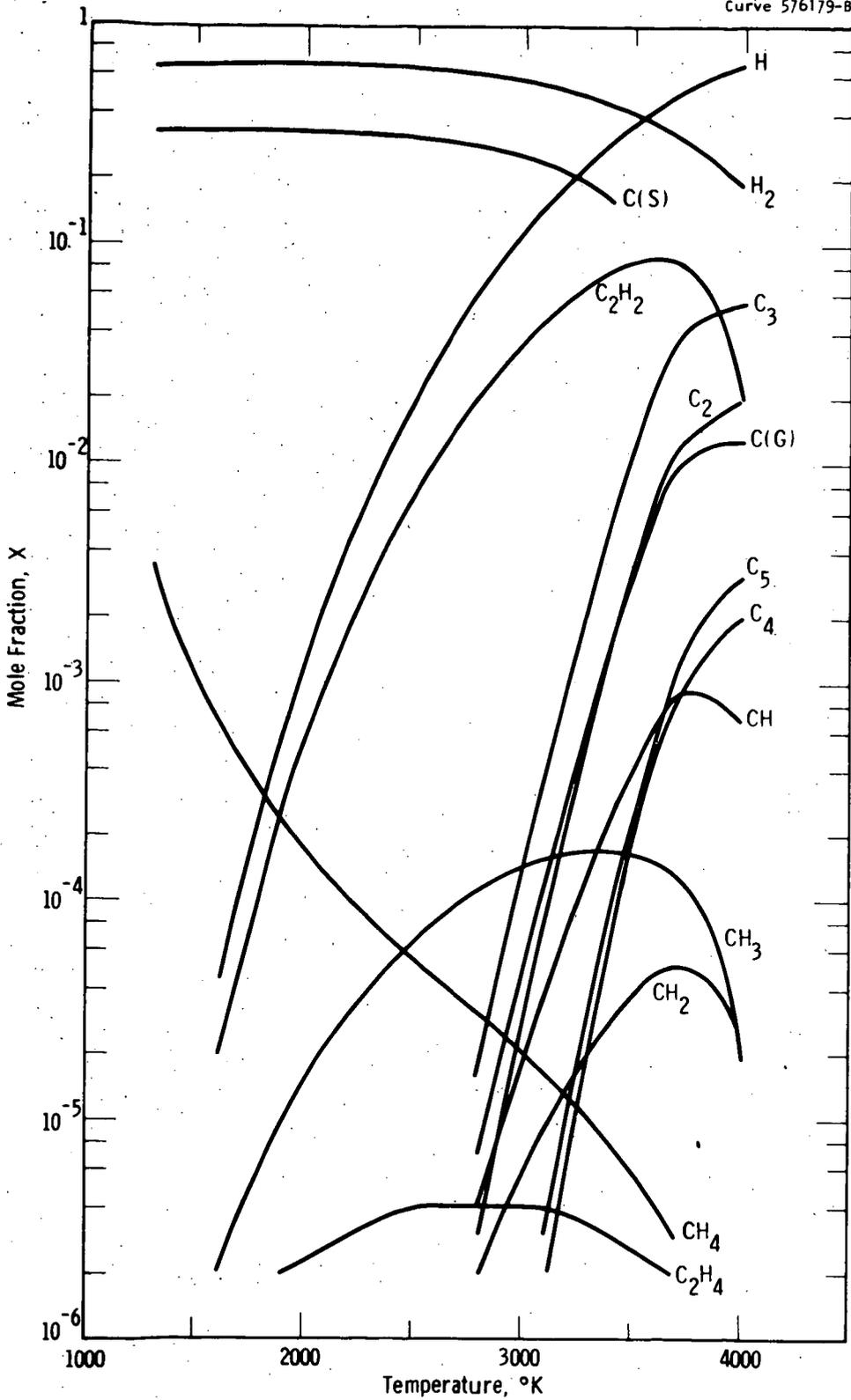


Fig. 1—Calculated $C + 2H_2$ as a function of temperature (Total P = 1 atm)

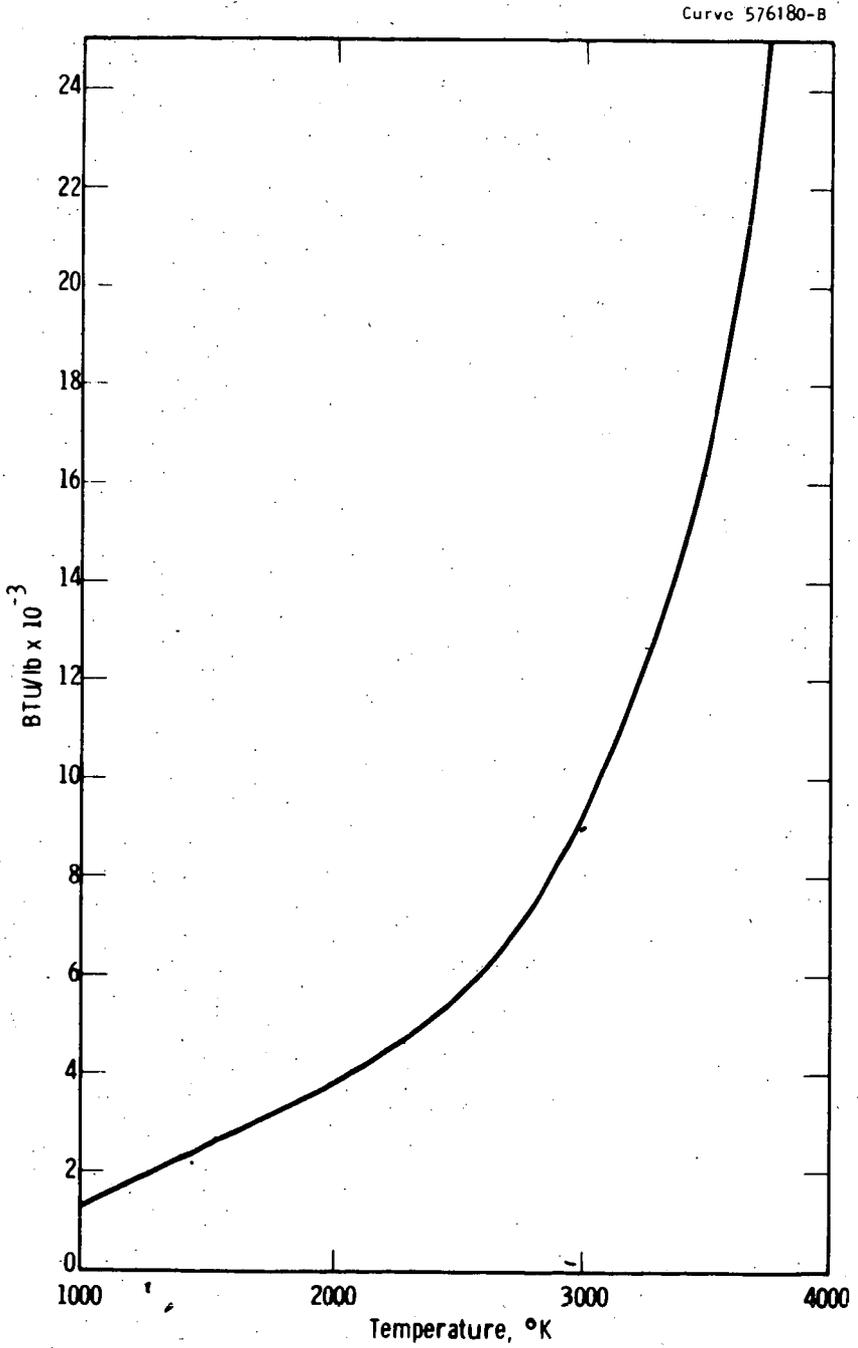


Fig. 2—Enthalpy vs temperature for $C + 2H_2$ at total pressure of 1 atm

Kinetics

It is apparent from the rapid flow reactions, such as the Hüels and the DuPont processes, that equilibrium is not obtained in the cracking of methane. This reaction, under optimum conditions, shows low carbon yields of about 5%. Also, there is present about 1% of ethylene among other minor hydrocarbon constituents. The kinetics of thermal decomposition of methane has been studied by many workers. The exact mechanism, however, remains unresolved. It is generally believed⁷ that two primary steps may take place near 2000°C:



The ΔH_{298}° for the reactions are 102 and 103 kcal, respectively. The overall monomolecular decomposition of methane is $k = 10^{14.88} \text{Exp}(-103 \text{kcal}/\text{RT})$, and the free radical reaction chain is apparently very short. The following chain is often postulated: $\text{CH}_4 \xrightarrow{k_1} \text{C}_2\text{H}_6 \xrightarrow{k_2} \text{C}_2\text{H}_4 \xrightarrow{k_3} \text{C}_2\text{H}_2 \xrightarrow{k_4} \text{polymeric products}$.

The ethane is presumably formed by the reaction $\text{CH}_3 + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_6 + \text{H}$, with the ethane dehydrogenating rapidly. At isothermal conditions it is shown that $[\text{C}_2\text{H}_6] / [\text{CH}_4] = 10^{-5}$ at 1800°K, thus C_2H_6 is not detected in the cracked products. The polymerization of acetylene to diacetylene is a second order reaction whose rate constant is relatively slow compared to the other monomolecular rates. Hydrogen is known to retard the decomposition of ethane, thus the formation of acetylene. Also, increasing the temperature in the neighborhood of 1100°C increases the rate of C_2H_2 formation. It appears, then, that maximum acetylene is obtained at temperatures higher than 1100°C and at short residence times at the high temperatures. In a rapid flow system there will be no hydrogen accumulation to decrease the acetylene formation.

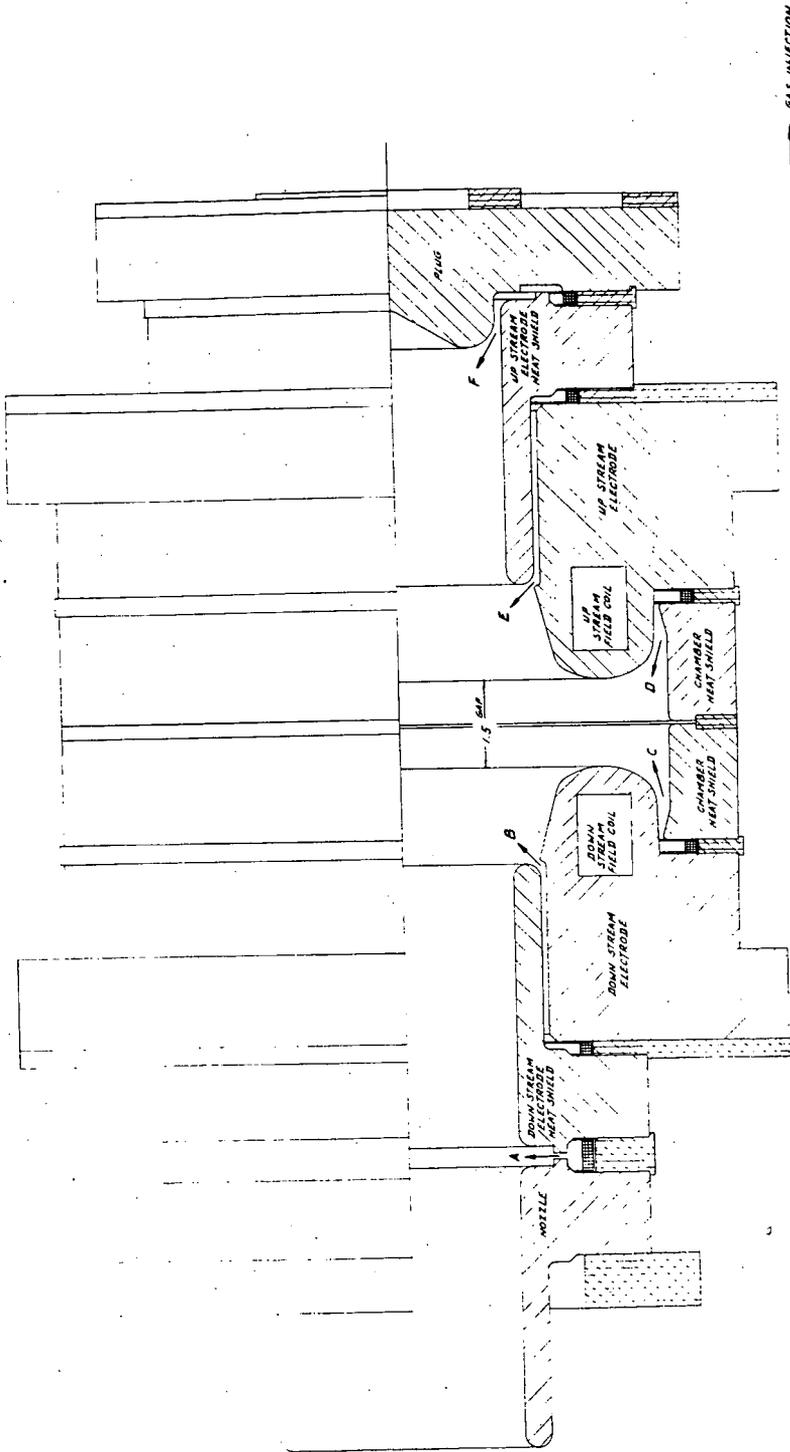
It is generally believed in methane cracking that the gas should be heated to at least 1500°C, at residence times in the neighborhood of one millisecond. It should be remembered in reactions in an arc-heater that the temperature gradient may be much greater than those obtained in the above kinetic studies.

Description of Rotating-Arc Heater

A cross-section of the heater used in this program is shown in Figure 3. One or more process gases can be added at the six locations designated "A" thru "F". With the arc established between the two toroidal electrodes, only the gas added at locations "C" and "D" will actually pass thru the arc zone. Some small amount (2 to 5% of total flow) must be added at the other four locations to keep the gaps clear of debris and prevent short circuiting of the electrodes.

All internal parts of the heater exposed to the gas are fabricated from copper or copper alloys. These parts are all water cooled. To prevent vaporization of metal from the electrode surface at the point of arc attachment, the arc is rotated around the gap at high speed. This is accomplished by the field coils which establish a magnetic field perpendicular to the arc column. The resulting force acts on the arc column causing it to rotate at speeds on the order of 2000 feet per second.

To start the heater, a thin metallic wire is inserted between the electrodes. Application of power causes a high current to flow and rapidly



← GAS INJECTION

MARC 30
ARC HEATER
DB 08165

Figure 3. Cross-section of Heater

vaporize the wire. The explosion of the wire provides an initial ionized path to establish the arc. In testing with hydrocarbons, the heater is usually started with an inert gas such as nitrogen. This allows the arc to stabilize without any solid by-products being formed in the heater. After several seconds, the nitrogen flow is stopped and hydrocarbon feed started.

The heater configuration shown in Figure 3 has been operated on both single phase A.C. and D.C. power. For A.C. arc operation, the field coils are separately powered from a D.C. power supply. When operated as a D.C. device, the field coils are connected in series with the arc and do not require a separate power supply.

Tests were conducted using both A.C. and D.C. power. Electrode gaps of 0.38, 0.75, and 1.5 inches were required to cover the power range from 90 to 2360 kilowatts into the arc. Stable arcs were maintained with currents as low as 780 amps. Currents of 3830 amps with methane and 9200 amps with nitrogen have been carried by the heater electrodes without damage.

The efficiency of the heater, calculated on the basis of electrical power and heat lost to the cooling water, has gone as high as 79%. Heat addition to the process gas has been as high as 19,900 Btu/lb. of CH_4 . The maximum methane flow in the heater is about 30 lbs/minute.

Chemical Tests

Tests have been run with methane of technical and C. P. grades. Propylene has also been cracked in the heater. The range of methane flow was from 0.04 to 0.275 lbs/sec. at arc power levels up to 2360 kilowatts. The gas was introduced into the heater at room temperature, and the flow was controlled by metering through a sonic orifice. At least three cylinders (15 lbs. methane when full) were opened to the manifold during a run. The pressure of the gas thus feeding into the heater was approximately 40 psig, and the total pressure in the heater chamber was 18 psia.

During a test the product gas was sampled by inserting a probe just inside of the heater nozzle. The probe was a water-cooled, concentric copper tube, with a 1/8 inch bore which was connected to the sampling manifold. The latter held 5 sample bottles, with a solenoid valve connected in parallel at each end of the bottle. The valves were remotely controlled from the instrument operating room. During a run the valves were all opened a few seconds after the nitrogen was turned on into the heater, and the system pumped continuously. At appropriate time intervals after the methane flame was started, the product gas was sampled by closing off the set of solenoid valves on any bottle. Thus, for any given run it was possible to obtain one or more samples at different periods. Since the quench rate is high in the probe, the gas samples should be representative of the composition at the nozzle. The chemical analyses of the product gas in all cases was made mass spectroscopically.

The power levels during any given run were varied after one to two minute intervals, usually by altering the current. The gas samples were taken at the end of a given power period. Simultaneously with the sampling, the electrical and flow data were recorded on the strip chart; subsequently, the current was stepped up or down. It should be noted that the arc reached stable equilibrium during any power level in the matter of a few seconds. The length of a given run varied from a few minutes to about 12 minutes.

The proprietary nature of this work prevents the authors from presenting the detailed data at the present time. However, the specific data presented will suffice to illustrate some of the important operating characteristics of the arc heater when used as a chemical processing tool.

TABLE I. Product Gas Analysis From Methane Run (Mole %)

H_2	CH_4	C_2H_2	C_2H_4	C_4H_2	Other HC
50.98	38.17	9.52	0.88	0.21	0.25

TABLE II. Composition of Products in Mole %

H_2	CH_4	C_2H_2	C_2H_4	C_4H_2	Other HC	C
46.3	34.7	8.7	0.8	0.2	0.2	9.1

TABLE III. Conversion of Reacted Methane to Products

C_2H_2	C	C_2H_4	C_4H_2	Other	% CH_4 Reacted
57.0	32.3	5.2	2.5	3.0	46.7

Table I shows the product gas analysis of a methane run. The material balance is then shown in Table II. This particular run corresponds to a methane conversion of 46.7%, as shown in Table III. The energy conversion for this run was 6.8 kwh/lb C_2H_2 . Depending on operating conditions, the acetylene concentration in the gas has ranged from 7-12 mole %, the other major constituents always being hydrogen and the unreacted methane. The energy conversion obtained was as low as 2.64 kwh/lb C_2H_2 . The methane conversion was increased appreciably when the arc-rotation was increased by increasing the field current. Although not yet optimized, methane conversions of 80% have been obtained in this way, where previously the conversion was only about 50%. The increased conversion obviously results from the better mixing and greater proportion of gas which passes through the arc.

The carbon content and its properties have varied with the operating conditions. The conversion to carbon varied from a few per cent to about 40% of the total carbon input. With A.C. power the carbon was generally of an amorphous nature, whereas at D.C. power at high enthalpy levels, the properties approached those of pyrolytic graphite. Thus, surface areas varied over almost one order of magnitude from about 20 to over 100 m^2/g . The purity of some samples, determined by a spark-source mass spectrometer, showed extremely low metal contamination (at least an order of magnitude less metal contamination than in spectroscopic carbon).

There are certain basic differences in uniformity of heating between A.C. and D.C. excitation. This arises from the alternating 60 cycle power cycle of the

A.C. excitation as opposed to the steady D.C. system. The latter allows a more uniform heating, with less temperature fluctuations; whereas the former shows the alternating pulses of relatively hot and cold volumes of gas as observed by high speed photography.⁹

The rotating arc heater has been in intermittent operation for a period of over a year. There have been many start-ups, with runs of duration up to approximately 12 minutes. The length of a run has been limited by the available power supply and cooling water. The heater has performed dependably with the original set of electrodes. Only difficulties encountered were under certain conditions in which excessive carbon deposited between the electrodes. However, a surprisingly large deposition of carbon may be tolerated in the heater, and still allow safe start-ups without removal of this carbon. It should be emphasized that start-up conditions are the most severe since large power surges are involved. It is felt that the heater is capable of continuous operation for periods up to 1000 hours, based on electrode and heater examination after repeated tests.

Discussion

From the equilibrium shown in Figure 1, the maximum acetylene concentration of about 15 mole % should be in the gas quenched from 3600°K. The C_2H_2 concentration decreases rapidly above and below the latter temperature. When the product gas analyses in this work are normalized by subtracting out the unreacted methane, the acetylene concentration remains at around 15 mole % over the wide range of enthalpy levels. It is apparent then that thermodynamic equilibrium is not attained, particularly at low enthalpies. At high enthalpies, however, the gas probably attains equilibrium and the average temperature is in the region of 3600°K. Since temperature measurements have not been made at low enthalpy levels, we can only conjecture that the average gas temperature is around 1500°K.

The low energy conversion of 2.64 kwh/lb. C_2H_2 is significantly lower than the 4.5 to 6.0 kwh/lb. C_2H_2 reported for the other arc processes. On examining the enthalpy requirements for this low conversion, it was found that 2.4 kwh is required just for the heat of reaction. Since sensible heat must be supplied, our value of 2.64 kwh/lb. appears too low. This determination obviously needs re-confirmation by further tests. It may be of interest, however, that a recently publicized electro-thermic process⁸ reports an energy conversion of 2-3 kwh/lb. C_2H_2 in the cracking of methane at around 2000°K.

From the dimensions of the rotating-arc heater, a plenum chamber of 80 in.³ is obtained. The average residence times of the gas, then, varied from 4 to 0.7 milliseconds in our tests.

The relative stability of acetylene during quench was qualitatively demonstrated by sampling the product gas with the 1/8-inch and a 2-inch sample probes. The gas analyses from both systems were very similar, in spite of the difference in quench rates.

Conclusion

A versatile rotating-arc heater, and some of its operating ranges, has been described. The device is of a short-arc type in which the gas is introduced in five positions. Thus two or more different gases may be easily heated together, and finely divided solids are not excluded. Methane flows up to about 30 lbs/min.

is possible at either A.C. or D.C. power inputs up to 2.4 megawatts into the arc. Thermal efficiencies as high as 79% have been obtained. The design of the heater is amenable to the direct heating of reducing inert and oxidizing gases.

Methane and propylene have been processed through the heater with some results for the former reported herein. Energy conversions at least comparable to other arc processes have been obtained. An added advantage is the relatively small physical dimensions of the heater. This feature allows higher thermal efficiencies.

References

1. C. W. Marynowski, R. C. Phillips, J. R. Phillips, and N. K. Hiester, I&EC Fundamentals, 1, 52 (1962).
2. H. Gladisch, Hydroc. Proc. & Pet. Ref., 41, 159 (1962).
3. a) Chemical Week, March 10, 1962, p. 69.
b) Belg. 604,989 (to DuPont).
4. a) M. N. Flooster and T. B. Reed, J. Chem. Phys., 31, 66 (1959).
b) R. F. Baddour and J. M. Iwasyk, Ind. Eng. Chem., Proc. Des. Dev., 1, 169 (1962).
5. "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1960.
6. R. L. Chambers and I. Tuba, "Properties of Combustion Gases for Magneto-hydrodynamic Processes," Westinghouse Report 62-1021 MHD-2502, Revised May 1964.
7. For brief review, see S. A. Miller, "Acetylene: Its Properties, Manufacture, and User," Vol. I, Academic Press, New York, 1965, pp. 371-382.
8. a) Chemical Week, November 21, 1964, p. 89.
b) J. Happel and L. Kramer, U.S. 3,156,733.
9. G. A. Kemeny, Progress Report #16, Cont. AF 40(600)-1034, by Westinghouse Electric Corporation, July 13, 1964.

EQUILIBRIA IN THE SYSTEM $2N_2 + H_2$ AND $N_2 + 8H_2$,
AND THERMODYNAMIC PROPERTIES OF N_2H_4 AT 1000° TO $5000^\circ K$

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Although high temperature equilibrium data on systems containing carbon, hydrogen, and nitrogen have been reported, the same type of data for the more simple system containing hydrogen and nitrogen¹ have not been reported. Both systems are of obvious interest in the chemistry of reactions in a high-temperature plasma.

We presently consider the equilibria in the systems $2N_2 + H_2$ and $N_2 + 8H_2$ at 1000° to $5000^\circ K$. Ideal gas behavior is assumed. The following species only are considered to be present in the gas: H_2 , N_2 , H , N , NH , NH_2 , NH_3 , N_2H_4 . Undoubtedly, there are other species and ions present, such as N_2H_3 , but the concentrations of these will be negligible compared to those considered here. It is expected that N_2H_4 will also be negligible, but we include this species because of its practical interest.

Eight equations are required in order to determine the concentrations of the eight components. Five equations express the equilibrium constants for the formation of H , N_2 , NH , NH_2 , and NH_3 , where the data are taken from the JANAF Thermochemical Tables.² The sixth equation, the equilibrium constant for formation of N_2H_4 , is calculated herein. The seventh equation expresses the total pressure as the sum of the partial pressures, $\sum_i P_i = P$. The eighth equation expresses the material balance; i.e., for the system $2N_2 + H_2$

$$2 P_{H_2} + P_H + 0.5 P_{NH} + 1.5 P_{NH_2} + 2.5 P_{NH_3} + 3 P_{N_2H_4} \\ - P_{N_2} - 0.5 P_N = 0,$$

and for the system $N_2 + 8H_2$

$$8 P_N + 16 P_{N_2} + 7 P_{NH} + 6 P_{NH_2} + 5 P_{NH_3} + 12 P_{N_2H_4} \\ - P_H - 2 P_{H_2} = 0.$$

The set of eight equations were solved for the different temperatures and pressures of one and a thousand atmospheres on a computer. A single pass in the computation was sufficient. Figures 1 to 4 summarize the results.

The partial pressure of N_2H_4 , as suspected, is negligible in all of the systems, although it goes through a maximum. The partial pressure of NH_3 decreases rapidly with increasing temperature, showing the low stability of this species at the high temperatures. It is interesting to note the stability of N_2 even at $5000^\circ C$, as evidenced by the small decrease in partial pressure of this species from 1000° to $5000^\circ K$.

There is only a very small effect on the concentration of the species NH , NH_2 , N_2H_4 , and NH_3 by varying the ratio of $N_2:H_2$. However, an increase in pressure from one to 1000 atmospheres does cause a slight shift in equilibrium, so that the relative concentrations of NH_3 , N_2H_4 , and NH_2 increases slightly.

Thermodynamic Properties of N_2H_4

Scott, et al,³ have reported thermodynamic properties of N_2H_4 to $1500^\circ K$. We extend these data to $5000^\circ K$ by using the more recent spectroscopic data of Giguere and Liu.⁴ The latter workers were unable to determine the symmetrical stretching (ν_2) and torsional (ν_7) vibrations, so that we use the values of Scott, et al, for these two frequencies. The three components of the moment of inertia, the potential barrier to internal rotation, the reduced moment calculated by Pitzer's formula,⁵ and the heat of formation at absolute zero are those given by Scott. Table I summarizes the spectroscopic data.

In the calculation of the equilibrium constants of N_2H_4 , the free energy functions of H_2 and N_2 were obtained from the tables of the U.S. Bureau of Standards.⁶ Table II summarizes the thermodynamic data.

The values of the thermodynamic functions calculated by us differ from those of Scott³ by 1.5 to 3.5% in the different functions in the range 1000° to $1500^\circ K$, since the vibrational contributions in this work are based on the more recent data of Giguere and Liu.⁴ The free energy of formation and $-\log K_p$ for this temperature region are about 1.5% and 2% higher, respectively, than those of Scott and co-workers.

Acknowledgement

We thank Miss Rosella Freedman for the computer calculations.

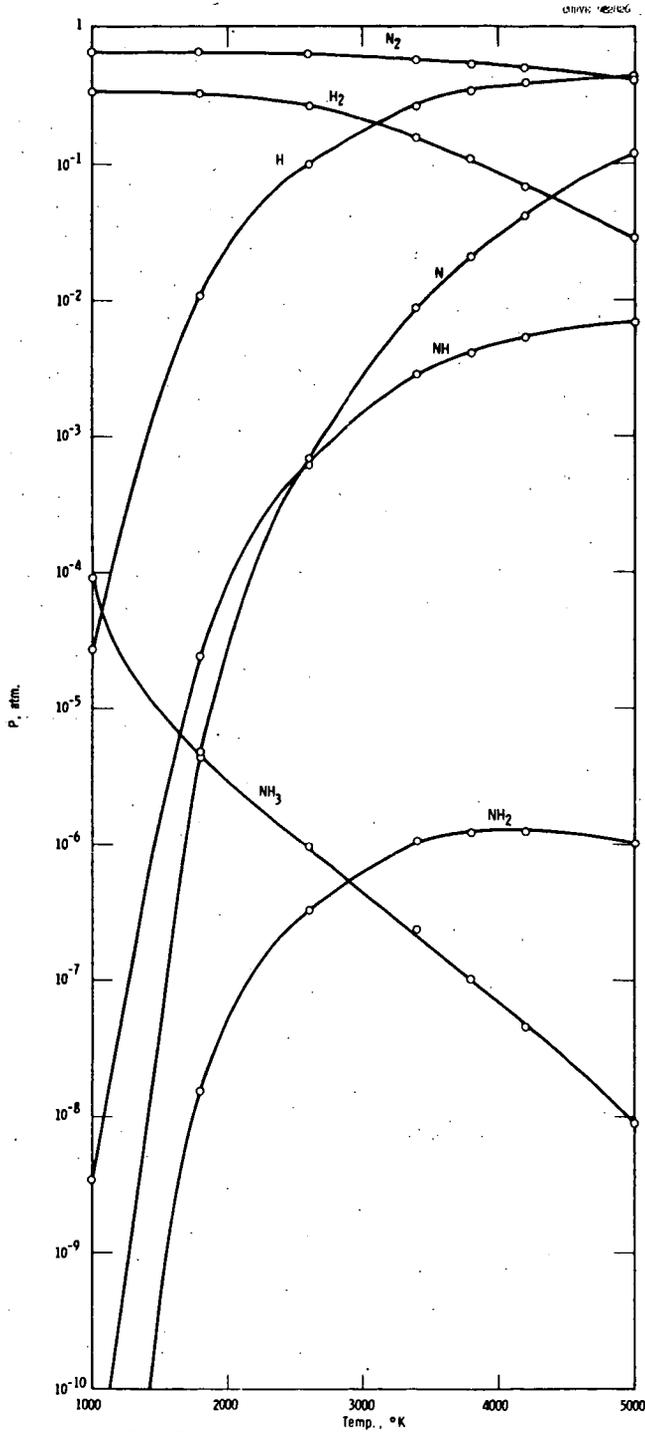


Fig. 1—Partial pressure as function of temperature for system $2N_2 + H_2$ at total pressure of 1 atmosphere.

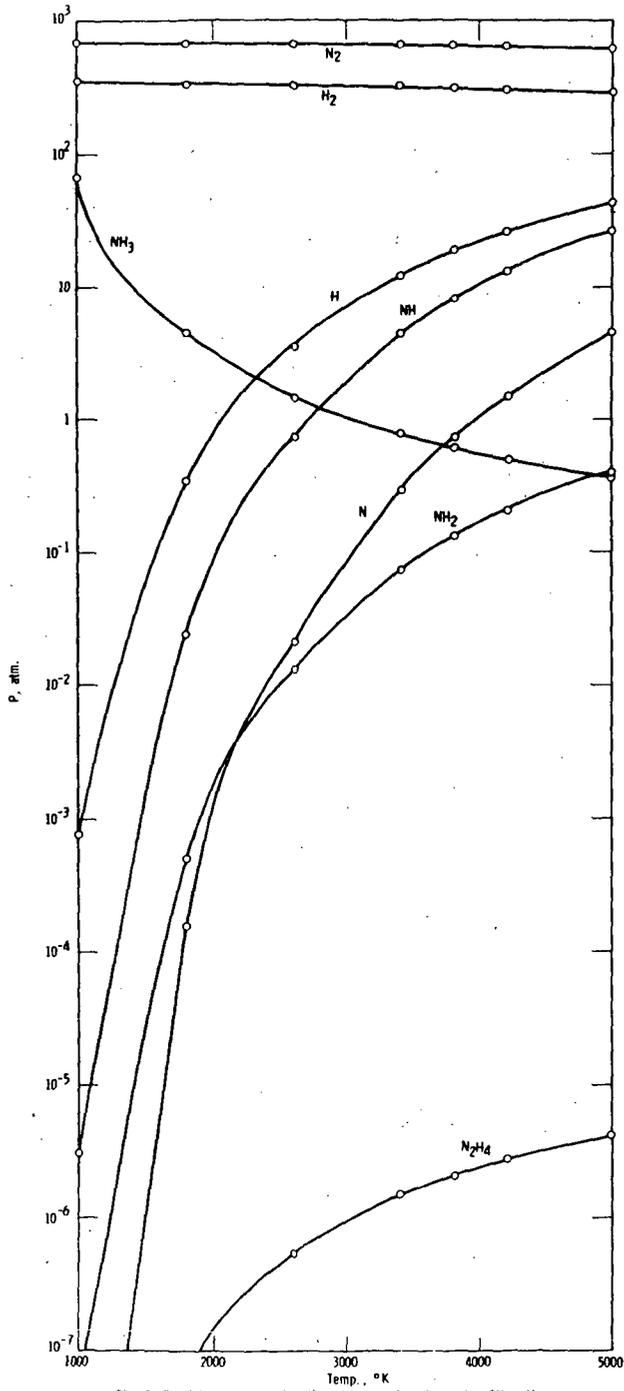


Fig. 2—Partial pressure as function of temperature for system $2N_2 + H_2$ at total pressure of 1000 atmospheres.

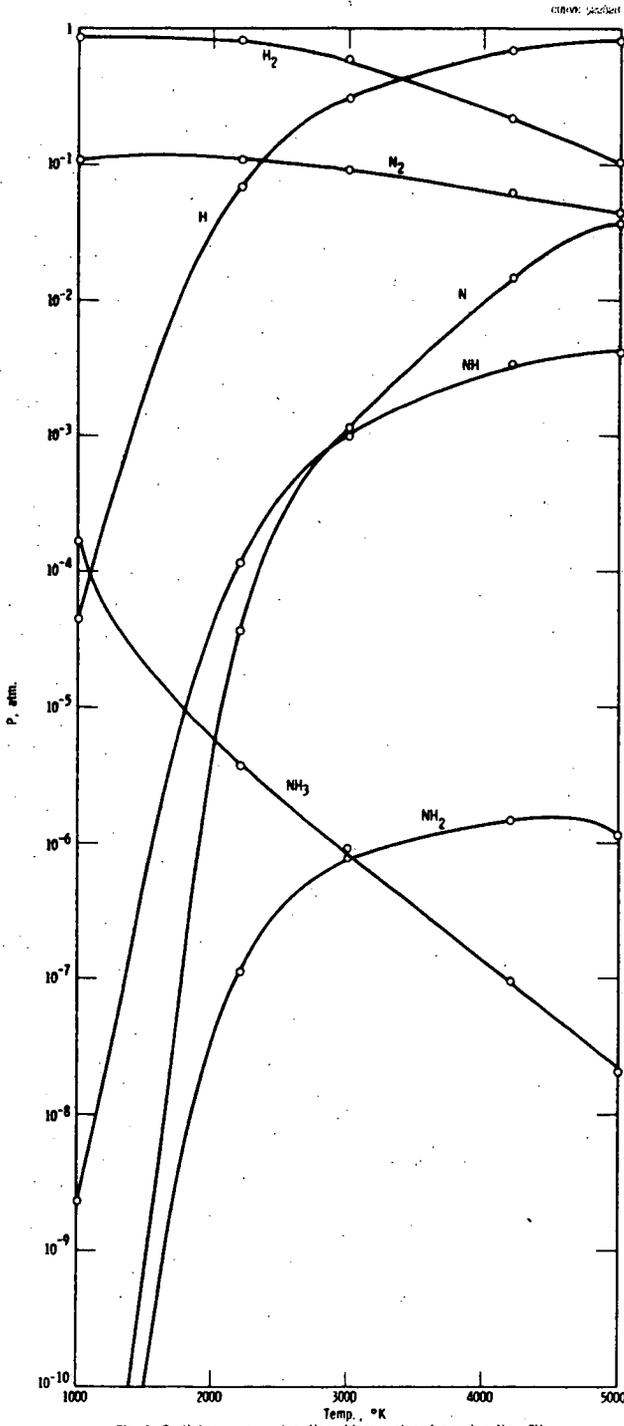


Fig. 3—Partial pressure as function of temperature for system $N_2 + 3H_2$ at total pressure of 1 atmosphere.

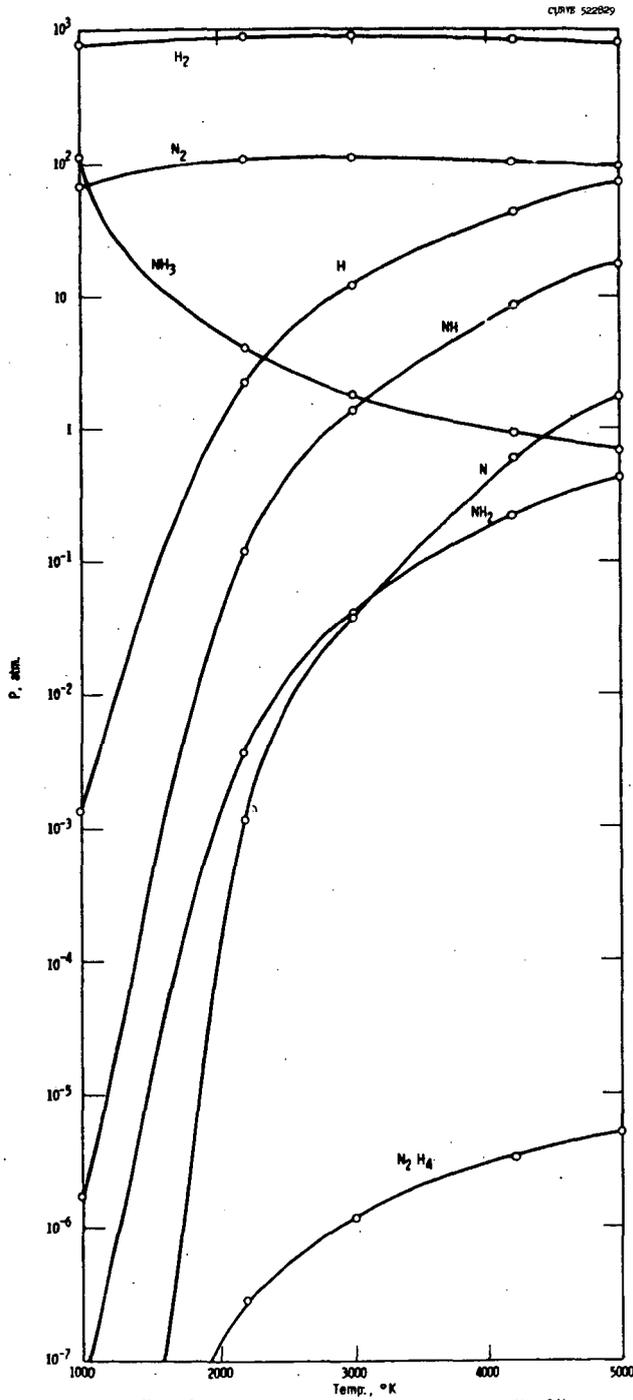


Fig. 4—Partial pressure as function of temperature for system $N_2 + 8 H_2$ at total pressure of 1000 atmospheres.

TABLE I

MOLECULAR DATA FOR HYDRAZINE

<u>Vibrational Frequency</u>			
<u>Mode</u>	<u>cm⁻¹</u>	<u>Mode</u>	<u>cm⁻¹</u>
γ_1	3325	γ_8	3350
γ_2	3160	γ_9 (doublet)	3280 3314
γ_3	1493	γ_{10}	1628
γ_4	1098	γ_{11}	1275
γ_5	960	γ_{12} (doublet)	933 966
γ_6	780		
γ_7	360		

Symmetry number (σ) = 2

Molecular Weight = 32.048

Moments of Inertia

$$I_A = 6.18 \times 10^{-40} \text{ g cm}^2$$

$$I_B = 35.33 \times 10^{-40} \text{ g cm}^2$$

$$I_C = 36.98 \times 10^{-40} \text{ g cm}^2$$

Reduced moment for internal rotation = $1.53 \times 10^{-40} \text{ g cm}^2$

Potential barrier height for internal rotation = 2800 cal/mole

$$\Delta H_0^{\circ} = 26,060 \text{ cal/mole}$$

Statistical weight of electronic ground state = 1

TABLE II

THERMODYNAMIC FUNCTIONS, FREE ENERGY OF FORMATION
AND EQUILIBRIUM CONSTANT OF N_2H_4 FROM 1000° TO 5000°K

Temp. °K	C_p , Cal/Mole	$\frac{H^\circ - H_0^\circ}{T}$ k Cal/Mole Deg.	S° , Cal/Mole/Deg.	$\frac{F^\circ - H_0^\circ}{T}$ k Cal/Mole Deg.	F_f° , k Cal/Mole	$-\log K_p$
1000	21.95	15.21	76.06	61.64	77.18	16.89
1800	26.60	19.39	90.40	71.65	122.88	14.94
2600	28.50	21.92	100.54	79.24	167.83	14.12
3400	29.38	23.60	108.30	85.37	212.09	13.65
3800	29.64	24.21	111.58	88.01	234.14	13.48
4200	29.84	24.75	114.54	90.46	256.04	13.34
5000	30.12	25.57	119.73	94.36	299.54	13.11

REFERENCES

1. Kroepelin, H., Kipping, D.E., and Pietruck, H., "Progress in International Research on Thermodynamic and Transport Properties," Ed. J. F. Masi and D. H. Tsai, pp. 626-648, American Society of Mechanical Engineers, Academic Press, New York, 1962.
2. "JANAF Thermochemical Tables," Vol. II, 1960.
3. Scott, D. W., Oliver, G. D., Gross, M. E., Hubbard, W. N., Huffman, H. M., J. Am. Chem. Soc., 71 2293 (1949).
4. Giguere, P. A., and Liu, I. D., J. Chem. Phys., 20, 136 (1952).
5. Pitzer, K. S., and Gwinn, W. D., J. Chem. Phys., 10, 428 (1942).
6. U. S. Bureau of Standards Circ. 564, 1955.

CATALYTIC DEHYDROGENATION OF LOW-TEMPERATURE LIGNITE PITCH

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ABSTRACT

Pitch obtained from the vacuum distillation of low-temperature lignite tar is not suitable for present commercial applications. To meet specifications for existing markets, the characteristics of the pitch must be changed. One method for modifying pitch is catalytic dehydrogenation. Palladium (30%) on CaCO_3 was chosen as the reference catalyst because it has given good results in other work. Various metal oxide catalysts were tested; nickel oxide gave the highest equivalent hydrogen removed, 14.8%. As a hydrogen-rich gas producer, nickel catalyst gave the highest yield with an off-gas containing 4.22 millimols of hydrogen per gram of pitch while palladium catalyst off-gas contained 1.22 millimols of hydrogen per gram of pitch. The best methane producing catalyst was palladium oxide with an off-gas containing 3.07 millimols of methane per gram of pitch. Aluminum was next with an off-gas containing 2.62 millimols of methane per gram of pitch.