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AN EVALUATION OF THE FIRE AND EXPLOSION HAZARDS OF OIL SHALE MINING AND PROCESSING

Prepared for

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16. Abstract

Oil shales differ from coals in that they contain less carbonaceous material, convertible to volatile hydrocarbons, and more inorganic rock. In all pre-commercial oil shale development, involving extensive full scale mining operations, there have been no explosions. However, large scale mine tests with oil shale dusts by the Bureau of Mines showed that propagating explosions could be induced under certain circumstances.

Laboratory tests were conducted on a broad spectrum of oil shale dusts to define chemical properties and to seek correlations with subsequently determined fire and explosivity properties. These latter properties, indicative of safety hazards, increased as the Fischer assay oil yield of the dusts increased and as particle size decreased.

Laboratory data were used to relate fire and explosivity properties of oil shales to those of coals and other carbonaceous materials and to assist in the identification and evaluation of potential hazardous situations which may be encountered in oil shale mining and processing.

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FOREWORD AND ACKNOWLEDGMENTS

This report was prepared by the Oil Shale Division of Tosco Corporation, 10100 Santa Monica Blvd., Los Angeles, California, under U.S. Bureau of Mines Contract No. J0275001. The contract was initiated under the Metal and Nonmetal Health and Safety Research Program. It was administered under the technical direction of Pittsburgh Mining and Safety Research Center with Mr. J. Kenneth Richmond acting as the Technical Project Officer. Ms. Darlene Wilson was the contract administrator for the Bureau of Mines.

This report is a summary of the work recently completed as part of this contract during the period June 16, 1977 to September 15, 1978. This report was submitted by the authors on September 15, 1978.

Tosco Corporation, with Denver Research Institute and under the guidance of the Bureau of Mines in Bruceton, Pennsylvania, has completed an initial investigation into the fire and explosive properties of oil shale, oil shale llsts, and associated gases. The timeliness of this work is evidenced by the increase in activity in oil shale development in Colorado and Utah, and the recent (September, 1978) fire in the Occidental Oil Shale, Logan Wash test facility in Colorado. Exploitation of our nation's vast resources of oil shale for the near future will require familiarization now with the potential hazards associated with this virgin industry and how to deal with these hazards.

When a projected one million barrel per day oil shale industry becomes a reality, approximately 42,000 individuals will be directly employed in mine and plant operations, assuming a productivity of 30 barrels of upgraded shale oil per man-shift. These individuals will represent about 87 million man-hours of work exposure per year in this industry alone. Acting now to assess the potential safety hazards associated with fire and explosions in oil shale mining and processing is of major concern. This study constitutes a first assessment by an organization other than a Federal agency to determine the safety aspects of oil shale mining and processing.

The following principal investigators and consultants are gratefully acknowledged for their assistance and expertise provided during this study:

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EXECUTIVE SUMMARY

Previous Test Work and Observations

Over three million tons of oil shale have been mined in Colorado by room and pillar techniques over a period of 34 years without a single explosive event taking place. It must be noted however, that two unplanned fires occurred in 1978.

A review of extensive literature on fire and explosivity properties of carbonaceous dusts shows that the particle size and organize volatiles content of the dust are important factors. A bituminous coal or gilsonite product having a high content of volatile matter would be more explosive, assuming the same particle size distribution, than would a carbonaceous dust of low volatile content such as carbon black and anthracite coal. Oil shales, even those considered to be high in potential oil yield, rest on the relatively low end of the organic volatile matter scale.

Large scale, experimental mine tests by Richmond and Miller (1977) established that oil shale dust will propagate an explosion initiated by a localized methane-air detonation. The test results showed that the total volatile hydrocarbon concentration necessary to propagate an explosion is about 0.05 oz/ft^3, a value that is the same for oil shale as for bituminous coal. The major difference in explosivity between oil shale and coal dusts is due to the much larger mass of oil shale required to produce 0.05 oz/ft^3 of volatile hydrocarbons in a mine opening.

In the initial design of the research program, a need for basic data on the chemical and physical properties of oil shale dusts and their corresponding laboratory fire and explosivity properties was demonstrated. These data would not only permit assessment of potential hazards but provide a systematic framework for future safety monitoring and setting of regulations.

Scope of Study

This study program was designed to identify and evaluate potential fire and explosion hazards in oil shale mining and processing by laboratory scale tests and provide recommendations for mitigation and safety monitoring.

Procedures Employed

Initially, a series of scenarios was compiled describing hypothetical fire and explosion incidents which could occur in oil shale mining, crushing, retorting, hydrocarbon processing and disposal of waste products. These scenarios were based on extensive Tosco Corporation experience in mining and processing. Central themes were combustion of broken and solid oil shale in a mine, propagation of a methane explosion by raw shale dust, combustion of raw oil shale dust below a crusher, fire initiated by a hot exhaust manifold, spontaneous combustion of crushed raw oil shale, explosion in a hot gas recirculation retort and a gas combustion retort, and explosion of spent shale in a surface retort. Other scenarios addressed the potential problem of explosion of high heating value gases in an in situ retort and a methane explosion in an in situ retort.

Subsequently, a laboratory testing phase was started. Oil shales used in the tests were selected so as to represent a broad spectrum of oil shale richness (potential hydrocarbon pyrolysis yield) and particle size ranges.

Extensive analyses were conducted for kerogen and organic carbon contents and for yields of hydrocarbon volatiles. After thorough analyses, the oil shales and pyrolysis products were subjected to laboratory fire and explosivity tests. Testing for oil shales followed standard Bureau procedures used extensively on coal, agricultural dusts, carbon black, and organic chemicals, in order to rate the relative hazard potential of oil shales to known materials. The Colony oil shale mine was selected and extensively sampled to evaluate the grade and quantity of oil shale dust remaining after earlier full scale mining operations. Finally, the laboratory data obtained were used to evaluate the scenarios previously formulated.

Major Findings

It was found that fire and explosivity properties of oil shale increase with oil shale richness and decreasing particle size. However, the data showed that oil shale dusts as rich as 35 gallon per ton Fischer assay oil yield had a very low tendency to ignite or explode compared to most coal dusts. These results are a reflection of the relatively low amounts of hydrocarbon volatiles in oil shales.

Data from the dust loading study in the Colony mine showed that the total potential yield of volatile hydrocarbons, assuming there had been no degradation due to aging, was about one tenth the amount required to fuel a propagating explosion.

Aging of oil shale dusts over a period of several years reduces the content of volatile hydrocarbons and the corresponding fire and explosivity properties.

The data and information from the completed program indicate that the hazard of dust explosions is less severe than the hazard of fire in mine muck piles or of the mine structure. Another hazard in mining appears to be that of gases and vapors produced by heating oil shale from fires in, or adjacent to, mine openings.

1.0 INTRODUCTION

1.1 Authorization and Background

The work performed in this study was conducted under Bureau of Mines Contract No. J0275001, awarded to Tosco Corporation on May 24, 1977. Work was effectively started on June 16, 1976 by Denver Research Institute (DRI) and Tosco's Rocky Flats Research Center near Golden, Colorado.

Almost every country in the world has deposits of oil shale. These deposits vary in size, grade, and economic importance. At present, only Estonia in the U.S.S.R. has a commercial oil shale industry which utilizes underground mining. The Estonian oil shale grade averages greater than 50 gallons per ton (gpt) and is used mostly as boiler fuel for electric power generation. Germany and Scotland have operated underground oil shale mines in the past which, because of the availability of lower cost crude oil, are presently uneconomic.

An oil shale industry in the U.S. has been on the verge of development for over 20 years. Since the recent increases in crude oil prices, commercialization appears to be closer than ever before. As an example, major oil shale development projects are presently underway in the Piceance Creek basin on Federal tracts Ca and Cb. Although both projects propose to use modified in situ retorting, considerable oil shale will have to be mined and brought to the surface for retorting and/or disposal. Modified in situ

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development, probably more than any other method, will require a close evaluation of the safety aspects of fire and explosion.

The explosivity of oil shale dust was first investigated by the Bureau in 1926 (Allison and Bauer, 1926). These tests consisted of gallery tests in an experimental facility used also for coal dust explosion testing. The results of those tests indicated that oil shale dust could be made to explode and that some precautions might be required to prevent oil shale dust explosions. Studies at the Pittsburgh Technical Support Center of MESA since 1974 indicate that some oil shale dusts are potentially explosive if the grade, organic content, and concentration are high enough.

During contract negotiations prior to award between Tosco and the Bureau, several changes were made in the Scope of Work, as originally set forth in the Request for Proposal. These modifications included performing all tests as a function of particle size and organic content of the oil shales, restricting testing to Colorado oil shales, and reducing the tests on retort gases to include only those representative of direct and indirect heating in above ground retorts and off gases from modified in situ retorting. In addition, Tosco and DRI were specifically instructed to follow the Bureau's procedures and to use the equipment as outlined in RI 5624 (Dorsett et al 1960) without modifications. This was necessary in order to establish a correlation between the tests on oil shale required by this contract with data from the extensive tests on other materials made by the Bureau at Bruceton, Pennsylvania.

1.2   Scope of Work

The objective of this study was to determine, by analysis and experiments, the fire and explosion potential of oil shale and oil shale

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dusts and vapors as they affect mining, crushing, spent shale handling, and processing. The work was divided into three phases. Phase 1 required the compilation of scenarios describing potential fire and explosion accidents for all proposed methods of oil shale development, processing, crushing and disposal. These scenarios were presented orally to the Bureau for review and approval.

Phase 2 included laboratory testing, collecting oil shale samples, developing the data necessary to evaluate Phase 1 scenarios, and determining if, and what, hazards may actually exist. The testing phase consisted of determining limits of flammability, minimum ignition energies and temperatures, fire spread rates and spontaneous combustion potential in relation to Fischer assays, organic carbon contents, and particle size.

The final phase, Phase 3, consisted of completing the Phase 1 scenarios in terms of data developed during the Phase 2 studies. The final report includes suggestions and recommendations for mitigating fire and explosion hazards, recommendations for regulations, if any are required, and suggestions for procedures to be used by safety inspectors in monitoring compliance with regulations, if any are required.

The completion of all three phases included presenting oral reports to the Bureau in Bruceton, Pennsylvania. A technical modification to the contract included collecting and analyzing the dust loading of the Colony mine at Parachute Creek, Piceance Creek basin, Colorado.

1.3   Report Contents

The approach used in compiling and preparing this study has been to divide the report into six sections consisting of an introduction, results and conclusions of phases 1, 2, and 3, conclusions of the study, and finally, the recommendations for future research programs. Sections 2.0 and 3.0 have

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been written so as to stand by themselves. Each section contains the conclusions for that portion of the study. Section 5.0 presents the overall conclusions resulting from collecting and analyzing data, and experience gained during the course of the study. The final section on recommendations outlines proposed research programs needed to answer questions or supply new data on the fire and explosivity properties of oil shale.

Three appendices are included that contain basic data referred to in the body of the report. Several papers written during the study concerning various phases of testing or equipment analysis, are also included. Laboratory Data Letters (LDL) by Tosco, completed before or during this study and referenced in the report text, are included in Appendix B.

2.0 PHASE 1 STUDIES

2.1 Purpose and Scope

The objective of Phase 1 was to identify potential fire and explosion hazards in oil shale mining and processing by creating a minimum of six representative scenarios of fire and explosion accidents. An extensive background in oil shale mining and retorting technology, along with detailed literature reviews, was used in creating these scenarios. All existing and planned mining, crushing, handling, and processing methods were considered in scenario development and hazard evaluation. Questions and hazards postulated by each scenario were then used to determine the course of laboratory testing in Phase 2. The purpose of the testing program was to develop and quantify data needed to evaluate the postulated hazards.

2.2 Review of Literature

A large body of literature, both technical and practical, exists on fire and explosion of carbonaceous dusts, chemical properties of oil shale and oil shale dusts, and mining and processing of oil shales. The ignition and explosion of dust is a complex phenomenon involving space-time variations in ignition energy, dust density, the physical and chemical properties of the dust, ambient conditions, and the nature of confinement (mine or laboratory model). Obviously, considering these numerous variations, it is a difficult

task to design a test apparatus and procedure that represents the actual full scale situation.

Fire tests have been carried out for years using techniques such as corner tests, pan fires, surface flammability, etc.; however, these techniques are not readily adaptable to oil shale rubble. In addition, past research on spontaneous combustion is not developed to the point of predicting auto-oxidation potential. Retort gas flammability is another area in which little research has been done. Retort gases are complex mixtures of hydrocarbons, hydrogen, hydrogen sulfide, and ammonia. Simple calculations (LeChatlier) can indicate a lower explosive limit, but how these compare to reality is debatable.

2.2.1 Fire and Explosivity of Carbonaceous Dusts

Using apparatus and procedures of Dorsett et al (1960), Jacobson et al (1961) studied the explosive hazards of agricultural dusts. Explosivity data were presented on 45 agricultural products. The authors suggest a number of ways to reduce dust explosion hazards, including good housekeeping, prevention of dust dissemination, elimination of ignition sources, use of an inert atmosphere or explosion-suppression devices, and venting.

Using similar procedures, Dorsett and Nagy (1968) investigated the explosivity of 73 chemical compounds and mixtures, 29 drugs, 27 dyes and 46 pesticides. The authors determined that the explosivity index increases as the dust particle size decreases. In addition, they found that organic compounds containing nitrogen tend to have high explosivity indexes and, further, that halogen substitution in organic molecules tends to reduce explosivity.

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The explosivity of a variety of carbonaceous dusts was investigated by Nagy et al (1965). Dust explosion data were obtained using the RI 5624 apparatus and procedures, Dorsett et al (1960). Materials studied included activated carbon, asphalt, charcoal, carbon black, coal, coke, gilsonite, graphite, lignite, pitch, tunnel dust and miscellaneous carbons. Their major conclusion was that the explosion hazard tends to increase as the volatile content of the dust increases.

In a review of investigations of coal mine explosions done in previous years at the Bruceton experimental mine, Hartmann (1957) reports a number of conclusions: (1) coal dust can produce widespread explosions in the absence of methane; (2) coarse coal dust, as coarse as 20 mesh, may take part in mine explosions, but the fine particles control the ease of ignition, the violence and the speed of flame propagation; (3) the combustible volatile content of coal has an important effect on the explosivity of coal dust; (4) any increase in the incombustible constituents of coal is accompanied by reduction in explosivity of the coal dust; (5) the presence of natural gas in the air current, even at concentrations below the lower explosive limit of methane, about 5%, enhances the ease of ignition of coal dust and makes it more difficult to arrest an explosion; (6) the minimum explosive concentration of fine bituminous coal dust in air was determined to be on the order of 0.05 ounces per cubic foot.

Hartmann further reported that coal dust deposited on rib and roof surfaces or on overhead timbers is generally a finer size, is more readily dispersable and ignitable, and constitutes a greater explosion hazard than coal dust on the floor. Further, explosions initiated by strong sources, that is, high energy sources, develop faster, do more damage, and are more difficult to arrest than explosions initiated by weak sources.

Other Bureau authors (Nagy et al, 1964) discuss properties of float coal dust, i.e., dust having a particle size of 74 microns (200 mesh) and less. These dusts are transportable in ventilating air currents, and similar dusts would be present in active oil shale mines. Full scale tests at the Bruceton experimental coal mine showed: (1) the intensity of an explosion, i.e., the product of pressure and flame velocity at the flame front, increased as the particle size of the coal dust decreased; and (2) the percentage of incombustible required to arrest explosion propagation increased with the quantity of float coal dust.

The effect of added rock dust on the explosivity of coal dust was reviewed in detail by Richmond et al (1975). Based on full scale mine explosion tests, Richmond and his co-workers demonstrated that increasing rock dust decreased flame speed, decreased flame pressure gradient, decreased length of flame travel and, above a certain level, converted an explosive propagation situation to non-propagating. Rock dust acts both as an inert ingredient and, in chemical decomposition, as an energy sink reducing the energy of an explosion.

Spontaneous combustion and its detection are discussed by Hertzberg (1978). The Bureau's approach is to directly measure spontaneous combustion by determining the rate of self-heating in an adiabatic calorimeter. Calorimeter data show that the various methods of evaluating relative reactivities correlate reasonably well with one another. The rate of temperature rise in the adiabatic calorimeter correlates well with the rate of production of carbon monoxide and carbon dioxide.

2.2.2   Chemical Properties of Oil Shale

Oil shale has been defined as "a wide variety of laminated, solidified mixtures of argillaceous (containing clay) sediments and organic matter having the common property of yielding oil upon destructive distillation, yet being but slightly susceptible to the action of solvents" (Guthrie, 1938).

Oil shales of the Green River Formation of Wyoming, Utah, and Colorado are lacustrine, sedimentary deposits of Eocene Epoch. These oil shales are a mixture of kerogen, a high molecular weight organic polymer, and an inorganic matrix consisting mostly of calcite and dolomite. A typical analysis of the minerals in oil shale is given as follows (Smith, 1969):

Component	Weight Percent
Dolomite	32
Calcite	16
Quartz	15
Illite	19
Albite	10
Microcline	6
Pyrite	1
Analcite	1

The calcite and dolomite provide a chemically basic environment for the kerogen and absorb heat if they are decomposed to the calcium and magnesium oxide components.

A typical analysis of the kerogen component is as follows (Smith, 1961):

Component	Weight Percent Organic Component
Carbon	80.52
Hydrogen	10.30
Nitrogen	2.39
Sulfur	1.04
Oxygen	5.75

The hydrogen to carbon ratio in kerogen is generally higher than ratios found in coal, but lower than ratios found in petroleum hydrocarbons. The

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nitrogen content of kerogen is responsible for the high nitrogen content of the produced shale oil.

The only feasible methods of converting the organic material in oil shale to useful hydrocarbons are gasification and thermal pyrolysis. Primary interest is in liquid hydrocarbons and thermal pyrolysis. Since in both oil shale and coal, thermal pyrolysis involves breaking carbon-carbon chemical bonds, the temperature requirements are quite similar. Retorting begins at about 800°F and proceeds vigorously in the range 900 to 1000°F. With oil shale averaging 33 gpt, the final product mixture contains about 82.4% spent shale (containing 5% organic carbon), 12.6 wt% condensed oil, 3.5 wt% gas having a heating value of around 700 Btu/scf and 1.2 wt% water. The large yield of processed shale, even with rich oil shales, represents a significant limitation on commercial processing. However, the relatively high hydrogen to carbon ratio of Green River oil shale kerogens permits high yields of vaporized hydrocarbon in comparison to coals.

As will be seen in the following sections, the presence of calcite and dolomite in oil shale, acting in similar fashion to rock dust used in coal mines, renders oil shale somewhat safer from a fire and explosivity standpoint. This is due to action as an inert ingredient and as a substance which absorbs heat on treatment at high temperature. In addition, the organic volatiles content of oil shales is low in comparison to most coals and other hydrocarbon materials.

2.2.3 Chemical Properties of Oil Shale Dust

Oil shales produced from secondary or tertiary crushers have particle sizes ranging from 3 to 4-inch size to fine powder. Raw shale feed for the TOSCO II retort has a size range of 0.5-inch to fine dust. It has been

repeatedly demonstrated that there is a relationship between the Fischer assay of a dust, taken from a common mass of crushed raw shale, and particle size. For example, Goodfellow (LDL, 1969) conducted screen analyses of feed raw shale to the TOSCO II retort and ran Fischer assays on representative samples of each of the screen size fractions. As a typical case, it was found that whole crushed oil shale with a top size of 0.5-inch and a head assay of 31.3 gpt, produced the following:

Screen Size (US Mesh)	Gpt
+20	32.1
-20 +40	25.2
-40 +80	24.6
-80	18.2

Richmond and Miller (1977) conducted screen analyses of mine and grind-house area dust taken at the Anvil Points mine. Screened fractions assayed ranged in size from +500 to -44 micrometers, and corresponding Fischer assay data showed a gradual decrease as the screen size decreased. In addition, Richmond showed that grinding an oil shale sample of 3/4" x 0" size to a nominal -200 mesh (-75 microns) did not decrease the Fischer assay.

Except for the concentration of inerts in the fine fractions and the surface oxidation of these high surface area materials, discussed in Section 2.2.4, oil shale fines have chemical properties which are very similar to larger sized oil shale particles.

2.2.4   Effect of Aging on Chemical Properties of Oil Shale

Crushed oil shale, one inch or larger in size, appears to be stable in long term storage at ambient atmospheric conditions. The surface of shale particles becomes oxidized, with the oxidized layer tending to protect the

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underlying oil shale matrix. However, in the case of oil shale dust, the resistance to oxidation is less, due to the high surface area to volume ratio.

Oil shale dusts, once formed in a mine or at a crusher site, will tend to oxidize slowly on standing thus affecting the fire and explosivity properties. Thorne et al (1951) reports that, in general, oil yields of preheated shales (200-300°C) decreased as the preheating periods and oxygen contents of the preheating gases were increased, and as the particle size of the samples was decreased.

Tests were conducted on artificial aging by Coomes and Sommer (1977). Oil shale samples ground to -65 mesh were spread in thin layers on aluminum trays and placed in an oven in contact with air for varying periods of time. Heating in this manner at 120°C for five days resulted in a decrease of Fischer assay oil yield to 77% of its original value. A corresponding reduction in the organic carbon content of the raw shale was significant but proportionately much less. The net result of aging under these circumstances is to decrease the Fischer assay oil yield, but in a manner disproportionate to the loss of organic carbon.

In tests carried out at a lower temperature (70°C), again in contact with air, the same -65 mesh oil shale suffered an oil yield loss to 84% of its original value in three months.

2.2.5   Fire and Explosive Properties of Oil Shale Dust

The earliest work on testing fire and explosivity properties of oil shale dust was conducted by the Bureau at Bruceton in 1926 (Allison and Bauer, 1926). The authors tested oil shale dust in a laboratory steel dust gallery made up of a steel pipe of 8 inches inside diameter and 17 feet long. A cloud of the test dust was raised in the pipe by means of compressed air and

a loose powder flame was fired into the dust cloud. Explosivity was determined by the flame length. Although information in the publication is not clear, the authors maintain that oil shale test samples, averaging in richness down to 8 gpt, were explosive. This conclusion is based on the fact that the test flame length exceeded the flame length of combustion of the igniting powder alone. Other information in the report does not support this conclusion. The authors state, however, that the oil shale dusts tested were explosive, and that their explosiveness increased with their combustible content.

Kawenski (1974) of the Bureau at Bruceton tested two samples of oil shale dust from the Colony Parachute Creek mine. One was an old mine dust sample taken from a mine pillar and the second an oil shale crusher dust. The former assayed 23 gpt and the latter 33 gpt. Using the equipment and procedures of RI 5624, minimum ignition temperatures of dust clouds obtained were 540 and 530°C, respectively. No ignition was observed in tests in the Hartmann lucite apparatus. However, in the steel Hartmann, the 33 gpt shale ignited at a dust concentration of 0.5 oz/ft^3 and above. The 27 gpt shale, old Colony mine dust, did not ignite in the steel Hartman apparatus at concentrations as high as 2 oz/ft^3.

Laboratory tests, utilizing the apparatus and procedures of RI 5624, were conducted on a series of oil shale samples varying in richness from 6.3 to 64.8 gpt and ground to -200 mesh (Kawenski and Jacobsen, 1974-1975). Utilizing the Godbert-Greenwald furnace, minimum ignition temperatures of dust clouds ranged from a high of 710°C for the 6.3 gpt sample to a low of 470°C for the 64.8 gpt sample. Experiments in the lucite Hartmann apparatus resulted in no ignition for samples having up to 30.9 gpt assay. Richer samples ignited with an average minimum concentration of 0.28 oz/ft^3

for the 33.6 gpt sample and 0.1 oz/ft^3 for the 64.8 gpt sample. Utilizing the pressure steel Hartmann apparatus, ignition was effected with 33.6 gpt and richer samples. In the richer samples, the minimum concentration of dust which underwent ignition decreased as the richness of the oil shale dust increased. Due to the fact that even the lean oil shales ignited and burned vigorously over a Bunsen burner, and that all samples ignited when heated by a hot surface, Bureau personnel drew the conclusion that all samples would present a dust explosion hazard. Data on tests in the Godbert-Greenwald furnace, which indicate that both dust clouds and dust layers of all tests were readily ignited, further supports the conclusion.

More definitive work has been done by Richmond and Miller (1977) of the Bureau at Bruceton. These investigators worked with oil shale samples from the Anvil Points mine, which were crushed and finally ground to a nominal -200 mesh size consist. These prepared dust samples were blended to make five large samples varying in average Fischer assay from 19 to 50 gpt. The dusts were tested by spreading in the experimental mine at Bruceton, followed by attempted explosions initiated by a mixture of natural gas and air. Results obtained were described as "propagating", "marginal", and "non-propagating".

A total of 17 tests were run in the Bruceton mine. The authors concluded that at least 0.05 ounces of volatiles per cubic foot of mine space were required for a propagating explosion. The volatiles were assumed to be equivalent to the sum of Fischer assay oil plus gas yields. In tests with addition of rock dust it was determined that rock dust is somewhat more effective in inhibiting explosions than is the inorganic matter in oil shale. This was believed to be due to the fact that the inorganic in oil shale is only about one half mineral carbonates, while rock dust is almost

entirely calcium carbonate. They also concluded that oil shale dust will propagate explosions at much greater incombustible content than in the case of coal dust/rock dust mixtures. Tentative explanations offered for this finding are that kerogen pyrolyzes at a lower temperature than coal and/or the kerogen pyrolysis products contain more hydrogen than coal.

The minimum concentration of volatiles, i.e., Fischer assay volatile combustibles, required for explosion is virtually independent of the amount of incombustibles in the oil shale dust over the range tested. The critical concentration of volatiles, 0.05 ounces per cubic foot, is about the lean explosive limit for most hydrocarbons and the same lean explosive limit as observed in the case of Pittsburgh coal for explosive propagation. The lean explosive limit of 0.05 ounces of volatiles per cubic foot of mine space is not claimed by the authors to be the final word on such matters, but represents a convenient and reasonable level and will be utilized extensively in Section 3.2.4 in evaluation of the data.

The authors also determined that a dust layer density of 0.2 pounds of 30 gpt oil shale per square foot would be required to form an explosive mixture on all six surfaces of a room 50 x 60 x 70 feet. This amounts to a layer of dust 0.038-inch thick which, as will be discussed in other sections, is much greater than has been found an existing oil shale mine.

Finally, the authors conducted some spontaneous ignition tests on oil shale dust and found that 46 gpt oil shale dust will ignite at a dust temperature of 130°C. A shale dust of 25 gpt richness required a dust temperature of 180°C for ignition.

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2.2.6 Problems Relating to Methane in Association with Oil Shales

There are two major problems relating to the presence of methane in coal mines. Methane layering may lead to explosive mixtures of methane in air, and the presence of methane in dust clouds may lead to a lowering of the minimum explosive dust concentration and ignition energy of the dust cloud. One of the purposes of this study was to determine if a synergism existed in methane/oil shale dust cloud emission and explosion tests. Results are discussed in Section 3.0. Another major concern was the presence of methane in oil shale mines. Kissell (1975) states that the experimental oil shale mine at Anvil Points was operated for many years without methane ever being detected in the ventilation air. However, Kissell, in separate tests, measured methane evolved from oil shale cores. With limited data, he has concluded that the amount of methane released by oil shale core is somewhat dependent on the distance from outcrop and the amount of overburden. In any case, the amounts of methane released are much lower than normally experienced with cores from coal mines.

More extensive work was published by Matta et al (1977) and indicated that oil shale samples would absorb methane under pressure. The amount absorbed and subsequently released was proportional to the pressure and, more interestingly, proportional to the richness or kerogen content. Additional tests with fresh oil shale cores confirmed that methane release increases with distance away from the outcrop and depth. It was also found that, with identical overburden and distance from the outcrop, methane release increased with oil shale richness. In all cases, methane evolution from oil shales was lower than that observed in coal cores by one order of magnitude.

A tentative conclusion may be reached that any methane problems in near surface oil shale mines will likely be due to leakage into the mine from adjacent gas pockets, and not to methane absorbed in oil shales.

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2.3   Summary of Oil Shale Mining Experience

This status report of oil shale mining experience and technology in the United States includes a brief description of the most prominent activities currently in progress. A first commercial oil shale project will have an unprecedented advantage over most mining operations started in new mining environments because of the numerous, prototype mining operations that have been successfully conducted in Colorado.

2.3.1   Anvil Points, Colorado, 1945-1956

The first large scale experiment in oil shale mining was authorized by Congress in 1944. The major objectives of mining were to feed a retort and develop and test mining methods and equipment that would produce large quantities of oil shale safely and at minimum cost.

The results of the Bureau's program (East and Gardner, 1964) provide a clear understanding of what was accomplished, how it was done, and set forth sensible goals for the oil shale venturers that followed. Rooms 60 feet wide were mined, pillars were 60 feet square. Mining was conducted before the advent of ammonium nitrate underground, so conventional powder was used. Drill hole size, depth, pattern and drill round dimensions suitable for the reach and capacity of equipment then available were optimized. Rock bolts were used and adapted for oil shale. Platforms for high scaling and roof control were developed and the first guidelines for using rotary drills in oil shale were established.

Anvil Points, run by the U.S. Bureau of Mines, replaced many uncertainties and mysteries about oil shale mining with facts. They also established an understanding of the behavior of oil shale around an opening, demonstrating that 80 feet was too wide for rooms at depths from 600 to 800

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feet, confirmed that room and pillar mining was a sensible method, and most importantly, established that oil shale could be mined safely with large equipment operating in large underground openings at low cost.

2.3.2   Union Oil Company, 1955-1958.

The Union mine is located in the lower east fork of Parachute Creek. With Utah Construction Company, the predecessor of Utah International, as their mining contractor, Union established an underground experimental mine for the purpose of feeding the Union retort, to determine the conditions underground, and to test mining methods and equipment. Underground mining consisted of a single adit 28 feet high by 30 feet wide extending 400 feet to a "Y" intersection from which two additional 110 foot drifts were driven. Over 70,000 tons of oil shale were mined during their experimental underground mining program.

Union experimented briefly with rotary drilling, achieving penetration rates as high as 13 feet per minute. Blasting studies proved for the first time that ammonium nitrate-fuel oil (ANFO) was safe and effective in the mining of oil shale. It was also noted that oil shale characteristically tends to break with some large pieces not consistent with the drill hole size and spacing.

In several instances, the Union work was an extension of the program left unfinished at Anvil Points. In particular, Union made a useful contribution to the advancement of drilling and blasting technology for oil shale mining and reaffirmed that oil shale could be safely mined from underground at high rates and low cost.

2.3.3   Mobil Oil Company, 1964-1968

Mobil Oil Company re-entered the Anvil Points demonstration mine in 1965, mining a small quantity of oil shale for retort feed. A new room and pillar experimental mine was opened nearby in late 1966 for the purpose of testing techniques and equipment for large scale mining. The target for this study was an oil shale bed 78 feet thick that included the richest part of the Mahogany Ledge.

The major objectives of the mining program were to collect geo-technical data useful to a rock mechanics research program, optimize drilling and blasting procedures and results, develop industrial engineering, data with economics, and test and evaluate equipment. These and other objectives provided information for a commercial mine design and cost estimate (Sellers, Haworth, and Zambas, 1972).

In the 13 months prior to April 1968, Mobil mined 500,000 tons at an average production rate of nearly 2,000 tons per working day. Although data collection and not production was the principal objective, mining rates to 4,000 tons per day were reached in order to test and optimize equipment and performance data. Using a basic room and pillar design, the experimental mine layout consisted of four parallel headings, 60 feet wide and 78 feet high, separated by rib-pillars 40 feet thick. Upper level headings 40 x 60 feet and a 38 x 60-foot bench on a lower level were used. The lower level system resembled quarrying.

Each heading round produced about 4,000 tons of broken oil shale. After completing the rooms, (headings or lanes), the rib-pillars were crosscut full height with a single blast, 78 x 40 x 40 feet, that produced about 9,000 tons.

Ventilation, hauling, and scaling together with other studies, established for Mobil that mining oil shale using large openings and a

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modified room and pillar method is technologically feasible and safe. These experiments also demonstrated that perhaps 80% of the oil shale could be recovered in overburden less than 600 feet thick.

2.3.4   Colony Development Operation, 1964-Present

The prototype mining program by Colony had the same general objectives as the test mine at Anvil Points and the Union Oil mine. However, it was intended to proceed directly from prototype mining into a 66,000 ton per day commercial mine (Crookston, 1975). To date Colony has mined more than 1,200,000 tons of oil shale to feed their semi-works retort operations and optimize mine design, economics, and equipment selection.

Initial plans are to use room and pillar mining with headings and benches in the richest 60-foot section of the Mahogany zone. The commercial mine will use rotary drills for both heading and bench, blasting with ANFO, non-electric primers, and rock bolts for roof control. Large mechanical scalers will remove loose rock from the face and ribs (the roof pulls to a clean parting), and loaders and trucks will move the oil shale to a primary crusher. Approximately 6,000,000 cubic feet per minute of air are required to provide fresh air to the mine and to dilute and remove fumes from blasting and diesel powered equipment.

2.3.5   Paraho, 1964-Present

With assistance from Cleveland Cliffs Iron Company, Western Division, Paraho is operating the old Anvil Points mine to supply feed for their retort operations. They have mined more than 300,000 tons of shale by the conventional room and pillar method, in mine openings that are a nominal 40 feet high by 55 feet wide (Pforzheimer, 1977). Although their objective is

production not research, they have demonstrated by their extensive operations
that large equipment can mine oil shale from large openings in a room and
pillar mine, safely and at minimum cost.

2.3.6   Occidental Oil Shale Company, 1973-Present

Mining will be the key to success of the modified in situ development
program on Mount Logan, near DeBeque, Colorado. Multiple levels of access to
large rubble-filled in situ retorts is a major mining undertaking. Mining of
these adits, drifts, crosscuts and raises, and the horizontal and/or vertical
slots inside the retorts, is done essentially by conventional mining.
However, the perfecting of a drill-blast technique that will rubblize oil
shale uniformly enough for satisfactory retorting operation and efficiency is
a difficult and ongoing project (Ridley, 1975).

Occidental and Ashland Oil Company are partners in developing Federal oil
shale tract C-b where large scale confirmation tests of rubblizing and
retorting techniques developed at Logan Wash are planned. Construction of
shafts and other facilities, in preparation for the advanced testing program,
will probably be completed in the mid 1980's.

2.3.7   Rio Blanco Oil Shale Company, 1973-Present

As with the Occidental modified in situ process, mining plays an
important role in the successful retorting with the RISE process for modified
in situ (Rio Blanco Project, 1978). Both commercial processes require
development of access by shafts, drifts, raises, and/or inclines to
facilitate rubblizing the retorts. The most significant difference in mining
is inside the retort. Whereas, Occidental excavates rock from the retort to

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provide swell room for rubblizing, Rio Blanco removes rubble by conventional sublevel mining methods to provide room for swell.

Rio Blanco is now sinking a shaft for their modular development phase program. They will burn several retorts to gain experience with their previously untested process, and to confirm the feasibility of their plans. The commercial phase is expected to commence by about 1987.

2.4 Summary of Oil Shale Processing

Oil shale processing has been under development in the United States for approximately 50 years without reaching true commercialization. Full scale commercial industries have existed in certain foreign countries. The fundamental steps in oil shale processing are mining and heating. These steps may be carried out underground, as in the modified in situ concept, or above ground in a variety of well developed processes.

The thermal or heat processing of mined oil shale involves steps of:

- Preheating.

- Retorting.

- Combustion to produce process heat.

- Processed shale cooling.

- Hydrocarbon recovery.

Generally, preheating of oil shale is conducted by contact with hot gases. This step reduces the heating requirements in the actual retorting step, which takes place at approximately 900°F. Retorting is effected by either direct heating, utilizing process heat from burning spent shale or part of the product mix, or by indirect heating, utilizing hot gases or hot solids.

2.4.1 Direct Fired Processing

The first major direct fired retort process of interest was the Nevada-Texas-Utah retort (NTU) investigated extensively by the Bureau at Anvil Points in the late 1940's. This concept involved burning a column of broken shale rock, from the top to the bottom, in a vessel using a downward flow of air and product gas for preheating, retorting and combustion. Product oil was removed from the cooled bottom of the retort and pumped to storage.

The modified in situ process involves the same concept operating underground. Sufficient oil shale is mined to provide void space in a rubble filled chimney created by explosive fracturing. Retorting is from top to bottom with the product oil recovered from a sump at the bottom of the rubble filled chimney.

Other examples of the direct fired concept are the Paraho direct retort, operated by the Paraho Group at Anvil Points, and the Union A retort, tested extensively by Union Oil Company at a site northwest of Rifle. The Paraho direct process utilizes combustion of a downwardly moving column of oil shale with the product hydrocarbon taken from the top of the retort. The Union A retort utilizes combustion of an upwardly moving column of oil shale with bottom removal of hydrocarbon products.

2.4.2 Indirect Fired Processes

Indirect fired processes can be segregated into those using hot gas and those using hot solids as the heat carrier. One process, utilizing hot gas, is the Paraho indirect concept, in which downward moving shale is heated to pyrolysis temperature by an upflow of externally heated product pyrolysis gas. The Union B concept is the reverse; an upward moving column of oil

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shale is heated to pyrolysis temperature by a downflowing stream of externally heated pyrolysis gas.

Processes involving the use of externally heated solids to provide process heat for oil shale pyrolysis are the TOSCO II and Lurgi. In the TOSCO II concept, oil shale moving through a horizontal rotating kiln is heated to pyrolysis temperature by ceramic pellets which have been fired by combustion of gas or oil in a separate heating vessel. The Lurgi concept involves similar heating, in a horizontal rotary kiln, of oil shale with hot shale ash obtained by burning the carbon on the spent shale obtained directly from the retort.

2.4.3   General Comments

Mining and feed preparation involves handling vast amounts of dry, dusty, carbonaceous solids. Safety considerations dictate an awareness and knowledge of conditions leading to spontaneous combustion, burning, ignition, and explosion. In preheating and retorting, a high temperature regime, 500 to 1400°F is required, in which carbonaceous solids and hydrocarbon vapors must be processed, separated, and recovered. Problems of handling hot, dusty carbonaceous solids are compounded by the presence of high temperature hydrocarbon streams. Fortunately, high temperature hydrocarbons are routinely and safely handled in refineries and petrochemical plants and by themselves, would not represent unfamiliar safety problems.

2.5   Identification of Hazards

The scenarios that were developed during Phase 1 helped provide a checklist of potential safety hazards. This checklist made it possible to identify the materials to be tested, and in part, the nature and extent of

the tests and experiments that were, and/or are necessary to establish, where scale is important, the hazards of full scale operations.

By this process, it became readily apparent that the fire and combustion hazards that are unique to oil shale are few in number when compared to the co-existent hazards that are associated with mining and processing oil shale. The associated hazards for the most part have been previously identified, and where necessary, their hazard measured and regulated. Therefore, for the purpose of this project, those hazards are of incidental, and not primary interest. A checklist of potential hazards is outlined below:

- **Oil Shale Derived Hazards**
  Raw shale in place
  Raw shale broken by blasting
  Crushed raw shales
  Raw shale dust
  Spent shale
  Spent shale dust
  Raw and processed shale oil
  Retort vapors, gases, and mists

- **Associated Hazards**
  Machinery and equipment
  Maintenance supplies, tires, belting, etc.
  Conveying equipment
  Methane
  Ammonium nitrate-fuel oil (ANFO)
  Dynamite and other explosives
  Explosive detonators and primacord
  Fuel, oil and grease
  Timber and frame structures
  Hydraulic fluid
  Trash and waste
  Oxygen and acetylene
  Butane, propane and natural gas space heaters
  Ventilation equipment, fans, doors, conduit, etc.
  Mine electricals
  Static electricity
  Natural phenomenon
  Welding and cutting
  Ground water

2.6   Scenarios

The preparation of scenarios was an important requirement of Phase 1. The definition of scenario, in terms of the preparation and application of the scenarios for this study, should be as expressed as follows: a scenario is not a prediction of what is likely, rather it is a statement of what is possible.

Concurrent with the identification of hazards (Section 2.5), thirteen scenarios were prepared. The derivation of the potential hazards was facilitated by these scenarios. In addition to the scenarios developed during Phase 1, three scenarios postulating the hazards of modified in situ mining and processing, were prepared. In order to achieve better balance among mining, crushing, materials handling and processing, three of the final scenarios are in mining, one in crushing, one in ore storage, three in surface retorting and three in in situ retorting.

2.6.1   Combustion of Broken and Solid Oil Shale in a Mine

During the last shift of a 20-shift work week, a front-end loader in a 30 by 50-foot heading has a hydraulic hose support bracket and coupling broken by a falling rock. The mishap occurs as it loads shale from the part of 2000-ton muck pile nearest a rib. The operator backs the machine 50 feet away from the muckpile, shuts it down, and sends the truck to another heading. During the process of backing up, flammable hydraulic fluid is sprayed on the rib and floor.

The hydraulic hose coupling is replaced and the bracket repaired by welding; by the end of the shift the machine is moved out of the heading. The portable ventilation fan directed into the heading is left on.

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During the twenty-first, or repair shift, smoke and fumes are detected by maintenance personnel. Before the source of the combustion is located and the fire extinguished, a substantial part of the muckpile and a portion of the rib that was sprayed with hydraulic fluid have been burned. The fire was started by sparks and slag from cutting and welding which ignited dust and shale rubble on the floor that had been sprayed with oil. Fire then spread along the floor to the oil soaked rib and to the muckpile. The fire also spread across some parts of the floor not sprayed with oil. Heat and flames from the fire in the muckpile spread also to the face and ribs adjacent to the muckpile. Fire and heat caused spalling of the roof and ribs which added to the fire and increased the depth of penetration of combustion into the roof and ribs.

This scenario raises the following questions:

- Combustibility of mine rubble.

- Propagation of combustion in ribs, and roof.

- Rate and intensity of combustion.

- Effect of intense heat on ribs, roof, and pillars, including spalling from thermal expansion, which could expose fresh surfaces, and the influence of joint and fracture density on the foregoing.

- Effect of oil shale grade on the ignition and propagation of combustion.

- Effect of the particle size distribution of the rubble.

- Relationship of Fischer Assay and Tosco Material Balance Assay to total volatile content and total combustible content.

2.6.2   Propagation of a Methane Explosion by Raw Shale Dust

A routine blast in a mine development heading at the end of the shift, ruptures a pocket of methane that had not been penetrated by drilling. The

ventilation fans are left on long enough to remove the smoke and fumes from blasting. The majority of the raw shale dust particles from the blast, settle on the muckpile, adding to the concentration of dust already deposited on the roof, ribs, and floor by previous blasting.

During the next shift, a ventilation work crew extends the ventilation pipe and moves the portable face fan forward in the heading. The main exhaust fan is turned off while the ventilation pipe is extended. At the same time, the portable fan is turned off and moved forward in the heading. During the interruption of air flow, the methane concentration at the new fan location reaches an explosive level. When the fan is turned on, an electric spark ignites the methane, resulting in an explosion, which is expanded and intensified by the raw shale dust in the heading. Loss of life and heavy damage extend well beyond the point where the explosion is propagated by the raw shale dust.

This scenario raises the following questions:

- Explosivity of raw shale dust.

- Concentration and grade of airborne raw shale dust necessary for detonation.

- Dust loading in and around openings in relation to the volume of the adjacent opening that is necessary to propagate an explosion.

- Ignition energy.

- Effect of particle size distribution (fineness) on explosivity.

- Intensity of a methane/oil shale dust explosion.

2.6.3 Combustion and/or Explosion of Raw Oil Shale Dust Below a Crusher

Probably the greatest concentration of airborne and settled dust in a crushing operation occurs in hoppers below crushers and screens.

A crusher hopper is empty. The hopper discharge conveyor is partly covered with raw shale. Typically, the hopper has several "shelves" piled with dust. A repairman enters through a side hatch to repair the hopper. While climbing into the hopper and dragging a cutting torch to the repair site, he knocks enough dust from shelves to cover the conveyor belt, which is also the hopper bottom, with a layer of dust. Before the heavy concentration of airborne dust subsides, he lights the cutting torch. One, or both, or neither of the following occurs: 1) the flame causes a dust explosion, 2) sparks and slag from cutting fall onto shelf dust and also the dust covered conveyor belt, causing a fire.

This scenario raises the following questions:

- Explosivity of airborne dust in a methane-free atmosphere.

- Rate and intensity of the explosion.

- Combustibility of dust by spark, slag or fire.

- Rate and intensity of combustion.

- Effect of grade and particle size distribution on explosivity, or combustibility of crusher dust.

2.6.4 Fire and/or Explosion from a Hot Exhaust Manifold

After a multiple-heading blast failed to detonate; two blasters drove to the vicinity of the charged headings to locate and eliminate the trouble. They separated, each to check several headings. When the first man was finished, he walked out, checking the main blasting line on the way. The second man soon followed. When they reached the blasting station, they realized their vehicle had been left in the mine. Knowing a large pillar would protect it from damage, they proceeded to detonate the explosive charges.

The engine in the vehicle had been left running. A poorly maintained exhaust manifold cooling system soon caused the exhaust manifold temperature to exceed the auto-ignition temperature of the layered shale dust on the exhaust manifold. The mine blast occurred just as the fire reached its maximum intensity. The burning shale caused the heavy concentration of airborne dust to explode. The explosion propagated by "shelf dust" extended well beyond the settling limits of the airborne dust from the blasts.

This scenario raises the following questions:

- Auto ignition temperature of raw shale dust.

- Explosivity of raw shale dust.

- Concentration and grade of airborne dust necessary for detonation and propagation of an explosion.

2.6.5   Spontaneous Combustion of Raw Oil Shale

At a commercial oil shale complex, a large stockpile of minus 10-inch crushed raw shale is required to ensure efficient and continuous mining operations and also accommodate the retort. About 40 percent of the coarse ore stockpile is live. The rest of the pile is drawn from infrequently and then only for short periods of time.

The secondary crushing plant includes 350 ton storage bins, each feeding one of several crushers. When a crusher is down, the storage bin may be unused for several weeks.

Spontaneous combustion begins in the "dead" part of the coarse ore stockpile, and continues without detection until several thousand tons are involved. The fire is controlled and eliminated by mixing the hot shale with cold shale as it is pushed into the reclaim feeders. This mix is cool enough to transport on the conveyor belt that feeds the secondary crusher bins. One

nearly empty, inactive bin is filled with the warm shale. The warm shale eventually re-ignites, the combustion is not detected until the heat, fumes and vapors are very evident.

This scenario raises the following questions:

- The potential for spontaneous combustion of raw oil shale.

- Effect on spontaneous combustion of grade, size distribution, chemical composition, moisture and weather.

- Safe temperature of cooled shale that will eliminate the possibility of re-ignition.

2.6.6   Fire and Explosion in a Hot Gas Recirculation Retort

A recycle gas compressor provides the pressure to circulate gas through the recycle gas heater, retort, and gas/oil separator in a hot gas recirculation retort. After several months of operation, the compressor develops a knocking sound causing a shut-down of the retort to allow inspection of the compressor bearings and rotor. During the shut-down, the compressor and the inlet and discharge piping, are completely dismantled. A worn bearing is discovered and after several delays the replacement bearing arrives and re-assembly of the compressor and associated piping is completed. Under pressure to complete reassembly of the inlet piping, an apprentice pipe-fitter fails to properly tighten the bolts on the compressor inlet flange.

As the start-up commences the retort is filled with shale, the recirculation gas heater is ignited, and the rubble heated by circulating gas from an adjacent retort. As retorting begins the gas recirculation rate is increased and a normal, slightly negative pressure develops at the compressor inlet, causing air to leak into the recirculating gas stream through the improperly installed flange.

A large oxygen concentration developes in the recirculating gas stream which would normally be detected by a continuous oxygen analyser on the retort off-gas line. However, water has accumulated and frozen in the sample lines leading from the main retort off-gas line to the oxygen analyser, rendering the analyser useless. The operators are concerned with bringing the retort up to its full production rate and are unaware of the dangerously high oxygen concentration in the gas.

The retorting rate increases as the firing rate in the recycle gas heater increases. The lead operator has been increasing the firing rate as rapidly as possible, until the temperature at the discharge of the recirculation gas heater and the oxygen/hydrocarbon gas ratio in the recycle gas reach the explosive limit. The recycle gas explodes and the tubes of the heater rupture. The lead operator responds immediately by shutting down both the recycle gas heater and the recycle compressor, however, a sufficient volume of pressurized recycle gas remains in the system to sustain a fire for several minutes after the initial explosive. The flame from this fire rises through the retort structure, severely damaging the retort. Flammable materials, including raw shale, spent shale, shale oil, and gas in the damaged and adjacent retorts and in reach of the flame, cause the fire to spread well beyond the site of the initial explosion.

This scenario raises the following questions:

- The auto-ignition temperature, combustibility and explosivity of rich shale gas mixed with various concentrations of air.

- The conditions under which raw shale, spent shale, shale oil and retort gases and vapors will sustain combustion.

2.6.7 Explosion of Spent Shale Dust in a Surface Retort

Spent shale from a hot solid recycle retort will be finely divided and contain from three to about six weight percent organic carbon content. After retorting, the spent shale is at about 900° F. It is cooled to 500-600° F in a rotary tube cooler before it is quenched with water in a moisturizing drum to about 14% moisture and 200° F. The moisturized material is discharged from the moisturizing drum onto a belt conveyor.

Under normal circumstances, water is pumped to the moisturizing drum by one of two pumps. Failure of one pump motor necessitates using a mobile crane to lift a replacement motor into position. A cable breaks, dropping the motor which cuts the power supply to the operating pump and stops the flow of water to the moisturizing drum. The hot end of the severed wire falls onto the pump stand, causing a short which trips a circuit breaker in the retort control room. The dry, hot spent shale, which is now discharging from the moisturizing drum, is picked up by a gusting wind, engulfing the retort structure in a cloud of spent shale dust. The control operator, noticing the moisturizer water pump has tripped, tries to restart the pump. The resulting spark from the wire against the pump stand initiates an explosion which propagates throughout the cloud of spent shale dust, causing severe damage to the structure.

This scenario raises the following questions:

- The explosivity of spent shale dust.

- The ignition temperature, carbon content and particle size required for a spent shale dust explosion.

- The dust concentration required to detonate and propagate an explosion of spent shale dust.

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2.6.8 Gas Combustion Retort Fire and Explosion

In a down-flow gas combustion retort, shale oil is carried out of the retort as a fine mist which is entrained in the retort off-gas. The oil is separated from the off-gas by cyclones, a condenser, and a wet electrostatic precipitator. A blower at the discharge of the electrostatic precipitator pulls the off-gas and mist from the top of the retort through a sequence of separators and directs the remainder to a gas recovery and treating system.

On several occasions in the previous weeks of operation, oil mist is carried over to the gas recovery and treating system. The operator notes that the oil degrades the solvents in the system and accumulates in the piping, causing upsets in the burners which use the retort off-gas as fuel. Because of this continuing problem, the graveyard shift operator is persuaded to sustain a brief shut-down to inspect the cyclones and the electrostatic precipitator. The supervisor for the retort area, not being convinced that the downstream problems originated in the retort, urges all personnel to complete their inspections and get the unit back into operation. No problems were discovered during the somewhat hurried equipment inspection of the cyclones.

The electrostatic precipitator had been inspected through a manway. Manway cover gaskets are required to be installed whenever the door has been opened. New gaskets were not available so the old gasket, judged to be in fair condition, was used. Reassembly of the gas/oil separation system is completed and the retort is started. Actually the oil mist carry-over was caused by a worn and loose connection in the electrostatic precipitator which had caused occasional disruptions of the unit's performance. The old gasket re-installed on the manway, leaks and allows air to be pulled into the precipitator. Soon after start-up, sufficient air has leaked into the

precipitator to form an explosive mixture of oilmist, low Btu gas, and air. An arc from the worn connector ignites the mixture causing the precipitator to explode. Oil within the precipitator and oil collector beneath the precipitator is ignited and scattered by the explosion covering a large area with burning oil.

This scenario raises the following questions:

- The flammability and explosivity of low Btu gas/oil, mist/air mixtures.

- The energy required to initiate an explosion of low Btu gas/oil, mist/air mixtures.

- The flammability of raw shale oil.

2.6.9   Explosion of Hot, Rich Gases From a Spent In Situ Retort

An in situ retort is shut down when the exit gas temperature rises, indicating that the retorting zone is near the bottom of the rubblized zone. After the gas flow is stopped, the unretorted shale in the hot rubble near the retort bottom continues to retort, eventually filling the retort with rich gases and vapor.

The process plan includes using the sensible heat remaining in the burned-out retort for preheating other retorts. This is accomplished by flowing low Btu gas from an operating retort through the hot rubble of the shut-down retort to pick up the available sensible heat. The low Btu gas, heated as it flows through the spent retort, is then passed through the fresh retort to accomplish the desired preheating. As the low Btu gas flows through the spent retort, it picks up both the sensible heat and the oil vapors and rich gas which have filled the rubble chamber since retorting was stopped. Normally, the preheat sequence is not started until the temperature in the spent retort has fallen below the auto-ignition temperature for retort

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gases. Due to faulty heat sensors, however, the heat is drawn off before the contents of the retort have sufficiently cooled. When the hot gases and oil vapors come in contact with the air in the new retort, they explode. The explosion is propagated by the shale dust in the rubble. The explosion ruptures the retort bulkheads and seals, damages the ignition monitoring control and recovery systems, and access to these areas. Retorting continues in the shut down retort, the rich gases and vapors flow through the heat transfer conduit, through the ruptured seals, and into active mining access.

This scenario raises the following questions:

- Explosivity of raw shale dust.

- Intensity of a retort gas/oil shale dust explosion.

- Dust load in the rubble necessary to propagate an explosion.

- The effect of rubble on an explosion in a retort.

2.6.10   Explosion of Retort Gases Leaking into a Rubblized In Situ Retort

When the combustion zone in an in situ retort reaches a rich section of oil shale the high temperature and shale grade, in combination with numerous joints and fractures, promote decomposition, spalling, and burning of the pillar. The burning continues until the wall of the retort is perforated. The hole continues to enlarge as the retorting zone descends and recycle gas forces gases and vapors into an adjacent, recently rubblized retort. An explosive mixture forms, consisting of retort gas from the operating retort and air in the new retort. When the ignition sequence for the new retort is initiated, the mixture explodes. The explosion, propagated by the oil shale dust in the rubble, quenches the starting flame, destroys the ignition monitoring control and recovery systems, and the retort seals and bulkheads. The loss of pressure and the explosion result in the shutdown of both

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retorts. Because of the high temperature of rubble in the spent retort, retorting continues with gases and vapors moving through the damaged bulkheads into active mine workings and intake airways.

This scenario raises the following:

- The effectiveness of retort pressure tests in predicting the pressure drop through retort walls of varying thickness and integrity of joints and fractures.

- The effect of temperature and pressure on rich layers of fractured and jointed oil shale that had provided measured resistance to pressure tests.

- The consequences of retort gases and vapors entering into active mining areas.

- The minimum gas richness that will ignite on contact with an open flame.

- The hazards of re-igniting a retort after retorting has been interrupted.

- The effect of oil shale grade on the resistance of the retort surfaces to combustion.

2.6.11   Methane Explosion, In Situ Retorting

After the first of several retorts in a cluster has been rubblized, it fills with an explosive concentration of methane from low pressure formation gas and from broken rubble. When the retort is ignited, the methane explodes, the explosion is propagated by dust in the rubble filled chamber. The explosion severely damages the retort ignition monitoring control and oil recovery systems, ruptures the bulkheads, and damages the access to the area.

This scenario raises the following questions:

- Explosivity of raw shale dust.

- Magnitude of an explosion originating and propagating in loosely packed and non-uniform rubble.

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- Effect of particle size distribution of dust and rubble on an explosion, e.g., dispersion and muffling.

- Intensity of a methane/oil shale dust explosion.

- Dust concentration as a percentage of rubblized oil shale (available dust).

2.7 Conclusions and Recommendations of Phase 1 Studies

The sequence of steps in conducting the Phase 1 study were as follows:

- Review of previous work on fire and explosivity properties of coal and other carbonaceous materials.

- Review of previous laboratory and mine scale studies on oil shale fire and explosivity.

- Review of practical field experience in oil shale mining, crushing and processing.

- Based on intensive study of the first three items, scenarios were written on what are believed to be potential fire and explosion accidents in oil shale mining, crushing, and processing.

- Review of the scenarios and the questions raised in each of them pointed to the need for certain laboratory tests on oil shale rubble and dust, spent shale dust, retort gases, and mixtures of flammable gases with oil shale dust.

It is not expected that laboratory tests alone would completely define the limits of oil shale mining and processing fire and explosivity properties. However, it is expected that the laboratory data, collected both on basic chemical and physical properties of oil shales and on their fire and explosivity properties, will provide useful information for estimating the degree of hazard and for providing criteria which could be translated into definitive fire and safety regulations.

Based on previous findings by Bureau personnel that the organic volatiles content of carbonaceous solids is critical in determining fire and explosivity properties, it was decided that the Fischer assay oil yield and total yield of volatile hydrocarbons from oil shale would be a most

significant factor. The relationship of Fischer assay hydrocarbon yields to other chemical and physical properties of oil shale, such as organic carbon content, kerogen content, and particle specific gravity, represent a useful expansion of property correlations which does not require excessive laboratory expenditures.

The most used laboratory test for fire and explosivity of carbonaceous solids are described in RI 5624 (Dorsett et al, 1960). A recent publication by Stull (1977) indicates current endorsement and continued use of the RI 5624 procedures for studying dust explosions.

In many practical mine situations, oil shale dusts encountered will have aged for a number of years in inactive areas of the workings. Since these dusts may be involved in fire and explosive events, it is considered necessary, as part of this study, to investigate properties of old dusts (eight to nine years) which can be collected from the Colony mine. Previous laboratory work has shown that aging of oil shale dusts causes a reduction in Fischer assay oil yield.

In addition to a study of new and aged oil shale dust, review of the scenarios indicated that information was needed on combustibility of oil shale mine rubble, spontaneous combustion properties of oil shale dust, upper and lower explosive limits of rich and lean retort gases (along with the corresponding minimum ignition energies), explosion properties of spent shale dust and certain tests on mixtures of dusts, hydrocarbon vapors and methane.

3.0 PHASE 2 STUDIES

3.1 Purpose and Scope

The primary objective of the Phase 2 studies was to reduce or eliminate the gaps in knowledge concerning the severity of the potential hazards identified in Section 2.0. A program was designed to produce, for laboratory testing, oil shale dusts ranging in richness from 10 to 35 gpt. Laboratory testing was conducted to determine the various chemical and physical properties of the oil shale dusts considered to affect fire and explosivity. These included analyses for organic carbon, Fischer assay to provide information on volatile and combustible products from pyrolysis, calculation of kerogen contents and analysis for pyritic sulfur. Subsequently, laboratory ignition, explosivity, and spontaneous combustion tests were conducted on the same samples, with data from all analyses and tests evaluated statistically. Ignition and explosivity tests were also conducted on a sample of Pittsburgh seam coal; the material against which other carbonaceous test materials are compared. Also, tests on Pittsburgh seam coal are valuable in relating laboratory results to the extensive full scale mine testing which has been done on this coal.

In addition, old mine dusts were collected from the Colony mine and from an 8 x 8-foot drift developed seven or eight years ago for mine studies. After removal of the old dust from the 8 x 8-foot drift, a heading round was drilled and blasted and new dust collected for assaying and testing. Spent

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shale was removed from the Parachute Creek spent shale embankment and prepared for testing in this study. Finally, oil shale rubble and rich retort gas were accumulated and tested in the appropriate manner.

3.2   Oil Shale Dust Sample Preparation and Analyses

Broken raw shale samples, collected from the Colony mine and Tosco core, were ground to -60 mesh and blended to provide standardized test samples for analysis at predetermined 10, 15, 20, 25, 30, and 35 gpt grades. Analytical data obtained from these samples provided a basis for comparison with dust ignition, explosivity, and spontaneous ignition test results obtained on the same oil shale dust samples.

In addition, from discussions with the Bureau and Mine Safety and Health Administration personnel, it became apparent that analytical and physical test data on oil shales may form part of the basis for future regulations directed to oil shale mining, crushing, and processing. These considerations dictated that the test materials be thoroughly characterized.

3.2.1   Development of Standard Size Consist

It has been shown that the explosivity of combustible materials, other than oil shale dust, increases as the particle size decreases (Jacobson et al, 1971; Jacobson et al, 1964) It seems reasonable to expect that this same relationship holds for oil shale dusts. Therefore, one property of dust test samples which must be defined is the particle size consist, i.e., the distribution of the various screen size fractions in the test sample. The following samples and associated data were selected:

- **Old mine dust.** Dust samples from an old 8 x 8-foot mine drift in the Colony mine.

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- **New mine dust.** Dust samples generated from a fresh blast in the same 8 x 8-foot mine drift. This is a total dust sample, including material which would be removed with the muck pile.

- **Colony mine dust.** Float dust collected from Room 1 of the Colony mine.

- **Richmond mine dust.** The dust used in an explosivity study reported by Richmond and Miller (1977).

These data were normalized to 100% -40 mesh and are shown in Figure 3.1, according to the particle size ranges adopted for this program: -40 +100 mesh; -100 +200 mesh; -200 +325 mesh; and -325 mesh. In the data surveyed the -325 mesh fractions were not further defined. The top size of 40 mesh was selected after discussions with the Bureau's technical debriefing committee at Bruceton on October 11, 1977 during the Phase 1 presentation of this contract.

The size distribution of broken coal and relatively fine crushed ore is excellently described by the Rosin-Rammler function (Taggart, 1945). This function is:

$$W_r = 100e^{-(\frac{D}{a})^b}$$

where W_r is the cumulative weight percent retained, D is the screen aperture size in millimeters, and "a" and "b" are equation constants. When the Rosin-Rammler function holds, a plot of log (log $100/W_r$) against log of D gives a straight line. When particle size data are being examined, the Rosin-Rammler function may be used as an aid in confirming sample integrity. The scale of the ordinate axis in Figure 3.1 is log (log $100/W_r$); however, the axis is labeled in units of cumulative weight percent retained for convenience.
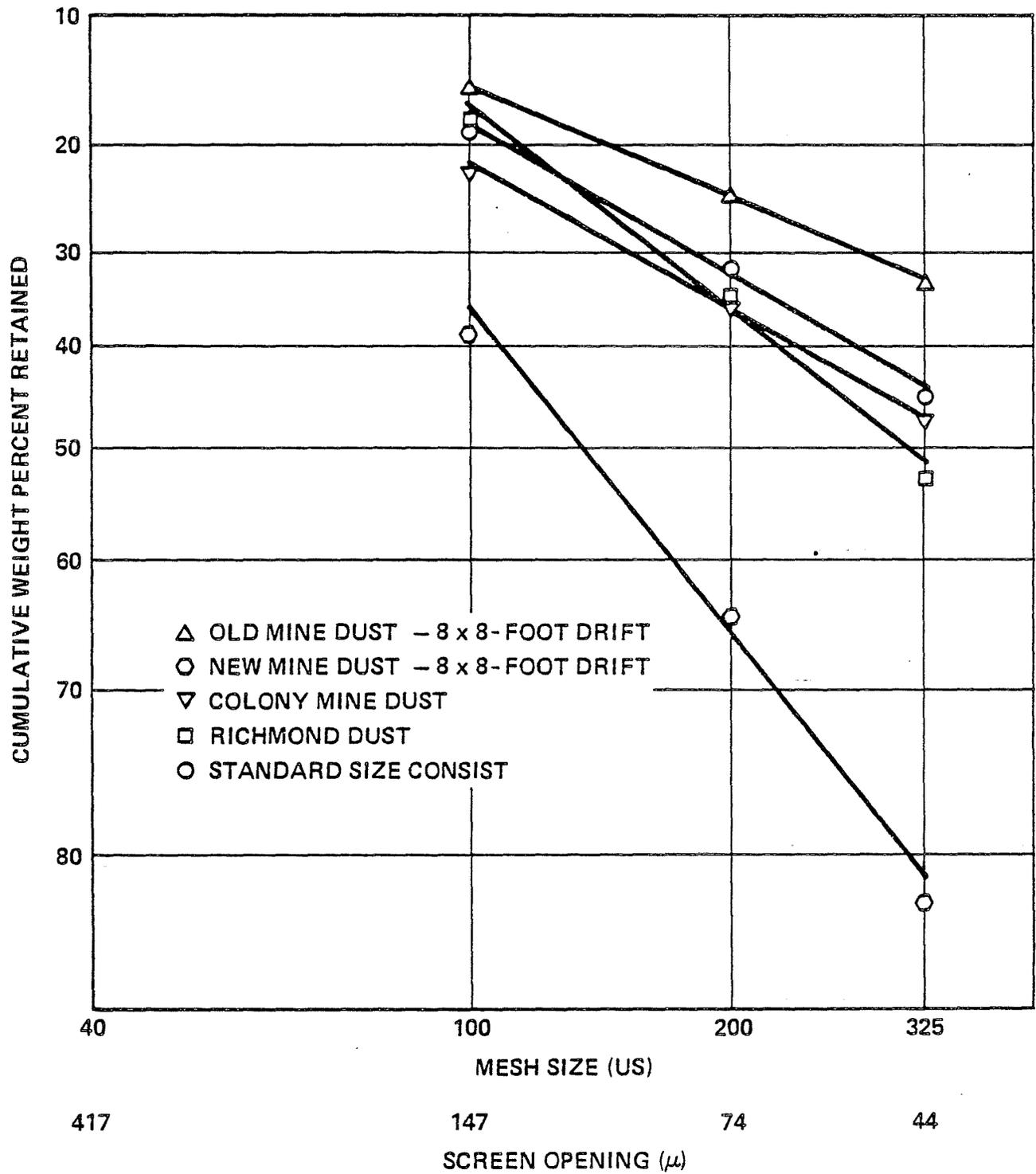
Figure 3.1   Rosin-Rammler Particle Size Distribution

Graphical analysis indicates that the Rosin-Rammler function provides a good fit to the old mine dust, new mine dust, and Colony mine dust. The new mine dust sample contains less -325 mesh material than the other selected samples, since it is the total sample of dust generated by the blast, much of it resting on muck that would normally have been removed. Thus the new mine dust sample contains more coarse material than the others, which more nearly represent float dust, and is somewhat coarser than that which would be involved in propagating mine dust explosions of the type discussed by Richmond and Miller (1977).

Table 3.1 presents the averages of the screen analyses discussed above and the selected standard size consist that is used throughout this work to rigidly define the four-component screen size distribution used in preparing oil shale and spent shale dust samples. This is done so that comparisons made in chemical and physical properties and in laboratory fire and explosivity properties will be independent of particle size distribution.

3.2.2 Laboratory Sample Preparation

The following subsections describe in general the techniques used to prepare oil shale dust samples for fire and explosivity testing. Care was taken to ensure all preparation methods resulted in reproducible and uniform samples with a minimum of distrubance to the basic chemical and physical properties.

3.2.2.1 Received Dust Samples

The standard procedure for screen analyses of material containing very fine particles is:

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Table 3.1

Average Particle Size And Selected Standard Size Consist

Mesh Size (US) Microns	-40 +100 417/147	-100 +200 147/74	-200 +325 74/44	-325 44/0
Old Mine Dust (8 x 8 ft drift)	15.3	9.6	8.5	66.6
New Mine Dust (8 x 8 ft drift)	38.6	26.2	17.6	17.6
Colony Mine Dust	22.8	13.3	11.4	52.5
Richmond Dust (1976)	18	17	18	47
Selected Standard Size Consist	19	13	13	55

- Dry screen the material using a range of screens from the coarsest size particles to 60 mesh.

- Wet screen the -60 mesh material using 100, 200 and 325 mesh screens.

All screen analyses were run in this manner whenever possible. When it was necessary to obtain large quantities of dry, fine material, dry screening was used. However, in dry screening this type material there is the possibility of plugging screens and as a consequence, not obtaining the proper screen fractions. An evaluation of this plugging potential was conducted using the procedures listed below:

- Dry screening to -60 mesh and then wet screening through -325 mesh.

- Dry screening the entire sample.

The results of the -60 mesh fractions were as follows:

Size Fraction	-60 Mesh Dry (wt%)	-60 Mesh Wet (wt%)
- 60 + 100	13.7	12.9
-100 + 200	26.1	25.2
-200 + 325	22.1	21.8
-325	23.6	25.6

Since the agreement is good, dry screens were used to obtain the separate fractions. Although the above evaluation was done on -60 mesh, a top size of -40 mesh was selected and used in all subsequent work. This minor change would not alter the previous conclusion that there is no significant difference between dry and wet screening of this material.

3.2.2.2 Mine Dust and Spent Shale Samples

Oil shale dust samples from the Colony mine and the 8 x 8-foot drift were blended and screened to remove all +40 mesh material. Spent shale retains

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from 1972 Colony operations (Coomes, 1974) were similarly prepared. The results are the four head samples described in Table 3.2. The screen sizes differ from those in Table 3.1 in that Table 3.1 described averages of previously collected materials and Table 3.2 shows the results of new preparations. Subsequently, a reconstituted standard size consist sample was prepared from the individual screen fractions of the four dusts. After a split of each head sample was screened, a portion from each of the screen fractions was blended to produce the reconstituted standard size samples. The as-produced spent shale size distribution is also given in Table 3.2.

3.2.2.3 Graded Series Samples

For this study a series of oil shale dusts with target Fischer assay oil yields of 10, 15, 20, 25, 30 and 35 gpt were chosen. These dust samples were prepared from the Mahogany zone of a selected oil shale core taken from the Tosco core storage facility (corehole TG 2-1, Section 21, NE 1/4 of the SW 1/4, T3S, R96W, Rio Blanco county, Colorado). Each selected core sample was ground to -40 mesh, and the total product is referred to as the "head sample".

Fischer assays of each head sample showed good agreement with the target oil yield except in the case of the first attempted 35 gpt sample. The product was lower in oil yield than anticipated and subsequently was designated the 31 gpt sample. A second attempt to prepare a 35 gpt sample was successful, and the sample was duly incorporated into the graded series. After each head sample was screened into the selected sizes, a portion of each of the screen fractions was blended to produce the reconstituted standard size distribution sample.

Table 3.2

Old, New, And Spent Shale Size Distribution, As-Produced

Sample Type	Mesh Size (US)	Colony Mine Dust	8 x 8 Foot Drift		Reconstituted Standard Size	Spent Shale
			New Dust	Old Dust		
F						
R	− 40 +100	23.0	23.2	22.6	19	16.3
A						
C	−100 +200	14.2	25.7	13.7	13	15.5
T						
I	−200 +325	7.5	20.6	10.3	13	11.2
O						
N	−325	55.3	30.5	53.4	55	57.1
S						

3.2.2.4 Sample Suite

A sample suite now prepared consists of old and new mine dusts, spent shale, and pulverized oil shale core samples. Each individual sample was tested for Fischer assay oil yield and total, mineral, and organic carbon. The reconstituted standard size samples were subjected to the Tosco Material Balance Assay (TMBA: i.e., Fischer assay in which the product gas is collected and analyzed), X-ray diffraction analysis at the Laramie Energy Technical Center, and determination of particle specific gravity. Certain selected samples were also analyzed for pyrite content. All samples were then transported to DRI for laboratory fire and explosivity testing.

In addition, an oil shale rubble sample was prepared for fire testing and gas samples were prepared, using Fischer assaying equipment, for ignition testing.

3.2.3 Analytical Procedures

As discussed previously, a detailed correlation of inherent chemical properties of oil shale dusts with the fire and explosivity test results was desired. These correlations would permit explanations of fire and explosive characteristics. The following subsections describe the analytical procedures used to evaluate the test samples.

3.2.3.1 Total Carbon Determination

Total carbon was determined using a carbon, hydrogen, nitrogen, oxygen analyzer operating on a combustion principle. In this method, all carbon, whether mineral or organic, is evolved and measured as carbon dioxide.

3.2.3.2 Mineral Carbon Determination

Mineral carbon was determined using the guidelines of ASTM D-1756 and involves evolution of inorganic carbon, as carbon dioxide, by treatment with mineral acid. The evolved carbon dioxide is trapped in Ascarite and the weight gain is determined.

3.2.3.3 Organic Carbon Determination

Organic carbon content is the arithmetic difference between total carbon and mineral carbon contents.

3.2.3.4 Fischer Assay Determination

Fischer and TMBA assays were conducted as described by Goodfellow and Atwood (1974). The two procedures are identical except that the product retort gas is collected, measured, and analyzed in the TMBA method.

3.2.3.5 Specific Gravity Determination

Particle specific gravities were determined by displacement of heptane with a weighed amount of solid sample.

3.2.3.6 Kerogen Determination

Kerogen contents were determined in both weight and volume percent using the procedures of Smith (1976).

3.2.3.7 Pyrite Determination

Pyrite determinations were conducted using the procedure of Smith (1964). This method incorporates lithium aluminum hydride treatment to evolve H_2S from the test sample.

3.2.3.8 X-Ray Diffraction

X-ray diffraction determinations of relative mineral contents were conducted at the Laramie Energy Technical Center, under the direction of J. Ward Smith. Results reported were relative and not absolute weight percentages.

3.2.4 Analytical Results and Discussion

Sample identification numbers for most of the samples used in this study are given in Table 3.3, illustrating the relationship to the study matrix. The designation "RF" stands for Rocky Flats. Laboratory analytical results on dusts prior to fire and explosivity testing and a brief discussion of each is presented in the following subsections.

3.2.4.1 Size Distributions As-Produced

The size distributions of samples produced from selected segments of oil shale core TG2-1, after grinding the entire sample to -40 mesh, are given in Table 3.4. The wide variation of these data and the importance of particle size in dust explosions point out the necessity of having a standard size consist not limited to the top size designation.

3.2.4.2 Total Carbon Data

Results of total carbon analyses are shown in Table 3.5. In a general way, to be discussed below, the total carbon value increases with oil shale richness and decreases with particle size. The major component of kerogen, the precursor of shale oil, is organic carbon which comprises a major part of the total carbon. In crushing, the kerogen component tends to concentrate slightly in the coarser fractions.

Table 3.3

Tosco Identification Numbers Assigned to Dust Samples

Graded Series	−40	−40 +100	−100 +200	−200 +325	−325	Reconstituted Standard Size Distribution
10 gal/ton	RF 5785	RF 5786	RF 5787	RF 5788	RF 5789	RF 5790
15 gal/ton	RF 5791	RF 5792	RF 5793	RF 5794	RF 5795	RF 5796
20 gal/ton	RF 5797	RF 5798	RF 5799	RF 5800	RF 5801	RF 5802
25 gal/ton	RF 5803	RF 5804	RF 5805	RF 5806	RF 5807	RF 5808
30 gal/ton	RF 5809	RF 5810	RF 5811	RF 5812	RF 5813	RF 5814
31 gal/ton	RF 5815	RF 5816	RF 5817	RF 5818	RF 5819	RF 5820
35 gal/ton	RF 6188	RF 6189	RF 6190	RF 6191	RF 6192	RF 6193
Mine Samples						
Colony Mine Dust	RF 5821	RF 5822	RF 5823	RF 5824	RF 5825	RF 5826
"New" Dust	RF 5833	RF 5834	RF 5835	RF 5836	RF 5837	RF 5838
"Old" Dust	RF 5839	RF 5840	RF 5841	RF 5842	RF 5843	RF 5844
Spent Shale	RF 5845	RF 5846	RF 5847	RF 5848	RF 5849	RF 5850
Coal Standard						
Pittsburgh Seam Coal	RF 6178*					

* Screen size is 80% −200 mesh.

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Table 3.4

Screen Analyses of Head Samples

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples							Standard Size Consist
		Nominal Richness							
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT	
F R A C T I O N S	− 40 +100	11.1	21.7	24.0	26.4	15.1	24.7	27.3	19
	−100 +200	36.7	36.1	24.6	27.3	38.5	25.7	20.7	13
	−200 +325	13.9	11.8	19.2	15.2	17.9	15.6	15.1	13
	−325	38.3	30.4	32.2	31.0	28.6	34.0	36.8	55

Table 3.5

Total Carbon Analyses

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples						
		Nominal Richness						
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT
As Produced	−40	11.4	11.6	15.7	16.8	19.5	20.4	20.0
F R A C T I O N S	− 40 +100	12.4	12.2	16.2	17.2	20.1	21.5	20.5
	−100 +200	11.7	11.7	15.8	17.1	19.9	20.6	20.2
	−200 +325	11.1	11.5	15.3	17.2	19.6	20.9	21.2
	−325	11.0	11.1	14.6	16.4	18.5	19.0	18.4
Reconstituted Standard Size	−40	11.4	11.4	15.3	16.7	19.3	19.8	19.4

3.2.4.3 Mineral Carbon Data

Data for mineral carbon contents of the graded series of oil shale test samples are shown in Table 3.6. Mineral carbon content does not appear to vary closely with particle size or with oil shale richness, since it is derived from the inorganic mineral component of oil shale, representing the major part of oil shale. Small variations in kerogen content do not have a significant effect on the mineral component.

3.2.4.4 Organic Carbon Data

Data for organic carbon content of the graded series of oil shale test samples are given in Table 3.7. The increase in organic carbon content with increasing shale richness is directly related to increased kerogen content. As with total carbon the organic carbon tends to concentrate in the coarser fractions when oil shale is crushed.

3.2.4.5 Fischer Assay Oil Yields

The actual Fischer assay oil yield data obtained are given in Table 3.8. Comparison of the as produced -40 mesh data with the target Fischer assay yield, given at the top of each column, illustrates the degree to which the target was met by careful selection of portions of oil shale core TG2-1. Note that, in general, the richness of the oil shale decreases with decreasing particle size, providing that the material representative of each particle size range is screened from a total mass of 40 mesh material. Richmond and Miller (1977) have shown that the Fischer assay oil yield is not affected by simply pulverizing a sample to a finer mesh size.

There is a very close relationship between Fischer assay oil yield and both total and organic carbon contents (Figure 3.2). This relationship was

Table 3.6

Mineral Carbon Analyses

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples Nominal Richness						
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT
As Produced	−40	5.7	5.0	5.9	5.5	5.1	5.6	4.2
F R A C T I O N S	− 40 +100	6.1	5.2	5.9	5.5	5.2	5.5	4.2
	−100 +200	5.8	5.1	5.9	5.4	5.2	5.6	4.3
	−200 +325	5.6	4.9	5.8	5.6	5.3	5.7	4.2
	−325	5.6	4.7	5.8	5.5	5.2	5.6	4.2
Reconstituted Standard Size	−40	5.7	4.9	5.8	5.5	5.2	5.6	4.2

Table 3.7

Organic Carbon Analyses

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples						
		Nominal Richness						
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT
As Produced	-40	5.7	6.6	9.8	11.2	14.4	14.7	15.8
F R A C T I O N S	- 40 +100	6.3	7.0	10.3	11.7	14.9	16.0	16.3
	-100 +200	5.9	6.6	9.9	11.7	14.7	15.0	15.9
	-200 +325	5.6	6.6	9.5	11.6	14.3	15.2	17.0
	-325	5.4	6.4	8.8	10.8	13.3	13.3	14.2
Reconstituted Standard Size	-40	5.7	6.5	9.5	11.2	14.1	14.2	15.2

Table 3.8

Fischer Assay Oil Yields in Gallons Per Ton (GPT)

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples						
		Nominal Richness						
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT
As Produced	−40	11.8	13.8	18.9	23.6	29.0	31.2	35.4
F R A C T I O N S	− 40 +100	12.7	14.5	22.1	24.7	30.4	34.1	37.3
	−100 +200	12.3	13.8	20.3	24.6	29.4	31.3	36.6
	−200 +325	11.5	13.6	19.5	23.8	29.4	32.2	37.8
	−325	10.9	12.7	18.0	21.2	26.2	30.5	31.3
Reconstituted Standard Size	−40	11.4	13.3	19.2	22.4	28.3	29.5	34.1
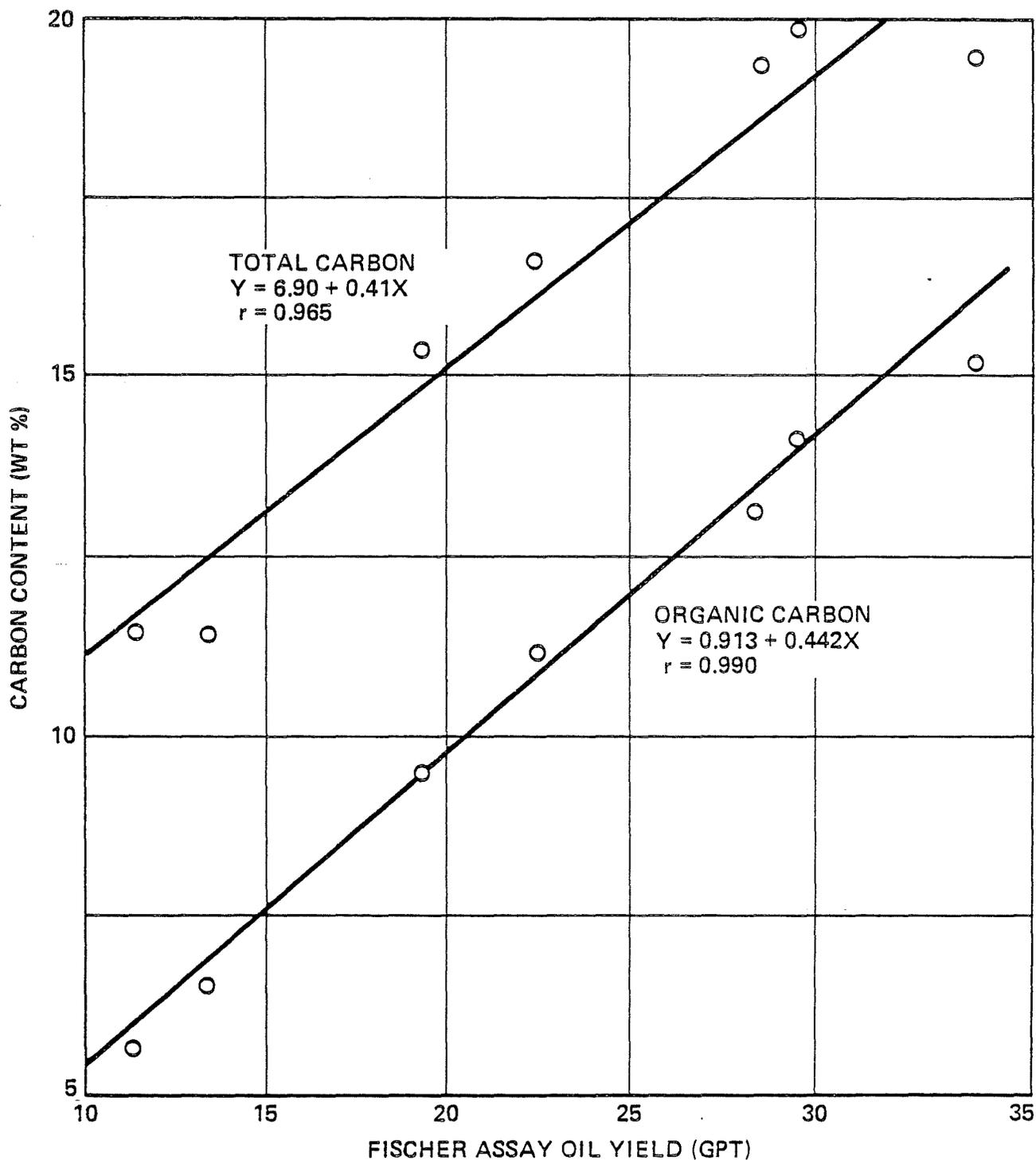
Figure 3.2   Fischer Assay Oil Yield As a Function of Total and
             Organic Carbon Contents: Graded Series -Reconstituted
             Standard Size Samples

previously reported by Stanfield et al (1951). The excellent correlation between organic carbon and Fischer assay oil yield has suggested that oil yields can be calculated from organic carbon data.

The relationship between mineral carbon and Fischer assay oil yield is shown in Figure 3.3. Although the correlation coefficient is poor, the noted general decrease in mineral carbon content as the amount of organic component increases could be predicted as simply a dilution effect.

3.2.4.6 Particle Specific Gravity

The linear relationship between particle specific gravity and Fischer assay oil yield is illustrated in Figure 3.4 (data in Table A.1). As can be seen, an increase in oil shale richness is accompanied by a systematic decrease in particle specific gravity. This relationship has been previously reported by Smith (1969) of the Laramie Energy Technical Center.

Fischer assay oil yields were calculated from particle specific gravity data and compared with actual experimental Fischer assay oil yields. The data are illustrated in Figure 3.5.

3.2.4.7 Screen Size Relationships

The relationship between screen size and Fischer assay oil yield and organic carbon content are illustrated in figures 3.6 and 3.7 (tables 3.5 and 3.7), respectively. A significant decrease in both Fischer assay oil yield and organic carbon content with decreasing screen size is illustrated. Reduction in size of a whole sample to increasingly finer particle size ranges does not affect Fischer assay yield and would not be expected to affect organic carbon content.
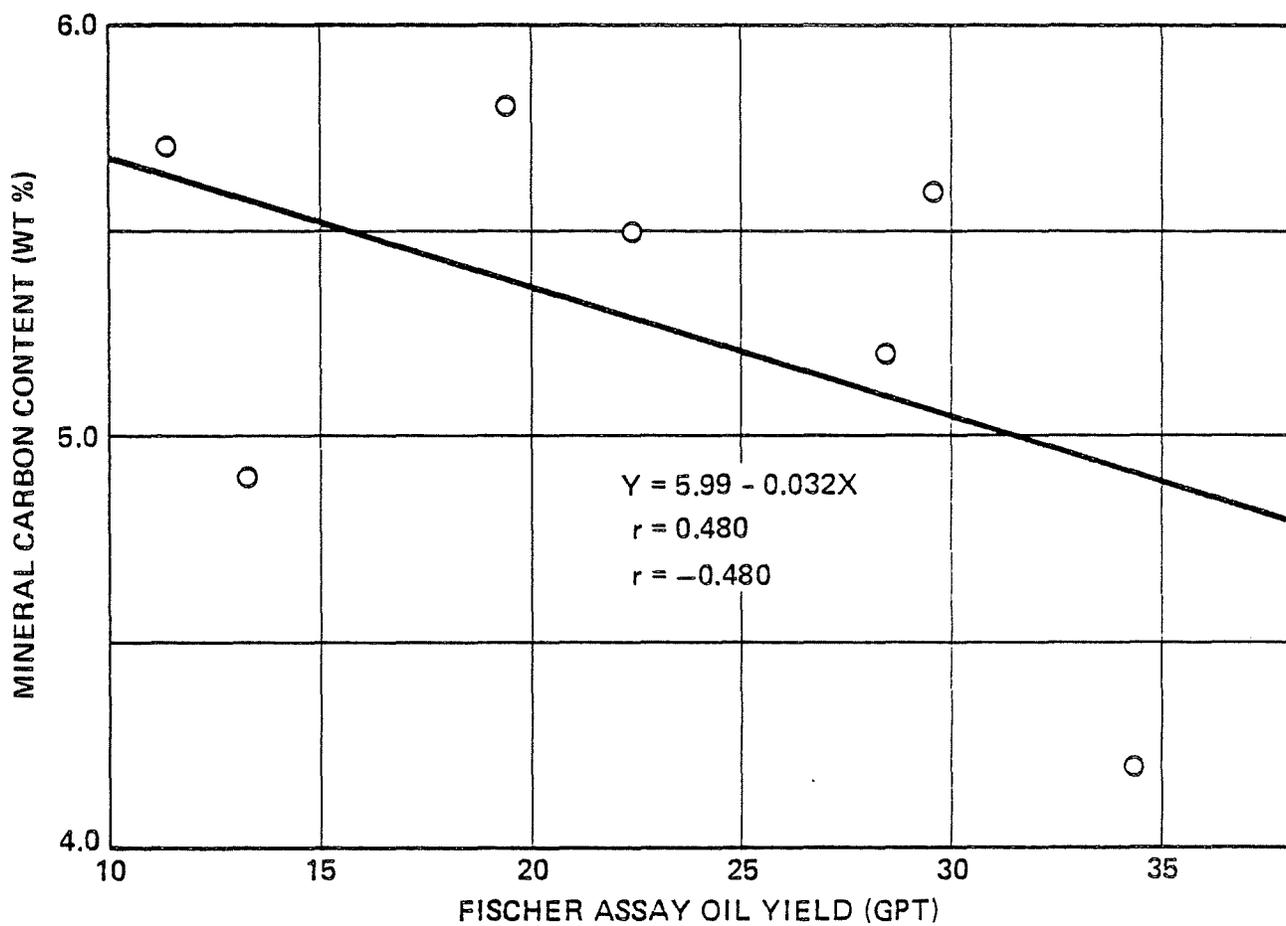
Figure 3.3 Fischer Assay Oil Yield As a Function of Mineral Carbon
Content: Graded Series — Reconstituted Standard Size
Samples
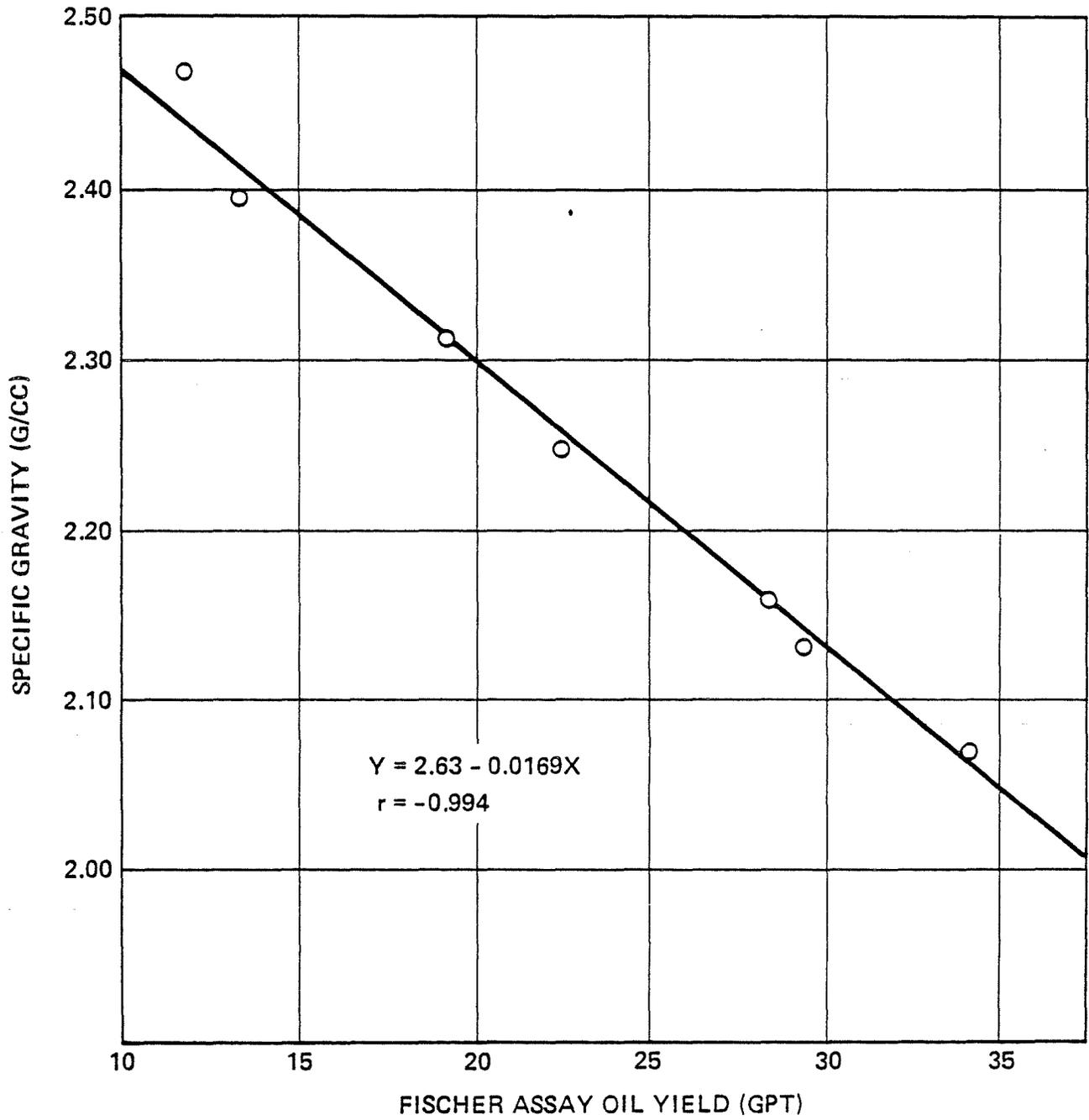
Figure 3.4 Relationship Between Fischer Assay Oil Yield and Particle
Specific Gravity: Graded Series - Reconstituted Standard
Size Samples

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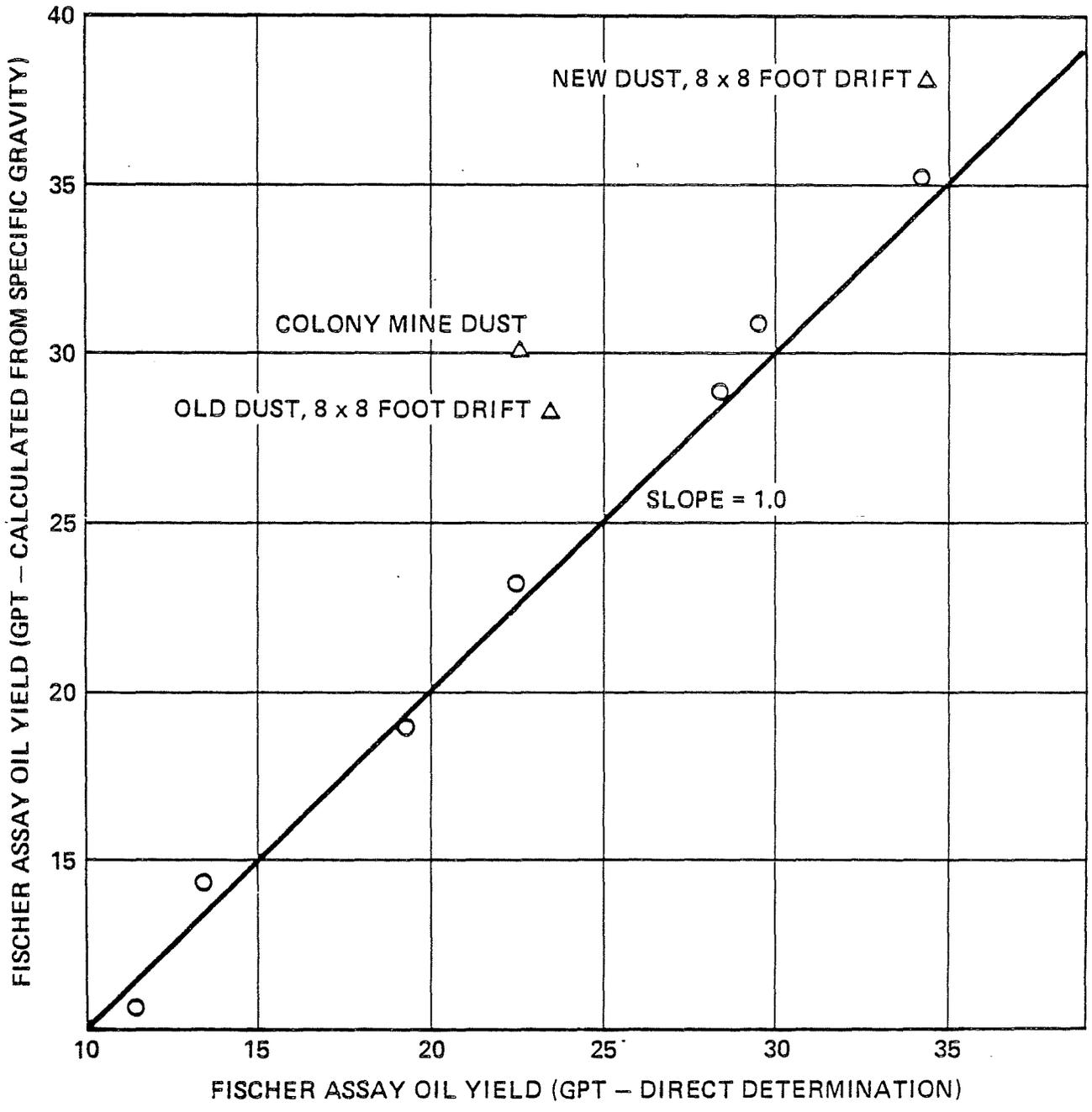
Figure 3.5 Experimental vs. Calculated Fischer Assay Oil Yields: Reconstituted Standard Size Samples
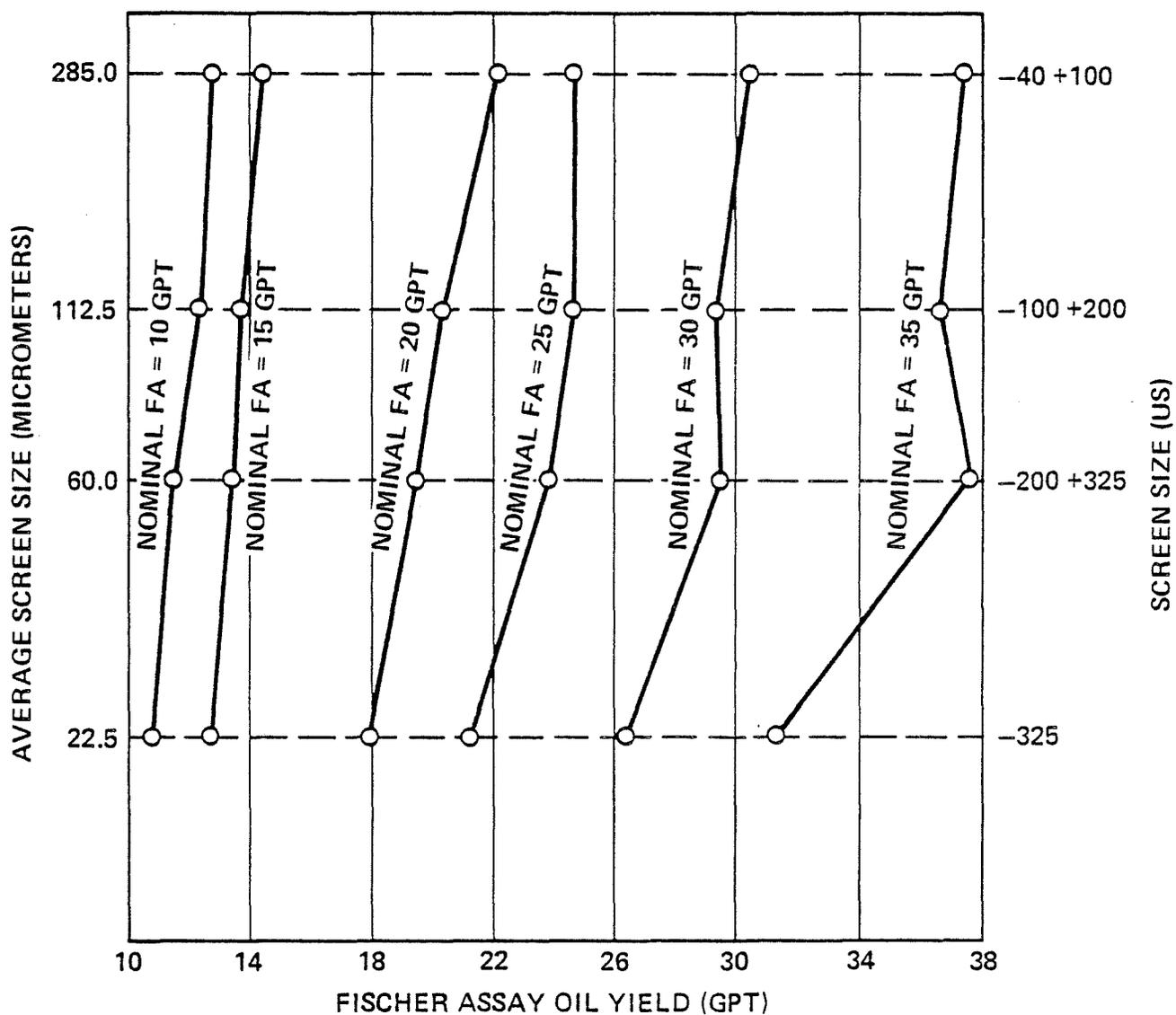
Figure 3.6   Screen Size vs Fischer Assay Oil Yield: Graded Series Samples
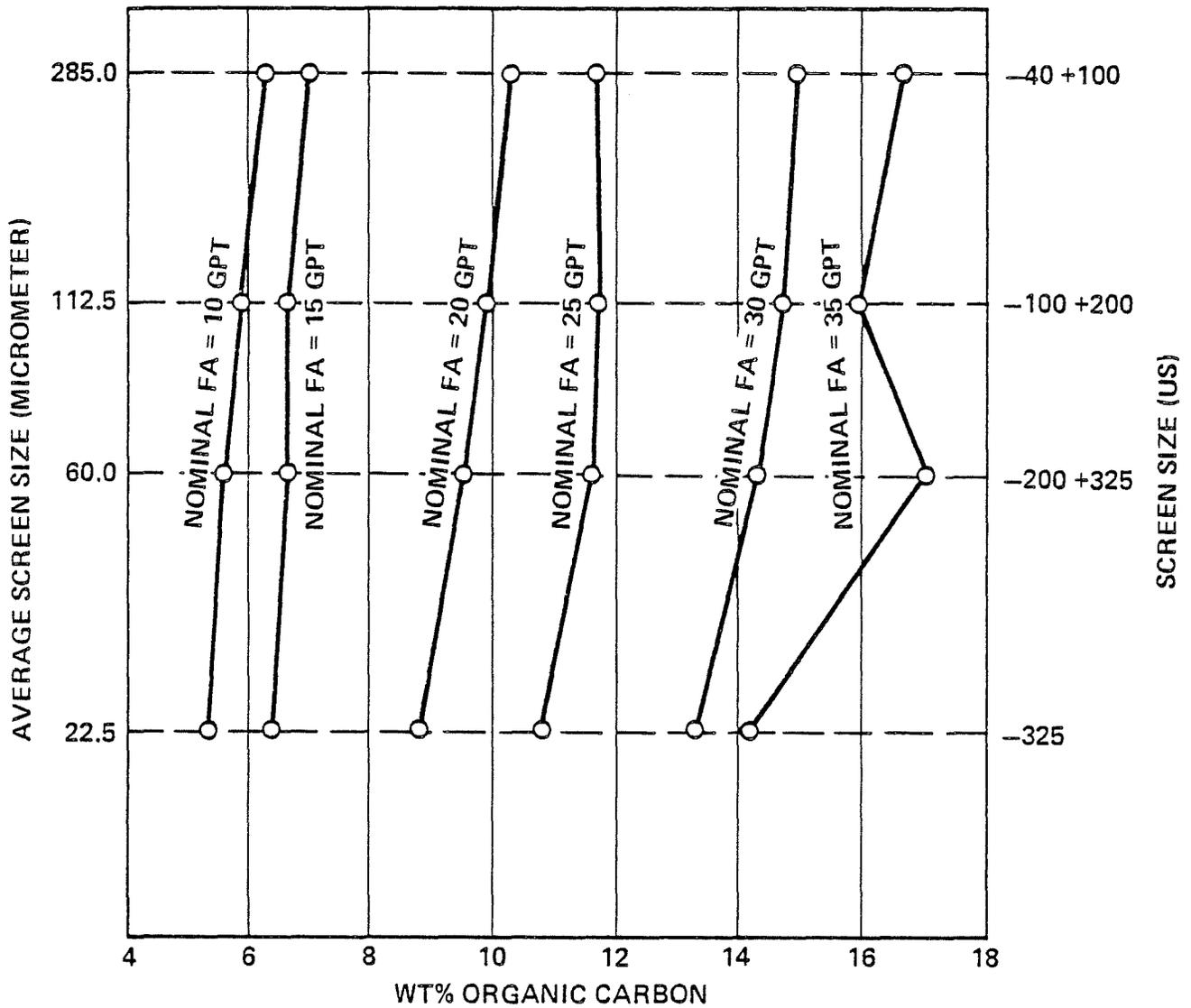
Figure 3.7   Screen Size vs. Fischer Assay Oil Yield: Graded Series Samples

3.2.4.8 Kerogen Content

Estimated kerogen contents of the graded series samples are given in tables 3.9 and 3.10. Table 3.9 gives the weight percent kerogen content, which is calculated by dividing the organic carbon content by 0.8052. The value, 0.8052, is the weight fraction of organic carbon in kerogen (Smith, 1961). Table 3.10 gives the volume percent kerogen content estimated from the Fischer assay oil yield (Smith, 1976).

In Figure 3.8 the relationships between both estimated volume percent kerogen and calculated weight percent kerogen with Fischer assay oil yield are plotted. The inversion of the linear relationships simply reflects the more rapid increase in volume percent rather than weight percent kerogen when plotted against Fischer assay oil yield.

3.2.4.9 Tosco Material Balance Assay

TMBA data (Goodfellow and Atwood, 1974) were obtained on all of the reconstituted standard size samples. The data are given in Table 3.11 for the graded series samples with detailed data printouts presented in Appendix A. Useful data for fire and explosivity studies would be the yield of total hydrocarbons. These data represent the total yield of volatile, combustible materials from each of the reconstituted standard size samples.

The close correlation of Fischer assay oil yield with total hydrocarbon yield is shown in Figure 3.9. The use of this relationship for other oil shale samples, on which only Fischer assay oil yields are known, should be restricted to Green River oil shales until further information is developed on shales from other regions.

Table 3.9

Calculated Kerogen Contents (wt %)

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples						
		Nominal Richness						
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT
As Produced	−40	7.1	8.2	12.2	13.9	17.9	18.3	19.6
F R A C T I O N S	− 40 +100	7.8	8.7	12.8	14.5	18.5	19.9	20.2
	−100 +200	7.3	8.2	12.3	14.5	18.3	18.6	19.7
	−200 +325	7.0	8.2	11.8	14.4	17.8	18.9	21.1
	−325	6.7	7.9	10.9	13.4	16.5	16.5	17.6
Reconstituted Standard Size	−40	7.2	8.1	11.8	13.9	17.5	17.6	18.9

Table 3.10

Calculated Kerogen Contents (vol %)

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples						
		Nominal Richness						
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT
As Produced	-40	16.9	19.2	24.5	29.1	34.0	36.0	39.3
F R A C T I O N S	- 40 +100	17.9	19.9	27.7	30.1	35.2	38.3	40.9
	-100 +200	17.5	19.2	26.0	30.0	34.3	36.0	40.3
	-200 +325	16.5	18.9	25.1	29.3	34.3	36.7	41.3
	-325	15.7	17.9	23.6	26.9	31.5	35.3	36.0
Reconstituted Standard Size	-40	16.4	18.6	24.8	28.0	33.4	34.4	38.3
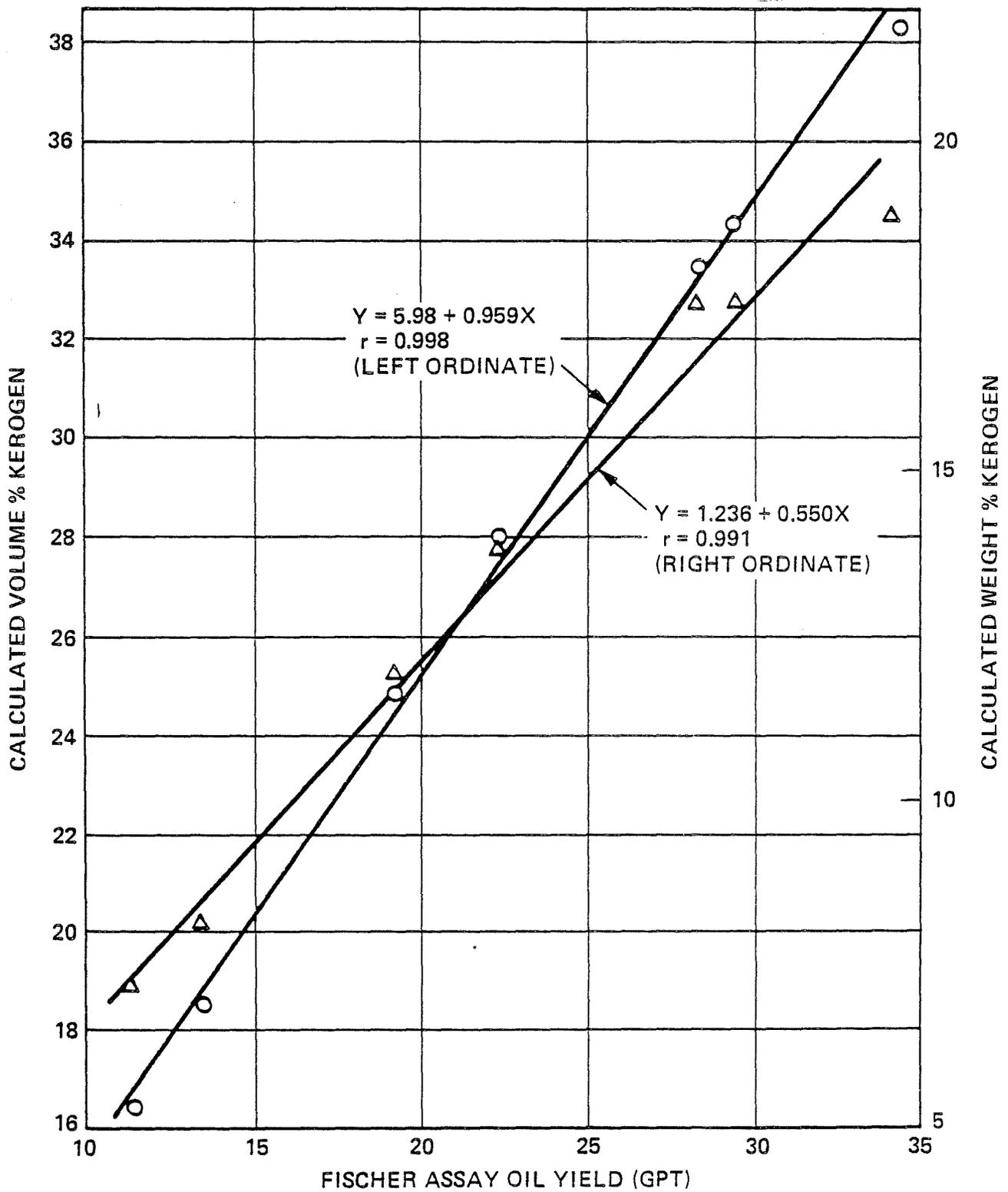
Figure 3.8 Calculated Kerogen Contents As a Function of Fischer Assay Oil
Yield: Graded Series – Reconstituted Standard Size Samples

Table 3.11

Tosco Material Balance Assay Data: Reconstituted Standard Size Samples

| | Graded Series Oil Shale Test Samples | | | | | | |
| | Nominal Richness | | | | | | |
	10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT
Sample RF Number	5790	5796	5802	5808	5814	5820	6193
Oil Yield: (gal/ton)	11.4	13.3	19.2	22.4	28.3	29.5	34.1
(lb/ton)	87.7	101.4	144.0	166.3	216.6	221.4	255.4
Oil Gravity ($^\circ$API)	27.0	23.6	26.1	27.4	22.6	25.9	26.2
Specific Gravity (60/60)	0.8927	0.9124	0.8976	0.8904	0.9181	0.8989	0.8975
Water Yield: (gal/ton)	1.7	2.6	3.0	3.5	2.2	2.8	0.9
(lb/ton)	13.9	21.9	25.1	29.1	18.0	23.0	7.2
Gas Yield: (scf/ton)	312	514	663	804	659	784	492
(lb/ton)	22.2	41.5	54.4	66.2	56.0	52.8	34.5
Total Hydrocarbon – Incl. H_2 and CO* (lb/ton)	97.5	112.4	159.8	182.8	236.6	245.4	275.9
Spent Shale Yield (lb/ton)	1869	1836	1772	1734	1707	1696	1685
Total Product Recovery (lb/ton)	1992.8	2000.8	1995.5	1995.6	1997.6	1993.2	1981.7

* This total includes the oil and all of the gas product except CO_2 and H_2S.
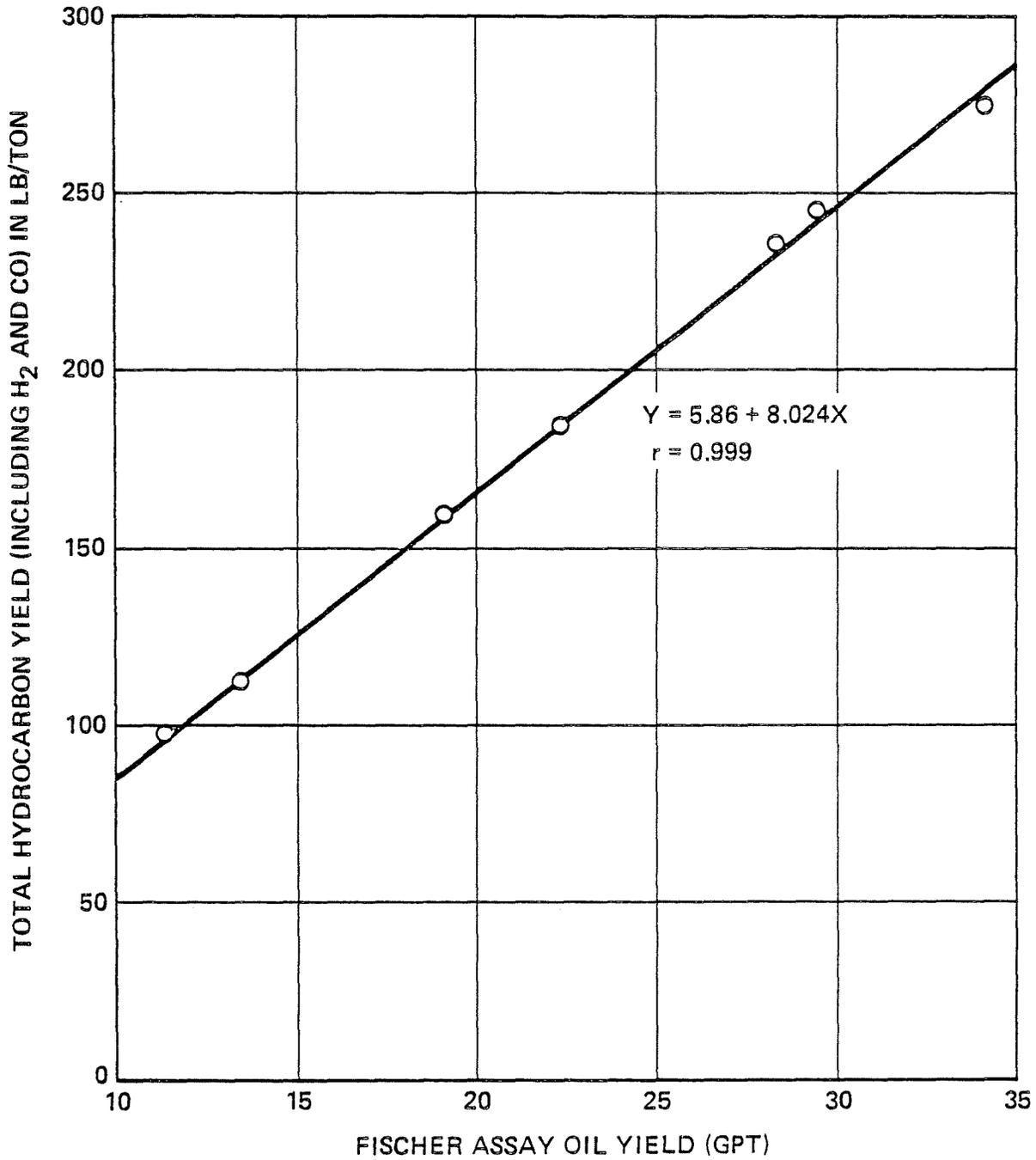
Figure 3.9 Total Hydrocarbon Yield vs. Fischer Assay Oil Yield: Graded Series - Reconstituted Standard Size Samples

3.2.4.10 Total Combustion Energy of Volatile Products

A useful extension for the TMBA data is the calculation and determination of combustion energy of volatile products. Higher heating values (HHV) for the oils produced by the TMBA have been determined by a bomb calorimeter method (ASTM D-271). Multiplying this value by the oil yield in pounds per ton of raw shale gives the total combustion energy of the oil produced from one ton of the oil shale as shown in Table 3.12. Further, the HHV's of gas produced were calculated from the gas analysis and are given in Btu per standard cubic foot. Multiplying this value by the total gas yield, in standard cubic feet, from one ton of oil shale gives the total combustion energy of product gas. The sum of the combustion energy for oil and gas is the total combustion energy of volatile products. Figure 3.10 illustrates the correlation between Fischer assay oil yield and the combustion energies of volatile products.

It is often convenient, in consideration of combustible or explosive dusts, to calculate the organic volatiles in ounces per cubic foot (oz/ft^3) expected from airborne dust. Figure 3.11 illustrates this relationship for oil shale dusts of various richness levels, assuming that dust loading in the mine opening is equivalent to an airborne concentration of one oz/ft^3. Also shown are the corresponding combustion energy levels. As an example, one oz/ft^3 of 20 gpt oil shale dust would produce 0.083 ounces of volatile combustibles per cubic foot having a combustion energy of 98.5 Btu per cubic foot, assuming the evolution of volatile combustible materials was the same as that obtained in Fischer assay.

Richmond and Miller (1977) concluded that the minimum concentration of oil shale volatiles for propagating full scale mine explosions was 0.05 oz/ft^3. Using the regression equation:

Table 3.12

Determination of Combustion Energy of Oil and Gas Volatile Products

	Graded Series – Reconstituted Standard Size Samples					
	10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	35 GPT
Nominal FA Oil Yield (gpt)	10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	35 GPT
Actual FA Oil Yield (gpt)	11.4	13.3	19.2	22.4	28.3	34.1
Fischer Assay Oil						
Yield (lb/ton of raw shale)	87.7	101.4	144.0	166.3	216.6	255.4
Higher heating value (HHV)(Btu/lb)	18,540	18,445	18,620	18,675	18,385	18,640
MM Btu/ton of raw shale	1.626	1.870	2.681	3.106	3.932	4.761
Fischer Assay Gas						
Yield (scf/ton of raw shale)	312	514	663	804	659	492
Calculated HHV (Btu/scf)	731	513	543	516	730	984
MM Btu/ton of raw shale	0.228	0.264	0.360	0.415	0.481	0.484
Total Combustion Energy of Fischer Assay Oil Plus Gas MM Btu/ton of raw shale	1.854	2.134	3.041	3.521	4.463	5.245
Volatile Combustibles in Dust at 1 Oz. of Dust/Cu. Ft.						
Oz. of volatiles*/cu. ft.	0.048	0.056	0.080	0.091	0.118	0.138
Combustion energy (Btu/cu. ft.)	57.9	66.7	95.0	110.0	139.5	163.9

*   Based on values for "Total Hydrocarbon – Including H_2 & CO" from preceding table.
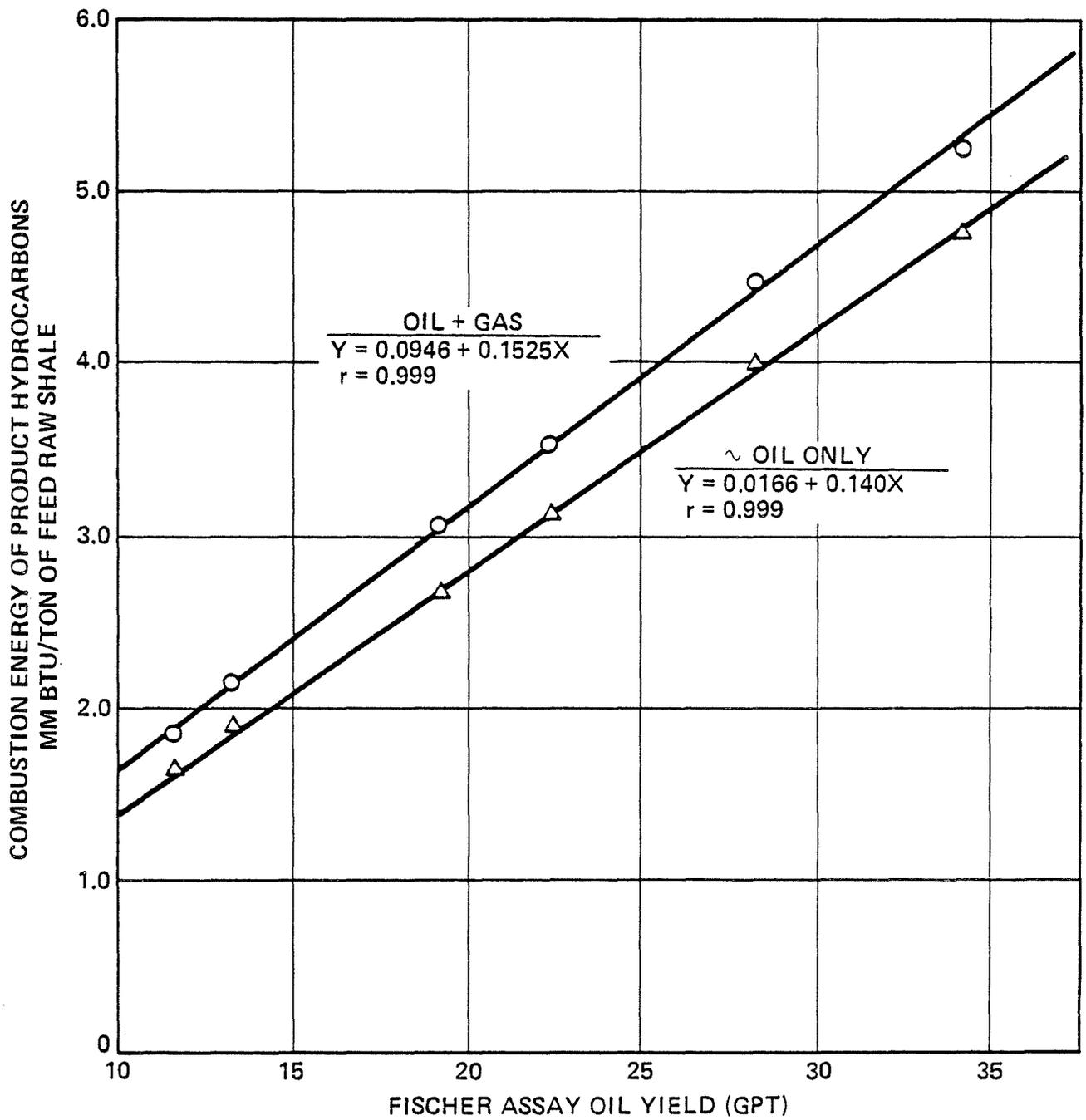
Figure 3.10   Total Combustion   Energy   of Product   Hydrocarbons   vs.   Fischer
Assay Oil Yield: Graded Series — Reconstituted Standard Size
Samples
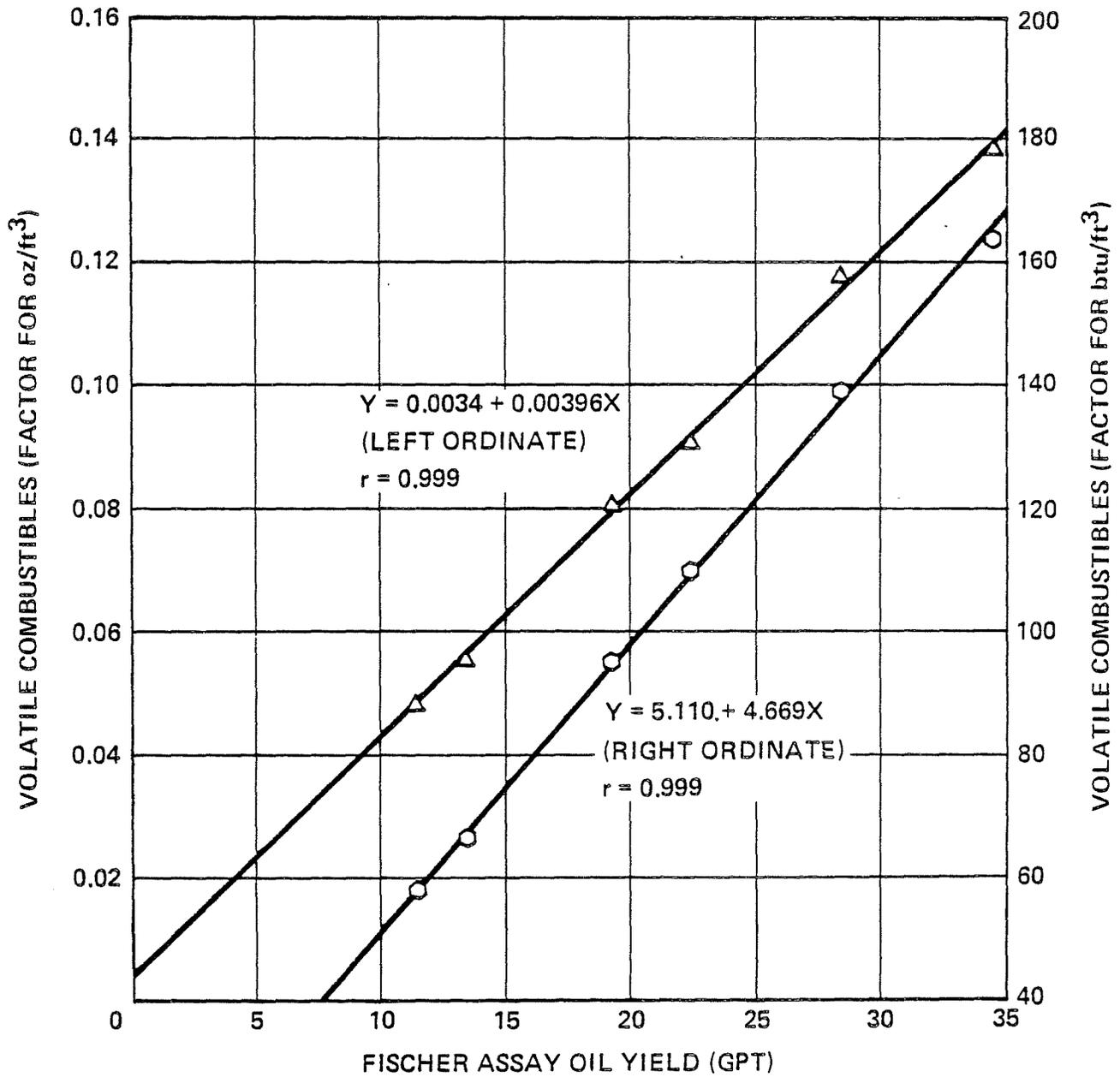
Figure 3.11 Volatile Combustibles vs. Fischer Assay Oil Yield: Graded Series — Reconstituted Standard Size Samples

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$$Y = 0.0034 + 0.00396X \text{ (Figure 3.11)},$$

where Y is in ounces of combustibles/ft^3 and X is in gpt, the various combinations which would produce 0.05 ounces of combustibles/ft^3 can be calculated as shown below:

Oil Shale Dust (gpt)	Dust Concentration (oz/ft^3) Giving 0.05 oz/ft^3 of Volatile Combustibles
10	1.162
15	0.796
20	0.605
25	0.488
30	0.409
35	0.352

These calculations show for example that with 25 gpt oil shale dust, the dust loading must be kept below 0.488 oz/ft^3 in order to maintain the potential for volatile combustibles below 0.05 oz/ft^3.

3.2.4.11 X-Ray Diffraction Data

In Table 3.13 the relative X-ray diffraction data on reconstituted standard size samples, as determined by Laramie Energy Technical Center, are presented. There does not appear to be any significant variation of mineral content with increasing Fischer assay yield.

It should be emphasized that these data are only relative. Typical values for calcite and dolomite in a Mahogany zone oil shale of the Green River Formation are 16 and 32 weight percent, respectively, of the mineral matter (Smith, 1969).

Calcite and dolomite in oil shale should act as rock dust (calcite), which is normally added to coal dust in a coal mine as an explosion

Table 3.13

Relative X-Ray Diffraction Data: Reconstituted Standard Size Samples

Graded Series Assay		Estimated Relative Percent				Indication
Nominal	Actual	Dawsonite	Quartz	Calcite	Dolomite	Pyrite
10	11.4	-	9	4	24	Yes
15	13.3	2	10	3	20	Yes
20	19.2	2	9	4	25	No
25	22.4	2	8	6	18	Yes
30	28.3	-	8	4	20	No
31	29.5	2	7	7	20	Yes
35	34.1	-	8	2	21	No

inhibitor. These mineral carbonates provide both an inert diluent to the kerogen and a heat sink which absorbs energy by chemical decomposition in an explosion. In a "limit explosion propagation" model postulated by Richmond and Liebman (1975), the heat of decomposition of rock dust, 766 Btu/lb, is part of the equation which is used to calculate available energy.

3.2.4.12 Old and New Mine Dusts

The old and new mine dusts were analyzed for total, mineral, and organic carbon, particle specific gravity, weight and volume percent of kerogen, Fischer assay oil yield, and TMBA. Data are in Appendix A, tables A.2 to A.6.

The total combustion energy of product gas and oil from TMBA determinations of old and new mine dusts are given in Table 3.14. The richness of the new dust in comparison with the old dust is apparent. It should also be noted, however, that data comparison of the old and new dusts, used in this study, have not been corroborated by other direct comparisons because of the unavailability of data from other sources.

Relative X-ray diffraction data on the old and new mine dust are given in Table 3.15. Indications were reported that the old mine dust had less pyrite and showed the presence of gypsum (calcium sulfate), not normally a component of oil shale (Smith, 1978), while the new mine dust did not indicate these alterations. Analyses for pyritic sulfur are described in a later section.

The effect of artificial aging of oil shale on Fischer assay oil yield was investigated by Coomes and Sommer (1977). The gradual reduction in oil yield is illustrated in Table 3.16. Similar effects, operating much more slowly, may have occurred in the mine.

Various relationships among data on all old and new mine dusts are illustrated in figures 3.12 through 3.17. Figures 3.12, 3.13 and 3.14

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Table 3.14

Determination of Combustion Energy of Oil and Gas Volatile Products:
Old and New Mine Dusts, Reconstituted Standard Size Samples

| | 8 x 8 Foot Drift | | Colony (Old) |
	Old	New	
Actual FA Oil Yield (gpt)	23.5	34.3	22.7
Fischer Assay Oil			
Yield (lb/ton of raw shale)	176.6	257.2	170.7
Higher Heating Value (HHV)(Btu/lb)	18,720	18,705	18,605
MM Btu/ton of raw shale	3.306	4.811	3.176
Fischer Assay Gas			
Yield (scf/ton of raw shale)	749.3	969.9	719.6
Calculated HHV (Btu/scf)	634.9	760.3	584.3
MM Btu/ton of raw shale	0.476	0.737	0.420
Total Combustion Energy of Fischer Assay Oil Plus Gas			
MM Btu/ton of raw shale	3.782	5.548	3.596
Volatile Combustibles in Dust at 1 Oz. of Dust/Cu. Ft.			
Oz of volatiles*/cu. ft.	0.095	0.144	0.099
Combustion energy (Btu/cu. ft.)	118.2	173.4	112.4

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* Based on values for "Total Hydrocarbon Including CO and H_2" from
preceding page.

Table 3.15

Relative X-Ray Diffraction Data Reconstituted Old and New Mine Dusts Samples

| | Estimated Relative Percent | | | | Indication |
	Dawsonite	Quartz	Calcite	Dolomite	Gypsum
Colony Mine (Old)	−	7	3	16	Yes
8 x 8 Foot Drift (New)	−	8	3	19	No
8 x 8 Foot Drift (Old)	2	8	4	19	Yes

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Table 3.16

Effect of Extended Preheat in Air
At 70°C on Oil Yield:
32 gpt Shale at −65 Mesh

Length of Preheat	Oil Yield (% of Fischer Assay)
0	100
1 month	94
2 months	90
3 months	84
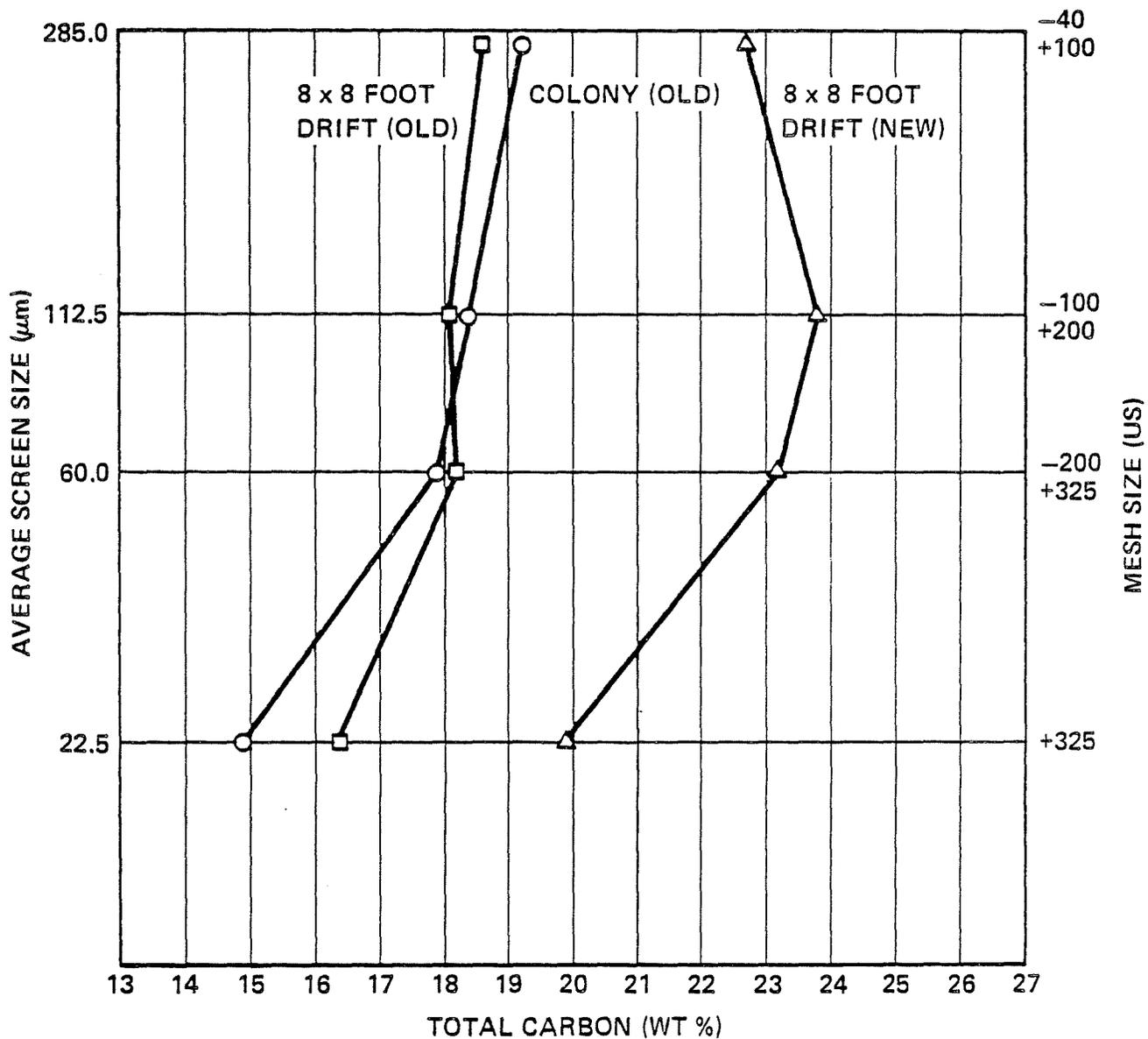
Figure 3.12   Relationship Between Screen Size and Total Carbon Content: Old
and New Mine Dusts
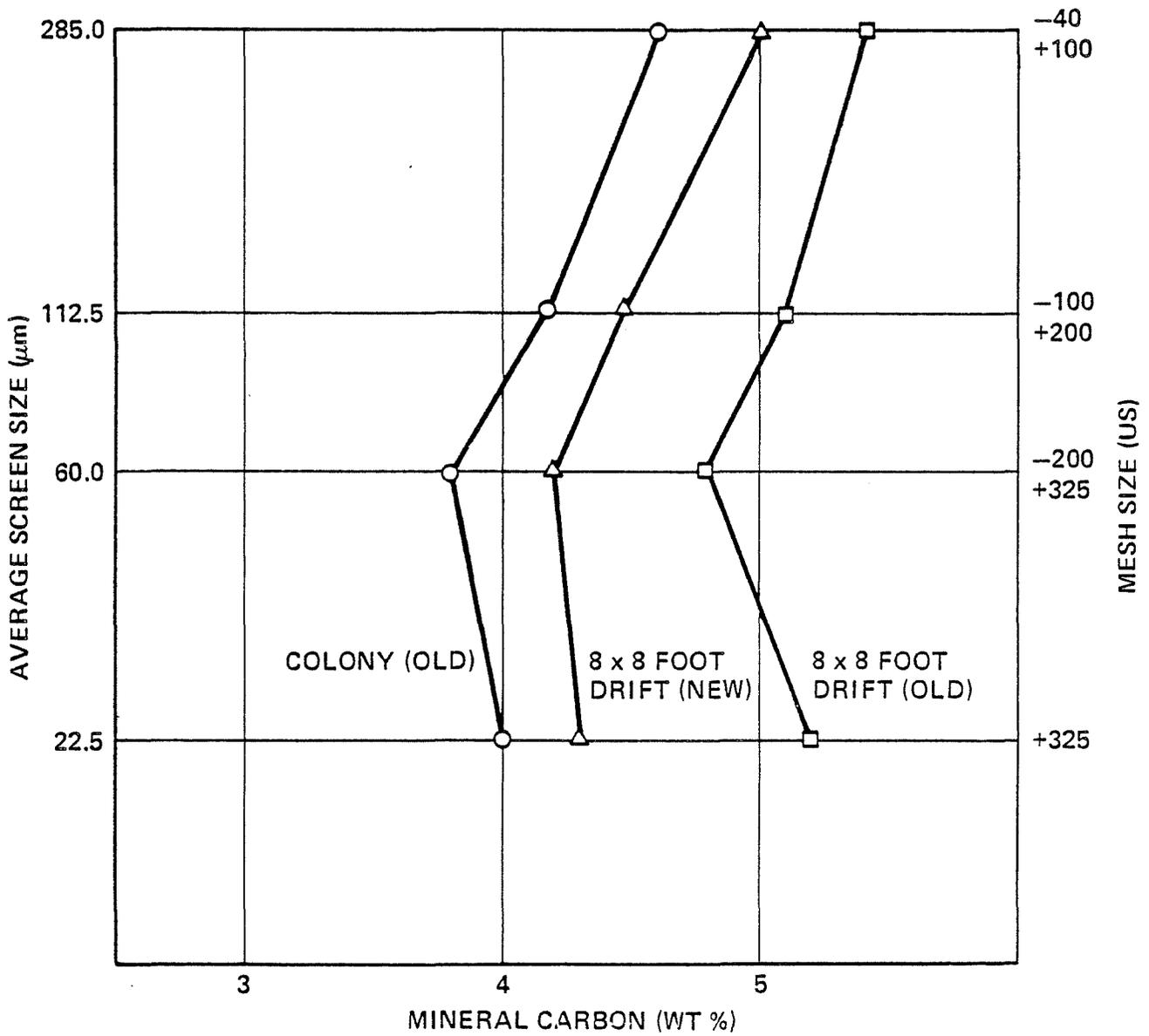
Figure 3.13   Relationship Between Screen Size and Mineral Carbon Content:
Old and New Mine Dusts
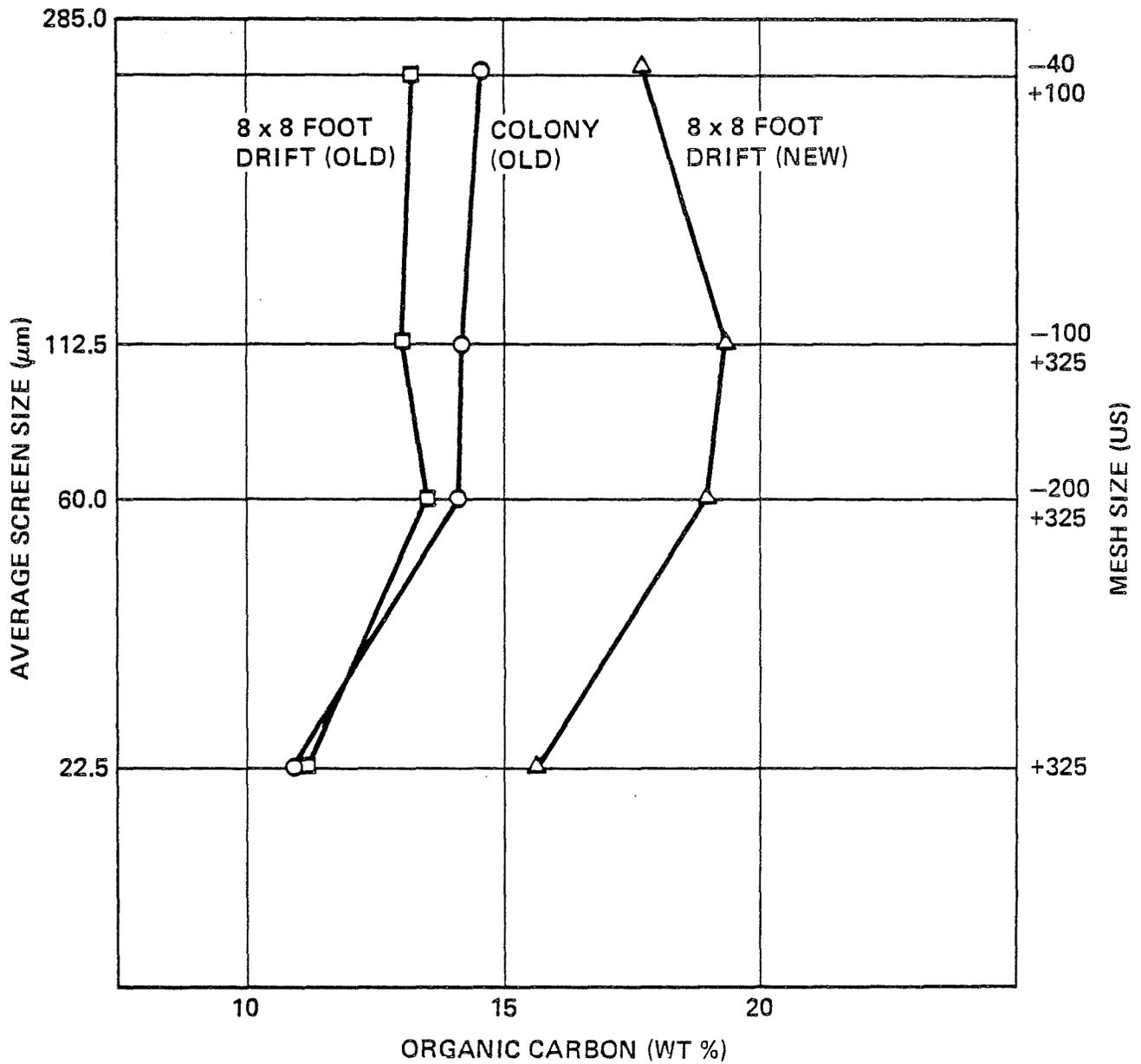
Figure 3.14 Relationship Between Screen Size and Organic Carbon Content:
Old and New Mine Dusts

describe the total, mineral and organic carbon content relationships. Total and organic carbon contents generally decrease with particle size, but there does not appear to be a correlation between mineral carbon content and screen size. Fischer assay oil yield-screen size relationships are shown in Figure 3.15. As expected, the Fischer assay oil yield decreases with screen size.

Figure 3.16 represents an attempt to construct a linear relationship between Fischer assay oil yields from new dust and from old dust in a situation where the particle size range has been fixed. It appears generally true that the old dust samples have oil yields approximately 10 gpt less than corresponding size fractions of new oil shale dust. The corresponding organic carbon relationship is given in Figure 3.17. Each of these relationships should be used cautiously until further data have been obtained.

3.2.4.13 Spent Shale Analyses

The size distribution of spent shale as-produced was shown in Table 3.2. The corresponding total, mineral and organic carbon contents are given in Table 3.17. Organic carbon content does not appear to vary with particle size.

3.2.4.14 Pyritic Sulfur Determination

Near the end of the study it was decided that determinations of pyritic sulfur content should be done, based on review of data on spontaneous combustion and indications from relative analysis by X-ray diffraction. The indications, described above, from X-ray diffraction data are that pyritic sulfur content was lower in old mine dust as compared to new mine dust. This is confirmed by the data in Table 3.18. An indication of a slight accumulation of pyritic sulfur in the -200 +325 mesh fraction is apparent.
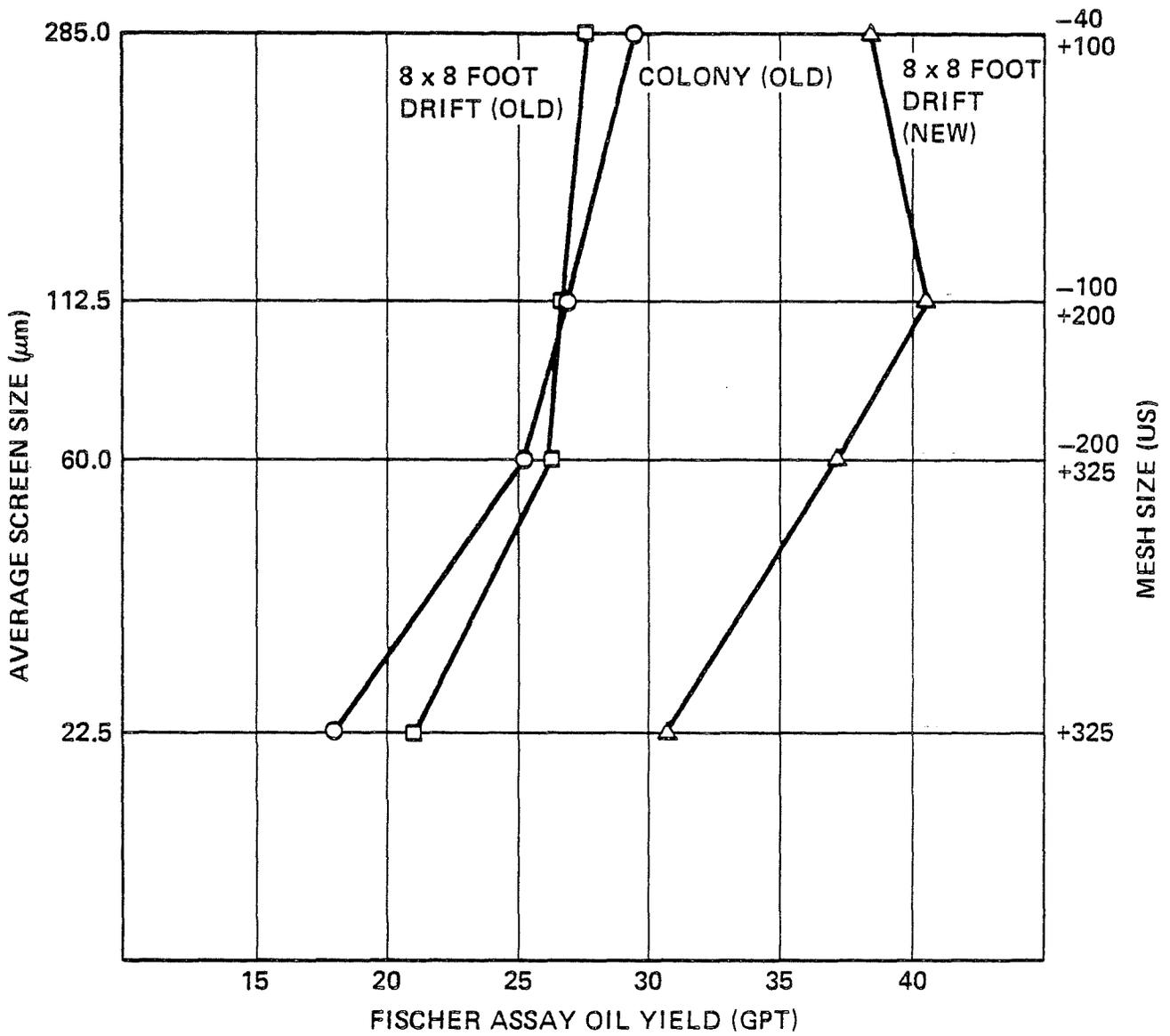
Figure 3.15 Relationship Between Screen Size and Fischer Assay Oil Yield: Old and New Mine Dusts
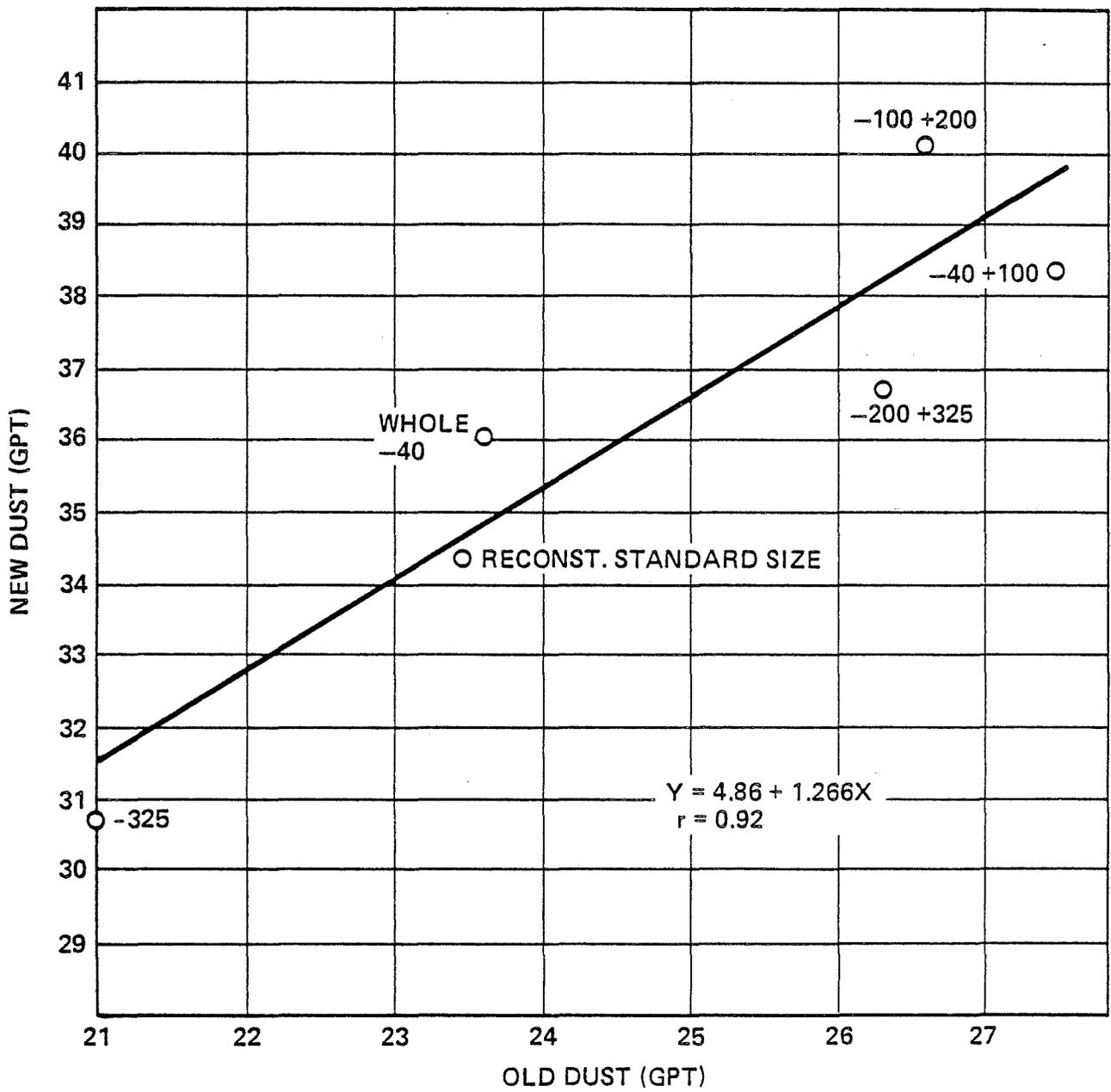
Figure 3.16   Fischer Assay Oil Yield Comparison Between Old and New Mine Dusts: 8x8-Foot Drift
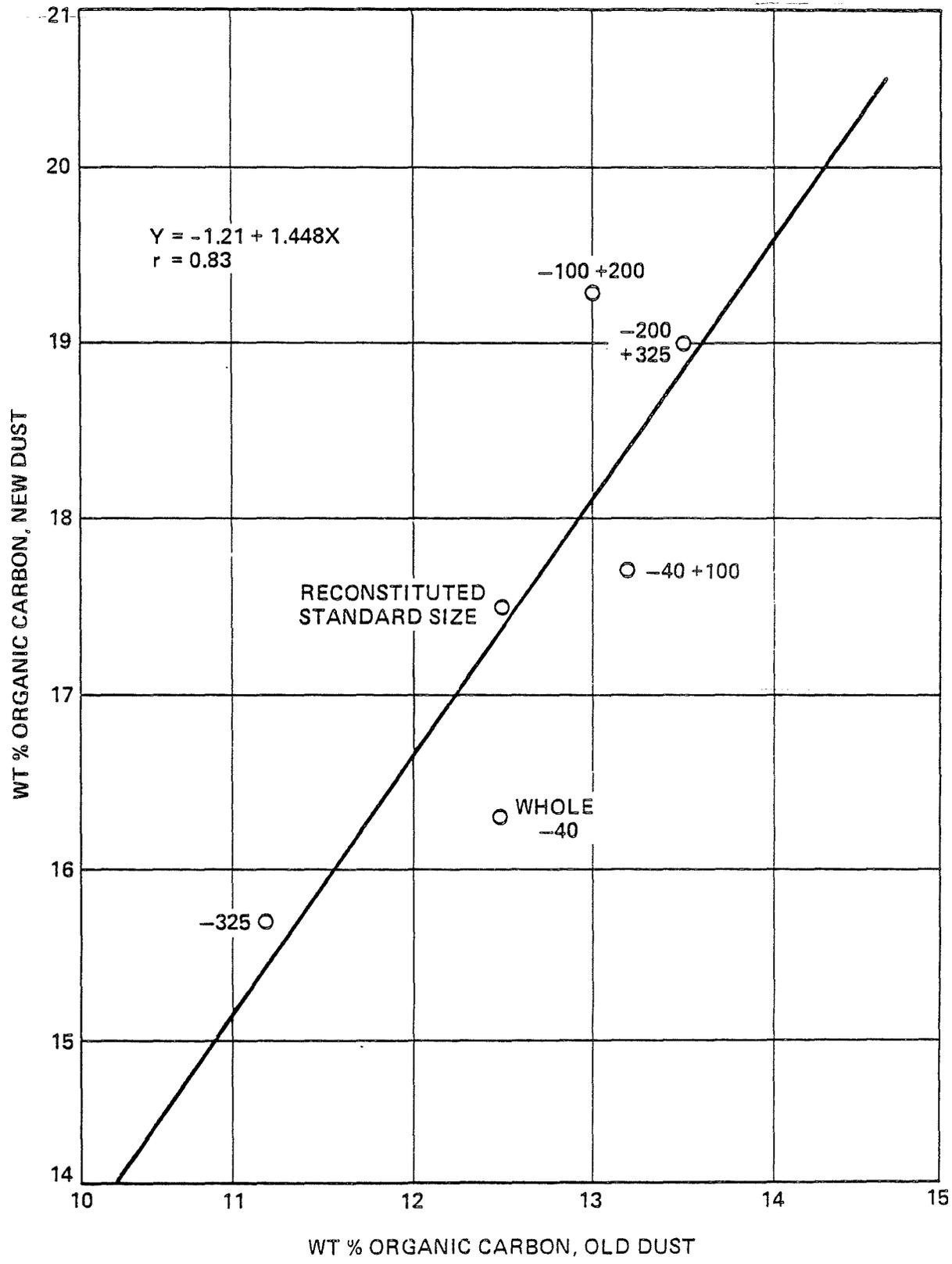
Figure 3.17 Organic Carbon Content Comparison Between Old and New Mine
Dusts: 8 x 8-Foot Drift

Table 3.17

Total, Mineral and Organic Carbon Contents: Spent Shale

Sample Type	Mesh Size (US)	Total Carbon (Wt%)	Mineral Carbon (Wt%)	Organic Carbon (Wt%)
As Produced	-40	9.8	5.6	4.2
F R A C T I O N S				
	- 40 +100	9.8	5.7	4.1
	-100 +200	10.1	5.4	4.7
	-200 +325	10.0	5.2	4.8
	-325	10.2	5.6	4.6
Reconstituted Standard Size	- 40	10.0	5.6	4.4

Table 3.18

Pyritic Sulfur Contents (Wt% Pyritic Sulfur)

| Sample Type | Mesh Size (US) | Graded Series Oil Shale Test Samples | | | | | | | Colony Mine | 8 x 8 Foot Drift | |
| | | Nominal Richness | | | | | | | | New | Old |
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT	Dust	Dust	Dust
As Produced	− 40										
F R A C T I O N S	− 40 +100										
	−100 +200			0.26			0.56	0.63			
	−200 +325			0.31			0.69	0.82	0.45	0.85	0.36
	−325			0.29			0.61	0.73			
Reconstituted Standard Size	− 40			0.27			0.60	0.69	0.33	0.72	0.31

Figure 3.18 illustrates a surprising relationship between pyritic sulfur and Fischer assay oil yield. Pyritic sulfur content appears to advance with Fischer assay oil yield. This is unexpected, since it is often assumed that the inorganic component is independent of the organic component from a chemical standpoint.

Inorganic sulfides, pyrites and others, are known to undergo spontaneous oxidation in the presence of moisture and oxygen (Nintemen, 1978). The relationship between pyritic sulfur content and the tendency to spontaneous combustion is discussed in a following section.

3.2.5   Dust Loading Study

Large scale explosion tests conducted by Richmond and Miller (1977), have established that medium grade oil shale dust in sufficient concentrations will propagate explosions initiated by methane. Phase 2 tests conducted within the confines of RI 5624 test procedures did not produce explosions. However, when the dust concentrations were modified by increasing pressure, evidence of explosions was observed. Although the differing results discussed above probably relate more to procedure and scale, it has nevertheless been clearly demonstrated that oil shale dust is explosive, at least in large scale tests.

As a result of the test work done by the Bureau on oil shale dust, several measurements were made (Richmond and Miller, 1977) on the dust concentration and grade components of the critical mass. It was determined that the concentration for the lower explosive limit of 30 gpt oil shale dust should be 0.3 g/l. To achieve that concentration in a room 50 x 60 x 70 feet, the average dust layer density on six surfaces would have to be about 0.098 gm/cm^2. Faced with this evidence, it is important that the
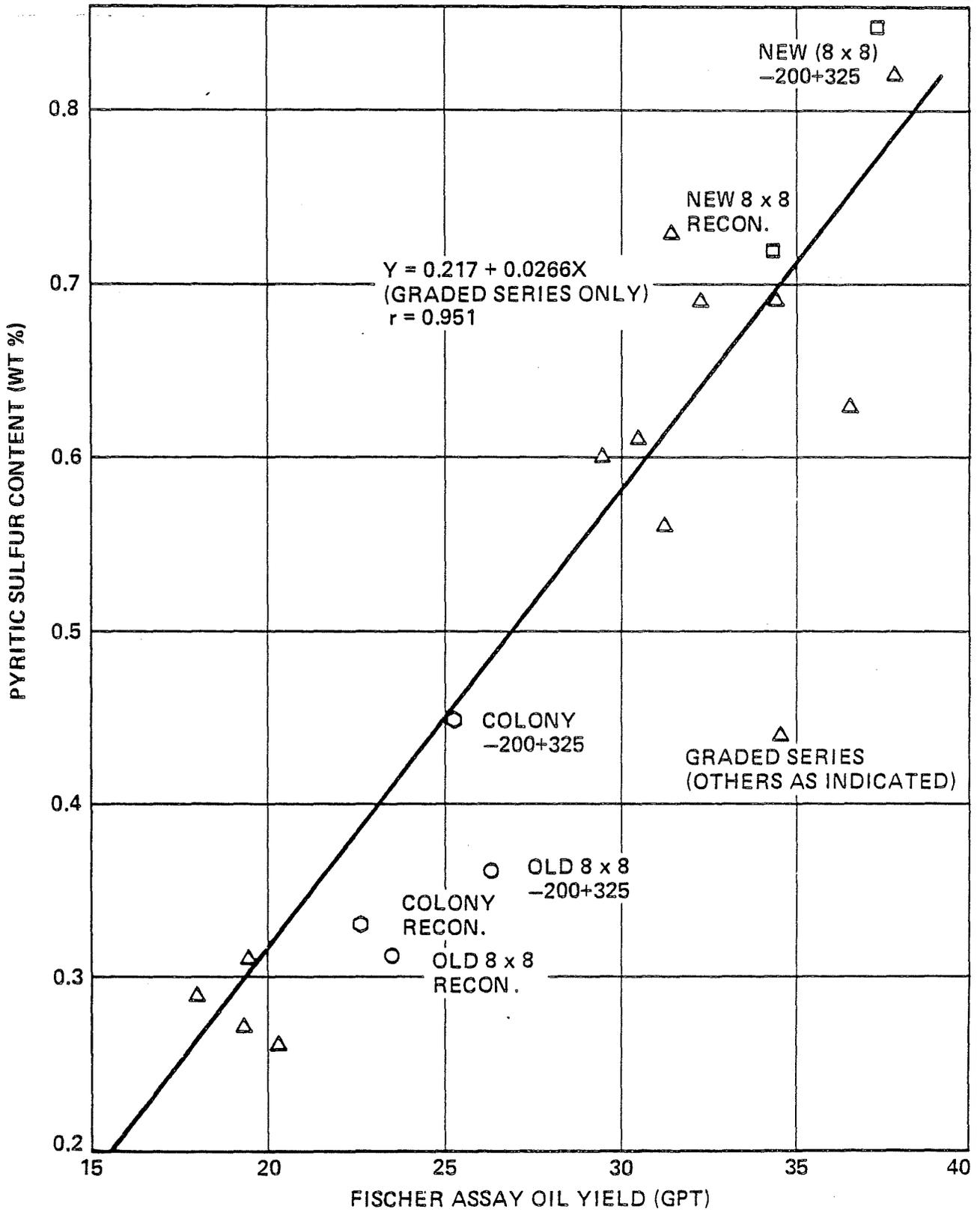
Figure 3.18 Pyritic Sulfur Content vs Fischer Assay Oil Yield

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components of the critical mass necessary for a dust explosion in an oil shale mine be further identified. The most obvious components of critical mass necessary for explosions of oil shale mine dust are dust layer density, average grade, particle size distribution, and grade of the most critical particle sizes of the dust found in a large oil shale mine.

3.2.5.1   Preliminary Program

As a first step toward establishing the components of critical mass, a preliminary program to collect basic information about the character and density of dust in the Colony oil shale mine was undertaken. In the preliminary program, 23 more-or-less random samples were collected. Three from areas 60 feet high, and the rest from areas on the upper level that are nominally 30 feet high. The procedure for taking these samples was to mark a vertical strip from roof to floor, then collect all of the dust in the strip with a high performance vacuum equipped with a brush-head. The dust layer density was determined for all of the samples. The particle size distribution and assay by particle size were determined for only two of the samples. The data for these samples, designated 222, are in Appendix A, Tables A.7 and A.8. These preliminary data, indicating an average dust load of 0.0053 gm/cm^2 are summarized in Table 3.19.

3.2.5.2   Modification Number 2

After the results of the preliminary investigation were compared with the postulated dust load necessary to propagate an explosion, the contract was modified to include more extensive measurements of the dust load in the Colony oil shale mine and, if possible, the Anvil Points mine. Permission to enter the latter facility was not obtained in time to collect and include

Table 3.19
Summary of Mine Dust Load Data

Description	Test No.	No. Samples	Wt% -40	Dust Load (gm/cm²)	-40 +100	-100 +200	-200 +325	-325	-40*	-40 +100	-100 +200	-200 +325	-325	Oil Yield Gal. Per Ton
						Particle Size Distribution								Oil Yield Gal. Per Ton
Selected Std. Dust					19.0	13.0	13.0	55.0						
Random Vertical Strips Roof to Floor	222	23	54.0	0.0053										
Random Vertical Strips Roof to Floor	122	12	57.7	0.0073	29.0	16.8	11.8	42.4	23.2	27.4	25.9	22.6	17.8	
Random Vertical Strips Main Haulageway	123	5	70.9	0.0172	8.7	6.7	10.4	74.2	12.8					
Mine Roof	124	5	87.7	0.0024	22.5	16.1	8.7	52.7	17.8					
Mine Rib, 30' x 50'	125	5	30.3	0.0200	39.8	16.0	11.7	32.5						
Mine Pillar 60' x 25'	126	5	38.8	0.0072	33.3	19.2	10.4	37.3						
Mine Floor	127	4	42.4	0.0550	30.9	9.0	45.0							
Horizontal Band Sample:	128	19	49.9	0.0087	24.9	11.4	7.4	56.4						

(Total area samples 2ft. wide at vertical center of ribs and pillars was 16,159 ft²)

*Head Sample

those measurements in this report. The measurements are, however, important to improving the present data base. Because mining has only recently been suspended at Anvil Points, it will also be possible to obtain valuable data about the grade of the dust relative to that of the shale being mined.

The program authorized by the contract modification included 12 additional random samples to complete the vertical strip sampling program initiated in the preliminary program. The sample locations were intended to test the differentiation in dust load and particle size relative to the mining sequence, mine height, and changes in ventilation patterns. The results of the 35 samples are not helpful to this determination. The data from all of the samples collected in the Colony mine relating to the analyses of the mine dust load are found in Appendix A, tables A.9 to A.14. Table 3.19 contains a summary of these data. Figures 3.19 and 3.20 are Colony mine maps showing the locations of the 122 and 222 series random samples and 123 to 128 series samples, respectively. Figure A.1, Appendix A, is a map of the mine showing areas of available access and mining roof height.

The vertical strip samples (Series 122, Table A.8) that were assayed averaged 23.2 gpt, with a range from of 20.3 to 25.8 gpt. The average dust load of the 35 samples (Series 122 and 222, Table A.8) is 0.0060 gm/cm^2, ranging from 0.0014 to 0.0298 gm/cm^2.

The rough texture of the vertical surfaces in an oil shale mine is a major factor in determining the dust load. The variations in dust load relate more to variations in surface texture than to local concentrations in dust loading for other reasons. The principal factor in texture is the slope of the major surfaces. No attempt was made to sort sample points by surface texture. The summary dust loading results, Table 3.19, illustrate quite well
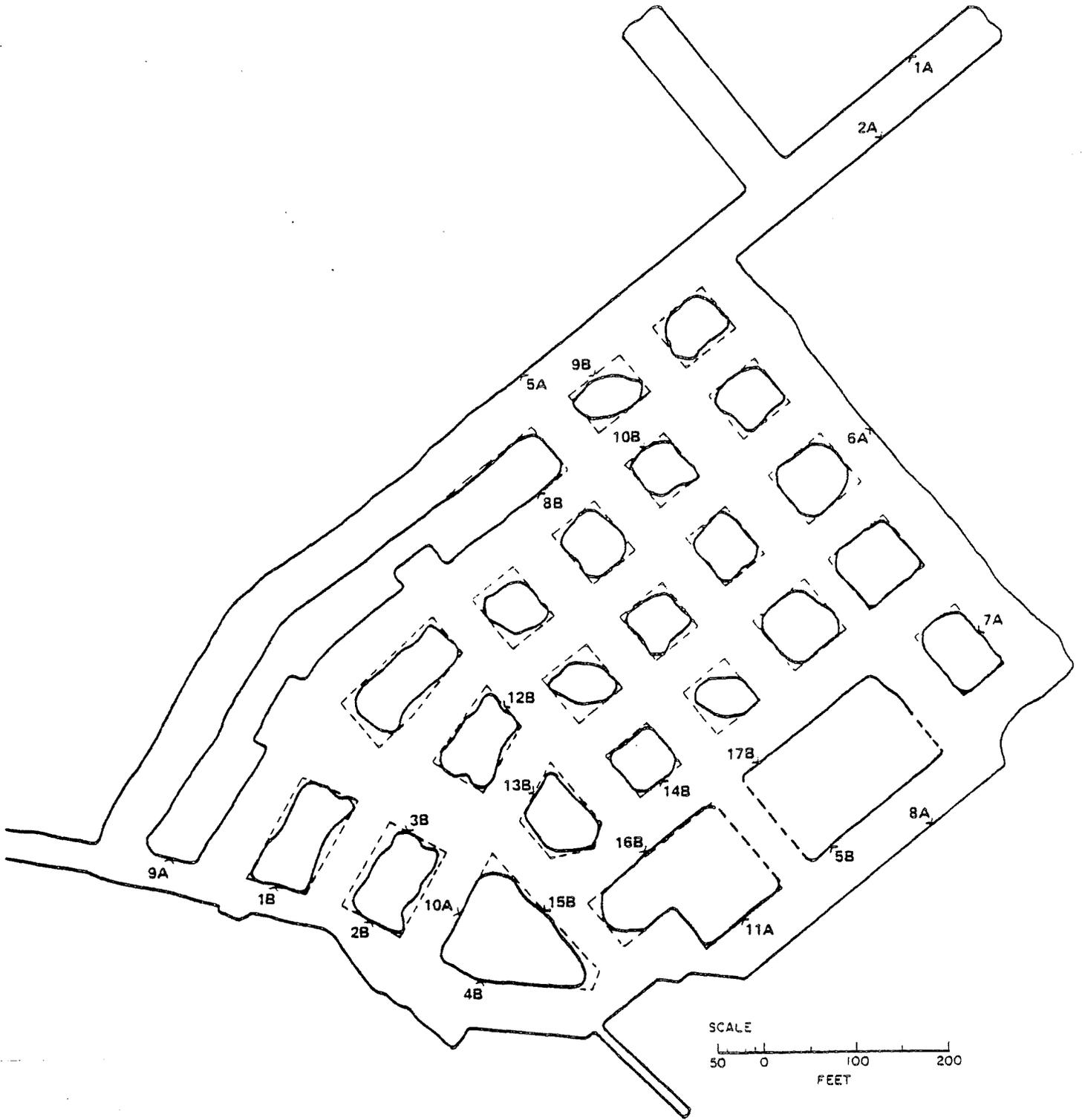
Figure 3.19   Sample Locations for Preliminary Program, Colony Mine: Series 122 and 222
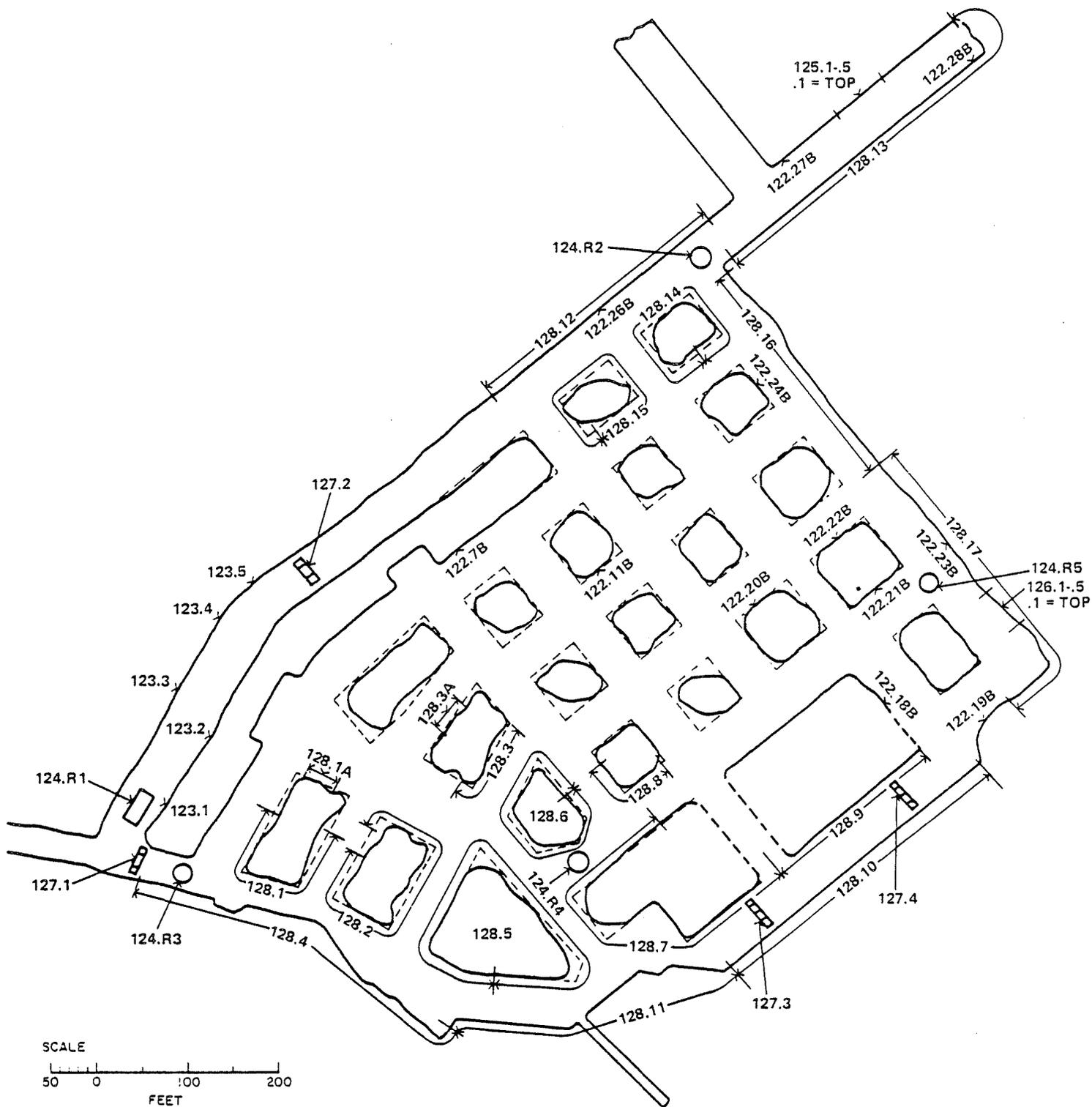
Figure 3.20 Sample Locations for Modification Number Two

the consistency of the results obtained by combining large numbers of samples (Series 122, 222, 128) as opposed to fewer and more location specific samples.

The volume of the Colony mine is approximately 19,300,000 cubic feet, covering about ten acres. The total surface area of the horizontal and vertical surfaces is about 1,200,000 ft^2. This area is too great to sample in detail.

In an effort to obtain basic data, the following sampling program was carried out.

- Dust loading on the rib of room one. This is a main haulageway through which more than 500,000 tons of shale were hauled. These five samples (Series 123), Table A.9, as expected, had a comparatively high dust load (.0172 gm/cm^2) and because the floor had been frequently graded and filled, had an assay of only 12.8 gpt. Only 30% of the dust collected was coarser than -40 mesh, indicating that road dust and the great distance from the face reduced the proportion of coarse fractions.

- Dust load on the mine roof samples (Series 124) Table A.9 covering a total area of 3,627 square feet were collected from five locations in the mine roof and had an average load of 0.0024 gm/cm^2, with an assay of 17.9 gpt. The mine roof is flat and quite smooth, and has relatively few places where dust will adhere.

- Dust load on the mine floor. This part of the program (Series 127) is an indicator only, of the dust load on a mine floor. Most haulageways will be covered with crushed shale, kept graded and moist. Other floor areas will often be wet and the dust load will be from sparse to heavy. The four samples, Table A.10, range in dust load from 0.3490 to 0.0576 gm/cm^2. The composite assay of the four samples is 16.0 gpt.

- Dust load on a rib 30 feet high. One 1,500 ft^2 area of a mine rib near a heading was sampled (Series 125), Table A.10, in five horizontal strips to check the size distribution and dust load near the most recently blasted area in the mine. It has been postulated that the heaviest concentrations of dust are to be found near actual faces, and that coarse and heavy dust loads in areas away from the face are continually reworked by air concussions from blasting, so as to drop out the coarser dust fractions and redistribute the finer dust fractions away from blasting operations. This theory has some support from these data which report a dust load of 0.0200 gm/cm^2.

- Dust load on a rib 60 feet high. One 1,250 ft^2 area of a pillar was sampled (Series 126, Table A.10) in five horizontal strips to check the dust load in one large area. The result, 0.0072 gm/cm^2, is well within the range of the average of the 35 random samples (Series 122, 222) and the strip samples (Series 128) which were 0.0060 and 0.0087 gm/cm^2, respectively.

- Horizontal band samples (Series 128, Table A.11). As stated earlier, none of the sample locations were selected because of surface texture. An examination of Tables A.9, A.10, and A.11 show that a horizontal band sample, collected at the mid-points of ribs and pillars over a large area of the mine, (without respect to surface texture) has the same relative range and average values as vertical strips over much of the same area. It is believed that these samples are quite representative of the dust loading on the vertical surfaces in the Colony mine. The band sample represents 6,332 ft^2 of surface, the random samples represent 6,920 ft^2 of surface.

- Validation of test sample collection procedures. Several checks of the efficiency of the vacuum were made. The most effective appeared to be spreading a weighed sample of -40 mesh dust on a smooth concrete floor, then weighing the dust recovered. One hundred percent of the dust was collected in the metal canister. The vacuum bag retained 97.4%. It was decided that recovering the small portion of the dust that went through the bag into the canister was too costly and time consuming to justify adding them to the sample. The effect of adding 2.6% to all of the samples is outside the accuracy of the results.

The foregoing data and information can be used to rank the potential dust hazard in the Colony mine, in terms of the airborne volatiles per cubic foot necessary to propagate an explosion. The pertinent data from tables 3.19, A.8, A.9, A.10, and A.11 are combined below to estimate the total amount of airborne dust that could be generated in the mine using nominal surface areas and volume:

Location	Area (ft^2)	Dust Load (oz/ft^2)	Dust (oz)
Mine roof	400,000	0.079	31,600
Mine floor	400,000	1.968*	787,200
Vertical surfaces	400,000	0.295	118,000
Total (mine volume = 19,300,000 ft^3)			936,800 = 0.0485 oz/ft^3

*Hartmann (1957) determined that dust on the floor contributes less to air explosion relative to it's volume than dust on roof and ribs.

The grade of the old dust in the Colony mine is about 20 gpt. Integrating a range of potential grades with the calculated airborne concentration (Figure 3.11 and the calculations following that figure), the explosive range of volatile combustibles is compared with those derived from the large scale experimental results of Richmond and Miller (1977) and other tests.

Grade (gpt)	Volatile Combustibles Conversion Factor	Volatile Combustibles in 0.0485 oz/ft^3 Dust (oz/f^3)	Equivalent Dust Load Density for 0.05 oz/ft^3 of Volatile Combustibles (oz/ft^3)
20	0.0826	0.0040	0.6053
25	0.1024	0.0050	0.4883
30	0.1222	0.0059	0.4092
35	0.1420	0.0069	0.3521

These comparisons of data with those from the one mine sampled so far indicates that the potential for explosions of oil shale dust in a mine may be very low.

3.2.5.3 Laboratory Program

A total of 55 samples were collected during the third phase of the program. These samples added to the 23 samples collected in Phase 2 and used for the Phase 3 study make up a total of 78 samples studied in Phase 3. The listing of the samples and their descriptions are given in Table A.12.

The samples were shipped to the Rocky Flats Research Center for the following analyses:

- Particle size distribution

- Modified Fischer assay (MFA)

- Organic carbon content

The analyses were used for determining the amount of -40 mesh dust in the mine and the richness (potential oil yield) of the dust.

For the purpose of this study, dust has been defined as material whose particle size is less than 40 mesh as measured on U.S. standard screens. Because of oversize material in the original 78 samples, it was necessary to screen the samples to obtain the -40 mesh material. The weight of this material was used to determine dust loading in the separate areas. Further screen analyses were then run on the -40 mesh material. The fractions determined were -40 + 100, -100 + 200, - 200 + 325 and -325 meshes. These screens were run to confirm or suggest appropriate adjustments in the "standard size distribution of oil shale dust" that was determined in Phase 2 of this study. The screen analyses on the samples largely substantiated the original size distribution. These analyses are presented in Table A.13.

As stated above, particle size distribution, MFA and organic carbon analyses were requested on selected dust samples; however, the quantity of some of the samples obtained was insufficient to run all the requested analyses, especially MFA. The primary purpose of modification number 2 was to determine the dust load in the mine. Time and cost restricted other analyses. Hence, MFA's were run only on specific samples. Organic carbon content correlates well with MFA; therefore, carbon analyses were run on the specified samples which were of insufficient quantity for MFA. Total and mineral carbon analyses were run since organic carbon in shale is determined as the difference between the total and mineral carbon in the shale. The MFA and carbon analyses are given in Table A.14.

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A linear regression was run on the samples analyses where both organic carbon and MFA had been run on a specific sample. The graph of the results is presented in Figure A.2. The linear regression line obtained in this study differs from that obtained for new mine dust.

3.3   Dust Explosivity

As previously discussed, dust explosivity is a complex subject. Three basic pieces of equipment have been developed by the Bureau to provide reproducible laboratory test results which are useful in providing comparisons of various carbonaceous dust but do not, of course, simulate the real world of underground dust explosions. These are the Godbert-Greenwald furnace and the steel Hartmann apparatus and lucite Hartmann apparatus. Detailed descriptions of the equipment and their use are presented in the next subsection. Presentation of the results of laboratory testing and discussions of the data then follow.

3.3.1   Apparatus and Laboratory Test Methods

The equipment used for the majority of dust testing consisted of the Godbert-Greenwald furnace, the lucite Hartmann, and the steel Hartmann. In general, the degree to which the test results using this equipment are representative of the "real-world" situation must be considered. As will be shown in the following subsections, the dust dispersion method raises questions as to the actual concentration at the time of dust ignition. The methodology used does not address parameters such as ambient pressure, temperature, and relative humidity. The equipment, as designed, makes no provisions to control these variables.

3.3.1.1 Godbert-Greenwald Furnace

The Godbert-Greenwald furnace, Figure 3.21, is used to determine the minimum ignition temperature at which a dust cloud will ignite. This furnace consists of a 1.438-inch diameter vertical alundum tube, nine inches long, wound with 21 feet of 18-gauge nichrome V wire. The windings are placed closer together toward the two ends than in the middle of the tube to obtain relatively even temperature throughout. The tube is mounted between two, 0.5-inch thick transite plates in a six-inch diameter sheet-metal cylinder with kieselguhr packing between the alundum tube and the sheet-metal shell. The top of the tube is connected by a glass adapter to a small brass chamber with a hinged lid for inserting the dust. A full-port solenoid valve between the dust chamber and a 500-milliliter air reservoir controls the air which disperses the dust. The air reservoir is connected to a hand-held bulb and a mercury manometer. Dust contained in the brass chamber is dispersed downward through the furnace by release of the compressed air in the reservoir. The pressure used for dispersion ranges from four to 20 inches of mercury, depending on the dispersibility of the material. Normally, 0.10 gram of dust is used in the test; however, the weight may be varied between 0.05 and 1.0 gram if the quantity affects the determination.

The temperature in the furnace is measured with a 22-gauge chromel-alumel thermocouple 0.031 inches from the furnace wall at mid-height. The furnace temperature at this point is maintained at the desired value by automatic control. Ignition is indicated by the appearance of flame below the mouth of the furnace. The ignition temperature is the minimum furnace temperature at which flame appears at the bottom of the furnace in one or more trials in a group of four. The smallest practical increment of temperature is 5°C; the highest temperature attained in the furnace is 1,000°C, (Dorsett et al, 1960).
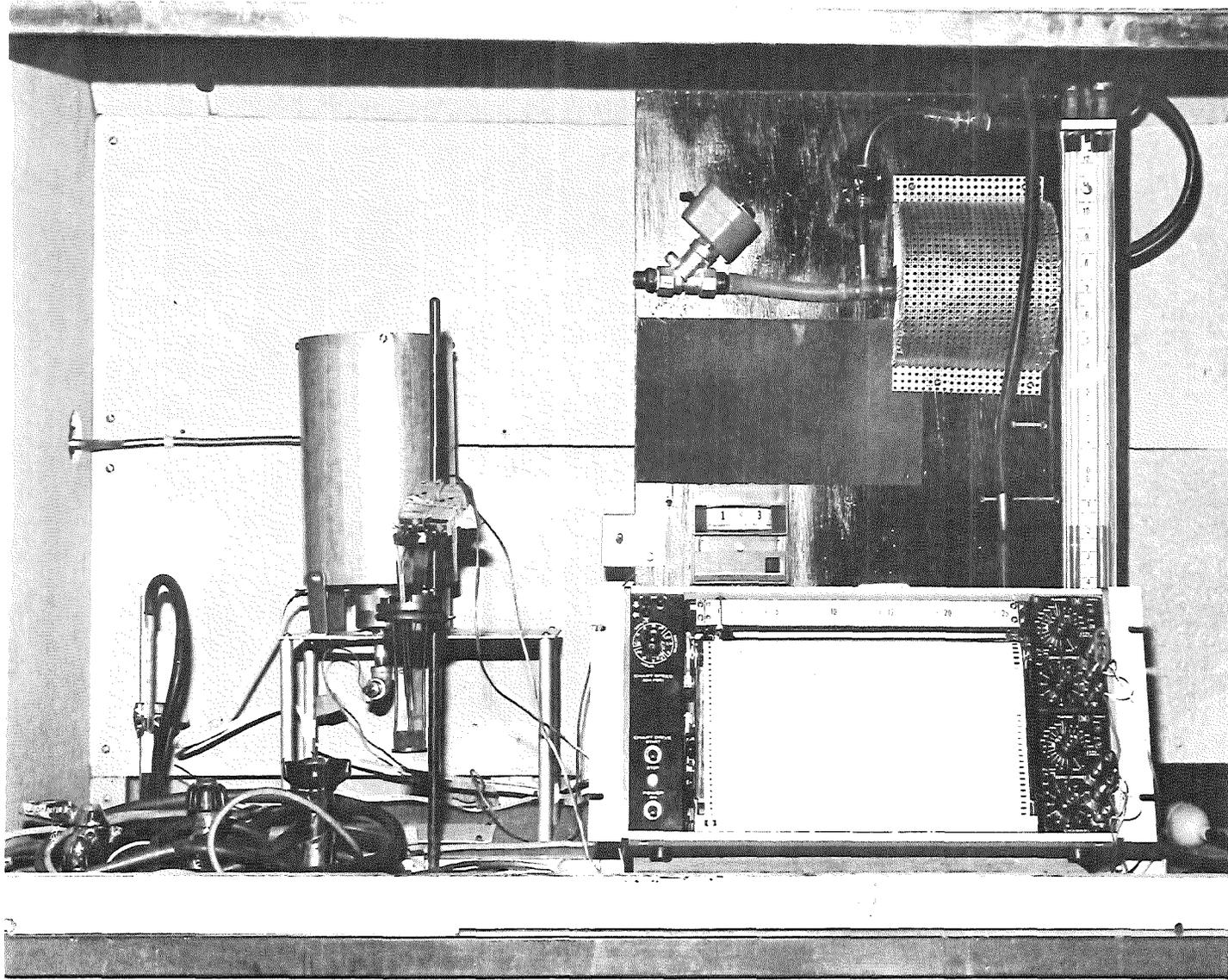
Figure 3.21 Godbert-Greenwald Furnace Apparatus

Additional data may be obtained by monitoring the intensity of the light from a He-Ne laser which passes through the dust cloud in the glass adapter. A particle density changes in this area may be observed before, during and after the dust explosion. A photoelectric detector may be placed to view the interior of the furnace to monitor the flash, if any, which is produced by the combustion. Both density variations and flash production outputs may be photographed from the screen of an oscilloscope for analysis.

3.3.1.2 Lucite Hartmann Apparatus

The minimum electrical energy required to ignite a dust cloud is determined in the lucite Hartmann apparatus (Figure 3.22). This equipment consists of a vertically mounted, 2.75-inch diameter combustion tube, 12 inches long and the auxiliary equipment to produce a dust dispersion. The tube, made of lucite, is attached to a cylindrical metal base by hinged bolts. The cup in the top surface of the base is machined to a somewhat hemispherical shape. The total volume of the chamber is 75 cubic inches. Dispersion is accomplished by the sudden release of air from an 80-cubic inch reservoir. The air flow, controlled by a 0.5-inch, full-port solenoid valve, passes into the chamber and impinges on a mushroom-like deflector which deflects the stream to sweep across the bottom of the dispersion cup. Optimum air pressure in the reservoir, determined by trial, ranges from 5 to 15 pounds per square inch gauge (psig). The quantity of dust in the cup ranges from 5 to 10 times the minimum explosive concentration. The top of the tube is covered with a filter-paper diaphragm which is pierced by a 1/8-inch hole and retained by a locking ring.

The igniting spark passes between pointed 20-gauge tungsten electrodes normally 0.25 inches apart. Preliminary trials are made by varying the electrode separation between 0.063 and 0.5 inches to determine whether the

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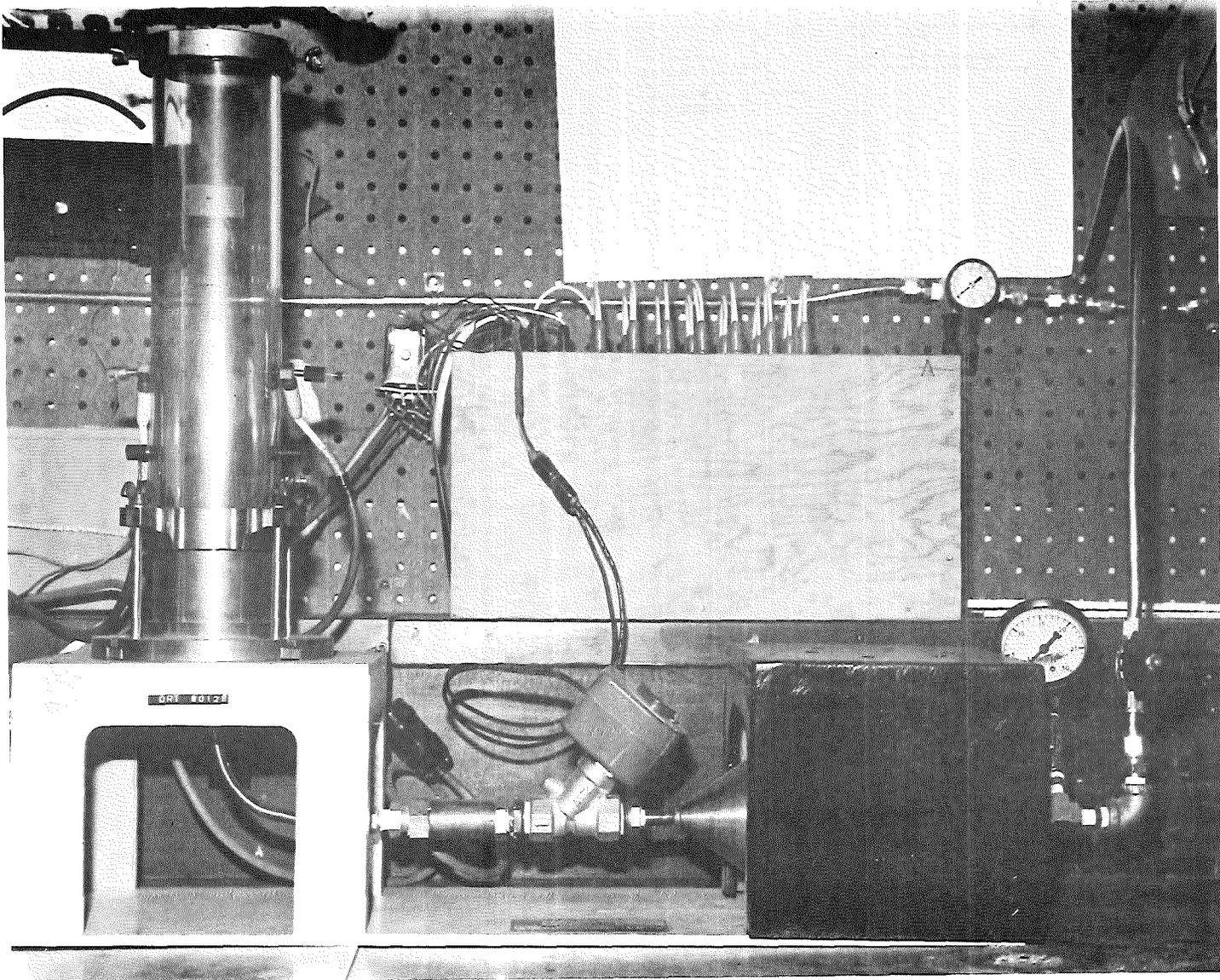
Figure 3.22   Lucite Hartmann Apparatus

distance affects the value of minimum energy. These electrodes are located at a distance of 2 inches and 4 inches above the base of the tube. The ignition spark is obtained by the discharging of oil-impregnated, paper-dielectric condensers with a capacitance range from two to 100 microfarads, which have been charged to a potential between 100 and 400 volts through a luminous tube transformer. An electronic timer, with adjustable delay, controls the spark discharge initiation and its duration during dust dispersal.

The spark energy is calculated as $0.5CV^2$, where C is the capacitance of the condensers in farads, and V is the charging potential in volts. The minimum energy for ignition of the dust cloud is the least energy required to produce flame propagation for a distance of four inches or more in the tube. At low energy values (five to 50 millijoules) the incremental capacitance is one microfarad; at higher energy values the increment is four microfarads. Four trials are made at each capacitance; however, if the dust ignites in the initial trials, lower energy is tried until a minimum is determined. The value of the minimum ignition energy obtained is only an approximation because some electrical energy is dissipated in the transformer circuit and some remains stored in the condenser. For this reason, relative rather than absolute values of energy are obtained.

The minimum explosive concentration of a dust is also determined in the Hartmann apparatus, except that a continuous induction spark source is used instead of the timed condenser discharge spark. This spark is created by supplying power to the luminous tube transformer from the 60 cycle, 118 volt power line and adjusting the secondary current to 23.5 milliamps. A weighed amount of dust is spread in a thin layer in the dispersion cup. The top of the Hartmann tube (lucite) is covered with a filter paper diaphragm held in place by a locking ring. A 0.063-inch hole is made in the center of the

filter paper to prevent pressure buildup from the dispersing air and the tungsten electrodes are adjusted to a gap length of 0.188-inch. The electric spark is struck and the dust cloud is formed in the lucite tube by releasing air from the reservoir; the air pressure usually ranges from five to 15 psig and is determined in preliminary trials.

Following ignition of the dust, sufficient pressure must develop to burst the filter-paper diaphragm; appearance of flame in the tube is not considered propagation. The pressure required to burst the paper diaphragm is about two to three psig, depending on the rate of pressure rise. If propagation occurs for a given weight of dust, the weight is reduced by a five-milligram increment and another trial made until a quantity is obtained which fails to propagate flame in any of four successive trials. The lowest weight at which flame propagates determines the minimum concentration. Tests are made with the electrodes two and four inches from the bottom of the tube. The average of the two weights is divided by the volume of the tube (75 cubic inches) for the value of the minimum concentration.

3.3.1.3 Steel Hartmann Apparatus

Pressure and rates of pressure rise developed by a dust explosion are determined in a closed steel Hartmann tube (Figure 3.23). Dust dispersion is accomplished by releasing air from a three cubic inch reservoir at 100 psig. The maximum pressure that can develop in the explosion tube from the dispersing air alone is 6.5 psig; however, because of rapid development of the dust explosion, the pressure from the dispersing air at the time of ignition is generally two to three psig. A full-port solenoid valve controls admission of the dispersing air and a check valve prevents the combustion
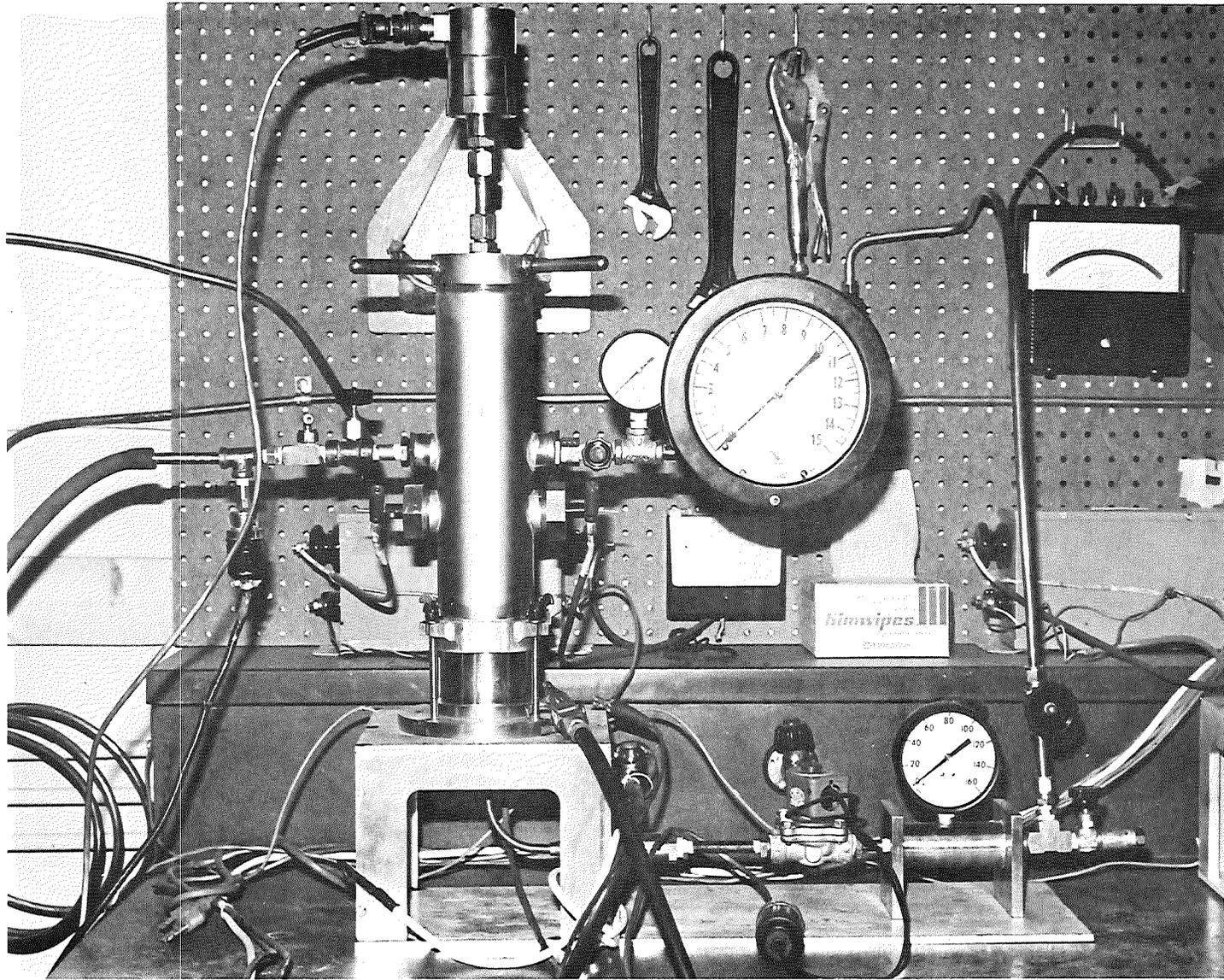
Figure 3.23 Steel Hartmann Aparatus

gases from flowing back into the dispersion reservoir. Ignition of the dust cloud is normally produced by a 23.5 milliampere continuous spark source identical to that used with the lucite Hartmann apparatus.

The explosion pressure is measured by an electronic transducer. The maximum pressure and the average and maximum rates of pressure rise developed in the explosion are determined from pressure-time record. The dispersion pressure (initial pressure in the tube at time of ignition) is subtracted from the peak explosion pressure to give a corrected maximum pressure. The average rate is obtained by dividing the maximum pressure by the time interval between ignition of the dust cloud and the occurrence of the maximum pressure. The maximum rate is the steepest slope of the pressure-time curve. Normally, explosion tests are made at dust concentrations of 0.10, 0.20, 0.50, 1.00, and 2.00 oz/ft^3.

3.3.2   Results of Dust Explosivity Testing

The Godbert-Greenwald furnace and lucite and steel Hartmann apparatus were fabricated by an outside contractor following the Bureau's blueprints. Upon receipt of the equipment certain modifications had to be made to improve operability and to correct manufacturing errors.

When the initial equipment set-up problems were solved, lycopodium and cellulose acetate powders were used as calibration materials. Results, when compared with the Bureau's data, were useful as a means of detecting some basic problems inherent in the test apparatus which became even more apparent as the calibration process continued.

Modification of the steel Hartmann became necessary because the data obtained were quite erratic. The original observation window fittings were modified to connect a vacuum pump for the extraction of ambient Denver

atmosphere. This ambient air was then replaced with air from a cylinder of compressed gas of a known composition. After this change in procedure, cellulose acetate data appeared consistent with the Bureau's results, and oil shale testing was begun. Lycopodium, cellulose acetate, and Pittsburgh seam coal were tested for comparison with Bureau data. These comparisons are presented in Table 3.20. Preliminary shale testing provided no justification for handling shale samples under an inert atmosphere and as a result, all samples tested were ground in air and desiccated for 48 hours as outlined in RI 5624 (Dorsett et al, 1960).

A dust testing program matrix became the basis of data reporting. By progressing across the testing matrix, from richer to leaner shales, it was expected that testing boundaries could be determined without examining all of the leaner fractions.

Preliminary testing was done in the lucite Hartmann to visualize the dust cloud dispersion and to determine whether the spark discharge occurred at the proper time. A high-speed movie film (500 frames per second) of the reservoir dumping reveals the inhomogeniety of the dust cloud. Evidently a nominal concentration based on total mass per total volume of the container is meaningless. Using the same film, a plot of the leading edge of the dispersed coal with time is presented in Figure 3.24. It can readily be seen that the coal front reaches the electrode gap approximately 30 milliseconds after dumping the air reservoir. Coal of -40+60 mesh takes 60 milliseconds to reach the electrodes.

Numerous tests were conducted in the Godbert-Greenwald furnace and lucite Hartmann apparatus to determine the statistical reproducibility of the results. Results of the tests are presented in tables A.15, A.16, and A.17 of Appendix A.

Table 3.20

Data Comparison

		Minimum Temp.(°C)	Minimum Conc.(g/l)	Minimum Energy (J)	Maximum Press(psi)	dp/dt (psi/sec)
Cellulose Acetate	Bur Mines	470	0.045	0.025	115	2400
		400	0.040	0.050	98	1500
	Tosco/DRI	455	0.033	0.044	94	2750
Lycopodium	Bur Mines	480	0.025	0.040	75	1500
	Tosco/DRI	490	0.022	0.045	76	3810
Pittsburgh Seam Coal	Bur Mines	610	0.055	0.060	68	1200
	Tosco/DRI	620	0.070	0.060	67	1105
Corn Starch*	Bur Mines	380	0.055	0.04	51	800
		390	0.045	0.04	99	1900
	Tosco/DRI	460	0.037	0.36	57	2306

*The corn starch agglomerated badly, even after desiccation; consequently it is not felt these data points are relevant.
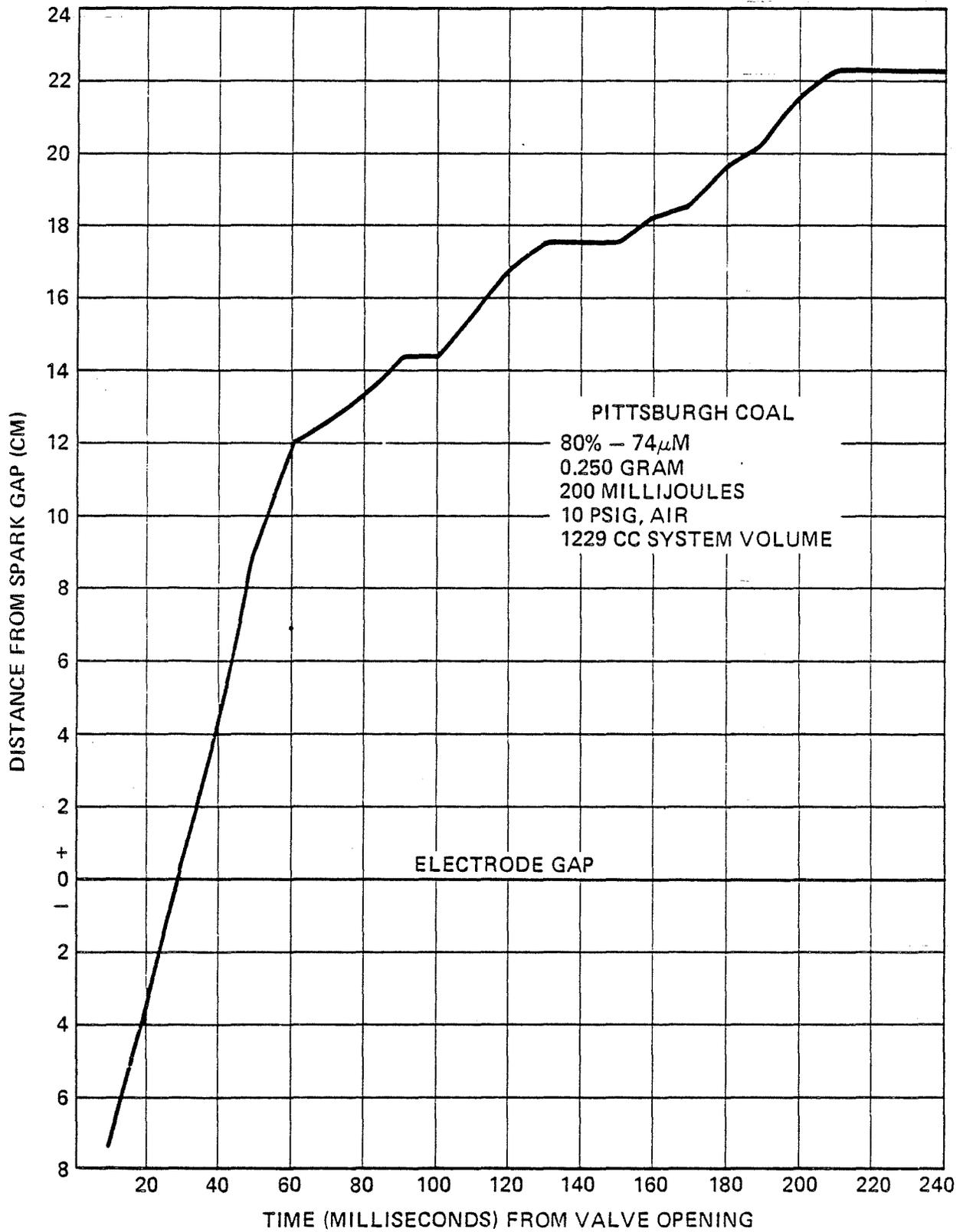
Figure 3.24   Leading Edge of Dispersed Coal vs. Time

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3.3.2.1 Minimum Dust Cloud Concentration

Oil shales of various grades were tested using the lucite Hartmann. The results of these tests are presented in Table 3.21. In no case was there ignition of the oil shale dusts observed.

In an attempt to achieve a more uniform dust dispersion, the reservoir pressure was increased to 25 psig (well outside the pressure called for in RI 5624). Selection of 25 psig was rather arbitrary, and based to some extent on the reservoir strength. Numerous tests were made with and without dust (no spark) to assure that the pressure pulse would not rupture the filter paper cap on the lucite Hartmann. Results of the higher pressure tests are presented in Table 3.22. The matrix was not completed because of time and the fact that the 25 psig reservoir pressure tests were outside the original scope of work.

3.3.2.2 Minimum Dust Cloud Ignition Energy

Using the lucite Hartmann apparatus, the minimum ignition energy (following RI 5624 procedures, e.g., 5-15 psig) was investigated. The results of these tests are outlined in Table 3.23. Again, as in the previous section, it was necessary to increase the reservoir pressure to 25 psig to obtain positive results. The data are tabulated in Table 3.24.

3.3.2.3 Minimum Dust Cloud Ignition Temperature

Using the Godbert-Greenwald furnace, the minimum ignition temperatures of all samples were determined. The results are presented in Table 3.25.

3.3.2.4 Maximum Pressure and Rate of Pressure Rise

Several higher grade oil shale samples were run in the steel Hartmann, however no explosions were observed. The oil shale, in all cases, failed to

Table 3.21

Minimum Concentration at 5 to 15 psig, Grams/Liter

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples Nominal Richness							Colony Mine Dust	8x8 Foot Drift		Spent Shale
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT		New Dust	Old Dust	
As Prod.	−40	(1)	(1)	(4)	(6)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
F R A C T I O N S	−40+100	(1)	(1)	(3)	(1)	(2)	(2)	(1)	(2)	(2)	(2)	(2)
	−100+200	(1)	(1)	(3)	(1)	(7)	(2)	(2)	(2)	(2)	(2)	(2)
	−200+325	(1)	(1)	(4)	(5)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
	−325	(1)	(1)	(4)	(1)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
Recon. Std. Size	−40	(1)	(2)	(4)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)

(1) No ignition at concentrations up to 4 grams/liter.
(2)   "   2   "
(3)   "   8   "
(4)   "   0.9   "
(5)   "   2.4   "
(6)   "   3.25   "
(7)   "   1.2   "

Table 3.22

Minimum Concentration at 25 psig, Grams/Liter

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples Nominal Richness							Colony Mine Dust	8x8 Foot Drift		Spent Shale
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT		New Dust	Old Dust	
As Prod.	-40					0.203	0.198	0.105	0.079	0.099	0.039	
F R A C T I O N S	-40+100					0.118						
	-100+200							1.096			1.310	
	-200+325					0.982	0.527	0.370	0.536	0.216	1.002	
	-325	0.087	0.087	0.057	0.045	0.061	0.076	0.063 0.043			0.071	0.041
Recon. Std. Size	-40	0.104	0.106	0.063	0.047	0.071 0.087	0.075	0.052 0.041	0.080 0.063	0.073 0.073	0.047 0.091	0.106

Table 3.23

Minimum Dust Cloud Ignition Energy at 5 to 15 psig (Joules)

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples Nominal Richness							Colony Mine Dust	8x8 Foot Drift New Dust	Old Dust	Spent Shale
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT				
As Prod.	-40								(1)	(1)		
F R A C T I O N S	-40+100							(1)				
	-100+200						(1)					
	-200+325				(1)	(2)			(1)	(1)		
	-325							(1)				
Recon. Std. Size	-40					(1)	(1)	(1)	(1)	(1)		

(1) Minimum ignition energy greater than 8 joules.

(2) At a dust loading 20 times minimum concentration.

Table 3.24

Minimum Dust Cloud Ignition Energy at 25 psig (Joules)

| Sample Type | Mesh Size (US) | Graded Series Oil Shale Test Samples Nominal Richness | | | | | | | Colony Mine Dust | 8x8 Foot Drift | | Spent Shale |
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT		New Dust	Old Dust	
As Prod.	-40					8.0	4.0	0.96	(1)	0.210	(1)	
F R A C T I O N S	-40+100											
	-100+200							0.215			0.355	
	-200+325					4.8	1.2	0.100	(1)	0.080	(1)	
	-325							(1)				
Recon. Std. Size	-40					(1)	(1)	(1)	(1)	0.420	(1)	

(1) Minimum ignition energy greater than 8 joules.

Table 3.25

Minimum Dust Cloud Ignition Temperature (°C)

Sample Type	Mesh Size (US)	Graded Series Oil Shale Test Samples Nominal Richness							Colony Colony Mine Dust	8x8 Foot Drift		Spent Shale
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT		New Dust	Old Dust	
As Prod.	-40	630	635	615	595	590	575	585	535	515	520	*
F R A C T I O N S	-40+100	730	*	720	*	740	*	*	*	*	*	*
	-100+200	655	660	630	620	635	590	605	580	560	580	*
	-200+325	620	595	570	585	565	550	560	550	495	520	*
	-325	620	610	600	560	530	550	560	515	475	590	*
Recon. Std. Size	-40	630	615	595	595	565	560	580	546	505	520	*

*Greater than 800°C

exhibit any pressure rise attributable to deflagration (slow burning). As a result of these negative tests, if the sample indicated no ignition in the lucite apparatus at RI 5624 conditions, it was not tested in the steel chamber.

3.3.3   Discussion of Dust Explosivity Testing

3.3.3.1 Minimum Dust Cloud Concentration

Table 3.26 presents correlation coefficients for minimum dust concentration from the lucite Hartmann vs. Fischer assay and organic carbon contents. Some correlation is evident, indicating only that minimum dust concentration appeared to decrease with increasing oil shale richness. The appropriate graphs are in Appendix A, on figures A.3 and A.4. Additional tests are needed to establish the degree of statistical significance and correlation.

3.3.3.2 Minimum Dust Cloud Ignition Energy

Little data were obtained for minimum ignition energies. Figure 3.25 presents a plot of minimum ignition energy versus Fischer assay for the graded series, showing a decrease in minimum ignition energy with increasing richness.

3.3.3.3 Minimum Dust Cloud Ignition Temperature

Correlations were made among many factors during initial assessment of the data. Table 3.27 shows the correlation coefficients between the minimum ignition temperatures and various assays. The data points used included only the graded series. Fair correlation is seen with Fischer assay and organic carbon. The lack of data in the -40+100 mesh series is due to the

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Table 3.26

Correlation of Minimum Explosive Concentration
With Fischer Assay Oil Yield and Organic Carbon Content
Graded Series Samples in Lucite Hartmann at 25 psig

Mesh Size (US)	Fischer Assay Oil Yield Correl. Coeff./No. Samples	Organic Carbon Correl. Coeff./No. Samples
-325	-0.52/7	-0.61/7
-40 Recon. Std. Size	-0.70/7	-0.70/7
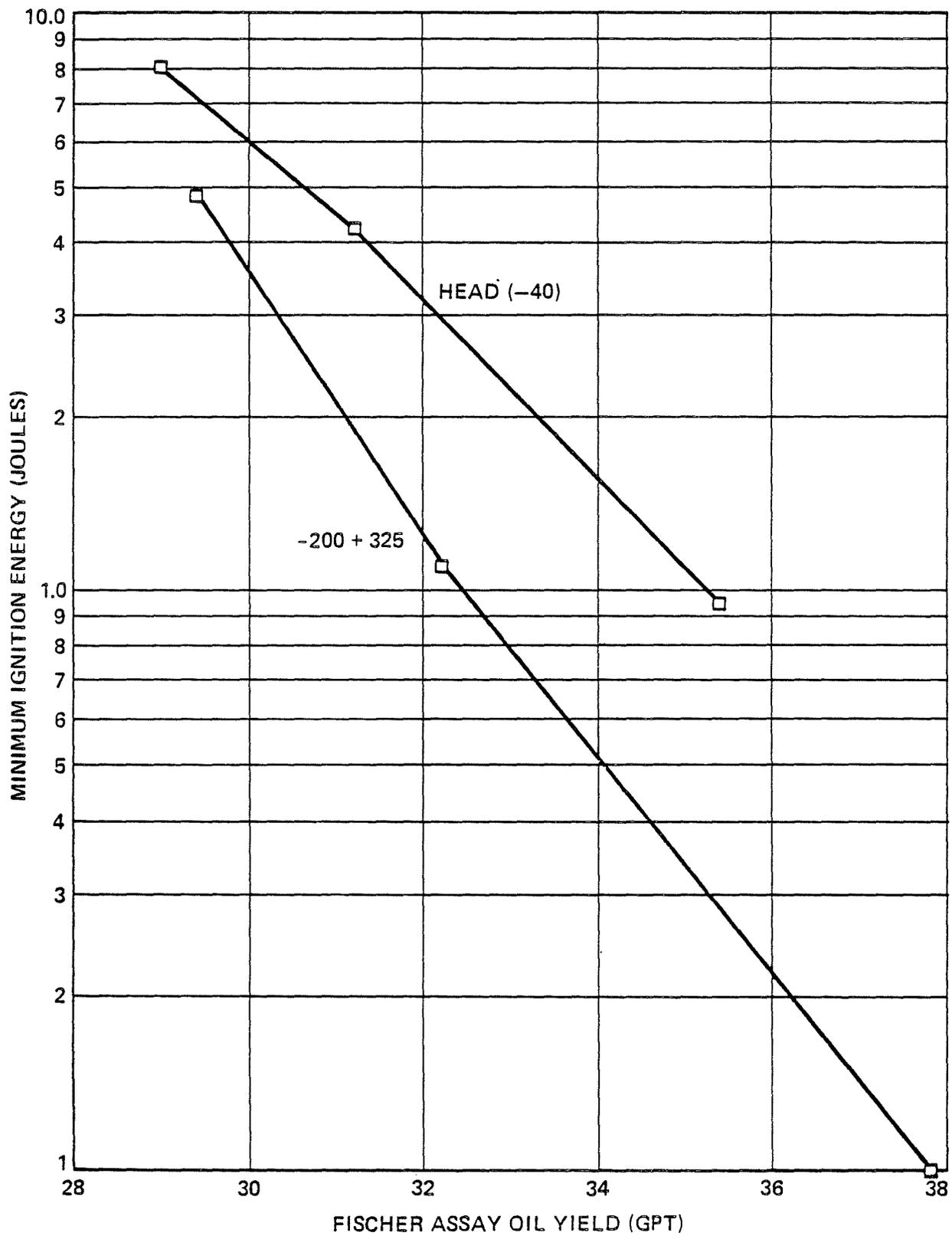
Figure 3.25 Minimum Dust Ignition Energy at 25 psig vs. Fischer Assay for
Graded Series Samples (Lucite Hartmann Apparatus)

Table 3.27

Correlation of Minimum Dust Cloud Ignition Temperature
with Oil Shale Properties, Grades Series Samples

Mesh Size (US)	Fischer Assay Oil Yield Correl. Coeff./No. Samples	Organic Carbon Correl. Coeff./No. Samples
-40 Head	-0.95/7	-0.95/7
-100 +200	-0.86/7	-0.85/7
-200 +325	-0.87/7	-0.88/7
-325	-0.87/7	-0.93/7
-40 Recon. Std. Size	-0.89/7	-0.93/7

temperature limitation of the Godbert-Greenwald furnace; test could not be made at temperatures above 800° C.

Figure 3.26 presents the correlation of Fischer assay with minimum ignition temperature of the graded series. It can be seen that the correlation is good (figures A.5 through A.9 of Appendix A present individual graphs of the data contained in Figure 3.26). Figure 3.27 presents the ignition temperature vs. Fischer assay for the mine dusts. No correlation coefficients are presented because only three data points were used; however, a general trend of decreasing minimum ignition temperature with increasing richness is evident.

Two additional correlations were made of minimum ignition temperature vs. total hydrocarbon content and total combustion energy. These are presented in figures 3.28 and 3.29, respectively, showing that minimum ignition temperature decreases as the amount of Fischer assay hydrocarbon evolution increases. Again, reasonable correlation is seen for the reconstituted standard size series.

3.3.3.4 Explosivity Index

An ignition sensitivity index can be determined by:

$$I.S. = \frac{(\text{Conc.})_{min} \ (\text{Energy})_{min} \ (\text{Temp})_{min}}{(\text{Conc.})_{min} \ (\text{Energy})_{min} \ (\text{Temp})_{min}} \left[\frac{\text{Sample}}{\text{Pittsburgh Coal}} \right]$$

An explosive severity index can be determined by:

$$E.S. = \frac{(\text{P})_{max} \ (dp/dt)}{(\text{P})_{max} \ (dp/dt)} \left[\frac{\text{Pittsburgh Coal}}{\text{Sample}} \right]$$

It is evident that if Pittsburgh seam coal is taken as a standard then both the I.S. and E.S. have a value of 1.0.

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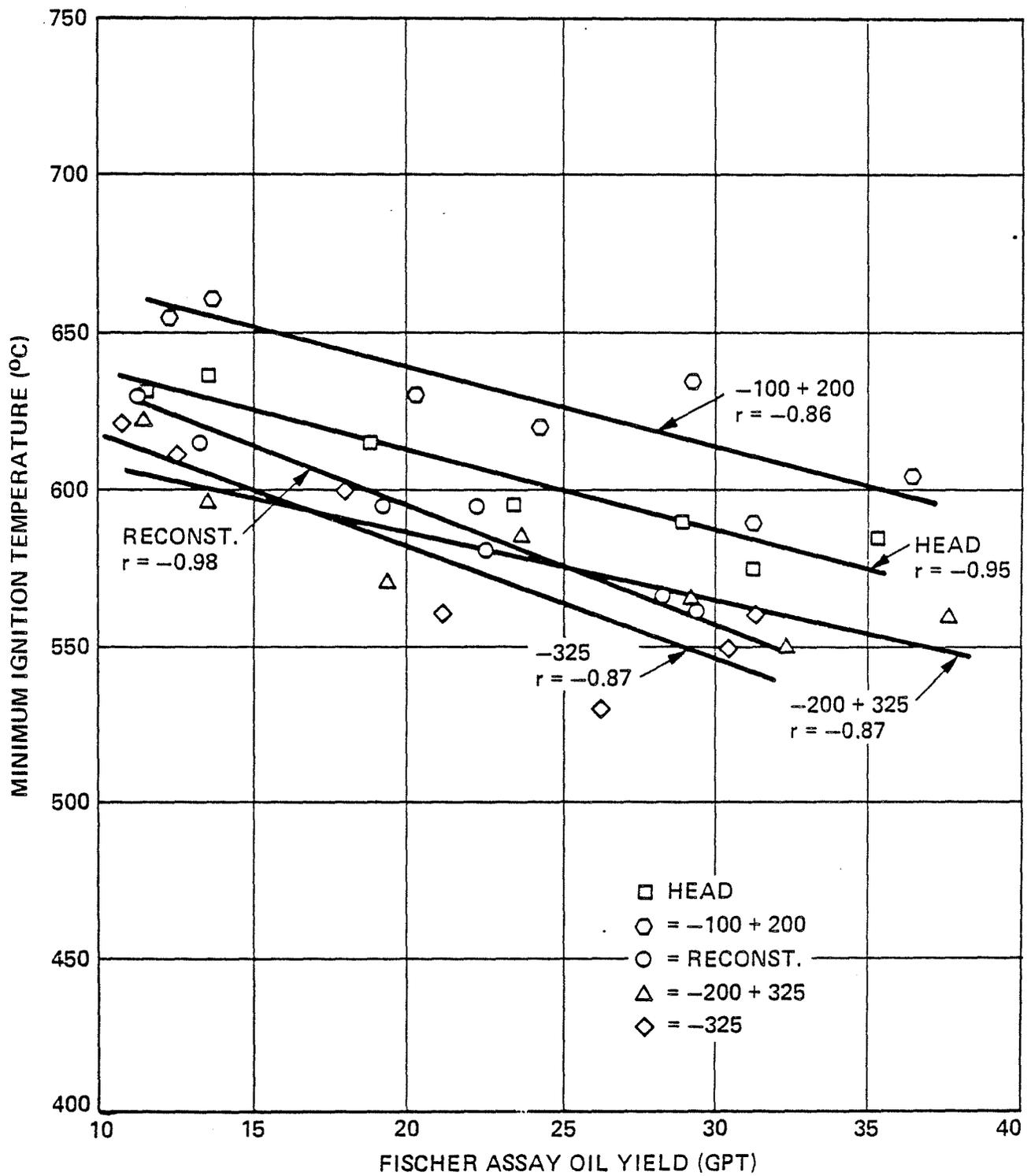
Figure 3.26   Minimum Dust Ignition Temperature vs. Fischer Assay For Graded
Series Samples (Godbert-Greenwald Furnace)
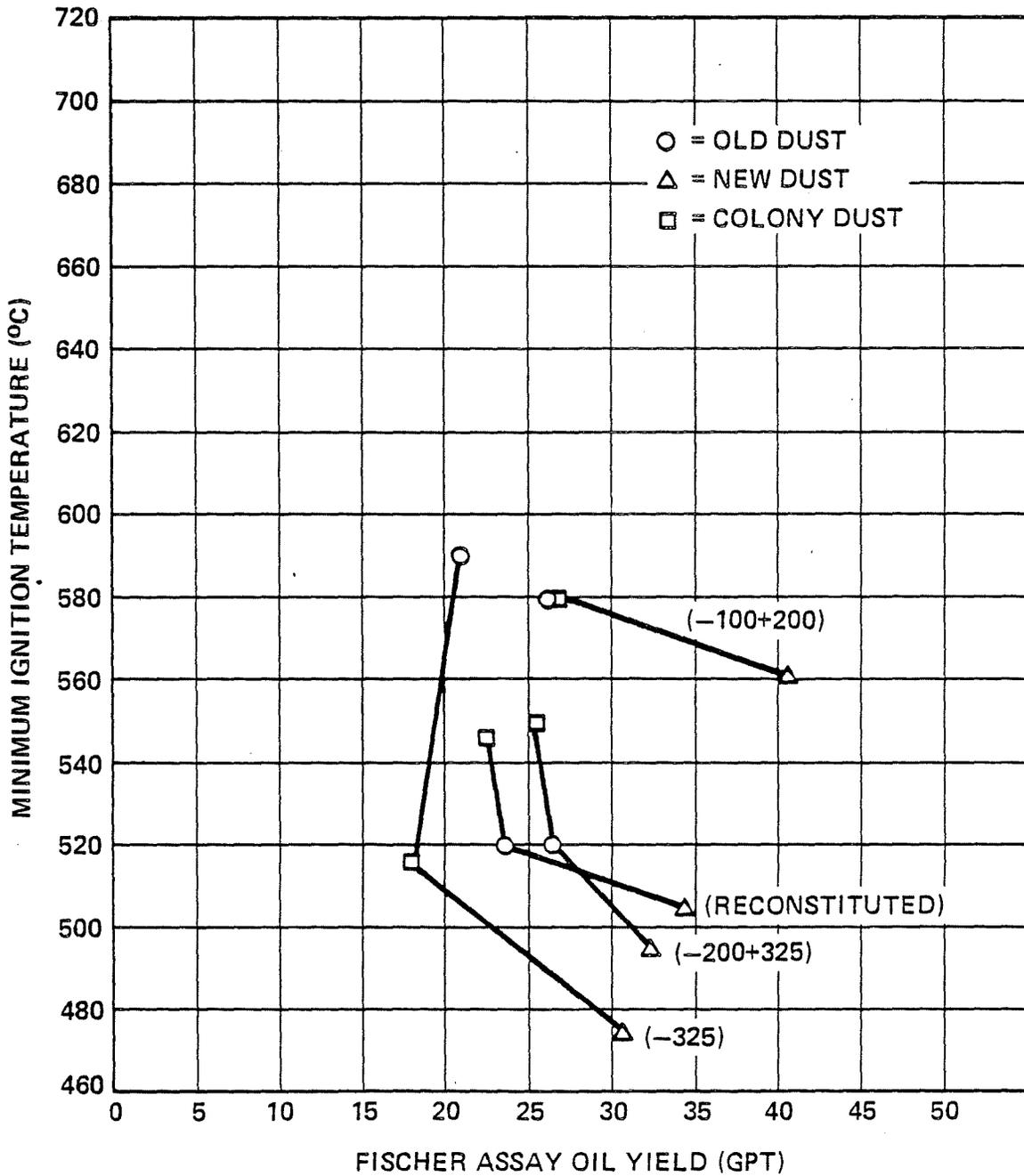
Figure 3.27 Minimum Dust Ignition Temperature vs. Fischer Assay For Mine
Dusts (Godbert-Greenwald Furnace)
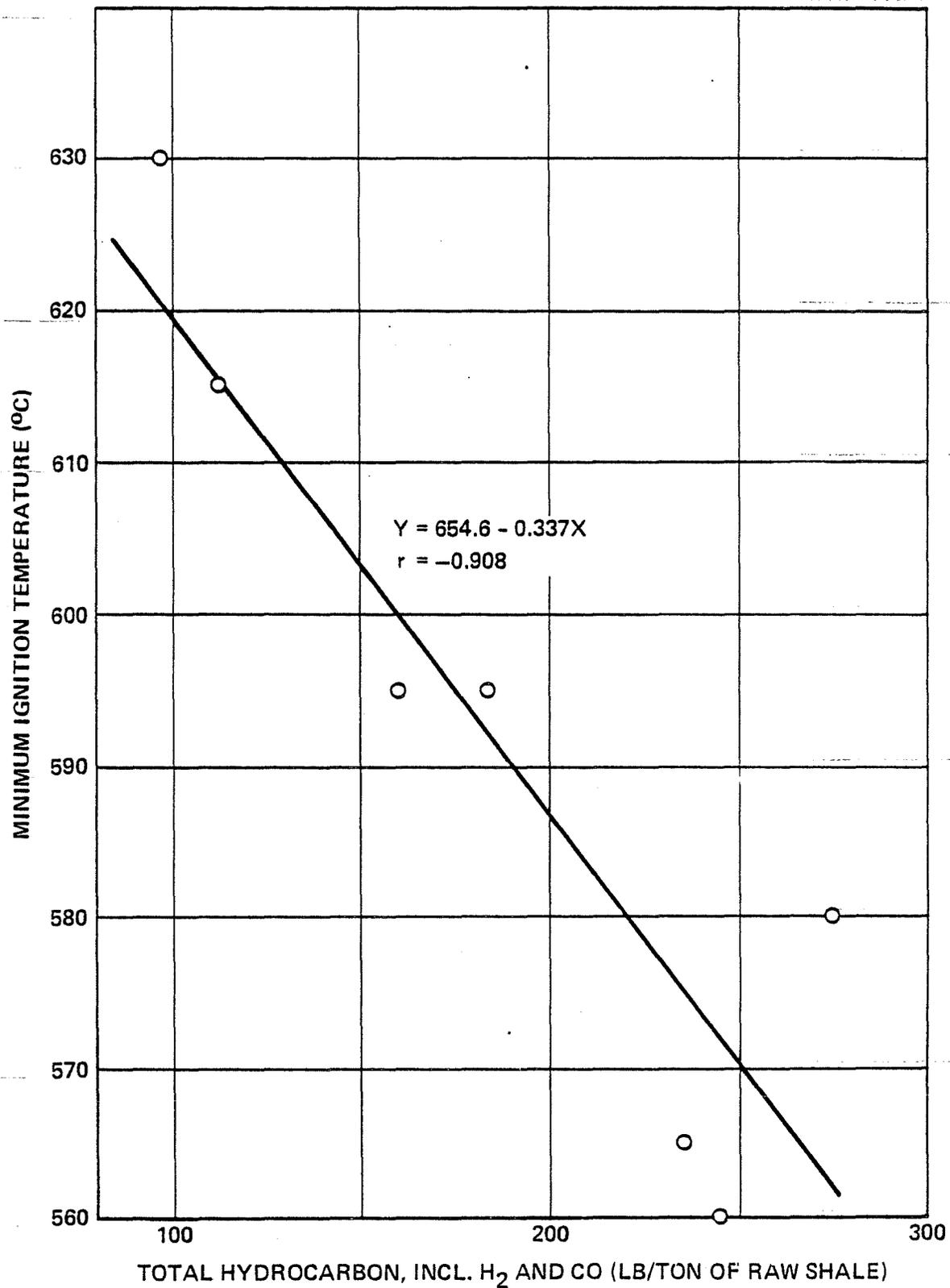
Figure 3.28 Minimum Ignition Temperature vs. Total Hydrocarbon Yield, Reconstituted Standard Size Samples
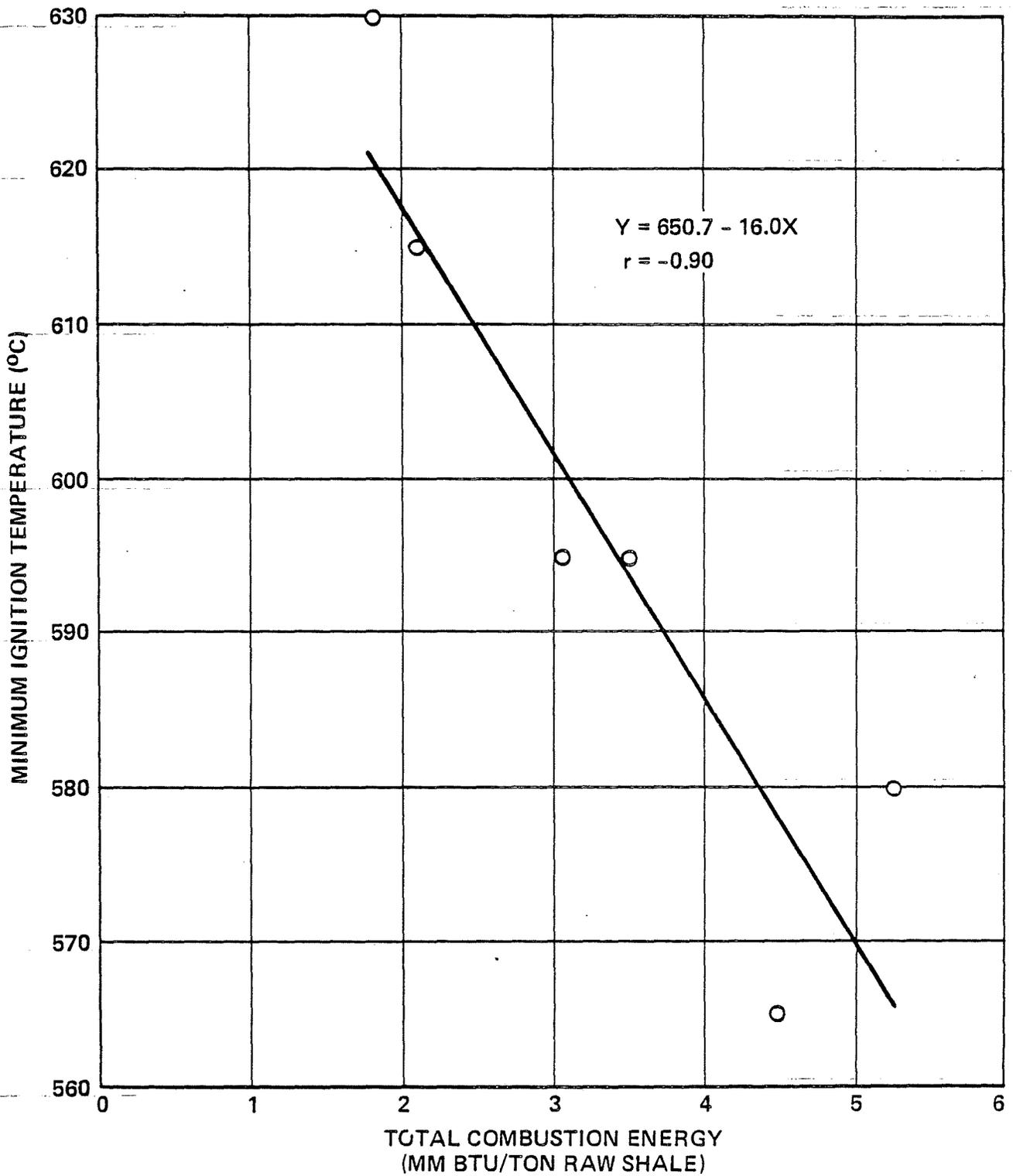
Figure 3.29 Minimum Dust Ignition Temperature vs. Total Combustion Energy
For Reconstituted Standard Size Samples

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When the I.S. and E.S. are multiplied together, an arbitrary explosivity index is obtained and is used for comparing the relative explosivity of a dust to Pittsburgh seam coal. The following indicates how these indices may be related to a subjective description of the hazard (Nagy et al, 1965).

Explosive Hazard Adjective Rating	Ignition Sensitivity Index	Explosion Severity Index	Explosibility Index
Weak	<0.2	<0.5	<0.1
Moderate	0.2 - 1.0	0.5 - 1.0	0.1 - 1.0
Strong	1.0 - 5.0	1.0 - 2.0	1.0 - 1.0
Severe	>5.0	>2.0	>10

Using the data obtained in the laboratory, oil shale dusts gave an explosivity index of approximately 0.0001. A comparison of explosivity indices for several materials is presented in Table 3.28.

3.3.3.5 General Comments on Dust Explosivity

Following the RI 5624 procedures, e.g., 5-15 psig reservoir pressure, no defined ignition was seen, that is, the filter paper disc was not ruptured. It must be pointed out that in several instances minor flaming was noted, but the flame did not propagate. This raises a question as to whether the size of the apparatus is causing some quenching. Appendix C contains a description of hydrocarbon explosion theory that describes the deflagration to detonation phenomenon.

Operating outside the RI 5624 pressure regime, i.e., 25 psig, oil shale dusts did ignite and propagate. While there certainly was a minor increase in oxidizer (air), it is felt that ignition resulted from a more homogeneous dispersion of the dust. A critical review of the apparatus and testing methods is presented in Appendix C.

Table 3.28

Comparison of Explosivity Indices

Gilsonite	>10
Lignite	$1.8 - >10$
Lycopodium	6.72
Cellulose Acetate	2.61
Pittsburgh Seam Coal	1.0
Carbon Black	$\ll 0.1$
Coke	$\ll 0.1$
Graphite	$\ll 0.1$
Oil Shale	~ 0.0001

In general, it appears that oil shale dust is not explosive within the limits defined by RI 5624. Oil shale dust was explosive only when the RI 5624 specified reservoir pressures were exceeded.

The effects of particle size on ignition and explosivity properties are rather pronounced. Examination of data in Table 3.22 show that, in general, when nominal Fischer assay oil yield is fixed, the minimum concentration required for ignition decreases as the particle size decreases. Data in Table 3.25 show fairly conclusively that the minimum ignition temperature in the Godbert-Greenwald furnace decreases with decreasing particle size of the test oil shale when nominal Fischer assay yields are maintained constant.

3.4   Methane Addition to Oil Shale Dust

The steel Hartmann closed bomb (initially decribed in Section 3.3) was used for methane addition testing. A modification to the Hartmann was made to permit evacuation of the air supply tube to ensure that accurate gas mixture compositions whould be created.

A reservoir solenoid was connected to an externally controlled 118 volt, 60 Hz line with the power off. A 0.616 gram sample of oil shale dust (0.5 g/1) was placed in the chamber and the apparatus assembled. All compressed air feed line and vacuum line valves were closed. The solenoid was actuated to the open position and methane added to the entire system until a low pressure gage indicated 5.5 psi. Following this the entire system was pressurized with air to 100 psig and the solenoid closed. The steel tube was then slowly vented until the internal pressure reached Denver ambient, approximately 650 torr.

This procedure resulted in the steel Hartmann tube and the 100 psig reservoir containing a 5% methane/air mixture at ambient pressure. Several

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tests were conducted on -200+325 mesh 35 gpt shale in this atmosphere. For comparison, tests were run with 5% methane/air alone, oil shale alone, an explosive mixture of methane/air (7%), Pittsburgh seam coal, and lycopodium.

3.4.1   Results of Methane Addition Tests

Figure 3.30 shows the pressure-time histories of oil shale, 5% and 7% methane/air mixtures alone, and that of combined oil shale and 5% methane/air mixture. The initial pressure rise of a few psi is the result of the reservoir dumping and is seen in all tests. It is noted that oil shale alone and a 5% methane/air mixture alone do not ignite. An explosive mixture (7%) of methane does ignite to give a peak pressure of approximately 90 psig. The mixture of 5% methane/air and oil shale ignites to give a peak pressure of approximately 65 psig.

Figure 3.31 indicates the pressure-time history of oil shale, Pittsburgh seam coal and lycopodium. This figure is included for comparative purposes.

3.4.2   Discussion of Methane Addition Tests

From there very limited tests, it appears that a synergistic effect exists between oil shale dust and a non-explosive mixture of methane/air, since the amount of methane added at 5% is quite small compared to the volatile hydrocarbon in the oil shale test sample. The synergism is implied in that the whole is greater than the sum of its parts. The mechanism of this enhanced ignition is not clearly defined. It may be that an ignition nucleus develops in the methane/air mixture (which normally would not propagate) with the increased temperature resulting in the oil shale retorting, thus changing the fuel/air ratio of the entire mixture. Obviously, many more tests would have to be made to define dust loadings, grade, size and methane limits.

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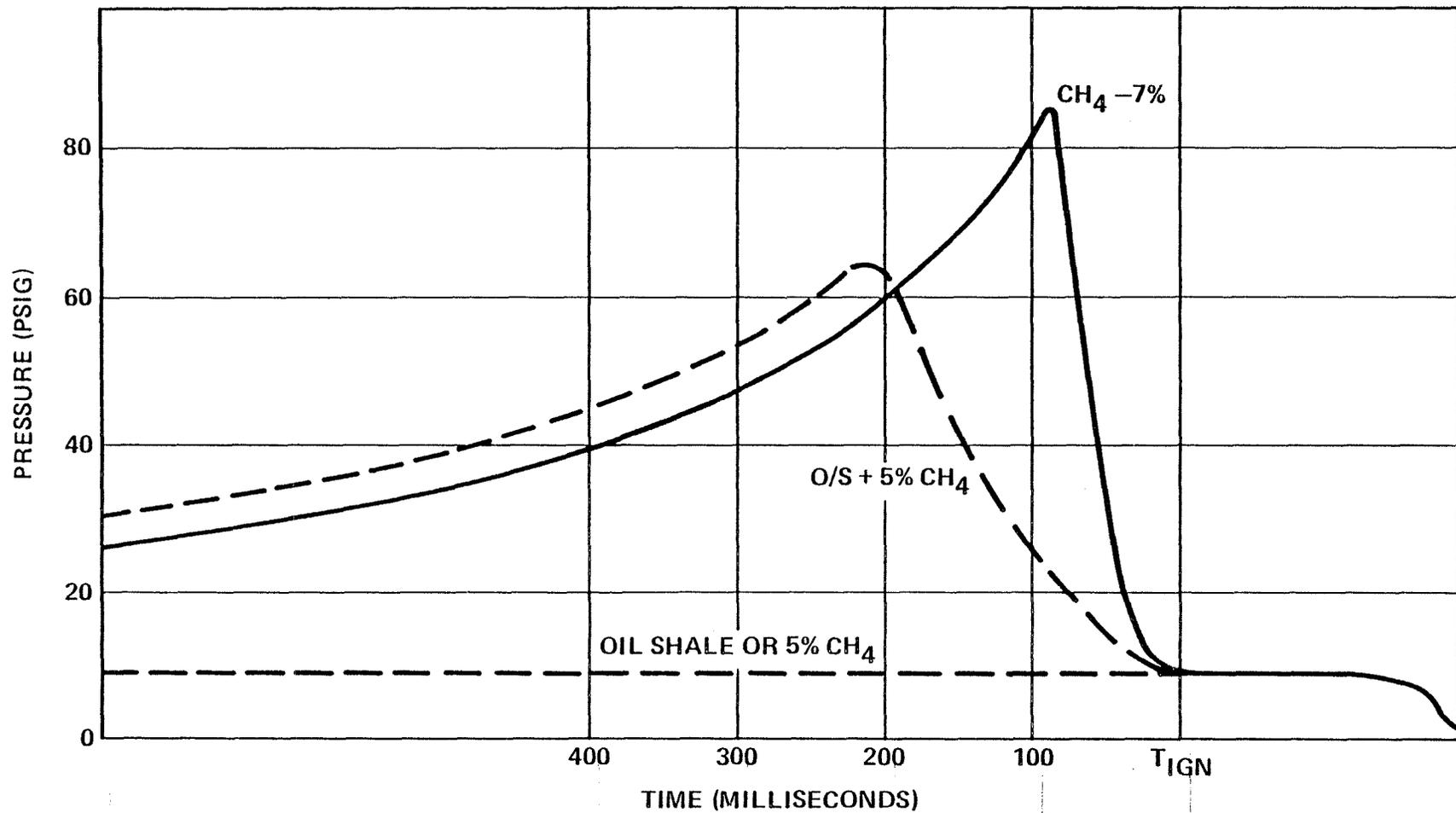
Figure 3.30   Methane/Air/Oil Shale Dust Interaction (Steel Hartmann Apparatus)

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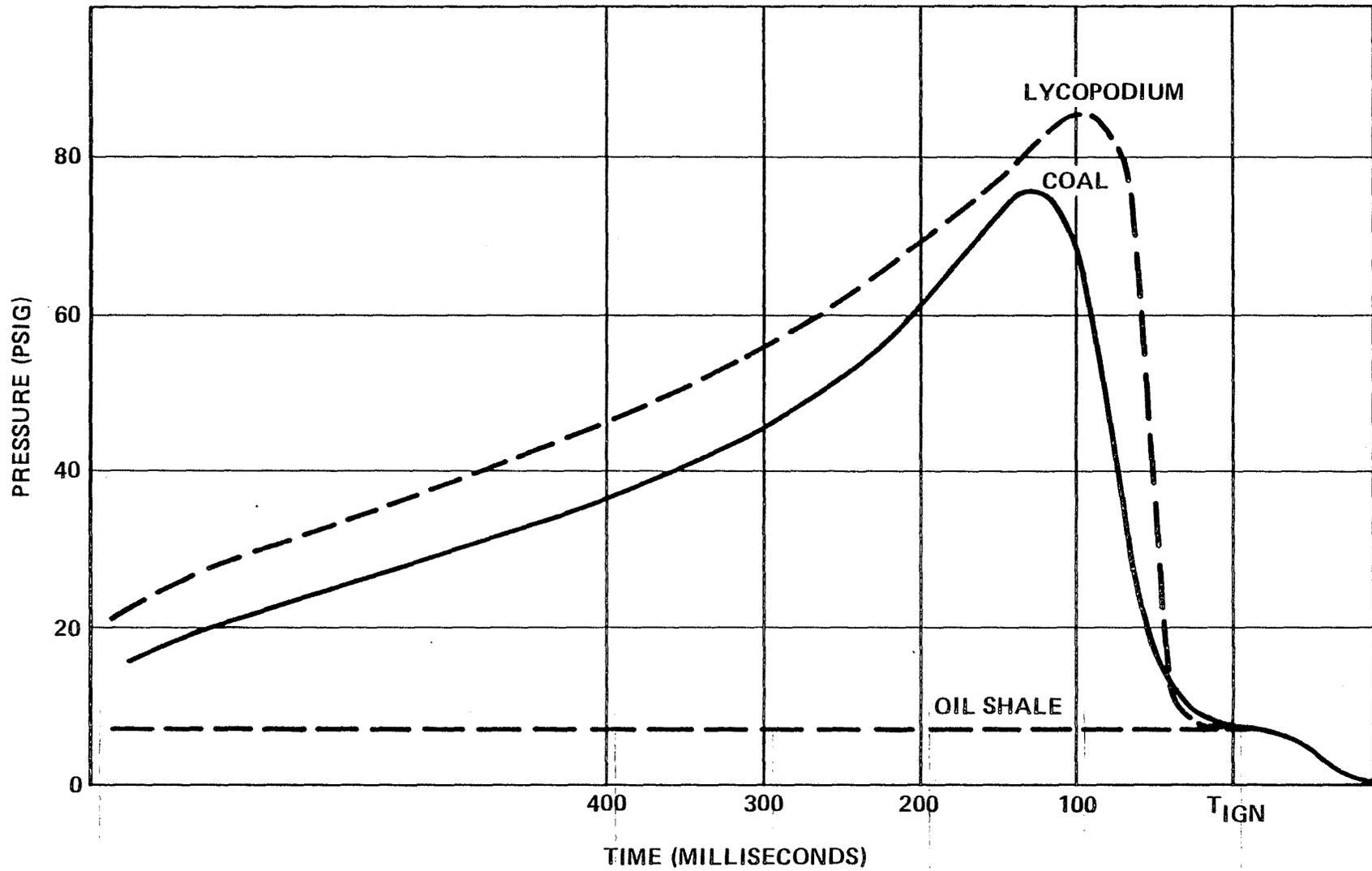
Figure 3.31 Pressure-Time Characteristics of Coal, Lycopodium, and Oil Shale Dust
(Steel Hartmann Apparatus)

3.5   Dust Layer Testing

Dust layers present a potential hazard if they are in contact with heat sources such as exhaust pipes. Using standardized techniques, oil shale dusts were characterized.

3.5.1   Apparatus and Procedures

3.5.1.1 Dust Layer Ignition Temperature

The ignition temperature of a dust layer is determined in a modified Godbert-Greenwald furnace. The glass adapter and fitting at the top of the furnace are removed and a flat disc containing an air inlet orifice is attached to the bottom transite plate. A sample of dust filling a 0.5-inch deep, one-inch diameter container, made of 40 mesh stainless steel with a 200 mesh stainless steel bottom liner, is suspended in the center of the heated furnace. The temperature of the dust (initially at room temperature) is measured by a chromel-alumel thermocouple centrally imbedded in the sample. A temperature-time record of the dust, along with that of the furnace, is obtained on a recording potentiometer. A stream of air, 30 cubic inches per minute, passes through the inlet orifice and flows upward into the furnace. At this flow rate, the dust will attain the same temperature as the furnace if combustion of the dust does not occur. The top surface of the dust is observed in a mirror above the furnace. Ignition is denoted by an inflection in the time-temperature record of the thermocouple imbedded in the dust.

In successive trials, the temperature of the furnace is reduced by increments until a minimum is obtained at which ignition of the dust just occurs. Temperature increments of 5°C are normally used. The duration of the test is regulated so the dust maintains the set temperature of the

furnace for a 5-minute period unless ignition occurs sooner (Dorsett et al, 1960).

In the study of ignition of dust layers, variations in diameter and depth of sample were investigated as well as the effects of air flow, duration of test, rate of heating and of preheating the dust. Trials were made with this apparatus in which appearance of a flash or flame was the criterion of ignition, rather than the inflection in the temperature-time record. Temperatures recorded by thermocouples imbedded in the sample are recorded at the time the heated sample begins to smoke. These temperatures are then averaged for each sample. The sample averages are averaged for each grade of shale. Results are subjected to a least-squares regression curve fit.

3.5.1.2 Dust Layer Ignition Energy

The electrical energy required for ignition of a dust layer is determined by discharge of a condenser at 400 volts through a layer of dust about 0.063-inches thick. The positive terminal of the condenser is connected to a pointed steel electrode and the negative terminal to a one-inch diameter steel platen holding the dust. In the test, the charged condenser is disconnected from the voltage source and the pointed electrode is lowered, by hand, toward the grounded plate until a spark discharges through the dust. After an ignition occurs, the platen is cleaned, a new dust layer placed and the process repeated at lower values of capacitance until a minimum is attained. Twenty trials are made at the minimum value of capacitance. The minimum energy is obtained by calculation from $0.5 \ CV^2$.

3.5.1.3 Dust Layer Hot Plate Test

This test was intended to simulate dust collecting on a hot surface with a flame source present. A thin layer of dust was spread on a conventional

hot plate and the temperature of the plate monitored. The temperature was set to 200°, 230°, and 260°C. A pilot flame was passed over the dust layer and observations made.

3.5.2   Results of Dust Layer Testing

In the few samples of dust tested, the nominal ignition temperature was 200°C. This value was determined by recording trace inflection point. By noting the temperature at which smoke appears, it seems that there is excellent agreement between this temperature and assay of the shale. Figure 3.32 plots the temperature at which smoke was observed, against the oil shale assay.

The hot plate test was conducted on nominal 35 gpt shale in the -200+325 size fraction. Only the 260°C hot plate temperature gave a visible flame when a pilot flame was introduced over the dust. This 260°C value correlates quite well with the values obtained at the Laramie Energy Technical Center (personal communication, Dr. J. Ward Smith).

Dust layer electric ignition tests have also been used for determining ignition temperature and were tried with oil shale and Pittsburgh seam coal. The validity of this test is quite doubtful; however, it was noted that oil shale dust did not ignite at 400 volts and 100 microfarads. Pittsburgh seam coal ignited at 400 volts and 30 microfarads.

3.5.3   Discussion of Dust Layer Testing

Dust layer testing was minimal and in some instances, the validity of the procedure is doubtful; nevertheless, the results did indicate that hot surfaces which increase the dust temperature can cause an ignition problem if an ignition source is present. The hot surface or heated dust layer
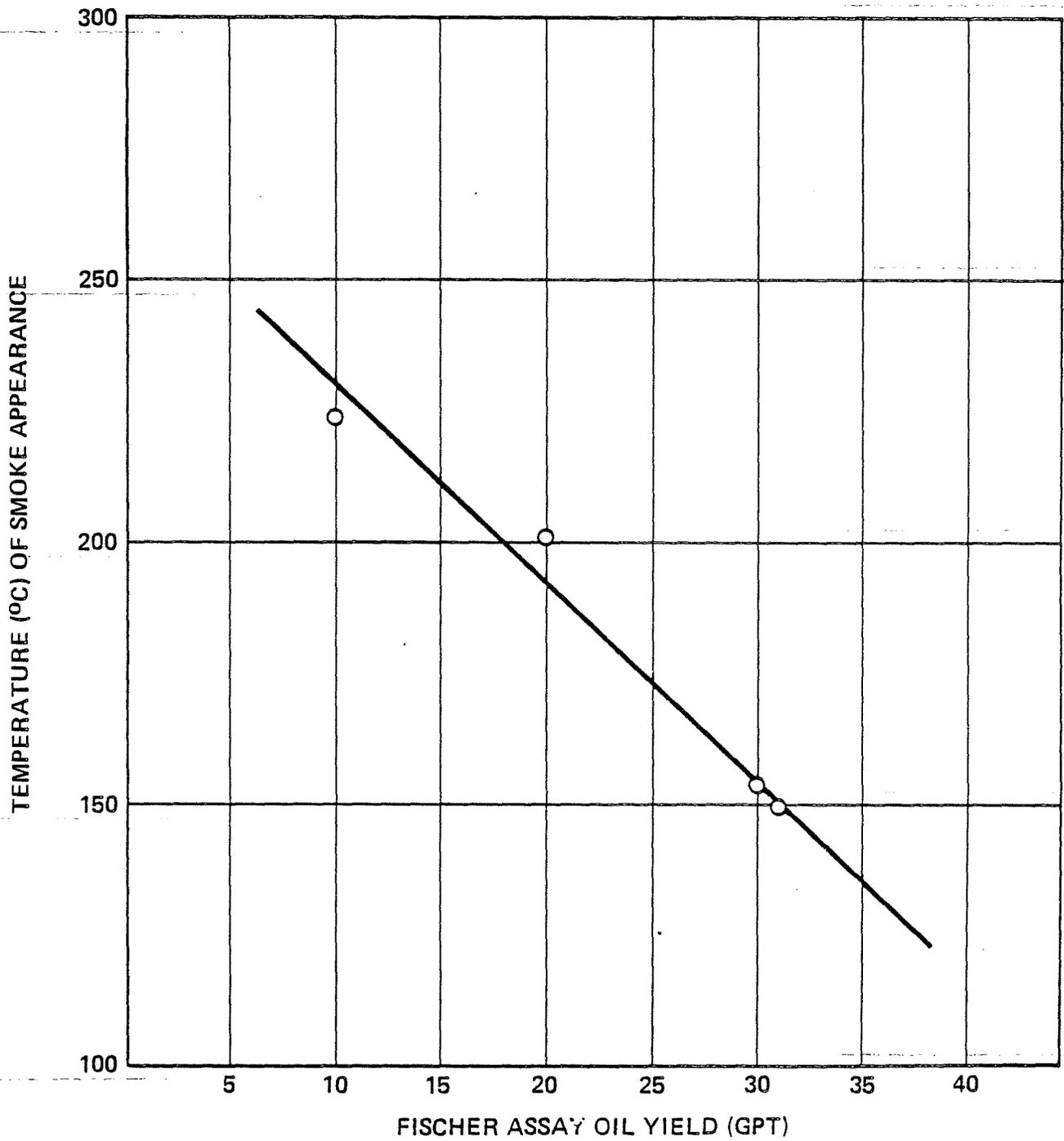
Figure 3.32   Dust Layer Testing: Temperatures   at   Which   Smoke   Appears   vs.
Fischer Assay Oil Yield

initiates retorting and it is apparently these flammable vapors that provide fuel for a continuing reaction. No attempt was made to identify these gases.

3.6 Rubble Fire Testing

A single test was conducted to determine the relative flammability of oil shale rubble. The intent of the test was to initiate a fire, then determine fire spread into the raw shale.

3.6.1 Procedure

An outdoor test was conducted by placing a high volume fan six feet downwind from the shale ignition source. A velometer was used to monitor the air flow which was held nominally at 100 feet per minute. A large galvanized drain pan was filled with minus 3-inch oil shale rubble assaying 44.3 gallons per ton. The shale was extended downwind from the pan approximately four feet. In total, 150 pounds of shale were used in the test.

One gallon of #2 diesel fuel was poured over the shale in the pan and allowed to accumulate. A second pan was filled with only one gallon of diesel fuel to serve as a control to assess when all of the fuel had been consumed. The pans were shielded from strong air currents and a diesel soaked flammable wick used to ignite both pans. A Locam camera was set up to photograph the test intermittently. Figure 3.33 schematically illustrates the test set-up.

3.6.2 Results of Rubble Fire Test

One minute after ignition, the control was burning well. The shale pan was burning only sporadically. Three minutes after ignition, the control reached its maximum intensity (subjective) with the shale pan gaining little intensity. After 12 minutes, the control pan fuel was almost exhausted;

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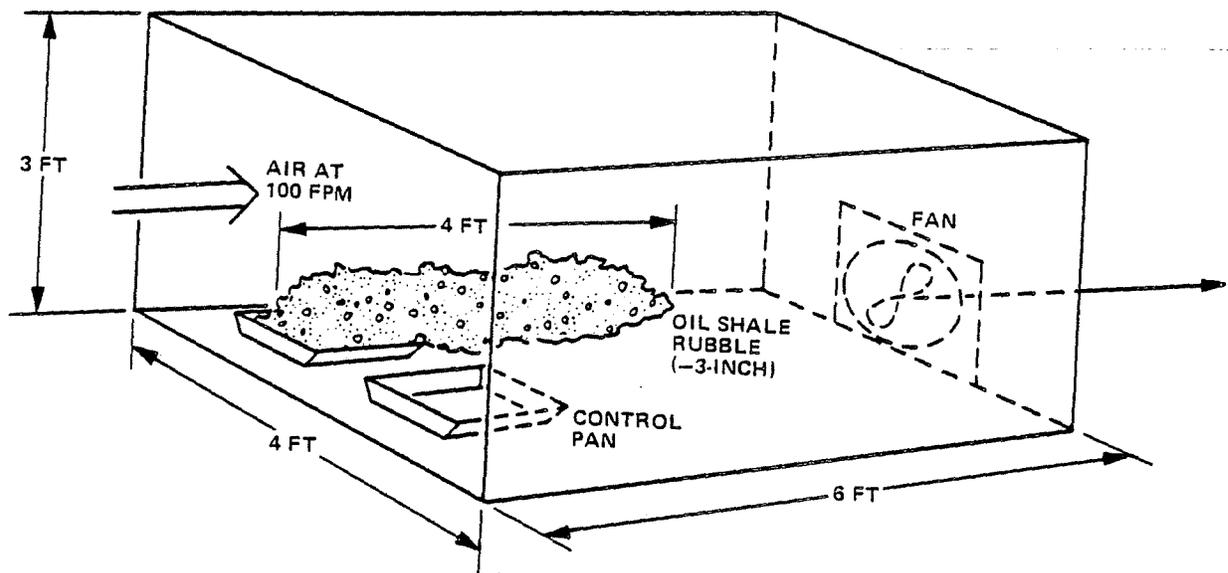
Figure 3.33 Schematic of Rubble Fire Test

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however, the flame in the shale was still quite small and had spread away from the pan less than one inch. At 14 minutes after ignition, the control flame extinguished; no additional flame spread was noted in the shale. Up to one hour and 45 minutes after ignition, an audible "crackling" was noted as well as hydrocarbon odors, with no additional flame spread. A small flame was still confined to the pan area.

3.6.3   Discussion of Rubble Fire Testing

The rubble in this single test was very difficult to ignite and would not sustain combustion without the presence of diesel fuel. It should be noted that rubble has been arbitrarily defined as minus three-inch. The smaller pieces of shale seemed to be consumed to a greater extent, thus the results of this single test should not be extrapolated to all rubble. The use of a pan may have substantially decreased the air flow through the rubble.

It is concluded that this single test is by no means indicative of rubble fires and that better defined tests and limits would be needed to fully ascertain the hazard potential of rubble fires.

3.7   Spontaneous Combustion

An accepted standardized test for determining the potential of materials to auto-oxidize has been in use for decades and uses an adiabatic furnace. The technique is extremely time-consuming and yields temperature-time data which is not amenable for comparative evaluations of materials. The test procedure used in this program has been widely accepted in Europe and is gaining popularity in the United States as a reliable indicator of spontaneous heating. Table A.18 in Appendix A present statistical reproduceability data on one oil shale dust peroxide test. The standard deviation is about 18% of the mean, indicating good reproduceablity

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3.7.1   Apparatus and Procedure

The test procedure for determining potential of spontaneous combustion is derived from a hydrogen peroxide test (Maceijasz, 1959). This relatively simple test procedure consists of the following steps:

- Ten grams of sample are crushed to a size of 63 micrometers or less.

- The sample is mixed with five milliliters of distilled water in a thermally insulated container.

- After allowing the sample and water to thermally equilibrate, 30 milliliters of 20% hydrogen peroxide are added to the sample.

- The temperature of the sample is monitored and the time required to increase temperature by $65^{\circ}C$ is recorded.

- The susceptibility or liability index "I" is calculated from: $I = 100/t$, where t is the time in minutes required to reach a temperature change of 65° C.

Increasing values of I indicate a greater liability for spontaneous combustion.

3.7.2   Results of Spontaneous Combustion Tests

Figure 3.34 presents typical temperature-time relationships, indicating various rates of temperature rise. No attempt was made to use any rate data. Table 3.29 presents the spontaneous combustion I value across the graded series and mine dusts. In general, the values range from two to 10 with an expected trend toward higher values with higher assay.

3.7.3   Discussion of Spontaneous Combustion Tests

Table 3.30 presents a summary of correlation coefficients between spontaneous combustion index and several assays, minimum ignition energy, and minimum temperature. Generally, the correlation is fair to good across assays within a single size fraction. Correlation within a particular assay

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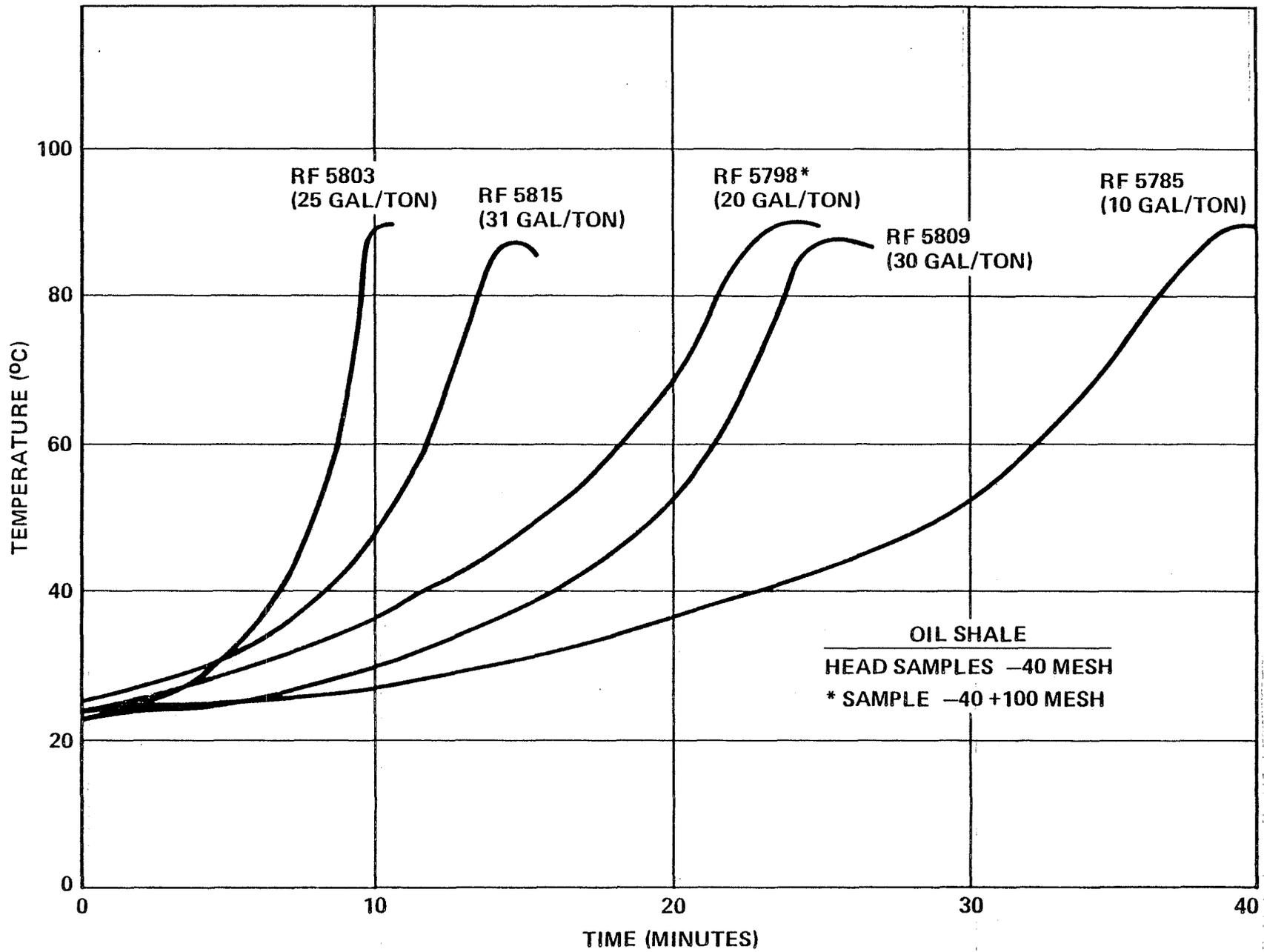
Figure 3.34   Temperature vs. Time for Hydrogen Peroxide Tests

Table 3.29

Spontaneous Combustion Index For Graded Series Mine Dusts and
Spent Shale Samples, Hydrogen Peroxide Test

| Sample Type | Mesh Size (US) | Graded Series Oil Shale Test Samples Nominal Richness | | | | | | | Colony Mine Dust | 8x8 Foot Drift | | Spent Shale |
		10 GPT	15 GPT	20 GPT	25 GPT	30 GPT	31 GPT	35 GPT		New Dust	Old Dust	
As Prod.	-40	2.5		5.9	10.1	4.1	7.2	7.2	5.2	7.6	2.5	4.4
F R A C T I O N S	-40+100	2.1		4.3		4.0	6.1	6.5	4.0	8.9	2.5	4.1
	-100+200	2.9		5.2		5.2	6.8	6.5	4.8	8.8	2.2	5.3
	-200+325	4.7		8.3		4.5	8.0	8.1	4.2	10.6	2.5	3.8
	-325	1.8		4.3		3.4	4.0	5.1	1.7	7.9	2.0	3.8
Recon. Std. Size	-40	2.2		4.0		3.2	4.9	5.4	3.6	9.9	2.4	4.4

Table 3.30

Correlation of Spontaneous Combustion Index with
Fischer Assay Oil Yield, Minimum Ignition Energy and
Minimum Ignition Temperature
(Graded Series Samples)

Mesh Size (US)	Fischer Assay Oil Yield Correl. Coeff./No. Smpls.	Organic Carbon Correl. Coeff./No. Smpls.	Min. Ign. Energy* Correl. Coeff./No. Smpls.	Min. Ign. Temp. Correl. Coeff./No. Smpls.
-40 Head	0.46/6	0.44/6	-0.90/3	-0.57/6
- 40 +100	0.92/5	0.88/5	---	---
-100 +200	0.91/5	0.90/5	---	-0.95/5
-200 +325	0.44/5	0.41/5	-0.98/3	0.61/5
-325	0.76/5	0.74/5	---	0.47/5
-40 Recon. Std. Size	0.82/5	0.77/5	---	-0.65/5

*Lucite Hartmann at 25 psig reservoir pressure

is widely variable with particle size. Spontaneous combustion index increases with Fischer assay oil yield and organic carbon content. Limited data show the spontaneous combustion index increases as minimum ignition energy and minimum ignition temperature of a dust cloud decrease. Typical plots are shown in the Appendix A, figures A.10 to A.21, for spontaneous combustion vs. organic carbon for the graded series and mine dust series.

Since auto-oxidation is not only a function of particle size, but pyritic sulfur as well, figures 3.35 and 3.36 show the relationship between pyrite and the I value. If spontaneous combustion were solely a function of pyrite, a postive correlation would be expected; however, from the plots it is evident that no such relationship exists. Thus, it is assumed that pyritic sulfur is only one influencing factor, with others obviously being particle size (surface area), moisture content, and organic material. By comparison, oil shale dusts are nominally in the range of two to 10, Pittsburgh seam coals on the order of 10, and western coals on the order of 20 to 30.

The test indicates only a relative index and does not imply oil shale is three to 15 times less likely to spontaneously combust than western coals; only that it is less likely. The fact that values were obtained in the range of two to 10 indicates that spontaneous combustion of rubble, fractured seams, etc., do have a liability to auto-oxidize. Examination of Table 3.29 also indicates that the spontaneous combustion index is not affected by particle size when the nominal Fischer assay oil yield is fixed.

3.8   Retort Gas Flammability

An oil shale retort gas (either surface or in situ) is a complex mixture of hydrocarbons, hydrogen, hydrogen sulfide, ammonia, carbon monoxide, carbon dioxide, and water in varying proportions. The concerns from a flammability standpoint are the upper and lower explosive limits and the minimum energy

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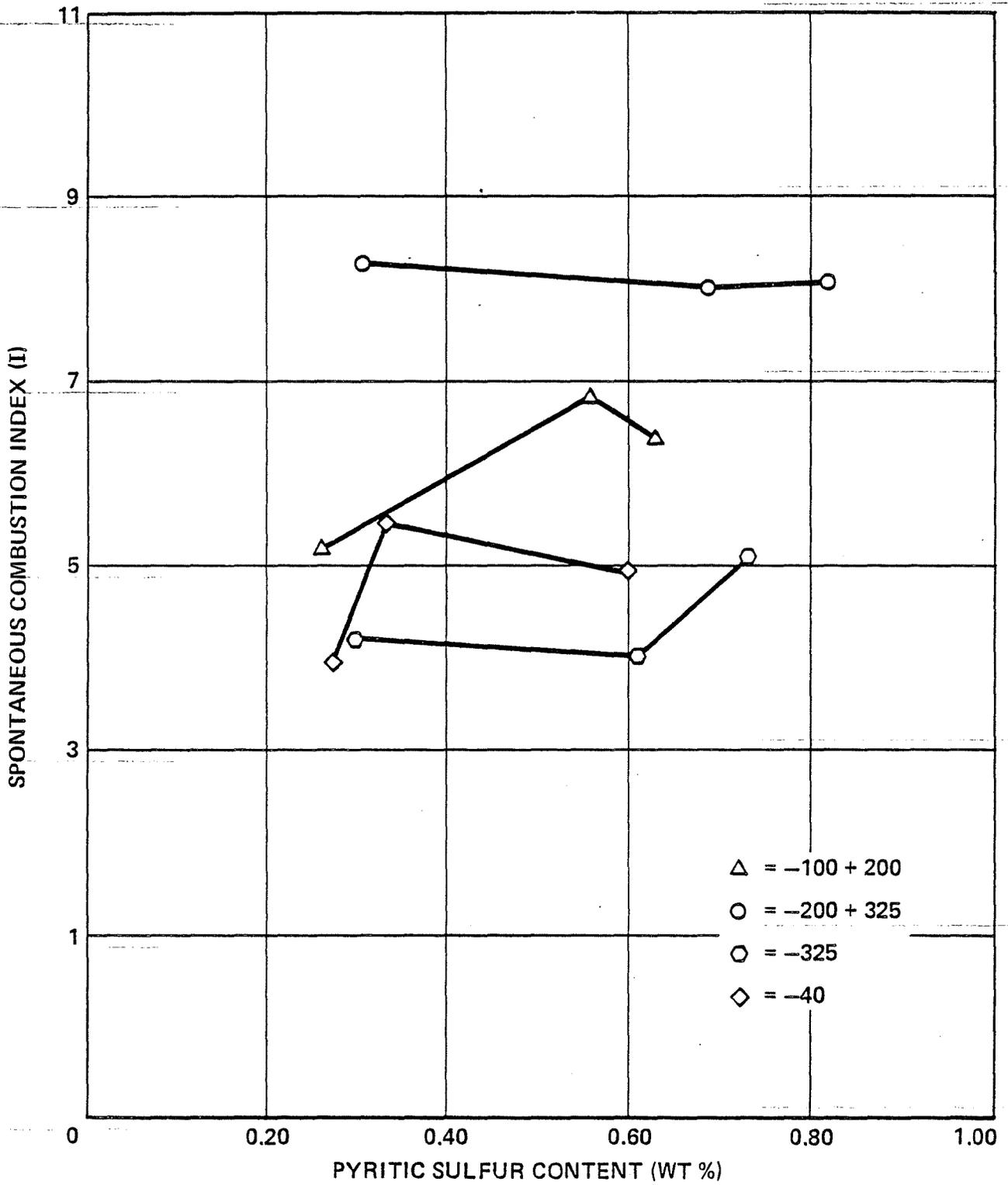
Figure 3.35 Spontaneous Combustion Index vs. Pyritic Sulfur Content For Graded Series Samples (Hydrogen Peroxide Test)
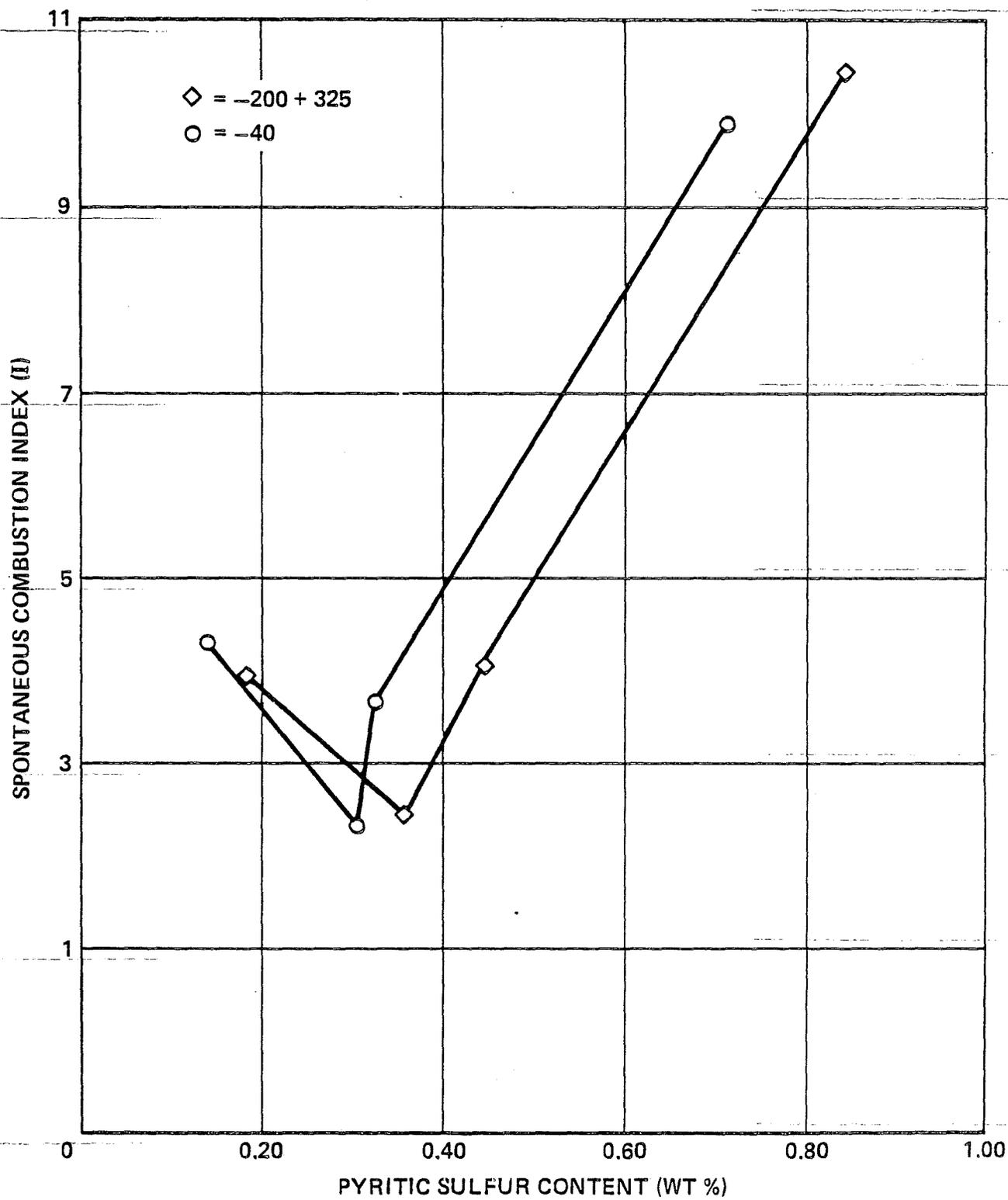
Figure 3.36 Spontaneous Combustion Index vs. Pyritic Sulfur Content For Mine Dusts (Hydrogen Peroxide Test)

required for ignition. In order to perform rough determinations of the explosive limits and the minimum ignition energy, an apparatus known as the PTB was used.

3.8.1   Apparatus and Procedure

The PTB apparatus (Figure 3.37) has been used for intrinsic safety testing for several years. It is basically a test apparatus made to create electric sparks in an explosive atmosphere. The sparks are created as a result of four rotating wire electrodes brusing the surface of a similarly rotating cadmium disc electrode. The electrodes operate in a chamber filled with the test mixture for a given length of time, during which at least 1,000 sparks are created. If ignition occurs, the gas is replaced and either the ignition current or the gas composition is changed. If ignition does not occur, the ignition current is increased and the test run again.

In order to be able to compare the results with the minumum igniting current (MIC) for methane, the PTB apparatus was run with the following settings: source voltage 24V; inductance 100 mH; 0.1778 mm diameter, 11 mm long tungsten wires; one mm overlap; Cd disc; 80 rpm; a negative test was run for 13 minutes (at least 2,500 sparks).

The test gas was generated from Fischer assays of 31.4 gpt oil shale and analyzed by gas chromatography. The analysis showed some variation in component ratios for the three batches.

Different mixture ratios were obtained using the technique of partial pressures. Approximately one liter of gas was required for each test, as a result, the number of test points obtainable from three to four liters of available gas was limited. Consequently, only a rough idea was obtained about the variation of minimum igniting current or minimum igniting energy as
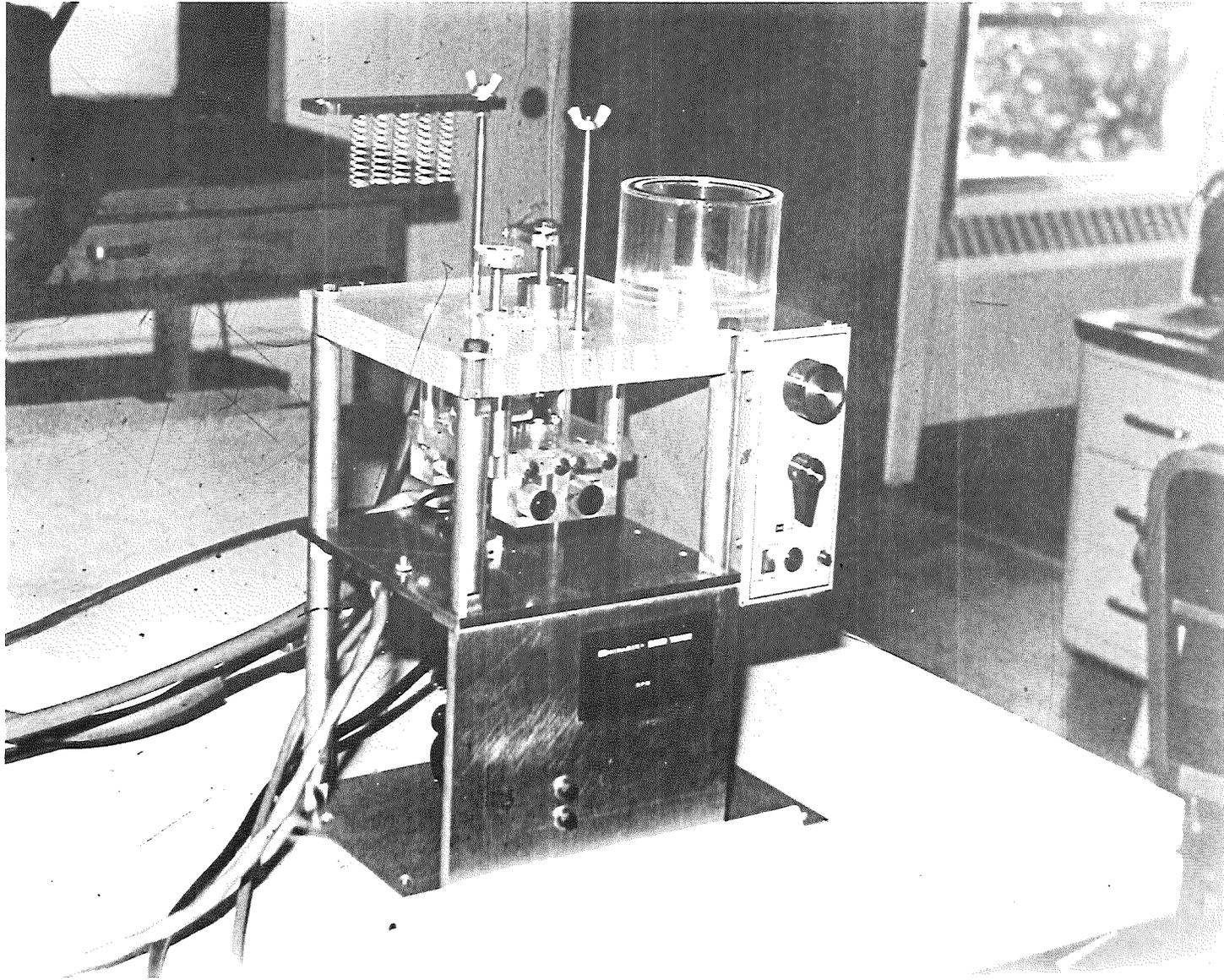
Figure 3.37 PTB Apparatus for Testing Gas Flammability

a function of mixture ratio. The testing was done at one atmosphere absolute, using 21.5% O_2 in N_2 for air.

3.8.2 Results of Retort Gas Flammability Tests

Typical gas compositions of high Btu retort gases from the Paraho and TOSCO II processes are presented in Table 3.31. Also presented are the lower explosive limits (L.E.L.) for each flammable component. Three samples of retort gas derived from a Fischer assay were tested in the PTB apparatus with composite results shown in Figure 3.38. The three gas compositions differed somewhat (see Appendix A, Figure A.15) which may account for the variability in results. Basically, the test indicates a L.E.L. around 5% retort gas in air and an upper explosive limit (U.E.L.) around 25 to 30%. The most dangerous mixture would appear to be approximately 15% with a minimum ignition energy of 0.23 millijoules and a minimum igniting current less than 0.1 amperes. The apparent "hump" in the U-shaped curve at 15% is unexplained.

3.8.3 Discussion of Retort Gas Flammability Tests

The L.E.L. was calculated, based on LeChatliers principle, for the Tosco and Paraho high Btu gases and for the Paraho low Btu gas, Table 3.32. The dry calculations were taken from the values in Table 3.31 with air, CO_2, and H_2O not calculated. The wet calculations included those values. While there is no substantiation for using the wet values (they do represent reality), they are included for comparative purposes. LeChatlier's principle is based on dry calculations and was originally intended for relatively simple fuel/air mixtures. Only one experimental point was determined and that seems to match quite well with the wet calculations. A note of caution - the ignition energy limit of the PTB is about one joule and to accurately determine the true L.E.L. and U.E.L. much more energy is needed. Thus, we

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Table 3.31

Typical Retort Gas Composition and Component Lower
Explosive Limits for TOSCO II and Paraho Processes (vol %)

	Paraho Indirect	TOSCO II	L.E.L.
H_2	17.4	23.23	4.0
Air	0.36	-	-
CO	1.91	3.12	12.5
CO_2	10.57	29.45	-
CH_4	22.53	14.48	5.3
C_2H_4	8.79	2.04	2.7
C_2H_6	3.16	5.44	3.0
C_3	1.62	5.66	2.2
C_4	0.47	4.01	1.9
C_5	1.15	2.31	1.4
C_6	0.57	2.80	1.2
H_2S	2.45	5.80	4.3
NH_3	0.92	-	15.0
H_2O	28.10	-	-
C_7	-	2.8	1.2
C_8	-	0.57	1.0
	100.00	99.99	
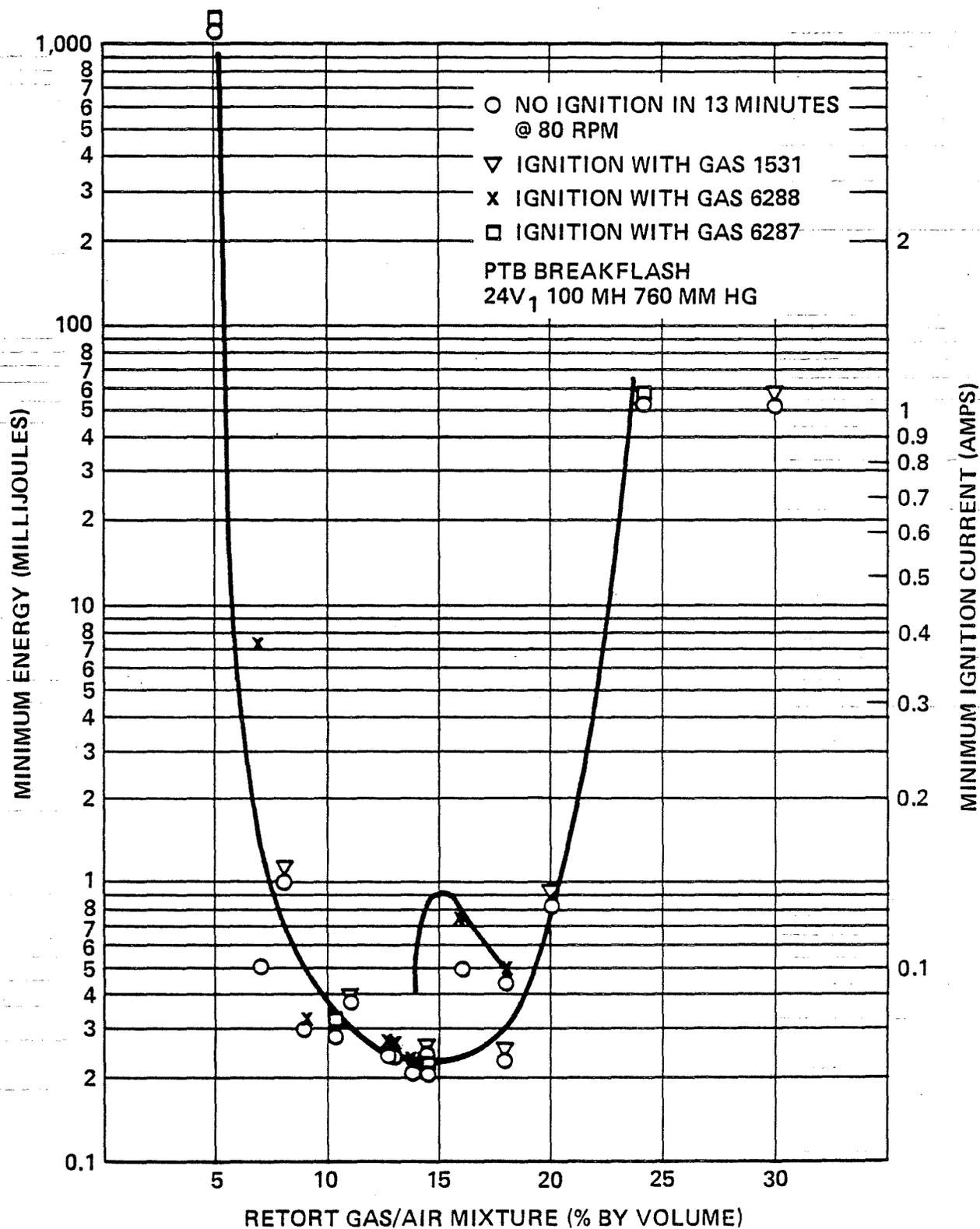
Figure 3.38 Minimum Igniting Current (Minimum Energy) vs. Retort Gas/Air Mixture for TOSCO II, Paraho Direct, and Paraho Indirect Processes (PTB Apparatus)

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Table 3.32

Lower Explosive Limits of Retort Gases for TOSCO II,
Paraho Direct, and Paraho Indirect Processes

Gas	L.E.L. (Vol. %)			
	Dry Calc.*	Dry Expt.	Wet Calc.*	Wet Expt.
TOSCO II	3.13	-	5.13	5
Paraho Direct (Low)	3.46	-	31.85	-
Paraho Indirect (High)	3.82	-	6.26	-

*Calculation based on LeChatlier's Principle

Table 3.33

Calssification of Gases on the Basis of
MIC and/or MESG Values

Group	Application	Either measurement is adequate if		Additional data is necessary if	
		MIC Range	or MESG Range	MIC Range	MESG Range
I	Mining Methane	1		0.8-0.9	
IIA	Industrial	0.9*	0.9mm		
II IIB	Gases & Vapors	0.5-0.8	0.55-0.9mm	0.45-0.5	0.5-0.55mm
IIC		0.45**	0.5mm**		

*Greater than
**Less than

cannot be sure that the true L.E.L. is not closer to 3% than to 5%. The real

value of the PTB lies in its ability to determine the minimum ignition energy.

The minimum igniting current for retort gas was approximately 70

milliamps. Under the same test conditions, the minimum current for the most

hazardous methane/air mixture was approximately 100 milliamps.

It is important to note that these limited experiments were conducted at

room temperature and 760 mm mercury pressure. An increase in temperature

(more likely for a true retort leak) would increase the explosivity and

reduce the energy or current required for ignition.

There are several methods and considerations for the classification of

explosive gas mixtures.

- For flame proof enclosures the gases and vapors can be grouped according to their maximum experimental safe gaps (MESG). The standard test apparatus and method used for determining MESG is described in the Publication 79-1 of the International Electrotechnical Commision (IEC).

- For the purpose of intrinsic safety, the gases and vapors can be grouped according to the ratio of their minimum igniting currents with that of laboratory methane. The standard method for determining the minimum igniting current (MIC) is described in the Publication 79-3 of the IEC.

- Grouping has also been done on the basis of similarity of chemical structure.

- In the 1930's and 1940's, the minimum igniting energies (MIC) were determined for the different mixtures as a function of volumetric mixture ratio (Lewis and von Elbe, 1961) and were used for classification. These tests were done with a high-voltage capacitive discharge system using flanged stationary electrodes.

- Additional information, that can be considered in the process of classification, are the minimum ignition temperature, flammability limits, maximum explosion pressure, etc.

It has to be emphasized that none of the above classification methods or

measurements can provide an absolute figure for the evaluation of the

explosion danger represented by the particular gas. Data obtained with the

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above methods are greatly influenced by the specifications of the test equipment, therefore can only be used with this limitation in mind.

According to the IEC Draft (1976) it is not necessary to execute all measurements on a particular gas in order to classify it. If the MESG or MIC data fall within the indicated range for the group, the gas can be classified on the basis of MESG or MIC alone. If the data fall on the border between groups, additional measurements are required for classification. The groups and limits recommended are given in Table 3.33.

On the basis of the test results, the retort gas apparently fits in the ISA Group IIB.

3.9   Conclusions of Phase 2 Studies

Newly prepared oil shale dusts of the graded series have analytical properties which are of value in predicting relative fire and explosivity tendencies. These are: organic carbon content, weight and volume percent kerogen contents, particle specific gravity, Fischer assay oil yield, total hydrocarbon yield from Fischer assay (TMBA), and combustion energy of total volatiles from Fischer assay (TMBA). Of these, the property most easily obtained is Fischer assay oil yield. All the remaining properties correlate to Fischer assay oil yield by simple linear regression relationships having correlation coefficients greater than 0.99.

The relationships developed for newly prepared oil shale dusts in this study will likely apply only to oil shales from the Mahogany zone in the Piceance Creek basin. Oil shales from deeper Piceance Creek basin formations, from other regions, and particularly from foreign countries, must be re-examined and new relationships developed.

Oil shale dusts which have aged for years in oil shale mines were studied and found to have property relationships which differ from those of new oil

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shale dusts. A major variation is that the amount of organic carbon in old dust required to produce a unit amount of Fischer assay oil is higher than in new dusts. However, based on limited data, the properties directly related to Fischer assay oil yield, total hydrocarbon yield, and combustion energy of total volatiles, do not appear to differ significantly from relationships established for new dusts.

Closed vessel tests, as described in RI 5624, and other tests were conducted on the prepared new and old oil shale dusts. Closed vessel tests included determination of minimum dust cloud concentration required for ignition, minimum dust cloud ignition temperature, minimum ignition energy, and explosion pressure and rate of pressure rise. In addition, dust layer data were obtained on smoke point (temperature at which smoke from combustion first appears) and on the tendency for spontaneous combustion. Comparisons of all of these data individually with Fischer assay oil yields (keeping screen size properties constant) gave fair to excellent correlations which showed that properties indicative of an increased tendency to fire and explosivity increase with Fischer assay oil yield.

It is interesting to correlate data on minimum explosive concentrations of dust and volatiles, obtained at a 25 psig lucite Hartmann reservoir pressure (Table 3.22), with full scale mine test data reported by Richmond and Miller (1977). The authors found that oil shale dust concentrations were potentially explosive if the content of Fischer assay organic volatiles was 0.05 oz/ft^3 or greater (see Table 3.34). Lucite Hartmann laboratory tests in this study gave minimum explosive dust concentrations, using experimental conditions modestly adjusted from RI 5624, which increased as the Fischer assay oil yields decreased.

In order to compare laboratory lucite Hartmann data with Richmond and Miller (1977) mine test results, it is necessary to reach a common data

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Table 3.34

Comparison of Minimum Explosive Volatiles Concentration
Data, Based on Fischer Assay--Laboratory and Mine Tests:
Reconstituted Standard Size Samples

LABORATORY

Sample	Minimum Explosive Concentration of Dust* (g/l or oz/ft^3)	Corresponding Minimum Explosive Concentration of Volatiles ** (g/l or oz/ft^3)
Graded Series - 11.4 GPT	0.104	0.005
Graded Series - 13.3 GPT	0.106	0.006
Graded Series - 19.2 GPT	0.063	0.005
Graded Series - 22.4 GPT	0.047	0.004
Graded Series - 28.3 GPT	0.079	0.009
Graded Series - 29.5 GPT	0.075	0.009
Graded Series - 34.1 GPT	0.046	0.006
Colony Mine Dust - 22.7 GPT	0.071	0.006
New Dust - 34.3 GPT	0.073	0.01
Old Dust - 23.5 GPT	0.069	0.007
Average	0.0733	0.0067
Standard Deviation	+0.02	+0.002

MINE (Richmond and Miller (1977)

Assay of Test Dust	Actual Mine Dust Concentration (g/l or oz/ft^3)	Corresponding Actual Concentration of Volatiles*** (g/l or oz/ft^3)	What Happened In Mine
46 GPT	0.15	0.030	Marginal propagation
46 GPT	0.30	0.060	Propagation
25 GPT	0.30	0.033	No propagation
25 GPT	0.30	0.033	No propagation
25 GPT	0.60	0.066	Propagation
34 GPT	0.30	0.045	Propagation
34 GPT	0.15	0.023	No propagation
50 GPT	0.15	0.033	No propagation
50 GPT	0.225	0.050	Propagation
19 GPT	0.40	0.032	No propagation
19 GPT	0.60	0.048	No propagation

*   From Table 3.23.
**   From regression equation of Figure 3.11.
*** Estimates by Richmond and Miller (1977). Corresponding calculations from regression equation of
      Figure 3.11 are close.

basis, namely ounces of volatile hydrocarbons per cubic foot of air space. Total volatile hydrocarbons in one ounce of dust were calculated from the regression equation of Figure 3.11:

$$Y = 0.0034 + 0.00396X$$

where Y is the total hydrocarbons in oz/ft^3 from one ounce of dust and X is the Fischer assay oil yield in gpt. The minimum explosive concentration of volatiles is then determined by multiplying "Y" from the above equation by the minimum explosive dust concentration from the lucite Hartmann tests (Table 3.34).

The average minimum explosive concentration of volatiles from laboratory tests is 0.0067 oz/ft^3 with a standard deviation of 0.002 oz/ft^3. (Note: examination of data in Table 3.34 shows that dust concentration in oz/ft^3, regardless of Fischer assay oil yield, would be just as reliable as volatiles concentration in predicting explosivity). Thus, the minimum concentration of volatiles in the Bruceton mine for explosive propagation was about 7.5 times larger than the minimum explosive concentration of volatiles in the laboratory apparatus. Note that concentrations of volatiles required for mine explosive propagation are compared with volatiles required for ignition in the lucite Hartmann apparatus. The difference in the mine and laboratory values is not of concern, but the apparent consistency of the ratio, if it can be confirmed, would increase the importance and significance of laboratory data in predicting oil shale dust explosions.

From the Colony mine dust loading studies an average dust load of 0.009 gm/cm^2 on the vertical mine surfaces was determined. This corresponds to a value for volatile hydrocarbons which is significantly lower than the minimum concentration of volatile hydrocarbons required for explosive propagation as determined by Richmond and Miller (1977). Even if the mine dust grade is

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increased to compensate for aging or oxidation, the volatile hydrocarbon concentration is still much lower than the 0.05 oz/ft^3 determined by the Bureau authors.

The extensive test and analytical work done on new and old oil shale dusts has provided a sound basis for delineating properties which relate to fire and explosivity tendencies. The relationship between laboratory test data and full scale mine fire and explosivity properties can, however, only be expressed in relative terms, i.e., 35 gpt oil shale dust is more likely to explode and the explosive mixture will have more energy than 30 gpt oil shale dust. When the full scale Bruceton mine test data allow a precise definition of the lower limits of an oil shale dust explosion system, using terms such as (1) content of Fischer assay combustible volatiles, (2) air to hydrocarbon volatiles ratio, (3) minimum explosive energy, and (4) particle size (surface area), the laboratory analytical and fire and explosivity test data can be used in a more effective manner in predicting safety hazards.

4.0 PHASE 3 STUDIES

The fundamental objectives of Phase 3 are (1) to complete the scenarios developed in Phase 1 by:

- Explaining how the hazards postulated in the scenarios could have been prevented or mitigated;

- Suggest techniques for suppressing accidental fires and explosions;

and, (2) prepare a final report including:

- The completed accident scenarios;

- Procedures for monitoring compliance with regulations;

- New data acquired with comparisons to data from the literature;

- Problems requiring solutions;

- Suggested research paths to solutions.

4.1 Data Gaps Filled by Study Program

Of the many questions raised by the scenarios in Section 2, the following summarizes many of these gaps that were filled during the testing in Phase 2. This summary is intended to be general as it relates to the scenarios.

4.1.1 Solid and Rubblized Oil Shale

Based on a simple rubble test (Section 3.6.2), the fire spread rate is slow and the flame is weak in intensity. It is assumed that the rate and intensity correlate with grade for a particular size rubble. While the

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rubble in the single test was nominally less than three-inch size, the smaller pieces were consumed more readily. The test did confirm the necessity of using material representative of crushed or blasted rock as it is apparent that particle size distribution and void volume are important factors in rubble fires.

4.1.2 Dust Layers

Based on minimal dust layer testing, Section 3.5.2, the ignition temperature of a thin dust layer is approximately 260°C. A fire hazard, may exist if an ignition source and other factors are present.

4.1.3 Dust Explosions

Based on 25 psig testing (Section 3.3.2) in the lucite Hartmann apparatus, the dust concentration required for an explosion is nominally less than one gram per liter. At this higher dispersion pressure, nominal grades from 10 gpt to 35 gpt exploded in the test apparatus. Energy required for dust ignition is nominally less than eight joules for grades ranging from 30 gpt to 35 gpt (lower grades not evaluated) based on the 25 psig testing. The overall explosivity index of oil shale dust is less than 0.0001, based on the data acquired in this program.

The effect of particle size distribution on dust explosions, appears to be one of coarser fractions inhibiting propagation (as seen in the head samples and the -40 +100 mesh samples).

The apparent synergistic effect of a non-explosive methane/air mixture on a non-explosive oil shale dust was demonstrated in a limited series of tests. The magnitude of the explosion was apparently less than an explosive methane/air mixture and indicated a peak pressure of about 65 psig.

The dust loads on mine surfaces necessary to propagate an explosion were not determined; however, typical dust loads from the Colony mine of approximately 0.009 gm/cm^2 are reported in Section 3.2.5.

4.1.4   Spontaneous Combustion

Oil shale indicates a liability to auto-oxidize (the I index is on the order of 2 to 10, Section 3.7.2). Generally, the liability increases with grade. Size (surface area), chemical composition (such as pyrite), moisture, and climate may all influence the liability, but their exact influence is unknown.

4.1.5   Retort Gas

From limited testing, Section 3.8.2, the limits of flammability of a rich retort gas are nominally 5% to 30%, with the most hazardous concentration being around 15% retort gas in air. The minimum ignition energy is approximately 0.23 millijoules. The effects of mixing retort gas with oil shale dust are not known, but we assume that an effect similar to the methane/oil shale will occur.

4.2   Completion of Scenarios

The completion of scenarios necessitated the development of data, through testing and experimentation, necessary to evaluate any postulated hazards. A careful comparison of RI 5624 test results with the data that was necessary to complete or amend the scenarios, demonstrates that large scale tests and perhaps amendments to the laboratory procedures should be devised. This comparison will expedite the scale-up of tests and/or the capability of accurately predicting full scale consequences from small scale tests.

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Inasmuch as many of the scenarios raise problems-in-common, completion of the scenarios is generally limited to dealing with a hazard in the first scenario in which it is presented. The method used for evaluating each of the scenarios is presented below:

- Conduct fault analyses.

- Define postulated oil shale derived hazards.

- Evaluate the effect of new data acquired in Phase 2 on the postulated hazards.

- Define means for prevention and mitigation of the hazards.

- Propose procedures for monitoring compliance with regulations.

- Propose means for detection and suppression of the hazards.

- Define problems requiring solutions.

- Formulate recommended paths to the solutions.

4.2.1   Fault Analysis Technique

Fault analysis (also called fault tree analysis) is a technique that provides an analysis of the causes of accidents or potential accidents. The approach, terminology, and symbols presented by Rankin and Tolly (1978), are used in this study. For those not familiar with this publication the following symbols are defined:
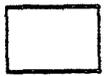
an output event that should be developed or analyzed further to determine how it occurs.
Example: fire, dust explosion,

an independent event and does not depend on other components in the system.

Example: gas leak, part failure.

a normal event expected to occur during a system operation.
Example: Retort, hopper, feed line.

an undeveloped event due to a lack of information or significance.
Example: Human error, cutting operations.

△   a transfer symbol that directs the reader to another part of the fault tree. Its purpose is to prevent repeating a sequence of events common to different areas of the fault tree.

⌂   an AND logic gate representing a condition in which all events below the gate (input) must be present for the event above the gate (output) to occur.

⌂   an OR logic representing a condition in which any of the events below the gate (input) will lead to the event above the gate (output).

A simplified schematic taken from the previously cited reference illustrates the use of these symbols (Figure 4.1).

Normally, in treating an accident system, either real or potential, probabilities can be assigned to each event and the likelihood of the undesired event occuring can be determined. In treating fault analysis for oil shale mining, handling, and processing, examples are taken from the created scenarios, implying that all events are likely to occur; consequently, probabilities of occurrence are not considered.

The fault trees in the following sections represent an analysis of each of the scenarios in Section 2.6. Each fault tree was analyzed for a "facts status", i.e., what is and is not known. A major portion of the recommended research, Section 6.0, reflects the unknown elements in the fault tree analyses.

4.2.2   Combustion of Broken and Solid Oil Shale, Scenario 2.6.1

Rubble on the mine floor soaked with hydraulic fluid is ignited by cutting and welding. The fire spreads to a muck pile, and to the adjacent roof and ribs of the opening.

a.   Fault Analysis:

Fact status of postulated oil shale derived hazards (Figure 4.2):

●   Combustibility of oil shale.

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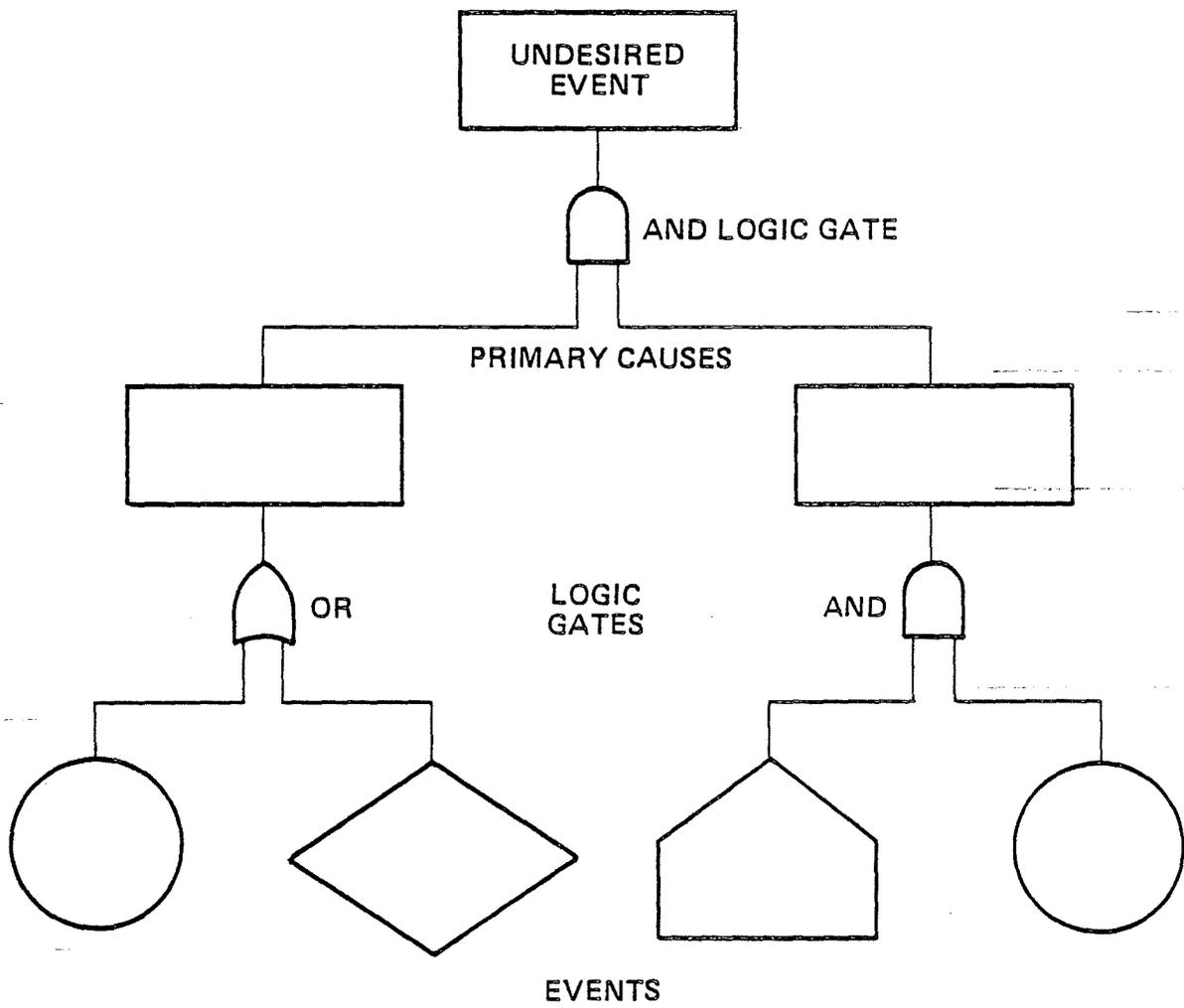
Figure 4.1   Example Fault Tree
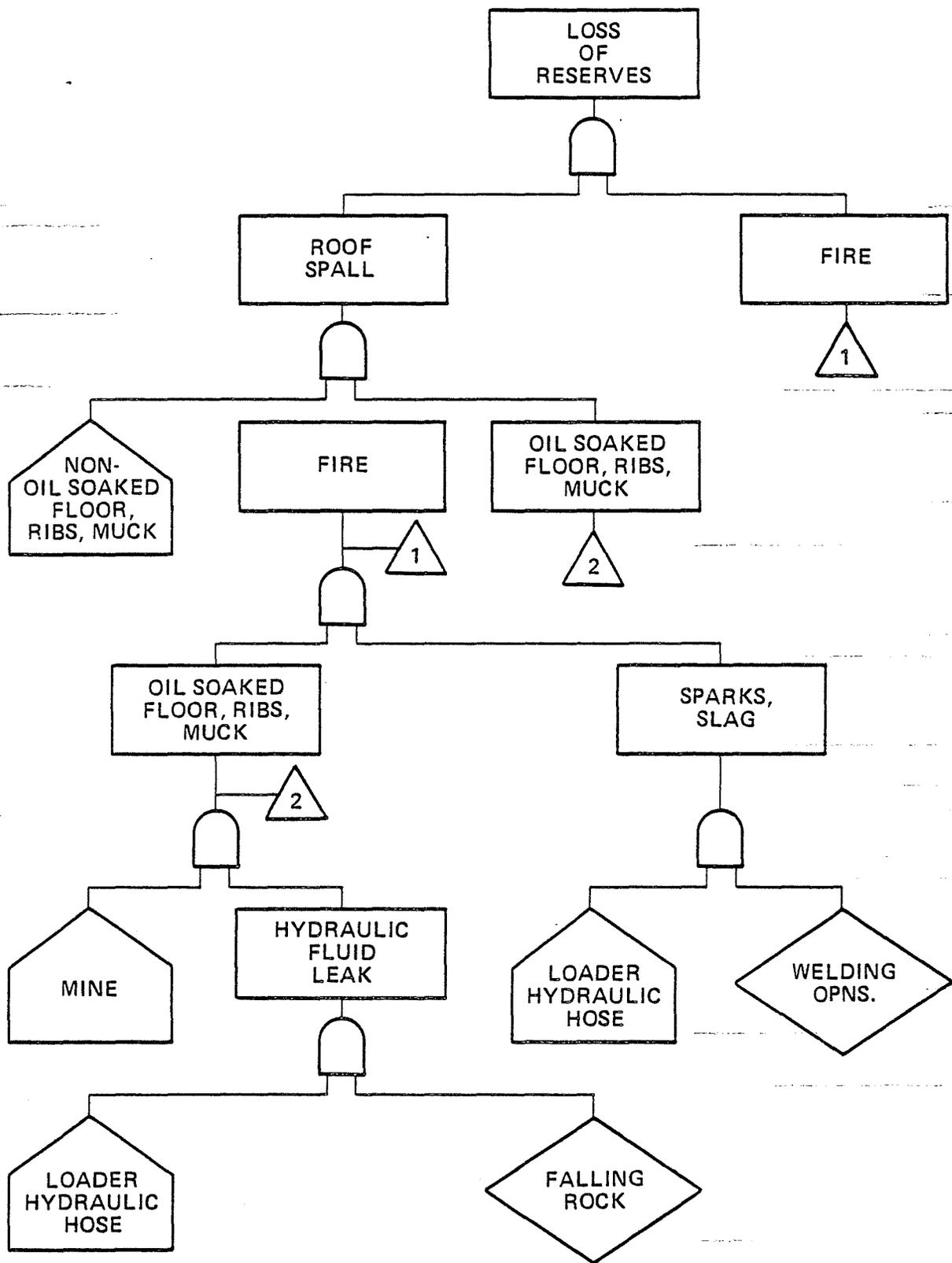
Figure 4.2   Fault Tree For Scenario 2.6.1: Combustiuon of Broken
and   solid Oil Shale in a Mine

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- Propagation of combustion from rubble into solid oil shale.

- Rate and intensity of combustion.

- Effect of combustion on mine surfaces.

- Effect of grade on ignition and propagation.

- Effect of particle size of rubble on combustion.

b. Effect of New Data on Postulated Hazards:

Although there were no provisions for rubble fires in the test program, one pan fire test was conducted. The results of this single modest effort failed to fully answer any of the above postulated hazards.

There is abundant evidence attesting to the combustibility of raw, broken oil shale. There is, however, much less available information about combustion of solid oil shale. The only available information on the latter is the evidence of combustion in weathered outcrops. Also, there may be some data to be found in the completed in situ retorts of Occidental Oil Shale Company's Logan Wash mine, and later from the in situ experiments by the Rio Blanco Project and the Laramie Energy Technical Center of DOE.

c. Prevention and Mitigation of Hazards:

- Use non-flammable hydraulic fluids.

- After using heat, fire, and spark producing equipment near raw shale rubble, check the area carefully for incipient combustion.

- Fire control equipment should be standard on all mine equipment and at other strategic locations.

- Mobile fire control equipment should be readily available to a mine with adit access, and inside mines with shaft or slope access.

- Ventilation and fire control doors and stoppings.

d. Procedures for Monitoring Compliance with Regulations:

No special techniques or procedures are required.

e. Detection and Suppression of Hazards:

No special techniques are required. As soon as oil shale begins to heat, prior to combustion, a distinctive and extremely unpleasant odor is produced. At the same time smoke is produced. State of the art detection devices may be useful, but would require case by case and location by location decisions of their need and usefulness.

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f.   Problems Requiring Solutions:

All of the questions raised by the scenarios, with the exception of combustibility, still need answers.

g.   Recommended Paths to Solutions:

Large scale rubble fire tests are required outside a mine for studying the hazard of fires in coarse ore stockpiles, and inside a mine for studying fires in muck piles and the effect of combustion on ribs, roof, floor and pillars. Some of the results obtained will probably replicate the effects of in situ retorting; most however, will not.

4.2.3   Propagation of a Methane Explosion by Raw Shale Dust, Scenario 2.6.2

A combination of events in a mine causes an explosion of methane which is propagated by oil shale dust on the mine surfaces.

a.   Fault Analyses:

Fact status of postulated oil shale derived hazards (Figure 4.3):

- Explosivity of raw shale dust.

- Dust load density on mine surfaces necessary to propagate an explosion.

- Concentration and grade of airborne dust necessary for a explosion.

- Ignition energy required.

- Effect of particle size distribution on the explosivity of oil shale dust.

- Intensity of a methane/oil shale dust explosion.

b.   Effect of New Data on Postulated Hazards:

By exceeding the guidelines for pressure in the Hartman apparatus, it was possible to generate an explosion of oil shale dust with laboratory tests. The laboratory tests (Section 3.3.2.1) found the explosivity or oil shale dust to be nominally less than 0.0001, and ignition energy of nominally less than eight joules. As a result of the Bruceton tests, Richmond and Miller (1978) calculated that an average load of 0.098 gm/cm^2 of dust on all surfaces of a 50 by 60 by 70-foot room was necessary to provide a 0.3 gm/1 concentration of airborne dust. This is the minimum
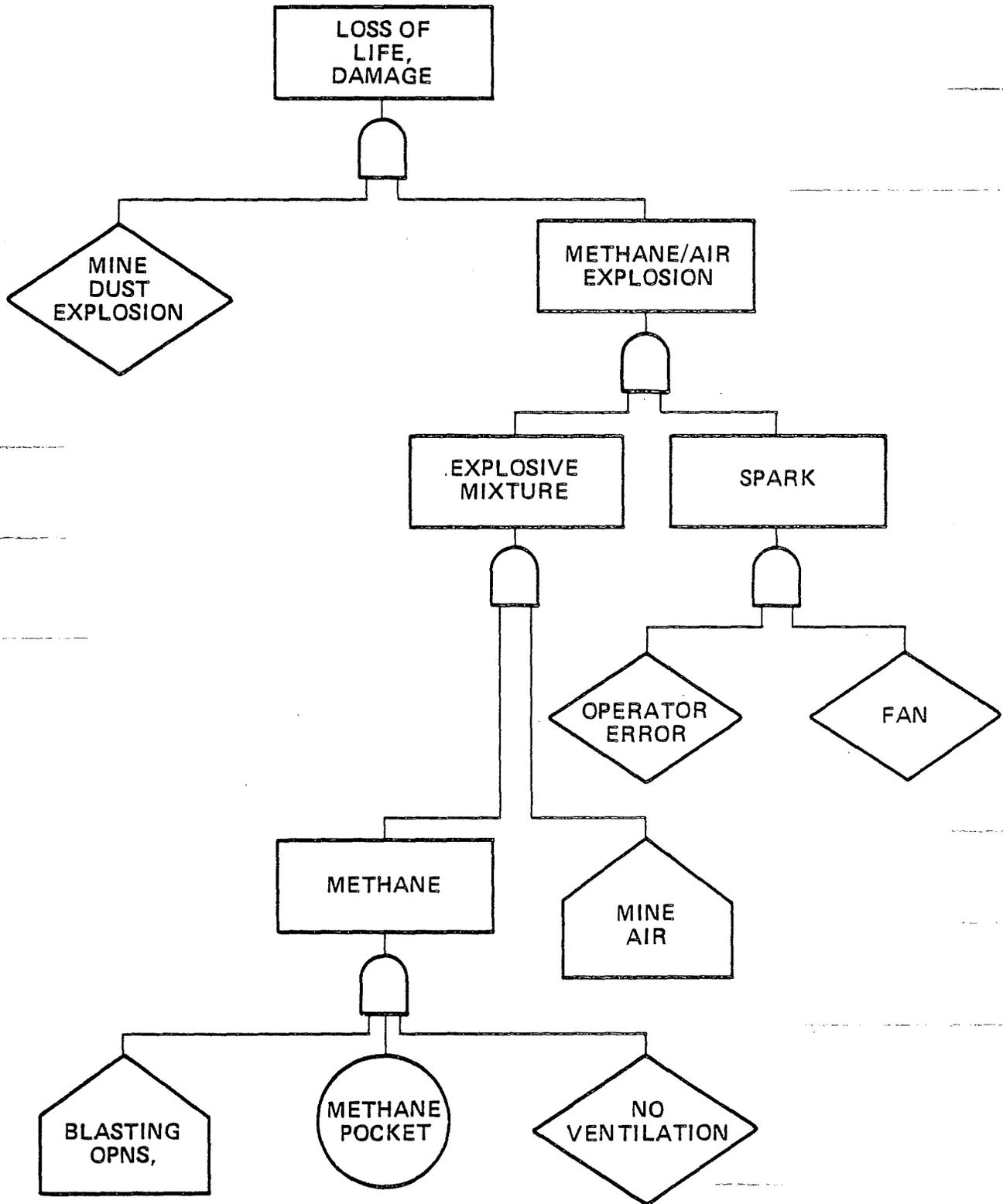
Figure 4.3   Fault Tree For Scenario 2.6.2: Propagation of a Methane
              Explosion by Raw Shale Dust

calculated concentration of dust assaying 30 gpt that is required to propagate an explosion of methane. The conclusions that were derived from the study of dust loading in the Colony mine, (Section 3.2.5) suggest that the dust load in an oil shale mine is about one-tenth (get from 5.1) the load necessary to propagate a methane explosion.

The testing program provided fundamental relationships between particle size and grade. Test results indicate coarse dust fractions inhibit ingition and a laboratory peak pressure of 65 psig for methane/oil shale dust explosion was obtained. The program also has provided some evidence about the time deterioration of the kerogen content of oil shale dust.

c.   Prevention and Mitigation of Hazards:

The results of large scale tests have established that oil shale dust propagates methane explosions. However, dust loading studies in a room and pillar oil shale mine indicate that not enough dust is, or will be, present to propagate an explosion. These diverse data leave us, at present, without a basis for establishing the hazard potential, if any exists. Nevertheless, prevention and mitigation of postulated hazards should be addressed, because investigations of the dust load and grade in other mining conditions may vary significantly in small openings, in rubblized shale, and close to active working faces.

State-of-the-art regulations prescribe monitoring, dilution and other procedures to prevent and mitigate methane derived hazards. The oil shale dust hazard has not yet been completely identified. However, if a hazard is found to exist, dilution with lime dust is not thought to be as practical, economic, or effective as occasional wetting of the offending surfaces with water.

d.   Procedure for Monitoring Compliance with Regulations:

If regulations for dust loading were found necessary, the dust load and grade relative to the adjacent excavated volume and the minimum safe airborne concentration must be determined. The dust loading would be determined by collecting dust from several areas with a small portable vacuum sweeper. If the weight per surface units exceeds the pre-determined maximum for the adjacent room dimensions, a Fischer assay would also be required. If the weight and grade of the dust samples, and specified number of check samples, exceed the allowable limits for that particular location, remedial action would be required.

e.   Detection and Suppression of Hazards:

State-of-the-art procedures are available for detecting and diluting methane hazards. The detection of an explosive dust hazard can be made by following the procedures outlined in 4.2.4.4. Suppression of a methane/oil shale dust explosion would be after-the-fact suppression of consequential fires and explosions.

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f.   Problems Requiring Solutions:

- The maximum dust loading in various sizes of mine openings, in rubblized oil shale, and the grade of the dust in relation to the grade of the section being mined.

- The minimum grade and the concentration of oil shale dust that will explode, or propagate the explosion of other substances.

- A laboratory or small scale test procedure that will be a reliable measure of full scale events.

g.   Recommended Paths to Solutions:

- Obtain dust loading data in all available mines now and as they continue to develop.

- By study and experiments, develop testing procedures and apparatus that will serve as a measure of the explosion hazard of oil shale dusts of all grades, and their concentrations in full-scale operations. One likely route to developing these protocols, may be by scaling down the Bruceton mine experiments to the smallest dimensions that can replicate the results of those experiments. The laboratory procedure that evolves would be used to establish the minimum grade and air borne concentration of dust that is explosive with and without methane. The suite of data that results will establish the minimum airborne concentration of all dusts in the explosive range. The explosive hazard of an oil shale dust could potentially be calculated once a correlation between minimum dust concentration by grade and grade of the mining section is established.

- Conduct additional oil shale dust explosions at Bruceton, using dust with particle size distributions representative of actual mine dust. These tests with oil shale dusts of lean, medium, and rich grades will be very useful in corroborating laboratory or small scale tests. They then can be useful in completing a suite of data for a wide variety of conditions of concentration, grade, temperatures, and methane and retort gases and vapor concentrations and richness.

- Learn more about the effect of aging on oil shale dusts.

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4.2.4   Combustion and/or Explosion of Raw Oil Shale Dust Below a Crusher, Scenario 2.6.3

The dust in a hopper below a crusher is scattered by a repairman, the heavy airborne concentration of dust is ignited and/or detonated by a cutting torch.

a.   Fault Analyses:

    Fact status of postulated oil shale derived hazards (Figure 4.4):

    ● Explosivity of raw shale dust cloud in a methane free atmosphere.

    ● Combustibility of dust layer from spark, slag, or flame.

    ● Rate and intensity of combustion of shale dust.

    ● Effect of grade and particle size distribution on explosivity or combustibility of crusher dust.

    ● Effect of a dust blanket on the combustibility of crushed oil shale.

b.   Effect of New Data on Postulated Hazards:

    The test procedures provided new data as described in Section 4.2.3. Other results and interpretations are reported in Section 3.3.2.

c.   Prevention and Mitigation of Hazards:

    The dust explosion hazard in mining is dependent on methane or retort vapors and the amount and grade of available dust. In all other raw shale handling and processing operations such as crushing, there could be heavy localized concentrations of dust that might be subject to heat and fire from numerous sources. If it is established that shale dust is explosive or combustible above specific concentrations and grades, prevention and mitigation would consist of, first, reducing the concentrations and second, eliminating the sources of ignition and detonation from potentially hazardous areas.

d.   Procedures for Monitoring Compliance with Regulations:

    Assuming a hazard could exist, state-of-the art procedures can be used to ascertain that potential sources of ignition and detonation are not allowed to contact combustible and/or explosive dusts.
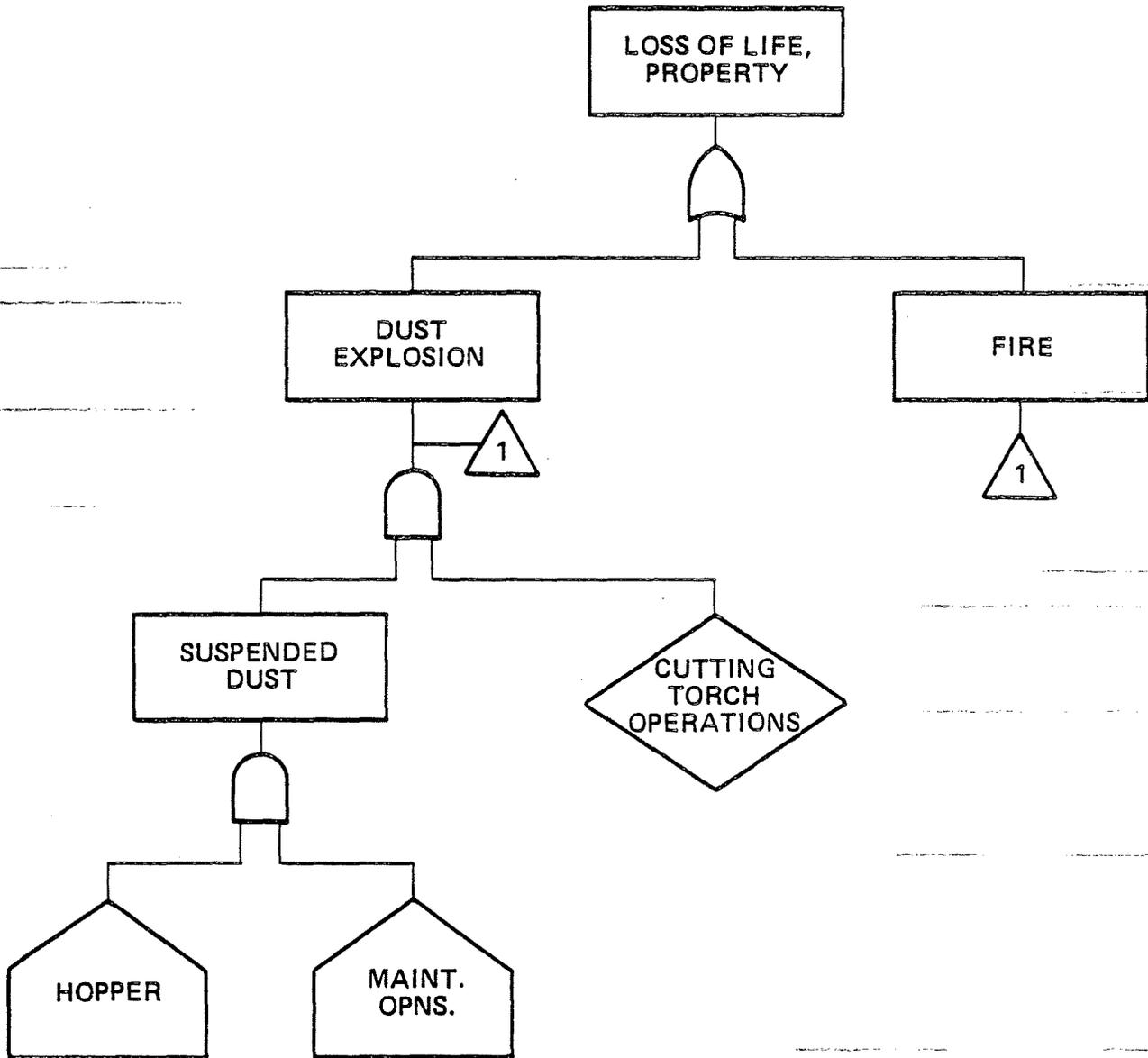
Figure 4.4   Fault Tree For Scenario 2.6.3: Combustion and/or Explosion of Raw Oil Shale Dust Below a Crusher

e. Detection and Suppression of Hazards:

Recognition of a potential hazard would be the result of establishing the minimum grade and minimum concentration of shale dust that is hazardous to fire and explosion. If either of these factors is absent, no hazard exists. Assays and measurements will establish compliance with regulations.

f. Problems Requiring Solutions:

* Determination of the explosivity of raw shale dust by size, consist and grade.

* Expand the combustibility testing of dusts, Section 3.3.3.

* Establish the rate and intensity of combustion of oil shale dust layers and piles as discussed in Section 2.6.4.

* Establish the effect of a dust blanket, or a high ratio of dust with broken oil shale, on combustibility.

g. Recommended Paths to Solutions:

* Hazard of dust explosivity as discussed in Section 4.2.3.

* Conduct experiments on combustion and heating to establish required data.

4.2.5 Fire and/or Explosion from a Hot Exhaust Manifold, Scenario 2.6.4

A layer of dust on a hot exhaust manifold is ignited at the time a mine round is blasted. The burning dust detonates the airborne dust cloud raised by the blast.

a. Fault Analyses:

Fact status of postulated oil shale derived hazards (Figure 4.5):

* Ignition temperature of raw shale dust.

* Explosivity of raw shale dust.

* Minimum concentration and grade of airborne dust necessary to detonate and propagate an explosion.

b. Effect of New Data on Postulated Hazards:

As described in Section 3.5.2, dust layer testing was minimal. RI 5624 procedures and an unconventional hot plate test demonstrated

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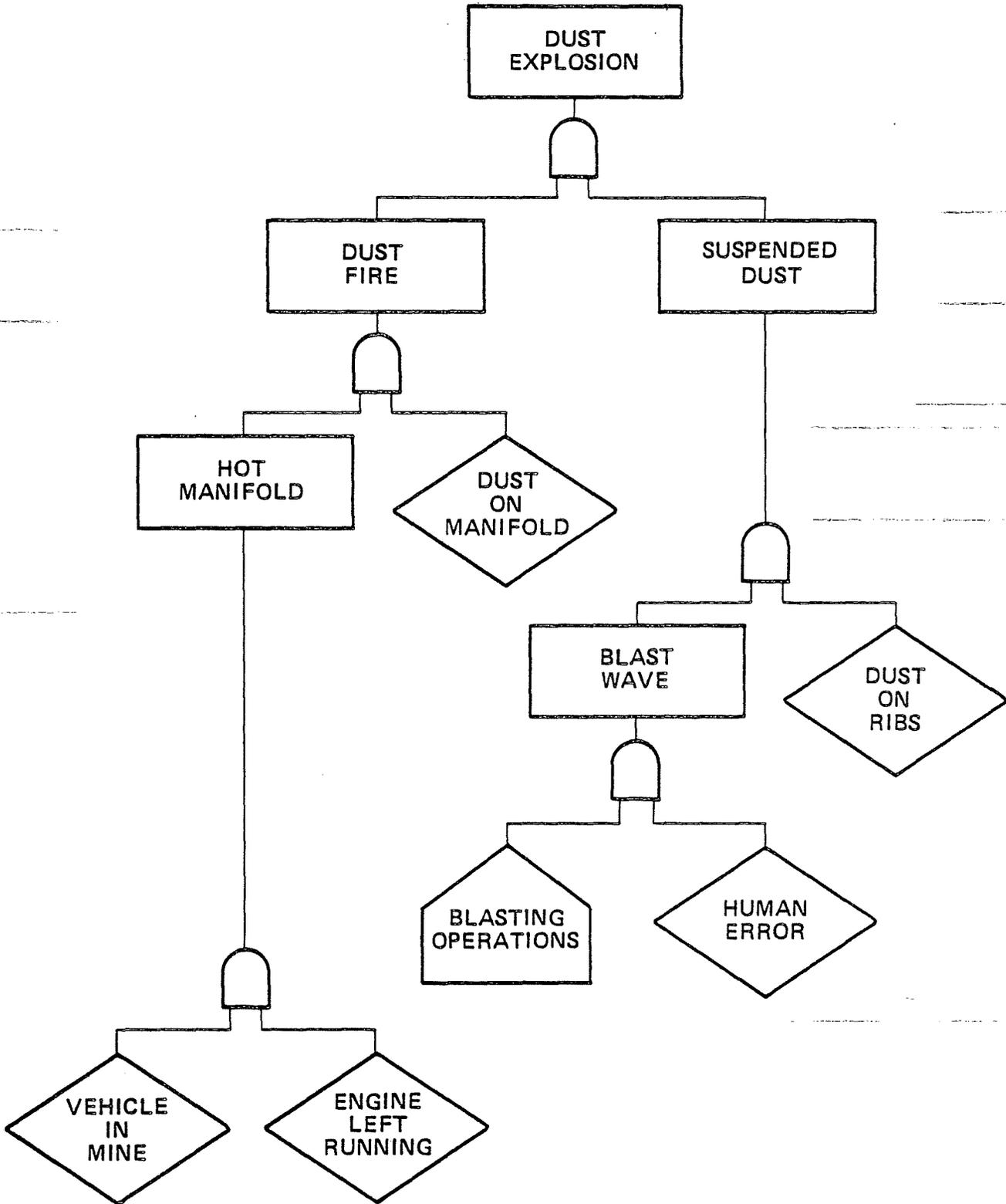
Figure 4.5   Fault Tree For Scenario 2.6.4:   Fire and/or Explosion From a
Hot Exhaust Manifold

that hot oil shale dust layers present a potential hazard, if an ignition source is present. The nominal ignition temperature is 260°. The ignition temperature correlates well with the grade.

c. Prevention and Mitigation of Hazards:

If additional studies and tests establish the combination of shale dust and the size, grade and concentration that will create a hazard; exhaust and other high temperature surfaces must be insulated or cooled. These techniques are state-of-the-art for coal mines.

d. Procedures for Monitoring Compliance:

An inspector would enforce regulations when an assay of the shale dust established a grade at or above a predetermined safe maximum, and the temperature of a hot surface with which the dust could come in contact was also at or above a predetermined safe maximum for the grade of this shale, and the potential for an ignition is present.

e. Detection and Suppression of Hazards:

As discussed in Section 4.2.4.

f. Problems Requiring Solutions:

- Ignition temperature(s) of raw shale dust.

- Maximum safe grade of shale dust for specified temperatures.

- Maximum allowable temperatures of hot surfaces for specified grade.

- State-of-the-art procedures need evaluating to establish their accuracy and/or applicability for this test.

- New test apparatus and procedures may be required.

g. Recommended Paths to Solutions:

- Establish a satisfactory procedure for conducting the necessary tests.

- Confirm maximum safe temperatures for all grades of shale.

4.2.6 Spontaneous Combustion of Raw Oil Shale, Scenario 2.6.5

Spontaneous combustion occurs in the "dead" portion of a large coarse ore stockpile on surface.

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a. Fault Analyses:

Fact status of postulated oil shale derived hazards (Figure 4.6):

- Potential for spontaneous combustion of oil shale.

- Effect of grade, size distribution, chemical compostion, moisture content, and climate.

- Effect of the shape of storage pile or bin.

- Safe temperature of cooled shale that will eliminate the possibility of re-ignition.

b. Effect of New Data on Postulated Hazards:

Oil shale dust was tested by using hydrogen peroxide to establish the tendency of oil shale to spontaneously combust. The test results are generally affirmative, with richer shales showing higher reactions. Large run-of-mine stockpiles of 30 to 35 gpt oil shale at Colony and Anvil points have shown no evidence of heating after more than 10 years. Crushed oil shale at Colony, however, has shown signs of heating. These occurrences were random with respect to time in storage, volume and shape of the pile, precipitation, and other effects. Moisture was the factor common to most observations.

Laboratory tests indicate a spontaneous combustion index for oil shale from 2 to 10, depending on richness. Using this same index Pittsburgh seam coal is 10 and Western coal is 20 to 30. Although the relative degree of combustibility of oil shale versus Pittsburgh coal is uncertain, it is "less likely" than coal.

c. Prevention and Mitigation of Hazards:

The potential for spontaneous combustion is principally a function of particle size and richness as determined from laboratory tests and actual experience (observations of R. B. Crookston from 1965-78). State-of-the-art techniques for preventing and mitigating the hazards in bituminous coal storagepiles are applicable to oil shale. These techniques include properly designed and constructed storage piles and cooling the heated coal with water and/or mixing it with cooler materials in the storage pile before being fed to the plant. The problem of spontaneous combustion of oil shale in closed bins and hoppers has much less hazard potential.

d. Procedures for Monitoring Compliance with Regulations

No special techniques would be required

e. Detection and Suppression of Hazards:

In cool weather, moisture will be concentrated above the areas in the pile that are heating. The strong, unpleasant odor from

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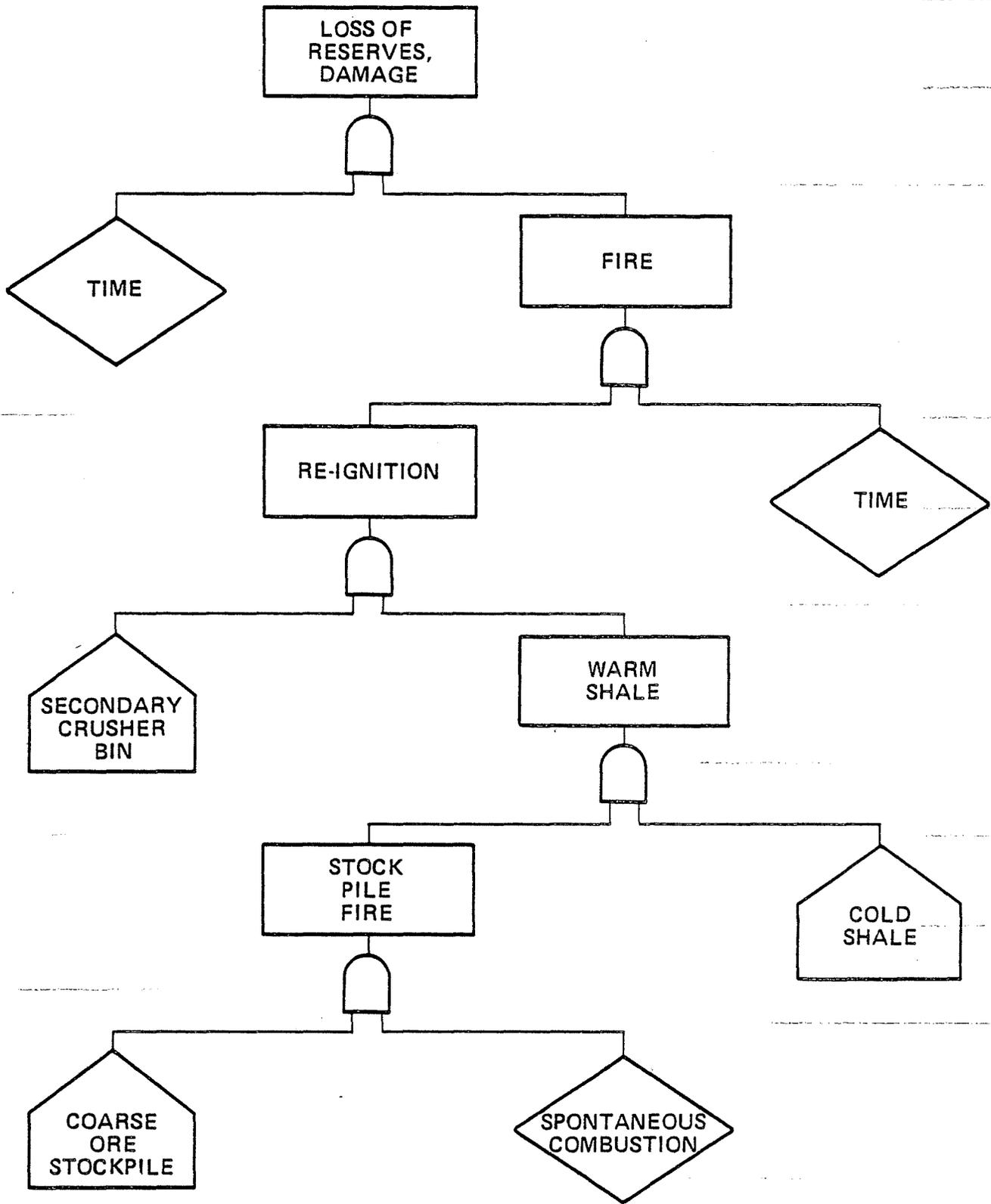
Figure 4.6   Fault Tree for Scenario 2.6.5:   Spontaneous Combustion of Raw
Shale

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retorting shale will be also present. The "hot spot" can be pinpointed by thermocouples located in "drive" pipes, or by excavating into the heated area. A small zone that is heating can be flooded with water through the "drive" pipe or by wetting the surface with sufficient water to cool the heated shale. When a heated zone is uncovered by excavation, and the material is below combustion temperature, it can be cooled by mixing with adjacent shale. If combustion is in progress, the combustion zone should be cooled with water before mixing.

f.   Problems Requiring Solutions:

None of enough magnitude that will require more than compilation of data from observations and field experience.

g.   Recommended Paths to Solutions:

No special solutions are required.

4.2.7   Fire and Explosion in a Hot Gas Recirculation Retort, Scenario 2.6.6

After repairing a hot recycle gas compressor, an air leak into the rich, hot recycle gas stream is undetected and the combination reaches explosive limits. The resulting explosion starts secondary fires of raw shale, spent shale, shale oil, and gas in the area.

a.   Fault Analyses:

Fact status of postulated oil shale derived hazards (Figure 4.7):

●   Auto-ignition temperature, flammability, and explosivity of rich retort gases and vapors in various combinations with air.

●   The conditions under which raw and spent shale, shale oil, and retort gases and vapors will ignite and sustain combustion.

b.   Effect of New Data on Postulated Hazards:

Tests on retort oil, gases, and vapors were limited to establishing the upper and lower explosive limits of high and low Btu retort gases. The lower limit of retort gas concentration in air was about 15%, the upper limit about 25 to 30%, and the minimum ignition energy about 70 milliamps. The most dangerous mixture appears to be about 15%. Under the same test conditions the most hazardous air/methane mixture has a minimum ignition energy of about 100 milliamps (Section 3.8.2).
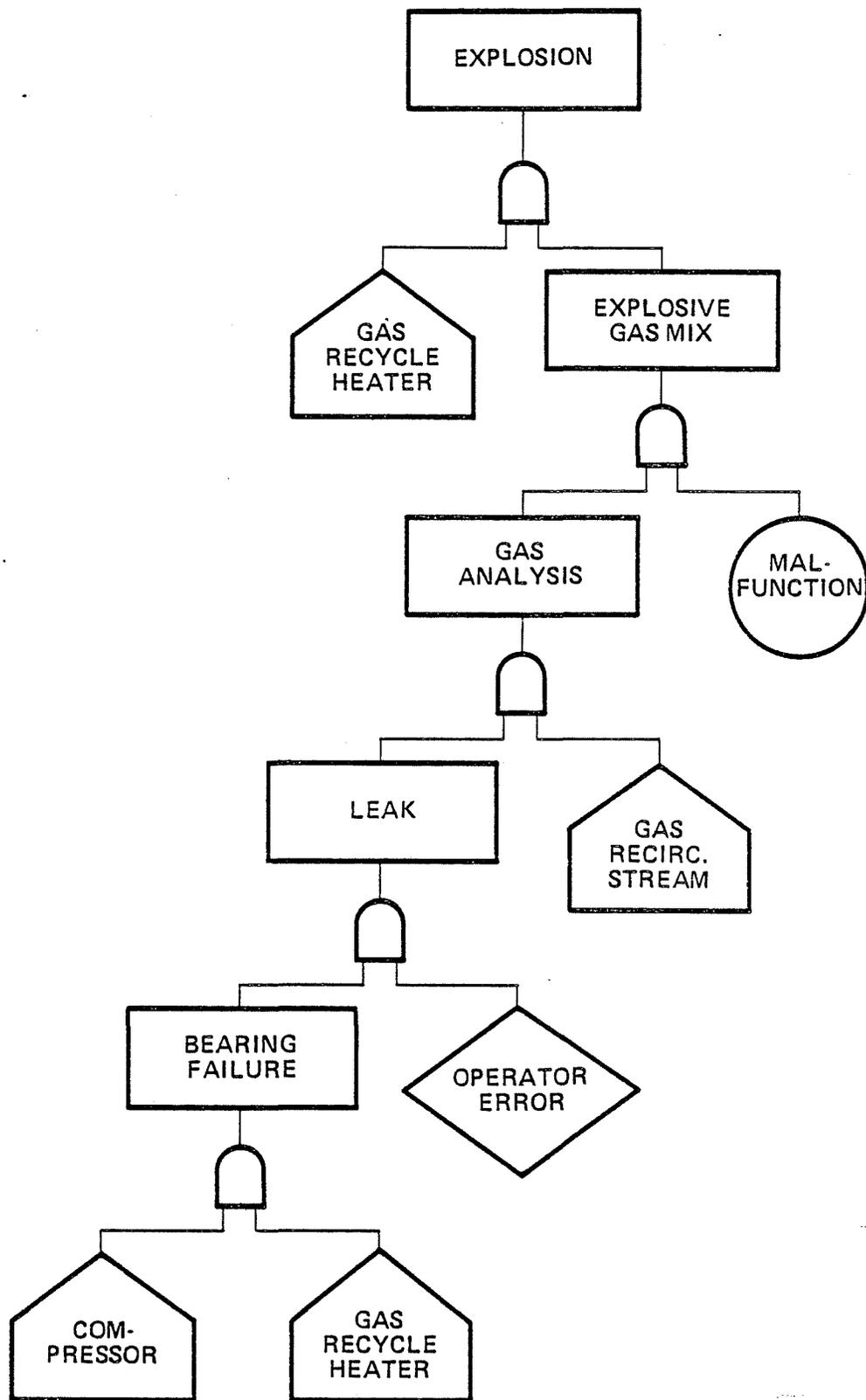
Figure 4.7   Fault Tree for Scenario 2.6.6:   Fire and Explosion in a Hot Gas
              Recirculation Retort

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The limits of flammability for raw and spent shales are not known, however, the ignition energy for the dust clouds are reported in Section 3.3.1.2.

c. Prevention and Mitigation of Hazards:

Every precaution should be taken to prevent oxygen from entering the hot recycle gas stream. Continuous monitoring and alarm devices should be placed at more than one location.

d. Procedures for Monitoring Compliance with Regulations:

The temperature, pressure, and analysis of the gas will be continuously monitored and recorded. An inspector will have information about the upper and lower explosive limits of the gas stream(s) for comparison purposes. He can also obtain samples directly from the gas stream for confirmation of the recorded results.

e. Detection and Suppression of Hazards:

Detection of a recycle gas hazard would be as discussed in Section 4.2.9. Suppression would be essentially the same as fire and explosion control techniques used in oil refineries.

f. Problems Requiring Solutions:

Investigate the minimum ignition energy, and upper and lower explosive limits of retort gas(es) and vapors as a function of temperature and concentration in air and with low Btu retort gases.

g. Recommended Paths to Solutions:

- Determine auto-ignition temperature of oil shale gases, mists, and vapors at temperatures ranging from 450°F to 1500°F.

- Determine the upper and lower explosive limits of oil shale gases, mists, and vapors at temperatures 450°F to 1000°F.

- Determine the effect on the foregoing, of diluting oil shale gases and vapors with low Btu retort gases.

- Determine the hazard level of each of the foregoing.

4.2.8   Explosion of Spent Shale in a Surface Retort, Scenario 2.6.7

An accident causes hot spent shale dust to be dispersed in a heavy air-borne concentration which is detonated by an electric spark.

a. Fault Analysis:

Fact status of postulated oil shale derived hazards (Figure 4.8):

- The explosivity of spent shale dust

- The ignition temperature, carbon content and particle size required for a spent shale dust explosion.

- The dust concentration and ignition energies required to detonate and propagate an explosion of spent shale dust.

b. Effect of New Data on Postulated Hazards:

The test procedures provided new data as described in Section 3.3.3. The ignition temperature of spent shale dust is nominally greater than 800°C (limit of apparatus) regardless of carbon content for any size range. The dust concentration of nominally two grams per liter (5-15 psig test) or less than 0.1 grams per liter (25 psig test), each required greater than 8 joules.
The laboratory program provided sufficient data and information on spent shale to establish that it has less liability as a hazard than lean oil shale dust.

c. Prevention and Mitigation of Hazards:

The same procedures, if any are required, that apply to extremely lean oil shale dusts, would apply also to spent shale dust.

d. Procedures for Monitoring Compliance with Regulations:

No special techniques or procedures will be required.

e. Detection and Suppression of Hazards:

Same as for Section 4.2.3d.

f. Problems Requiring Solutions:

If safety hazards are found for lean raw shale dust, then the research program suggested under Section 4.2.3g would apply.

g. Recommended Paths to Solutions:

Same as for Section 4.2.3g.

4.2.9 Gas Combustion Retort Fire and Explosion: Scenario 2.6.8

A mechanical malfunction in an electrostatic precipitator results in an air leak into the precipitator forming an explosive mixture of oil mist, low Btu gas and air. An electrical spark in the precipitator causes an explosion.
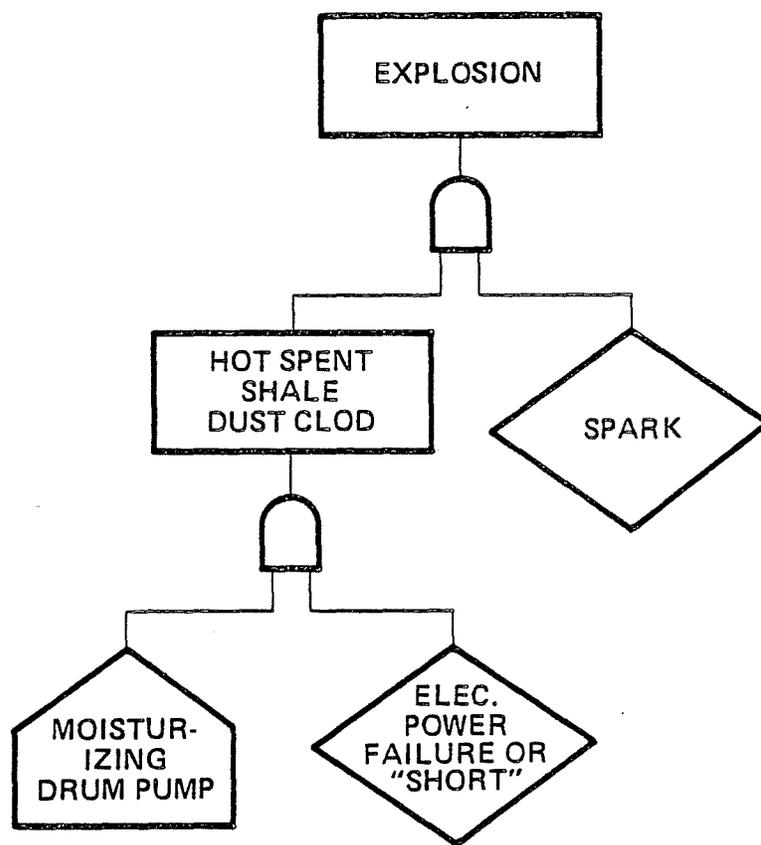
Figure 4.8   Fault Tree For Scenario 2.6.7:   Explosion of Spent Shale Dust
in a Surface Retort

a. Fault Analysis:

Fact status of postulated oil shale derived hazards (Figure 4.9):

- The flammability and explosivity of low Btu gas/oil mist/air mixtures.

- The energy required to initiate an explosion of low Btu gas/oil mist/air mixtures.

- The flammability of raw shale oil.

b. Effect of New Data on Postulated Hazards:

The results of the tests (Section 3.8), using the P.T.B. apparatus provide a reasonably good basis for evaluating the hazards of retort gases. Three retort gases derived from Fischer assays were tested for upper (UEL) and lower LEL explosive limits. The LEL for retort gas in air is about 5%, the UEL about 25 to 30% with a minimum ignition energy of 0.23 millijoules and a current less than 0.1 amperes. Retort vapors were not included in the test work.

c. Prevention and Mitigation:

Gases and vapors from retorting that are released from a retort circuit present the general type of hazard as methane. Prevention of hazards means prevention of retort leaks. Mitigation would be accomplished by the dilution and dispersion of the gases.

d. Procedures for Monitoring Compliance:

State-of-the-art procedures are available for monitoring the gases and vapors that evolve from retorting. Constant monitoring and recording devices should be located at carefully selected sites. Comparison would be made of these data with predetermined concentrations that are below the hazard level.

e. Detection and Suppression of the Hazard.

The same procedures as discussed in c. and d. of this section apply. Suppression of the resulting fires would follow standard practices for oil refineries.

f. Problems Requiring Solutions:

- Determine the flammability and explosivity of low Btu gas/oil mist/air mixtures for a range of gas, mist, air ratios.

- Determine the ignition energy required to initiate an explosion of low Btu gas/oil mist/air mixtures for a range of gas, mist, air ratios.

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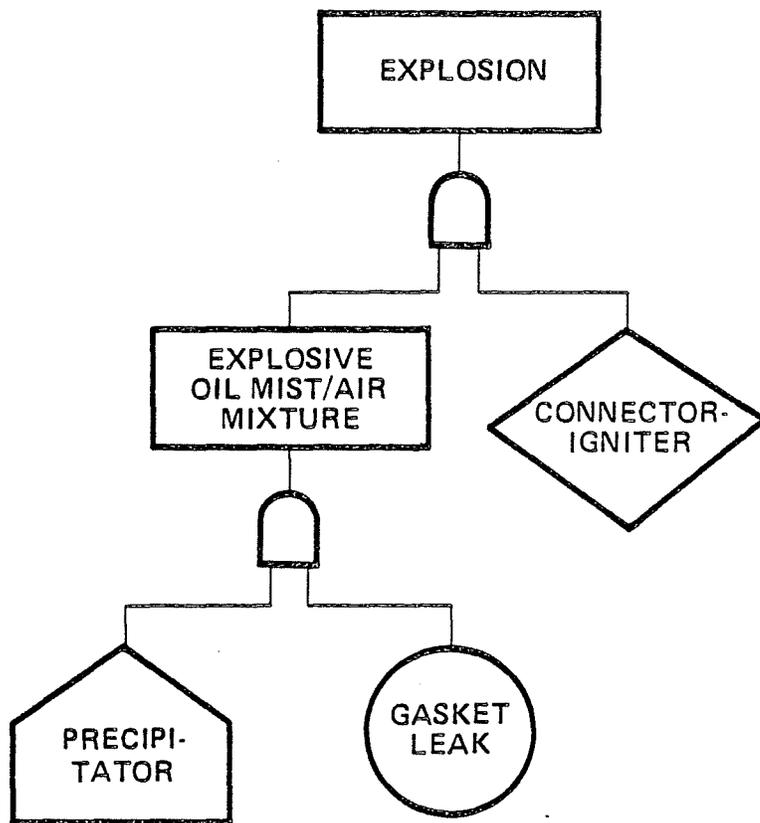
Figure 4.9   Fault Tree For Scenario 2.6.8:   Gas Combustion Retort Fire and
              Explosion

- Determine the effect of temperature on the foregoing.

- Establish the hazardous level for each.

g. <u>Recommended Paths to Solutions</u>:

The procedures developed as a solution in Section 4.2.7g would provide the required solutions.

4.2.10 <u>Explosion of Hot, Rich Gases from a Spent In Situ Retort, Scenario 2.6.9</u>

The sensible heat in a shut down retort is to be used to preheat a rubblized retort. The heat is transferred by flowing low Btu gas from an operating retort through the spent retort. The recycle gas also picks up rich gas and vapors. When the combination contacts the air in the rubblized retort, an explosion occurs which is propagated by the dust in the rubble.

a. <u>Fault Analysis</u>:

Fact status of postulated oil shale derived hazards (Figure 4.10):

- Auto-ignition temperature of retort gases and vapors.

- Explosivity or raw shale dust.

- Intensity of a retort gases and vapors/oil shale dust explosion.

- Dust load in rubble necessary to propagate an explosion.

- The effect of rubble on the intensity of an explosion in a retort.

b. <u>Effect of New Data on Postulated Hazards</u>:

The auto-ignition temperatures of the major components of raw shale oil range from about 500°F to 1200°F. The degree of their hazard is dependent upon the composition of the gases and vapors that are released from a retort over a range of retorting conditions and temperatures. Figure 3.3.2 shows typical compositions of retort gas. Tests on retort gases are reported in Section 4.2.9.

c. <u>Prevention and Mitigation of the Hazards</u>:

The hazard can be mitigated by establishing limits on the temperature relative to the composition of retort gases, and vapors with low Btu gases, that can be released from a spent retort.
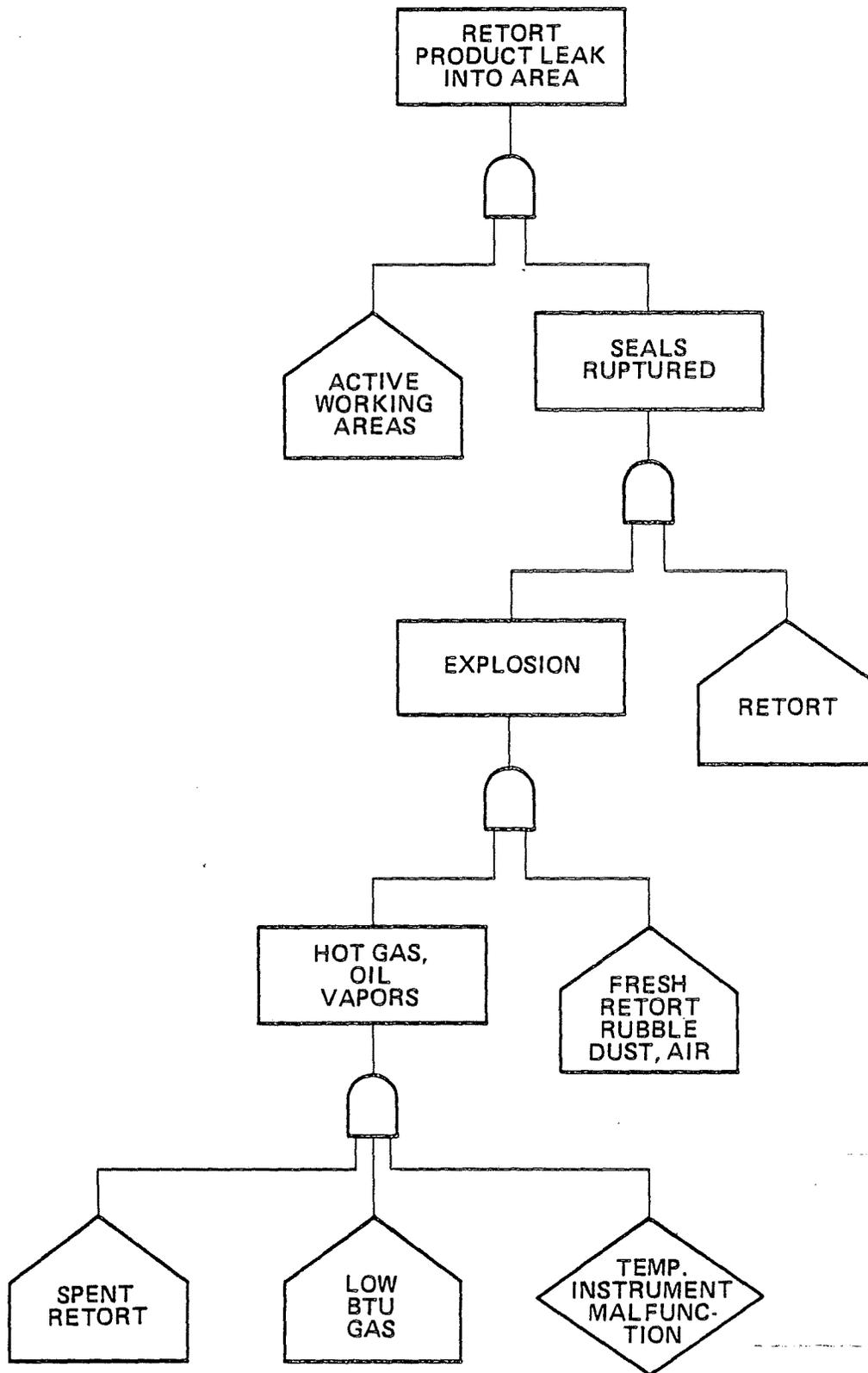
Figure 4.10   Fault Tree For Scenario 2.6.9:   Explosion of Hot, Rich Gases
From a Spent In Situ Retort

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d.   Procedures for Monitoring Compliance with Regulation:

       Before retort gases and vapors are released from a retort, the
temperature   and   the   gas/vapor   composition   would   be   within
predetermined safe limits.

e.   Detection and Suppression of the Hazard:

       Same procedure as for Section 4.2.9c.

f.   Problems Requiring Solutions:

       ●   Establish the auto-ignition temperature of a range of
             combinations of retort gases vapors and air.

       ●   Determine the liability of dust in rubble to propagate an
             explosion.

       ●   Determine the mitigating effect of rubble on an explosion
             originating in the rubble.

g.   Recommended Paths to Solutions:

       ●   Collect retort gases. Collect shale oil vapors generated
             at various temperatures. Using accepted fuels testing
             procedures determine auto-ignition temperatures for a
             range of combinations of gases, vapors and air.

       ●   Establish the load and grade of dust in broken shale
             rubble and compare the potential hazard to that of mine
             dusts.

       ●   Conduct explosion experiments, using rubble with particle
             size ratios similar to rubblized shale in an in situ
             retort. The experiments would measure by differences, the
             inhibiting effect of broken oil shale on the intensity of
             an explosion.

4.2.11   Explosion of Retort Gases Leaking into a Rubblized In Situ Retort,
          Scenario 2.6.10

The combustion zone burns through the rich shale section of a retort

wall, the recycle gas stream drives the rich gases and vapors into an

adjacent ready-to-be-fired retort. Ignition of the new retort, detonates an

explosion.

a.   Fault Analysis:

       Fact status of postulated oil shale derived hazards (Figure
       4.11):

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- Effectiveness of retort pressure tests

- Effect of temperature and pressure on rich, jointed and fractured, and moderately pressure resistant oil shale.

- Consequences of the products from retorting and combustion entering active mining areas.

- Minimum retort gas richness that will ignite.

- Hazard of re-igniting a retort after retorting has been interrupted.

- The reaction of a retort to the interruption of forced air flow.

- The effect of oil shale grade on the resistance of retort surfaces to combustion.

b. <u>Effect of New Data on Postulated Hazards:</u>

New data on gas flammability is reported in Section 3.8.2. The lower explosive limit in air is 3% to 5%. The composition of retort gases (Figure 3.3.2), retort vapors, and the products of combustion of oil shale all include lethal substances.

c. <u>Prevention and Mitigation of Hazards:</u>

- Consider the joint/fracture permeability of retort surfaces in the design of pillars between retorts.

- Install gas monitoring and alarm systems in mine workings.

- Sweep retorts with low Btu gases, and measure gas concentrations prior to ignition.

- Monitor retort pressure.

- Provide fail safe flow controls in retort gas inlet and exhaust conduits.

- Provide fail safe flow controls in mine air levels and ventilation openings.

d. <u>Procedures for Monitoring Compliance:</u>

- The concentration of gases, fumes and vapors in retorts before ignition, should comply with predetermined safe levels.

- Adequate detection and alarm system for monitoring gases and vapors would be maintained in active working places. Portable equipment would also be used by inspectors and safety personnel.
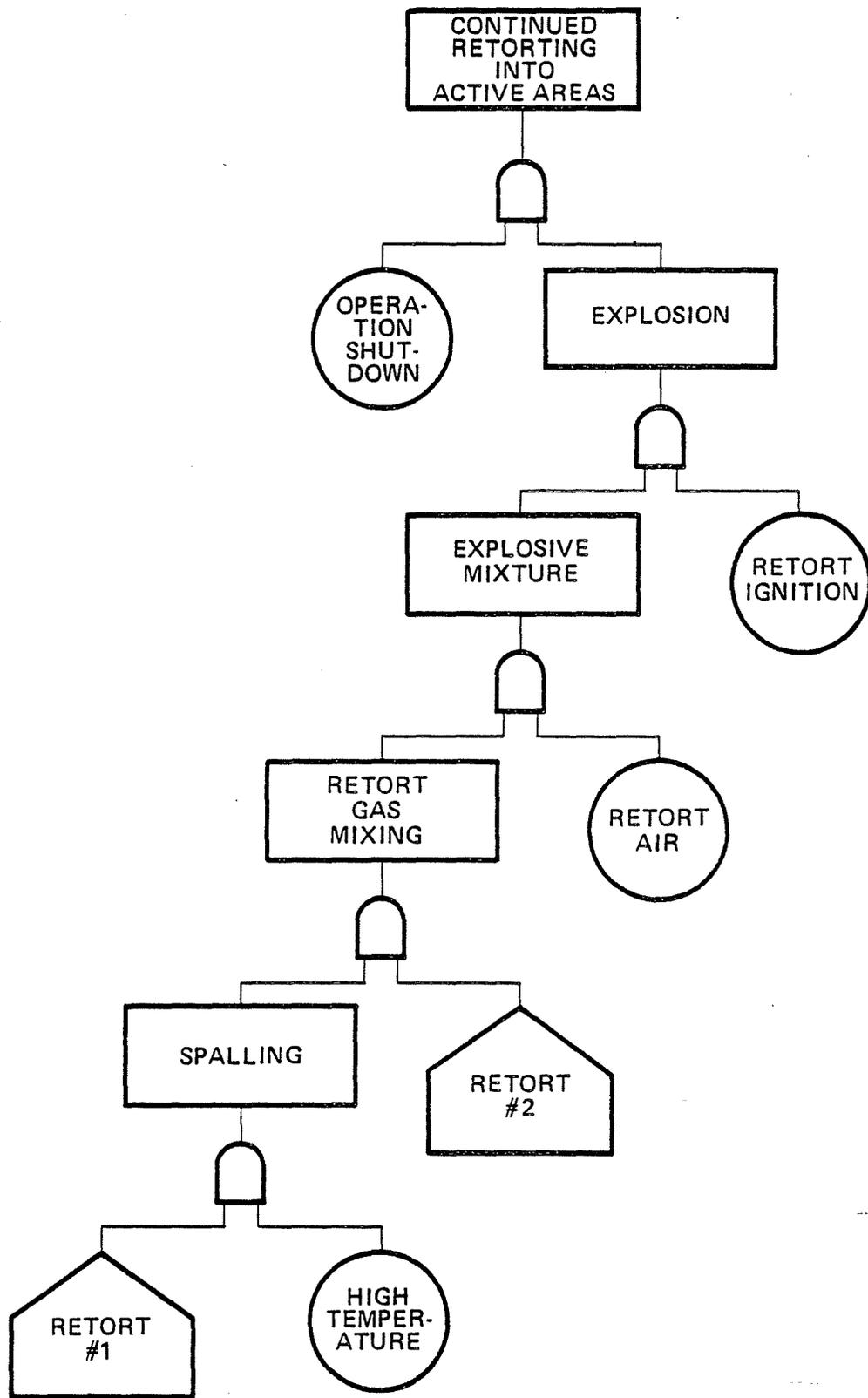
Figure 4.11   Fault Tree For Scenario 2.6.10:   Explosion of Retort Gases
Leaking Into a Rubblized In Situ Retort

e.   Detection and Suppression of Hazards:

   See 4.2.9c

f.   Problems Requiring Solutions:

   ● Establish the need for, and effectiveness of, in situ retort pressure tests.

   ● Determine the effect of combustion on the permeability of retort surfaces.

   ● Establish the potential for, and consequences of, retorting to continue in reverse fashion after blowers and/or compressors are shut down.

g.   Recommended Paths to Solutions:

   ● Practically all of the necessary data and information necessary to the solutions should come through cooperation between the segments of industry and government that are involved in in situ operations specifically and oil shale generally.

   ● Tests can be and/or are being devised and conducted by industry and by the Department of Energy that are intended to provide solutions to all of the potential problems that are presently evident.

   ● The specific tests should be devised to answer the problems posed in section preceeding.

4.2.12   Methane Explosion, In Situ Retort, Scenario 2.6.11.

   Methane which fills a rubblized retort is not purged before igniting the rubble. The resulting explosion is propagated by the shale dust in the rubble.

a.   Fault Analyses:

   Fact status of postulated oil shale derived hazards (Figure 4.12):

   ● Explosivity of oil shale dust

   ● Magnitude of an explosion originating in loosely packed, non-uniform rubble.

   ● Effect of particle size of dust and rubble on an explosion.

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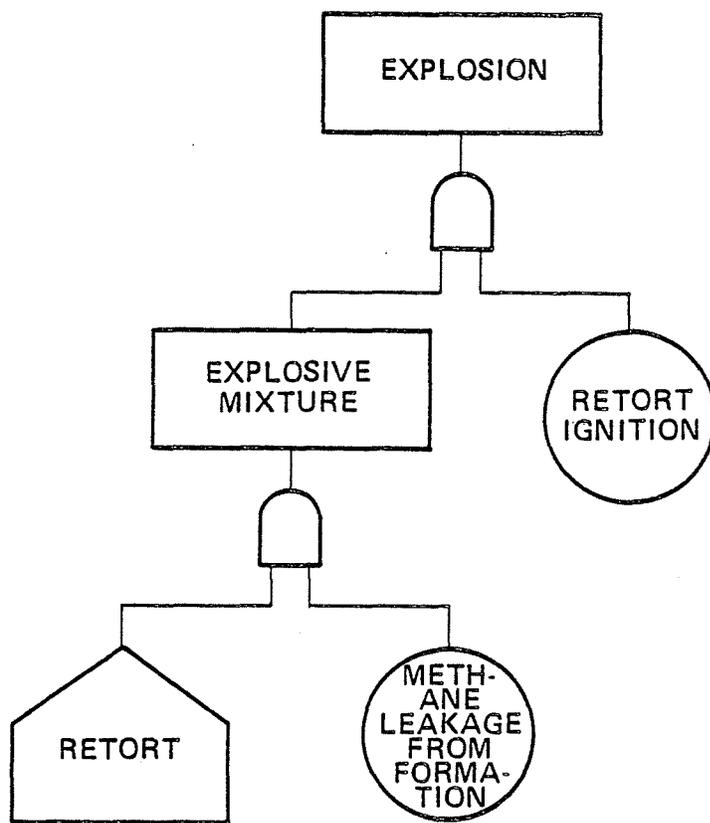
Figure 4.12   Fault Tree For Scenario 2.6.11:   Methane Explosion, In Situ Retorting

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- Intensity of methane/oil shale dust explosion

- Dust concentration in rubble.

b. **Effect of New Data on Postulated Hazards:**

New data discussed in Section 4.2.3 covers dust/methane explosions.

c. **Prevention and Mitigation of Hazards:**

The primary hazard here is methane. Similarly the only hazard that can be dealt with is methane. This can be accomplished by diluting and dispersing methane using low Btu retort gases or air to sweep the retort to a known safe gas level before ignition occurs.

d. **Procedures for Monitoring Compliance:**

The methane concentration in the retort should not exceed a predetermined safe level which can be checked before ignition of the retort.

e. **Detection and suppression of the Hazard:**

Procedures and equipment for monitoring the concentration of methane are well established.

f. **Problems Requiring Solution:**

- Determine the liability of dust in rubble to propagate an explosion.

- Determine the mitigating effect of rubble on an explosion originating in the rubble.

g. **Recommended Paths to Solution:**

Same as for dust on rubble parts of Section 4.2.10g.

4.3   **Additional Data Required to Complete Scenarios**

As was noted in the previous section, many gaps in data still exist. These gaps could not be filled under the time and economic constraints of this program. In order to complete the analysis of the scenarios, the following data are needed:

a. The combustibility, intensity of combustion and the fire spread rate in rubble as a function of grade and size distribution.

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b. The effect of an oil shale dust blanket on, or mixed with, rubble in propagating or restricting combustion.

c. The effect of gas combustion retorting continuing, with the air supply interrupted or reversed, and a determination of combustion and retort products as a function of temperature and time.

d. The mitigating effect of rubble as it relates to the propagation of an explosion which originates in the rubble.

e. The auto-ignition temperature, limits of flammability, and the minimum ignition energy of retort gases, vapors, and mists as a function of temperature and pressure.

f. The pressure-time history of a retort gas/air explosion.

g. The effect of retort gas/air mixtures with retort oil mists.

h. The effect of surface area, void spaces, chemical composition, and moisture on the liability of oil shale to spontaneously combust.

i. The need for, and effectiveness of, in situ retort pressure tests.

j. The effect of heat and combustion on the integrity and permeability of oil shale.

k. The dust load in oil shale mine openings of varying sizes relative to opening size, age of dust and proximity to active mine headings.

l. The grade of oil shale dust relative to the solid oil shale from which it is derived.

m. The explosivity of oil shale dust in large scale tests to validate the effect of particle size, grade and dust concentration on test parameters.

4.4   Safety Reviews and Inspections

Statutes on health and safety in mines are currently covered under Public Law 91-173, as amended by Public Law 95-164, titled: Federal Mine Safety and Health Act of 1977. Public Law 95-164 amended the Federal Coal Mine Health and Safety Act of 1969 and repealed the Federal Metal and Non-Metallic Mine Safety Act, essentially requiring all mining activities to fall under one set of statutes. The regulations now being promulgated are expected to be completed in the near future.

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Oil shale mines in Colorado are currently covered by the metal and non-metallic, non-gassy portion of the Act, because no methane gas has been found in current prototype operations. Modified in situ experiments have been permitted to operate under variances that allow the firing and combustion of a retort, or in essence, a controlled underground fire. Small concentrations of gas (presumed to be primarily methane) have been encountered in drilling and shaft sinking in portions of oil shale reserves away from any outcrop. In the final analysis, it is probable that each mine will be classified gassy or non-gassy on an individual basis.

4.4.1 Test Parameters to be Considered in Establishing Fire and Explosivity Regulations

All safety hazards that relate to solid oil shale and dust, also relate directly to the grade or oil content of oil shale. Every commercial oil shale facility will have a laboratory for oil shale evaluations, with Fischer assay equipment as the central feature. The laboratory would also have equipment to analyze the products of retorting and prerefining.

- Solid and broken oil shale: The grade of the oil shale section being mined, crushed, and processed is important to forecasting hazards that might exist or occur. Samples of core and broken oil shale will be routinely assayed to provide operating information. These assays will also provide an early indication of the grade of the dust being produced, the section being mined and the material being processed.

- Oil shale dust: The precise relationship can be determined for the grade of the shale being mined and the dust that is generated. Because each mine and the interval(s) being mined will have differing grades of shale. It is therefore important to establish the head assays versus the dust assays. Excepting for the aging factor of dust, the relationship of the grades of shale and dust remains constant for individual mines, if not for the entire Piceance Creek basin.

If oil shale dust is proven to be a hazard, a minimum allowable "safe" grade and maximum allowable airborne concentration would be established. Fischer assay yields and airborne dust concentrations could be translated into total volatiles per cubic foot (Section 3.2.4.10). Monitoring compliance would consist of as many as four steps: 1) if the relationship of head and dust assays is established as suggested, recognition or elimination of a potential hazard of dust may simply require comparison of the assay of the oil shale being mined to a published table applicable to all Piceance Creek basin oil shale; 2) to establish the site specific relationship of head and dust assay for the section(s) being mined; 3) if the grade of dust is determined to be in the potentially hazardous range, the dust concentration would then be determined by relating the dust load per unit of surface area to the adjacent mine openings (as described in Section 3.2.5), the result would then be compared with a specified table similar to the table in Section 3.2.4.10; and 4) if both the "potential" amount of airborne dust and the grade of the dust are determined to be in the hazardous range, the dust load would either be reduced in quantity by blowing the dust down with air/water or diluting the dust with a non-explosive material.

The Phase 2 studies suggest that the grade of oil shale dust is diminished with time. This factor should be recognized and treated separately if activity is resumed in old mine workings.

As described in the foregoing, regulations that are based on total volatile hydrocarbons or potential combustion energy may be readily equated with the potential hazard of mine dust.

If fire and explosivity regulations are necessary, Fischer assay data or other associated properties should be used as primary compliance criteria. If Fischer assay facilities are not available, it may be feasible to

determine particle specific gravities of an oil shale sample to calculate approximate Fischer assay yields. However, the presence of inert rock or other extraneous material in the sample might reduce the validity of specific gravity correlations. In addition, procedures for estimating Fischer assay oil yields by gas chromatographic and nuclear magnetic resonance tests have been developed. Further confirmation is needed before these relatively rapid procedures can be recommended.

4.4.2 Proposed Guidelines Concerning Safety and Inspections

A commercial oil shale facility must have a laboratory for oil shale evaluations, including Fischer assay equipment. Oil shale mine dusts would be collected for testing and the Fischer assay oil yield determined within a few hours. If the test dusts are not aged, the relationships described in Section 3.0 provide a means to estimate kerogen and organic carbon contents, and to estimate total hydrocarbon and combustion energy yields that may be produced upon heating the oil shale dusts. Regulations based on total volatile hydrocarbons or potential combustion energy released per cubic foot may be readily equated with the hazard of potential dust concentrations. These concentrations can be established by measuring the dust load on mine surfaces, then determining the maximum air borne dust concentration that can result in the adjacent mine openings. Fischer assay oil yields would establish the third parameter. Pyritic sulfur content can also be estimated and will be of interest in relation to spontaneous combustion potential. As indicated, the relationships defined will change with aged (surface oxidized) shale dusts. In addition, the relationships would, of necessity, need to be re-established in operations outside of the Mahogany zone of the Green River Formation.

5.0 CONCLUSIONS

The following conclusions can be drawn from the studies and experiments conducted under this contract.

a. More than 3,000,000 tons of oil shale have been mined from four room and pillar mines in the past 34 years without an accident attributable to the explosive hazards of oil shale dust.

b. There have been accidents during experiments and demonstrations that are attributable to the fire and explosion hazards of crushing, handling and processing oil shale.

c. Fire of mine muck piles and of the mine structure, may be a greater hazard in mining than dust explosions. Evidence of this is attributed to unplanned fires in the Occidental Logan Wash research facility and the Bureau's Horse Draw Experiental Facility. During both of these fires, excessive thermal spalling of oil shale caused closing of airways and contributed to the intensity of rubble fires.

d. Oil shale dusts in actual Bureau mine tests which, by a combination of dust loading and richness, will provide about 0.05 oz/ft^3 of volatile hydrocarbons or greater will undergo a propagating explosion.

e. There is not enough dust in the one large mine sampled, relative to the volume of the adjacent mine openings, to propagate an explosion.

f. The results of Phase 2 laboratory tests on the fire and explosivity properties of standard materials during calibration of the RI 5624 equipment correlated quite well with the work done by the Bureau and MSHA.

g. Laboratory tests, following the conditions specified in RI 5624 procedures, with oil shale dusts assaying nominally 10 to 35 gpt, and having particle sizes ranging from -40 mesh to -325 mesh, resulted in no ignition and explosion. It is therefore concluded that oil shale dust is not explosive when tested according to RI 5624.

h. Oil shale dusts assaying 10 to 35 gpt and -325 mesh did ignite and propagate in the lucite Hartmann apparatus at a reservoir pressure of 25 psig. It can then be said that oil shale dust is explosive when tested in RI 5624 apparatus, but with prescribed reservoir pressure exceeded. (Prescribed reservoir pressure is 5 to 15 psig.)

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i. Oil shale has an overall explosive index of 0.0001 compared with an index of 1.0 for Pittsburgh seam coal, indicating a lesser tendency of oil shale to explode.

j. Using a hot plate with a thin oil shale dust layer, of 35 gpt grade, and a pilot flame as an ignition source, the dust layer ignited at 260°C. It is concluded that oil shale dust layers can ignite at temperatures found in mining, handling, and retorting operations if an ignition source is present.

k. Oil yield and organic carbon content decrease with decreasing particle size of natural oil shale dust.

l. Fischer assay oil yields correlate reasonably well with minimum explosive concentration, minimum ignition energy, minimum ignition temperature, spontaneous combustion index and dust layer smoke point. In all cases, higher Fischer assay oil yields indicate increased tendencies to ignition and explosivity.

m. Fischer assay oil yield is the most convenient and useful test in evaluating the laboratory fire and explosive properties of oil shales. There are excellent correlations between Fischer assay oil yields and properties of oil shale that include total carbon, organic carbon, hydrocarbon yield from Fischer assay and particle specific gravity.

n. Preliminary studies indicate that the grade of oil shale dusts deteriorates with time. The rate will vary with factors such as temperature and (no data is available on humidity effects) particle size (surface area).

o. In all laboratory tests, using the peroxide method for spontaneous combustion, oil shale dusts indicated a potential to auto-oxidize. Oil shale is less liable to spontaneous combustion than typical western coals. Spontaneous combustion is influenced by surface area, chemical composition, and moisture content.

p. In a single test, fuel-soaked, three-inch oil shale rubble burned poorly and combustion did not spread into untreated oil shale rubble. From this one observation, it appears that that oil shale rubble burns with difficulty and combustion does not propagate under the test conditions.

q. In limited tests, a non-explosive 5% methane/air mixture (a lower explosive limit of 5.3%) and a non-explosive oil shale dust did ignite and explode. The conclusion is that a non-explosive methane/air mixture enhances the explosivity of oil shale dust.

r. Oil shale retort gas appears to be more dangerous than methane in terms of minimum ignition energy. Since gases may be grouped according to the ratio of their minimum igniting current with that of methane, the retort gas gives a ratio of 0.9, classifying it in the ISA II B group (for which ethylene is the laboratory standard).

6.0 RECOMMENDED RESEARCH PROGRAMS

The purpose of this section is to recommend to the Bureau necessary follow-up programs to supplement this report. To truly assess the fire and explosion hazards of oil shale mining, handling, and retorting, the following programs are recommended.

6.1 Flammability of Retort Gas and Vapor

Two important aspects are seen here: (1) the minimum ignition energy (M.I.E.), and (2) the limits of flammability. Of these, we feel the M.I.E. is the most critical. In a gas leak there will be, at some time and some place, an explosive mixture. Knowing the L.E.L. and U.E.L. may therefore be somewhat academic. The real factor subject to control is the M.I.E. It is recommended that the Bureau investigate the M.I.E. of retort gases and vapors as a function of temperature and pressure. The pressure is important in in situ or modified in situ retorting and a laboratory program can adequately determine the M.I.E. for various retort gases and vapors.

A corollary program which ultimately should be conducted (though at a lower priority) is the determination of the L.E.L. and the U.E.L., again as a function of temperature and pressure.

6.2 Rubble Fire Tests

It is recommended that the U.S. Bureau of Mines investigate the flammability of oil shale rubble. We visualize three important factors that

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need to be addressed: (1) the composition of the evolved gas, (2) the flame spread mechanism and rate, and (3) the temperature profile with time both in the rubble and in the atmosphere. It is important that a well designed test be planned that controls air flow and approaches an adiabatic condition, e.g., underground. Rubble should be characterized by screening waste dumps, muck piles, and other sources of rubble. Surface fires (as caused by burning timber, oil spills, etc.) should be examined as well as fires inside the rubble (spontaneous combustion). As part of this investigation, means of extinguishment should be studied. It may be found that if ventilation is cut off, explosive gas mixtures from the heated shale may build up.

6.3   Improved Test Apparatus

From high-speed photographs, it is evident that the dust concentration at time of ignition has little relation to the measured concentration. An improved standard test apparatus is needed, not only for oil shale but for other dusts as well. It would be the intent of this improved apparatus to better simulate full-scale gallery tests. Modifications in existing equipment would certainly help, but the physical size of the Hartmann equipment is limiting. It is recommended that the U.S. Bureau of Mines make an intensive investigation toward improvement of the current apparatus and to consider elements such as: a more uniform dispersion of dust by methods such as air blast, free fall, or levitation with a more accurate measurement of the dust density at the electrode area at the time of ignition; a wide range of characterized ignition sources; a scale-up of the system which could be a larger Hartmann (this is currently in use at the Bureau), up to a shock tube-type facility. Test conditions should be rigorously defined, e.g., temperature, pressure, humidity. Particle size should be more closely

defined. We feel that a size such as -200 mesh with no lower size cutoff will cause misleading results.

6.4   Flammable Gas/Dust Mixtures

From the preliminary results obtained on methane/air/oil shale dust, it is felt a program investigating this phenomenon is essential. It is recommended that a program investigating the effects of methane and retort gas on oil shale dusts be conducted. Furthermore, the retort gas should be both high and low Btu gas and at both high and ambient temperatures. This program would closely couple with that recommended in Section 6.2.1.

6.5   Continued Tests in the Bruceton Mine, U.S. Bureau of Mines

Extensive further tests should be carried out in an actual full scale mine with varying amounts of lean and rich oil shale dusts, to establish the minimum requirement of organic volatiles for propagating explosions. This would be a continuation of work previously reported by Richmond and Miller (1977).

6.6   Mine Dust Load Studies

Existing oil shale mines should be thoroughly sampled and the dust tested to determine the dust loading and the richness of the dust. This data would be used to determine if sufficient potential hydrocarbon volatiles are present, or would be present under current operations, to provide an explosive propagation. The relationship of the grade of the oil shale being mined to the dust are important determinations.

6.7   Minimum Hydrocarbon Volatiles for Ignition in Laboratory Tests

Further work should be done in the Hartmann lucite test apparatus to establish the minimum requirement of hydrocarbon volatiles from oil shale which would undergo ignition and explosion. Information obtained should be compared with similar data for explosive propagation in full scale mine tests to determine if a reliable relationship between the laboratory and full scale test results can be established.

6.8   Oil Shale Dust-Methane Interactions

Further work should be done in the lucite Hartmann apparatus with various grades and amounts of oil shale dust and methane concentrations to determine combinations which will lead to minimum explosive conditions and to attempt to determine a true methane equivalency of various grades of oil shale dusts.

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APPENDICES

APPENDIX A

Table A.1

Particle Specific Gravities
Graded Series – Reconstituted Standard Size Samples

Nominal Oil Yield (GPT)	Actual Oil Yield (GPT)	Particle Specific Gravity (gm/cm^3)
10	11.4	2.463
15	13.3	2.393
20	19.2	2.314
25	22.4	2.245
30	28.3	2.160
31	29.5	2.133
35	34.1	2.073

Table A.2

Total, Mineral and Organic Carbon Contents Old and New Mine Dusts Table 16

Sample Type	Mesh Size (US)	Total Carbon (wt%)			Mineral Carbon (wt%)			Organic Carbon (wt%)		
		Colony Mine Dust	8 x 8 Ft Drift New Dust	8 x 8 Ft Drift Old Dust	Colony Mine Dust	8 x 8 Ft Drift New Dust	8 x 8 Ft Drift Old Dust	Colony Mine Dust	8 x 8 Ft Drift New Dust	8 x 8 Ft Drift Old Dust
As Produced	−40	16.8	22.1	17.5	4.1	4.6	5.0	12.7	17.5	12.5
F R A C T I O N S	− 40 +100	19.2	22.7	18.6	4.6	5.0	5.4	14.6	17.7	13.2
	−100 +200	18.4	23.8	18.1	4.2	4.5	5.1	14.2	19.3	13.0
	−200 +325	17.9	23.2	18.2	3.8	4.2	4.8	14.1	19.0	13.4
	−325	14.9	19.9	16.4	4.0	4.3	5.2	10.9	15.7	11.2
Recon. Std. Size	−40	16.6	21.3	17.5	4.2	5.6	5.0	12.4	16.3	12.5

Table A.3

Particle Specific Gravities of Reconstituted Standard Size Samples
Old and New Mine Dusts

Sample	Particle Specific Gravity (g/cm^3)
Colony Mine Dust	2.144
8 x 8 Foot Drift	
New dust	2.035
Old Dust	2.171

Table A.4

Calculated Kerogen Contents of Old and New Mine Dusts

| | | Weight Percent | | | Volume Percent | | |
| | | | 8 x 8 Ft Drift | | | 8 x 8 Ft Drift | |
Sample Type	Mesh Size (US)	Colony Mine Dust	New Dust	Old Dust	Colony Mine Dust	New Dust	Old Dust
As Produced	-40	15.8	21.7	15.5	28.6	39.9	29.1
F R A C T I O N S	- 40 +100	18.1	22.0	16.4	34.3	41.7	32.7
	-100 +200	17.6	24.0	16.1	32.1	43.3	31.8
	-200 +325	17.5	23.6	16.8	30.6	40.8	31.6
	-325	13.5	19.5	13.9	23.6	35.5	26.7
Recon. Std. Size	-40	15.4	20.2	15.5		38.5	29.0

Table A.5

Fischer Assay Data – Old Yields in Gallons Per Ton
Old and New Mine Dusts

Sample Type	Mesh Size (US)	Colony Mine Dust	8 x 8 Ft Drift New Dust	Old Dust
As Produced	–40	23.0	36.1	23.6
F R A C T I O N S	– 40 +100	29.4	38.3	27.5
	–100 +200	26.9	40.5	26.6
	–200 +325	25.2	37.2	26.3
	–325	18.0	30.7	21.0
Reconstituted Standard Size	– 40	22.7	34.3	23.5

Table A.6

Old and New Mine Dust
Reconstituted Standard Size Samples
Tosco Material Balance Assay Data

| | | Colony Mine Dust | 8 x 8 Ft Drift | |
			New Dust	Old Dust
Oil Yield:	(gal/ton)	22.7	34.3	23.5
	(lb/ton)	170.7	257.2	176.6
Oil Gravity (°API)		25.8	25.8	25.4
Specific Gravity (60/60)		0.8998	0.8996	0.9017
Water Yield:	(gal/ton)	8.7	3.4	4.2
	(lb/ton)	73.0	28.7	35.3
Gas Yield	(scf/ton)	729	970	749
	(lb/ton)	50.5	66.8	53.1
Total Hydrocarbon – Incl. H_2 + CO* (lb/ton)		189.5	287.8	197.7
Spent Shale Yield (lb/ton)		1704	1646	1733
Total Product Recovery (lb/ton)		1998.2	1998.7	1998.0

* This total includes the oil and all of the gas product except CO_2 and H_2S.

Table A.7

Mine Dust Load Preliminary Program 30 and 60 Ft. Vertical Strips

Sample No.	Wt. % -40M	Area (ft^2)	Wt-40 (gm)	Dust Load (gm/ft^2)	Dust Load (gm/cm^2)
222.1A	56.5	138.1	290.5	2.1	0.0023
222.2A	39.3	138.1	558.4	4.9	0.0043
222.5A	36.6	136.6	511.1	3.7	0.0040
222.6A*	64.2	300.0	1656.4	5.5	0.0059
222.7A*	43.2	290.0	1853.9	6.4	0.0069
222.8A	45.5	138.1	660.5	4.8	0.0052
222.9A	50.4	141.2	183.2	1.3	0.0014
222.10A	66 2	140.4	678.6	4.8	0.0052
222.11A	54.1	146.2	356.9	2.4	0.0026
222.1B	21.3	151.2	216.3	1.4	0.0015
222.2B	69.0	140.4	217.6	1.6	0.0017
222.3B	65.6	199.4	1222.7	6.1	0.0066
222.4B	35.6	140.4	209.5	1.5	0.0016
222.5B	30.3	146.2	88.7	0.6	0.0006
222.8B	66.2	142.5	3945.5	27.7	0.0298
222.9B	64.6	146.9	1669.9	11.4	0.0123
222.10B	70.8	142.5	872.8	6.1	0.0066
222.12B*	73.4	315.6	3093.1	9.8	0.0105
222.13B	68.0	199.4	716.8	3.6	0.0039
222.14B	34.0	147.4	536.9	3.6	0.0039
222.15B	69.0	160.0	619.4	3.9	0.0042
222.16B	60.6	156.9	610.3	3.9	0.0042
222.17B	57.7	146.9	211.2	1.4	0.0015
Avg's	54.0				0.0053

Table A.8

Mine Dust Load Preliminary Program*
30 and 60 Ft.** Vertical Strips

Sample No.	Wt. % -40M	Area (ft²)	Wt-40 (gm)	Dust Load (gm/ft²)	Dust Load (gm/cm²)
122.7B	73.3	300.0	1776	5.9	.0064
122.11B**	83.7	300.0	1647	5.5	.0059
122.18B**	39.9	301.5	1511	5.0	.0054
122.19B**	41.4	283.5	597	2.1	.0023
122.20B**	70.7	300.0	2447	8.2	.0088
122.21B**	48.6	300.0	3576	11.9	.0128
122.22B**	51.4	300.0	708	2.4	.0025
122.23B**	69.9	300.0	2333	6.8	.0073
122.24B	68.9	206.0	3961	19.2	.0207
122.26B	63.2	1390.0	1119	8.1	.0087
122.27B	54.9	136.5	653	4.8	.0059
122.28B	28.6	149.5	204	1.4	.0015
Avg's	57.7				.0073
Avg First 23	54.0				.0053
Weighted Avg.	55.3				.0060

*Preliminary random sampling program completed under modification no. 2

Table A.9

Mine Dust Load Preliminary Program*

Sample No.	Wt. % -40M	Area (ft²)	Wt-40 (gm)	Dust Load (gm/ft²)	Dust Load (gm/cm²)
30 Ft. vertical strips in main haulageway					
123.1	81.5	139.0	4255	30.6	0.0330
123.2	70.9	129.5	1063	8.2	0.0088
123.3	67.6	146.5	2152	14.7	0.0158
123.4	60.6	144.0	1128	7.8	0.0084
123.5	69.5	147.5	2745	18.6	0.0200
Avg's	70.9				0.0172
Samples from mine roof					
124.R1	81.6	800.0	1501	1.88	0.0020
124.R2	86.1	706.9	585	0.83	0.0009
124.R3	90.9	706.9	1123	1.59	0.0017
124.R4	88.0	706.9	649	0.92	0.0010
124.R5	92.1	706.9	568	0.64	0.0066
Avg's	87.7				0.0024

* Sample 50 ft. long of rib in a 30 ft high room.

Table A.10

Mine Dust Load Preliminary Program*

Sample No.	Wt. % -40M	Area (ft^2)	Wt-40 (gm)	Dust Load (gm/ft^2)	Dust Load (gm/cm^2)
Five horizontal strip samples, on above the other, each 50ft long on 30ft rib in room 1					
125.1	81.5	200	8140	40.7	0.0438
125.2	37.4	200	1683	8.4	0.0090
125.3	29.7	200	3641	18.2	0.0196
125.4	37.4	200	1103	5.5	0.0059
125.5	38.7	200	4303	21.5	0.0232
Avg's	44.9				0.0200
Five horizontal strip samples, one above the other, each 25ft long on 60ft rib in cross cut six.					
126.1	31.0	250	1548	6.2	0.0067
126.2	53.3	250	750	3.0	0.0032
126.3	33.2	250	1281	5.1	0.0055
126.4	35.0	250	245	1.0	0.0011
126.5	41.3	250	4500	18.0	0.0194
Avg's	38.8				0.0072
Four strip samples from mine floor					
127.1	41.0	37.5	12197	325.0	0.3498
127.2	46.5	37.5	5284	143.6	0.1546
127.3	40.0	75.0	4900	65.3	0.0703**
127.4	41.1	75.0	4011	53.5	0.0576**
Avg's	42.1				0.1550

*Samples from haulageway that have been backfilled and maintained but not moisturized.
**From floor in working area.

Table A.11

Two-Foot Wide Band Samples Taken From Mid-Point on 30ft* High Ribs and Pillars

Sample No.	Wt. % −40M	Area (ft^2)	Wt−40 (gm)	Dust Load (gm/ft^2)	Dust Load (gm/cm^2)
128.1	62.7	380	3417	9.0	0.0097
128.1A	53.2	50	361	7.2	0.0078
128.2	60.1	568	2728	4.8	0.0052
128.3	45.8	240	2908	12.1	0.0130
128.3A***	70.5	50	317	6.3	0.0068
128.4	36.9	400	3404	8.5	0.0092
128.5	53.3	914	4957	5.4	0.0058
128.6	60.0	240	762	3.2	0.0034
128.7	35.9	520	3830	7.4	0.0079
128.8	42.0	80	269	3.4	0.0036
128.9	30.4	250	1848	7.4	0.0080
128.10	43.6	460	1015	2.2	0.0024
128.11	31.2	300	780	2.6	0.0028
128.12	50.7	340	1927	5.7	0.0061
128.13	32.3	520	1613	3.1	0.0033
128.14	63.7	220	1592	7.2	0.0078
128.15	71.5	180	5193	28.8	0.0311
128.16	58.3	280	4235	15.1	0.0163
128.17***	48.6	340	4523	13.3	0.0143
AVG's	49.9				0.0087

continuation of sample 128.1 on same pillar
continuation of sample 128.3 on same pillar
***60ft high rib

Table A.12

Fire and Explosivity Study Dust Sample Receiving Log

Sample Designations		Sample	
Colony Mine No.	Rocky Flats No.	Weight (Grams)	Sample Description
122.7B	6358	2423	Band width 5', band height 59.9', pillar height 61.3'
122.11B	6361	1967	60.4' from top pillar, height 63'
122.18B	6372	3788	Band width 5', band height 60.3', pillar height 62.4'
122.19B	6373	1441	Band width 5', band height 56.7', pillar height 60.6'
122.20B	6359	3470	Band width 5', band height 61.2', pillar height 62.3'
122.21B	6357	7359	Band width 5', band height 60.0', pillar height 61.1'
122.22B	6356	1377	Band width 5', band height 57.7', pillar height 59.3'
122.23B	6360	2988	Band width 5', band height 58.7', pillar height 60.0'
122.24B	6374	5750	Band width 5', band height 41.2', pillar height 42.7'
122.26B	6375	1997	Band width 5', band height 27.8', pillar height 27.8'
122.27B	6376	1360	Band width 5', band height 27.3', pillar height 28.3'
122.28B	6377	716	Band width 5', band height 29.9', pillar height 31.0'
123.1	6362	5221	Band width 5', band height 27.8', pillar height 29.8'
123.2	6364	1500	Band width 5', band height 25.9', pillar height 27.7'
123.3	6366	3180	Band width 5', band height 29.2', pillar height 29.7'
123.4	6368	1861	Band width 5', band height 28.8', pillar height 30.8'
123.5	6370	3950	Band width 5', band height 29.6', pillar height 30.0'
124.1	6388	1840	20'-40'
124.R2	6371	680	30' diameter roof
124.R3	6389	1235	(None)
124.R4	6390	737	(None)
124.R5	6391	617	(None)

Table A.12

Fire and Explosivity Study Dust Sample Receiving Log (cont.)

Sample Designations		Sample	
Colony Mine No.	Rocky Flats No.	Weight (Grams)	Sample Description
125.1	6378	9990	4'
125.2	6379	4500	4' strip 20'-16'
125.3	6380	12260	12'-16'
125.4	6381	2950	8'-12'
125.5	6382	11120	4'-8'
126.1	6363	4995	45'-55'
126.2	6365	1407	35'-45'
126.3	6367	3860	(None)
126.4	6369	700	30' diameter roof
126.5	6387	10900	5'-15'
127.1	6383	29750	(None)
127.2	6384	11580	(None)
127.3	6385	12250	Rm 6
127.4	6386	9760	Rm 6
128.1	6393	5450	190' x 2'
128.1A	6392	680	2' x 25'
128.2	6395	4540	2' x 284'
128.3	6396	6350	2' x 120'
128.3A	6394	450	2' x 25'
128.4	6397	9300	2' x 200'
128.5	6398	9300	2' x 458'
128.6	6399	1270	2' x 120'
128.7	6400	10670	2' x 260'
128.8	6401	640	2' x 40'
128.9	6402	6080	2' x 125'
128.10	6403	2225	2' x 230'
128.11	6404	2500	2' x 150'
128.12	6405	3800	2' x 170'
128.13	6406	4995	2' x 260'
128.14	6407	2500	2' x 110'
128.15	6408	1090	2' x 90'
128.16	6409	7264	2' x 140'
128.17	6410	9080	2' x 170'

Table A.13

Fire and Explosivity Study
Dust Sample Screen Analyses[1]

Sample Designations		Screen Analysis of Head Sample (Wt%)		Screen Analysis of -40 Mesh Portion of Sample (Wt%)			
Colony Mine No.	Rocky Flats No.	+40	-40	-40 +100	-100 +200	-200 + 325	-325
122.7B	6358	26.7	73.3	25.4	19.6	11.0	44.0
122.11B	6361	16.3	83.7	14.9	13.4	5.5	63.2
122.18B	6372	60.1	39.9	44.4	22.4	10.8	22.4
122.19B	6373	58.6	41.4	36.1	19.8	12.5	31.6
122.20B	6359	29.5	70.5	33.7	17.0	11.0	38.3
122.21B	6357	51.4	48.6	28.6	15.1	12.2	44.1
122.22B	6356	48.6	51.4	29.3	17.5	10.9	42.3
122.23B	6360	30.1	69.9	29.1	18.5	10.1	42.3
122.24B	6374	31.1	68.9	21.7	14.1	19.6	44.6
122.26B	6375	36.8	63.2	17.0	12.2	9.3	61.4
122.27B	6376	45.1	54.9	22.2	14.2	19.1	44.5
122.28B	6377	71.4	28.6	44.5	16.9	3.8	34.8
123.1	6362	18.5	81.5	6.1	5.2	17.6	71.1
123.2	6364	29.1	70.9	7.7	5.8	10.5	76.0
123.3	6366	32.3	67.7	12.7	8.9	6.2	72.2
123.4	6368	39.4	60.6	6.4	4.7	4.6	84.3
123.5	6370	30.5	69.5	10.9	9.0	13.0	67.1
124.1	6388	18.4	81.6	22.7	17.6	8.4	51.3
124.R2	6371	13.9	86.1	23.6	14.9	8.9	52.6
124.R3	6389	9.1	90.9	21.1	16.0	8.7	54.2
124.R4	6390	11.4	88.6				
124.R5	6391	7.9	92.1				
125.1	6378	18.5	81.5	40.5	15.5	14.2	29.8
125.2	6379	62.6	37.4	41.3	13.4	16.1	29.2
125.3	6380	70.3	29.7	40.1	15.2	11.9	32.8
125.4	6381	62.6	37.4	39.0	16.0	8.5	36.5
125.5	6382	61.3	38.7	38.3	19.6	7.7	34.4
126.1	6363	69.0	31.0	37.3	16.4	6.4	40.0
126.2	6365	46.7	53.3	17.7	20.6	13.4	48.4
126.3	6367	66.8	33.2	36.6	16.9	10.4	36.1
126.4	6369	65.0	35.0	31.1	22.5	11.0	35.4
126.5	6387	58.7	41.3	42.7	19.7	11.2	26.3
127.1	6383	59.0	41.0	28.4	14.8	7.2	49.6
127.2	6384	53.5	46.5	32.6	17.5	10.8	39.1
127.3	6385	60.0	40.0	30.7	14.0	9.2	46.1
127.4	6386	58.9	41.1	31.9	14.2	8.8	45.0

Table A.13

Fire and Explosivity Study
Dust Sample Screen Analyses[1] (cont.)

Sample Designations		Screen Analysis of Head Sample (Wt%)		Screen Analysis of −40 Mesh Portion of Sample (Wt%)			
Colony Mine No.	Rocky Flats No.	+40	−40	−40 +100	−100 +200	−200 + 325	−325
128.1	6393	37.3	62.7				
128.1A	6392	46.3	53.2	24.9	11.4	7.4	56.4
128.2	6395	39.9	60.1				
128.3	6396	54.2	45.8				
128.3A	6394	29.5	70.5				
128.4	6397	63.1	36.9				
128.5	6398	46.7	53.3				
128.6	6399	40.0	60.0				
128.7	6400	64.1	35.9				
128.8	6401	58.0	42.0				
128.9	6402	69.6	30.4				
128.10	6403	56.4	43.6				
128.11	6404	68.8	31.2				
128.12	6405	49.3	50.7				
128.13	6406	67.7	32.3				
128.14	6407	36.3	63.7				
128.15	6408	28.5	71.5				
128.16	6409	41.7	58.3				
128.17	6410	51.4	48.6				
222M1A	6180A	43.5	56.5				
222M2A	6180B	60.7	39.3				
222M5A	6180C	63.4	36.6				
222M6A	6180D	35.8	64.2				
222M7A	6180E	56.8	43.2				
222M8A	6180F	54.5	45.5				
222M9A	6180G	49.6	50.4				
222M10A	6180H	33.8	66.2				
222M11A	6180I	45.9	54.1				
222M1B	6181A	78.7	21.3				
222M2B	6181B	31.0	69.0				
222M3B	6181C	34.4	65.6				
222M4B	6181D	64.4	35.6				
222M5B	6181E	69.7	30.3				
222M8B	6181F	33.8	66.2				
222M9B	6181G	35.4	64.6				
222M10B	6181H	29.2	70.8				
222M12B	6181I	26.6	73.4				
222M13B	6181J	32.0	68.0				
222M14B	6181K	66.0	34.0				
222M15B	6181L	30.1	69.9				
222M16B	6181M	39.4	60.6				
222M17B	6181N	42.3	57.7				

(1) U. S. Standard Screen sizes

Table A.14

Fire and Explosivity Study
Dust Sample Modified Fischer and Carbon Analyses

Sample Designation		Modified Fischer Assay (gal oil/ton shale)					Carbon Analyses (Wt%) (Total/Mineral/Organic)				
Colony Mine No.	Rocky Flats No.	-40*	-40+100	-100 +200	-200 +325	-325	-40*	-40 +100	-100 +200	-200 +325	-325
122.7B	6358	21.9					17.11/4.34/12.77	19.35/4.28/15.07	17.61/4.37/13.24	16.78/4.33/12.45	15.19/4.53/10.66
122.11B	6361	21.0					15.55/3.63/11.92	16.24/3.43/12.81	15.60/3.47/12.13	16.43/3.13/13.30	14.44/3.67/10.77
122.18B	6372	20.3					15.68/4.04/11.64	17.27/4.12/13.15	16.31/4.15/12.16	14.62/3.59/11.03	12.79/3.49/9.30
122.19B	6373	25.2					17.52/4.63/12.89	19.11/4.94/14.17	18.16/4.47/13.69	16.38/4.02/12.36	14.40/3.97/10.43
122.20B	6359	26.8					18.72/4.45/14.27	20.31/5.31/15.00	18.66/4.81/13.85	16.57/4.25/12.32	16.80/3.94/12.85
122.21B	6357	21.0	21.6	21.9	19.7	16.6	15.97/4.35/11.62	16.67/4.85/11.82	16.60/4.46/12.14	14.56/3.86/10.70	13.16/3.86/9.30
122.22B	6356	26.2					18.67/4.48/14.19	19.40/5.13/14.27	20.42/4.77/15.65	20.67/4.42/16.25	17.38/3.93/13.45
122.23B	6360	21.7	25.8	25.9	22.0	18.0	16.27/4.28/11.99	17.46/5.01/12.45	17.11/4.40/12.71	16.37/4.11/12.26	14.20/3.92/10.32
122.24B	6374	23.7	36.1	33.1	26.2	17.4	15.68/3.93/11.75	19.46/4.45/15.01	19.69/4.10/15.59	17.10/4.02/13.08	14.93/4.12/10.81
122.26B	6375	20.0					14.95/3.54/11.41	20.02/4.18/15.84	17.61/3.74/13.87	15.90/3.26/12.64	12.71/3.46/9.25
122.27B	6376	25.3					15.62/4.03/11.59	19.67/4.42/15.25	18.31/4.22/14.09	16.55/4.03/12.52	14.75/4.05/10.70
122.28B	6377	25.7					17.49/4.35/13.14	18.95/4.95/14.00	18.04/4.48/13.56	16.48/3.80/12.68	14.15/3.68/10.47
123.1	6362	14.8	(Fischer assay oil yield)								
123.2	6364	13.5	(on composite of equal)								
123.3	6366	17.4	(weights of -40 mesh shale)								
123.4	6368	16.6	(from 123 series dust is)								
123.5	6370	14.9	(17.8 gpt)								
222M1A	6180A						20.12/3.88/16.24				
222M2A	6180B						17.04/4.05/12.99				
222M5A	6180C						17.97/4.07/13.90				
222M6A	6180D						15.49/4.20/11.29				
222M7A	6180E						16.63/4.44/12.19				
222M8A	6180F						16.62/4.24/12.38				
222M9A	6180G						14.54/3.30/11.24				
222M10A	6180H						13.64/3.12/10.52				
222M11A	6180I						15.91/3.64/12.27				
222M1B	6181A						16.36/3.22/13.14				
222M2B	6181B						15.72/3.71/12.01				
222M3B	6181C						17.24/3.45/13.79*				
222M4B	6181D						16.50/3.08/13.42				
222M5B	6181E						17.70/4.64/13.06				
222M8B	6181F										
222M9B	6181G						14.82/3.99/10.83				
222M10B	6181H						17.08/3.92/13.16				
222M12B	6181I						15.97/3.71/12.26				
222M13B	6181J						17.84/4.99/12.85				
222M14B	6181K						17.19/3.89/13.30				
222M15B	6181L						16.55/3.42/13.13				
222M16B	6181M						16.29/3.84/12.45				
222M17B	6181N										

* -40 mesh head sample

Table A.15

Statistical Reproducibility
Minimum Ignition Temperature
Godbert-Greenwald Furance

Lycopodium

Minimum Ignition Temp. (Y)			
500°C	495°C	495°C	495°C
485°C	495°C	495°C	

Minimum Temperature Values

3460

Average ($\overline{X}$)

494.29°C

Standard Deviation

4.50°C

90% Confidence (Z = 1.96

485.47	494.29	503.10

S_x = 0.9% of the mean

Table A.16

Statistical Reproducibility
Minimum Ignition Concentration (9/1)
Lucite Hartmann Apparatus (25 psig)

Pittsburgh Seam Coal (RF 6178)

Minimum Ignition Conc. (X)

| 0.167 | 0.167 | 0.161 |
| 0.164 | 0.163 | 0.150 |

Minimum Conc. Values

0.972

Average ($\overline{X}$)

0.162

Standard Deviation

0.006

95% Confidence (Z = 1.96)

0.150   0.162   0.174

S_x = 3.9% of the mean

Table A.17

Statistical Reproducibility
Minimum Ignition Energy (Joules)
Lucite Hartmann Apparatus (25 psig)

Lycopodium

Minimum Ignition Energy (X)	
0.020	0.020
0.015	0.020
0.025	0.015

Minimum Ignition Values
0.115

Average ($\overline{X}$)
0.019

Standard Deviation
0.004

95% Confidence (Z = 1.96)		
0.012	0.019	0.026

S_x = 19% of the mean

Table A.18

Statistical Reproducibility
Spontaneous Combustion Test (1)
(Hydrogen Peroxide Test)
Shale Dust RF 5836

Spontaneous Combustion (x)

14.5	8.73	10.25
12.1	10.87	10.1

Spon. Comb. Values

66.55

Average ($\bar{X}$)

11.09

Standard Deviation

2.00

95% Confidence Level

7.18	11.09	15.01

S_x = 18% of the mean

Table A.19

Composition of Gases Used in Ignition Testing
(Gases Produced in Fischer Assay)

Component	RF 6287	RF 6288	PB 1531
Helium*	0.95	4.32	0
Oxygen	2.14	1.81	3.46
Nitrogen	8.06	7.33	13.88
Hydrogen	20.24	20.09	18.58
Carbon Monoxide	2.72	2.71	3.14
Carbon Dioxide	23.16	25.48	24.90
Hydrogen Sulfide	5.17	5.03	5.39
Methane	12.09	12.53	13.80
Ethane	4.95	4.71	5.01
Ethylene	1.76	1.77	1.50
Propane	3.14	2.79	2.59
Propylene	2.19	2.11	2.07
iso-Butane	1.26	0.19	0.10
n-Butane	1.39	1.22	0.93
Butylenes	3.04	2.06	1.38
C_5's	3.04	2.00	1.41
C_6's	1.75	2.42	1.52
C_7's and higher	2.93	1.43	0.34
Total	99.98	100.00	100.00

* Used as a sweep gas
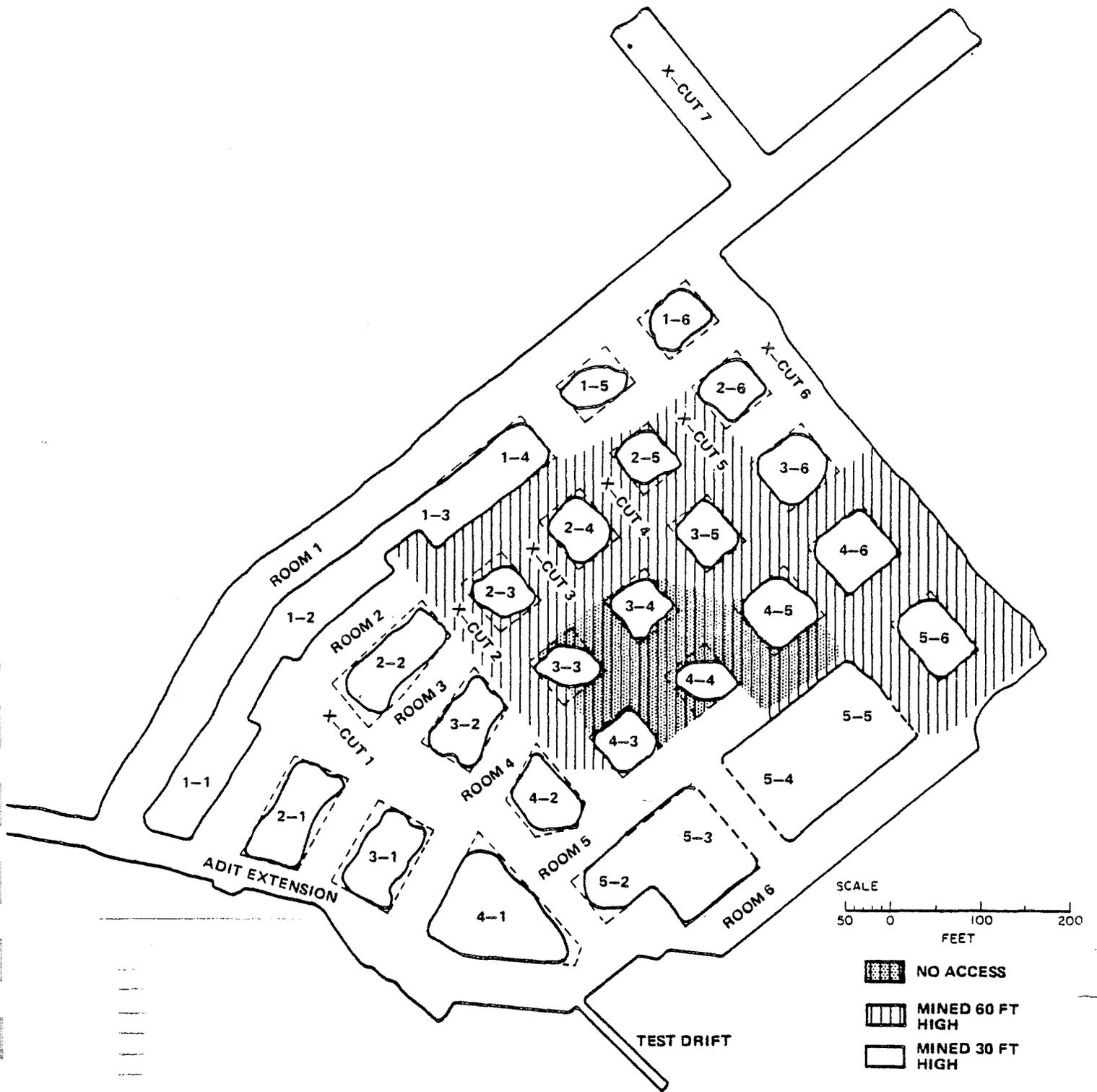
Figure A.1   Room Heights in the Colony Mine
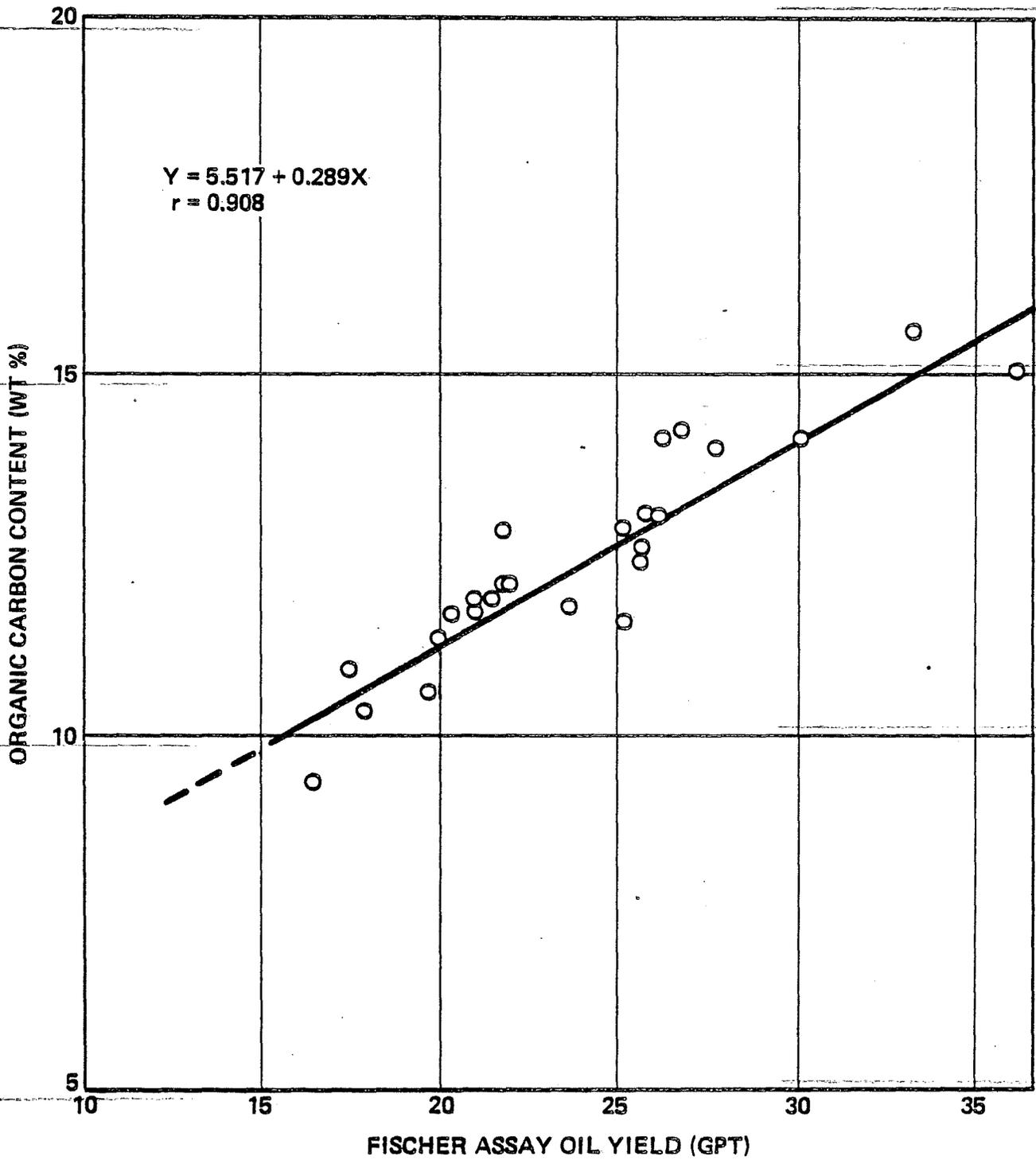
Figure A.2   Fischer Assay Oil Yield as a Function of Organic Carbon
             Content
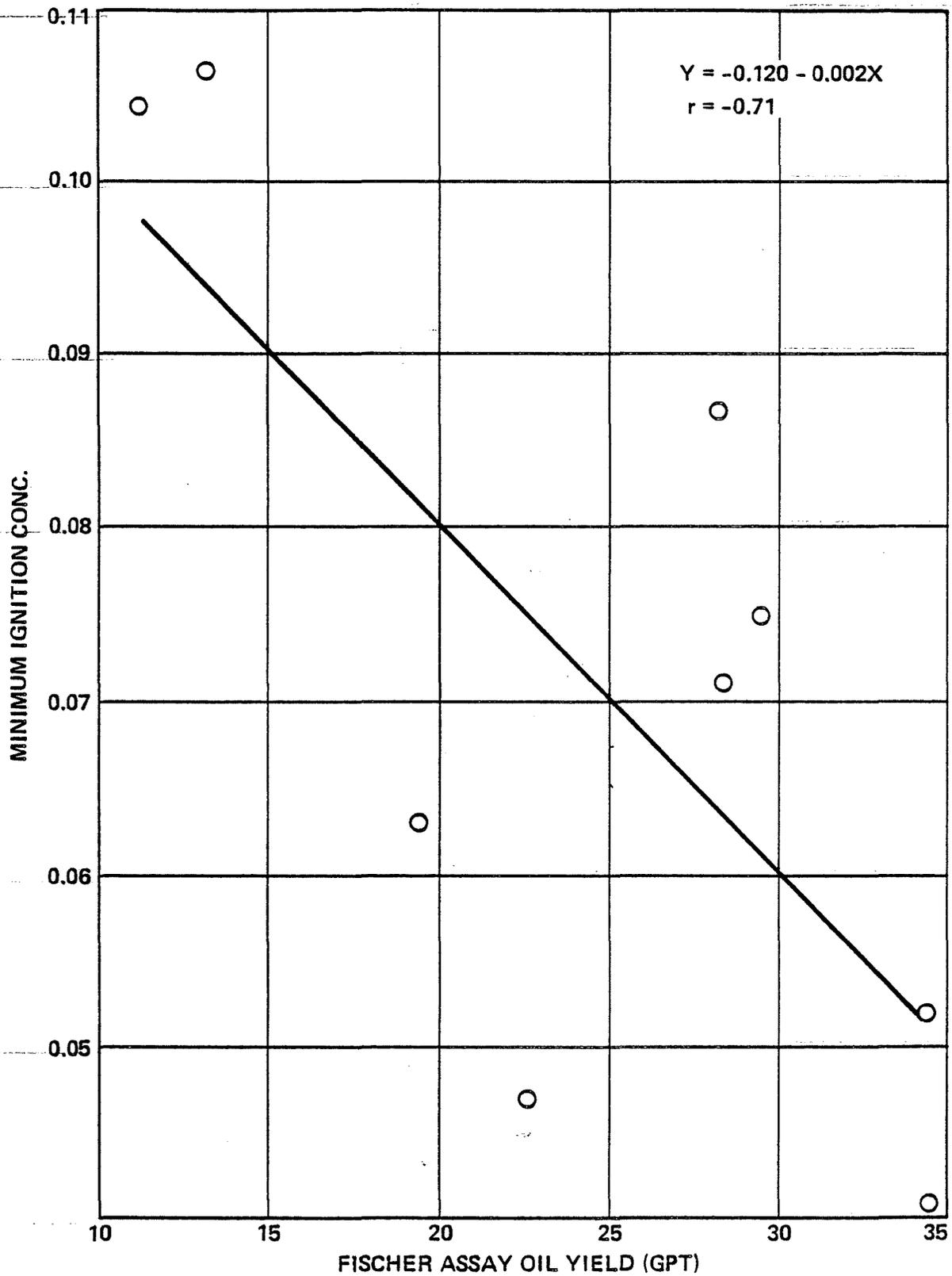
Figure A.3   Minimum Ignition Concentration at 25psig vs. Fischer Assay Oil Yield: Graded Series (Reconstituted Standard Size) Samples
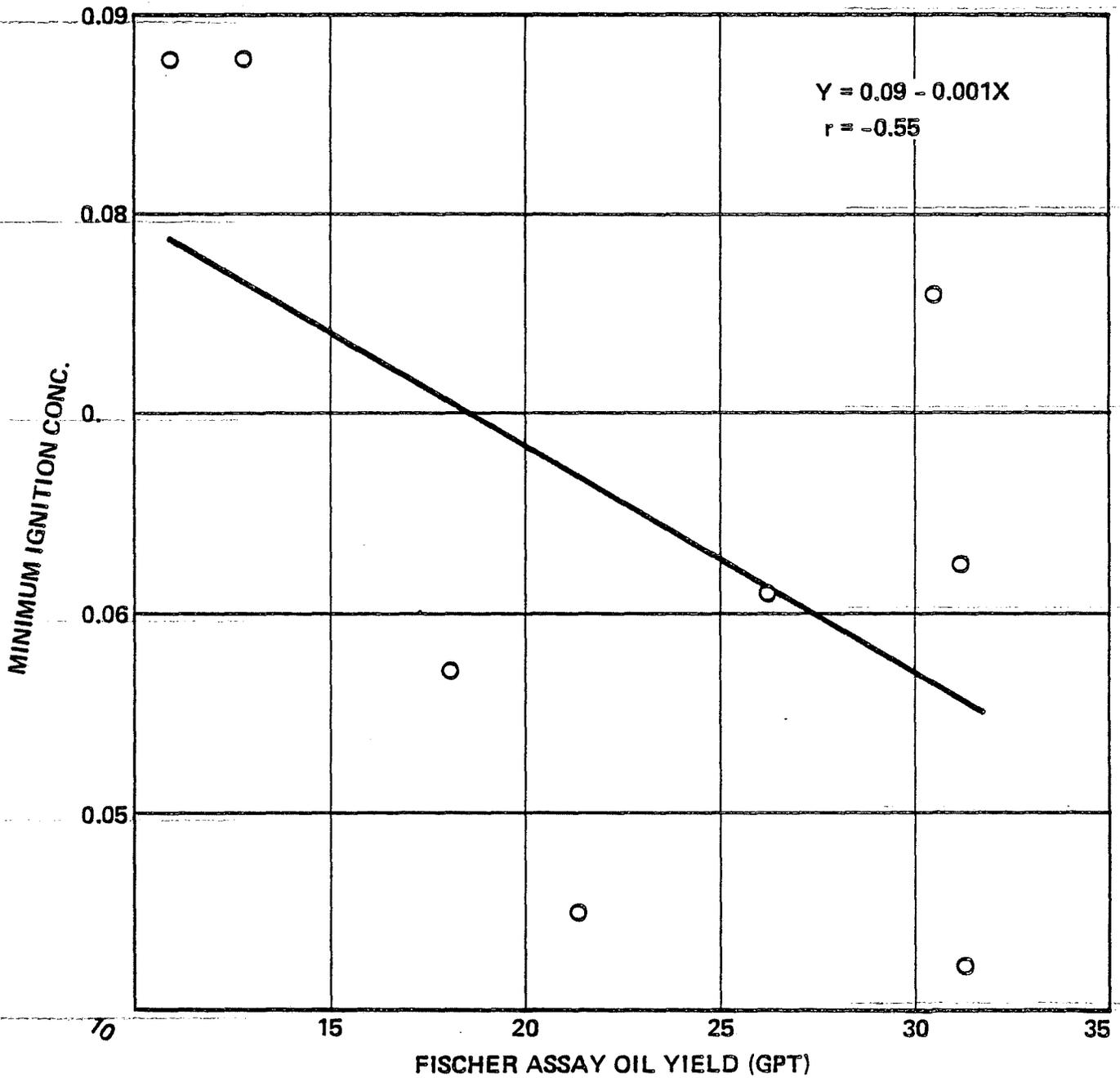
Figure A.4   Minimum Ignition Concentration at 25psig vs. Fischer
               Assay Oil Yield: Graded Series (-325 Mesh) Samples

The chart shows a plot with:
- Y-axis: MINIMUM IGNITION TEMPERATURE (°C) GODBERT-GREENWALD FURNACE, ranging from 450 to 700
- X-axis: FISCHER ASSAY OIL YIELD (GPT), ranging from 15 to 35

Equation shown on chart:
$$Y = 660.83 - 2.45X$$
$$r = -0.95$$
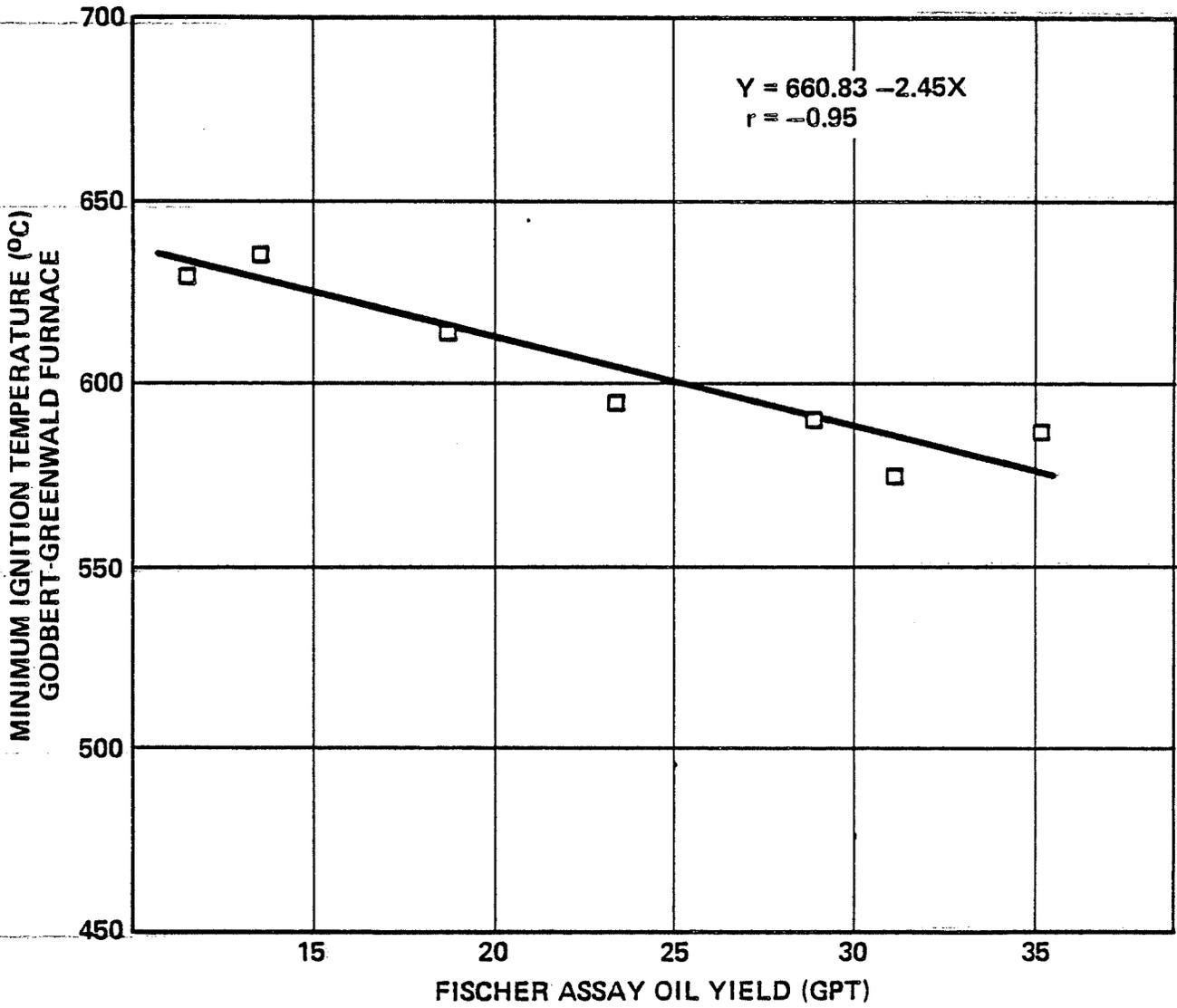
Figure A.5   Minimum Ignition Temperature vs. Fischer Assay Oil
             Yield: Graded Series (Head) Samples
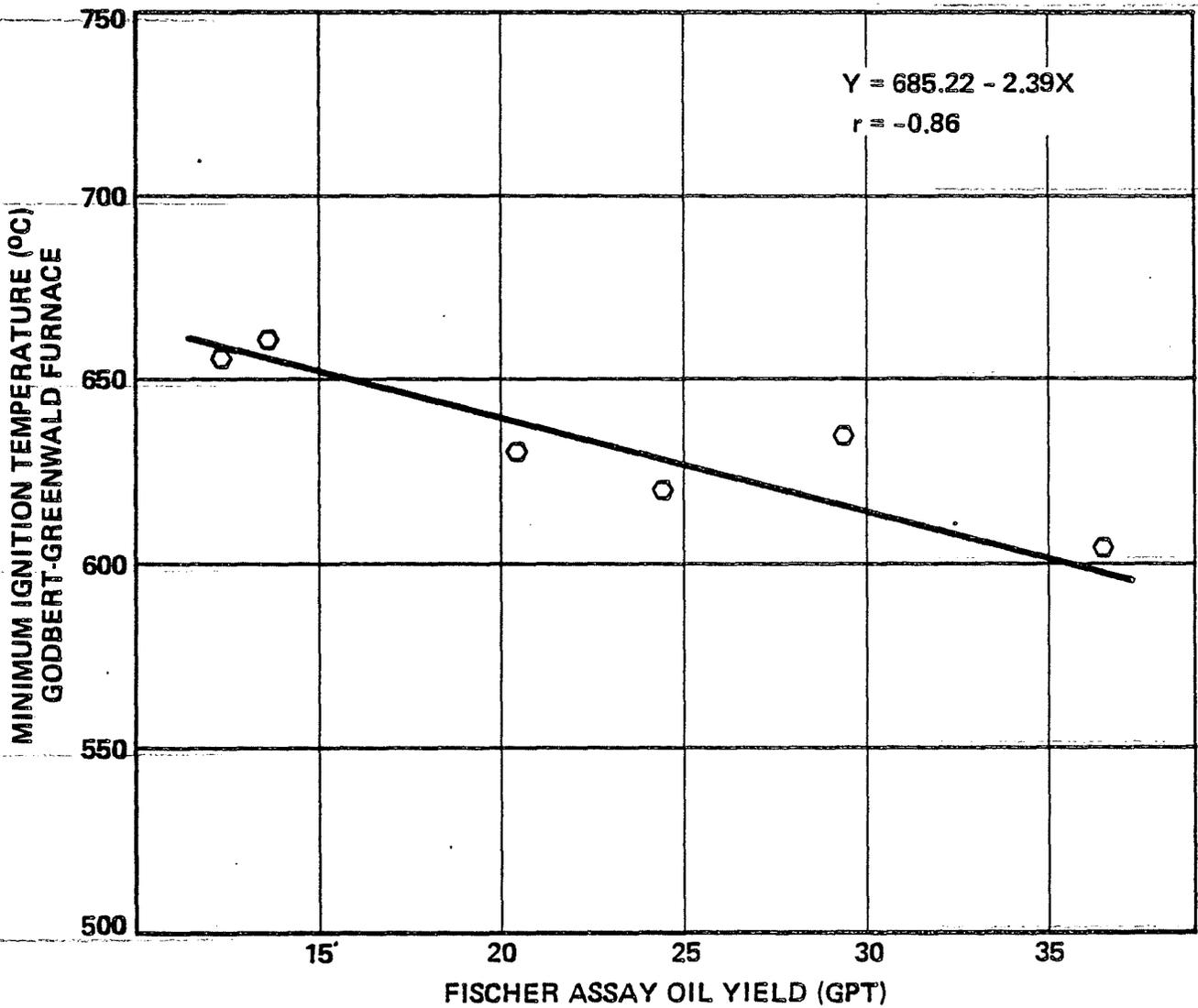
Figure A.6   Minimum Ignition Temperature vs. Fischer Assay Oil
Yield: Graded Series (-100 +200 Mesh) Samples
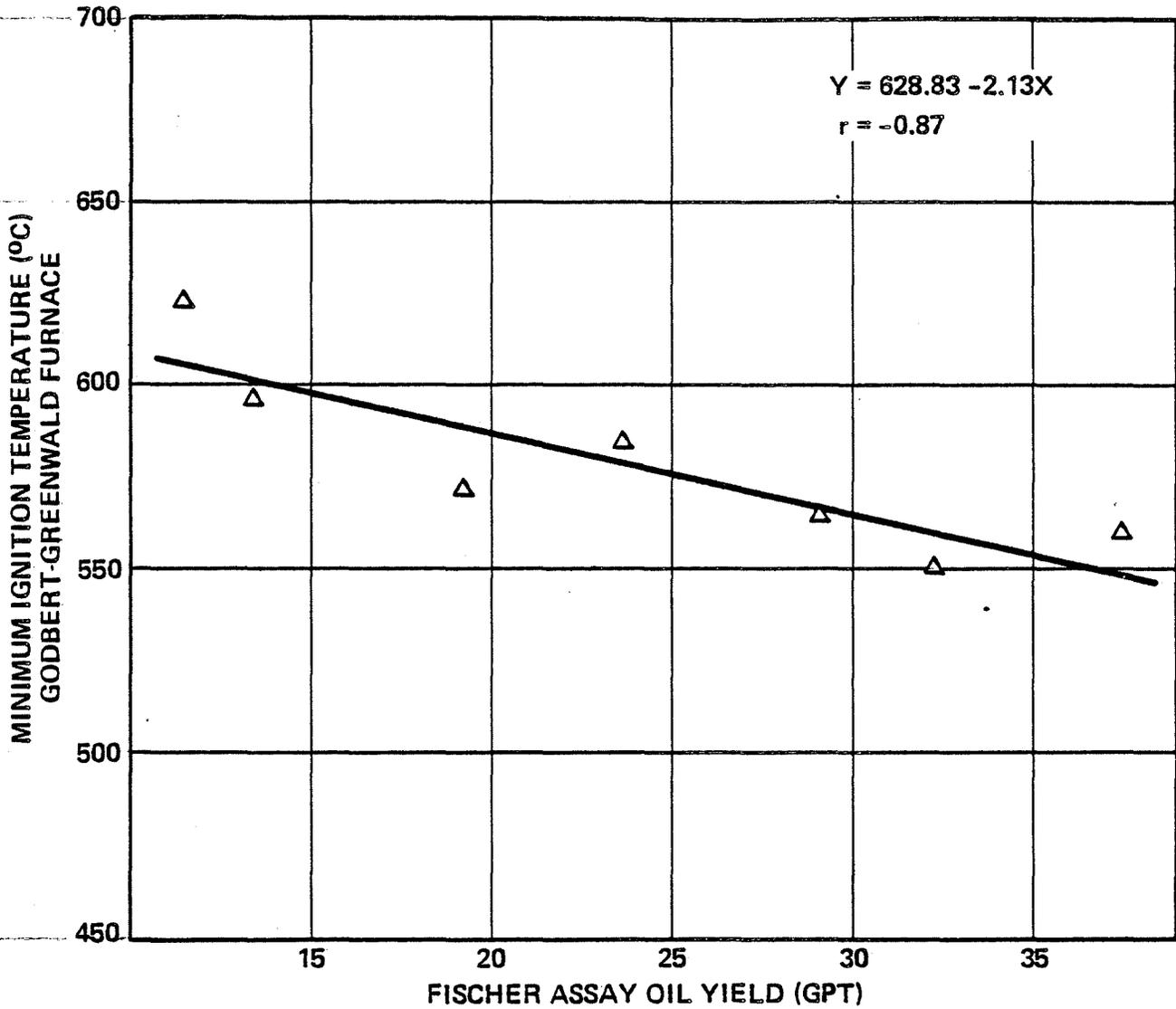
Figure A.7   Minimum Ignition Temperature vs. Fischer Assay Oil
               Yield: Graded Series (-200 +325 Mesh) Samples
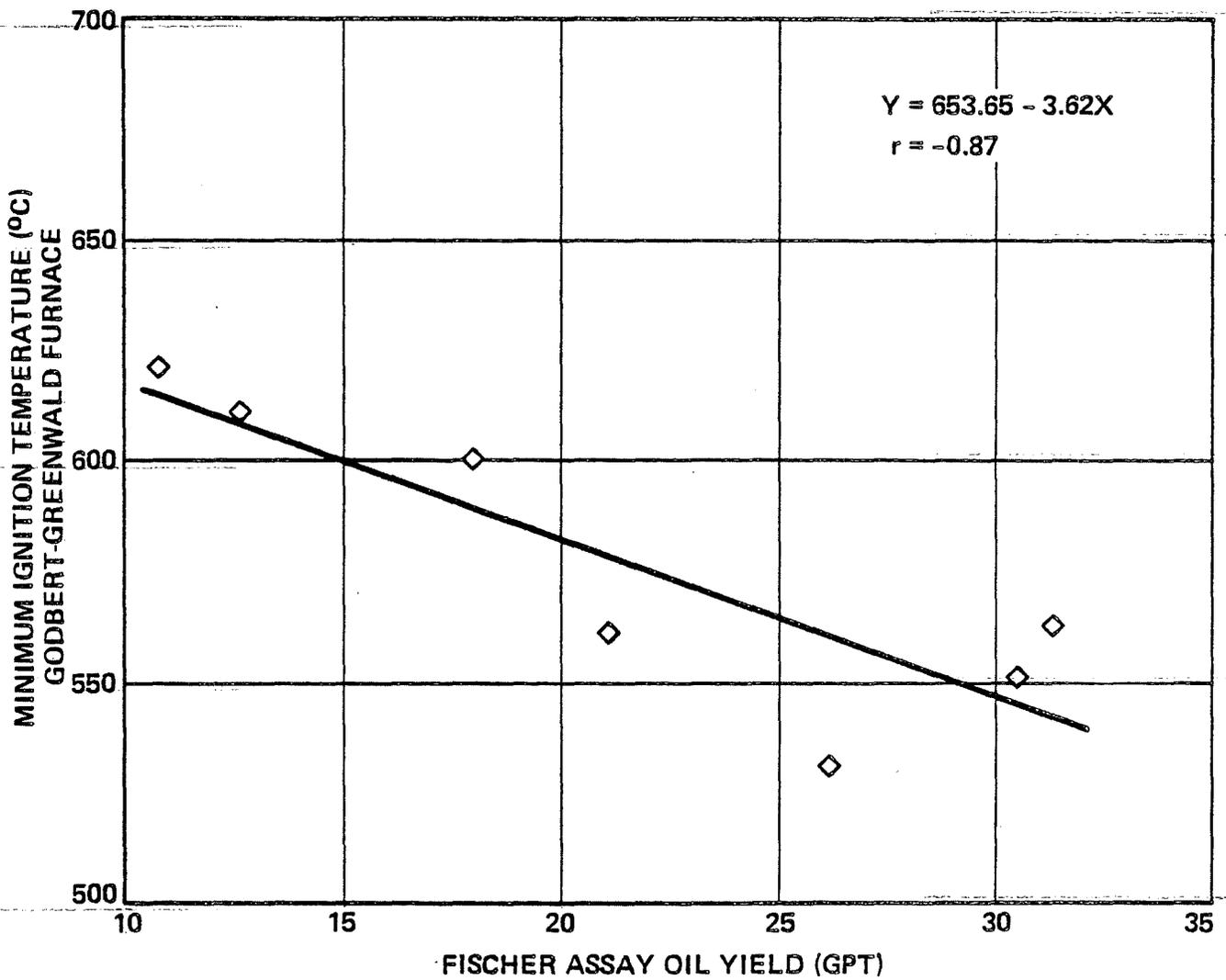
Figure A.8   Minimum Ignition Temperature vs. Fischer Assay Oil
               Yield: Graded Series (-325 Mesh) Samples
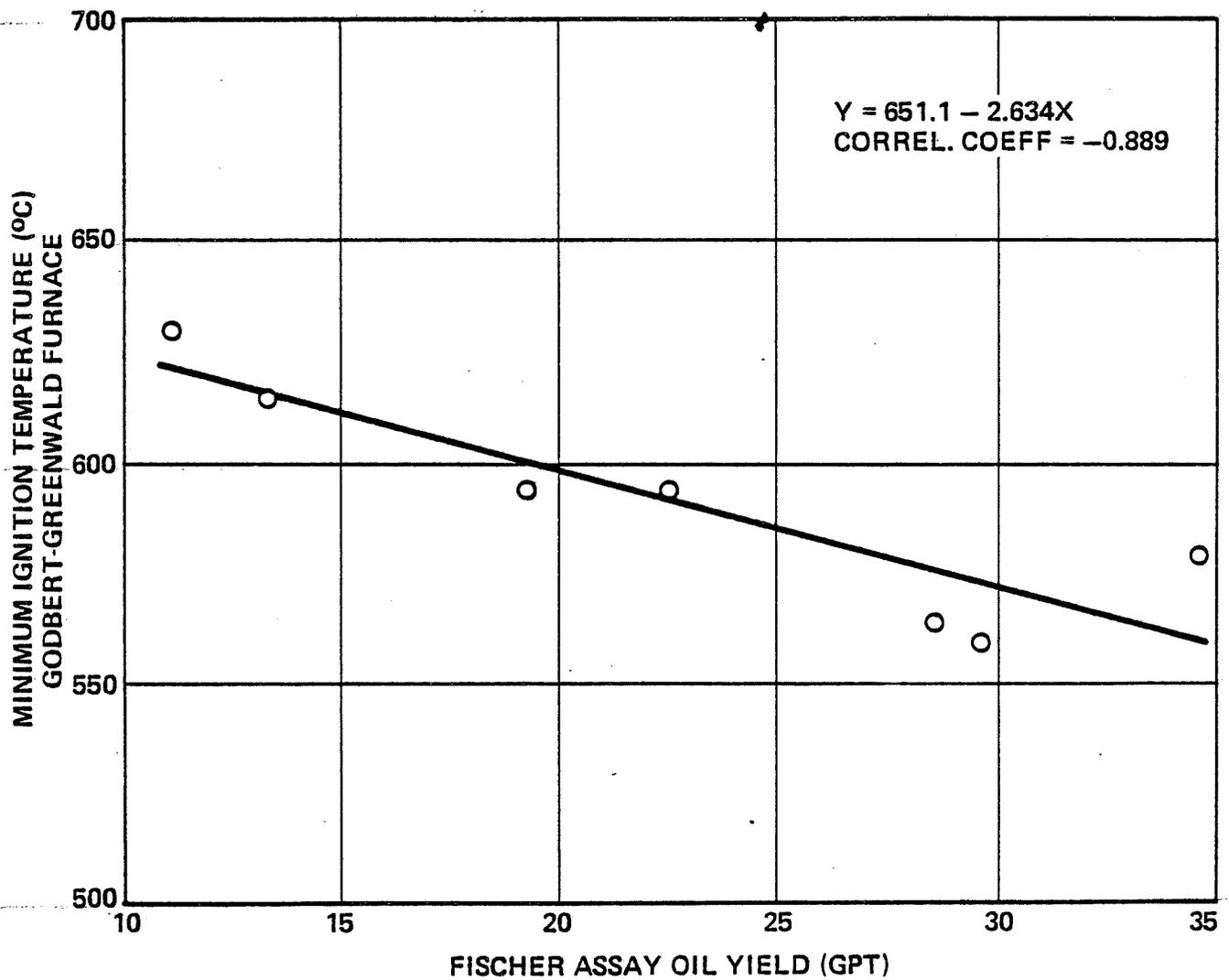
Figure A.9   Minimum Ignition Temperature vs. Fischer Assay Oil
              Yield: Graded Series (Reconstituted Standard Size)
              Samples
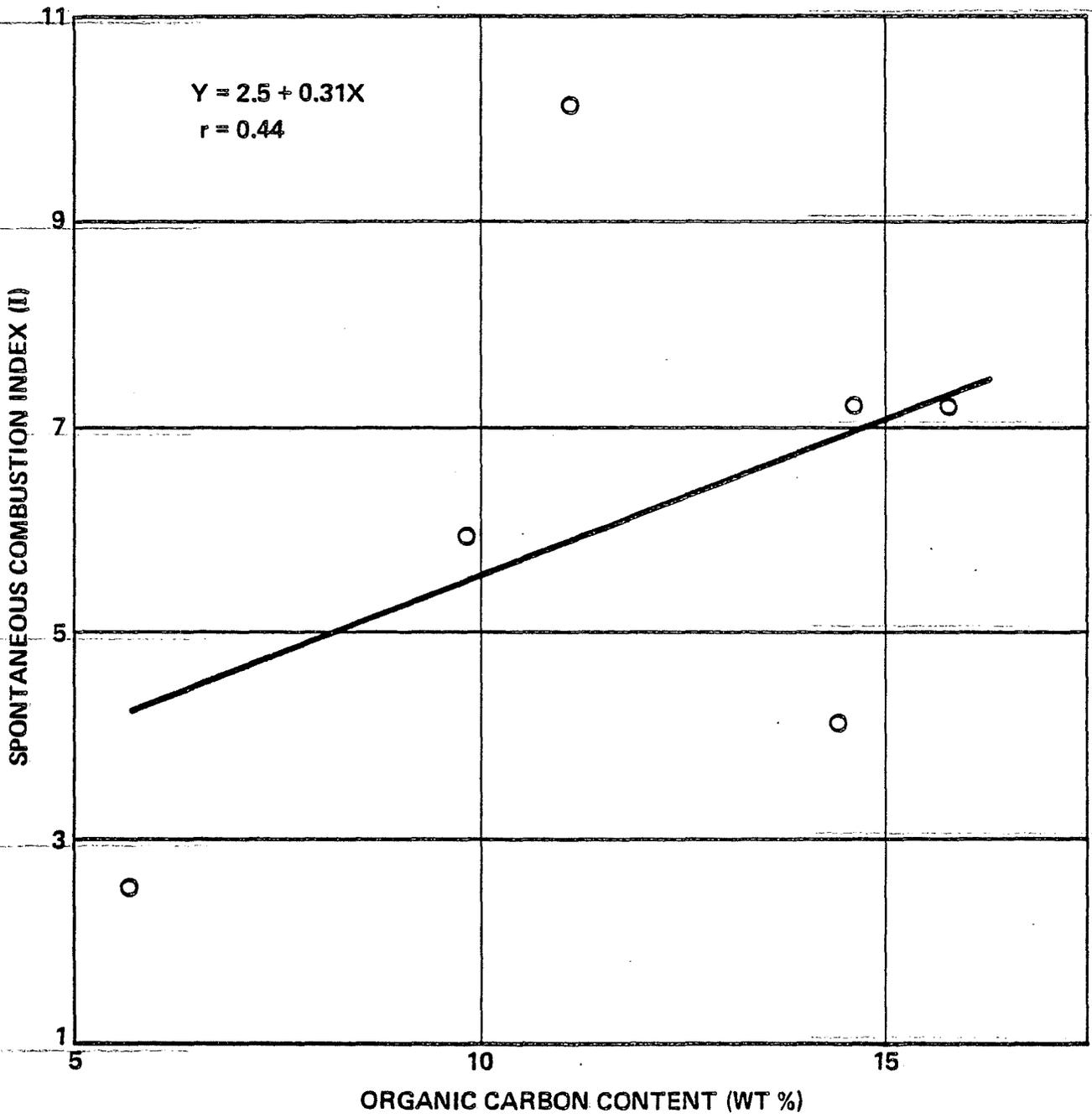
Figure A.10   Spontaneous Combustion Index vs. Organic Carbon
               Content: Graded Series (Head) Samples
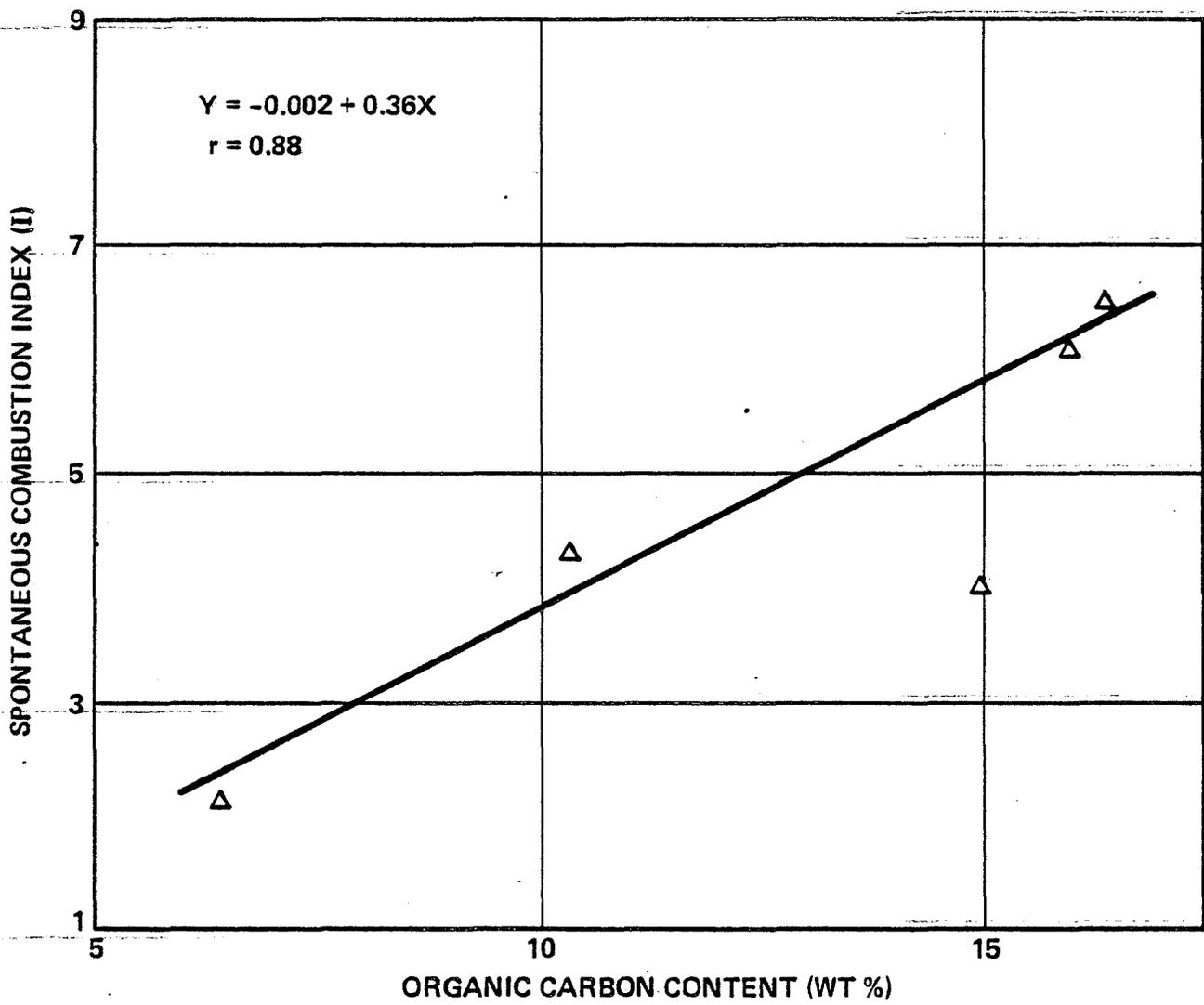
Figure A.11   Spontaneous Combustion Index vs. Organic Carbon
                Content: Graded Series (-40 +100 Mesh) Samples
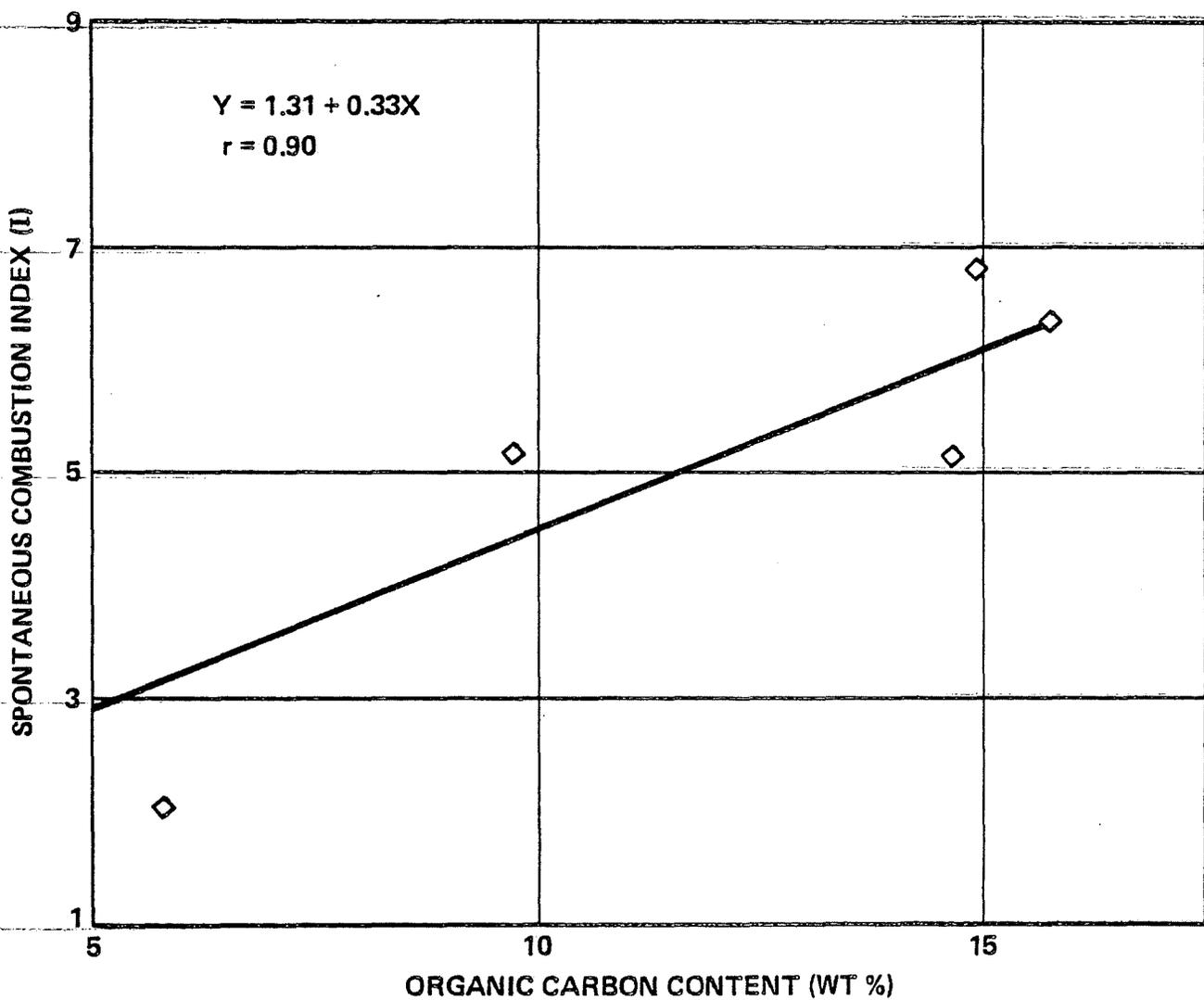
Figure A.12   Spontaneous Combustion Index vs. Organic Carbon
Content: Graded Series (-100 +200 Mesh) Samples
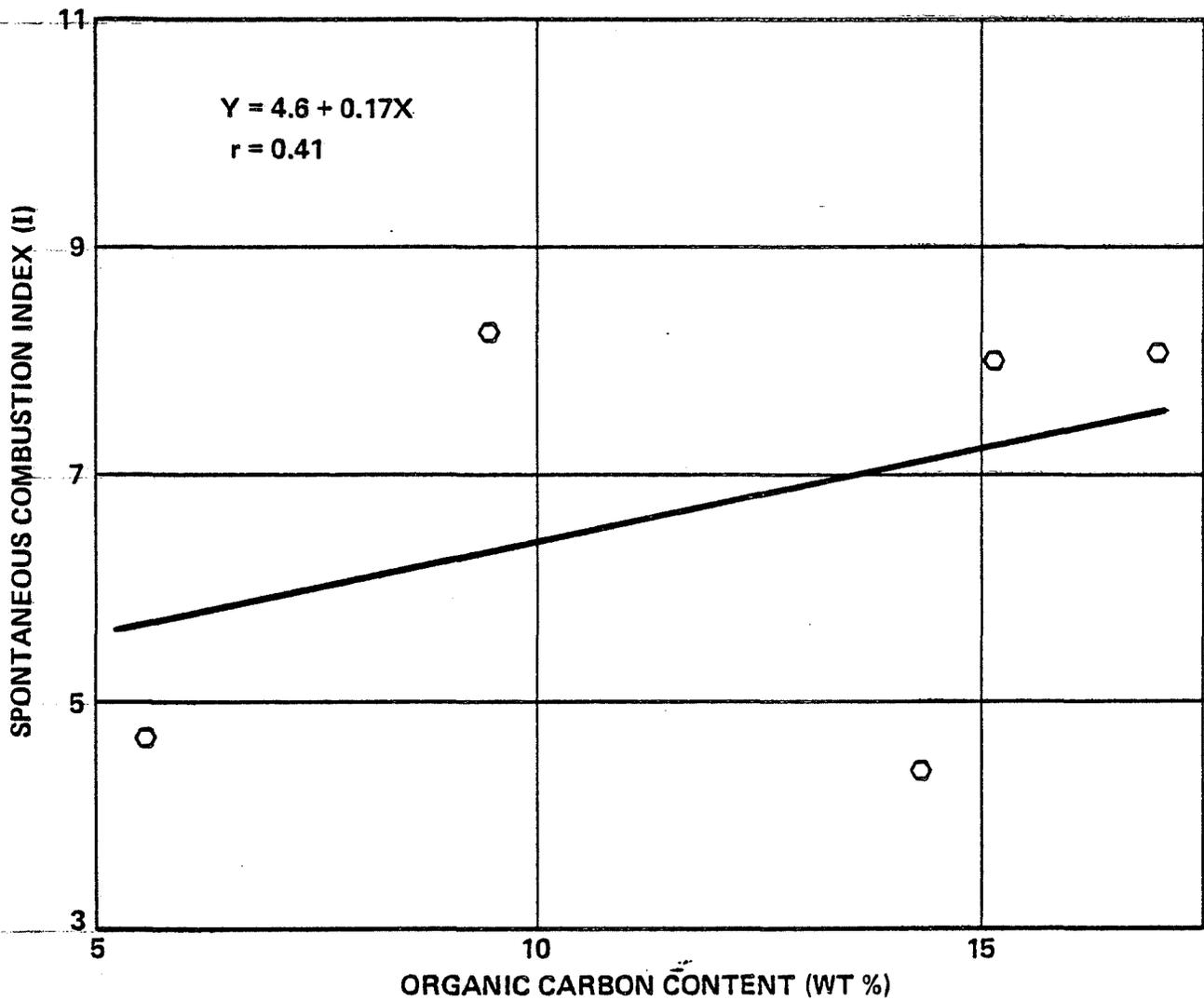
Figure A.13   Spontaneous Combustion Index vs. Organic Carbon
Content: Graded Series (-200 +325 Mesh) Samples
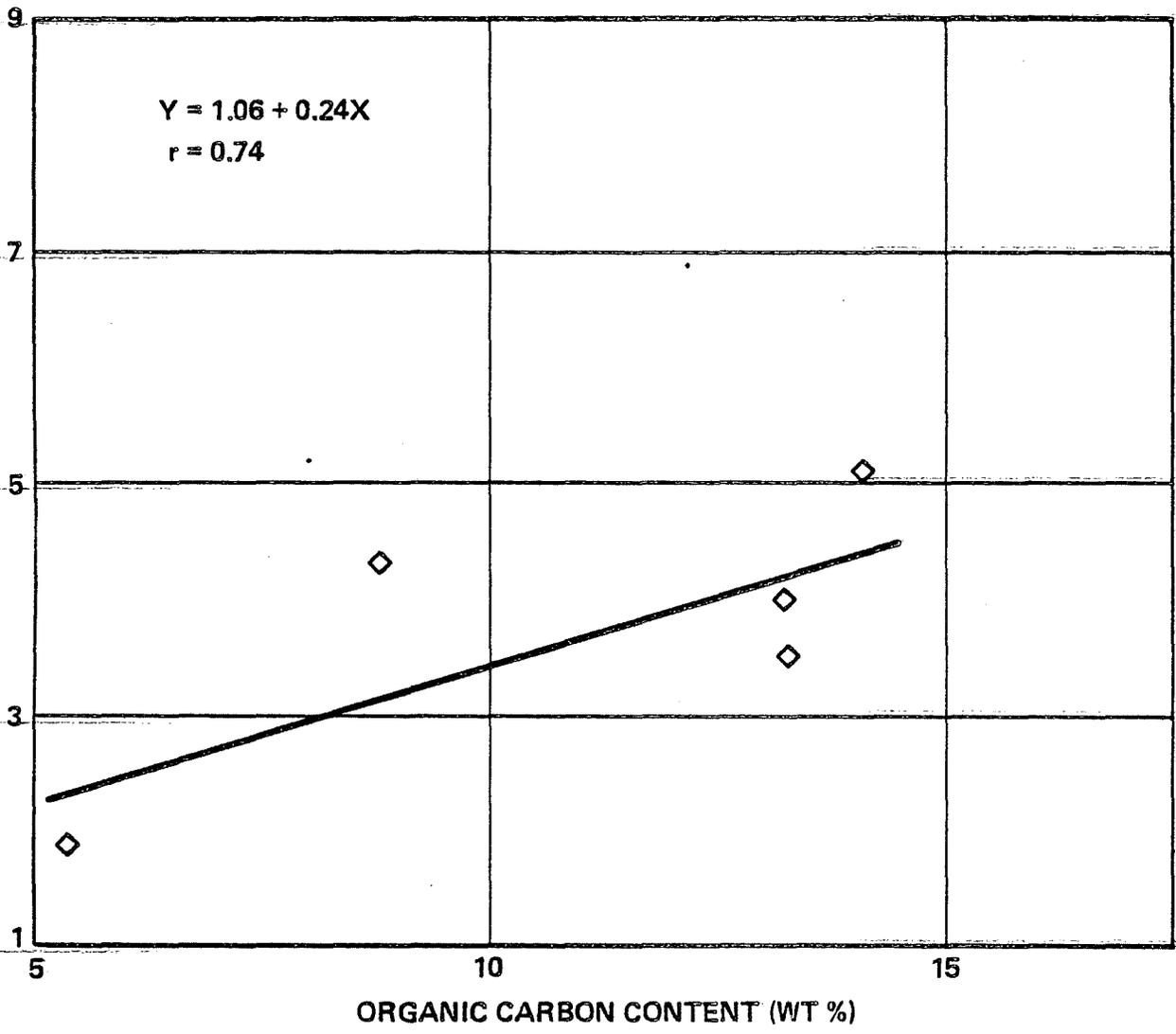
Figure A.14   Spontaneous Combustion Index vs. Organic Carbon
            Content: Graded Series (-325 Mesh) Samples
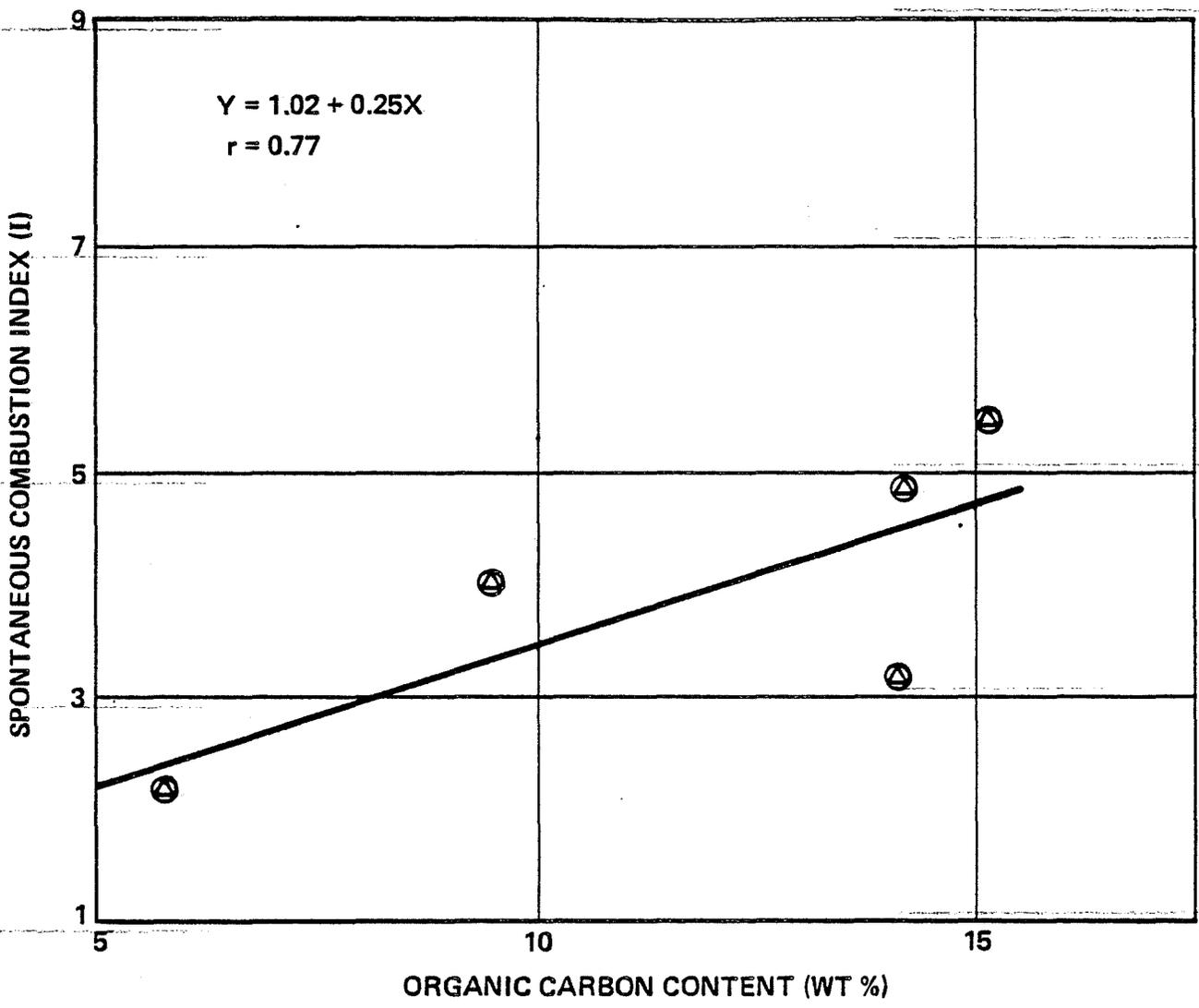
Figure A.15   Spontaneous Combustion Index vs. Organic Carbon
                Content: Graded Series (Reconstituted Standard Size)
                Samples
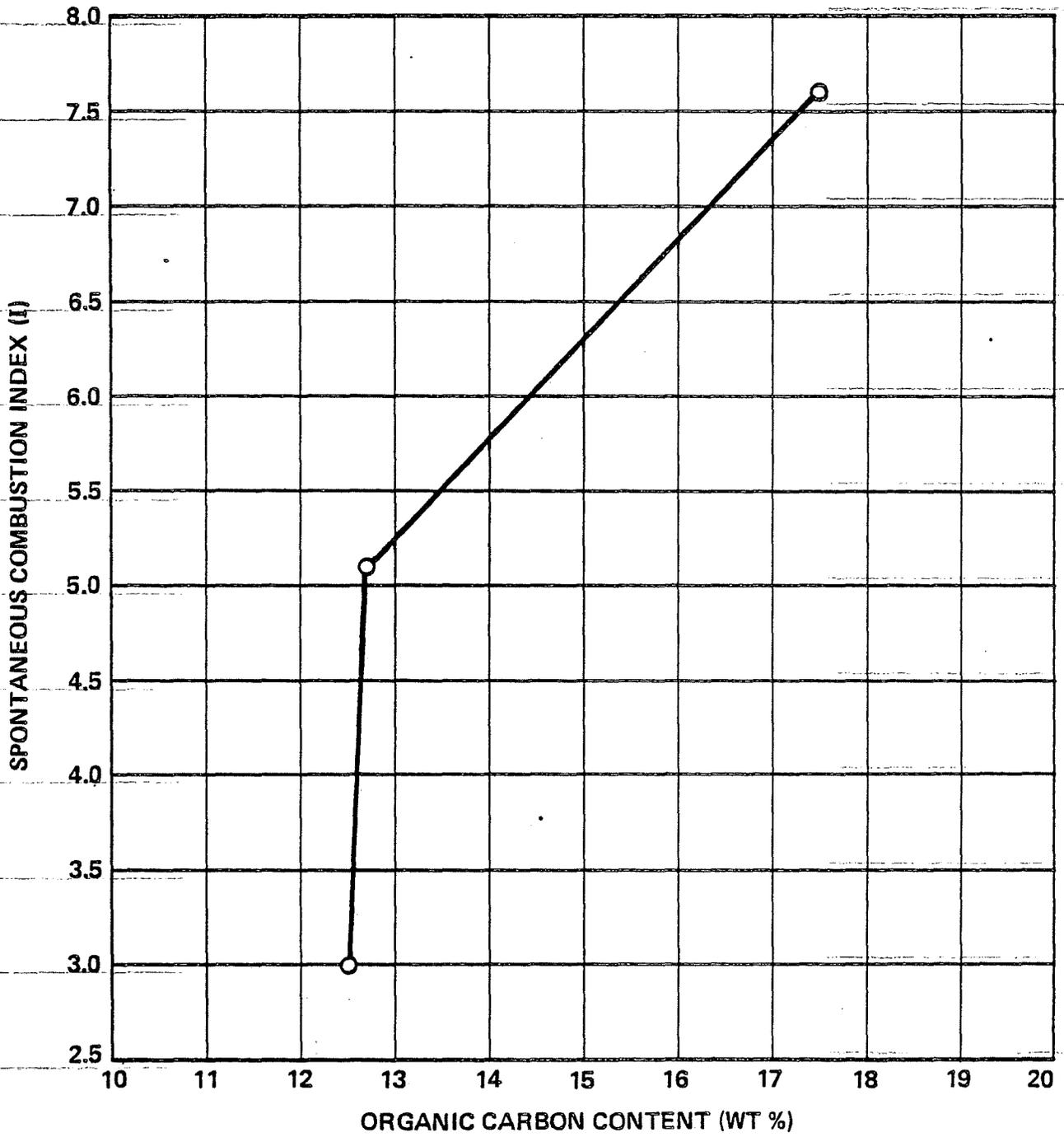
Figure A.16   Spontaneous Combustion Index vs. Organic Carbon
               Content: Mine Dust (Head) Samples
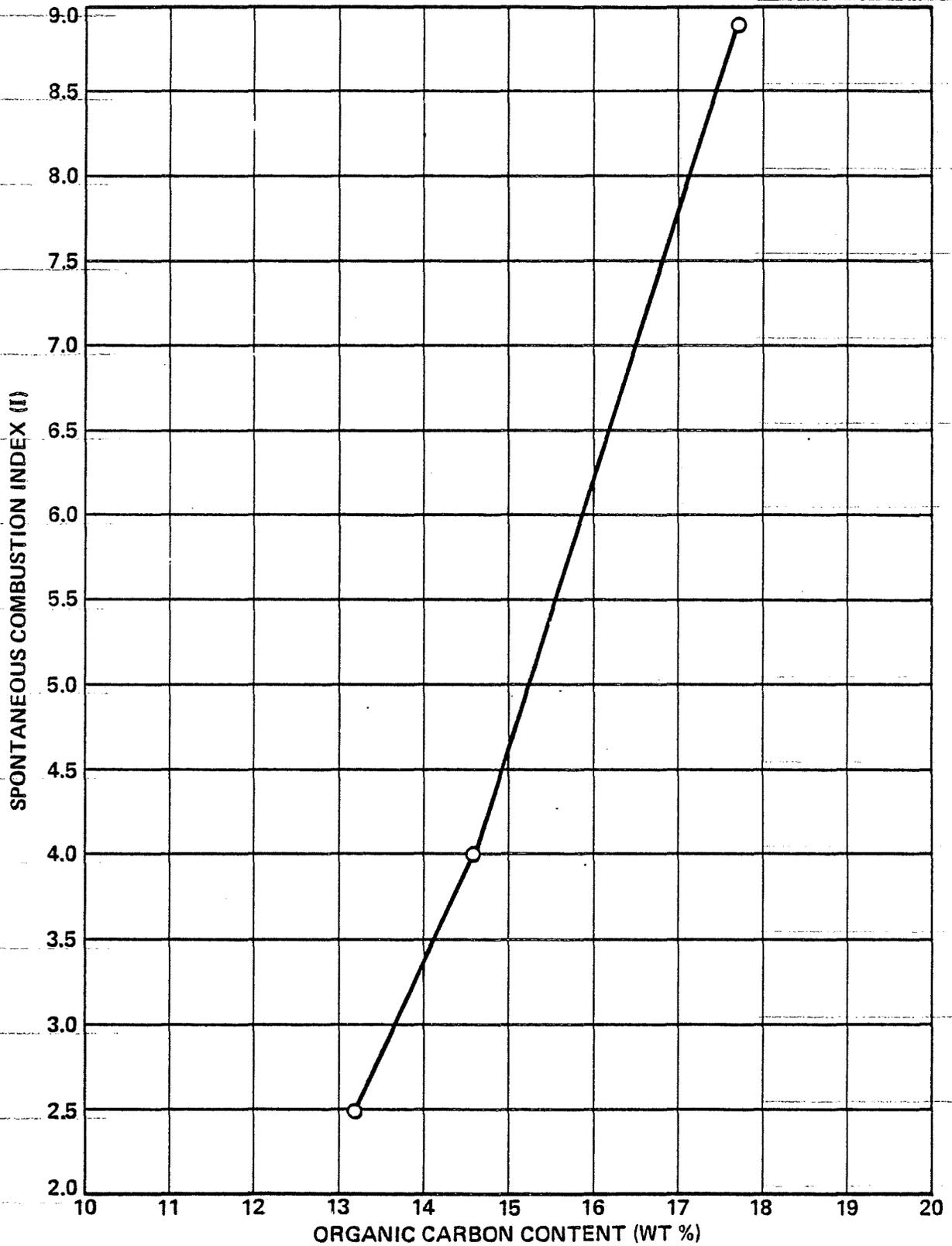
Figure A.17   Spontaneous Combustion Index vs. Organic Carbon
Content: Mine Dust (-40 +100 Mesh) Samples
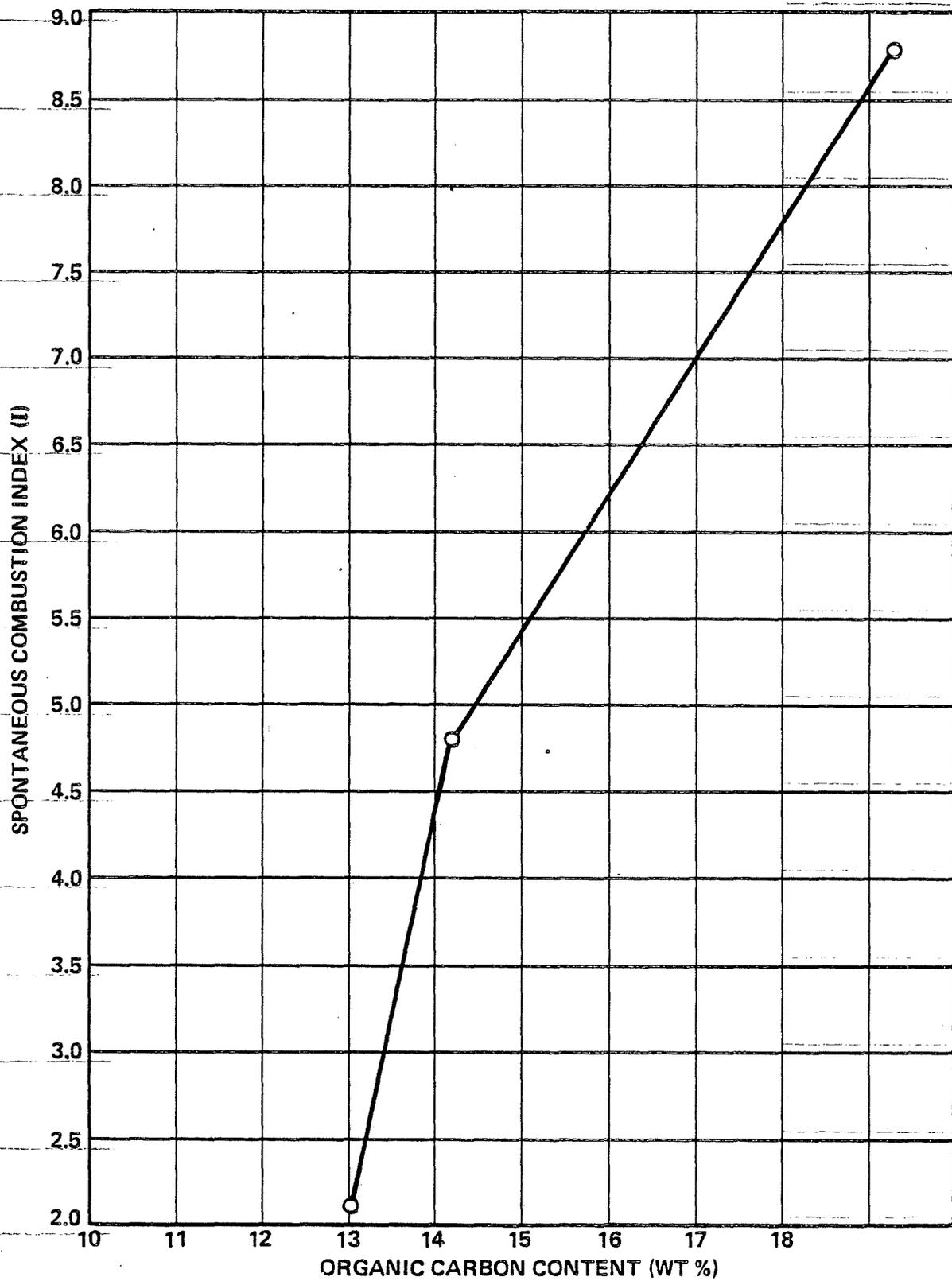
Figure A.18   Spontaneous Combustion Index vs. Organic Carbon
Content: Mine Dust (-100 +200 Mesh) Samples
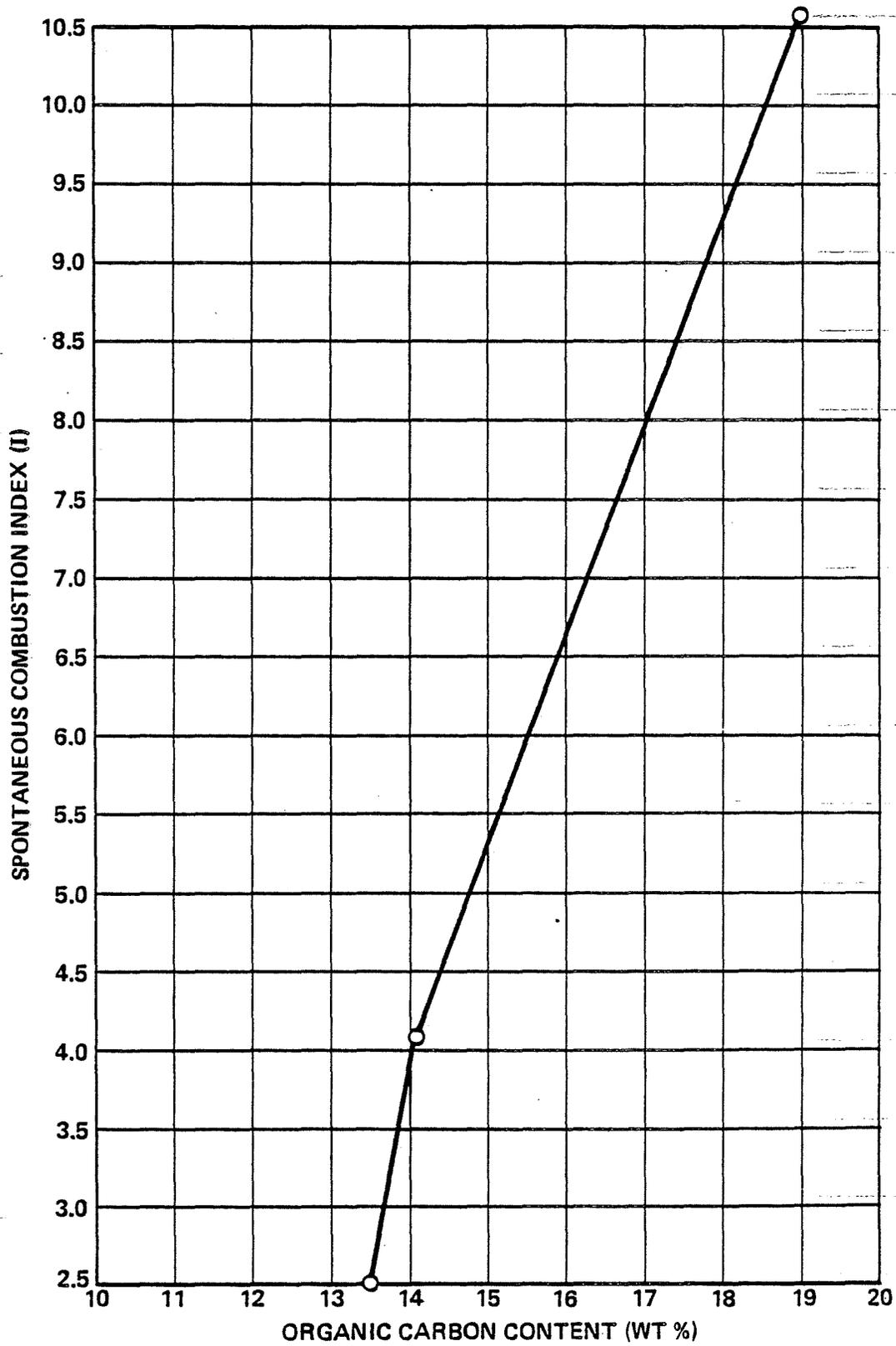
Figure A.19   Spontaneous Combustion Index vs. Organic Carbon
Content: Mine Dust (-200 +325 Mesh) Samples
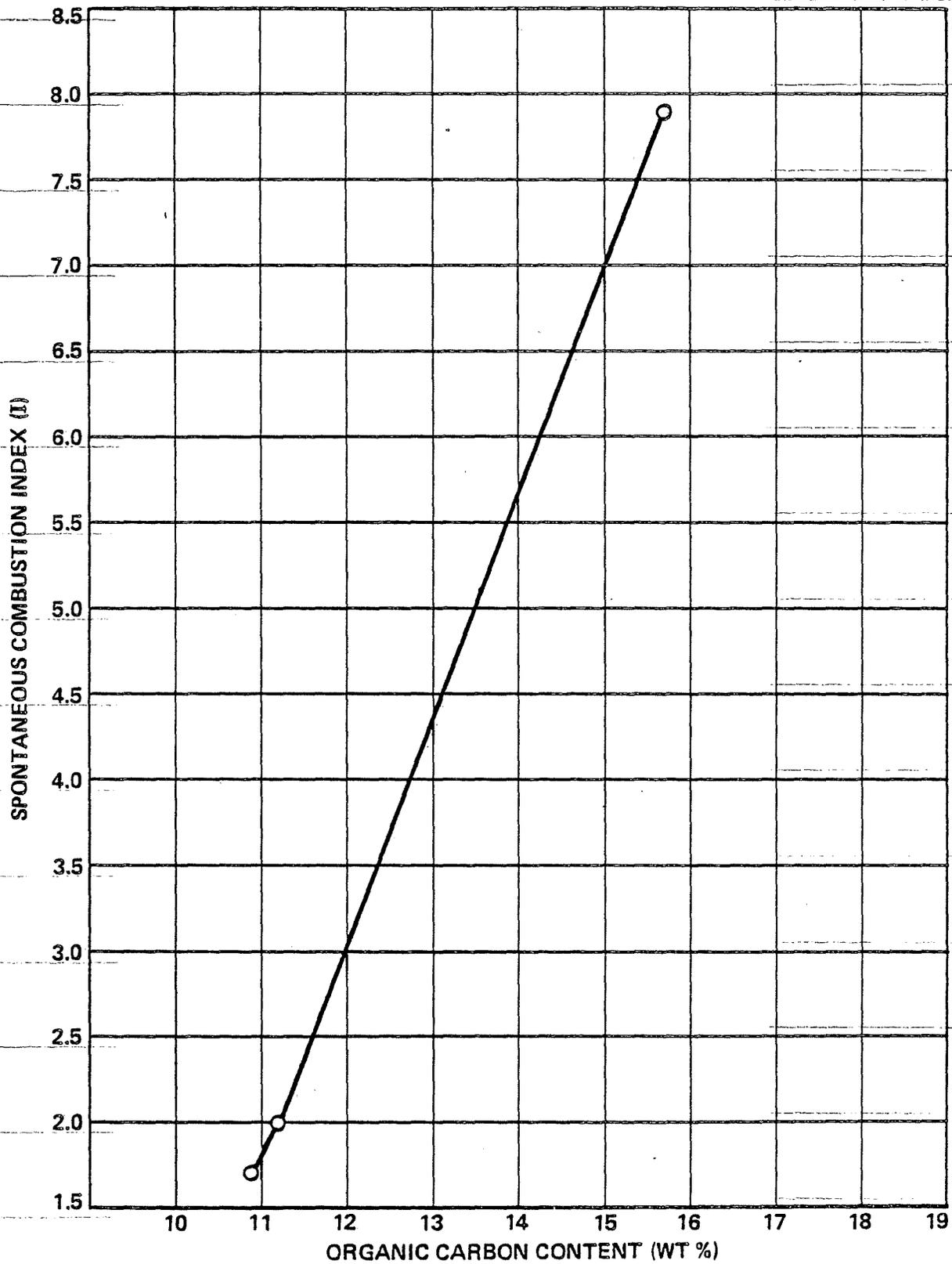
Figure A.20   Spontaneous Combustion Index vs. Organic Carbon
Content: Mine Dust (-325 Mesh) Samples
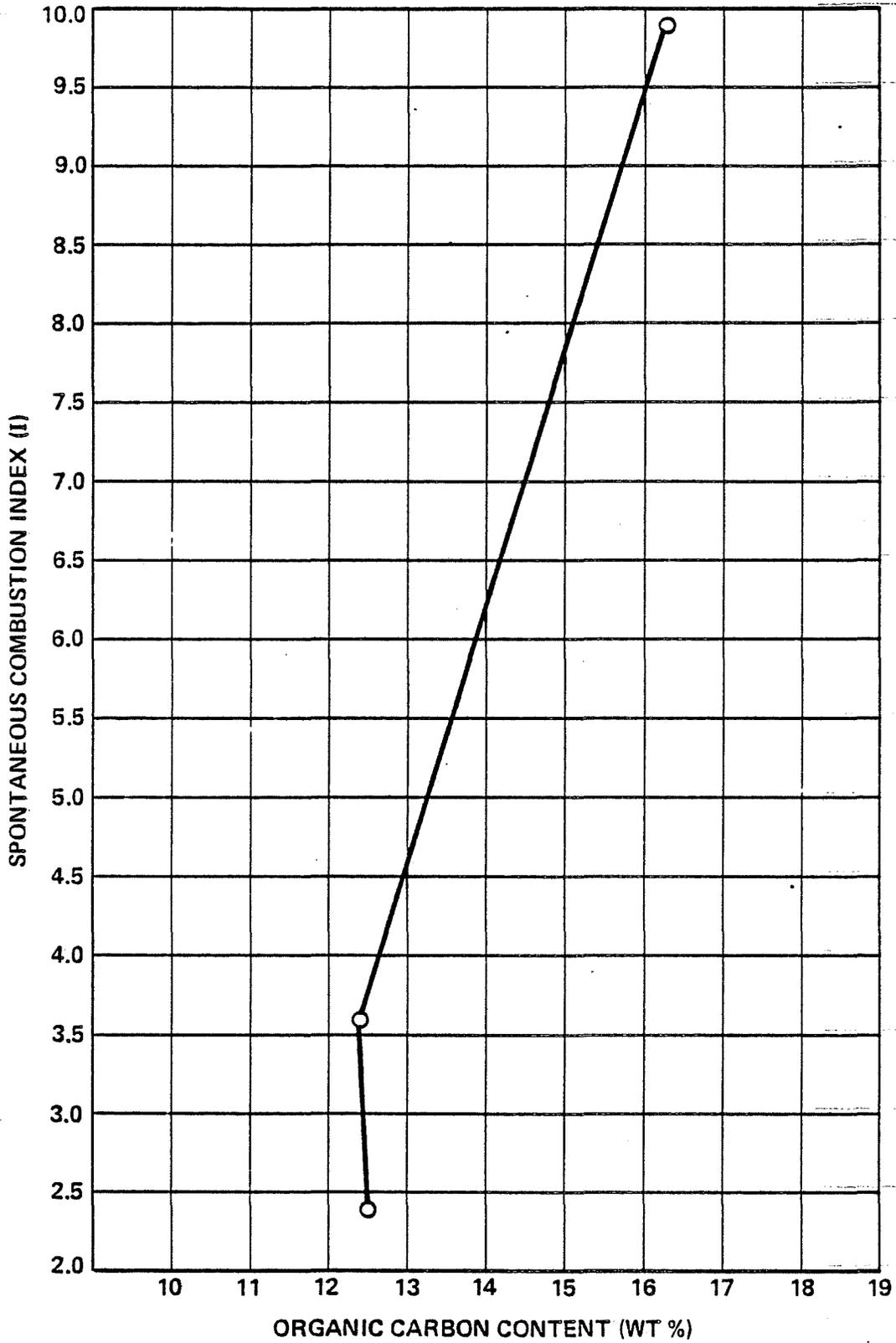
Figure A.21   Spontaneous Combustion Index vs. Organic Carbon
              Content: Mine Dust (Reconstituted Standard Size) Samples

SAMPLE NUMBER   RF5790
SAMPLE DESCRIPTION   10 GPT RECON
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   PB1539

FISCHER ASSAY YIELDS

OIL (LB/TON)	87.7	
(GAL/TON)	11.8	
API GRAVITY	27.0	
GAS (LB/TON)	22.1	
(SCF/TON)	310.5	
WATER (LB/TON)	13.9	
(GAL/TON)	1.7	
SS (LB/TON)	1868.7	
TOTAL (LB/TON)	1992.4	
VARIANCE (PC)	-.4	

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	0.45	0.51
CO	0.91	1.04
CO2	10.95	12.48
H2S	1.38	1.57
C1	2.08	2.37
C2	1.30	1.49
C2-	0.46	0.52
C3	1.00	1.14
C3-	0.84	0.95
I-C4	0.05	0.05
N-C4	0.43	0.49
C4-	0.71	0.81
C5	0.78	0.89
C6	0.57	0.65
C7	0.23	0.27
C8	0.01	0.02
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	19.4		22.1
(SCF/TON)		295.0	
C4 & HEAVIER(LB/TON)	90.5		103.2
(GAL/TON)		12.3	
API GRAVITY		29.0	
TOTAL HYDROCARBONS	97.5		111.2
(INCL. H2 & CO, LB/TON)			

FISCHER ASSAY GAS ANALYSIS

```
        SAMPLE NUMBER          RF5790
     SAMPLE DESCRIPTION        10 GPT RECON
      FISCHER ASSAY NO.        PB1539
  TERMINAL TEMP. DEG. F        932
```

COMPONENT MOLE PERCENT

Component	Mole Percent
H2	27.39
CO	3.98
CO2	30.37
H2S	4.94
C1	15.85
C2	5.29
C2-	1.99
C3	2.76
C3-	2.42
I-C4	0.10
N-C4	0.91
C4-	1.55
C5	1.34
C6	0.81
C7	0.29
C8	0.02
C9	0.00
SUM	100.00

```
     AVERAGE MOLE WT              27.03

 LBS C IN GAS/TON SHALE           10.25
       PERCENT CARBON             46.27

BTU VALUE OF GAS (CALC.)
     BTU/SCF (GROSS)             731.55
       BTU/SCF (NET)             667.00
```

READY

TOSCO ASSAY NUMBER   PB1539
SAMPLE NUMBER   RF5790
SAMPLE DESCRIPTION   10 GPT RECON

TERMINAL TEMP =	932
SAMPLE =	100.83100
RESIDUE =	94.21100
TOTAL LIQUID =	5.12200
WATER =	0.70000
OIL DENSITY =	0.89270

1 GAS BOMBS

BAROMETRIC PRESS. MM =	608.0
BOMB PRESS IN HG =	2.4
BOMB TEMP DEG F =	77.0

	BOMB 1
VOLUME LITERS	1.22
O2	0.97
N2	2.92
H2	17.19
CO	2.50
CO2	19.06
H2S	3.10
C1	9.95
C2	3.32
C2-	1.25
C3	1.73
C3-	1.52
I-C4	0.06
N-C4	0.57
C4-	0.97
C5	0.84
C6	0.51
C7	0.18
C8	0.01
C9	0.00
SUM	66.65

```
                    SAMPLE NUMBER        RF5796
                 SAMPLE DESCRIPTION      15 GPT RECON
                   TERMINAL TEMP         932 DEG. F
                 FISCHER ASSAY NO.       PB1527
```

FISCHER ASSAY YIELDS

```
    OIL   (LB/TON)                      101.4
          (GAL/TON)                      13.3
        API GRAVITY                      23.6

    GAS   (LB/TON)                       41.5
          (SCF/TON)                     514.4

    WATER (LB/TON)                       21.9
          (GAL/TON)                       2.6

    SS    (LB/TON)                     1835.6

    TOTAL (LB/TON)                     2000.4

    VARIANCE  (PC)                        0.0
```

			(LB/100 LB)
GAS	(LB/TON)		(FA OIL)
H2	0.59		0.58
CO	1.27		1.25
CO2	27.48		27.11
H2S	3.01		2.97
C1	2.35		2.32
C2	1.46		1.44
C2-	0.70		0.69
C3	1.05		1.03
C3-	0.87		0.86
I-C4	0.01		0.01
N-C4	0.42		0.42
C4-	0.78		0.77
C5	0.82		0.81
C6	0.54		0.53
C7	0.12		0.11
C8	0.01		0.01
C9	0.00		0.00

ADJUSTED YIELDS

```
    C3 & LIGHTER(LB/TON)    38.8                        38.2
              (SCF/TON)             499.1

    C4 & HEAVIER(LB/TON)   104.1                       102.7
              (GAL/TON)              13.8
             API GRAVITY             25.4

    TOTAL HYDROCARBONS     112.4                       110.8
    (INCL. H2 & CO, LB/TON)
```

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER   RF5796
SAMPLE DESCRIPTION   15 GPT RECON
FISCHER ASSAY NO.   PB1527
TERMINAL TEMP. DEG. F 932

COMPONENT MOLE PERCENT

Component	Mole Percent
H2	21.65
CO	3.34
CO2	46.02
H2S	6.51
C1	10.82
C2	3.58
C2-	1.83
C3	1.75
C3-	1.52
I-C4	0.01
N-C4	0.54
C4-	1.02
C5	0.85
C6	0.47
C7	0.09
C8	0.01
C9	0.00
SUM	100.00

AVERAGE MOLE WT   30.56

LBS C IN GAS/TON SHALE   15.44
PERCENT CARBON   37.24

BTU VALUE OF GAS (CALC.)
BTU/SCF (GROSS)   513.21
BTU/SCF (NET)   467.51

READY

TOSCO ASSAY NUMBER   PB1527
SAMPLE NUMBER   RF5796
SAMPLE DESCRIPTION   15 GPT RECON

TERMINAL TEMP =	932
SAMPLE =	100.34000
RESIDUE =	92.09000
TOTAL LIQUID =	6.18700
WATER =	1.10000
OIL DENSITY =	0.91240

1 GAS BOMBS

BAROMETRIC PRESS. MM =	604.0
BOMB PRESS IN HG =	2.4
BOMB TEMP DEG F =	77.0

	BOMB 1
VOLUME LITERS	1.98
O2	0.42
N2	1.89
H2	12.51
CO	1.93
CO2	26.59
H2S	3.76
C1	6.25
C2	2.07
C2-	1.06
C3	1.01
C3-	0.88
I-C4	0.00
N-C4	0.31
C4-	0.59
C5	0.49
C6	0.27
C7	0.05
C8	0.00
C9	0.00
SUM	60.09

```
                    SAMPLE NUMBER      RF5802
                 SAMPLE DESCRIPTION    20 GPT RECON
                   TERMINAL TEMP       932 DEG. F
                 FISCHER ASSAY NO.     PB1526
```

FISCHER ASSAY YIELDS

```
      OIL   (LB/TON)                        144.0
            (GAL/TON)                        19.2
         API GRAVITY                         26.1

      GAS   (LB/TON)                         54.4
            (SCF/TON)                        663.3

      WATER (LB/TON)                         25.1
            (GAL/TON)                         3.0

      SS    (LB/TON)                       1771.5

      TOTAL (LB/TON)                       1995.0

      VARIANCE  (PC)                         -.3
```

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	0.79	0.55
CO	1.42	0.99
CO2	37.42	25.98
H2S	1.15	0.80
C1	2.89	2.01
C2	2.15	1.49
C2-	0.88	0.61
C3	1.56	1.08
C3-	1.35	0.94
I-C4	0.07	0.05
N-C4	0.79	0.55
C4-	1.18	0.82
C5	1.40	0.97
C6	0.97	0.67
C7	0.32	0.22
C8	0.03	0.02
C9	0.00	0.00

ADJUSTED YIELDS

```
   C3 & LIGHTER(LB/TON)     49.6                      34.4
               (SCF/TON)            636.6

   C4 & HEAVIER(LB/TON)    148.8                     103.3
               (GAL/TON)             20.1
            API GRAVITY             28.3

   TOTAL HYDROCARBONS      159.8                     111.0
   (INCL. H2 & CO, LB/TON)
```

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER	RF5802
SAMPLE DESCRIPTION	20 GPT RECON
FISCHER ASSAY NO.	PB1526
TERMINAL TEMP. DEG. F	932

COMPONENT MOLE PERCENT

Component	Mole Percent
H2	22.49
CO	2.90
CO2	48.59
H2S	1.93
C1	10.34
C2	4.09
C2-	1.79
C3	2.02
C3-	1.83
I-C4	0.06
N-C4	0.78
C4-	1.21
C5	1.13
C6	0.65
C7	0.18
C8	0.01
C9	0.00
SUM	100.00

AVERAGE MOLE WT	31.06
LBS C IN GAS/TON SHALE	21.89
PERCENT CARBON	40.27

BTU VALUE OF GAS (CALC.)

BTU/SCF (GROSS)	543.03
BTU/SCF (NET)	494.98

```
          TOSCO ASSAY NUMBER        FB1526
             SAMPLE NUMBER          RF5802
          SAMPLE DESCRIPTION        20 GPT RECON


              TERMINAL TEMP =          932
                     SAMPLE =        99.61000
                    RESIDUE =        88.23000
               TOTAL LIQUID =         8.42300
                      WATER =         1.25000
                OIL DENSITY =         0.89760



                   1 GAS BOMBS
             BAROMETRIC PRESS. MM =     604.0
                 BOMB PRESS IN HG =       2.4
                 BOMB TEMP DEG F =       77.0
                              BOMB 1
       VOLUME LITERS            2.53
       O2                       0.64
       N2                       2.25
       H2                      17.34
       CO                       2.24
       CO2                     37.47
       H2S                      1.49
       C1                       7.97
       C2                       3.15
       C2-                      1.38
       C3                       1.56
       C3-                      1.41
       I-C4                     0.05
       N-C4                     0.60
       C4-                      0.93
       C5                       0.87
       C6                       0.50
       C7                       0.14
       C8                       0.01
       C9                       0.00
       SUM                     80.00
```

```
            SAMPLE NUMBER      RF5808
         SAMPLE DESCRIPTION    25 GPT RECON
            TERMINAL TEMP      932 DEG. F
         FISCHER ASSAY NO.     PB1525
```

FISCHER ASSAY YIELDS

OIL	(LB/TON)	166.3
	(GAL/TON)	22.4
	API GRAVITY	27.4
GAS	(LB/TON)	66.2
	(SCF/TON)	804.5
WATER	(LB/TON)	29.1
	(GAL/TON)	3.5
SS	(LB/TON)	1733.9
TOTAL	(LB/TON)	1995.5
VARIANCE	(PC)	-.2

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	0.93	0.56
CO	1.59	0.96
CO2	43.29	26.02
H2S	6.42	3.86
C1	2.84	1.71
C2	2.22	1.34
C2-	0.90	0.54
C3	1.83	1.10
C3-	1.44	0.87
I-C4	0.06	0.04
N-C4	0.88	0.53
C4-	1.30	0.78
C5	1.38	0.83
C6	0.93	0.56
C7	0.15	0.09
C8	0.03	0.02
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	61.5		36.9
(SCF/TON)		777.4	
C4 & HEAVIER(LB/TON)	171.1		102.8
(GAL/TON)		23.3	
API GRAVITY		29.2	
TOTAL HYDROCARBONS	182.8		109.9
(INCL. H2 & CO, LB/TON)			

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER	RF5808
SAMPLE DESCRIPTION	25 GPT RECON
FISCHER ASSAY NO.	PB1525
TERMINAL TEMP. DEG. F	932

COMPONENT MOLE PERCENT

Component	Mole Percent
H2	21.83
CO	2.68
CO2	46.34
H2S	8.87
C1	8.36
C2	3.48
C2-	1.52
C3	1.95
C3-	1.61
I-C4	0.05
N-C4	0.71
C4-	1.09
C5	0.91
C6	0.51
C7	0.07
C8	0.01
C9	0.00
SUM	100.00

AVERAGE MOLE WT	31.18
LBS C IN GAS/TON SHALE	23.88
PERCENT CARBON	36.08

BTU VALUE OF GAS (CALC.)

BTU/SCF (GROSS)	515.79
BTU/SCF (NET)	470.22

READY

```
TOSCO ASSAY NUMBER      PB1525
    SAMPLE NUMBER       RF5808
SAMPLE DESCRIPTION      25 GPT RECON
```

```
TERMINAL TEMP =         932
       SAMPLE =         99.52600
      RESIDUE =         86.28200
 TOTAL LIQUID =         9.72700
        WATER =         1.45000
  OIL DENSITY =         0.89040
```

```
          2 GAS BOMBS
BAROMETRIC PRESS. MM =  606.1
 BOMB PRESS IN HG =     2.4
 BOMB TEMP DEG F =      77.0
```

	BOMB 1	BOMB 2
VOLUME LITERS	2.61	0.41
O2	0.36	0.39
N2	1.57	1.64
H2	14.34	36.00
CO	1.97	3.05
CO2	39.77	16.52
H2S	7.95	0.97
C1	6.00	10.54
C2	2.51	4.28
C2-	1.15	1.51
C3	1.48	1.95
C3-	1.18	1.89
I-C4	0.04	0.04
N-C4	0.54	0.72
C4-	0.83	1.09
C5	0.68	0.99
C6	0.38	0.57
C7	0.05	0.10
C8	0.01	0.01
C9	0.00	0.00
SUM	80.81	82.26

SAMPLE NUMBER   RF5814
SAMPLE DESCRIPTION   30 GPT RECON
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   PB1517

FISCHER ASSAY YIELDS

OIL (LB/TON)	216.6	
(GAL/TON)	28.3	
API GRAVITY	22.6	
GAS (LB/TON)	49.7	
(SCF/TON)	659.1	
WATER (LB/TON)	18.0	
(GAL/TON)	2.2	
SS (LB/TON)	1707.4	
TOTAL (LB/TON)	1991.8	
VARIANCE (PC)	-.4	

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	0.86	0.40
CO	1.52	0.70
CO2	24.57	11.34
H2S	5.22	2.41
C1	3.55	1.64
C2	3.26	1.51
C2-	0.72	0.33
C3	2.55	1.18
C3-	1.94	0.90
I-C4	0.13	0.06
N-C4	1.10	0.51
C4-	1.66	0.77
C5	1.67	0.77
C6	0.82	0.38
C7	0.09	0.04
C8	0.05	0.02
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	44.2		20.4
(SCF/TON)		626.8	
C4 & HEAVIER(LB/TON)	222.2		102.6
(GAL/TON)		29.4	
API GRAVITY		24.4	
TOTAL HYDROCARBONS	236.6		109.2
(INCL. H2 & CO, LB/TON)			

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER   RF5814
SAMPLE DESCRIPTION   30 GPT RECON
FISCHER ASSAY NO.   PB1517
TERMINAL TEMP. DEG. F 932

COMPONENT MOLE PERCENT

H2	24.61
CO	3.12
CO2	32.11
H2S	8.79
C1	12.77
C2	6.24
C2-	1.47
C3	3.32
C3-	2.65
I-C4	0.13
N-C4	1.09
C4-	1.71
C5	1.35
C6	0.55
C7	0.05
C8	0.03
C9	0.00
SUM	100.00

AVERAGE MOLE WT	28.59
LBS C IN GAS/TON SHALE	21.64
PERCENT CARBON	43.53

BTU VALUE OF GAS (CALC.)

BTU/SCF (GROSS)	729.75
BTU/SCF (NET)	666.28

READY

```
          TOSCO ASSAY NUMBER        PB1517
             SAMPLE NUMBER          RF5814
          SAMPLE DESCRIPTION        30 GPT RECON

               TERMINAL TEMP =          932
                     SAMPLE =        99.90600
                     RESIDUE =       85.29100
               TOTAL LIQUID =        11.72200
                      WATER =         0.90000
                OIL DENSITY =         0.91810


                    1 GAS BOMBS
             BAROMETRIC PRESS. MM =      614.0
                BOMB PRESS IN HG =         2.4
                BOMB TEMP DEG F =         82.4
                                  BOMB 1
          VOLUME LITERS              2.48
          O2                         0.36
          N2                         1.51
          H2                        18.75
          CO                         2.38
          CO2                       24.46
          H2S                        6.70
          C1                         9.73
          C2                         4.75
          C2-                        1.12
          C3                         2.53
          C3-                        2.02
          I-C4                       0.10
          N-C4                       0.83
          C4-                        1.30
          C5                         1.03
          C6                         0.42
          C7                         0.04
          C8                         0.02
          C9                         0.00
          SUM                       78.05
```

SAMPLE NUMBER   RF5820
SAMPLE DESCRIPTION   31 GPT RECON
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   PB1524

FISCHER ASSAY YIELDS

OIL (LB/TON)		221.4
(GAL/TON)		29.5
API GRAVITY		25.9
GAS (LB/TON)		52.8
(SCF/TON)		784.0
WATER (LB/TON)		23.0
(GAL/TON)		2.8
SS (LB/TON)		1696.0
TOTAL (LB/TON)		1993.2
VARIANCE (PC)		-.3

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	1.25	0.56
CO	1.66	0.75
CO2	23.24	10.50
H2S	5.59	2.52
C1	5.16	2.33
C2	3.51	1.58
C2-	1.34	0.60
C3	2.61	1.18
C3-	2.15	0.97
I-C4	0.12	0.05
N-C4	1.23	0.56
C4-	1.73	0.78
C5	1.84	0.83
C6	1.16	0.52
C7	0.20	0.09
C8	0.04	0.02
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	46.5		21.0
(SCF/TON)		747.7	
C4 & HEAVIER(LB/TON)	227.7		102.8
(GAL/TON)		30.7	
API GRAVITY		27.8	
TOTAL HYDROCARBONS (INCL. H2 & CO, LB/TON)	245.4		110.8

FISCHER ASSAY GAS ANALYSIS

```
           SAMPLE NUMBER        RF5820
        SAMPLE DESCRIPTION      31 GPT RECON
        FISCHER ASSAY NO.       FB1524
     TERMINAL TEMP. DEG. F      932
```

COMPONENT MOLE PERCENT

Component	Mole Percent
H2	30.18
CO	2.87
CO2	25.54
H2S	7.93
C1	15.59
C2	5.64
C2-	2.31
C3	2.87
C3-	2.47
I-C4	0.10
N-C4	1.02
C4-	1.49
C5	1.25
C6	0.66
C7	0.10
C8	0.02
C9	0.00
SUM	100.00

```
      AVERAGE MOLE WT                 25.53

  LBS C IN GAS/TON SHALE             24.16
         PERCENT CARBON              45.74

BTU VALUE OF GAS (CALC.)
         BTU/SCF (GROSS)            749.24
          BTU/SCF (NET)            682.35
```

READY

TOSCO ASSAY NUMBER   PB1524
SAMPLE NUMBER   RF5820
SAMPLE DESCRIPTION   31 GPT RECON

```
         TERMINAL TEMP  =        932
                SAMPLE  =        100.16300
               RESIDUE  =         84.93700
          TOTAL LIQUID  =         12.24000
                 WATER  =          1.15000
           OIL DENSITY  =          0.89890


               1 GAS BOMBS
        BAROMETRIC PRESS. MM  =     600.0
           BOMB PRESS IN HG  =       2.4

           BOMB TEMP DEG F  =       77.0
                        BOMB 1
VOLUME LITERS            2.98
O2                      0.20
N2                      1.12
H2                     18.85
CO                      1.79
CO2                    15.95
H2S                     4.95
C1                      9.74
C2                      3.52
C2-                     1.44
C3                      1.79
C3-                     1.54
I-C4                    0.06
N-C4                    0.64
C4-                     0.93
C5                      0.78
C6                      0.41
C7                      0.06
C8                      0.01
C9                      0.00
SUM                    63.78
```

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER   RF6193
SAMPLE DESCRIPTION   35 GPT RECON
FISCHER ASSAY NO.   PB1533
TERMINAL TEMP. DEG. F   932

COMPONENT MOLE PERCENT

Component	Mole Percent
H_2	27.75
CO	4.01
CO_2	16.02
H_2S	10.94
C1	16.83
C2	6.98
C2-	2.24
C3	3.74
C3-	3.38
I-C4	0.09
N-C4	1.60
C4-	2.09
C5	2.29
C6	1.47
C7	0.53
C8	0.04
C9	0.00
SUM	100.00

AVERAGE MOLE WT	26.55
LBS C IN GAS/TON SHALE	18.09
PERCENT CARBON	52.46

BTU VALUE OF GAS (CALC.)
BTU/SCF (GROSS)   983.84
BTU/SCF (NET)   900.08

READY

1

```
                    SAMPLE NUMBER      RF6193
                    SAMPLE DESCRIPTION 35 GPT RECON
                    TERMINAL TEMP      932 DEG. F
                    FISCHER ASSAY NO.  PB1533
```

FISCHER ASSAY YIELDS

```
    OIL   (LB/TON)                      255.4
          (GAL/TON)                      34.1
       API GRAVITY                       26.2

    GAS   (LB/TON)                       34.5
          (SCF/TON)                     492.2

    WATER (LB/TON)                        7.2
          (GAL/TON)                       0.9

    SS    (LB/TON)                     1684.7

    TOTAL (LB/TON)                     1981.7

    VARIANCE  (PC)                       -.9
```

		(LB/100 LB)
GAS	(LB/TON)	(FA OIL)
H2	0.72	0.28
CO	1.46	0.57
CO2	9.15	3.58
H2S	4.85	1.90
C1	3.50	1.37
C2	2.73	1.07
C2-	0.81	0.32
C3	2.14	0.84
C3-	1.85	0.72
I-C4	0.07	0.03
N-C4	1.21	0.47
C4-	1.52	0.60
C5	2.12	0.83
C6	1.62	0.63
C7	0.68	0.27
C8	0.06	0.02
C9	0.00	0.00

ADJUSTED YIELDS

```
    C3 & LIGHTER(LB/TON)   27.2               10.7
               (SCF/TON)        452.3

    C4 & HEAVIER(LB/TON)  262.6              102.8
               (GAL/TON)        35.5
             API GRAVITY        27.9

    TOTAL HYDROCARBONS    275.9              108.0
    (INCL. H2 & CO, LB/TON)
```

```
         TOSCO ASSAY NUMBER        PB1533
            SAMPLE NUMBER          RF6193
         SAMPLE DESCRIPTION        35 GPT RECON


              TERMINAL TEMP =         932
                     SAMPLE =       98.74100
                    RESIDUE =       83.17400
               TOTAL LIQUID =       12.96100
                      WATER =        0.35300
                OIL DENSITY =        0.89750


                     1 GAS BOMBS
           BAROMETRIC PRESS. MM =       609.0
                BOMB PRESS IN HG =        2.4
                BOMB TEMP DEG F =        75.2
                                  BOMB 1
           VOLUME LITERS            2.58
           O2                       0.94
           N2                      23.14
           H2                      14.76
           CO                       2.13
           CO2                      8.52
           H2S                      5.82
           C1                       8.95
           C2                       3.71
           C2-                      1.19
           C3                       1.99
           C3-                      1.80
           I-C4                     0.05
           N-C4                     0.85
           C4-                      1.11
           C5                       1.22
           C6                       0.78
           C7                       0.28
           C8                       0.02
           C9                       0.00
           SUM                     77.26
```

SAMPLE NUMBER   RF5826
SAMPLE DESCRIPTION   COLONY MINE DUST RECON
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   PB1534

FISCHER ASSAY YIELDS

OIL (LB/TON)		170.7
(GAL/TON)		22.7
API GRAVITY		25.8
GAS (LB/TON)		52.8
(SCF/TON)		719.6
WATER (LB/TON)		73.0
(GAL/TON)		8.7
SS (LB/TON)		1703.5
TOTAL (LB/TON)		2000.0
VARIANCE (PC)		-.0

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	1.43	0.84
CO	2.25	1.32
CO2	33.98	19.90
H2S	0.00	0.00
C1	0.04	0.03
C2	2.96	1.73
C2-	1.06	0.62
C3	2.15	1.26
C3-	1.92	1.13
I-C4	0.10	0.06
N-C4	0.94	0.55
C4-	1.61	0.94
C5	1.58	0.93
C6	1.78	1.04
C7	1.02	0.60
C8	0.00	0.00
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	45.8		26.8
(SCF/TON)		681.7	
C4 & HEAVIER(LB/TON)	177.7		104.1
(GAL/TON)		24.1	
API GRAVITY		28.3	
TOTAL HYDROCARBONS	189.5		111.0
(INCL. H2 & CO, LB/TON)			

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER	RF5826
SAMPLE DESCRIPTION	COLONY MINE DUST RECON
FISCHER ASSAY NO.	PB1534
TERMINAL TEMP. DEG. F	932

COMPONENT MOLE PERCENT

Component	Mole Percent
H2	37.55
CO	4.23
CO2	40.67
H2S	0.00
C1	0.15
C2	5.17
C2-	1.99
C3	2.56
C3-	2.40
I-C4	0.09
N-C4	0.85
C4-	1.51
C5	1.17
C6	1.10
C7	0.54
C8	0.00
C9	0.00
SUM	100.00

AVERAGE MOLE WT	27.81
LBS C IN GAS/TON SHALE	22.86
PERCENT CARBON	43.30

BTU VALUE OF GAS (CALC.)

BTU/SCF (GROSS)	584.32
BTU/SCF (NET)	532.16

.

READY

```
        TOSCO ASSAY NUMBER      FB1534
          SAMPLE NUMBER         RF5826
      SAMPLE DESCRIPTION        COLONY MINE DUST RECON


            TERMINAL TEMP =         932
                   SAMPLE =       98.67400
                  RESIDUE =       84.04500
             TOTAL LIQUID =       12.02200
                    WATER =        3.60000
              OIL DENSITY =        0.89980



                1 GAS BOMBS
        BAROMETRIC PRESS. MM =      606.0
           BOMB PRESS IN HG =        2.4
           BOMB TEMP DEG F =        73.4
                            BOMB 1
VOLUME LITERS                2.89
O2                           0.69
N2                           7.00
H2                          25.63
CO                           2.89
CO2                         27.76
H2S                          0.00
C1                           0.10
C2                           3.53
C2-                          1.36
C3                           1.75
C3-                          1.64
I-C4                         0.06
N-C4                         0.58
C4-                          1.03
C5                           0.80
C6                           0.75
C7                           0.37
C8                           0.00
C9                           0.00
SUM                         75.94
```

SAMPLE NUMBER   RF5838
SAMPLE DESCRIPTION   NEW DUST RECON
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   PB1530

FISCHER ASSAY YIELDS


```
OIL    (LB/TON)                      257.2
       (GAL/TON)                      34.3
    API GRAVITY                       25.8

GAS    (LB/TON)                       66.8
       (SCF/TON)                     969.9

WATER  (LB/TON)                       28.7
       (GAL/TON)                       3.4

SS     (LB/TON)                     1645.5

TOTAL  (LB/TON)                     1998.2

VARIANCE  (PC)                        -.1
```

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	1.45	0.56
CO	2.44	0.95
CO2	29.15	11.33
H2S	7.10	2.76
C1	6.69	2.60
C2	4.92	1.91
C2-	1.30	0.51
C3	3.05	1.18
C3-	2.25	0.87
I-C4	0.17	0.07
N-C4	1.42	0.55
C4-	2.17	0.84
C5	2.52	0.98
C6	1.62	0.63
C7	0.47	0.18
C8	0.08	0.03
C9	0.00	0.00

ADJUSTED YIELDS

```
C3 & LIGHTER(LB/TON)    58.3                     22.7
           (SCF/TON)              922.1

C4 & HEAVIER(LB/TON)   265.7                    103.3
           (GAL/TON)               35.9
        API GRAVITY                27.9

TOTAL HYDROCARBONS     287.8                    111.9
(INCL. H2 & CO, LB/TON)
```

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER   RF5838
SAMPLE DESCRIPTION   NEW DUST RECON
FISCHER ASSAY NO.   PB1530
TERMINAL TEMP. DEG. F   932

COMPONENT MOLE PERCENT

Component	Mole Percent
H2	28.32
CO	3.40
CO2	25.89
H2S	8.14
C1	16.34
C2	6.38
C2-	1.81
C3	2.70
C3-	2.09
I-C4	0.11
N-C4	0.96
C4-	1.51
C5	1.39
C6	0.74
C7	0.19
C8	0.03
C9	0.00
SUM	100.00

AVERAGE MOLE WT   26.10

LBS C IN GAS/TON SHALE   30.60
PERCENT CARBON   45.81

BTU VALUE OF GAS (CALC.)
BTU/SCF (GROSS)   760.33
BTU/SCF (NET)   692.76

READY

```
TOSCO ASSAY NUMBER      PB1530
   SAMPLE NUMBER        RF5838
SAMPLE DESCRIPTION      NEW DUST RECON


   TERMINAL TEMP =         932
          SAMPLE =       98.10000
         RESIDUE =       80.71000
    TOTAL LIQUID =       14.02700
           WATER =        1.41000
     OIL DENSITY =        0.89960


           1 GAS BOMBS
   BAROMETRIC PRESS. MM =      612.0
      BOMB PRESS IN HG =        2.6
      BOMB TEMP DEG F =        77.0
                        BOMB 1
VOLUME LITERS            3.52
O2                       0.04
N2                       1.45
H2                      19.83
CO                       2.38
CO2                     18.13
H2S                      5.70
C1                      11.44
C2                       4.47
C2-                      1.27
C3                       1.89
C3-                      1.46
I-C4                     0.08
N-C4                     0.67
C4-                      1.06
C5                       0.97
C6                       0.52
C7                       0.13
C8                       0.02
C9                       0.00
SUM                     71.51
```

SAMPLE NUMBER   RF5844
SAMPLE DESCRIPTION   OLD DUST RECON
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   PB1531

FISCHER ASSAY YIELDS

OIL	(LB/TON)	176.6
	(GAL/TON)	23.5
	API GRAVITY	25.4
GAS	(LB/TON)	53.1
	(SCF/TON)	749.3
WATER	(LB/TON)	35.3
	(GAL/TON)	4.2
SS	(LB/TON)	1732.8
TOTAL	(LB/TON)	1997.8
VARIANCE	(PC)	-.1

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	1.15	0.65
CO	2.11	1.20
CO2	31.75	17.98
H2S	0.19	0.11
C1	4.69	2.66
C2	3.32	1.88
C2-	0.98	0.55
C3	1.97	1.12
C3-	1.57	0.89
I-C4	0.12	0.07
N-C4	0.87	0.49
C4-	1.47	0.83
C5	1.51	0.86
C6	1.04	0.59
C7	0.35	0.20
C8	0.00	0.00
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	47.7		27.0
(SCF/TON)		718.9	
C4 & HEAVIER(LB/TON)	182.0		103.0
(GAL/TON)		24.5	
API GRAVITY		27.4	
TOTAL HYDROCARBONS	197.7		112.0
(INCL. H2 & CO, LB/TON)			

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER   RF5844
SAMPLE DESCRIPTION   OLD DUST RECON
FISCHER ASSAY NO.   PB1531
TERMINAL TEMP. DEG. F   932

COMPONENT MOLE PERCENT

Component	Mole Percent
H_2	29.03
CO	3.81
CO_2	36.50
H_2S	0.28
C1	14.83
C2	5.58
C2-	1.76
C3	2.26
C3-	1.89
I-C4	0.11
N-C4	0.76
C4-	1.32
C5	1.08
C6	0.62
C7	0.18
C8	0.00
C9	0.00
SUM	100.00

AVERAGE MOLE WT   26.85

LBS C IN GAS/TON SHALE   24.05
PERCENT CARBON   45.30

BTU VALUE OF GAS (CALC.)
BTU/SCF (GROSS)   634.88
BTU/SCF (NET)   577.17

1

```
       TOSCO ASSAY NUMBER      PB1531
         SAMPLE NUMBER         RF5844
       SAMPLE DESCRIPTION      OLD DUST RECON

         TERMINAL TEMP =          932
                SAMPLE =        98.31700
               RESIDUE =        85.18000
          TOTAL LIQUID =        10.41800
                 WATER =         1.73700
           OIL DENSITY =         0.90170


              1 GAS BOMBS
       BAROMETRIC PRESS. MM =      612.0
          BOMB PRESS IN HG =        2.4
          BOMB TEMP DEG F =        77.0
                          BOMB 1
    VOLUME LITERS           2.76
    O2                      0.00
    N2                      1.50
    H2                     16.45
    CO                      2.16
    CO2                    20.68
    H2S                     0.16
    C1                      8.40
    C2                      3.16
    C2-                     1.00
    C3                      1.28
    C3-                     1.07
    I-C4                    0.06
    N-C4                    0.43
    C4-                     0.75
    C5                      0.61
    C6                      0.35
    C7                      0.10
    C8                      0.00
    C9                      0.00
    SUM                    58.16
```

SAMPLE NUMBER   RF6302
SAMPLE DESCRIPTION   COLONY MINE RUBBLE
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   1537

FISCHER ASSAY YIELDS

OIL (LB/TON)		324.8
(GAL/TON)		44.3
API GRAVITY		29.6
GAS (LB/TON)		60.8
(SCF/TON)		946.5
WATER (LB/TON)		15.9
(GAL/TON)		1.9
SS (LB/TON)		1595.3
TOTAL (LB/TON)		1996.8
VARIANCE (PC)		-.2

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	1.56	0.48
CO	2.38	0.73
CO2	18.42	5.67
H2S	6.61	2.04
C1	8.08	2.49
C2	4.93	1.52
C2-	1.25	0.39
C3	3.60	1.11
C3-	2.66	0.82
I-C4	0.21	0.06
N-C4	1.71	0.53
C4-	2.51	0.77
C5	2.95	0.91
C6	2.35	0.72
C7	1.51	0.47
C8	0.04	0.01
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	49.5		15.2
(SCF/TON)		884.9	
C4 & HEAVIER(LB/TON)	336.0		103.5
(GAL/TON)		46.5	
API GRAVITY		31.6	
TOTAL HYDROCARBONS	360.5		111.0
(INCL. H2 & CO, LB/TON)			

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER	RF6302
SAMPLE DESCRIPTION	COLONY MINE RUBBLE
FISCHER ASSAY NO.	1537
TERMINAL TEMP. DEG. F	932

COMPONENT MOLE PERCENT

H2	31.21
CO	3.41
CO2	16.76
H2S	.7.76
C1	20.21
C2	6.56
C2-	1.79
C3	3.26
C3-	2.53
I-C4	0.14
N-C4	1.18
C4-	1.79
C5	1.66
C6	1.11
C7	0.61
C8	0.01
C9	0.00
SUM	100.00

AVERAGE MOLE WT	24.33
LBS C IN GAS/TON SHALE	31.84
PERCENT CARBON	52.40

BTU VALUE OF GAS (CALC.)

BTU/SCF (GROSS)	900.10
BTU/SCF (NET)	820.52

READY

```
        TOSCO ASSAY NUMBER      1537
          SAMPLE NUMBER         RF6302
      SAMPLE DESCRIPTION        COLONY MINE RUBBLE


          TERMINAL TEMP =          932
                 SAMPLE =        99.40100
                RESIDUE =        79.28900
           TOTAL LIQUID =        16.93200
                  WATER =         0.79100
            OIL DENSITY =         0.87830



              1 GAS BOMBS
      BAROMETRIC PRESS. MM =        606.0
        BOMB PRESS IN HG =           2.4
        BOMB TEMP DEG F =           71.6
                             BOMB 1
     VOLUME LITERS           3.91
     O2                      1.99
     N2                      7.87
     H2                     21.99
     CO                      2.40
     CO2                    11.81
     H2S                     5.47
     C1                     14.24
     C2                      4.62
     C2-                     1.26
     C3                      2.30
     C3-                     1.78
     I-C4                    0.10
     N-C4                    0.83
     C4-                     1.26
     C5                      1.17
     C6                      0.78
     C7                      0.43
     C8                      0.01
     C9                      0.00
     SUM                    80.31
```

SAMPLE NUMBER   RF6286
SAMPLE DESCRIPTION   GAS EXPLOSIVITY STUDY
TERMINAL TEMP   932 DEG. F
FISCHER ASSAY NO.   PB1538

FISCHER ASSAY YIELDS

OIL (LB/TON)	232.0	
(GAL/TON)	31.4	
API GRAVITY	28.5	
GAS (LB/TON)	35.6	
(SCF/TON)	553.2	
WATER (LB/TON)	23.0	
(GAL/TON)	2.8	
SS (LB/TON)	1705.9	
TOTAL (LB/TON)	1996.5	
VARIANCE (PC)	-.2	

GAS	(LB/TON)	(LB/100 LB) (FA OIL)
H2	0.95	0.41
CO	1.41	0.61
CO2	10.56	4.55
H2S	3.16	1.36
C1	4.19	1.81
C2	3.46	1.49
C2-	0.85	0.37
C3	2.22	0.95
C3-	1.67	0.72
I-C4	0.08	0.03
N-C4	1.89	0.81
C4-	1.38	0.59
C5	1.73	0.74
C6	1.45	0.63
C7	0.54	0.23
C8	0.08	0.03
C9	0.00	0.00

ADJUSTED YIELDS

C3 & LIGHTER(LB/TON)	28.5		12.3
(SCF/TON)		513.0	
C4 & HEAVIER(LB/TON)	239.2		103.1
(GAL/TON)		32.8	
API GRAVITY		30.4	
TOTAL HYDROCARBONS	253.9		109.4
(INCL. H2 & CO, LB/TON)			

FISCHER ASSAY GAS ANALYSIS

SAMPLE NUMBER   RF6286
SAMPLE DESCRIPTION   GAS EXPLOSIVITY STUDY
FISCHER ASSAY NO.   PB1538
TERMINAL TEMP. DEG. F   932

COMPONENT MOLE PERCENT

Component	Mole Percent
H_2	32.45
CO	3.44
CO_2	16.44
H_2S	6.34
C1	17.96
C2	7.87
C2-	2.08
C3	3.44
C3-	2.72
I-C4	0.09
N-C4	2.23
C4-	1.69
C5	1.66
C6	1.17
C7	0.37
C8	0.05
C9	0.00
SUM	100.00

AVERAGE MOLE WT	24.39
LBS C IN GAS/TON SHALE	19.37
PERCENT CARBON	54.41

BTU VALUE OF GAS (CALC.)
BTU/SCF (GROSS)	931.04
BTU/SCF (NET)	849.19

READY

```
     TOSCO ASSAY NUMBER      PB1538
       SAMPLE NUMBER         RF6286
    SAMPLE DESCRIPTION       GAS EXPLOSIVITY STUDY

          TERMINAL TEMP =          932
                 SAMPLE =      99.91800
                RESIDUE =      85.22500
           TOTAL LIQUID =      12.74100
                  WATER =       1.15000
            OIL DENSITY =       0.88430


                 1 GAS BOMBS
    BAROMETRIC PRESS. MM =         608.0
        BOMB PRESS IN HG =           2.4
         BOMB TEMP DEG F =          77.0
                             BOMB 1
VOLUME LITERS                  2.43
O2                             1.95
N2                             6.39
H2                            13.86
CO                             1.47
CO2                            7.02
H2S                            2.71
C1                             7.67
C2                             3.36
C2-                            0.89
C3                             1.47
C3-                            1.16
I-C4                           0.04
N-C4                           0.95
C4-                            0.72
C5                             0.71
C6                             0.50
C7                             0.16
C8                             0.02
C9                             0.00
SUM                           51.05
```

APPENDIX B

THE OIL SHALE CORPORATION
18200 WEST HIGHWAY 72
GOLDEN, COLORADO 80401
303/279-7721
CABLE ADDRESS: "TOSCOPETRO"

September 30, 1974   IOIOU SANTA MONICA BOULEVARD
LOS ANGELES, CALIFORNIA 90067

Dr. Paul D. Kilburn
Colony Development Operation
1500 Security Life Building
Denver, Colorado 80202

Re: Materials for Carcinogenic Testing

Dear Paul:

This letter is to provide you with the background information available on the samples furnished to the Eppley Institute for Research in Cancer for biological and chemical testing. The samples to be utilized in the biological testing program are listed in the following table:

SAMPLES FOR BIOLOGICAL TESTING

Sample Number	Description
219-9-2	Processed shale
207-64-2	Raw shale
207-66-4	Shale oil coke
218-25-1	Lift pipe effluent

Detailed descriptions of the above samples are given in Appendix 1.

The samples to be analyzed chemically for known carcinogenic compounds include the above samples plus the samples listed in the following table:

SAMPLES FOR CHEMICAL ANALYSIS

Sample Number	Description
219-11-2	Scrubber emissions
219-1-1	Scrubber foam solids, composite
207-57-4	DRI processed shale
219-9-6	Whole shale oil
FF-379-4	Hydrotreated shale oil
————————	This sample is not yet chosen

Detailed descriptions of the above materials are given in Appendix 2.

Additional information is presently being obtained on many of the above samples. This information will be forwarded as soon as is practical.

Should you have any questions concerning the data, please let me know. If you find, during the coarse of the experiment, that additional analyses are required, or that specific samples need attention, I will attempt to furnish the information.

Very truly yours,
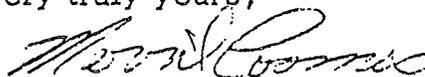
R. MERRIL COOMES
Organic Research Group Leader
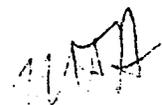
Approved (MTA)

RMC/dt
Encs

cc: Dr. Philippe Shubik
    Dr. Lawrence Wallcave

bcc: Dr. J. A. Whitcombe
     Dr. B. L. Schulman
     Mr. F. C. Haas
     Mr. L. Goodfellow
     Mr. C. M. Smits
     Mr. W. D. Shay, Esq.

Appendix 1

Sample 219-9-2, Processed Shale

The processed shale sample was obtained from the interior of the processed shale disposal pile at Parachute Creek on June 18, 1974. A sample from the interior was used in order to eliminate the effects of leaching and surface contamination. Twenty-two 55-gallon drums were obtained under the supervision of R. E. Smith, ARCO.

Representative samples from each drum were examined for total extractable organic material using benzene and a Soxhlet extractor. Sample 219-9-2 is a composite of the six drums which, when extracted, gave amounts of extracts closest to the average value of all twenty-two drums. The weight percent extractable organic material was 0.2484. The elemental analysis of the organic extractable material is being performed at the present time.

The particle size distribution was determined dry with an Allen-Bradley sonic sifter apparatus and wet, with acetone as the solvent. The results of these analyses are given in Table 1.

Table 1

PARTICLE SIZE DISTRIBUTION

Particle Size	Dry		Wet	
	Wt%	Σ Wt%	Wt%	Σ Wt%
+ 60	39.3	39.3	37.8	37.8
− 60 + 80	1.5	40.8	0.5	38.3
− 80 + 100	3.9	44.7	2.9	41.2
−100 + 200	4.4	49.1	10.4	51.6
−200 + 325	14.6	63.7	7.9	59.5
−325 (44μ)	36.4	100.1	40.6	100.1

The material with a particle size less than 325 mesh (−44μ) was analyzed for particle size distribution in the respirable range by the Coors Laboratories. This data is given in Table 2 and is shown graphically in Figure 1.

The elemental analysis of sample 219-9-2 for heavy metals is being performed by the Instrumental Analysis Division of Commercial Testing and Engineering Company, Golden, Colo.

Table 2

PARTICLE SIZE DISTRIBUTION OF PROCESSED SHALE
(Minus 325 mesh)

Particle Size (μ)	Percent by Weight Greater than Size	
	Wt%	Σ Wt%
40	---	---
30	.5	0.5
20	6.6	7.1
15	11.6	18.7
10	18.3	37.0
7	11.8	48.8
5	8.0	56.8
3	21.1	77.9
1	15.8	93.7
0.5	1.3	95.0
0.1	5.0	100.0

Figure 1

MSA SEDIMENTATION PARTICLE SIZE ANALYSIS

Sample No. 224-11-2 Material Spent Shale

Run with Whitby Size Analyzer
Method ASTM Recommended

Sedimentation Liquid: 0.25% Neofat – Xylene
Feeding Liquid: Neofat – Xylene – Acetone
Dispersing Agent: Neofat

PERCENT BY WEIGHT GREATER THAN SIZE

EQUIVALENT SPHERICAL PARTICLE DIAMETER, MICRONS
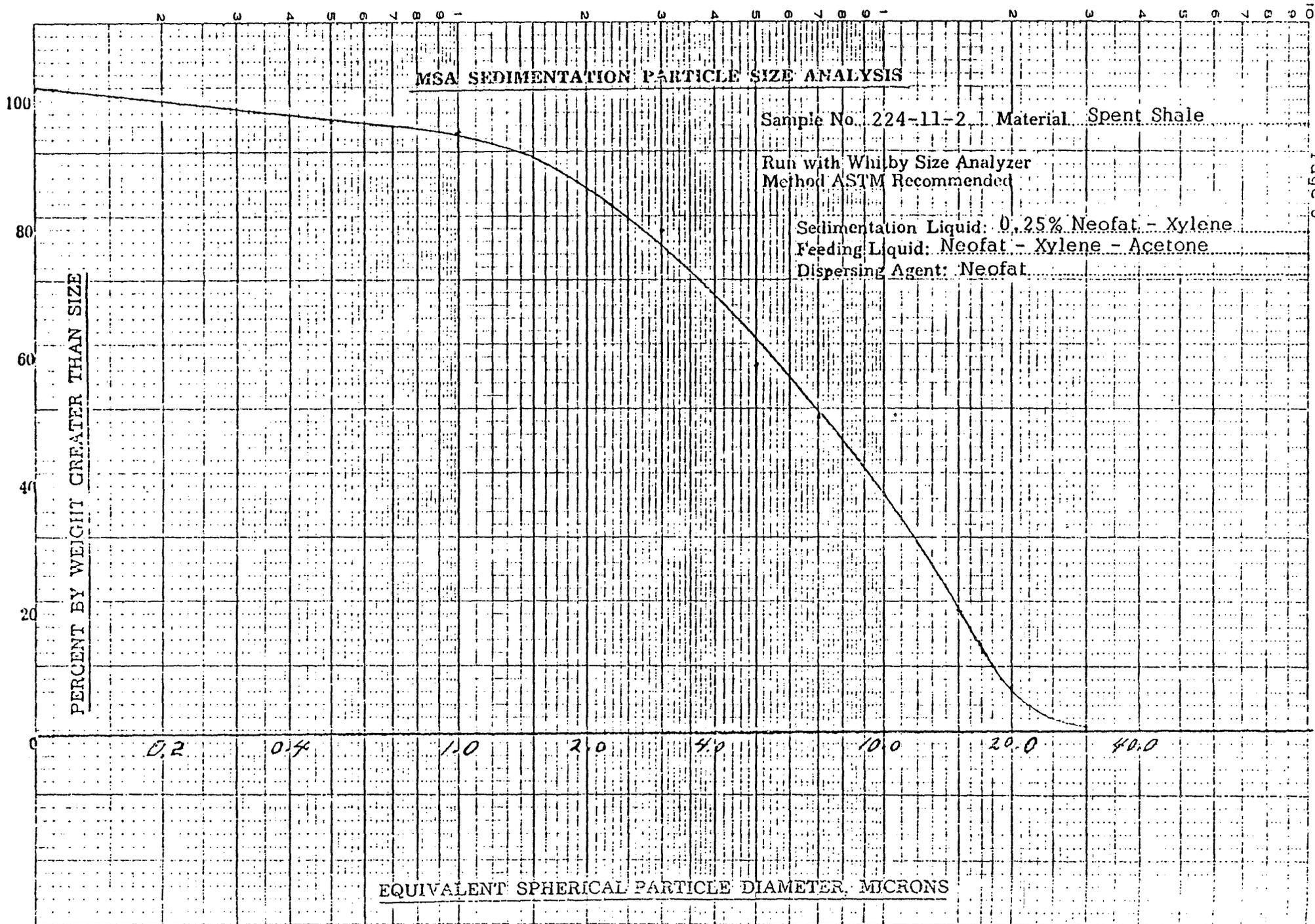
The following trace metal analysis was performed by spark ionization mass spectroscopy on a different composite processed shale sample produced at the Parachute Creek semi-works retort. These results were reported in Laboratory Data Letter 72-69, "Spent Shale Analyses", August 17, 1972, by F. C. Haas.

TRACE ANALYSIS OF SPENT SHALE

Element	Concentration (ppm)	Element	Concentration (ppm)
Aluminium	Major	Magnesium	Major
Antimony	0.39	Manganese	34
Arsenic	7.2	Molybdenum	4.9
Barium	32	Neodymium	1.2
Beryllium	35	Nickel	11
Bismuth	0.36	Niobium	3.4
Boron	140	Phosphorus	670
Bromine	0.01	Potassium	4600
Cadmium	0.14	Praseodymium	0.25
Calcium	Major	Rubidium	29
Cerium	1.6	Samarium	0.44
Cesium	1.2	Scandium	2.4
Chloride	72	Selenium	0.08
Chromium	49	Silicon	Major
Cobalt	39	Silver	< 0.01
Copper	15	Sodium	Major
Europium	0.12	Strontium	69
Fluorine	1700	Sulphur	1500
Gadolinium	0.40	Terbium	0.07
Gallium	2.2	Thorium	0.77
Germanium	0.40	Tin	0.11
Indium	Standard	Titanium	570
Iodine	< 0.01	Tungsten	0.42
Iron	3600	Uranium	0.99
Lanthanum	1.4	Vanadium	29
Lead	10	Yttrium	1.2
Lithium	850	Zinc	13
		Zirconium	9.3

Sample 207-64-2, Raw Oil Shale

The raw shale, 207-64-2, was obtained as dust material from the commercial crusher at Parachute Creek. This type of raw shale, a fine dust, would be potentially more hazardous to humans than the other raw shale material available from a commercial operation. Sample 207-64-2 was supplied to the TOSCO Laboratories in May 1974 by Bob Crookston. There are ten pounds of material available for biological and chemical testing. The weight percent extractable organic material is 2.014%.

Elemental analysis of the organic extract was determined and found to be:

Element	Wt%
Carbon	83.42
Hydrogen	11.57
Nitrogen	0.78
Sulfur	1.25
Oxygen	2.76
Total	99.78

The dry particle size distribution of this raw oil shale was determined with an Allen-Bradley sonic sifter apparatus. The wet screen analysis utilized acetone as the solvent. The results of these analyses are shown in Table 3.

Table 3

PARTICLE SIZE DISTRIBUTION OF RAW OIL SHALE

Particle Size	Dry Screen Wt%	Dry Screen Σ Wt%	Wet Screen Wt%	Wet Screen Σ Wt%
+ 60	1.76	1.76	---	---
- 60 + 80	1.56	3.32	---	---
- 80 + 100	1.37	4.69	0.2	0.2
-100 + 200	16.99	21.68	18.7	18.9
-200 + 325	20.12	41.80	24.6	43.5
-325 (44μ)	58.20	100.00	56.5	100.0
	100.0%		100.0%	

The material with a particle size of less than 325 mesh
(-44μ) was analyzed for particle size distribution by Coors
Laboratories. The data is given in Table 4 and is shown graph-
ically in Figure 2

Table 4

PARTICLE SIZE DISTRIBUTION OF RAW OIL SHALE
(Minus 325 mesh)

Particle Size (μ)	Percent by Weight Greater than Size	
	Wt%	Σ Wt%
40	.2	0.2
30	13.8	14.0
20	30.8	44.8
15	20.6	65.4
10	14.0	79.4
7	10.3	89.7
5	5.6	95.3
3	3.7	99.0
1	1.0	100.0

An elemental analysis[1] of typical raw oil shale from
the Green River formation is given in Table 5.

The elemental analysis for the whole sample 219-9-2
is presently being determined for carbon, hydrogen, nitrogen,
sulfur and oxygen.

The free silica content of raw oil shale is in the range
of 6.9 to 8.6 volume percent,[2][3] The actual silica content
of sample No. 207-64-2 is presently being determined.

---

[1]E. W. Cook, "Elemental Abundances in Green River
Oil Shale", Chemical Geology, 11, 321 (1973).

[2]F. C. Haas, "Silica Analysis on Dow Shale", Labora-
tory Data Letter 71-21, May 7, 1971.

[3]M. M. Gutierrez, "Silica Analysis", Laboratory Data
Letter 71-66, December 14, 1971.

Table 5

ELEMENTAL CONCENTRATION OF GREEN RIVER OIL SHALE

Element	Concentration (ppm)	Element	Concentration (ppm)	Element	Concentration (ppm)
Li	680	Zr	7.4	Gd	0.3
Be	28	Nb	2.7	Tb	0.06
B	112	Mo	3.9	Dy	0.3
F	1360	Ru	< 0.1	Ho	0.06
Cl	58	Rh	< 0.1	Er	0.22
Sc	1.9	Pd	< 0.1	Yb	0.20
Ti	456	Ag	< 0.01	Lu	< 0.1
V	23	Cd	0.11	Hf	< 0.1
Cr	39	In	Standard	Ta	0.03
Mn	27	Sn	0.??	W	0.03
Co	31	Sb	0.?1	Re	< 0.1
Ni	9	Te	< 0.?	Ps	< 0.1
Cu	12	I	< 0.01	Ir	< 0.1
Zn	10	Cs	1.0	Pt	< 0.1
Ga	18	Ba	26	Au	< 0.1
Ge	0.3	La	1.1	Hg	< 0.1
As	5.8	Ce	1.3	Tl	0.11
Se	0.06	Pr	0.2	Pb	8
Br	0.01	Nd	1.0	Bi	0.29
Rb	23	Sm	0.35	Th	0.62
Sr	55	Eu	0.1	U	0.79
Y	1.0				

NO. 340-L310 DIETZGEN GRAPH PAPER   EUGENE DIETZGEN CO.
SEMI-LOGARITHMIC   MADE IN U. S. A.
3 CYCLES X 10 DIVISIONS PER INCH

Figure 2

MSA SEDIMENTATION PARTICLE SIZE ANALYSIS

Sample No. 224-11-4   Material   Crusher Dust

Run with Whitby Size Analyzer
Method ASTM Recommended

Sedimentation Liquid: 0.25% Neofat – Xylene
Feeding Liquid: 0.25% Neofat – Xylene – Acetone
Dispersing Agent: Neofat

PERCENT BY WEIGHT GREATER THAN SIZE

EQUIVALENT SPHERICAL PARTICLE DIAMETER, MICRONS

Page 8

Sample 207-66-4, Shale Oil Coke

The coke sample 207-66-4 is a composite of the product from three coking tests performed by Union Oil Company for Colony Development Operation. The coke was produced by coking shale oil bottoms. The individual samples of coke have been extensively analyzed. The results have been reported in Laboratory Data Letter 73-83, "Assays of Union Coke Distillates and Coke Samples Produced from Shale Oil Bottoms", October 11, 1973, by M. T. Atwood.

Weight percent extractable organic material was found to be dependent on the length of time the extraction continued. Generally, a Soxhlet extraction is essentially complete after 48 hours. Table 6 gives the amount of material extracted after given time intervals.

Table 6

EXTRACTABLE MATERIAL FROM SHALE OIL COKE

Time (hrs)	Wt% Extracted	Σ Wt% Extracted
32	0.278	0.278
64	0.107	0.385
98	0.053	0.438
130	0.044	0.482
164	0.034	0.516
194	0.029	0.545

The elemental analysis of the total combined organic extract is presently being determined.

The particle size distribution of 207-66-4 was not determined. The composite sample was made from material which was ground to less than one half square inch.

The elemental analysis of 207-66-4 (whole sample) was:

Carbon	86.66
Hydrogen	4.06
Nitrogen	4.59
Sulfur	0.45
Ash	0.67
Oxygen (by difference)	3.57
Total	100.00

The analysis of heavy metals in 207-66-4, by atomic absorption, has been reported in Laboratory Data Letter 73-83, "Assays of Union Oil Coke Distillates and Coke Samples Pro-Duced from Shale Oil Bottoms", October 11, 1973, by M. T. Atwood. The values given in Table 7 are averages of the analyses for the individual coke samples.

Table 7

ELEMENTAL ANALYSES OF SHALE OIL COKE

Element	Concentration (ppm)	Element	Concentration (ppm)
Aluminum	92	Molybdenum	1.0
Antimony	< 3	Nickel	38
Calcium	520	Potassium	14
Chromium	1.7	Silicon	67
Cobalt	9.2	Silver	< 0.1
Copper	4.0	Sodium	1.1
Iron	493	Tin	< 4
Lead	< 5	Titanium	5.7
Magnesium	144	Vanadium	10.1
Manganese	3.5	Zinc	4.5

Arsenic ranges from 60 to 90 ppm, determined by Union Oil.

Sample 218-25-1, Lift Pipe Effluent

    The lift pipe and scrubber systems of the Rocky Flats
pilot plant were operated at commercial design specifications
during August 8, 9 and 12, 1974. During this operation, envi-
ronmental engineers from Ryckman/Edgerly/Tomlinson & Assoc-
iates, Inc. (RETA) collected effluent from the scrubber stack
by two methods: EPA approved Method No. 5, and with two
Hi Vol samplers at the stack exit. Paper filters were used to col-
lect the Hi Vol samples. This sample should be representative of
particulate material emitted to the atmosphere during commercial
oil shale operations. The combined solids from the Hi Vol sam-
plers form sample 218-25-1. A total of 200 grams of material
was collected. The individual samples were collected for periods
of one hour each.

    The weight percent extractable organic material was 9.45.
The elemental analysis of the organic extractable material is
presently being determined. The particle size distribution of
218-25-1 was determined by wet screen analysis and the results
are shown in Table 8.

<div align="center">Table 8</div>

<div align="center">PARTICLE SIZE DISTRIBUTION OF LIFT PIPE EEFLUENT</div>

Particle Size	Wt%	Σ Wt%
+ 60	2.02	2.02
- 60 + 80	2.60	4.62
- 80 + 100	1.45	6.07
-100 + 200	4.05	10.12
-200 + 325	2.31	12.43
-325 (44μ)	86.57	100.00

    The material with a diameter less than 44μ was analyzed
by the Coors Laboratories. The data is given in Table 9 and also
shown graphically in Figure 3.

Table 9

PARTICLE SIZE DISTRIBUTION OF LIFT PIPE EFFLUENT
(Minus 325 mesh)

Particle Size (μ)	Percent by Weight Greater than Size	
	Wt%	Σ Wt%
30	0.1	0.1
20	0.3	0.4
15	0.6	1.0
10	0.5	1.5
7	1.0	2.5
5	2.4	4.9
3	32.2	37.1
1	59.1	96.2
0.5	2.8	99.0
0.1	1.0	100.0

The elemental analysis for trace metals is being performed
by the Instrumental Analysis Division of Commercial Testing &
Engineering Company, Golden, Colorado. The trace metals will
be determined by spark source ionization mass spectroscopy,
using indium as an internal standard. The elemental analysis
of the whole sample 218-25-1 is being determined for carbon,
hydrogen, nitrogen, sulfur and oxygen.

Figure 3

MSA SEDIMENTATION PARTICLE SIZE ANALYSIS

Sample No. 224-11-3   Material   Hi Vol

Run with Whitby Size Analyzer
Method ASTM Recommended

Sedimentation Liquid: 0.25% Neofat – Xylene
Feeding Liquid: 0.25% Neofat – Xylene – Acetone
Dispersing Agent: Neofat

PERCENT BY WEIGHT GREATER THAN SIZE

EQUIVALENT SPHERICAL PARTICLE DIAMETER, MICRONS
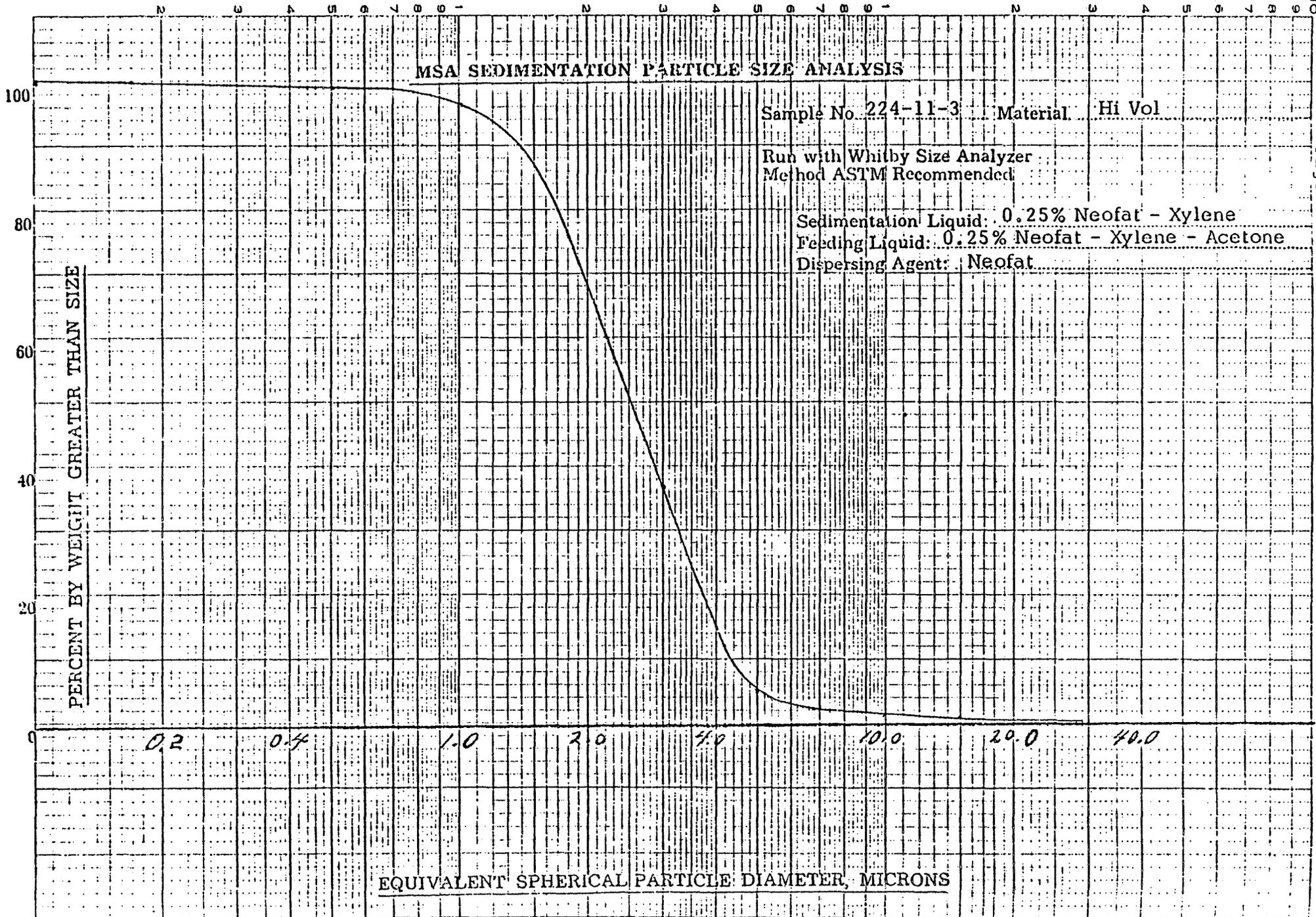
Appendix 2

Sample 219-11-2, Scrubber Emissions

This material is the organic extractables from the particulate material collected by environmental engineers from Ryckman/Edgerly/Tomlinson & Associates, Inc. (RETA). The sample was collected at the scrubber exit of the pilot plant at Rocky Flats. During the period of collection, August 8, 9 and 12, the lift pipe and scrubber systems were operated at proposed commercial conditions. These operating conditions insure that the sample is as representative as experimentally possible of the effluent from commercial oil shale operations.

The sampling system and method were in accordance with the EPA approved stack sampling Method No. 5.[4] The total weight of solid material collected was 8.1588 grams, leaving about 7.5 grams available for chemical analysis. The organic extractables from this material should weigh approximately 0.75 grams. The exact weight percent extractable organic material will be reported with delivery of the extract.

An elemental analysis for heavy metals is presently being performed by the Instrumental Analysis Division of Commercial Testing & Engineering Company, Golden, Colorado. The elemental analysis of the whole sample 219-1102, for carbon, hydrogen, nitrogen, and ash, will soon be determined.

This sample should be chemically similar to extracts of raw oil shale and scrubber foam solids. The similarity may prove useful in the chemical analysis of this small sample.

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[4] Federal Register, Vol. 36, No. 247, December 23, 1971, p. 24888.

Sample 219-1-1, Scrubber Foam Solids

This sample, 219-1-1, is a composite of the solids
from scrubber foam formed during the March 1974 operation
of the Rocky Flats pilot plant. This solid material, trapped by
the scrubber, should be similar to the material released into
the atmosphere during commercial oil shale operations.

Scrubber foam contains 13.5% solids.[5] These solids
were removed from the water by vacuum filtration. The solids
were then air dried. The weight percent organic extractable
material, based on the weight of the dried solid, was 11.21.

Elemental analysis shows that the organic extractables
have the following compositions:

Element	Wt%
Carbon	76.57
Hydrogen	10.20
Nitrogen	0.71
Sulfur	0.80
Oxygen	11.65
Total	99.93

The dry particle size distribution of 219-1-1 was deter-
mined using an Allen-Bradley sonic sifter apparatus and the
results are shown in Table 10.

Table 10

PARTICLE SIZE DISTRIBUTION OF SCRUBBER FOAM SOLIDS

Particle Size	Wt%	Σ Wt%
+ 60	1.59	1.59
- 60 + 80	1.19	2.78
- 80 + 100	0.99	3.77
-100 + 200	1.39	5.16
-200 + 325	3.57	8.73
-325 (44μ)	91.27	100.00

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[5]R. M. Coomes, "Scrubber Foam Solids and Effluent
Analyses, Elemental and Fischer Assay", Laboratory Data Letter
74-45, June 4, 1974.

Sample 207-57-4, Denver Research Institute Processed Shale

This sample of processed shale was supplied to TOSCO by Dr. Josef Schmidt-Collerus of the Denver Research Institute (DRI). This sample is representative of the material furnished to DRI by Colony Development Operation. The sample, 207-57-4, was split from the bulk sample under the direct supervision of Dr. Schmidt-Collerus.

This processed shale has been examined extensively for the organic composition of the organic extractable material. The chemistry of this sample is reported in detail in the First Annual Report, "The Disposal and Environmental Effects of Carbonaceous Solid Wastes from Commercial Oil Shale Operations", by Dr. Josef Schmidt-Collerus of DRI. A copy of this report has been furnished to Dr. Wallcave at the Eppley Institute for Research in Cancer.

Weight percent extractable organic material (TOSCO) was 0.185, in a 24-hour interval. The dry particle size distribution was determined with an Allen-Bradley sonic sifter for the DRI processed shale. The wet screen particle size distribution was determined utilizing acetone as the solvent. These analyses are reported in Table 11.

Table 11

PARTICLE SIZE DISTRIBUTION OF DRI SPENT SHALE

Particle Size	Wet		Dry	
	Wt%	Σ Wt%	Wt%	Σ Wt%
+ 60	35.7	35.7	49.6	49.6
- 60 + 80	8.6	44.3	9.1	58.7
- 80 + 100	5.9	50.2	6.9	65.6
-100 + 200	13.7	63.9	7.5	73.1
-200 + 325	8.7	72.6	12.1	85.2
-325 (44μ)	27.4	100.0	14.7	99.9

Sample 219-9-6, Whole Shale Oil

Sample 219-9-6 originated from the March 1974 pilot plant operation at Rocky Flats. This sample is a composite of several fractions of the oil formed during this operation. The API gravity at $60^{\circ}F$ is 19.8, and specific gravity at $60^{\circ}F$ is 0.9352. These values are typical for raw shale oils produced by the TOSCO II process. The sample 219-9-6 was supplied unfiltered.

The elemental analysis of sample 219-9-6 is presently being determined. Elemental analyses of typical raw shale oils give the following average composition:

Element	Wt%
Carbon	84.7
Hydrogen	11.3
Nitrogen	1.8
Sulfur	0.8
Oxygen	1.4
Total	100.0

Literature values[6] for benzo[a]pyrene (BaP) content of American shale oils are in the range of 30-40 ppm. Alkyl substituted BaP's were not identified in the literature reports.

[6]Cahnmann, H. J., Anal. Chem., 27, 1235 (1955).

Sample FF-379-4, Hydrotreated Shale Oil

This sample of shale oil was hydrotreated by Union Oil Company, using a commercial type catalyst. This treatment reduces the sulfur and nitrogen content, making the product valuable commercially. Sample FF-379-4 was hydrotreated until it contained less than 0.05% nitrogen.

Analysis for BaP in the hydrotreated oil, FF-379-4, at the TOSCO Laboratories indicated that the hydrotreating process does not alter the BaP content. ·

The elemental analysis of FF-379-4 was found to be:

Element	Wt%
Carbon	86.02
Hydrogen	13.35
Nitrogen	0.035
Sulfur	5 ppm
Oxygen	0.0047

The elemental analysis of FF-379-4 has been reported in Laboratory Data Letter 73-76, "Assays of Union Oil Shale Oil Samples, Interim Report", by M. T. Atwood. This analysis is shown in Table 12.

Table 12

TRACE METALS IN OIL SAMPLE FF-379-4

Element	ppm	Element	ppm
Aluminum	< 0.1	Molybdenum	< 0.08
Antimony	< 0.2	Nickel	< 0.06
Arsenic	< 0.003	Potassium	0.04
Calcium	0.02	Silicon	< 0.2
Chromium	< 0.04	Silver	< 0.01
Cobalt	< 0.08	Sodium	0.005
Copper	0.01	Tin	< 0.3
Iron	< 0.02	Titanium	< 0.1
Lead	< 0.6	Vanadium	< 0.1
Magnesium	0.01	Zinc	0.02
Manganese	< 0.03		

THE OIL SHALE CORPORATION

INTER OFFICE MEMORANDUM

LABORATORY DATA LETTER 69-

FROM: L. Goodfellow

TO: W. L. McDonnell

DATE: June 16, 1969

FILE NO.: 5100-3

SUBJECT: Fischer Analyses of Lift Pipe Tests

SUMMARY

The Fischer Assays of the raw shale samples from the last lift pipe tests are attached. Material balances on each test are shown. The replicate analyses on the samples are presented to show the variations in the assay.

DISCUSSION

In general, the assay balances are good. Minor difficulties were encountered in some samples with insufficient shale in particular size fractions. Two samples were scratched because of insufficient sample.

The assays are misleading to some extent due to the variations in particle size and the results should probably be reduced to original screen analyses for interpretation.

The duplicate and replicate assays are in general, good. In some cases, especially in the -40 +80 fraction, there was insufficient sample to grind in the Raymond Mill and hence a good sample split could not be made.

LG/kh
attachs.

_____
Approved (MTA)

cc: J. A. Whitcombe
L. H. Yardumian
R. H. Beaver
J. H. Barney

Sample Number Date Time Description % Moisture	01-253 May 5, 1969 1515-1815 Raw Shale 1.0				01-254 May 5, 1969 1515-1815 Retort Feed			
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	99.9	30.8		2.4	100.0	31.5		2.1
+0.5	0				0.3			
-0.5 +0.371	4.7				11.3			
-0.371 +4	20.9 77.4	33.0	25.5	2.4	30.2 91.2	32.7	29.8	1.9
-4 +10	36.5				40.8			
-10 +20	15.3				8.6			
-20 +40	9.0	29.1	2.6	2.6	3.3	26.9	0.9	2.0
-40 +80	6.7	26.7	1.8	3.0	3.0	23.6	0.7	2.3
-80	6.8	21.3	1.4	4.1	2.5	17.2	0.4	3.1
Yield By Head Assay			30.8				31.5	
Yield By Fraction Assay			31.3				31.8	
% Variance			+1.6				+1.0	

Sample Number	01-255				01-256			
Date	May 5, 1969				May 5, 1969			
Time								
Description	Raw Shale				Retort Feed			
% Moisture	1.03							
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.1	30.6		2.5	100.1	30.3		2.3
-0.5 +0.371	4.4 ⎫				7.6 ⎫			
-0.371 +4	25.3 ⎬ 79.3	32.6	25.8	2.4	32.8 ⎬ 83.3	32.1	26.7	2.2
-4 +10	35.5 ⎪				31.8 ⎪			
-10 +20	14.1 ⎭				11.1 ⎭			
-20 +40	8.1	27.8	2.2	2.9	6.1	25.6	1.6	2.2
-40 +80	5.8	25.0	1.4	3.2	5.0	22.7	1.1	2.6
-80	6.9	19.6	1.4	4.3	5.7	17.0	1.0	3.3
Yield By Head Assay			30.6				30.3	
Yield By Fraction Assay			30.8				30.4	
% Variance			+0.7				+0.3	

	01-258				01-257			
Sample Number	01-258				01-257			
Date	May 4, 1969				May 4, 1969			
Time	1200-1500				1200-1500			
Description	Raw Shale				Retort Feed			
% Moisture	0.89							
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.1	29.8		2.6	100.0	29.6		2.4
+0.5					0.5			
-0.5 +0.371	5.5				6.5			
-0.371 +4	17.8				31.4	31.1	26.1	2.3
	(71.2)				(83.9)			
-4 +10	30.8	32.2	22.9	2.4	33.6			
-10 +20	17.1				11.9			
-20 +40	10.7	27.8	3.0	2.8	6.6	25.7	1.7	2.3
-40 +80	8.3	25.6	2.1	3.2	4.8	21.1	1.0	1.8
-80	9.9	19.8	2.0	3.9	4.6	14.9	0.7	3.0
Yield By Head Assay			29.8				29.6	
Yield By Fraction Assay			30.0				29.5	
% Variance			+0.7				-0.3	

Sample Number Date Time Description % Moisture	01-259 May 7, 1969 1830-2130 Raw Shale 0.78				01-260 May 7, 1969 1830-2130 Retort Feed 			
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.0	33.0		2.6	100.0	30.6		2.4
+0.371	9.3				7.6			
-0.371　　+4	32.5				31.2			
-4　　+10	34.1 } 86.2	33.5	28.9	2.4	32.8 } 82.9	31.5	26.1	2.1
-10　　+20	10.3				11.3			
-20　　+40	5.6	30.2	1.7	2.6	6.6	27.8	1.8	2.2
-40　　+80	4.1	27.7	1.1	3.4	5.2	25.1	1.3	2.3
-80	4.1	21.5	0.9	4.9	5.3	18.4	1.0	2.8
Yield By Head Assay			33.0				30.6	
Yield By Fraction Assay			32.6				30.2	
% Variance			-1.2				-1.3	

Sample Number Date Time Description % Moisture	01-261 May 6, 1969 Raw Shale 1.75				01-262 May 6, 1969 Retort Feed			
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.0	34.4		2.2	100.0	31.2		2.3
+0.371	18.0				13.1			
-0.371 +4	44.3				42.4			
-4 +10	22.3 91.2	35.1	32.0	2.3	24.0 87.2	32.9	28.7	1.9
-10 +20	6.6				7.7			
-20 +40	4.0	31.3	1.2	2.6	4.8	26.7	1.3	2.1
-40 +80	2.8	29.6	0.8	3.2	3.8	24.5	0.9	2.1
-80	2.1	25.3	0.5	3.9	4.1	17.8	0.7	2.6
Yield By Head Assay			34.4				31.2	
Yield By Fraction Assay			34.5				31.6	
% Variance			+0.3				+1.3	

Sample Number	01-263R				01-264R			
Date	May 7, 1969				May 7, 1969			
Time	2130-0030				2130-0030			
Description	Raw Shale				Retort Feed			
% Moisture	2.19							
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.0	32.8		2.6	100.0	30.8		2.1
-0.5 +0.371	6.9				10.5			
-0.371 +4	29.4				36.4			
-4 +10	34.8 } 84.3	32.9	27.7	2.5	30.4 } 87.5	32.2	28.2	1.9
-10 +20	13.2				10.2			
-20 +40	7.8	30.8	2.4	2.9	5.4	26.9	1.4	1.9
-40 +80	5.2	29.2	1.5	3.3	3.9	22.6	0.9	2.1
-80	2.8	24.9	0.7	4.3	3.2	16.0	0.5	2.3
Yield By Head Assay			32.8				30.8	
Yield By Fraction Assay			32.3				31.0	
% Variance			-1.5				+0.6	

Sample Number	01-267R				01-268			
Date	May 8, 1969				May 8, 1969			
Time	1630-1930				1630-1930			
Description	Raw Shale				Retort Feed			
% Moisture	4.08							
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.0	32.8		2.4	100.0	31.4		2.2
+0.371	10.4				11.5			
-0.371 +4	33.8				31.3			
-4 +10	31.8 87.3	33.4	29.2	2.4	30.5 85.7	32.7	28.0	2.0
-10 +20	11.3				12.4			
-20 +40	5.3	30.2	1.6	2.9	6.1	27.6	1.7	2.3
-40 +80	3.2	29.2	0.9	3.2	4.3	26.0	1.1	2.5
-80	4.3	23.6	1.0	4.5	4.0	21.1	0.8	2.9
Yield By Head Assay			32.8				31.4	
Yield By Fraction Assay			32.7				31.6	
% Variance			-0.3				+0.6	

Sample Number Date Time Description % Moisture	01-269 May 11, 1969 0600-0900 Raw Shale 2.53				01-270 May 11, 1969 0600-0900 Retort Feed			
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.0	32.8		2.5	100.0	29.4		1.7
−0.371	10.6				12.4			
−0.371 +4	40.9				37.1			
−4 +10	28.9 88.6	33.5	29.7	2.4	28.5 87.3	31.3	27.3	1.7
−10 +20	8.2				9.3			
−20 +40	4.4	30.5	1.3	3.0	5.3	26.0	1.4	1.9
−40 +80	3.2	29.2	0.9	3.4	3.5	23.4	0.8	2.0
−80	3.9	24.5	1.0	4.1	3.9	16.0	0.6	2.5
Yield By Head Assay			32.8				29.4	
Yield By Fraction Assay			32.9				30.1	
% Variance			+0.3				+2.0	

Sample Number	01-272R				01-271R			
Date	May 12, 1969				May 12, 1969			
Time	1630-1830				1630-1730			
Description	Raw Shale				Retort Feed			
% Moisture	3.66							
Screen Size (U. S. Standard)	Wt. % (%)	Oil (Gal/Ton)	Wt. % x Oil Yield	Water (Gal/Ton)	Wt. % (%)	Oil (Gal/Ton)	Wt.% x Oil Yield	Water (Gal/Ton)
Head	100.0	32.3		2.6	100.0	31.2		2.1
+0.371	10.8 ⎫				12.8 ⎫			
-0.371 +4	37.5 ⎬ 88.2	33.0	29.1	2.5	43.8 ⎬			
-4 +10	30.7 ⎥				29.4 ⎬ 93.1	32.0	29.8	2.0
-10 +20	9.2 ⎭				7.1 ⎭			
-20 +40	4.3	30.5	1.3	2.9	3.3	25.5	0.8	2.2
-40 +80	2.8	29.8	0.8	3.4	2.0	24.6	0.5	2.2
-80	4.6	23.4	1.1	4.8	1.6	18.0	0.3	2.8
Yield By Head Assay			32.3				31.2	
Yield By Fraction Assay			32.3				31.4	
% Variance			0				+0.6	

LIFT PIPE TESTS
DUPLICATE AND REPLICATE ANALYSES
FISCHER ASSAY OIL YIELD (GPT)

Sample No.	Head Assay	Screen Size			
		+20	+40	+80	-80
01-253	31.4	33.2	28.8	25.8	23.4
	30.8	32.8	29.3	26.7	21.2
	30.8			26.6	21.3
01-254	31.4	32.8	27.0	23.5	17.2
	31.6	32.5	26.8	23.7	17.2
01-255	30.6	32.5	28.0	24.6	19.8
	30.6	32.7	27.6	25.3	19.3
				26.0	
01-256	30.2	32.2	25.2	22.5	17.0
	30.3	31.9	25.9	22.9	16.9
			25.7		
01-257	29.5	31.0	25.5	21.9	15.1
	29.5	31.2	25.8	21.3	14.7
01-258	30.0	32.2	27.6	25.6	19.8
	29.5	32.1	27.9	25.6	19.8
01-259	31.6	33.6	30.1	27.1	21.6
	31.1	33.4	30.2	27.8	21.4
	33.0	32.1		27.5	
01-260	30.6	31.5	27.8	25.2	18.4
	30.5	31.4	27.8	24.9	18.4
01-261	34.5	36.0	31.2	29.4	25.5
	34.3	35.2	31.4	30.2	25.0
		35.0		29.7	
01-262	31.2	33.0	29.6	24.3	17.8
	31.2	32.8	29.4	24.7	17.7
	30.5				
01-263	32.6	32.7	29.9	28.1	25.1
	33.0	33.1	30.7	29.2	24.7
	30.4		30.8	30.4	

Sample No.	Head Assay	+20	+40	+80	-80
01-264	30.8	32.2	26.9	22.5	16.2
	29.4	32.1	26.9	23.4	15.7
	30.7			22.6	
01-265	Sample Scratched				
01-266	Sample Scratched				
01-267	32.8	33.4	30.4	28.9	23.6
	32.8	30.8	30.0	29.6	23.5
		33.5			
01-268	31.4	32.8	27.6	26.0	21.2
	31.3	32.7	27.6	25.9	21.0
01-269	33.0	33.5	30.5	28.6	24.5
	32.0	33.5	30.4	29.3	24.5
	32.5		29.9	29.1	
01-270	29.5	31.2	26.0	23.3	15.8
	29.3	31.4	25.9	23.4	16.2
				24.2	
01-271	31.3	32.1	25.2	24.6	18.2
	31.0	31.8	25.8	24.5	17.7
01-272	32.3	33.0	30.7	29.7	23.6
	32.3	33.1	30.3	29.7	23.3

APPENDIX C

HYDROCARBON EXPLOSION THEORY

This paper deals with the basic physical characteristics of hydro-
carbon-air explosions in closed chambers. Gaseous explosions take place
by two essentially different mechanisms: deflagration and detonation.
In deflagration, combustion of the fuel-air mixture is accomplished via
an ordinary flame front, which propagates at relatively low velocity into
the unburned gases. In detonation, the combustion zone is attached to a
pressure discontinuity (a shock wave) which advances at supersonic velo-
city into the fuel-air mixture. The essential features of deflagration-
type explosions are described in Section 1, while detonation phenomena are
treated in Section 2. The conditions under which a deflagration process
can be transformed into a detonation are described in Section 3. Finally,
the question of energy required to initiate deflagration or detonations is
discussed in Section 4.

1.0 DEFLAGRATION PHENOMENA

The process of deflagration is nothing more than combustion of a
mixture of a fuel and oxidant by an ordinary flame front. If a cylin-
drical tube, which is open at both ends, is filled with such a mixture
and ignited at one end, a flame front will propagate at a low velocity
(of the order of a few centimeters per second to a meter per second,
typically) through the tube.

The structure of a deflagration wave is as follows: the combustion
zone itself is a region of high temperatures, resulting from the release
of the heat of combustion of the fuel. Some of this heat is conducted
ahead of the flame front, raising the temperature of the adjacent unburned

gases to the point that the combustion reaction is initiated. The speed

of flame propagation is thus governed by the rate of heat transfer into

the unburned gases and the ignition temperature of these gases. The gases

expand on passage of the flame front, due to the large temperature increase,

but they are vented out the ends of the tube. The pressure pulse associated

with combustion in this situation is thus very small (Jost, 1946; Lewis and

von Elbe, 1961).

When the same process is carried out in a closed vessel, the final

result is quite different. The flame front initially advances in the same

manner as described above. However, the burned gases are not free to expand

into the environment. Since the velocity of the flame front is initially

much lower than the speed of sound, the increase in temperature behind the

flame front will be transformed into an increase in pressure which is

nearly uniform throughout the entire volume of the confined enclosure.

Roughly, the pressure increase in the enclosure will be directly proportional

to the mass fraction of the gases which have been burned.

The flame front will not advance with constant velocity in a closed

vessel. The expansion of the burned gases will compress the unburned

gases, and the flame front will acquire a velocity component due to the

net motion of all of the gases in the enclosure. In addition, the pressure

increase will produce a near-adiabatic heating of the unburned gases, thus

bringing the gas temperature closer to its ignition temperature. This

also leads to an acceleration of the flame front. In some cases, these

processes can continue smoothly until all the gases in the enclosure have

been burned. However, there are at least two other possible outcomes:

- First, the adiabatic compression of the unburned
  gases may raise their temperature to the auto-
  ignition point, and ignition may occur at one or
  more points well in advance of the flame front.
  In this case, all the remaining unburned gases
  will burn in a very short time, producing a very
  rapid rise in pressure and temperature in the
  enclosure.

- The second possibility, which is more probable,
  is that the deflagration wave may accelerate (as
  described above) to the point that it turns into
  a detonation wave. Since this wave will be prop-
  agating into a gas whose pressure is much higher
  than the initial pressure in the enclosure, it can
  produce very high transient pressures (Brinkley
  and Lewis, 1958).

1.1 Deflagration Pressures

The qualitative features of the pressure-time history of deflagration-

type explosives have been discussed above. In general, deflagration of

hydrocarbon-air mixtures in confined enclosures results in final pres-

sures which are six to ten times greater than the initial pressure. For

a variety of hydrocarbons, the explosion pressure for a stoichiometric

fuel-air mixture at atmospheric pressure is in the range of 100 to 115

psig, which corresponds to an absolute pressure ratio of eight to nine

(Figure 1). The pressure falls off as the fuel-air ratio departs from

stoichiometric.

If the initial pressure of the mixture is greater than one atmosphere,

the final explosion pressure will be correspondingly greater; that is,

the ratio of explosion pressure to initial pressure (on an absolute

pressure basis) will be approximately constant for a given fuel-air

ratio. This results from the simple fact that the pressure rise is

directly proportional to the heat of combustion, and the heat of combus-

tion per unit volume is approximately proportional to the quantity of fuel and oxygen per unit volume.

1.2 Deflagration Temperatures

The detailed distribution of temperatures resulting from a deflagration explosion in a confined enclosure is quite complicated (Lewis and von Elbe, 1961) because different portions of the gas are subjected to different thermodynamic histories. The gas near the ignition source is burned at essentially the initial operating pressure, and later compressed when the remainder of the gas is burned. The last sample of gas, on the other hand, is compressed to nearly the final explosion pressure before it is burned. Lewis and von Elbe show that this results in a temperature gradient in the enclosure, the first gas to burn having the highest final temperature and the last gas to burn having the lowest final temperature. As a first approximation, the normal flame temperature (combustion taking place at ambient pressure) may be used to estimate the final explosion temperature.

Table 1 (Lewis and von Elbe) shows flame temperatures for a number of combustible mixtures, both for fuel-air and fuel-oxygen flames. For fuel-air mixtures, these temperatures are estimated in the range of 2,000 degrees Centigrade.

In any real situation, the exact value of gas temperature is somewhat uncertain. The burned gases may lose energy by radiation (especially if incandescent particles are present, as will be the case when fuel-rich or poorly mixed gases are burned) as well as by conduction to the walls. The important point is that the pressure in the enclosure is determined by the gas temperature. As long as the gas remains confined, the pressure will

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TABLE 1

Flame Temperatures

COMBUSTIBLE	DILUENT	PERCENT COMBUSTIBLE	FLAME TEMP. $^{\circ}C$
Hydrogen	Air	31.6	2045
			2047[1]
	O_2	67.0	2487
		73.0	2527
		78.0	2660
		82.0	2427
Hydrogen Atoms	---	---	?3760[2]
Carbon Monoxide	Air	20.0	1650[3]
		25.0	1930[3]
		32.0	2100[3]
		37.0	2000[3]
		45.0	1850[3]
		55.0	1560[3]
	O_2	20.0	1850[3]
		30.0	2400[3]
		40.0	2680[3]
		60.0	2905[3]
		70.0	2925[3]
		80.0	2805[3]
		90.0	1800[3]

See footnotes at end of table.

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TABLE 1
(Continued)

COMBUSTIBLE	DILUENT	PERCENT COMBUSTIBLE	FLAME TEMP. $^{\circ}C$
Methane	Air	10.0	1875
Ethane	Air	5.8	1895
Propane	Air	4.15	1925
Butane	Air	3.2	1895
Isobutane	Air	3.2	1900
Acetylene	Air	9.0	2325
	O_2	18.0	2927
		33.0	3007
		44.0	3137
		50.0	2927
Ethylene	Air	7.0	1975
Propylene	Air	4.5	1935
Butylene	Air	3.4	1930
Ammonia	Air	21.0	1700
60% NH_3 + 40% ($3H_2$ + N_2)	Air	26.0	1745
40% NH_3 + 60% ($3H_2$ + N_2)		27.5	1770
20% NH_3 + 80% ($3H_2$ + N_2)		32.5	1815
10% NH_3 + 90% ($3H_2$ + N_2)		35.0	1850

(1) Calculated.
(2) Estimated for hydrogen torch
(3) Calculated, ±10° to allow for different H_2O content.

decay only by cooling of the explosion products. Thus, heat transfer to the walls of the enclosure governs both the pressure-time and temperature-time histories.

1.3 Deflagration Characteristic Times and Propagation Velocities

Typical laminar flame speeds in hydrocarbon-air mixtures are of the order of a few centimeters to a few tens of centimeters per second. If such velocities persisted throughout the entire process of burning a hydrocarbon-air mixture in an enclosure with dimensions of the order of a kilometer, it is obvious that several thousand seconds would be required for the process to go to completion (i.e., the event would involve times of the order of an hour). However, as discussed above, the combustion in an enclosed volume is inherently a self-accelerating process. In fact, in Section 3, arguments are advanced which suggest that it is unlikely that deflagration in a large volume of irregular geometry can proceed far without making the transition to detonation.

On the assumption that detonation does not occur, the characteristic times for increase of pressures in a deflagration explosion will be of the order of many seconds, or perhaps some minutes. The effects of the explosion will thus differ little from a gradual increase in the static pressure in the enclosure. Also, it has been shown that the characteristic time for pressure and temperature decay will also be relatively long, probably of the order of hours or even days, because it depends on heat transfer rates from hot gases to the walls in an enclosure of large dimensions.

1.4 Deflagration Composition Limits

Table 2, taken from Lewis and von Elbe (1961), shows limits of flam-

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TABLE 2

Limits of Inflammability of Gases and Vapors with Air[1]

COMPOUND	FORMULA	LIMITS OF FLAMMABILITY	
		LOWER	UPPER
Paraffin Hydrocarbons			
Methane	CH_4	5.3	15.0
Ethane	C_2H_6	3.0	12.5
Propane	C_3H_8	2.2	9.5
Butane	C_4H_{10}	1.9	8.5
Isobutane	C_4H_{10}	1.8	8.4
Pentane	C_5H_{12}	1.5	7.8
Isopentane	C_5H_{12}	1.4	7.6
2,2-Dimethylpropane	C_5H_{12}	1.4	7.5
Hexane	C_6H_{14}	1.2	7.5
Heptane	C_7H_{16}	1.2	6.7
2,3-Dimethylpentane	C_7H_{16}	1.1	6.7
Octane	C_8H_{18}	1.0	6.0
Nonane	C_9H_{20}	0.8	---
Decane	$C_{10}H_{22}$	0.8	5.4

1. Data from H. F. Coward and G. W. Jones, Limits of Flammability of Gases and Vapors. U.S. Bureau of Mines Bulletin No. 503 (1952).

TABLE 2
(Continued)

COMPOUND	FORMULA	LIMITS OF FLAMMABILITY	
		LOWER	UPPER
Olefins			
Ethylene	C_2H_4	3.1	32.0
Propylene	C_3H_6	2.4	10.3
Butene-1	C_4H_8	1.6	9.3
Butene-2	C_4H_8	1.8	9.7
Amylene	C_5H_{10}	1.5	8.7
Actylenes			
Acetylene	C_2H_2	2.5	80.0
Aromatics			
Benzene	C_6H_6	1.4	7.1
Toluene	C_7H_8	1.4	6.7
o-Xylene	C_8H_{10}	1.0	6.0
Cyclic Hydrocarbons			
Cyclopropane	C_3H_6	2.4	10.4
Cyclohexane	C_6H_{12}	1.3	8.0
Methylcyclohexane	C_7H_{14}	1.2	---
Terpenes			
Turpentine	$C_{10}H_{16}$	0.8	---
Alcohols			
Methyl Alcohol	CH_4O	7.3	36.0
Ethyl Alcohol	C_2H_6O	4.3	19.0
Allyl Alcohol	C_3H_6O	2.5	18.0
η-Propyl Alcohol	C_3H_8O	2.1	13.5
Isopropyl Alcohol	C_3H_8O	2.0	12.0
η-Butyl Alcohol	$C_4H_{10}O$	1.4	11.2

mability for various hydrocarbons in air. Comparison of these tables with the explosion pressure curves in Figure 1 shows that the limits of flammability coincide quite closely with the fuel-air ratios at which the explosion pressures approach zero. In other words, any gas mixture which will burn will also undergo a deflagration explosion.

2.0 DETONTATION PHENOMENA

Detonations are distinguished from deflagrations by their propagation mechanism. In deflagration, the combustion zone is propagated forward by conduction of heat into the unburned gas, raising its temperature to the ignition point. In detonation, the combustion reaction is so rapid that a pressure jump, generated by a very rapid release of the heat of combustion, moves into the unburned gas. The heating of the gas by this pressure jump raises the gas temperature to the point that the combustion reaction rate remains high enough to sustain the pressure wave. A detonation wave in essence consists of a shock wave followed immediately by a zone of very rapid combustion.

The following simple experimental model illustrates a detonation wave in more detail: a length of pipe, closed at both ends, is filled with a detonable gas mixtures, and a detonation is initiated at one end. Figure 2 gives several instantaneous "snapshots" of the pressure distribution along this pipe at different instants of time. The pressure ahead of the detonation wave is denoted by p_0. The detonation wave (points A_1, A_2, and A_3 at times t_1, t_2, and t_3, respectively), moving at a constant (supersonic) velocity, increases the gas pressure to the value p_1, and simultaneously sets it in motion in the positive x direction. Since the gas at the left-hand
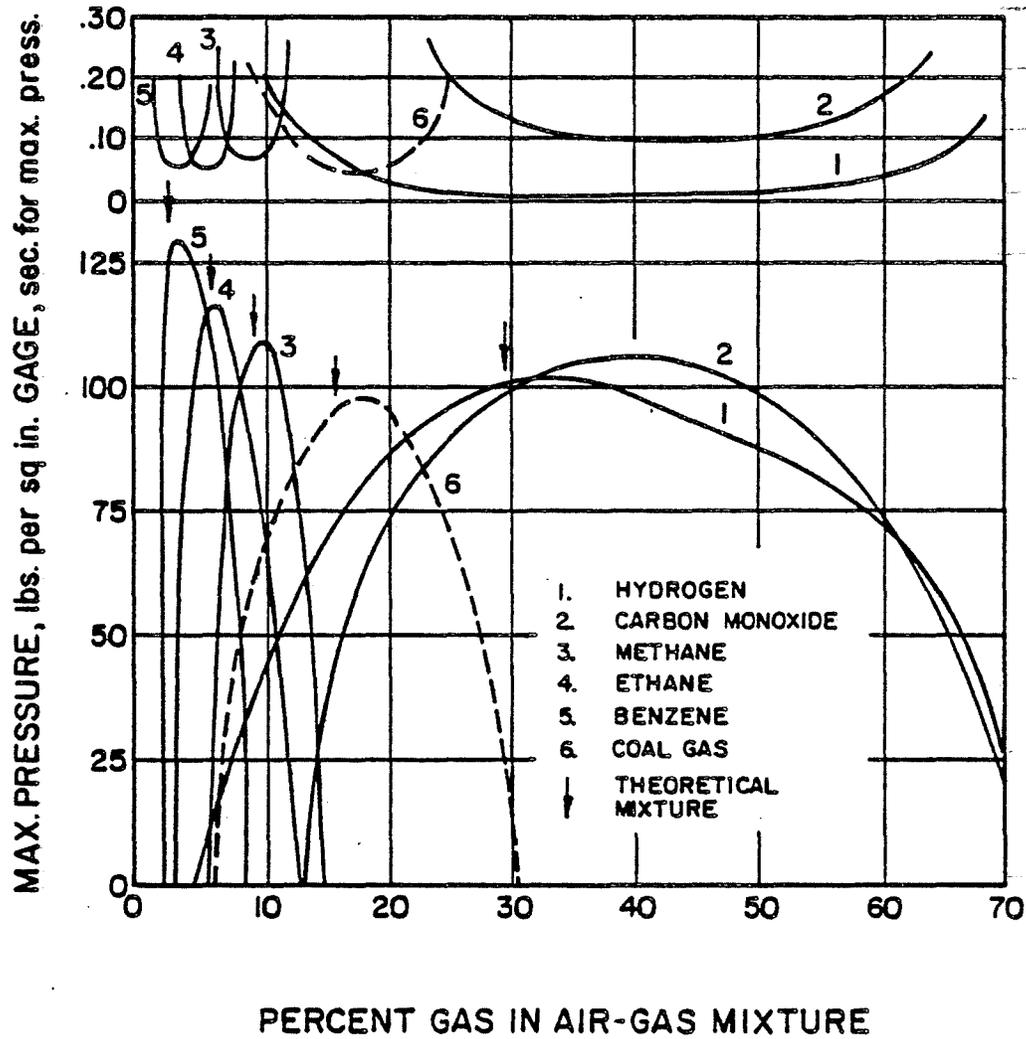
FIGURE 1

EXPLOSION TIME AND PRESSURE FOR MIXES OF GAS AND AIR
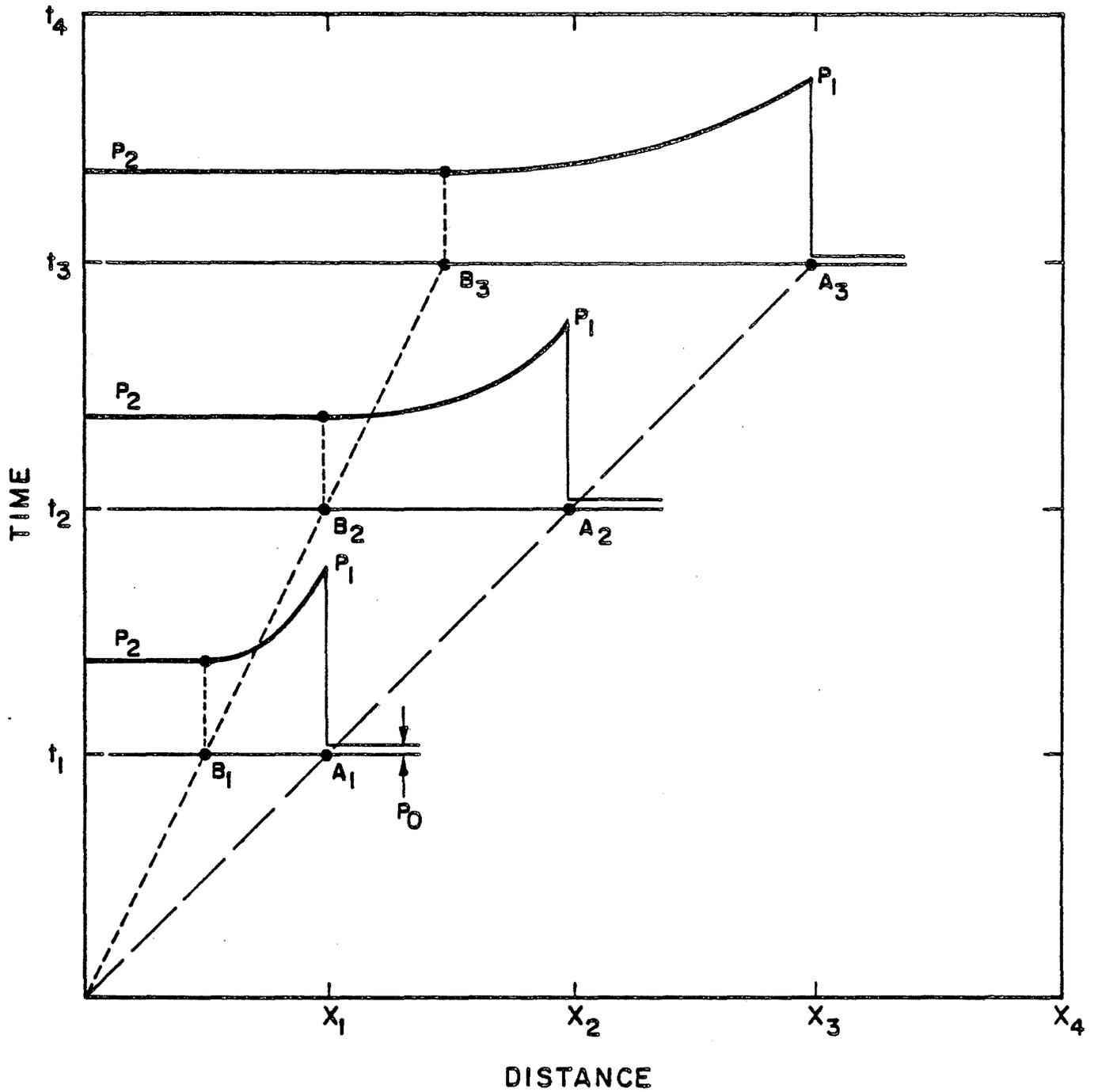
FIGURE 2

PRESSURE — DISTANCE PROFILES IN A IDEAL
DETONATION WAVE AT DIFFERENT TIMES

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end of the pipe must be at rest (or else it would pull away from the end plate and leave a vacuum there), there must be a rarefaction wave following the detonation wave which serves the function of decelerating the burned gases in the wake of the detonation wave and bringing them to rest where the pressure p_2 is less than p_1. Since continuous pressure signals (as distinguished from pressure discontinuities, or shock waves) move at the local velocity of sound, the tail of the rarefaction wave, where the pressure attains the value p_2 (points B_1, B_2, and B_3 at times t_1, t_2, and t_3, respectively) propagates forward at a steady velocity which is less than the detonation wave velocity. This difference between velocities of the front and tail of a detonation wave results in the spreading of the wave form illustrated by the three "snapshots" shown in Figure 2.

2.1 Propagation Velocities

For hydrocarbon-air mixtures, the detonation wave velocity is typically in the range 1,500 to 2,000 m/sec. Figure 3 shows detonation velocities for propane-air mixtures as a function of the propane concentration (Burgess et al, 1968). These values are also representative of other hydrocarbon-air mixtures when the fuel concentration is adjusted for stoichiometry. The velocity of sound in the hot, burned gases behind the detonation wave is typically about 800 to 900 m/sec, or about half the detonation velocity.

2.2 Detonation Pressures

Zeldovich and Kompaneets (1960) have shown that the pressure at the detonation front, p_1 in Figure 2, is about twice the pressure generated when the fuel-air mixture is burned at constant volume, i.e., the final pressure resulting from a deflagration explosion. Thus, from Section 1.1,

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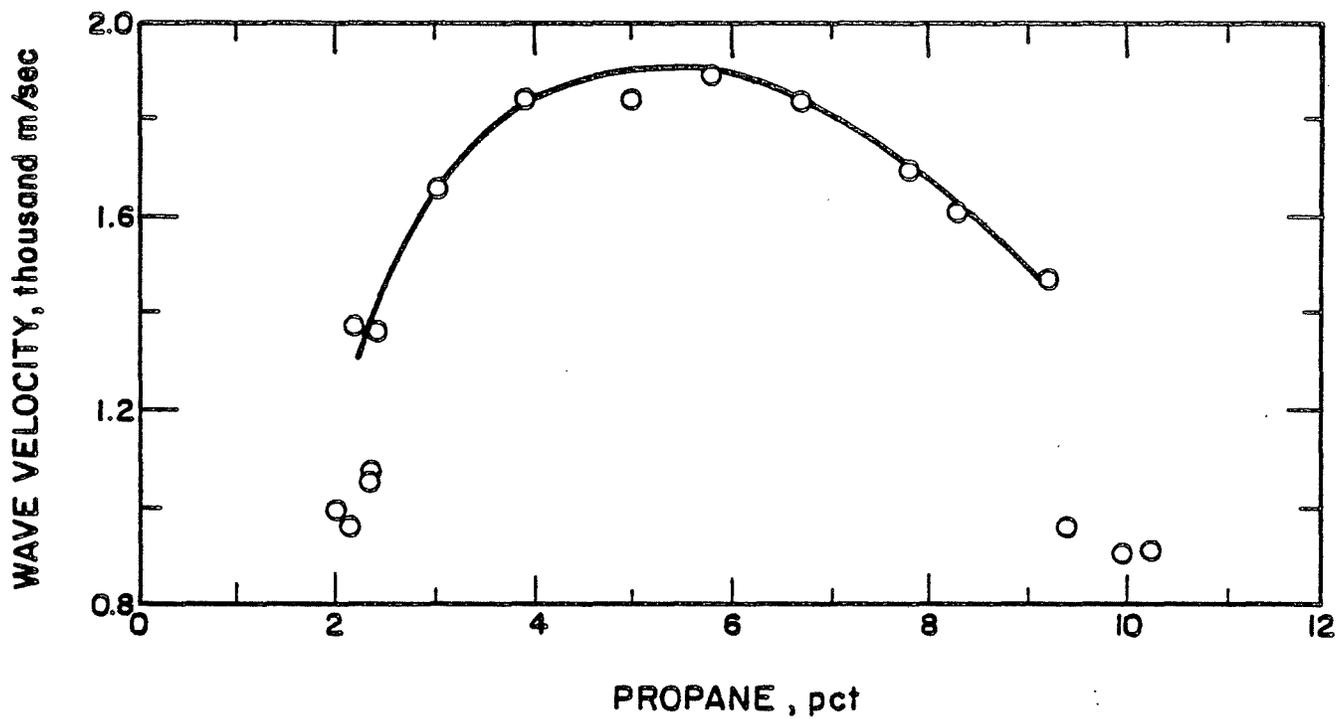
FIGURE 3

DETONATION WAVE VELOCITY AS A FUNCTION OF FUEL
CONCENTRATION FOR PROPANE - AIR MIXTURES INITIATED WITH
IOG OF PETN IN THE CRAWSFORD - JONES APPARATUS

p_1 is about 16 to 18 times as great (absolute) as the initial cavern

pressure for a stoichiometric fuel-air mixture. This estimate is generally

in agreement both with experiment and with more exact theoretical treatments

of detonation phenomena.

Experiments described by Burgess et al (1968) show that the steady

pressure, p_2, behind the tail of the rarefaction wave is about 0.4 p_1,

or about 80 percent as great as the pressure produced by a deflagration

explosion.

When the detonation wave impinges on the far end of the pipe, it is

reflected back in the negative x direction. Reflection of an ordinary

acoustic wave doubles the peak pressure. For waves of large amplitude,

the pressure increases by more than a factor of two; at the pressures of

detonation waves the factor is closer to 2.5. In any case, wave reflec-

tion will be a transient effect since the reflected wave will be rapidly

attentuated as it moves through the region of falling pressure behind

the incident wave (the region between the points A and B in Figure 2).

After the reflected waves have damped out and pressure equilibrium

has been established in the pipe, the steady pressure level in the system

will be less than but may be approximated to be the same as that resulting

from a deflagration explosion. This again simply results from the fact

that the total amount of heat available from combustion of a given gas

mixture is the same, regardless of the mechanism by which combustion takes

place.

As with deflagration explosions, the absolute pressures generated

at any point in the detonation process are basically directly proportional

to the initial pressure, for a given fuel-air ratio. Doubling the initial pressure will very nearly double the peak detonation pressures and the steady pressure level reached after the transient effects have died away.

The main differences between detonation and deflagration explosion pressures are thus seen to be the rate of pressure rise, and the existence of the transient pressure peak at the front of the detonation wave. Detonation, perhaps surprisingly, is a more predictable process than deflagration. The low propagation velocity of deflagration allows the early stages of the deflagration process to affect the environment in which the later stages of deflagration take place; thus, depending on the particular fuel-air mixture and the characteristics of the container in which the explosion takes place, there are a variety of possible outcomes in the later stages of a deflagration explosion (Section 1.0). A detonation wave, on the other hand, moves so rapidly that the unburned gas is "unaware" that anything is happening until the detonation wave front arrives.

2.3 Detonation Temperature

Temperatures at the detonation front are higher than those in the tail of the wave, due to the pressure ratio p_1/p_2. The magnitude of this temperature difference is of the order a few hundred degrees Centigrade. The final temperature after equilibration of pressure in the enclosure, however, will be essentially the same as that resulting from a deflagration explosion.

Since thermal effects during the passage of the detonation wave itself will be small, because of the short times involved, the important thermal effects will be the long-duration processes taking place after all transients

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have died away. Thus, the temperature information presented in Section 1.2 can be used for detonation as well as deflagration processes.

2.4 Characteristic Times

The characteristic times concern primarily the duration of the pressure transients at the front of the detonation wave. The essential information has already been presented in Section 2.1. The duration of the pressure transient is directly proportional to the distance traveled by the detonation wave from its point of initiation. Assuming that the detonation wave velocity is 1,800 m/sec, and that the tail of the detonation wave moves at half this velocity, the duration of the pressure transient is given by

$$t = x/1,800$$

where x is the distance from the point of initiation of detonation in meters, and t is the time in seconds.

The decay of pressure after the initial transients are past will again depend on the rate of heat loss from the hot gases, just as in the case of deflagration explosions (Section 1.0).

Since the duration of a pressure transient relative to the dynamic characteristics (natural vibration periods) of geotechnical, civil and mechanical systems determines the nature and magnitude of structural response, the increase in duration with distance from the point of initiation is a significant aspect of a detonation relative to potential damage. It is noted here that the above relation is based on observations in shock tubes under laboratory conditions which are significantly different from those anticipated in underground caverns.

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2.5 Detonation Composition Limits

The question of detonation limits is somewhat more complicated than that of deflagration limits. The usual definition of the detonation limit is the fuel-air ratio beyond which a stable detonation wave cannot exist; that is, the heat released by combustion is just marginally able to drive a shock wave strong enough to bring the fuel-air mixture to a temperature at which the combustion reaction is fast enough to follow the pressure wave. Beyond the limit, the combustion zone will lag behind the shock, thus separating the shock from its energy source. The shock will then decay with time, and the combustion front will degrade to a deflagration.

However, an externally driven shock wave can propagate as a detonation for some distance into a mixture whose composition is outside the limits of stable detonation. Such a wave will eventually decay and degrade into a separate shock and deflagration, as above (Jost, 1946). Nevertheless, Burgess et al (1968) have observed such "overdriven" detonation waves in propane-air mixtures containing 30 percent propane, whereas the normal flammability limit of propane in air is 9.5 percent; the waves propagated for several meters distance without being degraded into separate shock and deflagration waves. Table 3 shows expected upper and lower limits of detonability for several fuel-oxygen and fuel-air systems.

3.0 THE DEFLAGRATION-DETONATION TRANSITION

This discussion is largely based on the paper by Brinkley and Lewis (1958) who state the following general observations:

- A combustion wave propagating from the closed end of a container filled with an explosive mixture whose normal burning velocity is sufficiently high accelerates continuously. If the container is sufficiently large, such a flame will accelerate to a detonation wave.

TABLE 3

LIMITS OF DETONABILITY

MIXTURE	LOWER LIMIT PERCENT FUEL	UPPER LIMIT PERCENT FUEL
H_2-O_2	15	90
H_2-air	18.3	59
CO-O_2, moist	38	90
CO-O_2, well dried	--	83
$(CO + H_2)$-O_2	17.2	91
$(CO + H_2)$-air	19	59
NH_3-O_2	25.4	75
C_3H_8-O_2	3.2	37
i-C_4H_{10}-O_2	2.8	31
C_2H_2-O_2	3.5	92
C_2H_2-air	4.2	50
$C_4H_{10}O$(ether)-O_2	2.6	> 40
$C_4H_{10}O$-air	2.8	4.5

- The details of the transition are strongly influenced by the geometry of the confining vessel insofar as the geometry affects the reflection of pressure waves generated by the ignition source or by the combustion wave itself. It has been observed, for example, that the transition to detonation may occur at the instant that the combustion wave interacts with a pressure wave originating at the ignition source and reflected from the wall.

- The transition is facilitated by the presence of turbulence in the flame front. Turbulence in the flame front generates additional pressure pulses, which in turn acts to intensify the turbulence itself. It is thus a self-enchancing phenomenon. Turbulence can be induced by obstacles placed in the path of the flame front or by wall irregularities.

- The compression and heating of the unburned gases ahead of the combustion front also produces an increase of the flame velocity. This is a weaker mechanism than turbulence for enhancing the transition to detonation. It could theoretically, however, lead to an increase in detonation pressures. If a large fraction of the combustible mixture is burned by a deflagration mechanism before detonation sets in, the remaining unburned gas will be at a pressure much higher than the original pressure. Brinkley and Lewis cite an example in which a deflagration produced a fivefold compression of the unburned gases before detonation began; this resulted in a fivefold increase in the detonation pressure, i.e., to nearly 100 atmospheres. On reflection from a rigid wall, a transient pressure of over 200 atmospheres would be generated in this instance.

The generation of pressure pulses by turbulence in the flame front is primarily the result of wrinkling of the flame front and subsequent collapse of flame segments upon pockets of unburned gases. In this circumstance, the trapped gases burn nearly instantaneously giving rise to pressure transients. The same effect can be produced by placing obstacles in the path of the flame front, so that the front divides as it passes around the obstacle and collapses upon itself on the far side.

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A room-and-pillar structure furnishes irregular surfaces to induce turbulence and obstacles to promote flame-front collapse. Thus, strong arguments can be advanced for the hypothesis that any ignition of fuel-air mixtures will very rapidly produce a detonation wave. There is thus little probability that a substantial fraction of the volume will burn by deflagration, with the resulting enhancement of detonation pressures as cited above in the last indented statement.

4.0 IGNITION SOURCES

The minimum energy required to cause ignition in a flammable mix may be defined by the following events:

- Somewhere in a volume of combustible gas a small source of energy is located.

- When energy is released "instantaneously", a hot spherical volume is created.

- The temperature at the center of this sphere will change with time; ignition occurs when this temperature never decreases.

- The minimum ignition energy is the least energy input which causes ignition under these conditions.

The limits of flammability and minimum ignition energy have been investigated and reported for many substances as discussed previously and shown in Table 2 for flammability limits. Similar limits apply to butane, pentanes, propane, hexanes, gasoline, and tetramethyl pentane, according to Coward and Jones (1952). In general, upper limits of flammability are around eight percent for these hydrocarbons although the limits for tetramethyl pentane are given as 0.9 to 4.9 percent. The minimum ignition energy for these same hydrocarbons lies between 0.25 and 0.30 millijoules.

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It should be noted that ignition energies discussed above correspond to sources which have a very large power density. Zabetakis (1965) states that power density requirements are greater than one megawatt per cubic centimeter. This implies that an ignition source of 0.3 millijoule be extremely concentrated and rapid. When the source energy is diffuse, the total energy requirements may be quite large.

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AN EVALUATION OF THE FIRE AND EXPLOSION HAZARDS
OF OIL SHALE MINING AND PROCESSING

"Review of Dust Explosibility Testing Methods and Apparatus"

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1.0 Introduction

The explosibility of dust has been the subject of many investigations conducted in laboratories and galleries. The purpose of these experiments was to obtain a comparative assessment of the severity of explosions that could develop, and to determine the limits of ignition expressed in dust concentrations, energy required to ignite, or in ignition temperatures.

The development of dust ignition is a very complex phenomenon involving the time-space variation of the energy provided by the ignition source, the time and space variation of dust density, the physico-chemical properties of the dust, ambient conditions and container (see Table 1). It is therefore an extremely difficult task to design a test apparatus and procedure which would represent extreme conditions and would yield absolute limits. At the same time it seems desirable to design such an apparatus which would imitate the practical conditions at which dust ignition might occur. The third consideration is that the apparatus should preferably be of laboratory size for the sake of convenience and expenses but the data obtained should be translatable into or applicable to large scale practice.

2.0 Survey of Different Test Apparatus, Methods, and Results

As a compromise derived from the above considerations, three basic apparatus were developed by the Bureau of Mines, namely the Godbert-Greenwald furnace[1], the Hartmann lucite test bomb and the modified version of this, the Hartmann steel bomb[2].

2.1 The Godbert-Greenwald Furnace

The Godbert-Greenwald furnace is used for determing the ignition temperature of dusts. The procedure is as follows. The dust sample is identified by running a proximate analysis and by sieving it through 200 mesh (particle size is < 75 μm). A given amount (normally 0.1 g) sample of dust is blown into a preheated oven through a given pipe system using an air blast coming from a reservoir of a given volume (500 cm^3) and pressure (4-20 in.Hg). The other end of the oven is open. The lowest temperature of the oven at which ignition occurs is labelled as the ignition temperature of the dust cloud.

2.2 The Hartmann Lucite Chamber

The Hartmann lucite chamber is a 1.23 liter vertical chamber closed with a filter paper on the top and having a dust dispersing mushroom at its bottom. The dust, spread out on the bottom, is lifted up by an airblast coming from a 500 cm^3 reservoir filled with air to 5-15 psig pressure. The dust cloud is ignited by a spark between two needle shaped electrodes

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TABLE 1

Factors Affecting the Dust Explosion

I. Initiator	Energy Volume Duration Temperature Position Pressure
II. Dust	Volatile content Inert content Petrographic composition Particle size Concentration Physico-chemical properties
III. Atmosphere	Temperature Pressure Oxygen concentration Flammable gas type Flammable gas concentration Motion (flow, turbulence, etc.)
IV. Space (container)	Shape Size Roughness of wall Material of wall Temperature of wall Openings for pressure release

positioned at a given height in the chamber. The apparatus is used for obtaining two kinds of data, namely the minimum explosive concentration (m.e.c.) and the minimum igniting energy (m.i.e.)

For the determination of the minimum explosive concentration a continous spark is created first by feeding a high voltage transformer connected to the drill-rod electrodes from the main supply. The dust concentration is varied until no ignition occurs out of four trials. Then the position of the electrodes is changed and again the concentration is sought where no ignition (indicated by the burst of filter paper) occurs in four trials. The mean value of these two concentrations is labelled as the minimum explosive concentration.

The same apparatus is used for the determination of the minimum igniting energy but the test parameters and procedure is somewhat different. The electrodes are placed to 4 inches height (11.6 cm) and the electrode material is tungsten. The sequence is different to the extent that instead of having a continuous discharge, the transformer is fed by switching a charged-up capacitor onto it. The duration of the discharge is very short in comparison to the time it takes for the dust to settle down again. For this reason the correct timing of the spark is essential.

At a given dust concentration (normally five to ten times the m.e.c.) the lowest energy stored in the capacitor with which ignition can be obtained is designated as the minimum igniting energy. The criterion for ignition in this case is whether the observed flame is 4 inches or longer.

2.2.1 The Ignition Sensitivity Index

The above three parameters all have a smaller value when it is more difficult to ignite a dust. Although strictly they don't represent a real life situation, because the dust concentration at which the minimum igniting energy is measured is not identical with the concentration at which the lowest ignition temperature is obtained, nor with the minimum explosive concentration, arbitrarily an ignition sensitivity index was created by multiplying these three values and relating the multiple to the same multiple for Pittsburgh coal.

2.3 Hartmann Steel Bomb

The Hartmann steel bomb is similar to the lucite tube except that it is a closed steel cylinder. It is used for obtaining data on the pressure-time function generated by the ignition. The dust is blown in by an airblast coming from an 80 cm^3 reservoir charged with air at 100 psig. The dust concentration is fixed at 0.5 oz./cu ft., the igniting spark energy is fixed by prescribing "23.5 mA current" in the secondary, feeding the spark.

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The faster the pressure reaches its maximum and the higher that value is, the more damage will be caused. Thus the multiple of the maximum rate of pressure rise and of the pressure maximum can be used as a measure of the explosion severity. This multiple for a given dust divided by the same multiple for Pittsburgh coal is called the explosion severity index.

The arbitrary multiple of the explosion severity index and ignition sensitivity index is called overall explosibility index and is used for categorizing the different dusts[3] (see Table 2).

Table 2

Explosive Hazard Adjective Rating	Ignition Sensitivity Index	Explosion Severity Index	Overall Explosibility Index
Weak	< 0.2	< 0.5	< 0.1
Moderate	0.2 - 1.0	0.5 - 1.0	0.1 - 1.0
Strong	1.0 - 5.0	1.0 - 2.0	1.0 - 10
Severe	> 5.0	> 2.0	> 10

2.4 Experimental Work and Results Obtained with the Apparatus
    Developed at the Bureau of Mines

The effect of dust concentration, admixed inert powder and admixed moisture on the explosibility were investigated by Nagy, et al[4]. The test apparatus used for the investigations was the Hartmann steel bomb. The materials tested were Pittsburgh coal, cornstarch, etc.

The most important findings were as follows:

● The decrease in oxygen concentration reduces the maximum pressure nearly linearly.

● The increase of the admixed inert decreased the maximum pressure.

● A very small amount of admixed moisture might increase the maximum pressure at low concentrations but after that it also reduces the maximum pressure.

● The rate of pressure rise also decreases with the addition of inert power and/or moisture.

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- Both the maximum pressure and the maximum rate of pressure increase first with the dust concentration. In this range the oxygen consumption is increasing proportionally and the combustion products tend to be CO_2 and H_2O. After reaching the maximum, which does not necessarily occur at the same dust concentration for the maximum-pressure and maximum-pressure-rate curves, the oxygen consumption levels off, the after explosion analysis of the gas products indicates the presence of CO, methane, hydrogen and unsaturated hydrocarbons, i.e., the combustion process is incomplete. The dust concentration at which the pressure maximum is the highest is considered as the equivalent to a stoichiometric concentration. As the concentrations approach the higher explosive limit, the analysis of gas composition and the decrease of maximum pressure indicate a decreasing chemical activity.

- The investigation of the importance of particle size indicated that, if a wider range of particle sizes is present, the explosion characteristics will be determined by the smallest particles. The larger sizes, whether they are combustibles or inert, won't effect the explosion. The limit above which the particles do not participate was found to be 425 µm for cornstarch.

Hartmann[5] et al have investigated the explosive characteristics of several ranks of coal, using the apparatus developed by the Bureau of Mines. The most important findings can be summarized as follows:

- The ignition temperature of dust clouds is decreasing with the volatile content, and is about 200°C less in pure oxygen than in air. The dust layer ignition temperature is approximately 2-3 times lower than that of the dust cloud.

- Both the minimum energy and the minimum concentration are decreasing with increasing volatile content in the 0-50% region and compared to air are lower in pure oxygen.

- The maximum pressure and maximum rate of pressure increases with the volatile content and are higher in pure oxygen. These results confirm that the danger of dust ignition is greater in pure oxygen and that the higher volatile content gives a more dangerous situation up to about 40% volatile content determined on dry, mineral free basis.

- There is a most dangerous dust concentration for every material.

- At a given dust concentration the particle size distribution influences the overall explosibility index considerably. For instance, for 45µ particle size, the ignition sensitivity index is 18.4 times higher than for 75µ size, using segregated fractions of Pittsburgh coal.

These results clearly indicate that the presently used sample identification namely that the sample is "through 200 sieve" is not adequate since the amount of smaller particles which is not known will influence the results considerably.

- The maximum explosion pressure and the rate of pressure rise were found to increase linearly with the initial pressure determined by the ratio of the steel chamber volume to the volume of the reservoir and the overpressure in it.

- The moisture content above 8% signigicantly reduces the ignition sensitivity.

- The relative flammability of the dust is increased with the increase in oven temperature.

- Release of explosions to adjoining larger spaces of limited volume might result in strong explosions in the adjoining space.

2.5   Large Scale Test Apparatus

2.5.1   115 Liter Steel Bomb

For large scale purposes a 115 liter cylindrical steel bomb was designed by D. Reeh[6] at the Dortmund Experimental Mine. Its operation is similar to that of the steel Hartmann bomb. Approximately 0.225 sec after starting to introduce the dust (blown in short blasts by a pneumatic regulator) an explosive compound is triggered which releases about 5 Kj energy. The apparatus is used for obtaining pressure-time and explosive limit data. The explosion coefficient is calculated as:

$$K = \frac{dp}{dt}\bigg|_{max} \cdot \frac{P_{max}}{\Delta t}$$

where Δt is the time elapsed between initiation and reaching the maximum pressure p_{max}. In the terminology developed by the Bureau of Mines the explosion severity index is defined as

$$\varepsilon = \frac{dp}{dt}\bigg|_{max} \cdot P_{max}$$

No arguments have been given to justify either of these definitions. It would seem desirable to make some comparisons to determine which of the indices is more meaningful. Dust concentrations produced by this system are in the $0 - 2.500 \times 10^{-2}$ g/m^3 range (0-1.44 oz/cu in).

The most important observation derived from the experimental data are as follows:

- Coals containing more volatiles have a wider explosive limit range.

- The explosion coefficient appears to be inversely proportional with the ash content.

- The explosion coefficient as a function of particle size shows a maximum at a given particle size. For cooking coal this maximum is at $\simeq$ 20 μm.

2.5.2 Palmer's Free Fall Apparatus

The small scale dust testing results have to be related to practical, large scale operations. In order to relate the small scale testing data to practice a 25 cm diameter 5.2 m long test apparatus was built by the Fire Research Station in Borehamwood[7] and already classified dusts were retested with it. The dust was fed from a hopper onto a screw conveyor which fed the explosion tube. The dust was dispersed at the top and was allowed to fall freely. After measuring the dust concentration by collecting dust for a given time on a given surface area and establishing the on-set of steady state conditions the dust was ignited toward the lower end of the tube and the extent of flame propagation was observed. It was confirmed that the dust distribution within a 17 cm diameter area was reasonably uniform. This apparatus was used for determining the flammability limits of different dusts, dust and inert (magnesium oxide) mixtures, etc.

The results showed that dusts or dust mixtures classified Class III or II with the small scale test apparatus did not propagate explosion in this apparatus. Most of the dusts and dust mixtures classified marginally Class I with the small scale apparatus did however, propagate in the large scale apparatus.

Thus it seems that the small scale tests are meaningful to the extent that if a dust or dust mixture is found not to propagate explosions using a small source of ignition with the small scale tests then it won't propagate explosion on a larger scale either. The minimum amount of inert dust required to prevent propagation using small or large scale apparatus were also found to be in good agreement.

2.5.3 Japanese Toothed Rotating Drum Apparatus

The systematic investigation of dust explosions is hindered by the difficulties encountered in obtaining a known, repeatable, homogeneous dust cloud. In an attempt to provide a better controlled dust cloud W. Ishihama and H. Enomoto[8] developed a rotating toothed explosion chamber.

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Three kinds of teeth cover the inner wall of the drum. First, the dust is evenly distributed on the bottom of the stationary chamber; then the chamber is rotated. After 5 seconds of rotation the dust cloud is ignited by a spark. It was found that the rotation speed of the drum had to be varied according to particle size and was critical in obtaining a homogeneous mixture of a given concentration. Up to five seconds, the uniformity was improving, later on the uniformity in the axial direction decreased. The apparatus is suitable for creating dust concentrations up to 4000 g/m^3 with $\simeq$ 6% error. It is a closed system thus is suitable for obtaining pressure data.

This apparatus was further improved[9] and was used for extensive experimental work on aluminum and magnesium dusts, which showed rather different behavior at higher dust concentrations.

The most important conclusions derived by the authors from work with the above apparatus were as follows:

1. Maximum pressure increases with volatile matter content at a given particle size.

2. Maximum pressure decreases as the particle size increases at a given volatile matter content.

3. The explosion range increases toward higher concentrations as the volatile matter content increases and/or the particle size decreases. The concentration at which the maximum pressure is the highest, increases as the volatile matter content increases and/or particle size decreases.

These results seem to indicate that mainly the surface of the particle participates in the ignition process.

2.5.4 Bureau of Mines' closed explosion vessels

The Hartmann steel chamber has a relatively small volume and a specific cylindrical shape, thus raises the question of 1) how the vessel size and shape would influence the development of an explosion, and 2) how the turbulence caused by dispersing the dust effects the explosion. In order to get an answer to these questions the Bureau of Mines conducted an extensive study[10] using cellulose acetate, cornstarch coal dust, methane-air and propane-air mixtures and igniting them in vessels of different sizes (0.018-905 cu. ft) and shapes (spherical, cylindrical, cubical rectilinear). The most signigicant results derived from the study were as follows:

1. The maximum pressure developed by the gas or dust explosion is a closed vessel and is independent of the vessel size and shape if heat loss to the vessel is negligible.

2. If heat loss isn't negligible (duct shaped vessel, with ignition source being near to a wall) the maximum pressure will decrease.

3. The rate of pressure rise is affected by the volume and shape of the vessel. It was found to be proportional to the ratio of the surface area of the vessel to its volume. Explosions in non spherical vessels have greater rates of pressure rise than in equal-volume spherical vessels.

4. Initial turbulence was found to increase the rate of pressure rise considerably but influence the maximum pressure only slightly.

5. A change in the initial pressure produced a proportional change in the maximum pressure.

6. A change in the initial temperature produced an inverse change in maximum pressure.

7. The size, kind and position of ignition source did influence the rate of pressure rise but only slightly affected the maximum pressure.

In summary it seems that the maximum pressure is much less sensitive than is the rate of pressure rise to changes in experimental conditions (such as vessel size, shape, ignition source, turbulence, etc.). Since the explosion severity proposed by the Bureau of Mines is the multiple of these factors it will be sensitive to experimental conditions. Thus without specifying the conditions the explosion severity is meaningless. The explosion severity index which relates the explosion severity of a dust to that of the Pittsburgh coal dust has a relative value only if the test conditions for the two dusts were exactly identical. From the above results it appears that the index proposed by D. Reeh[6] would be even more dependent on the experimental circumstances and less characteristic of the dust itself.

2.6 Test Galleries

The best approximation of real life conditions can be obtained by using test galleries. Unfortunately, due to the large scale, setting up the test is time-consuming, expensive, and extensive instrumentation is required.

The experimental galleries can provide very extensive and complex data, and can be used to investigate the propagation process, in detail. Several countries such as the U.S.A., England, Germany, etc.) have therefore experimental galleries.

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2.7.3 Work Pertaining to the Chemical Analysis of Coal Samples

In order to identify the coal samples or similar materials, a proximate analysis and ultimate analysis is run usually on the samples. These analyses are standardized[19,20,21] and well known. The problem with these tests is that they take several hours to complete. For instance, a proximate analysis[18] (assay of the volatile matter, fixed carbon and ash content) involves separate analyses for moisture (1.5 h) volatiles (> 2h) and ash (~1h). The carbon is calculated as a difference, which makes this figure rather inaccurate.

The same data could be obtained with a Thermogravimetric Analyzer (e.g., Perkin Elmer TGS-2) in 15 minutes. The data presented by Culmo[21] indicates that the numbers obtained with the TGS-2 and the ASTM methods agree well. For the classification of coal by rank[20] and for assessing its calorific value the ultimate analysis[21] (determination of percent carbon, hydrogen, sulfur, nitrogen, and oxygen by the difference) is used. Culmo shows that these data can also be obtained much faster (13 min.) using the Model 240 Elemental Analyzer, of course, the sample handling preparation has to be adopted to suit the circumstances followed for the treatment of coal samples in the ASTM methods.

The shortcomings of the standard proximate analysis method compared to the TG method are that the former is time consuming requires rigidly controlled conditions for weight, temperature, time atmosphere, is subject to operator accuracy, and it does not measure the fixed carbon directly. The TGS-2 uses much smaller sample (5-10 mg versus 1 g), thus further homogenization and particle size reduction is necessary to get representative sample.

Another advantage of the TG method is that the data output is more informative. The readings on the Thermogram are given in weight percent, the temperature is also marked on the abscissa thus the different reasons for weight loss such as evaporation of water, exodus of volatiles can readily be related to the temperature. When, as a final step, oxygen atmosphere is introduced, the subsequent weight loss can be related to the carbon content and the residual weight gives the ash content.

It is felt that although the thermogravimetric method cannot give information directly on the explosibility of the dust itself, it would give a more complex picture about the sample and would give detailed breakdown on the moisture and volatiles which in turn greatly influence the explosiveness thus might be a more informative test. Presumably, the minimum ignition temperature of the dust could also be obtained with this method choosing the test conditions and interpreting the thermogravimetric and/or differential scanning calorimetry data.

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3.0 Discussion

3.1 The Coal Particle Combustion

It is of interest to compare Howard and Essenhigh's[18] results with
that of J. Nagy, et al[4], I. Hartmann, et al, D. Reeh[6] and Ishihama[8]
on the importance of particle size and volatile content.

According to Nagy, et al. the larger particle sizes (> 425 μ for corn-
starch) regardless of their chemical composition did not influence the
explosion pressure, i.e., did not participate in the explosion. Hartmann,
et al, showed that the igniting sensitivity index was increasing with
decreasing particle size. Reeh showed that the explosion coefficient
was increasing with the decrease in particle size until it reached a
maximum which for cooking coal was found to be ~ 20 μm. It therefore
seems that around < 15-20 μm size for coal the combustion of the particle
is instantaneous and complete thus further decrease in size cannot increase
the severity of explosion.

Howard's findings (that the volatile content above a certain particle
size will prohibit the total combustion of the particle itself) can also
explain the trend observed by Ishihama, namely that the increase in vola-
tile matter content and the decrease in particle size have similar effects,
both increasing the explosion severity.

3.2 Comments on the Testing Apparatus and Methods Used by the
    Bureau of Mines

In the course of the last 20 years, the Bureau of Mines have done an
extensive amount of work in trying to categorize the different dusts.[2,5,22,23]
Since the testing with the originally developed Godbert furnace and
Hartmann lucite and steel apparatus was intended to be used for the com-
parative evaluation and classification of dusts, this consideration
at the same time proved prohibitive as far as modifications in the test
apparatus or method were concerned.

In the meantime, considerable research has been done using these
apparatuses and others (discussed previously in Chapter 2) in an
attempt to better understand the process of dust ignition and to have
better control over the parameters influencing it.

In the light of these findings, it seems appropriate to evaluate the
effectiveness of the apparatuses in fulfilling their intended purpose and
the validity of the data obtained with them.

3.2.1 Evaluation of the Godbert-Greenwald Ignition Temperature Test

The lowest temperature of the oven at which ignition is observed is labelled as the "ignition temperature" of the dust cloud. The so obtained "ignition temperature" cannot have absolute value for several reasons:

1. The dust dispersion is far from being homogeneous during tests. The density of dust is varying in time and space as a function of the air blast parameters, particle size, etc. Thus relating the ignition temperature to any dust density is incorrect.

2. There is no assurance that any part of the dust is at the same temperature as the oven at the time of ignition.

The dust is cold, the air in the reservoir is cold, and the blast caused by releasing the air from the pressurized reservoir has a nominal isothermal volume of 500 cm^3 x (1.13 - 1.67) depending on the overpressure in the reservoir. Since the volume of the oven is only 227 cm^3, it is obvious that most of the dust picked up by the blast wave is blown right through the tube furnace into the open. As most of the air-dust mixture passes through the tube in a very short time it does not seem to have much chance to reach any significant temperature. Only the tail end of the blast carrying very little dust and remaining in the tube could eventually reach the temperature of the oven, unless the gravitational free fall would cause the particle to drop out of the oven earlier. Using Stokes equation, the ultimate velocity achieved by a coal sphere of 75 μm diameter at 0°C in air would be approximately 18 cm/sec. Thus, within one second, as an extreme duration, the dust will leave the oven. The other opportunity for ignition occurs when the front of the "cold" blast wave hits the hot air in the oven.

Which of the two phenomena is, in fact, the cause of ignition in the test is not known at present; it presumably varies. It seems that depending on which phenomenon causes the ignition the ignition temperature number might be different.

It is felt that by identifying the cause of ignition and by modifying the test parameters, lower ignition temperatures could be obtained for dusts. From the data available for different dusts it appears that the ignition temperature for dust clouds in generally 1.2 - 3 times higher than for dust layers. This is presumabaly due to the air flow in case of dust testing being much faster in order to get the dust suspended but, at the same time, causing excessive cooling. If the dust would be fed continuously into the oven and would just free fall through it the ignition temperatures would probably be significantly lower.

Although another test apparatus[8] has been designed to provide free fall of particles without turbulence it has not been used for determining ignition temperatures.

3.2.2 Comments on the Minimum Igniting Energy Test Using the Lucite Tube

The minimum igniting energy is defined as the lowest capacitor energy which when it is fed through a high voltage transformer into the spark is able to cause at least 4 inch long flame propagation.

The shortcomings of the method and definitions are as follows:

1. The dust density as a function of time and space is changing during the test. Since the dust density goes through a wide scale of values it is extremely critical at which point the spark should be created.

2. The dust density-time function is influenced by the pressure in the reservoir and by the amount of dust used in the test. Thus it seems that in order to determine the minimum spark energy still able to cause ignition, it would be necessary to determine when the dust density reaches its maximum at the electrodes, what its instantaneous value is and initiate the spark at that instant. To our knowledge this is not done at all at present.

3. Also the labelling of the energy stored in the capacitor as the energy required to cause ignition is incorrect as it was discussed in Chapter 2.7. The energy that should be measured is the energy transferred to the spark. The difference between the stored energy and spark energy can be very signigicant, particularly if a high voltage transformer of undefined equivalent circuit is transferring the energy to the spark.

4. It is not known how the wall effect influences the energy required for ignition in the test chamber.

5. As a consequence of these the minimum igniting energies determined with the lucite tube cannot be used neither as an absolute value nor as a relative value to characterize the energy necessary to ignite a particular dust.

   In order to have absolute value it should be proven that every one of the parameters influencing the ignition was at its most favorable value for ignition during the test.

   In order to have relative value it should be proven that nothing whatsoever was different in the test setup, parameters and procedure but the kind of dust specimen and the parameter investigated. Of course, if two different dusts ignite with different energies then the capacitor value has to be altered to achieve this, at the same time the time constant, losses, etc., will automatically change in the igniting circuit hence the criterion for relative validity is forfeited.

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3.2.3 Comments on the Minimum Explosive Concentration Test Using the Lucite Tube

The dust density as a function of time and space is changing during the test. The spark power is presumed to stay constant during the test thus at some density the dust ignites. If the test condition indeed represents the minimum concentration that can be ignited, then the ignition again has to occur when the dust concentration is the highest around the electrodes. The maximum instantaneous dust concentration can be significantly higher than the average value obtained by dividing the amount of dust into the total volume. Hence, the so obtained average number is probably much lower than the real minimum explosive concentration.

3.2.4 Comments on the Explosibility Severity Index Test

It was shown that the maximum pressure is more independent of the test conditions than the maximum rate of pressure rise is. The explosibility index, which is created by multiplying these two factors, will therefore be also influenced by the test conditions. Since the Hartmann steel bomb does create a higher than ambient initial pressure but due to its shape the losses to the wall could be significant; it might not give high maximum pressure compared to other vessels.

It was shown that the maximum rate of pressure is proportional to the ratio of vessel surface to its volume and increases with turbulence. Since the Hartmann steel tube is realtively small, that ratio is high, and also, considerable turbulence is caused by the air blast. The apparatus is likely to give high maximum rate of pressure values compared to other larger or spherical vessels. These expectations were not confirmed by Nagy, et al. who's measurements are presented in Table 3. These data indicate that:

a. The Hartmann apparatus does not produce the highest

$$P_{max} \times \frac{\Delta p}{\Delta t} \text{ max value,}$$

b. The maximums occur at different dust concentrations. Particularly the rate of pressure maximum does vary with vessel size.

c. Even when the index is created by relating the multiple for a given dust to the multiple obtained for Pittsburgh coal with the same apparatus the so obtained explosion severity index can vary quite significantly.

In summary, the explosion process is far too complex for being represented meaningfully by the explosion severity index.

TABLE 3. Explosion Severity Index Generated from Data Obtained by Nagy, et al[10]

Material	Pittsburgh Coal		Cornstarch		Cellulose Acetate	
Measured Parameter	Max. Press. psia	Max. Rate of Pr. psi/sec	Max. Press. psia	Max. Rate of Pr. psi/sec	Max. Press. psia	Max. Rate of Pr. psi/sec
Max. Reached at Dust Conc.	0.4 oz/cu.ft.	0.4 oz/cu.ft.	0.8 oz/cu.ft.	0.4 - 0.8 oz/cu.ft.	0.8 oz/cu.ft.	0.2 - 0.8 oz/cu.ft.
Vessel Size cu. ft.						
0.043 Hartmann	92	1800	120	1200 at 0.6	110	5000 at 0.8
.32	120	3400	125	6500 at 0.4	128	3500 at 0.6
1.	140	1900	103	4000 at 0.4	116	2200 at 0.8
485.	118	300	110	800 at 0.8	113	600 at 0.2

explosion severity index (relating to Pittsburgh coal data obtained with the same vessel

Vessel Size cu. ft.			
0.043	1	0.869	3.32
.32	1	1.99	1.09
1.	1	1.54	0.96
485.	1	2.48	1.91

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3.2.5 Comments on Sample Preparation.

It was shown by several workers[5,7] that the particle size has a considerable influence on both the ignition sensitivity and explosion severity. Consequently, for the proper identification of the sample not only the approximate analysis and/or ultimate analysis should be given but the particle size distribution should also be determined.

According to the presently used procedure the sample is passed through a 200 mesh sieve and the percent of dust that passed through is stated. This is clearly not adequate. In order to properly identify the sample, a detailed particle size distribution should be required since the smallest particles will have the greatest influence on the explosion. It appears that the dust explosibility test results would be much more meaningful if both the humidity and the particle size distribution would deliberately be set to specified values instead of just recording what those numbers happen to be.

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INTRODUCTION

Retorting may be defined as the heating or decomposing of the organic content of a material into recoverable hydrocarbons. Green River oil shale is a fine-grained sedimentary rock which consists of a mixture of solid organic matter (called kerogen) and inorganic matter such as dolomite, calcite, quartz, clay, and other minerals. It is the kerogen content of oil shale that decomposes when retorted, while most of the inorganic rock minerals are unaffected by the relatively low temperature (425 to 550°C) needed for the rapid pyrolysis of kerogen.

Methods for retorting oil shale may be separated into two broad categories:

- Surface retorting of mined oil shale.
- In situ retorting of fractured, leached, or rubblized oil shale.

Retorts for mined shale may be grouped into three basic types:

- Direct Heating By Combustion - heat for pyrolysis is supplied by controlled combustion within the retort. This is accomplished by controlling the amount of air admitted to the retort to supply oxygen for the combustion reaction. Retorted vapors and combustion flue gases are withdrawn from the retort, and then are cooled and separated for hydrocarbon recovery.

- Indirect Heating Using Recycle Gas - uses an externally heated recycle gas to supply heat for pyrolysis, thus eliminating combustion within the retort. No air is added to the retort, consequently the by-product gas is a high-Btu gas suitable for upgrading into pipeline quality gas.

- Indirect Heating Using A Solid Heat Carrier - a solid heat carrier (usually spent shale or ceramic balls) is recycled to the retort after being externally heated. By intimate solid-to-solid heat transfer, the kerogen is recovered as high-Btu gas and raw shale oil.

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SURFACE RETORTING PROCESSES

A number of proposed surface retorting methods have been developed to various stages in anticipation of a commercial oil shale industry. Presented below is a brief summary of these methods now in use or currently being developed.

DIRECT HEATING PROCESSES

Paraho Gas Combustion Process

A group of seventeen private companies, led by Standard Oil of Ohio and Development Engineering, Inc., are currently developing an improved version of the gas combustion process, referred to as the Paraho Process. This development is an outgrowth of work on the Gas Combustion Process carried out in 1945-1955 by the U. S. Bureau of Mines at Anvil Points, Colorado. A sketch of this process is presented in Figure 1.

Important features of the Paraho process are:

- Retort is a vertical kiln through which shale flows downward in contact with a rising gas stream.

- Retort is divided into four zones.
  1. Shale preheat zone,
  2. Retorting zone,
  3. Spent shale combustion zone, and
  4. Spent shale ash cooling zone.

- Oil is separated as a mist from combustion gases, and part of the gas is recycled back to the retort.

- Products are a low-Btu (100 Btu/scf) product gas, shale oil, and spent shale ash.

- Developments by the Paraho group include:
  1. Improved shale distributor at the top of the retort,
  2. Improved discharge grate to control the flow pattern of solids, and
  3. An improved gas distributor.

- Process is limited to shale feed size of 1/2 to 3 inches.

Union Oil Process (Type A)

This gas combustion process, as shown by Figure 2, has been developed by Union Oil Company of California since operation of a 1200 ton-per-day demonstration plant in the mid-1950's.
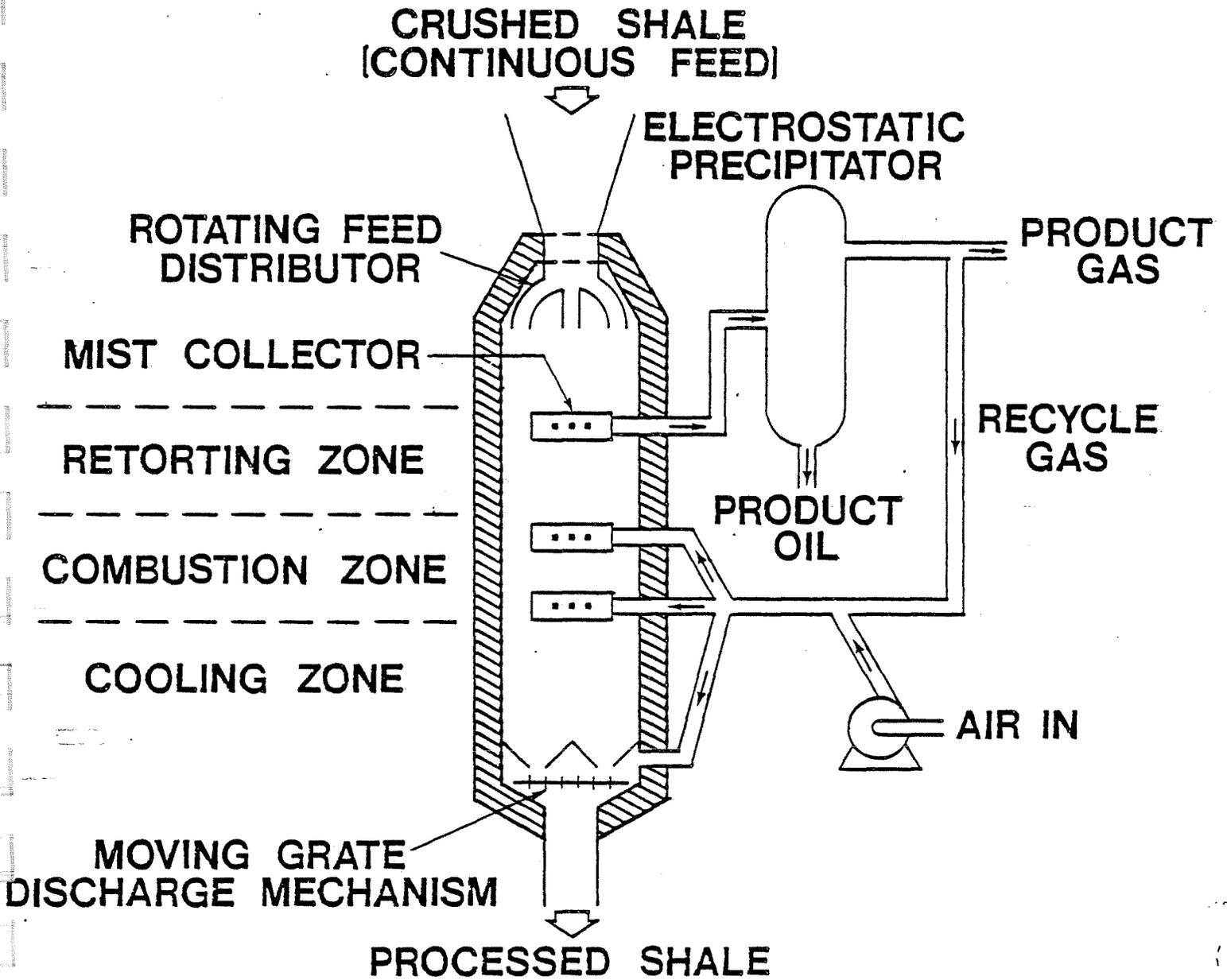
FIGURE 1

PARAHO GAS COMBUSTION PROCESS

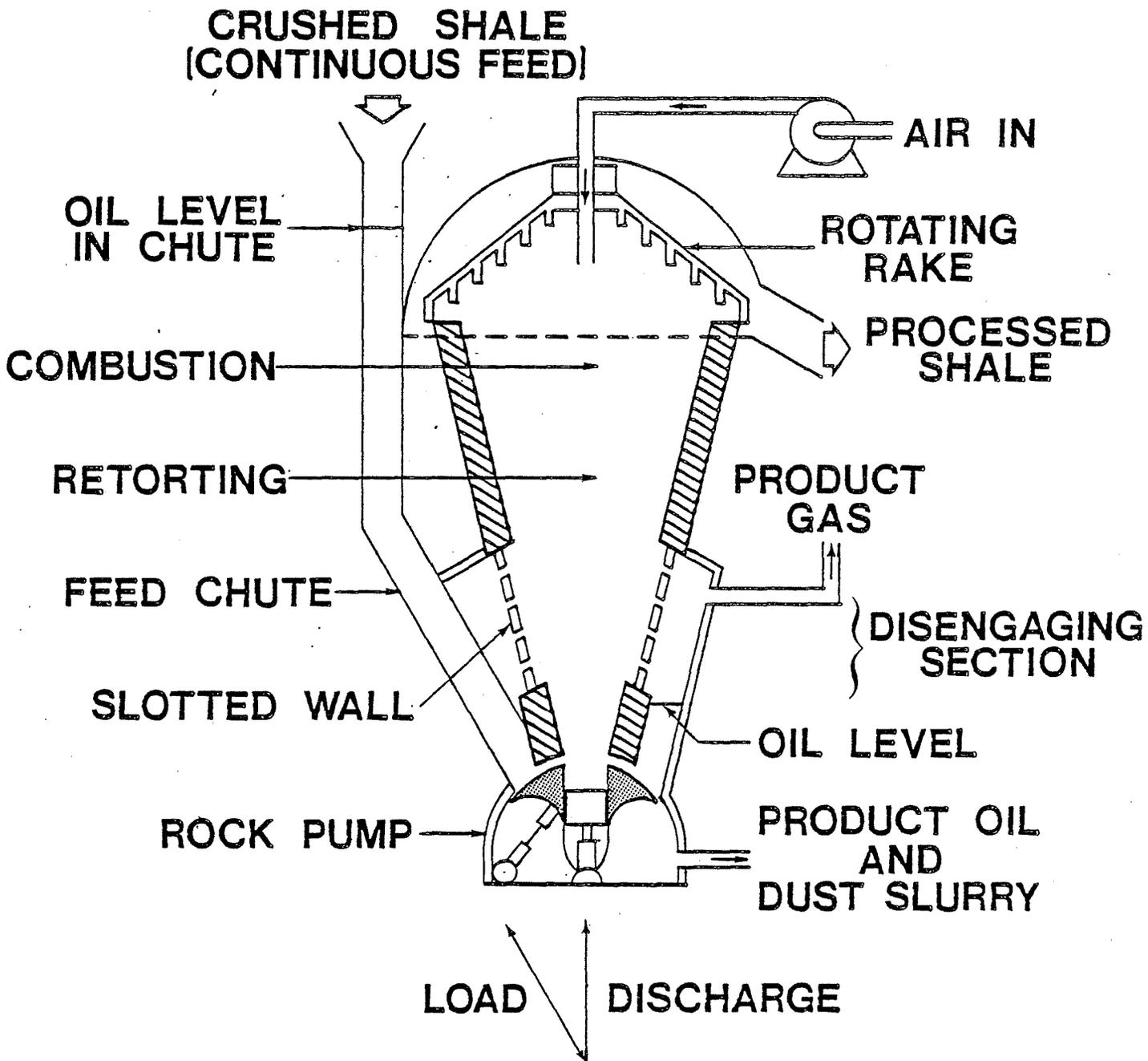CRUSHED SHALE
[CONTINUOUS FEED]

ELECTROSTATIC
PRECIPITATOR

ROTATING FEED
DISTRIBUTOR

PRODUCT
GAS

MIST COLLECTOR

RECYCLE
GAS

RETORTING ZONE

PRODUCT
OIL

COMBUSTION ZONE

COOLING ZONE

AIR IN

MOVING GRATE
DISCHARGE MECHANISM

PROCESSED SHALE

FIGURE 2

UNION GAS COMBUSTION PROCESS

CRUSHED SHALE
(CONTINUOUS FEED)

AIR IN

OIL LEVEL
IN CHUTE

ROTATING
RAKE

PROCESSED
SHALE

COMBUSTION

RETORTING

PRODUCT
GAS

FEED CHUTE

DISENGAGING
SECTION

SLOTTED WALL

OIL LEVEL

ROCK PUMP

PRODUCT OIL
AND
DUST SLURRY

LOAD   DISCHARGE

Highlights of the Union Process are:

- The vertical kiln retort is fed by an oscillating piston-type "rock pump" which forces solids upward through the retort.
- Retort gases flow downward countercurrent to shale flow, and oil mist and combustion flue gases exit the bottom of the retort.
- Carbon is burned from the spent shale when gas combustion occurs.
- Fines cannot be included in the retort feed.
- Products are a low Btu gas, full-range shale oil, and spent shale ash.

Kiviter Process

The Kiviter Process is similar in principles of operation to the gravity flow gas combustion retort developed by the Bureau of Mines except that the Kiviter retort includes a special preheating section near the top of the retort. The Kiviter retort processes shale feed in the size range of 1 to 5 inches, and cannot accept fines. The Russians are constructing a 1000 metric ton-per-day unit using this type of retort in Estonia. Figure 3 shows the basic features of the Kiviter retort.

INDIRECT HEATING USING RECYCLE GAS

Petrosix Process

Petrobras, the Brazilian national oil company, is developing an indirectly heated retorting process referred to as the Petrosix Process, shown by Figure 4. Important features of the Petrosix retort are:

- Retort is a vertical kiln equipped with a shale distributor at the top and a discharge grate at the bottom.

- Shale flows vertically downward through hot gases recycled from retort products and externally heated in in a tubular fired heater. Carbon is not burned from the spent shale.

- Oil is removed as a mist along with the recycle gas from the top of the retort.
- Fines cannot be handled by this type of retort.
- Products are a high-Btu gas, full range shale oil, and spent shale.
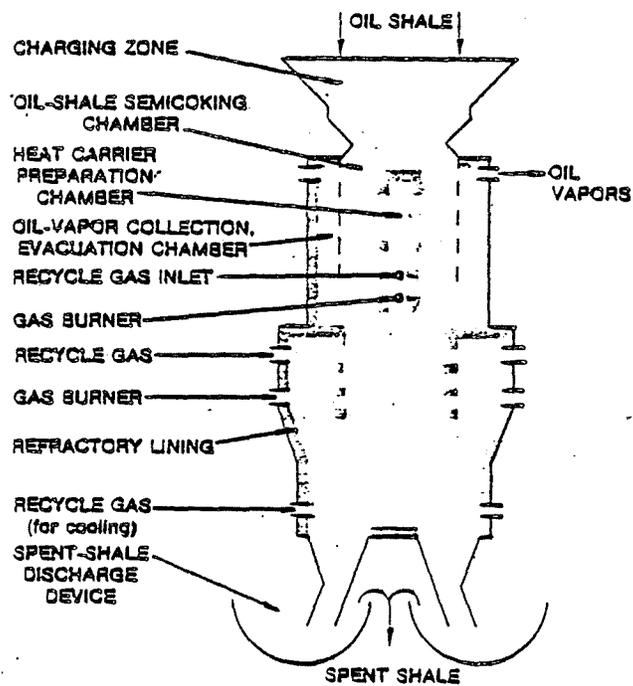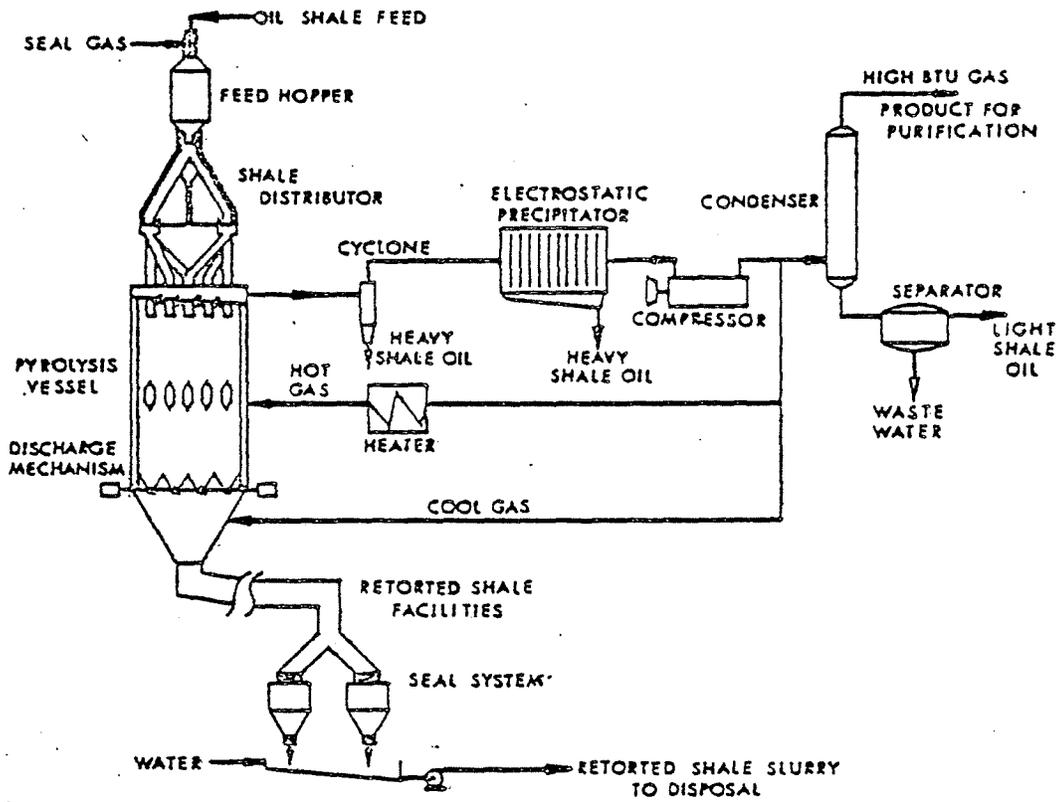
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FIGURE 3

KIVITER PROCESS

Diagram labels, top to bottom along the left side:
CHARGING ZONE
OIL-SHALE SEMICOKING CHAMBER
HEAT CARRIER PREPARATION CHAMBER
OIL-VAPOR COLLECTION, EVACUATION CHAMBER
RECYCLE GAS INLET
GAS BURNER
RECYCLE GAS
GAS BURNER
REFRACTORY LINING
RECYCLE GAS (for cooling)
SPENT-SHALE DISCHARGE DEVICE

Top label: OIL SHALE
Right label: OIL VAPORS
Bottom label: SPENT SHALE

FIGURE 4

PETROSIX PROCESS

SEAL GAS — OIL SHALE FEED

FEED HOPPER

SHALE DISTRIBUTOR

CYCLONE

ELECTROSTATIC PRECIPITATOR

CONDENSER

HIGH BTU GAS PRODUCT FOR PURIFICATION

COMPRESSOR

SEPARATOR

LIGHT SHALE OIL

PYROLYSIS VESSEL

HOT GAS

HEAVY SHALE OIL

HEAVY SHALE OIL

WASTE WATER

DISCHARGE MECHANISM

HEATER

COOL GAS

RETORTED SHALE FACILITIES

SEAL SYSTEM

WATER — RETORTED SHALE SLURRY TO DISPOSAL

Union Oil Process (Type B)

The Union Oil Company is developing their rock pump retort to utilize externally heated recycle gases rather than heat from combustion within the retort to provide pyrolysis heat. A high-Btu gas is produced as a by-product and the carbon content of the spent shale is not utilized. The Union Recycle Gas Process is presented in Figure 5.

Union Oil Process (Type SGR)

The Union Oil Company's Steam Gas Recirculation Process, as shown by Figure 6, burns the spent shale carbon residue in a separate combustor vessel and uses the hot combustor flue gas to reheat the recycled retort gases and generate steam.

Paraho Recycle Gas Process

The Paraho group is developing the recycle gas mode of their retort, and operating principles are similar to the Petro-six retort. The basic features of this process are illustrated in Figure 7.

Superior Oil Process

The Superior Oil Company is developing a process utilizing a traveling circular grate retort adapted from equipment utilized in iron ore pelletizing. A sketch of the Superior retorting process is illustrated in Figure 8.(1) Highlights of the process are:

- Retort is a traveling circular grate.
- The process benefits from recovery of both the mineral content (dawsonite and nacohlite) of the oil shale as well as recovery of the shale oil.
- Heat for retorting is supplied by either gas combustion or recycle of hot gases into the hooded retort zone.
- Products are a full range shale oil, recovered nacohlite and dawsonite, and either a high or low-Btu gas.

(1) U.S. Patent 3325395, Figure 1, January 13, 1967.

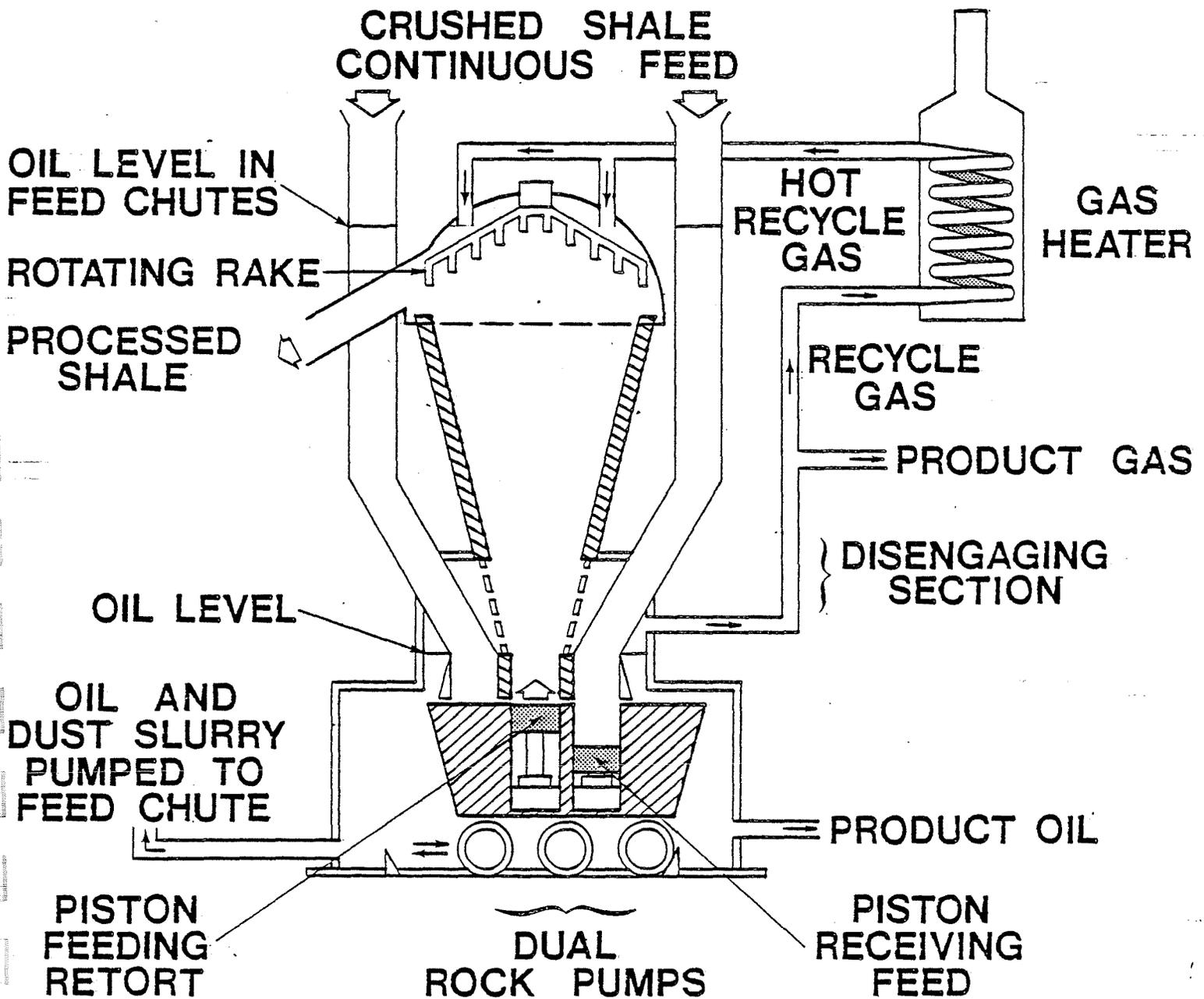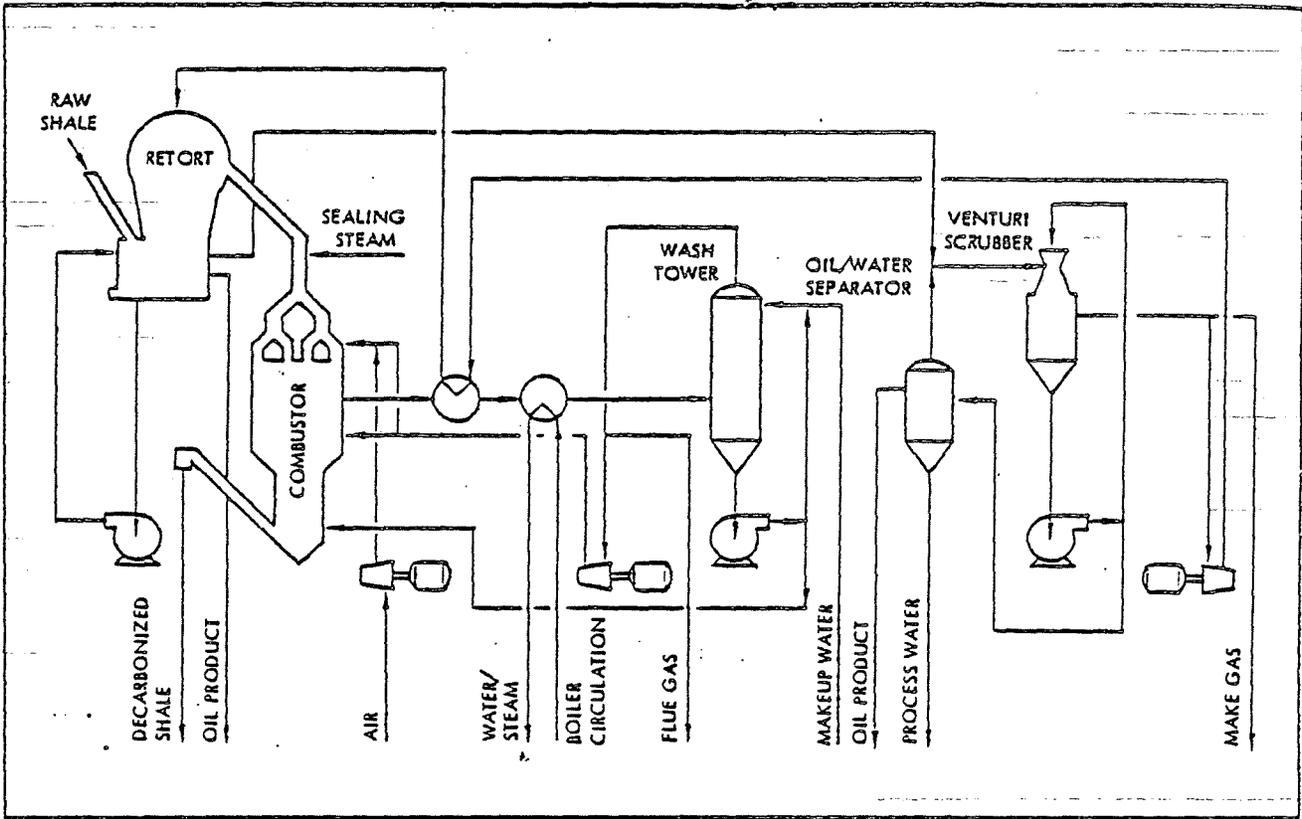FIGURE 5

UNION RECYCLE GAS PROCESS

CRUSHED SHALE
CONTINUOUS FEED

OIL LEVEL IN
FEED CHUTES

ROTATING RAKE

PROCESSED
SHALE

HOT
RECYCLE
GAS

GAS
HEATER

RECYCLE
GAS

PRODUCT GAS

DISENGAGING
SECTION

OIL LEVEL

OIL AND
DUST SLURRY
PUMPED TO
FEED CHUTE

PRODUCT OIL

PISTON
FEEDING
RETORT

DUAL
ROCK PUMPS

PISTON
RECEIVING
FEED

FIGURE 6

UNION SGR PROCESS

FIGURE 7

PARAHO RECYCLE GAS PROCESS

CRUSHED SHALE
CONTINUOUS FEED

ELECTROSTATIC
PRECIPITATOR

ROTATING FEED
DISTRIBUTOR

PRODUCT
GAS

MIST COLLECTOR

GAS
HEATER

RETORTING ZONE

PRODUCT
OIL

HEATED
RECYCLE GAS

COOLING ZONE

COOL RECYCLE GAS

MOVING GRATE
DISCHARGE MECHANISM
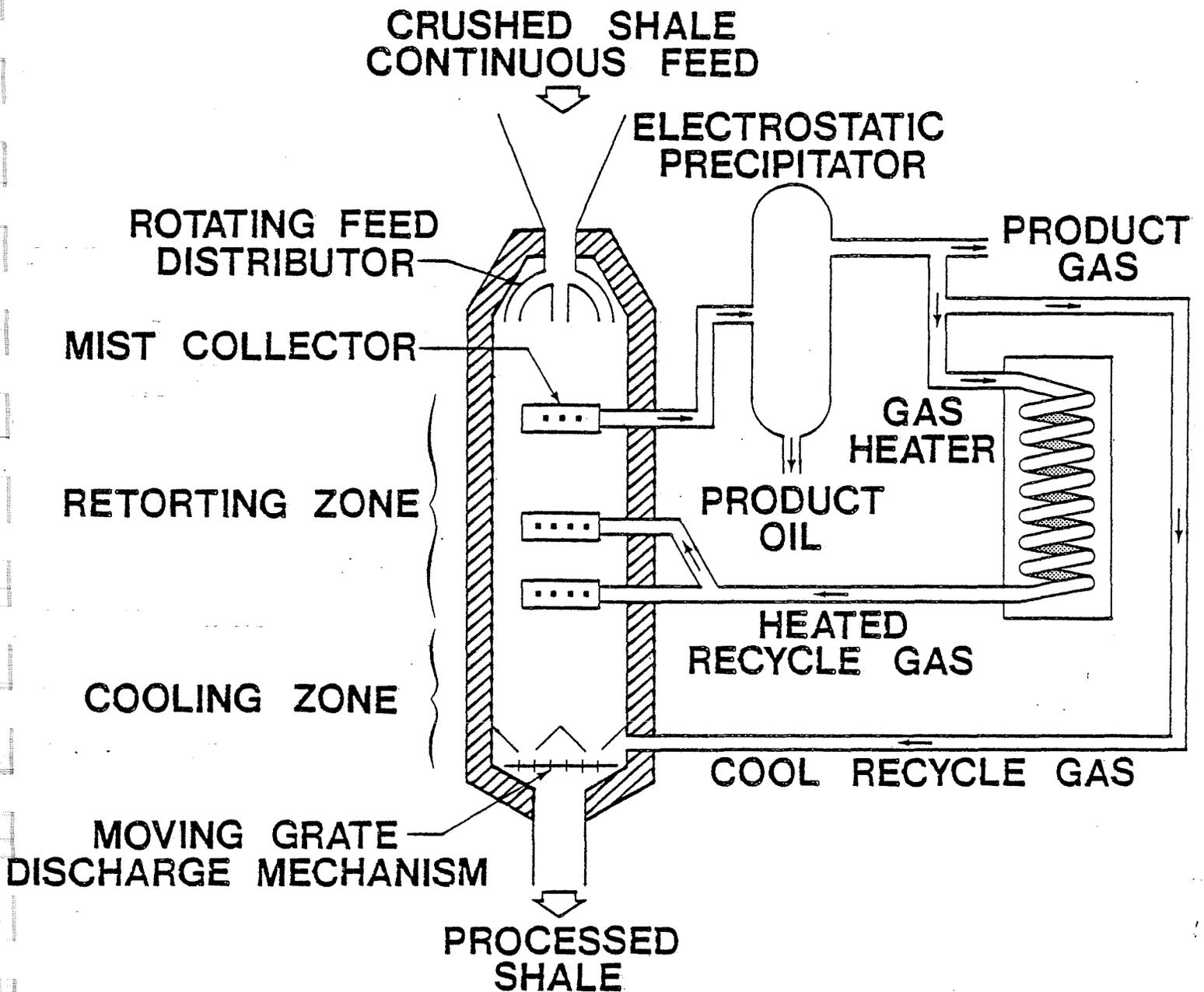
PROCESSED
SHALE

FIGURE 8

SUPERIOR PROCESS

FIRST ZONE — SECOND ZONE

AIR 1025 $^T/_D$

VENT 1520 $^T/_D$

1500°F — 1000°F

RAW FEED 5000 $^T/_D$

45 MIN. — 45 MIN.

1332.5 FT.² — 1332.5 FT.²

SPENT SHALE 3905 $^T/_D$

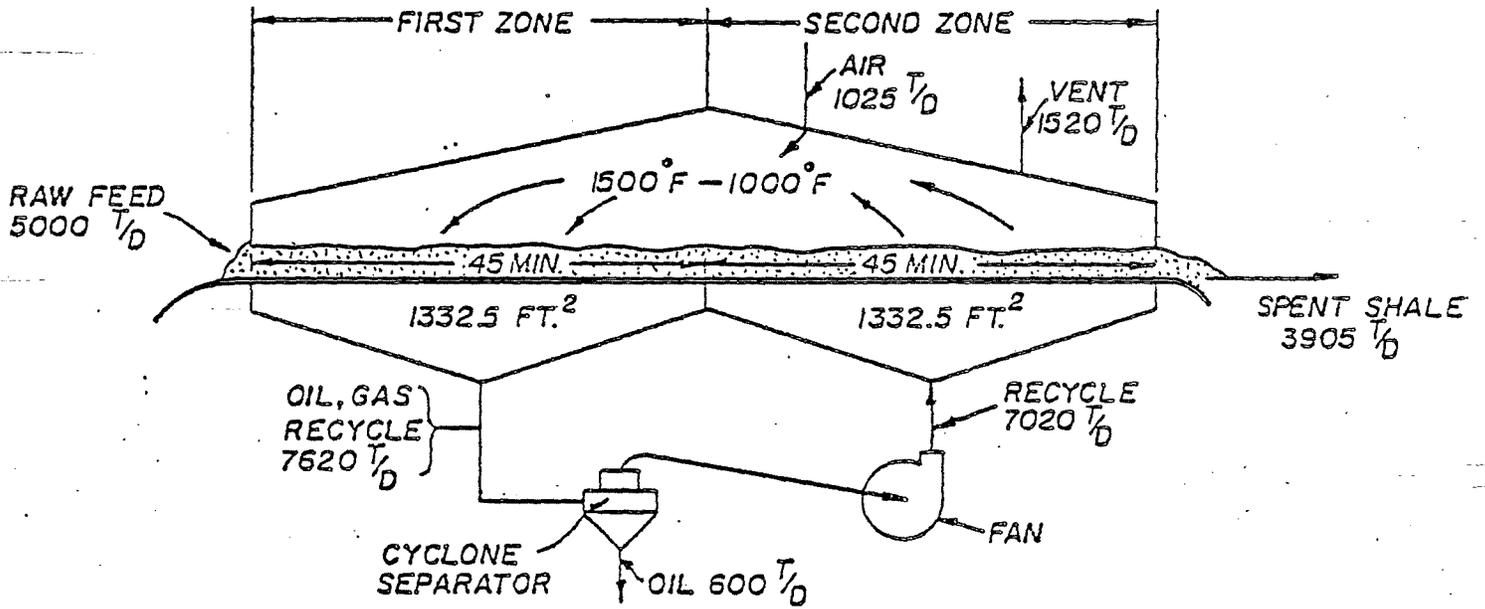OIL, GAS RECYCLE 7620 $^T/_D$

RECYCLE 7020 $^T/_D$

FAN

CYCLONE SEPARATOR

OIL 600 $^T/_D$

INDIRECT HEATING USING A SOLID HEAT CARRIER

TOSCO II Process

The TOSCO II Process, as shown in Figure 9, has been in development by Tosco Corporation since the mid-1950's, and has been successfully demonstrated at a 1000 ton-per-day semi-works plant near Grand Valley, Colorado.

Highlights of the TOSCO II process are:

- The retorting vessel is a rotary drum operated under positive pressure to prevent combustion with air from occurring in the retort.

- The heat-carrying medium for transfer of pyrolysis heat is a circulating load of ceramic balls heated in a separate furnace.

- Minus 1/2-inch shale feed, including fines, is pre-heated in a dilute-phase fluidized lift pipe system using heat from the ball heater flue gases.

- The balls are separated from the pyrolysis vapors and spent shale by a perforated rotating cylinder called a trommel.

- Carbon is not burned from the spent shale.

- Pyrolysis vapors exit the retort through a cyclone and are cooled and separated into a high-Btu gas and several distillation cuts of shale oil products.

Lurgi-Ruhrgas Process

The Lurgi-Ruhrgas Process, illustrated by Figure 10, was developed by the Germans in the 1950's for low-temperature carbonization of sub-bituminous coal. Processing of Colorado oil shale has been tested in a 25 ton-per-day pilot plant.

Important features of the Lurgi-Ruhrgas process include:

- Retorting occurs by mixing shale with hot carrier solids in a sealed screw-type conveyor.

- Pyrolysis heat is derived from a circulating stream of sand or spent shale which is heated in a dilute-phase lift pipe by burning carbon from the spent shale.

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● Retort products are a high-Btu gas, a full range shale oil, and spent shale ash.

Galoter Process

The Galoter Process (also known as the UTT Process) is a surface retorting process developed by the Russians that utilizes hot spent shale ash as the solid carrier to provide pyrolysis heat. A process sketch is shown in Figure 11. Highlights of the process are:

● Shale is preheated by utilizing low level heat from the flue gas generated by burning the carbon from the spent shale.

● Preheated shale and hot ash are retorted in a rotating drum.

● Spent shale is burned in an air-blown firebox and the hot ash is separated from the flue gas in cyclones before being recirculated to the retort.

● High level heat from the hot burner flue gas is used to generate steam.

● Process prefers 1/8 to 1/4-inch shale feed size, although the retort can accept fines.

● Retorting temperature may vary from 500°C to maximize production of liquid shale oils, to 800°C to favor retort gas production.

RETORT PRODUCTS

Although gas and solid products from the surface retorting of oil shale differ depending on which process is used, the condensed shale oil liquid products are very similar in terms of gravity and composition. Table 1 illustrates the approximate oil properties from the Union Oil, Paraho, and TOSCO II Processes.

Gas and solids product composition vary due to the following process differences:

● Light hydrocarbon product vapors from pyrolysis may be diluted with combustion flue gases in the direct-fired gas combustion process or yielded as a high-Btu gas product in the recycle gas or solid heat carrier processes.

TABLE 1

Shale Oil Properties

	Union A[2,3]	Paraho[4,5]	TOSCO II[6,7]
Inspections			
API Gravity	19.7	19.3	21
Specific Gravity	0.936	0.9383	0.928
Sulfur, Wt%	1.0	0.61	0.7
Nitrogen, Wt%	1.8	2.2	1.9
Pour Point, °F	85	85	25(8)
Carbon Residue, Wt%	5.6	1.4	4.6
Distillation, Volume %			
Naphtha (IBP-392°F)	2.7	1.3	18
Light Distillate (392-595°F)	14.3	18.8	20
Heavy Distillate (595°-807°F)	34.7	26.7	28
Residuum	48.0	53.1	34 (calc)
Loss	0.3	0.1	

(2) Stevens, R.F. et al, Analysis of Crude Shale Oil, USBM RI 4898, 1952.

(3) Hartley, F.L., Oil Shale: Another Source of Oil for the United States, Oil Daily's Third Annual Synthetic Energy Forum, 1974.

(4) Applied Systems Corp. for Office of Naval Research, Executive Summary Report, The Production and Refining of 10,000 Barrels of Crude Shale Oil into Military Fuels, 1975.

(5) Cameron Engineers Inc., Synthetic Fuels Quarterly Report, Vol. 13, No. 2, June 1976.

(6) Whitcombe, J.A., and Vawter, R.G., The TOSCO II Oil Shale Process, 79th National Meeting, AIChE, March 16-20, 1975.

(7) Cameron Engineers, Synthetic Fuels Data Handbook, 1975.

(8) After mild heat treatment, U.S. Patent 3,284,336.

FIGURE 11

GALOTER PROCESS

NOTE: TOTAL CAPACITY IS 3,750 TONS/DAY
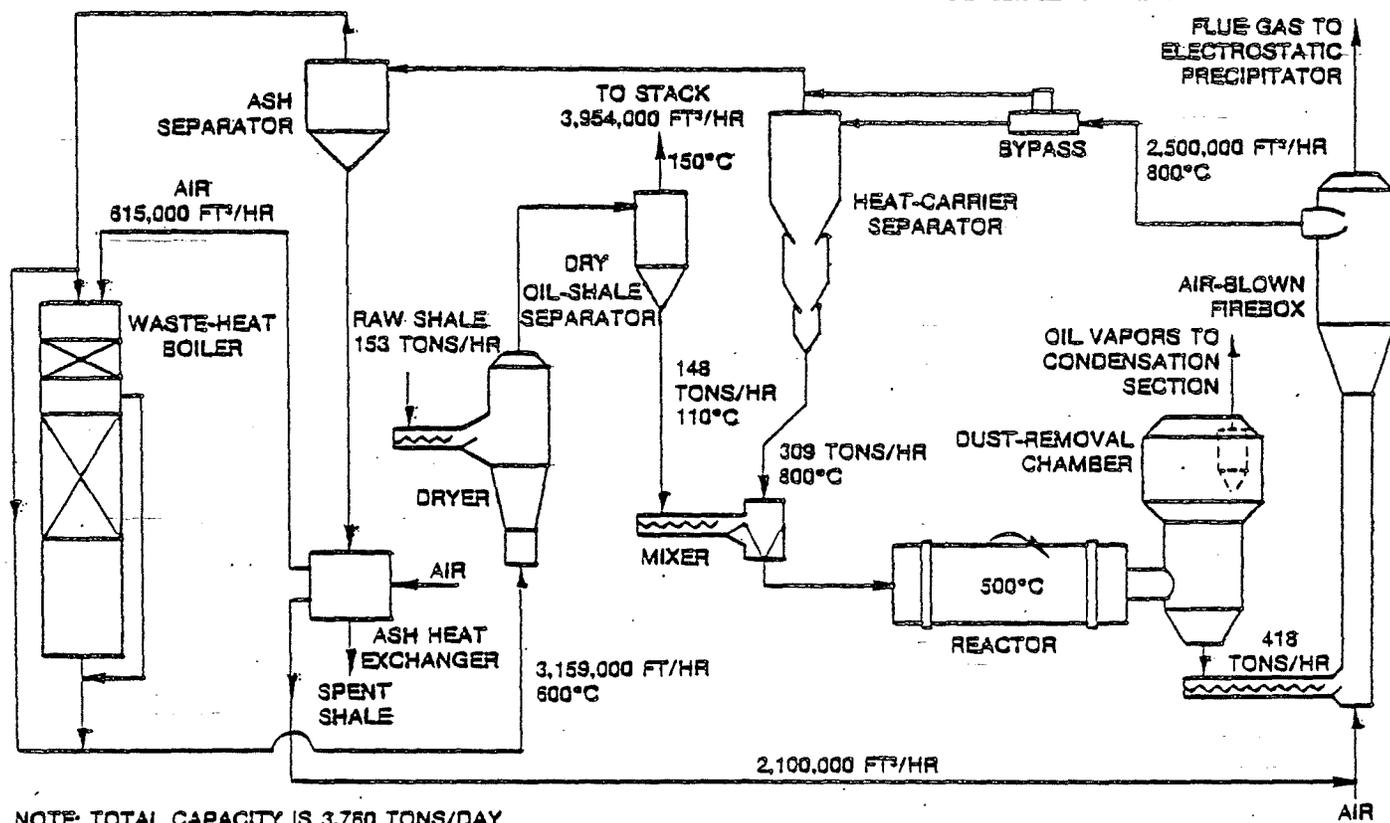
- Spent shale product contains unburned carbon in the TOSCO II or recycle gas processes, or is a relatively carbon-free ash product in the gas combustion or Lurgi-Ruhrgas processes. Also, spent shale particle size is significantly smaller for the TOSCO II spent shale (0.007 cm geometric mean particle diameter) than for the other processes, such as the gas combustion process (0.205 cm geometric mean diameter) (9).

Product composition for the high-Btu gas from the TOSCO II Process and low-Btu gas from the Union Gas Combustion Process are given in Table 2. Table 3 shows the composition of the TOSCO II spent shale.

(9) Synthetic Fuels Data Book, Cameron Engineers, 1975 Tables 82 and 80.