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DOE/PC/50261--T3

THIRD QUARTERLY TECHNICAL PROGRESS REPORT

Investigate the Effectiveness of Calcium-Treated Coals
In the Capture of Sulfur Gases Generated in
Staged Fired Combustors

September 1, 1983

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Third Quarterly Technical Progress Report

Investigate the Effectiveness of Calcium-Treated Coals
In the Capture of Sulfur Gases Generated In
Staged Fired Combustors

U.S. Department of Energy
Pittsburgh Energy Technology Center
U.S. DOE Contract No. DE-AC22-82PC50261

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Energy and Environmental Engineering, Inc.
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SUMMARY

This is the third quarterly report on the project to "Investigate the Effectiveness of Calcium Treated Coals in the Capture of Sulfur Gases Generated During Combustion". In this quarter's work, a new procedure was developed to add calcium to pulverized coal. The method has been found to increase the calcium content of bituminous coal to 12% calcium by weight, which corresponds to a Ca/S ratio of greater than 2.

Progress was also made on the combustion test facility this quarter. A new modification of the low-flow coal feeder has made that system steady and reliable. With the furnace wired and plumbed, and the other subsystems complete, the facility is almost ready to burn the treated coals.

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INTRODUCTION

A number of processes which utilize calcium to desulfurize coal combustion gases have been investigated in the past with varying degrees of success. Limestone injection into a single stage combustor, for one, has been shown to be inadequate to remove sulfur gases. As an alternative to mixing particles of limestone and coal together, it is possible to bond the calcium directly into the coal matrix.

Imbedding the calcium in the coal provides for intimate contact between the calcium and the sulfur gases produced during combustion. The imbedded calcium is then able to react with the devolatilized sulfur gases before they escape the coal particle. Moreover, diffusion distances between the sulfur species and the calcium are much shorter in the case of calcium impregnated coal than in the case of coal-limestone particle mixing. Shorter diffusion distances would lead to faster reaction times and hence to greater calcium utilization.

In this project to "Investigate the Effectiveness of Calcium Treated Coals in the Capture of Sulfur Gases Generated in Staged Fired Combustors", the sulfur capture mechanism described above will be tested for ultimate use in a staged fired combustor. It is anticipated that the use of calcium treated coals in a staged fired combustor will reduce both SO_x and NO_x emissions. By staging the combustion of coal, the generation of NO_x by two well known mechanisms: the oxidation of nitrogen in the fuel; and the high temperature free radical attack on molecular nitrogen (Zeldovich mechanism) is reduced.

In staged combustion, the first stage is operated in a fuel rich or reducing atmosphere. This technique results in conversion of complex fuel nitrogen species to a series of cyanogen, oxycyanogen, and ultimately, amine species. If sufficient energy is extracted from the first stage before admixing more air and injections into the second stage, the adiabatic flame temperature can be lowered to below 1800°K, where the thermal Zeldovich mechanism becomes less significant.

By utilizing calcium impregnated coals as the feed to a staged fired combustor, the emission of acid gases, both SO_x and NO_x may be reduced. In this experimental program, sulfur capture by calcium impregnated coals will be investigated. The atmospheres encountered by the treated coals in the test furnace will be similar to those of different sections in a staged combustor.

OBJECTIVES

The objectives of this program are threefold:

- (1) To develop and test methods to fix calcium ions into the coal matrix;

- (2) To determine the effectiveness of sulfur capture by calcium treated coals as a function of coal type, calcium fixation method, coal particle size, combustion temperature, equivalence ratio and particle residence time;
- (3) To develop a model of sulfur capture by calcium treated coals which will describe the dependence of sulfur retention on the above mentioned experimental parameters.

TASKS

To meet the objectives outlined above, the research program has been divided into six tasks. A brief description of these tasks is presented below.

Task 1 - Literature Review and Coal Selection

The literature will be reviewed for reports on previous work on methods of impregnating calcium in coal and for sulfur retention data of coals in which calcium has been fixed. Three types of coal will be selected for use in this study. The coals will be selected according to the following criteria:

- o they are well characterized;
- o high potential for use in coal water mixtures;
- o high sulfur and low calcium content; and
- o three coals should have a distribution of rank characteristics.

Task 2 - Design and Construction of Test Facility

A combustion test facility will be designed and built which will allow variation of the following experimental parameters:

- (a) coal feed rates;
- (b) initial coal particle size feed;
- (c) fuel equivalence ratio;
- (d) combustion temperature; and
- (e) particle residence time.

Task 3 - Development of Calcium Fixation Procedures

A method to bond calcium within the coal matrix, in such a way that it will not leach out in the aqueous phase, will be developed. The following variables will be tested for their effect on calcium fixation:

- (1) coal particle size;
- (2) concentration of organic acid in solution;
- (3) soaking temperature;
- (4) soaking time; and
- (5) acid identification.

Task 4 - Pretreating Coal for Combustion Study

Using the impregnation method determined by Task 2 to be most effective, 1 kilogram of each of the three selected coals will be treated with calcium for use in the combustion experiments.

Task 5 - Experimental Investigation of Sulfur Capture

A combustion test program will be carried out using the apparatus constructed in Task 2. Carbon and sulfur contents of the coal feed materials,

the post combustion char and the combustion gases will be analyzed. A material balance of carbon and sulfur species will be calculated for each run, in order to ensure the credibility of the experimental and analytical set-ups and to better understand the reactions taking place in the test furnace.

Task 6 - Model Development

A model of sulfur capture in calcium impregnated coal will be developed. Past models will serve as a starting point for the model; the data collected in Task 5 will guide model development. A conceptual model will first be formulated, the appropriate mathematics developed to describe the concept and the solution to the mathematical formulation will then be devised.

PROGRESS

During this quarter, the work effort was focused primarily on two tasks: Development of Calcium Fixation Procedures and the Design and Construction of the Combustion Test Facility. In the development of calcium treatment methods, a new approach to calcium impregnation of high rank coals has been discovered which yields to encouraging results. With the new method, the investigators have produced bituminous coal samples containing up to 12% calcium by weight. In task 2, the build-up of the test facility, a revised design of the coal feeder has led to the development of a steady and reliable low flow feed system. With the feeder satisfactorily developed, the test facility is nearly complete. These two major accomplishments, as well as the rest of the progress made in this quarter, are described in the sections below.

Task 2 Design and Construction of Test Facility

To describe the progress which has been made in the design and construction of the combustion facility, this facility has been conceptually divided into five separate subunits: the coal feeder; the gas feed system (both air for combustion and argon for quenching); the laminar flow furnace; the char and gas collection probe; and the gas analysis system. During this quarter's work, progress has been made in the design and construction of all of these components. This progress is described, by unit, below.

Coal Feeder

The operation of the low flow coal feeder has warranted considerable attention, because its precision and accuracy is a critical determinant of the whole combustion system reliability. After numerous tests on the feed system developed during last quarter's work, it was decided that modification of the system was required to improve its performance. Simple but significant changes in the design were made which dramatically increased the reliability of the coal feed rates it produced. The feeder now being calibrated is a substantial improvement over the previous system. It can deliver coal at the desired flow rates, with the required steadiness and repeatability. With only calibration left for the development requirements of this device, its satisfactory operation is, for the most part, assured.

Figure 1
Low Flow Fluidized Bed Coal Feeder

A sketch of the feeder is shown on the following page. The major improvements/additions to the system which have been made since last quarter are:

- 1) A jewel bearing fit into the top of the coal feed tube is utilized as a critical flow orifice for gas-solid flow. This roughly sets the coal flow to the desired range.
- 2) A venturi added to the bottom of the coal feed tube. This serves to "pull" the coal down the tube.
- 3) A cam operated valve system is attached below the venturi to pulse air back through the coal feed tube at regular intervals. This unclogs the tube and minimizes the feed rate fluctuations due to slowly decreasing flow (caused by static buildup in the tube).

The operation of the feeder is as follows. The coal is fluidized by air entering at inlet A. The fluidized coal flows through a hypodermic needle which has been fitted with a toroid shaped jewel at the tip. The jewel serves to constrict the needle and establish a range of possible coal flow rates through the tube. Both the jewels and the tubes are interchangeable so that different ranges of flow rates can be produced by varying the inner diameters of these components. At the base of the needle is a venturi. Air enters at inlet B to provide the venturi air which pulls the coal down the tube. Underneath the venturi is tygon tubing and a cam which rotates at 25 revolutions per minute. As the cam rotates, it closes off the flow through the tubing every 2 seconds for 0.3 seconds. This pulsing forces air and coal to backwash through the feed tube and clear the needle of clogs. The method to clear the clogging in the system (which results primarily from the static electricity in the coal) is the critical part of the feed system. At very low or quite high feed rates the clogging is not much of a problem. The rates required for this experimental program seem to require the coal to flow in a density range where the flow is particularly sensitive to clogging and instabilities.

With this system there is no need for vibration to shake the clogged coal from the tubes. The system is thus steady and reliable. The feed is pulsed, as opposed to continuous, flow. The pulsed nature of the feed rates should be reduced as the coal flows through a reasonable length of narrow tubing into the furnace. One further method is being investigated to minimize the pulsing of the flow. This modification entails adding a constriction at the end of the system, after the tygon tubing and cam arrangement. This will slow the coal stream when it is flowing and consequently continue to feed the coal when the main stream is being flushed back up the tube.

Flow rate is controlled by fluidizing air velocity, chamber pressure and venturi flow rate, as well as with the needle size and jewel size in the needle.

As the fluidizing air velocity increases the density of the bed decreases, causing an increase in the coal flow rate. It appears to be that the less dense the bed, the easier it is for the coal to flow into a small tube opening. As the density increases, clogging at the tip of the needle may decrease the number of particles which are able to enter the tube. Adjustment of the fluidizing air flow rate is the primary means to set coal flow rate.

The venturi air flow rate is also important in establishing the quantity and nature of coal flow from the feeder. As venturi air is increased, the flow of coal decreases. The reason this occurs may be that pressure builds up just upstream of the venturi as the flow rate of air is increased. Regulating the venturi air does help in controlling coal feed rate, but the range of air flow rates available for use is limited for combustion reasons. In an attempt to minimize the amount of air that enters the furnace with the coal stream, the use of venturi air is restricted to a low flow range.

Increasing the pressure in the fluidizing chamber serves to steady the bed and decrease the coal flow rate variations. The higher the pressure above the bed, the denser and more consistent is the bed. This leads to steadier flow.

Work is being conducted to calibrate the feeder. Unless difficulties arise in this final task, the feeder will be ready by September 1st.

Furnace

The laminar flow tube furnace has been installed in the laboratory. In July, the furnace was wired and plumbed. Initial tests on the furnace indicate that the temperature controller and programmer work well. A platinum rhodium thermocouple (type R) has been purchased for use as a temperature probe to map the temperature profile in the furnace. Initial test firings went to 900°F without any problem. The initial tests were to check the cooling system and the temperature controller function.

The interior of the furnace must be modified slightly in order for it to be used as a continuous combustion system. The preheater and flow straightener elements must be added to the interior of the furnace. The bulkheads of the furnace which support the alumina muffle tube lining must be modified to allow insertion of the collection probe (at the bottom) and the coal feed and air feed tubes (at the top). A picture of the furnace system is shown on the following page. The specifications of this Astro group 1000 A furnace are included in Appendix A.

Gas Flow Control

Critical flow orifices will be used to control the flow of gases in the combustion system. It was decided that a rotameter-type gas flow meter does not have the accuracy required for flow control in this system. Argon flow, serving as the quench gas, will be controlled by a critical flow orifice and measured by a Teledyne Hastings Raydist mass flow meter (whose operating mechanism is a hot wire anemometer). The same system, critical flow orifice control and hot wire anemometer mass flow measurement, will be used to control and measure the flow of combustion air into the furnace.

Probe

The gas and char collection probe has been built according to the design presented in the previous quarterly report.

Sulfur Gas Analysis

Sulfur dioxide levels in the gas stream will be measured with a continuous SO₂ analyzer. Arrangements with DOE in Pittsburgh are taking place to

Figure 2
Laminar Flow
Tubular Furnace

obtain an infra-red analyzer. As presently arranged, a Mine Safety Appliance model 303 infra red SO₂ analyzer will be delivered by the first week in September.

As pretreatment of the gas for sulfur analysis, the particulates and water vapor will be removed from the gas stream. The particulates will be removed with a filter in the collection probe. The water vapor will be removed with a length of a Permapure drier. This dryer passes the gas stream through a membrane which is permeable to water vapor only. A vacuum or a dry gas purge around the membrane tubes draws out the water from the gas stream. About 1 liter per minute of the combustion gases will be drawn off the main stream for drying and analysis.

Summary

Each component of the system is nearly completed. Assembly of the components is now the remaining task to be performed for task 2. Since the design phase is completed, the remaining work is to assemble the parts and to clarify the test schedule and procedures.

Task 3 Development of Calcium Fixation Procedures

Introduction

As pointed out in the last quarterly report, conventional ion exchange methods are unsuccessful in adding an adequate amount of calcium (a minimum Ca/S molar ratio of 1.0) to the high rank bituminous coals. A new approach to increasing the calcium content of these high rank coals was investigated this quarter.

The new concept lies in the use of a reaction between calcium acetate and carbon dioxide in the aqueous phase (in the presence of ammonia) to precipitate CaCO₃ into the coal sample. It is anticipated that this precipitation reaction will take place in the pores of the coal. Coal is a porous solid with an extensive network of pores. Most of the pores are larger than 6 angstroms, and the reacting ions, Ca⁺⁺, NH₄⁺, OH⁻ and CO₂ gas can all diffuse through these pores. It can be said that in principle the reaction could be made to take place inside the coal matrix.

Some experiments were conducted to investigate the new process. A slurry of coal and ammoniated calcium acetate solution was pressurized with CO₂ to 1000psi. The results of this new calcium impregnation method are very encouraging. The calcium content of two types of bituminous coals treated in this manner were increased to 12 percent by weight, from an original concentration of less than 1/2 of one percent. The calcium concentration present in the coal after treatment corresponds to a calcium to sulfur concentration ratio of greater than 2.

The new pressurized impregnation method is a very different process from the methods initially investigated to bond calcium in the coal pores. The original experiments relied on the ion exchange properties of coal to bond calcium in the coal matrix. The amount of calcium which could be introduced into the coal matrix seemed to be limited by two factors: the quantity of sites in the coal matrix on which the calcium was to bind and the accessibility of these sites to calcium ions in aqueous solution. As was hypothesized in the work of Freund and Lyon at Exxon, the bonding may be

carboxylic or phenolic groups. The bonding of additional calcium into the coal would be limited if the quantity of carboxylic groups were low (as is in the case of high rank coals in which little oxidation has taken place) or if the carboxylic groups existed in micropores of the coal which are physically inaccessible to calcium ions in an aqueous solution (i.e. because of excessive surface tension forces resisting the penetration of a solution into the pores.) In an effort to overcome the basic limitations of an ion exchange process, a new approach was investigated.

Experimental Work in Calcium Treatment Methods-Procedures and Results

The experimental procedures used in the new impregnation method are described below. Also presented are the results of the experiments and a discussion of these results. Some limited combustion tests conducted to further investigate the process are also described.

I. Experiment 1 Coal, Calcium Acetate, and Ammonium Hydroxide in Aqueous Solution Pressurized with Carbon Dioxide

A. Experimental Procedure

A sample of 20 grams of coal was soaked in 50 milliliters of 1.00 molar calcium acetate solution. The solution was ammoniated with 10 ml of a 30% by weight ammonium hydroxide (NH_4OH) solution. The coal in solution was placed in a stainless steel cylindrical vessel and pressurized to 1000. psi by pumping CO_2 into the vessel. The pressure was maintained in the vessel for two hours. The pressure was then released, and the mixture was filtered through a 5 micron membrane filter. The treated coal sample was dried in a dessicator. After the coal sample was dried, the sample was sent to a coal analysis lab to determine the calcium content of the coal. Calcium content was determined by the ASTM method D3682. Specifics of this test are presented in Appendix B.

It should be noted that except for the CO_2 pressurization step, the treatment procedure is the same as that used in the ion exchange tests of last quarter.

B. Results

The results of the tests are presented below. Tables 1 and 2 display a coal analysis performed on treated and untreated Illinois #6 and Pittsburgh #8 coals.

Table 1
Analysis of Treated and Untreated Illinois #6 coal

<u>Sample type</u>	<u>calcium wt %</u> <u>(untreated)</u>	<u>calcium wt%</u> <u>(pressurized w/CO_2)</u>	<u>calcium wt%</u> <u>(soaked, no pressure)</u>
Illinois	0.411	12.08	1.34

Table 2
Analysis of Treated and Untreated Pittsburgh #8 Coal

<u>Sample Type</u>	<u>calcium wt %</u> <u>(untreated)</u>	<u>calcium wt %</u> <u>pressurized w/CO_2)</u>	<u>calcium wt %</u> <u>(soaked, no pressure)</u>
Pittsburgh	0.055	11.87	0.46

As can be seen, large increases in the calcium concentration of the coal sample occurs after pressurized impregnation. The calcium to sulfur ratio of the coal has increased to 2.5. (This ratio was only increased to about 0.30 in the ion exchange tests conducted at atmospheric pressure.)

Leaching tests were conducted on the treated coal samples. Results of these tests indicate that less than one percent of the added calcium leaches out of the coal into the water. That the calcium does not leach out supports the idea that calcium carbonate is being formed, since calcium carbonate is insoluble in water. The leaching tests also imply that the calcium carbonate may have been formed in pores that are not accessible to the wash water at atmospheric pressure.

Sulfur determinations were made on the treated and untreated coal samples. The sulfur test is a high temperature (2400°F) combustion test in pure oxygen. (ASTM method D3177 Method B. The standards for this test are presented in Appendix B). The sulfur in the coal is measured as it is released as SO₂ in the combustion gas. The sulfur content of the combustion gases of the treated coals was 25% of the expected quantity, based on the sulfur content of the untreated coal. In other words, only 25% of the sulfur expected to be in the coal came out as SO₂. This implies that the impregnation procedure produces a coal which retains a high percentage of the sulfur in the ash during a combustion process.

It was desired to study the importance of the various components of this calcium impregnation technique. To determine whether CO₂ was taking part in the reaction, a test was conducted using air, instead of carbon dioxide, as the pressurizing gas. If the high pressure gas were only serving to force the calcium into the micropores of the coal matrix, the type of gas used should not have a significant effect on the quantity of calcium deposited in the pores.

II. Experiment 2: Calcium Acetate, Ammonium Hydroxide and Coal in Aqueous Solution Pressurized with Air to 1000 psi

A. Procedure

The procedure of this experiment was the same as the previous experiment, except that the pressurizing gas was air instead of carbon dioxide. The coal was soaked in 50 mls of a 1 molar calcium acetate solution. 10 mls. of a 30% ammonium hydroxide solution were added. The mixture was placed in a cylindrical vessel and pressurized to 1000 psi with air. The pressure was held for 2 hours. The coal was then filtered and dried in a desiccator. When the coal was dry it was sent out for analysis.

B. Results

The results of the air pressurization tests are shown in Table 3. These data show that coal samples in a solution of ammoniated calcium acetate which have been pressurized with air to 1000 psig contain significantly less calcium than the samples which were pressurized with CO₂. The samples pressurized by air did contain, however, far more calcium than samples treated at atmospheric conditions, as shown in Table 3.

Table 3
Effect of Pressurization by Air on Bituminous Coals Treated with
Ammoniated Calcium Acetate

<u>Coal Type</u>	<u>Calcium wt.%</u> <u>(untreated)</u>	<u>Calcium wt.%</u> <u>(tr.@1 atm.)</u>	<u>Calcium wt.%</u> <u>(tr. @1000psi air)</u>	<u>Calcium wt.%</u> <u>(tr.@1000psiCO₂)</u>
Illinois #6	0.411	1.34	1.66	12.08
Pittsburgh #8	0.055	0.46	3.00	11.87

When the samples are treated in the presence of air, the calcium is probably deposited into the coal by means of an ion exchange process. The additional quantities of calcium which are deposited in samples which have been treated under pressure, as compared to those treated under atmospheric conditions is due to the large surface area made available for ion exchange when the pressure forces calcium acetate solution into the micropores of the coal. Comparing the quantities of calcium which were deposited into the Pittsburgh #8 coal to the amounts deposited into the Illinois #6 coal, one can conclude that the pore structure of the two coals is quite different. The difference in pore structure could determine the amount of increased surface area which becomes available for ion exchange when pressure is applied.

The role of the ammonium hydroxide was briefly studied as well. A test was conducted using CO₂ as the pressurizing gas above a slurry of Pittsburgh #8 coal and a solution of calcium acetate alone, without any ammonium hydroxide. Again, if the CO₂ was only being utilized as a pressurizing gas and was not taking part in a reaction, the omission of the ammonium hydroxide should have little effect on the amount of calcium added to the coal.

III. Experiment 3: Calcium Acetate Solution and Coal Suspension
Pressurized with Carbon Dioxide to 1000 psi for 2
Hours

A. Procedure

A sample of Pittsburgh #8 coal was soaked in calcium acetate solution (1 molar) and pressurized with CO₂ to 1000 psi for 2 hours. The procedure for this experiment was the same as for Experiment 1 except that no ammonium hydroxide was added to the solution. The coal sample was then filtered and dried, the sample sent out for calcium analysis.

B. Results

The final calcium content in the sample treated without the ammonia was only 0.196%. This shows that the presence of ammonium hydroxide is essential to the impregnation process.

IV. Combustion Tests

A combustion test was performed to make a preliminary evaluation of the effectiveness with which the treated coal captured sulfur. In this experiment, a comparison was made between the amount of sulfur gases released when treated coal was burned, and the amount of sulfur gases released when untreated coal was burned in a mixture of coal and CaCO₃. The amount of

calcium present in the two samples was equivalent, but their contact with the coal was different. Both samples were burned in an excess of oxygen at 2400°F in a crucible. Sulfur emissions from the untreated coal mixed with calcium carbonate particles were double those released from the calcium treated coal sample.

Discussion and Conclusions

The increase in the calcium content of coal which can be achieved by a pressurized reaction between carbon dioxide, calcium acetate and ammonium hydroxide is dramatic and encouraging. The tests which were described in the previous paragraphs were conducted in order to understand the process by which this new method is depositing calcium into the coal. The use of all three components of the treatment: carbon dioxide, calcium acetate and ammonium hydroxide seems to be necessary for a maximum increase in the calcium content of the coal to be observed.

The increase in calcium concentration of the coal which occurs after calcium acetate treatment and CO₂ pressurization appears to operate by a different mechanism than the ion exchange process which occurs in unpressurized conditions. The CO₂ pressurized process may be adding calcium to the coal by a precipitation process. In this hypothesis, calcium carbonate is being formed in the coal by a reaction between the calcium acetate and the carbon dioxide dissolved in the water. The ammonium hydroxide serves to keep the solution basic, so that the CO₂ will dissolve in it. It may be envisioned that pores, cracks and available surface area in the coal matrix are being filled with calcium carbonate particles. These CaCO₃ particles may vary in size from the molecular level to being a few microns in diameter.

The ammonium hydroxide may also serve to combine with the acetic acid which remains after the calcium ion is bound into CaCO₃. Buildup of acetic acid would dissolve the CaCO₃ and drive the CO₂ out of solution. The necessity of a counter ion to combine with the acetate ion may be the reason that treatment without the ammonium hydroxide is not nearly as successful as treatment with it.

APPENDIX A

Specifications for ASTRO Furnace

Features

The Astro 1000A Group of graphite element resistance furnaces has become the standard for the high temperature laboratory. Several models are available with hot zone sizes, temperature, and controlled atmosphere capabilities to meet a wide variety of small volume production and laboratory requirements.

Operating environments are inert and dry reducing atmospheres with pressure capabilities to 15 psig positive. Vacuum operation is also possible at temperatures up to 2300°C. The addition of optional muffle tube assemblies permits working in oxidizing or wet reducing atmospheres.

The basic system includes the furnace, support column with swivel mounting bracket, manual power supply, and water-cooled flexible power leads. Some of the additional features are as follows:

Easy Access to Work

Straight through access permits loading from either end. Multiple radial and axial ports permit viewing and instrumentation access to the hot zone during operation.

Rapid Response

Heat up to maximum temperature in less than 30 minutes. Cool down time to 100°C is typically 2 to 3 hours.

High Temperature

Temperatures to 3000°C in inert and reducing atmospheres.

Horizontal or Vertical Operation

Systems include swivel mounting bracket and flexible power leads.

Easy Maintenance

The long life heating element can be replaced in less than 10 minutes.

Optional Accessories

Among the many standard furnace accessories available are: Alumina Muffle Tube Assembly, Hydraulic Hearth Lift, Cooling Chamber, Gas and Vacuum Controls, Automatic Temperature Control/Program/Record.

Typical Applications

Melting, Sintering, Annealing, Metallizing and Brazing, Crystal Growing, Hot Pressing, Spectroscopy, Mechanical and Physical Properties Testing, DTA and TGA, Pyrolyzing.

Furnace Construction

The furnace shell is heavy-wall, seamless extruded 6061-T6 aluminum with an anodized exterior. The bulkheads are hard anodized aluminum and the doors are nickel-plated copper. The shell and bulkheads have integral water-cooling passages. Important safety features of the chamber design are the absence of water-wetted welds and brazed joints in the furnace interior. External surface temperatures are maintained at 65°C or less. O-ring seals are Viton. Other models are available for use with corrosive atmospheres; these are constructed of stainless steel and nickel-plated copper materials.

The furnace has 3 radial and 2 axial 1½"-16 threaded ports. One radial port is equipped with a 0.63 (16 mm) diameter viewing window with anti-fog gas diffuser. All other ports are plugged but will accept the addition of optional sight windows, thermocouples, feedthroughs, and valved adaptors. Additional radial ports can be optionally added.

The hot zone has straight through access for convenient loading from either end. Sight hearths in both ends of the furnace serve as thermal baffles, and in the vertical position, will support the work. A graphite tray is optionally available for attachment to either hearth to support work during horizontal operation.

Power connections are both at one end of the furnace through radially mounted, water-cooled, copper feedthroughs, providing unimpeded access to the bulkheads and doors. Electrical contact between the feedthroughs and the element is made by simple, clamp-type connectors.

System Models

Hot Zone Size	Temperature In Helium	Model	Power Supply
2.44" dia. x 6" long (62 mm x 153 mm)	2650°C 3000°C	1000-2560-FP-12 1000-2660-FP-20	12 KVA 20 KVA
3.0" dia. x 6" long (76 mm x 153 mm)	2500°C 2850°C	1000-3060-FP-12 1000-3060-FP-20	12 KVA 20 KVA
3.5" dia. x 6" long (89 mm x 153 mm)	2200°C 2650°C	1000-3560-FP-12 1000-3560-FP-20	12 KVA 20 KVA
4.5" dia. x 6" long (114 mm x 153 mm)	2000°C 2275°C	1000-4560-FP-12 1000-4560-FP-20	12 KVA 20 KVA

Special Models are available with hot zone lengths to 24 inches (610 mm).

Specifications

Heating Elements. High Density Graphite Resistance Element.

Hot Zone Dimensions. 4.5 inches diameter max. (114 mm)

6.0 inches long max. (153 mm).

Insulation (Thermal). Graphite Felt Pack.

Maximum Temperature. To 3000°C.

Ultimate Vacuum Level. 10⁻³ torr (0.13 Pa) at 2000°C.

Positive Pressure Maximum. 15 psig.

Facility Requirements.

Electric: 208/230 volt, 60 Hz, single phase or 220 volt, 50 Hz, single phase

Water: 2.5 gpm at 50 psid; 65-85°F (9.5 l/min. at 345 KPa; 18-30°C).

Inert Gas: 0.2 to 2.0 SCFH minimum.

Vacuum: A mechanical vacuum purge pump is recommended.

Space: Maximum floor area: 5' x 5' (1.3 m x 1.3 m) including access.

Height: 7' (2.1 m).

Installation: Systems are complete and require only connection to user supplied sources of power, cooling water and operating gas/vacuum.

APPENDIX B

ASTM Standards for Calcium and Sulfur Analysis

ASTM Method D3682
Test for Calcium Content in Coal

12. Calcium Oxide (CaO)

12.1 Preparation of Standards—Prepare standard solutions containing 1 to 10 ppm Ca and 10 ml of lanthanum solution per 100 ml. Dilute with the blank solution as described in 11.2.

12.2 Blank Solution—Use blank solution as described in 11.2.

12.3 Sample Solution—Use Solution 2 as described in 8.3.4.

12.4 Atomic Absorption Operating Conditions—Use a calcium hollow-cathode lamp and set the monochromator at 422.7 nm. Use an air-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

12.5 Determination—Read the absorbance values for the blank solution, the standard solutions, and the sample solution.

$$\text{CaO, \%} = [(C - B)/(A - B)] \times N \times 2.80$$

where:

A = absorbance of standard nearest *C*,

B = absorbance of blank,

C = absorbance of sample, and

N = Ca in standard, ppm.

ASTM Method D3177
Test for Total Sulfur in Coal

Designation: D 3177 - 75 (Reapproved 1982)

Standard Test Methods for
TOTAL SULFUR IN THE ANALYSIS SAMPLE OF
COAL AND COKE¹

This standard is issued under the fixed designation D 3177; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These methods cover three alternative procedures for the determination of total sulfur in samples of coal and coke. Sulfur is included in the ultimate analysis of coal and coke.

1.2 The procedures appear in the following order.

	Sections
Method A—Eschka Method	5 to 8
Method B—Bomb Washing Method	9 to 11
Method C—High-Temperature Combustion Method	12 to 16

2. Applicable Documents

2.1 *ASTM Standards:*

D 346 Collection and Preparation of Coke Samples for Laboratory Analysis²

D 1193 Specification for Reagent Water³

D 2013 Preparing Coal Samples for Analysis²

D 2015 Test for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter²

D 3173 Test for Moisture in the Analysis Sample of Coal²

D 3176 Ultimate Analysis of Coal and Coke²

D 3180 Calculating Coal and Coke Analyses from As-Determined to Different Bases²

3. Summary of Methods

3.1 *Eschka Method*—A weighed sample and Eschka mixture are ignited together, and the sulfur is precipitated from the resulting solution as barium sulfate (BaSO_4). The precipitate is filtered, ashed, and weighed.

3.2 *Bomb Washing Method*—Sulfur is precipitated as BaSO_4 from oxygen-bomb calorimeter washings, and the precipitate is filtered,

ashed, and weighed.

3.3 *High-Temperature Combustion Method*

—A weighed sample is burned in a tube furnace at a temperature of 1350°C in a stream of oxygen. The sulfur oxides and chlorine formed are absorbed in a hydrogen peroxide (H_2O_2) solution yielding hydrochloric (HCl) and sulfuric (H_2SO_4) acids. The total acid content is determined by titration with sodium hydroxide (NaOH), and the amount of sodium chloride (NaCl) resulting from the titration of the HCl is converted to NaOH with a solution of mercuric oxycyanide ($\text{Hg}(\text{OH})\text{CN}$). This sodium hydroxide is determined titrimetrically and used to correct the sulfur value which is equivalent to the amount of H_2SO_4 formed during combustion of the coal.

4. Sample

4.1 The sample shall be the material pulverized to pass No. 60 (250- μm) sieve in accordance with Method D 2013 or Method D 346.

4.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Method D 3173, so that calculation to other than the as determined basis can be made.

4.3 Procedures for converting as determined sulfur values obtained from the analysis sample to other bases are described in Method D 3176 and Method D 3180.

4.4 Standard Reference Material (SRM)

¹ These methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke.

Current edition approved May 30, 1975. Published August 1975. Originally published as D 3177 - 73. Last previous edition D 3177 - 73.

² Annual Book of ASTM Standards, Part 26.

³ Annual Book of ASTM Standards, Part 31.

ASTM Method D3177
Test for Total Sulfur in Coal, Cont'd.

1631-Sulfur in Coal* consists of three different low-volatile coal samples, each of which has a certified sulfur content. Sulfur values obtained by analyzing these coals, using any of the three methods described in this standard, may be used for checking the accuracy of analytical results.

ALTERNATIVE PROCEDURES

Method A—Eschka Method

5. Apparatus

5.1 *Gas (Note 1) or Electric Muffle Furnace, or Burners*, for igniting the sample with the Eschka mixture and for igniting the barium sulfate (BaSO_4).

NOTE 1—Gas may contain sulfur compounds.

5.2 *Crucibles or Capsules*—Porcelain capsules, $\frac{7}{8}$ in. (22 mm) in depth and $1\frac{3}{4}$ in. (44 mm) in diameter, or porcelain crucibles of 30-ml capacity, high or low form, or platinum crucibles of similar size shall be used for igniting the sample with the Eschka mixture. Porcelain, platinum, alundum, or silica crucibles of 10 to 15-ml capacity, shall be used for igniting the BaSO_4 .

6. Reagents.

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Available Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type IV conforming to Specification D 1193.

6.3 *Barium Chloride Solution (100 g/litre)*—Dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and dilute to 1 litre with water.

6.4 *Bromine Water (Saturated)*—Add an excess of bromine to 1 litre of water.

6.5 *Eschka Mixture*—Thoroughly mix 2 parts by weight of light calcined magnesium oxide (MgO) with 1 part of anhydrous sodium carbonate (Na_2CO_3). Both materials should be

as free as possible from sulfur.

6.6 *Hydrochloric Acid (1 + 1)*—Mix equal volumes of concentrated hydrochloric acid (HCl , sp gr 1.19) and water.

6.7 *Hydrochloric Acid (1 + 9)*—Mix 1 volume of concentrated hydrochloric acid (HCl , sp gr 1.19) with 9 volumes of water.

6.8 *Methyl Orange Indicator Solution (0.2 g/litre)*—Dissolve 0.02 g of methyl orange in 100 ml of hot water and filter.

6.9 *Sodium Carbonate, Saturated Solution*—Dissolve approximately 60 g of crystallized sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) or 22 g of anhydrous sodium carbonate (Na_2CO_3) in 100 ml of water, using a sufficient excess of Na_2CO_3 to ensure a saturated solution.

6.10 *Sodium Hydroxide Solution (100 g/litre)*—Dissolve 100 g of sodium hydroxide (NaOH) in 1 litre of water. This solution may be used in place of the Na_2CO_3 solution.

7. Procedure

7.1 *Preparation of Sample and Mixture*—Thoroughly mix on glazed paper approximately 1 g of the sample, weighed to nearest 0.1 mg, and 3 g of Eschka mixture. The amount of sample to be taken will depend on the amount of BaCl_2 solution required in accordance with 7.3. Transfer to a porcelain capsule or porcelain crucible, or a platinum crucible, and cover with about 1 g of Eschka mixture.

7.2 *Ignition*—Heat the crucible over an alcohol, gasoline, or gas flame as described in 7.2.1, or in a gas or electrically heated muffle as described in 7.2.2 for coal and in 7.2.3 for coke. The use of artificial gas for heating the sample and the Eschka mixture is permissible only when the crucibles are heated in a muffle.

7.2.1 Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter which tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 min, gradually increase the temperature, and occasionally stir

* Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Bureau of Standards, Washington, D.C. 20234.

³ "Reagent Chemicals, American Chemical Society Specification," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Ross, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

ASTM Method D3177
Test for Total Sulfur in Coal, Cont'd.

ASTM D 3177

until all black particles have disappeared, which is an indication of the completeness of the procedure.

7.2.2 For Coal—Place the crucible in a cold muffle and gradually raise the temperature to $800 \pm 25^\circ\text{C}$ in about 1 h. Maintain this maximum temperature until on stirring all black particles have disappeared (about $1\frac{1}{2}$ h).

7.2.3 For Coke—Place the crucible in a warm muffle (about 200°C) and gradually raise the temperature to $800 \pm 25^\circ\text{C}$ in about 30 min. Maintain this maximum temperature until on stirring all black particles have disappeared.

7.3 Subsequent Treatment—Remove the crucible and empty the contents into a 200-ml beaker and digest with 100 ml of hot water for $\frac{1}{2}$ to $\frac{3}{4}$ h, while stirring occasionally. By decantation, filter, and thoroughly wash the insoluble matter with hot water. After several washings in this manner, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 ml, with 10 to 20 ml of saturated bromine water, make slightly acid with HCl, and boil to expel the liberated bromine. Make just neutral to methyl orange with NaOH or Na_2CO_3 solution; then add 1 ml of HCl (1 + 9). Boil again and add slowly from a pipet, while stirring constantly, 10 ml or more of BaCl_2 solution. The BaCl_2 solution must be in excess. If more than 10 ml of BaCl_2 solution is required, reduce the weight of sample to about 0.5 g and repeat the ignition and digestion. Continue boiling for 15 min and allow to stand for at least 2 h, or preferably overnight, at a temperature just below boiling. Filter through an ashless paper and wash with hot water until 1 drop of silver nitrate (AgNO_3) solution produces no more than a slight opalescence when added to 8 to 10 ml of filtrate.

7.3.1 Place the wet filter containing the precipitate of barium sulfate (BaSO_4) in a weighed platinum, porcelain, silica, or Alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow to burn with flame. After the paper is practically consumed, raise the temperature to approximately 925°C and heat to constant weight.

7.4 Blanks and Corrections—In all cases a

correction must be applied. Either a reagent blank may be run exactly as described above, using the same amount of all reagents that were employed in the routine determination, or a more accurate correction may be made by analyzing a weighed portion of a standard sulfate using the prescribed reagents and operations. If the latter procedure is carried out once a week, or whenever a new supply of a reagent is used, for a series of solutions covering the approximate range of sulfur concentrations in the samples, it is only necessary to add to or subtract from the weight of BaSO_4 determined for the sample, the deficiency or excess found by the appropriate "check" determination. This procedure is more accurate than the simple reagent blank because, for the amounts of sulfur in question and the conditions of precipitation prescribed, the solubility error for BaSO_4 is probably the largest one to be considered. Barium sulfate is soluble* in acids and pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, if very high-purity reagents are used or extra precaution is exercised, there may be no sulfate apparent in the "blank." In other words, the solubility limit for BaSO_4 has not been reached or at any rate not exceeded; consequently, some sulfate in the sample may remain in solution or redissolve.

8. Calculation

8.1 Calculate the sulfur content as follows:

$$\text{Sulfur, \% in the analysis sample} = \frac{(A-B) \times 13.738}{C}$$

where:

- A* = grams of BaSO_4 precipitated,
B = grams of BaSO_4 correction, and
C = grams of sample used.

*Method B—Bomb Washing Method**

9. Reagents

9.1 Purity of Reagents—(Sec 6.1.)

9.2 Purity of Water—(Sec 6.2.)

* *Journal of the American Chemical Society*, JACSA, Vol 32, 1910, p. 588, Vol 33, 1911, p. 829.

* Selvig, W. A., and Fieldner, A. C. "Check Determinations of Sulfur in Coal and Coke by the Eschka, Bomb-Washing and Sodium Peroxide Fusion Methods," *Industrial and Engineering Chemistry*, JECHA, Vol 29, 1927, pp. 729-733.

ASTM Method D3177
Test for Total Sulfur in Coal, Cont'd.

ASTM D 3177

9.3 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

9.4 *Bromine Water* (Saturated)—(See 6.4.)

9.5 *Hydrochloric Acid* (1 + 1)—(See 6.6.)

9.6 *Sodium Carbonate Solution*—Dissolve 20.90 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 litre. The Na_2CO_3 should be previously dried for 24 h at 105°C.

9.7 *Wash Solution*—Dilute 1 ml of a saturated solution of methyl orange to 1 litre with water.

10. Procedure

10.1 *Ignition*—Sulfur is determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination (Method D 2015). The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified under the calorimetric determination (Sections 4 to 8 of Method D 2015). The bomb shall stand in the calorimeter water for not less than 5 min after firing.

10.2 *Subsequent Treatment*—Remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape at an approximately even rate so the pressure is reduced to atmospheric in not less than 1 min. Bombs equipped with valves other than needle valves, such as compression valves, shall be provided with a device so the valve can be controlled to permit a slow and uniform release of the gases. Open the bomb and examine the inside for traces of unburned material or sooty deposit. If these are found, discard the determination. Wash carefully all parts of the interior of the bomb, including the capsule, with a fine jet of water containing methyl orange (9.7) until no acid reaction is observed. It is essential to wash through the valve opening in the case of bombs equipped with compression valves, or other types of valves with large openings, as considerable spray may collect in such valve openings.

10.3 Collect the washings in a 250-ml beaker and titrate with standard sodium carbonate solution (9.6) to obtain the "acid correction" for the heating value, as specified under the calorimetric determination D 2015. Adjust the pH to 5.5 to 7.0 with dilute NH_4OH , heat the

solution to boiling, and filter through a qualitative paper. Wash the residue and paper thoroughly five or six times with hot water. To the filtrate and washings, amounting to about 250 ml, add 1 ml of saturated bromine water (9.4) and sufficient HCl (9.5) to make it slightly acid. Boil the solution to expel the excess bromine. Adjust the acidity, precipitate, and determine the sulfur as specified under the Eschka method, Sections 5 to 8.

*Method C—High-Temperature Combustion Method**

11. Apparatus

11.1 *Tube Furnace*—Capable of heating a tube approximately 34-mm external diameter over a length of 150 mm to a temperature of 1350°C. It is heated electrically using either silicon carbide resistance rods or a resistance wire.

NOTE 2—Induction furnace techniques may be used provided it can be shown that they meet the precision requirements of Section 17.

11.2 *Combustion Tube*—Approximately 28-mm internal diameter with a 3-mm wall thickness and 750 mm in length, which is gas tight at working temperature. A high-temperature porcelain or zircon straight refractory tube has been found most efficient. It requires a silica (12.12) adaptor with a flared end that just fits inside the combustion tube and serves as an exit for the gases. Alternatively, the combustion may be carried out in a tapered end tube that is directly connected to the elbow of the fritted gas bubbler (12.8) or to a 10/30 standard-taper ground joint which is attached to a borosilicate glass right-angle bend. The temperature at the tapered end of the tube should be high enough to prevent condensation in the tube itself.

11.3 *Oxygen Cylinder*, fitted with pressure regulator and needle valve to control flow rate of oxygen.

11.4 *Flowmeter*, for measuring an oxygen flow rate of 300 ml/min.

* Based on the method of Mott, R. A., and Wilkinson, H. C., "Determination of Sulfur in Coal and Coke By the Sheffield High Temperature Method," *Fuel*, FUEL 8, Vol 35, 1956, p. 6. This method is designed for the rapid determination of sulfur in coal and coke. It is not applicable to coals or coal density fractions that have been subjected to treatment with chlorinated hydrocarbons because of the potentially high acidity of the combustion gases.

ASTM Method D3177
Test for Total Sulfur in Coal, Cont'd.

D 3177

11.5 *Sample Combustion Boats*—Iron-free, unglazed porcelain or zircon boats. A convenient size is 100 mm long, 19 mm wide, and 11 mm deep.

11.6 *Heat-Resistant Wire*, 1.5 mm thick with bent end to remove boats from combustion tube.

11.7 *Silica Pusher or Heat-Resistant Rod*, with a disk end for pushing the combustion boat into the hot zone. The pusher passes through a T-piece which is fitted into a rubber stopper at the inlet end of the combustion tube. The open end of the T-piece is sealed with a rubber tube or one-holed stopper to permit movement of the pusher and prevent escape of oxygen which enters at the side limb of the T. The rubber stopper or tube should be changed periodically to avoid leakage.

11.8 *Gas Absorption Bottles with Fritted Disk*, 125-ml capacity, for gas absorption. Fritted glass end porosity should be 15 to 40 μ m. The bottle should be of such a diameter that the fritted end is covered by peroxide solution to a depth of at least 50 mm. The bottles are fitted, in a series of two per combustion tube, to the outlet end of a combustion tube. Alternatively a single narrow gas absorber may be used so that the fritted bubbler is covered to a depth of at least 90 mm.

11.9 *Vacuum Regulating Bottle*, containing mercury with an open-ended tube dipping into it.

11.10 *U-tube*, packed with soda-asbestos.

11.11 *Vacuum Source*.

11.12 *Silica Adaptor*, 300 mm long by 8 mm in outside diameter and flared at one end to 26 mm.

12. Reagents

12.1 *Purity of Reagents*—(See 6.1.)

12.2 *Purity of Water*—(See 6.2.)

12.3 *Aluminum Oxide (Al_2O_3)*, finely divided and dried at 1350°C.

12.4 *Hydrogen Peroxide (H_2O_2) Solution*—One volume percent (50 ml of 30 % H_2O_2 with 1450 ml of water). The pH is adjusted (using NaOH or H_2SO_4 as appropriate) to that which is used for the end point in the titration. Solutions should be discarded after 2 or 3 days.

12.5 *Indicator*—Indicators that change color (titration end point) between pH 4 and 5

are recommended, but in no case should the pH exceed 7. Adequate lighting and stirring to ensure proper detection of the end point is essential. A choice of indicators or use of a pH meter is permitted. Directions for preparing two acceptable mixed indicators are as follows:

12.5.1 Mix 1 part methyl red solution (dissolve 0.125 g in 60 ml of ethanol and dilute to 100 ml with water) with 3 parts bromocresol green solution (dissolve 0.083 g in 20 ml of ethanol and dilute to 100 ml with water). Discard the mixed solution after 1 week.

12.5.2 Mix equal volumes of methyl red solution (dissolve 0.125 g in 60 ml of ethanol and dilute to 100 ml with water) and methylene blue solution (dissolve 0.083 g in 100 ml of ethanol and store in a dark glass bottle). Discard the mixed solution after 1 week.

12.6 *Mercuric Oxycyanide $Hg(OH)CN$* (Note 3)—One g/80 ml of water. Prepare fresh solution every 2 or 3 days.

NOTE 3—This is a highly poisonous substance and will explode when touched with a flame or by percussion.

12.7 *Soda-Asbestos*, 8 to 20 mesh.

12.8 *Sodium Hydroxide (NaOH) Solution*, 0.050 N.

12.9 *Sulfuric Acid (H_2SO_4)*, 0.050 N.

13. Procedure

13.1 Raise the temperature of the furnace to 1350°C at such a rate that the combustion tubes will withstand the thermal shock. Measure 100 ml of 1 % H_2O_2 (12.4) into two gas absorption bottles so that at least 50 mm of the fritted disk is covered in the first bottle, or pour the whole amount into a single absorption bottle. Assemble the apparatus as shown in Fig. 1 except do not connect the rubber tube from the oxygen supply to the soda-asbestos U-tube. Draw air through at about 350 ml/min. The rate of flow can be adjusted by changing the depth of penetration into the mercury of the open-ended glass tube in the vacuum regulating bottle. Connect the oxygen supply to the U-tube and adjust the rate of flow of oxygen to 300 ml/min. This flow rate, at a temperature of 1350°C, will prevent the formation of oxides of nitrogen. The preliminary adjustment to 350 ml/min of air ensures that the connections at the outlet end of the combustion tube are under

ASTM Method D3177 Test for Total Sulfur in Coal, Cont'd.

ASTM D 3177

taken from the same bulk sample after the last stage of reduction should not differ by more than the following:

	%
Coal containing less than 2 % sulfur	0.10
Coal containing 2 % sulfur or more	0.20
Coke	0.05

17. High Temperature Combustion Method

17.1 *Repeatability*—Results of two consecutive determinations carried out on the same sample in the same laboratory by the same

operator using the same apparatus should not differ more than 0.05 % sulfur for all coal and coke.

17.2 *Reproducibility*—The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ more than the following:

	%
Coals containing less than 2 % sulfur	0.15
Coals containing 2 % sulfur or more	0.25
Coke	0.15

FIG. 1 High-Temperature Combustion Tube Furnace for the Determination of Total Sulfur in Coal.

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ASTM Method D3177
Test for Total Sulfur in Coal, Cont'd.

D 3177

slightly reduced internal pressure and no leak of combustion products will occur.

13.2 Weigh about 0.5 g of the analysis sample (Note 4) to the nearest 0.1 mg and spread evenly in a combustion boat previously lined with a thin layer of Al_2O_3 (0.02 to 0.05 g); then cover with approximately 0.5 g of Al_2O_3 .

NOTE 4—It may be necessary to grind coals of high mineral matter content to pass through a No. 100 (150- μm) sieve.

13.3 Put the charged boat into the inlet end of the combustion tube so that the center of the boat is 270 mm from the center of the combustion tube hot zone, and if necessary readjust the rate of flow of oxygen to 300 ml/min. Move the boat forward a distance of 30 mm at the beginning of each minute with the exception of the sixth minute, for the next 10 min. The boat should be left at the fifth minute position until the seventh minute to ensure a slow heating rate. At the end of the 10-min period the combustion boat will be in the center of the hot zone. Withdraw the pusher after each movement to prevent distortion of the rod. Keep the boat in the hot zone for an additional 4 min. Disconnect the gas absorption bottles and withdraw the boat onto a sheet of asbestos. This heating program has been established for all types of coal, and where it is shortened for a particular coal, results should be checked against those obtained by using the longer heating schedule.

13.4 Pour the content of the absorption bottles into a suitable titration flask. Wash the bottles and the interior of the silica adaptor with water (12.2) and add the washings to the flask. Add 5 or 6 drops of indicator solution and titrate with 0.050 *N* NaOH solution (12.8). The total acidity, due to oxides of sulfur and chlorine, is given according to the following reactions:

13.5 After titration, the chloride ion is present in solution as NaCl. Convert the NaCl to NaOH by adding 20 ml of $\text{Hg}(\text{OH})\text{CN}$ (13.6) solution (sufficient for coals containing up to 1.2 % chlorine):

13.6 Titrate the liberated NaOH with the

0.050 *N* H_2SO_4 (12.9). Make a blank determination in the same manner but without sample.

14. Calculation

14.1 Calculate the percentage sulfur in coal as follows:

$$S = \frac{1.603 [F_1(a-a_1) - F_2(b-b_1)]}{W}$$

where:

- S* = percent sulfur in coal,
- a* = millilitre of NaOH solution used in full determination,
- a*₁ = millilitre of NaOH solution used in blank determination,
- b* = millilitre of H_2SO_4 used in full determination,
- b*₁ = millilitre of H_2SO_4 used in blank determination,
- F*₁ = normality of the NaOH solution,
- F*₂ = normality of the H_2SO_4 solution, and
- W* = grams of coal taken.

15. Report

15.1 The results of the sulfur analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

15.2 Use the percentage of moisture in the sample passing a No. 60 (250- μm) sieve to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Specifications D 3176 and D 3180.

PRECISION

16. Eschka and Bomb-Washing Methods

16.1 *Repeatability*—Results of two consecutive determinations carried out on the same sample in the same laboratory by the same operator using the same apparatus should not differ more than the following:

	%
Coal containing less than 2 % sulfur	0.05
Coal containing 2 % sulfur or more	0.10
Coke	0.03

16.2 *Reproducibility*—The means of results of duplicate determinations carried out by different laboratories on representative samples