

DR. ARTHUR M. SQUIRES
RECIPIENT OF
1973 STORCH AWARD

THE HENRY H. STORCH AWARD

Friends of Dr. Henry H. Storch established the Award in 1964 as a memorial to him for his outstanding achievements as a physical chemist and a research director. Dr. Storch's major work involved fundamental research on the chemistry of coal and on engineering studies of coal utilization. Much of this work was accomplished while he was director of research at the U. S. Bureau of Mines from 1928 to 1951. The Award, administered by the Division of Fuel Chemistry, is given annually to a U. S. citizen who has contributed most to fundamental or engineering research on the chemistry and utilization of coal, or related materials, in the preceding five years. The Award consists of a plaque and an honorarium of \$100, which are presented at the Fall National Meeting of the American Chemical Society.

Biography

Arthur M. Squires is Professor and Chairman, the Chemical Engineering Department of the City College of the City University of New York. There he heads a fifteen-man research team working under a grant from the RANN Program (of the National Science Foundation) to convert coal into clean fuels.

Born in Neodesha, Kansas (March 21, 1916), he completed elementary and high school in Higginsville and Columbia, Missouri, respectively. In 1938, the University of Missouri granted him an A.B. with distinction in chemistry. In 1947, he obtained a Ph.D., in physical chemistry, under the late John Kirkwood at Cornell University.

Dr. Squires' interest in engineering was aroused during World War II through his association with Manson Benedict, now of M.I.T., whom he assisted in the process design of the Oak Ridge gaseous diffusion plant for concentrating Uranium-235. Subsequently he became Assistant Director (1946-1951) and Director (1951-1959) of Process Development at Hydrocarbon Research, Inc.,

where he worked on producing synthesis gas from natural gas, fuel oil, and coal. From 1959 to 1971, he served as a consultant to various chemical process industries. In 1967, Dr. Squires joined the faculty of Chemical Engineering, City College of the City University of New York as a full Professor; and in 1970 he was elected Chairman of the Department.

Dr. Squires holds sixteen U. S. patents dealing with fuel processing, gas cleaning, fluid-particle technology, and power generation; and he has published more than thirty papers in these fields.

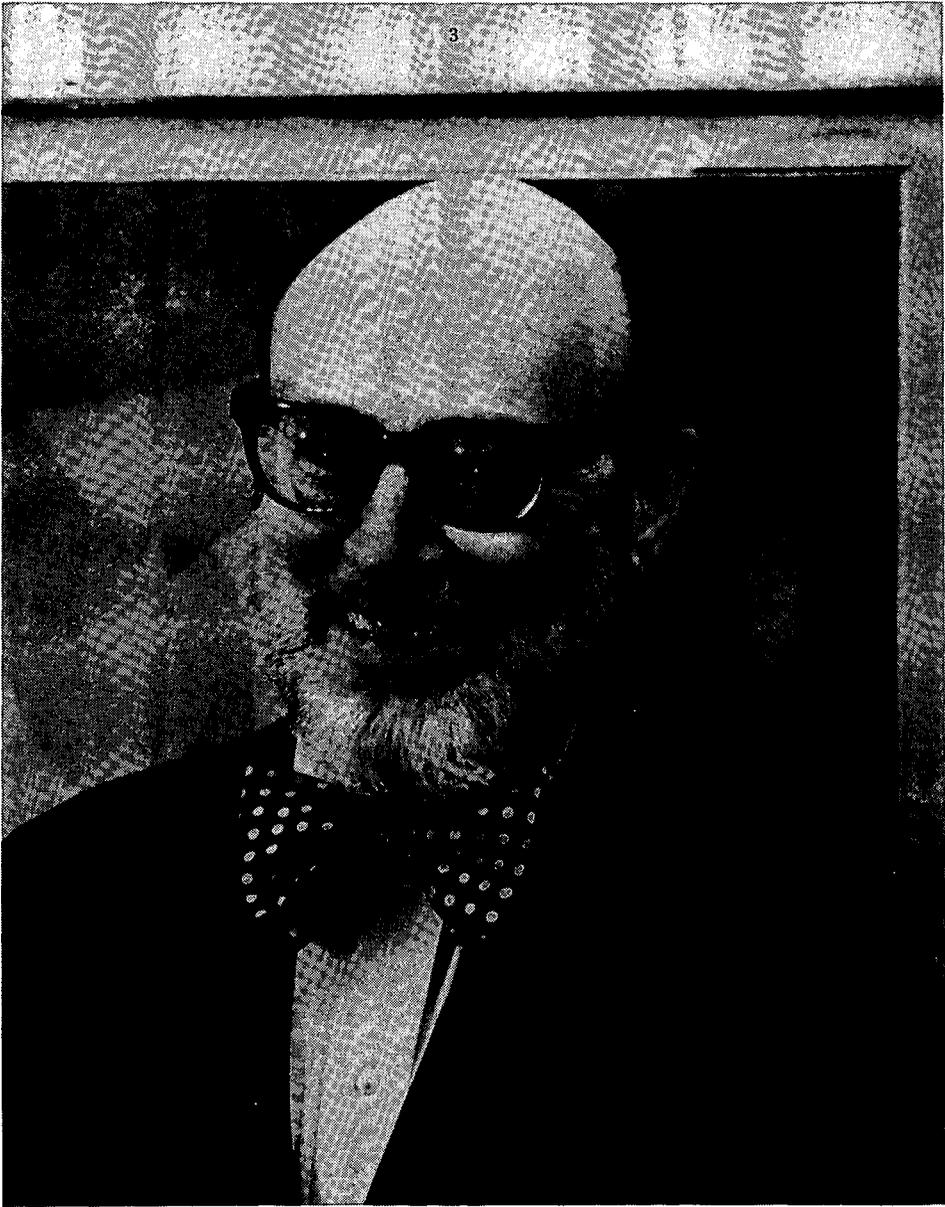
Dr. Squires is a member of various chemical and engineering societies, here and abroad, and is a Fellow of the American Association for Advancement of Science. Among his committee memberships are: Committee on Environmental Alteration, and Ad Hoc Committee of the American Society of Mechanical Engineers for Setting Goals for Energy Research.

For many years, Dr. Squires has had a deep interest in the arts, particularly music. He played a leading role in the formation of New York Pro Musica and is a member of its board of directors. He was a soloist for the group, and even now finds time for singing lessons. In addition, he plays the harpsichord for relaxation.

THE DIVISION OF FUEL CHEMISTRY
HENRY H. STORCH AWARD

Established 1964

Irving Wender	1964
Everett Gorin	1965
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Robert W. Van Dolah	1972
Arthur M. Squires	1973



Gasifying Coal in High-Velocity Fluidized Beds, Arthur M. Squires,
Department of Chemical Engineering, The City College of The City
University of New York, New York, New York 10031

Two distinct arts of fluidization arose independently from (1) Winkler's 1922 invention for gasifying crushed coal fluidized at about 15 ft/sec, and from (2) Lewis and Gilliland's discovery in 1938 that a bed of a fine catalyst remained "stationary" when fluidized at 1 ft/sec even though this was beyond the Stokes-Law settling velocity for the powder.

(1) Development of the first art led to processes treating crushed solids of natural origin; also, to agglomerating beds of two kinds: (a) accreting beds that produce dense beads, and (b) the Godel ash-agglomerating bed.

(2) Development of the second art led to higher velocities in both regenerator and cracking zone of the fluid cracker. Recently Lurgi has shown that a "fast fluidized bed" of a fine powder recirculating at 10 to 15 ft/sec displays good thermal communication between an exothermic zone near the bottom of a column and endothermicity elsewhere in the column.

Experiments and concepts for gasifying coal in fluidized beds will be reviewed in light of the two fluidized-bed arts. It appears that high-velocity beds will have many advantages for producing low-Btu gas to serve gas turbines in combined-cycle power systems.

SULFUR REMOVAL FROM HOT PRODUCER GAS

by

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INTRODUCTION

To obtain clean gas from coal, gasification and gas cleanup must be considered jointly in view of today's clean environment regulations. Much of the coal sulfur appears in the gas, and in addition, solid and tar particulates are present in concentrations that vary with the gasification process and coal composition. All gasification concepts undergoing development include some type of gas cleaning. Conventional practice could be followed using commercial equipment, but this requires gas cooling and scrubbing with liquid solutions. Disposal of liquid and solid wastes is required, and provision for recovering coal tar is necessary.

Low-Btu fuel gas for power generation is receiving serious consideration by the electric utilities because it offers a timely solution to the shortage of low-sulfur fuel. High-sulfur coals can be converted into gas and cleaned of sulfur before being burned for power generation. Commercialization of this practice will make large quantities of high-sulfur coal available for generating electricity. Probably the least complicated system for converting coal into low-Btu fuel gas is pressure gasification using mine-run coal which may have any free-swelling index from low to high and includes lignite.

Gasification in a fixed bed has been widely used commercially for over one hundred years and is still used today. Historically, the fixed-bed gas producer has required a feed of noncaking, lump-sized coal or coke. Recently, the Bureau of Mines at Morgantown, W. Va., has gasified many coals including strongly caking Pittsburgh seam (1),^{1/} high-volatile A bituminous (FSI 8-1/2), and coal 50 percent smaller than 1/4-inch screen size (run-of-mine) (2). These pioneering developments have demonstrated that deep, continuous stirring or agitation of the fuel bed is essential and beneficial to the gasification process. The bed stirring promotes gasification reactions and gas quality by breaking massive coke formations and maintaining permeability of the bed for better contact between gas and fuel. The stirring employed in this work is much more extensive than ever used previously, and it warrants being distinguished by being called the stirred fixed-bed, or simply the stirred bed to distinguish it from the conventional fixed bed.

^{1/} Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

The Morgantown Energy Research Center of the U.S. Bureau of Mines has evaluated many solid sorbents as an acceptor for hydrogen sulfide in hot producer gas. Results of those studies using simulated producer gas at 1,000° to 1,500° F have been reported in earlier papers (3)(4). This paper reports results obtained with a sintered iron oxide sorbent and gas from the stirred-bed producer.

EXPERIMENTAL

A mixture of iron oxide (hematite Fe_2O_3) and fly ash was the best sorbent found among more than thirty-two materials tested. Primary requirements were that the sorbent be readily available and relatively inexpensive, have reasonable sorption capacity and useful life, be easily regenerated for repeated use, and resist fusion or disintegration over the useful temperature range. Fly ash (as received) could be formed into a durable and regenerable sorbent, but its sorption capacity was improved by adding iron oxide, increasing the concentration to 36 percent from 15 percent originally present. Other oxides found in this fly ash but inactive included silica 35 percent, alumina 18 percent, and small percentages of oxides of calcium, magnesium, sodium, potassium, and titanium. Iron oxide concentrations greater than 40 percent were unsatisfactory because the bed fusion temperature was lowered and fusion took place during normal operations.

Pilot quantities of the fly ash-iron oxide sorbent were made by two catalyst manufacturers by mulling and extruding the mixture to form 1/4-inch-diameter cylinders with 1/4- to 3/8-inch lengths, which were then sintered to develop hardness. Mercury porosimeter measurements showed pore volume of one new sorbent was 0.36 cc per gram, but this decreased to 0.13 cc per gram and remained constant after 30 regenerations, as shown in figure 1. Surface area measured by nitrogen absorption ranged from 4.2 to 6.5 square meters per gram.

RESULTS AND DISCUSSION

Two sorption-regeneration cycles were completed, cleaning gas generated by the stirred-bed producer using Upper Freeport coal. Gas composition is given in figure 2. Gas from the producer was transferred to the sorbent bed at system pressure of 120 psig via a heated pipeline. Bed temperatures were controlled to give 1,100° and 1,200° F, and flow rates were adjusted to give gas hourly space velocities of 710 and 940, respectively. Hydrogen sulfide concentration averaged 380 grains per 100 scf, and the gas contained approximately 1/2 pound of dust, 1 pound of tar, and 5 pounds of steam per 1,000 scf. Figure 3 shows hydrogen sulfide in the gas leaving the sorbent bed had its concentration reduced to 10 and 20 grains per 100 scf and did not

increase until after six hours on steam. Removal was 95 percent and 97 percent effective with respect to hydrogen sulfide. Tar was not removed by the sorbent.

Data were obtained for cleaning the gas from Western Kentucky No. 9 coal using 820 hourly space velocity. Average H_2S concentrations in the feed gas were 588, 518, and 478 grains per 100 cubic feet and respective bed temperatures were 1,100°, 1,200°, and 1,300° F. Sorption capacity increased markedly as bed temperature increased. Figure 4 shows the grams of H_2S removed per gram of sorbent until concentration in gas leaving the bed reached 100 grains per 100 scf. The amount removed increased linearly between 1,100° and 1,300° F. Breakthrough was reached after approximately 4-1/2, 6, and 6-1/2 hours, respectively.

Reaction mechanism is chemisorption, whereby hydrogen sulfide diffuses throughout the sorbent and reacts with Fe_2O_3 forming FeS and FeS_2 . Analyzing the spent sorbent indicated the empirical composition was $FeS_{1.3}$. Iron oxide, Fe_2O_3 , was regenerated and the sulfur released as SO_2 by passing air or oxygen over the hot bed. With oxygen regeneration, the effluent gas was pure SO_2 until some oxygen passed through unreacted after regeneration was 90 percent complete.

CONCLUSIONS

Sintered sorbent made of iron oxide and fly ash is effective for removing hydrogen sulfide at temperature up to 1,500° F. Long life is indicated for this sorbent when used in a fixed bed. Its activity is good for the 1/4-inch-diameter extrusion, the only size for which data were obtained, but reduction in size should increase its activity.

REFERENCES

1. Lewis, P. S., A. J. Liberatore, and J. P. McGee. Strongly Caking Coal Gasified in a Stirred-Bed Producer. BuMines Rept. of Inv. 7644, 1972, 11 pp.
2. Shultz, F. G., and P. S. Lewis. Hot Sulfur Removal From Producer Gas. Proc., Third Internat. Conf. on Fluidized-Bed Combustion, Hueston Woods State Park, Ohio, Oct. 29-Nov. 1, 1972, 6 pp, 7 figs.
3. Shultz, F. G. Removal of Hydrogen Sulfide From Simulated Producer Gas at Elevated Temperatures and Pressures. Proc., Second Internat. Conf. on Fluidized-Bed Combustion, Hueston Woods State Park, Ohio, 1970, 6 pp, 3 figs.
4. Shultz, F. G., and J. S. Berber. Hydrogen Sulfide Removal from Hot Producer Gas with Sintered Absorbents. J. Air Poll. Cont. Assoc. 20, 93-97 (1970).

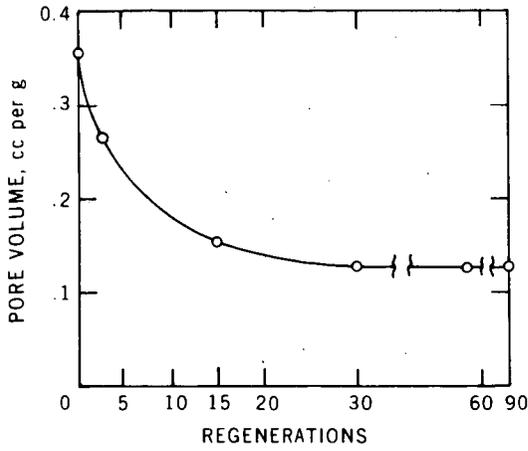


FIGURE 1. - Pore Volume Reaches Constant Value After 30 Regenerations

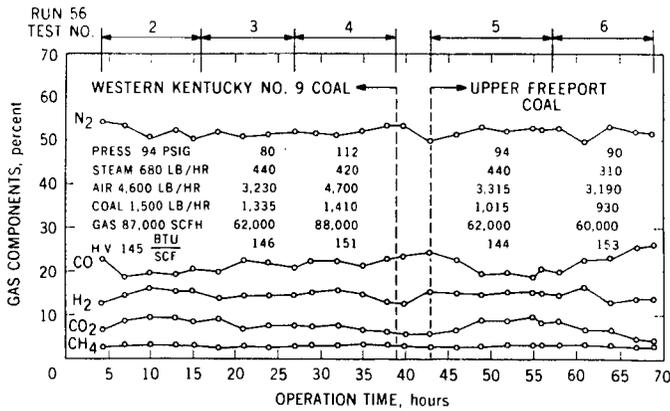


FIGURE 2. - Producer Gas Composition

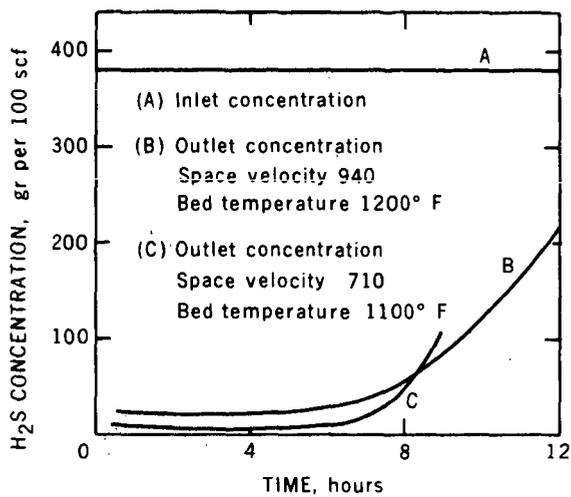


FIGURE 3. - Removing H₂S from Producer Gas

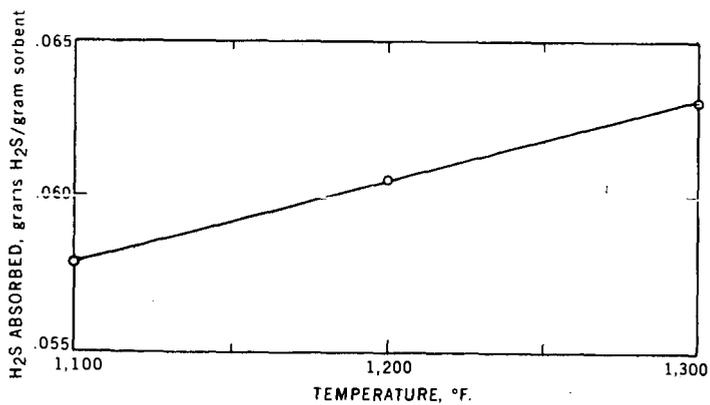


FIGURE 4. - Total H₂S Absorbed by an Fe₂O₃ Fly Ash Bed Until 100 grains/100 ft³ Breakthrough Occurred

The Panel Bed Filter for Simultaneous Removal of Dust and Sulfur, Kun-Chieh Lee, Robert Pfeffer, and Arthur M. Squires, Department of Chemical Engineering, The City College of The City University of New York, New York, New York 10031

An old idea is to treat a gas by causing it to flow in the horizontal direction across a bed of a granular solid disposed in a tall, narrow "panel". The bed may be held in place, for example, by louvered walls that resemble venetian blinds.

Efficiencies beyond 99.99% have been measured for removal of redispersed fly ash from air at normal temperature. After a test, fly ash filter cake and a controlled amount of filter solid are removed by applying a surge backflow of gas from the clean side of the panel.

The paper will discuss problems yet to be faced in scaling up the device to commercial size and in projecting its performance at high temperatures, where a reactive filter solid might be used to remove sulfur species as well as dust.

Coal for Peak Power

Henrik Harboe

STAL-LAVAL (Great Britain) Ltd.

In the ensuing debate about new forms of coal utilisation for power generation the attention has - often wrongly - been focused on mid load and base load plant but, it is most important also to look carefully at the problem of using coal for the generation of peak power.

Large variations in demand between night and day produce problems that the generating industry will always have to live with. This means that a lot of plant must be capable of stopping and starting once or twice in every day - with the associated need for changing the load of the installed capacity over large areas very rapidly. The giant-size base-load steam plants now being installed do not have these essentially flexible characteristics, and yet they will be required to meet such exacting duties if they - in the traditional way - are shifted down in the merit order as they get old. The alternatives are either to dissipate - during the night - some of the generated electricity as heat (seriously being put forward in some circles as the only practical, low-cost, method of dealing with the problem) or to tackle the overall question of reconciling generation method with load pattern.

One most effective course that can be adopted fills up the night time troughs in the demand curves by the introduction of power storage. Hydro-pumped power storage is an established technique that will soon reach the end of its limited exploitation potential and, quite naturally, it becomes more expensive as the less and less obvious sites are taken over and developed. An alternative method uses the storage of air under pressure, a technique that has not yet been exploited but which, because it will develop from known and tried techniques, shows excellent promise. Air storage power as such does not require large forward strides or jumps in technology, it is only a matter of marrying two known, experienced, branches of engineering: building and operating large industrial gas-turbines and the techniques of forming large underground caverns by mining, tunnelling, or leaching.

Up to 20% of the installed capacity of some power systems could in the future be air storage power and it is therefore necessary, already now, to look at the various possibilities for using coal as the primary fuel for such plant.

Fig. 1 shows by way of an example what can be achieved by employing a substantial amount of air storage power. Fig. 1a shows the 24 hour variation in electricity demand for a U.S. utility. The horizontal lines indicate the contribution of the various generating units on the system: several big units have to be turned down very severely every night and a large number of units have to be stopped and started every day.

By contrast has been shown on Fig. 1b the load pattern which the conventional plants would have to follow - the bold line - if 20% of the installed capacity was provided by six air storage units. These units would generate, on average, 8 hours per day. Assuming that our total installed capacity will increase fivefold between 1970 and year 2000, we see that air storage plants in year 2000 could represent as much capacity as we had installed in total in 1970 and the electrical energy generated by these plants could be well over half of our total 1970 production.

The principle of air storage power requires the use of gas-turbine equipment where the compressor(s) can be separately driven by an electric motor at such times as surplus, and therefore cheap, electricity supplies are available. Excess electricity production at night from ultra-large generating sets which must be run continuously and cannot be shut down or controlled on a divided-day basis is becoming very freely available and will become a serious "disposal problem" as nuclear plants proliferate. Air storage provides a use for this surplus production and a most economic method of using gas-turbines to cater for peak demands in day time.

During the day compressed air from storage is taken to the combustion chambers where it is heated up and then expanded through the turbine component to produce peak power. With this arrangement approximately three times as much day time output is available from an equal-capacity gas turbine installation than in the normal way - when two-thirds of the turbine output is needed to drive the compressor. Today, gas-turbines having 70 to 80 MW output are in routine production and use. It is a simple and straightforward matter to extend this to the construction of air storage units of 200 to 300 MW.

It is not the intention of this paper to draw comparisons between hydro-pumped storage power and air-storage power; such comparisons can only be made in specific cases where the authority concerned is fortunate enough to have a choice available in a given power system area.

This is an examination of air-storage power compared with conventional gas-turbines with and without steam turbines in combined-cycle installations. For these two main considerations there are the added

alternatives of fuelling by High-Btu gas and Low-Btu gas derived from coal. As a major consideration, these two fuels are compared with the direct combustion of coal in a fluidised-bed air heater operating in conjunction with air-storage plant.

The need to improve the efficiency of open cycle gas-turbines and combined cycle units is forcing designers of gas-turbines to strive for inlet temperatures of well over 2000 °F. In turn, this demands a clean fuel and we see how - with coal as the main fossil fuel - this has led to all the interest in coal gasification and low-Btu gas in particular.

Although an air-storage plant is basically a gas-turbine - albeit used in a very special way - there is not the same demand for very high turbine inlet temperatures. An economical analysis - which is not gone into here - shows that it is more rewarding to go to high storage pressures. Since a very high turbine inlet temperature is not a prerequisite for a good air-storage plant it has been natural to study the possibility of using coal fired fluidised bed air heaters instead of going the detour around coal gasification.

The simplest form of gas-turbine combined with a fluidised-bed heater is seen in Fig. 2. The air from the compressor is divided into two streams: primary combustion air, about 30 per cent of the total, goes through the bed, providing 10 to 20 per cent excess air for the combustion. This leaves the bed at 1600 °F (870 °C) after which it passes through two stages of cyclone separation.

Secondary air is passed through a closed-tube bundle immersed in the bed and is heated to 1427 °F. (775 °C); this bed-cooling air is mixed with the cyclone-separated air before entering the turbine at an average temperature of 1472 °F (800 °C).

By today's standard 1472 °F is a very conservative inlet temperature, but at a bed temperature of 1600 °F fluidised bed combustors have optimum performance: maximum sulphur removal by absorption into limestone or dolomite fuel additives, low vapour pressure of the alkali component in the ash and no melting of the ash. At this temperature the formation of nitrous oxides is low and particularly so when the combustion takes place under pressure as in this proposal.

This concept of a coal burning gas turbine is radically different from previous attempts to burn coal in gas-turbines. Firstly the feed consists of crushed coal in pea-sized lumps of which only a small amount is inadvertently reduced to dust. Previously, all the fuel was pulverised specially and expensively. There is now, therefore, a much smaller amount of airborne particles to be separated from

the exhaust gases before these are passed to the turbine. It is also of importance that these particles have not been sintered whereas, previously, all fuel passed through the intensely hot high-temperature combustion zone, where all the ash was sintered and became highly abrasive, before being cooled by dilution air. Thirdly there is not now a corrosion problem superimposed on the erosion problem since, due to the lower temperature, the vapour pressure of the alkali component of coal ash in a fluidised bed is only a small fraction of that in conventional combustion systems. The cyclones, finally, have to deal with only one third of the mass flow compared with previous systems.

For air storage plant, where the air compression is done separately during the night, the specific fuel consumption during the day is barely influenced by the turbine inlet temperature - with reasonable preheating of the air from the storage cavern it will be around 4600 Btu/kWh.

A proposal for an air storage plant incorporating a pressurised fluidised bed air heater is shown on Fig. 3. If a storage pressure as high as 50 atmosphere is used it is natural to introduce reheat and let the actual combustion take place at about 10-12 atmosphere pressure. All the cold air from the storage cavern is preheated in an exhaust heat recuperator, it then passes through a high pressure tube bundle in one section of the fluidised bed where it is heated and subsequently expanded through a high-pressure air turbine. After the H.P. turbine the air is divided in two flows, as in the simple gas-turbine arrangement, with one stream going through cooling tubes to be reheated before joining the exhaust gases and expanded through the low-pressure turbine.

The air mass flow of this proposed 260 MW reheat air storage plant corresponds to the mass flow of a 70 MW conventional gas-turbine now in production. This gives an idea of how much more the hardware is utilised in an air storage arrangement.

In the following, very coarse, comparison of the cost of an air-storage-fluidised bed-air-heater with other alternatives is made a number of assumptions and the results are shown in a diagram, Fig. 4 :

- capital cost of gas turbines	\$ 100/kW
- capital cost of combined cycle	\$ 135/kW
- capital cost of air storage plant:	
"above ground"	\$ 75/kW
storage cavern: "0" hour/day	\$ 25/kW
12 " /day	\$ 65/kW

- capital cost of high-Btu gas plant supplying a generating station which uses 10,000 Btu/kWh \$ 250/kW
- capital cost of low-Btu gas plant supplying a generating station which uses 10,000 Btu/kWh \$ 125/kW
- The capital cost of fluidised bed air heaters have been studied in some depth and the best estimate now is that a fluidised bed air heater with all coal and ash handling facilities will add \$ 40/kW to the cost of a 260 MW reheat air storage plant.
- gas turbine efficiency (for late 1970's) 35%
- combined cycle efficiency 46%
- efficiency of high-Btu gas plant 70%
- efficiency of low-Btu gas plant 85%
- cost of coal 40 cent/MBtu
- capital charges 15%
- Operating costs for air storage plant can be divided into two parts:-
 - (a) The cost of night time energy supplies. With a night/day energy ratio of 0.66 (i.e. 0.66 kWh spent for compression of air for each 1 kWh generated during the day), and an assumed marginal fuel consumption for base load plants during the night of 9000 Btu /kWh, the cost for night night energy is 6000 Btu/kWh x the specific fuel cost. For simplicity it is considered that night time supplies of energy would at present come from coal-fired stations. Eventually, when night time energy is provided by nuclear plants, operating costs will be reduced still further - and make air storage even more competitive.
 - (b) The cost of fuel used during the day. The direct day time fuel consumption - also called the in situ fuel consumption - can be 4600 Btu/kWh.

Therefore, $a + b = 6000 + 4600 = 10,600$ Btu/kWh, which is the total primary fuel consumption needed by an air storage plant using a fluidised-bed air heater. This is the fuel consumption which is used here as the reference value for all comparisons.

- variations in fuel consumption for different alternatives are converted to capital cost equivalent so that all comparisons can be done on capital cost diagrams alone. This is possible when the same initial fuel is used throughout.
- high-Btu gas will be produced on a continuous basis in large plants and stored for use intermittently by peak power plants. Therefore the capital cost for gas making plant is taken in proportion to the number of hours per day - out of 24 - which the peak load plant is intended to operate.
- low-Btu gas will be produced at power station site when needed, partly because it is "bulky" and partly to avoid the losses in cooling it down for storage. Designers of low-Btu gas plants should note that such plant will be required to stop and start every day!

The specific capital cost figures used in Fig. 4 to correct for variations in primary (i.e. coal) fuel consumption has been worked out in the following tables: I, II and III. 12 hours per day is used as reference time (12 hours per day during 11 month corresponds to 4000 hours per year). At zero hours per day there is of course no adjustment.

Table I

Air Storage

		Fluidised Bed *	High-Btu Gas	Low-Btu Gas
Indirect night fuel, Btu/kWh		6000	6000	6000
Primary day fuel, - " -		4600	6600	5400
Total	Btu/kWh	10600	12600	11400
Variation	- " -	Datum	+2000	+ 800
\$/kW at 4000 h/year (12h/day)		Datum	+ 21	+ 9

* Or natural gas or oil as fuel in conventional combustion chambers.

Table IIGas Turbine (Secondary fuel consumption 9750 Btu/kWh)

	Primary fuel consumption Btu/kWh	Compared with Air Storage Btu/kWh	\$/kW at 4000 h/year
High-Btu gas :	13,900	+ 3300	+ 35
Low-Btu gas :	11,500	+ 900	+ 10

Table IIICombined-Cycle Plant (Secondary fuel consumption 7400 Btu/kWh)

	Primary fuel consumption Btu/kWh	Compared with Air Storage Btu/kWh	\$/kW at 4000 h/year
High-Btu gas :	10,600	\pm 0	\pm 0
Low-Btu gas :	8,750	- 1850	- 20

Looking now at Fig. 4 one sees in alternative "a" that an air storage plant for less than 6 hours operation per day should burn high-Btu gas if this can be produced on a large scale in a plant which operates continuously. But, for longer operating hours it pays to employ fluidised bed air heaters. For the demand curve shown on Fig. 1 this would mean three units gas fired and three units with fluidised bed air heaters - these last three units generating three times as much electricity as the first three.

In alternatives "b" and "c" is shown - in heavy broken line - for comparison the most economical air storage cost called "datum". Only combined cycle plant ("c") operating for more than 15 hours

per day will be competitive with air storage plant - and then one is out of the peak load regime, but not necessarily out of the two-shift regime.

In summing up one can highlight a number of important features of air storage plant:

- it allows base load plant to be operated in a true base load mode by filling up the night trough in the demand.
- when built near load centres - as it should be - it then causes less air pollution than any other alternative: 4600 Btu/kWh in situ fuel consumption.
- its maximum output is not reduced at high ambient temperature - a problem with conventional gas turbines and combined cycle plant.
- it does not require excessive turbine inlet temperatures and is therefore well suited to its invariable duty of daily stops and starts.
- the relatively low turbine inlet temperature allows the use of fluidised bed air heater, which in turn makes it possible to use coal of very low and varying quality.
- the combination with fluidised bed air heaters does not alter the ability to stop and start every day: when air and fuel is cut off the bed will stay warm for days.
- it should be operated at nearly constant turbine inlet temperature - by throttling fuel and air simultaneously - and therefore shows very good part load efficiency.

In planning the development of new generating plant, using coal as the primary fuel, it is important to remember that none of the new ideas now being discussed will make an effective impact until we are well into the 1980's. In the mean time we see lots of large base load plant being put on stream - plant which will have to remain in a near base load mode of operation throughout its life. Nuclear power in particular will want to stay in the base load area - and towards year 2000 may account for 50% of all installed capacity. Altogether this makes it exceedingly important to guide the coal-power developments in such a direction that it allows these new breed of plant to operate in peak load and intermittent modes and air storage plant may prove very competitive in our endeavours to provide clean power from dirty fuel.

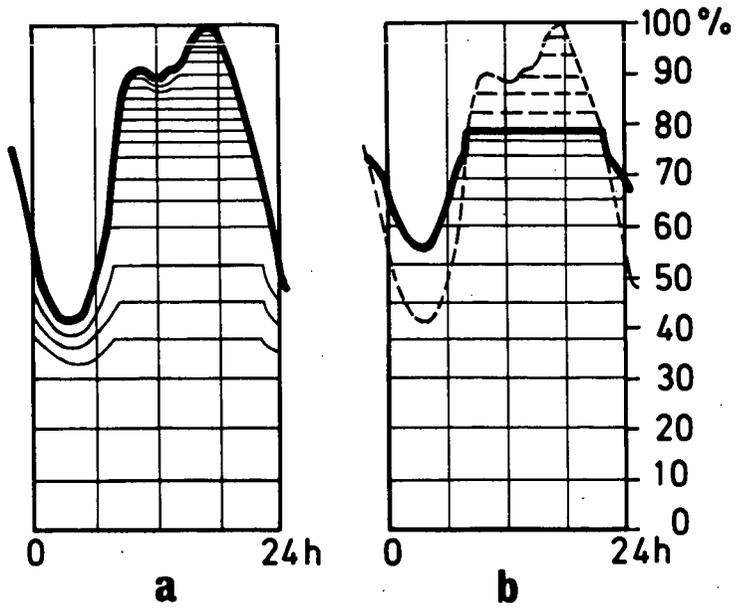


Fig. 1. Example of a daily load curve in an electricity supply system (a) and the effect of introducing 20% air storage power (b).

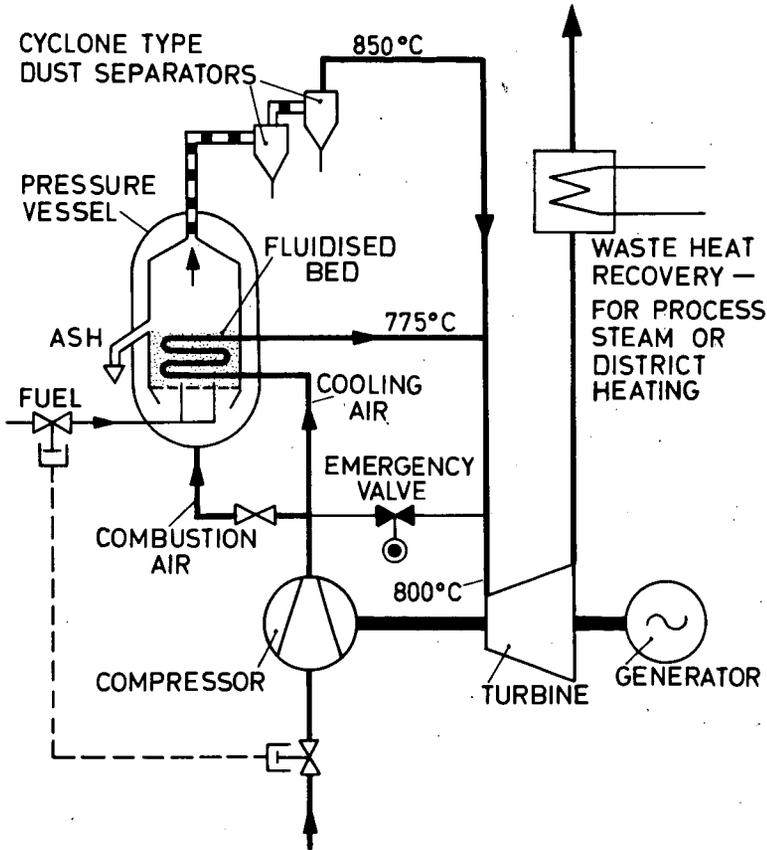
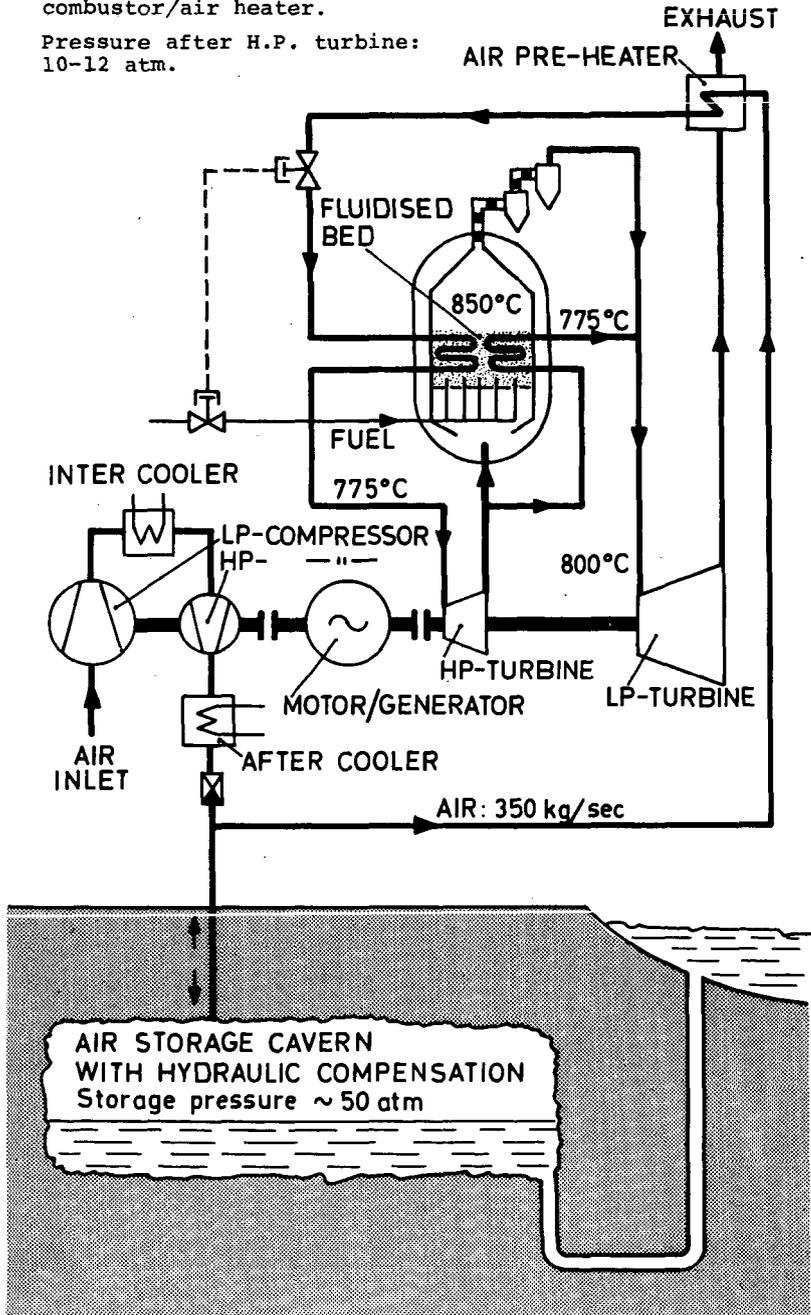


Fig. 2. Open cycle gas turbine with pressurised fluidised bed combustor/air heater.

Fig. 3.

260 MW reheat air storage plant
with pressurised fluidised bed
combustor/air heater.

Pressure after H.P. turbine:
10-12 atm.



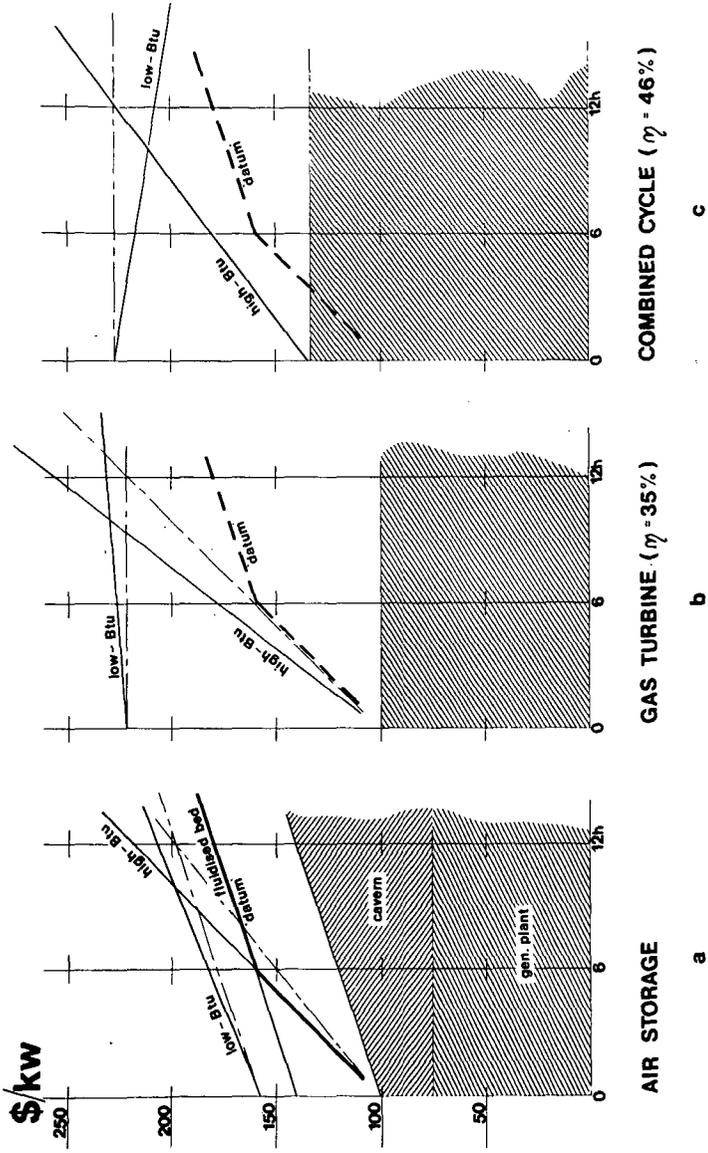


Fig. 4. Capital cost comparison of different types of peak power plant as function of operating hours per day. All using coal as primary fuel and all normalised to 10,600 Btu/kWh primary fuel consumption.

ADVANCED FUEL PROCESSING FOR ADVANCED POWER GENERATION. D. H. Archer, D. Berg.
Westinghouse Research Labs., Pittsburgh, Pa. 15235.

The use of coal (and possible residual oil) for power generation in the United States will increase threefold in the next 20 years. Advanced power plants are being developed to reduce the environmental and economic impact of this growth. Emissions of SO₂, NO, and particulates and discharge of heated water are minimized. Capital costs of equipment and construction are reduced; operating efficiency in fuel usage is increased over that of conventional steam power plants. Such plants involve the processing of coal (or oil) under pressure to produce either clean, pressurized fuel products by means of a fluidized bed gasification system or clean, pressurized combustion products by means of a fluidized bed combustion boiler system. Power production is carried out by combined cycle generation. Gas turbines burn the fuel gases and/or expand the combustion products; steam turbines expand steam provided by heat recovery and/or fluidized bed boilers. Combined cycle plants are low in cost because their standardized components are shop fabricated. High cost engineering, field assembly and erection are minimized. Such plants are also high in efficiency because the gas turbine directly and effectively utilizes high temperature combustion gases. And fluidized bed combustion boilers appear capable of economic producing steam at temperatures and pressures higher than conventional boilers. Several variations of coal (or oil) processing can be combined in various configurations with combined cycle generation equipment, boilers, and gas cleaning apparatus. Overall power plant capital cost reductions greater than 20% and operating efficiency increases greater than 25% appear feasible.

Combustion of Coal in a Bed of Fluidized Lime

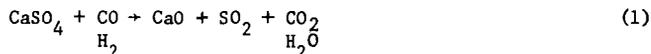
R. R. Bertr nd, R. C. Hoke, H. Shaw, A. Skopp

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Under Contract to the Office of Research & Monitoring -
US Environmental Protection Agency

A program is being conducted for the Environmental Protection Agency to develop a regenerative limestone process for fluidized bed coal combustion and desulfurization. The potential of fluidized bed combustor for air pollution control is good because the intimate gas-solid contacting in a fluidized bed promotes high SO₂ removal efficiency on suitable materials such as limestone or dolomite.

A schematic diagram of the process is shown in Figure 1. In the combustor, the sulfur in the coal is burned to SO₂ which then reacts with the lime to form CaSO₄. The system under study involves transferring the partially sulfated lime from the combustor to a separate regeneration vessel where the sulfated lime is regenerated according to the reaction



The regenerated stone (CaO) can then be returned to the combustor for further use, thereby substantially reducing the fresh limestone requirement. The off gas from the regenerator has a high SO₂ concentration and can be used as feed to a by-product sulfur or sulfuric acid plant.

Previous Studies

Various laboratories have studied fluidized bed coal combustion over the past few years. The results of the studies have shown that coal can be burned efficiently with over 90% removal of SO₂ and with reduced NO_x emissions. Regeneration of sulfated limestone has been studied using a number of regeneration methods. The method currently under study has been shown to give 6-10% SO₂ in the product gas when carried out at 1 atm and about 2000 F. The recycled lime was also shown to maintain a reasonably high level of activity after 7 combustion/regeneration cycles.

Economic studies carried out by Westinghouse Research Laboratories under contract to EPA⁽¹⁾ have indicated that operation of the combustor and regenerator at higher pressures, approximately 10 atm, would be significantly more economical than atmospheric pressure operation. As a result, the current studies are being made at higher pressures.

Objectives

Objectives of the current experimental program consist in (1) investigating the factors influencing the reduction of NO_x emissions in fluidized bed combustion, and (2) studying the regeneration of sulfated lime at pressures up to 10 atm.

EXPERIMENTAL RESULTSFactors Affecting NO_x Emissions

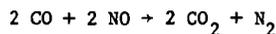
It was determined previously that NO_x emissions measured at the low temperatures occurring in fluidized bed combustion are formed by oxidation of nitrogen compounds in the coal. Oxidation of atmospheric N₂ occurs only at higher temperatures.

In this study, the effect of temperature, excess air and fluidized bed material on NO emissions was measured. The effect of temperature using a bed of CaSO_4 in the combustor is shown in Figure 2. As temperature decreases, NO emissions drop and drop rather sharply below 1500°F. The effect of excess air using a bed of CaSO_4 is shown in Figure 3. Actual NO emissions decreased as excess air (percent O_2) was increased. However, when the emissions were normalized to a constant gas volume (at 3% O_2), the NO emissions increased as the excess air increased. The NO formation rate was thus increased by the higher average oxygen concentration in the bed. The effect of bed material is shown in Figure 4. CaSO_4 gave lower emissions than alundum. With a CaO bed, the emissions were high initially, but as the bed sulfated, the emission level approached that of CaSO_4 .

One consistent explanation for these results is the reaction of NO with CO. CO emissions are higher at the lower temperatures and at lower excess air conditions. The higher CO levels then give lower NO emissions. The effect of bed materials appears to be a catalytic effect.

Reactions of NO and CO

The reaction of CO and NO was studied further in fixed bed units. The effect of bed material, temperature and feed gas composition were studied. In a dry system, CaSO_4 catalyzed the reaction slightly and showed a small effect of temperature, but alumina and an empty bed gave essentially no reaction. However, the addition of water enhanced the reaction and gave the same NO conversion regardless of the presence of the bed material. But when CaO was used as the bed material in a dry system, a very rapid reaction occurred which gave over 90% conversion of the limiting reactant as shown in Table 1. The reaction proceeded in 1/1 molar ratio of CO and NO suggesting the reaction



CO_2 was then added to the feed and reduced the conversion significantly over both calcined limestone and calcined dolomite. This is shown in Table 1.

TABLE 1

<u>BED SOURCE</u>	<u>NO-CO REACTIONS</u>					
	<u>CALCINED LIMESTONE</u>			<u>CALCINED DOLOMITE</u>		
<u>INLET GAS COMP.</u>						
NO ppm	1400	1800	860	1400	1990	840
CO ppm	940	1870	990	900	2080	980
CO_2 %	0	0	17	0	0	16
<u>OUTLET GAS COMP.</u>						
NO ppm	400	20	640	350	240	680
CO ppm	10	160	770	20	100	830
CO_2 %	0	0	17	0	0	17
<u>CONV. (%)</u>	99	99	26	98	95	16

TEMPERATURE: 1600°F

RES. TIME: 0.3 SEC

The most likely explanation for these effects is a kinetic limitation caused by the presence of the CO_2 . Formation of CaCO_3 and inhibition caused by chemical reversibility were considered as possible explanations, but were ruled out after closer examination.

Reactions of NO and SO₂

Studies of the reaction of NO and SO₂ were also made in a fixed bed reactor. The effects of bed material and temperature were studied. The results show that NO and SO₂ do not react in the vapor phase or over alundum or CaSO₄. However, a reaction does occur over partially sulfated lime and appears to be dependent on SO₂ concentration. Further rate studies indicated a 0.5 order dependence on the NO concentration. Temperature had a negative effect on the rate, decreasing the rate with increasing temperature. A proposed mechanism for the reaction involves the reversible formation of CaSO₃ intermediate from CaO and SO₂. The sulfite then reacts with NO to form N₂ and CaSO₄. However, it is known that the sulfite becomes unstable in the temperature range where the SO₂/NO reaction rate drops and this instability is the probable explanation for the negative temperature effect.

Two Stage Combustion

The reactions of NO with CO suggest the possible lowering of NO emissions by operating a staged combustion system. Air would be injected at two points in the combustor giving an O₂ lean section at the bed inlet. This should promote NO reduction because of the relatively high CO levels. The second step would then complete combustion. The fluid bed combustor was then modified to operate in a staged fashion. As the ratio of the amount of air added to the second stage to the amount added to the first stage increased, the NO emissions dropped from 600 to 200 ppm. Although these conditions may not be feasible in commercial operation, the principal of staged combustion appears attractive.

Regeneration of Sulfated Limestone

Regeneration studies were carried out in fixed and fluidized beds using CaSO₄ at pressures up to 10 atm.

Concentrations of SO₂ in the off gas as high as 7.5% have been measured at pressures up to 6 atm. At 10 atm, the highest SO₂ concentration measured to date is 3%. Comparisons were also made with SO₂ levels estimated from equilibrium calculations made by Argonne National Laboratory⁽²⁾. In general, the measured SO₂ concentrations were 40-50% of the equilibrium levels. Further work is planned in the fluidized bed regeneration unit to determine the SO₂ levels attainable at pressures up to 10 atm as a function of temperature, regeneration gas composition and flow rate, particle size and sulfated lime source. Activity maintenance of various stones will also be measured by cycling the stones between a pressurized combustor and the regenerator unit.

BIBLIOGRAPHY

- (1) Archer, D. H., et al., Evaluation of the Fluidized Bed Combustion Process Vol. I, Westinghouse Research Laboratories, Pittsburgh, Pa., Under contract to EPA.
- (2) Jonke, A. A., et al., Reduction of Atmospheric Pollution By the Application of Fluidized-Bed Combustion, Argonne National Laboratory Monthly Progress Report No. 38, December, 1971, Under agreement with EPA.

Fluidized Bed Combustion -
 Lime Regeneration System

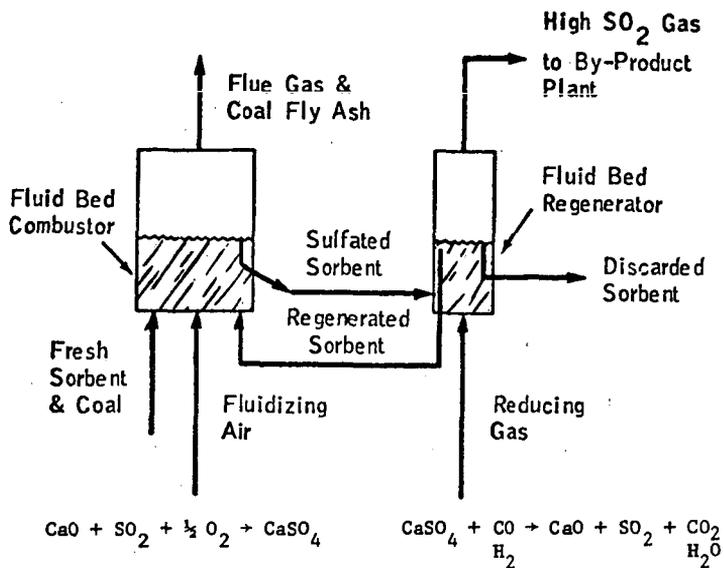


FIGURE 2

NO EMISSIONS AS A FUNCTION OF BED TEMPERATURE

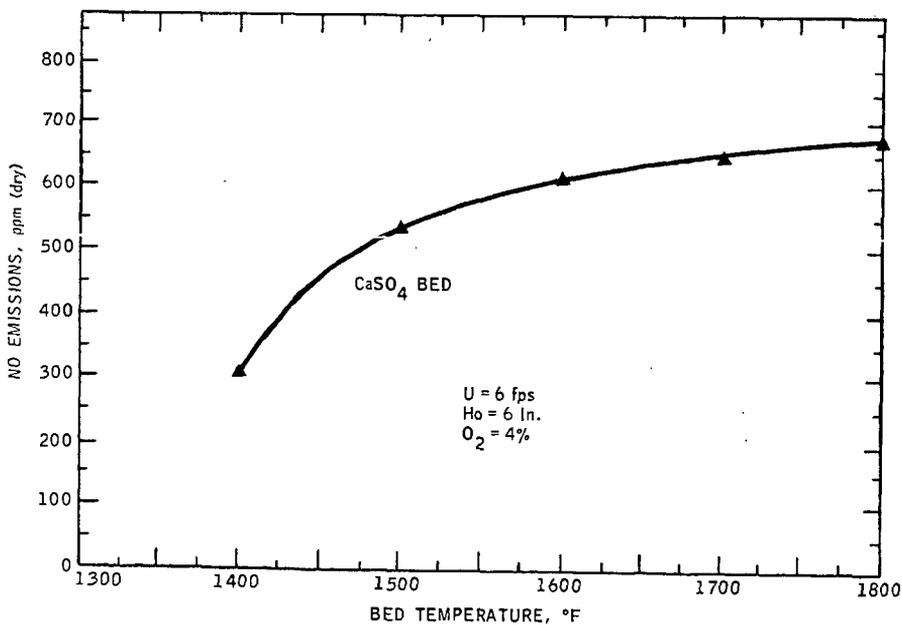


FIGURE 3

EFFECT OF O₂ IN FLUE GAS ON NO EMISSIONS (CaSO₄ BED)

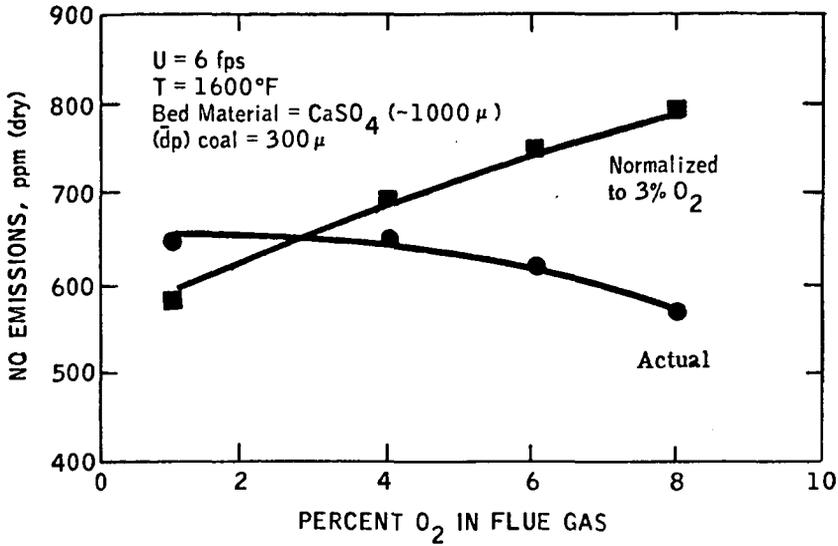
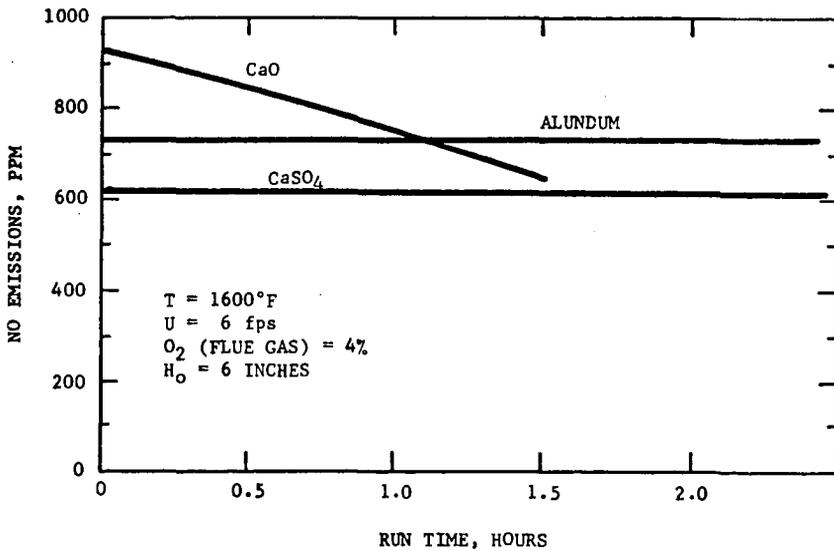


FIGURE 4

NO EMISSIONS USING DIFFERENT BED MATERIALS



PRETREATMENT OF BITUMINOUS COALS FOR
PRESSURE GASIFICATIONGeorge P. Curran, Bedrich Pasek,
Melvyn Pell, and Everett GorinResearch Division
Consolidation Coal Company
Library, Pennsylvania 15129INTRODUCTION

Eastern steam coals become fluid when heated through the temperature range of 700 to 850°F, and therefore require pretreatment to prevent caking at gasification conditions. Pretreatment via preoxidation has been studied for processes under development by Consol, IGT and the USBM.

Consolidation Coal Co. has carried out work for the past several years on the development of a fluidized bed gasification process for the production of low-sulfur fuel gas from high-sulfur caking bituminous coals. Progress reports have been published^(1,2,3,4) from time to time giving the status of the development.

The process involves gasification with air and steam in a fluidized bed of the pretreated coal at temperatures in the range of 1700-1750°F and at pressures of about 15 atmospheres. The pretreatment method studies most intensively is that of preoxidation.

Two criteria are used to evaluate the effect that preoxidation requirements have on economics. The first is the percent preoxidation required as compared with the adiabatic quantity, i.e., the amount of oxidation by heat balance to sustain the reaction at the desired temperature. With percent preoxidation defined as pounds O₂ reacted/100 pound dry coal fed, this relationship is illustrated in Figure 1. If the percent preoxidation exceeds the adiabatic level, the reactor becomes more complicated because of the need for cooling by indirect heat transfer and the heat released cannot be utilized efficiently.

The other criterion for preoxidation relates to the fluidization behavior of the preoxidized coal product. In order to operate the gasifier at a practical throughput, it is necessary to use a relatively coarse feed, and for the preoxidized coals to have a relatively high particle density. These properties are required in order to permit operation at reasonable gas velocities without excessive entrainment and to maintain the required bed inventory to satisfy the demands of the gasification kinetics.

The difficulties involved in meeting these criteria when preoxidizing Pittsburgh Seam coal at pressure have led to exploratory work on a pretreatment process in which the fluid coal is smeared out over seed char particles to produce a dense noncaking gasifier feedstock. The technique has been designated the "Seeded Coal Process."

The "Seeded Coal Process" in principle would actually utilize the natural fluidity of the coal. In the process visualized, char would be circulated at a high rate by means of a lift gas through a draft tube immersed in a normal fluidized bed. Coal and fine size seed char would be fed into the draft tube. The external fluid bed would be maintained at 1000-1400°F either by injection of air or hot fluidizing gas from a gasification step.

The coal would melt, smear out over the surfaces of the seed char and external bed material, and then solidify on completion of pyrolysis.

BACKGROUNDPreoxidation

Pretreatment via preoxidation has been studied by many investigators as a means of rendering caking coals operable for subsequent processing. The degree and severity of pretreatment required is a function of the type of processing the coal will be subjected to and the conditions under which the process is operated, i.e., temperature, pressure and gas composition, as well as the particular type of processing equipment used.

The following are some specific examples of the effect of operating conditions on fluid bed processing. First, it may be noted that more severe pretreatment is required for processes that operate under pressure as compared to those that operate at atmospheric pressure.

The effect of increasing total pressure is illustrated by the two experimental observations outlined below. Ordinarily, Pittsburgh Seam coal cannot be fed directly into a gasifier. However, a highly caking Pittsburgh Seam coal was successfully processed in 1949 in an atmospheric pressure one ton per hour fluid bed gasification unit without any pretreatment⁽⁵⁾ whatsoever. The above admittedly was accomplished at a relatively low coal throughput rate of 25 lb/hr-ft², but the effect of higher rates was not explored.

The other observation was, that in processing noncaking subbituminous coals at 20 atmospheres pressure in the hydrodevolatilizer of the CO₂ Acceptor Process, agglomeration of the bed solids occurred unless the coal feed was pretreated by mild preoxidation.⁽⁶⁾ The need for pretreatment here may be affected also by the presence of a substantial partial pressure of H₂, i.e., 5.5 atmospheres.

The work on the development of the Synthane Process at the USBM⁽⁷⁾ illustrates the fact that successful operation of a pressurized fluidized bed gasification process with bituminous coal requires that the feed be pretreated by preoxidation.

Work at IGT on the development of the Hydrogasification Process,^(8,9,10) again illustrates the need for severe pretreatment to establish operability in the fluidized bed processes operated at high total pressures, i.e., ca. 1000 psig. The high partial pressure of hydrogen in the hydrogasifier may also intensify the need for pretreatment.

A large experimental effort was carried out in the laboratories of Consolidation Coal in the 1950's to define the minimum severity of pretreatment via preoxidation required to establish operability in a subsequent atmospheric pressure fluidized bed carbonizer operated at 950°F. The aforementioned work has not been published, but the salient conclusions are given here.

The severity of pretreatment may be minimized by maximizing the amount of associated thermal treatment, i.e., pretreatment temperature and residence time. There is, however, for each specific coal a maximum pretreatment temperature that may be used above which the pretreatment process itself becomes inoperable. For highly caking Pittsburgh Seam coals, the "optimum" pretreatment temperature is in the range of 750-800°F.

The procedure finally adopted⁽¹¹⁾ was a mild preoxidation at temperatures below the plastic zone, i.e., <600°F, followed by final preoxidation at temperatures within the plastic zone, i.e., at 725-800°F. The total preoxidation required for the LTC process was in the range of 5-8 wt %, and increased with increasing fluidity of the coal being processed.

The use of preoxidized coal for fluidized bed⁽¹²⁾ reduction of calcium sulfate at temperatures of 1825-1875°F but at low pressures, i.e., 8 psig, has also been described. In this instance, 5.3 wt % preoxidation of the feed coal at 8 psig and 700°F was sufficient to prevent defluidization due to coking. The same highly fluid Pittsburgh Seam coal, Ireland Mine, and the same particle size (28 x 100) was used as in the work to be discussed here.

Forney,⁽¹³⁾ et al. studied the effect of the variables on ease of pretreatment of caking coals in a fluidized bed. They concluded, in accord with other investigators, that higher temperatures, increased residence time and decreased particle size all decreased the amount of preoxidation required to make the feed coal noncaking.

The development of the Synthane Process for gasification of bituminous coal most closely parallels the work reported here as far as the need for pretreatment is concerned. The small-scale pilot work⁽¹⁴⁾ used a free fall, dilute-phase preoxidizer to pretreat the coal. With very fine Pittsburgh Seam coal, i.e., 70% through 200 mesh, less than 8 wt % preoxidation was sufficient to decake the feed coal.

The large Synthane pilot plant now under construction will, however, incorporate a more complex two-stage pretreatment procedure. This is considered necessary since the coarser feed coal size (-14 M x 0) to be used necessitates more severe pretreatment. The first stage is a fluid bed preoxidizer operated at 40 atm and 750°F, followed by a second precarbonization stage which is conducted by free fall of the preoxidized coal against the product gases through the extended free board zone of the gasifier. With this system approximately 8 wt % preoxidation is considered to be adequate to achieve operability with a Pittsburgh Seam coal.⁽¹⁵⁾

Seeded Coal Process

A demonstration of the technique which is to be applied to the "Seeded Coal Process" was successfully carried out in the low-temperature carbonization section of the CSF Coal Liquefaction Pilot Plant at Cresap, West Virginia.⁽¹⁶⁾ The feed material, in this instance, was somewhat different and constituted the underflow from the hydroclone separation of the extraction effluent. Coal extract in this case was used instead of the fluid coal and the extraction residue was used instead of the seed char. Other differences were that the mixture was sprayed into the draft tube as a slurry and operating temperatures and pressures were lower, i.e., 825-925°F and approximately 4 psig, respectively.

In this particular installation, a 36" I.D. carbonizer was employed in which there was installed a 6" I.D. x 11' high draft tube. Solids were circulated through the draft tube by injection of about 3500-4500 SCFH of lift gas into the bottom of the tube. The feed was sprayed into the circulated char stream within the draft tube by means of a nozzle 3 feet above the lift gas injection point.

Solids circulation rates of the order of 100,000 lb/hr were achieved in this device, while complete operability and product size control was maintained with extract feed rates up to 200 lb/hr. The ratio of extraction residue solids-to-extract was in the range of about 1.5/1 to 3/1. The above throughput rates do not necessarily represent the capacity of the system since higher extract feed rates were not available and consequently were not tested.

The above results led to an attempt to apply the same system to coal even though coal is a less fluid material than extract and the operating conditions, particularly the pressure required, are more severe.

EQUIPMENT AND PROCEDURE

Bench-Scale Unit

A flow diagram of the experimental preoxidation unit is shown in Figure 2. The reactor is shown with the draft tube in place as for seeded coal tests. Preoxidations were generally carried out without the draft tube unless otherwise stated. Coal was fed at a known rate through a rotary feeder into a pneumatic lift line which conveyed it into the bottom of the reactor. Pretreated coal overflowed a weir and was collected in a separate product receiver.

For the seeded coal and draft tube runs, several reactor configurations were employed as shown in Figures 3 and 4. Another feeder was used for the seed char and an additional line was installed for accelerating gas to the draft tube. The reactor was 4" I.D. with an active bed height of 40". The reactor internals were constructed of type 310 stainless steel.

Fluidizing gas was metered through rotameters. It entered the top of the reactor through a preheat coil into the bottom of the bed where it reversed direction and fluidized the bed. Preoxidizer outlet gas generally contained some heavy tar and pitch which would rapidly plug the solids filters and the outlet piping. This was alleviated by installing two parallel tar receivers to collect the heavy material.

After passing through the coolers, the gas was depressured and analyzed. The analytical train consisted of a continuous paramagnetic oxygen analyzer and infrared SO₂, CO₂ and CO analyzers. In addition, the gas was selectively sampled for intensive chromatographic analysis.

Laboratory Test for Gasifier Operability

To judge the likelihood of caking in the gasifier, a laboratory test was developed which consisted of fluidizing a sample in a quartz tube reactor with nitrogen, and then immersing the reactor into a fluidized sand bath furnace for three minutes. The temperature in the reactor reached 1500°F within two minutes. If no agglomeration occurred, the material would surely be operable in the gasifier. Samples which showed slight agglomeration might be operable in the gasifier since the coal is fed in with a stream of air.

The FSI method has been used by previous investigators⁽¹³⁾ to test for decaking for subsequent gasification. We have found this method unsuited to our system since samples with FSI values as low as 1 were inoperable in the gasifier.

Similarly, the Gieseler plastometer was also used for the same purpose. The maximum fluidity of an operable feedstock was below the level that can be quantitatively measured, i.e., <0.1 DDPM.

EXPERIMENTAL RESULTS

Bench-Scale Preoxidation of Illinois No. 6 Coal

Three runs were made with Illinois No. 6 coal from Consol's Hillsboro Mine. This coal can be classified as weakly caking. Tests with a standard Gieseler plastometer showed a maximum fluidity of only 2.8 DDPM.

The conditions of the runs are summarized below:

System Pressure: 15 atm (206 psig)

<u>Run Number</u>	<u>5P1</u>	<u>5P2</u>	<u>6P</u>
Temperature, °F	750	800	810
Inlet O ₂ Partial Pressure, atm.	0.31	0.32	0.25
Fluidizing Velocity, ft/sec (top of bed)	0.29	0.29	0.29
Percent Preoxidation	11.9	11.5	8.7

Run data, properties of the preoxidized products, material balances and distribution of oxygen in the products are given in Tables 1 through 4.

The first runs were made with the level of preoxidation conservatively above the adiabatic level, 11.7%.

Upon completion of the 750°F portion of Run 5P1, the temperature was raised to 800°F via the electrical preheaters in order to obtain a more highly devolatilized product. Both runs were completely operable.

In Run 6P, the amount of preoxidation was reduced to approach the adiabatic level. The temperature was increased slightly to 810°F, compared to 800°F in Run 5P2.

In Run 6P, the pressure drop across the fluidized bed increased continuously. Microscopic examination of the chemical analysis of the final bed material drained from the reactor showed that ash particles had accumulated in the bed during the run. Ash and pyritic sulfur balances on the product coal and bed material showed that 10.55% of the dry feed coal had accumulated in the bed compared with 10.29% as obtained by difference in the overall weight balance, as shown in Table 3. A check of the chart records for Run 5P2 also showed an increase in pressure drop across the bed, but to a lesser extent than in Run 6P. In Table 3 the accumulations in Runs 5P1 and 5P2 were obtained by differences in the overall weight balances, in view of the good agreement between the measured and difference values shown in Run 6P. The nominal retention times shown in Table 1 are corrected for the presence of accumulated ash.

The preoxidized coal products from Runs 5P2 and 6P were fed to the bench-scale gasifier operated at simulated process conditions shown in Table 5. Both gasification tests were completely operable with no traces of agglomeration. All further work concentrated on the Ireland Mine feedstock.

Bench-Scale Preoxidation of Pittsburgh Seam Coal

The coal used for these tests was from Consol's Ireland Mine. To the best of our knowledge, this is the most fluid of the Pittsburgh Seam coals. The maximum fluidity is >37,000 DDPM, i.e., greater than can be measured in the standard Gieseler plastometer. Successful preoxidation of Ireland Mine coal would ensure applicability of the process to any other coal.

For the initial experimental program, a severe level of preoxidation was chosen deliberately with the intent of suppressing completely any tendency toward caking at gasification conditions. A long nominal retention time, 60 minutes, was chosen to ensure adequate exposure to O₂ for those particles at the low end of the retention time distribution which is characteristic of a continuously fed fluidized bed. With these constraints, the inlet O₂ partial pressure fell in the range of 0.4-0.5 atm.

Run 1P

Run data and properties of the preoxidized coal products are listed in Tables 6 and 7. The run proceeded without apparent difficulty, except for a disturbingly large temperature gradient across the fluidized bed, until the desired amount of product was

fed. During the run, the temperature at the bottom typically was 580°F and the profile showed an increase to 700°F at about 25" above the bottom with constant temperature to the top of the bed at 40".

On disassembly of the reactor it was found to be partially choked with large chunks of agglomerated coal. The presence of agglomerates distorted the normal mixing pattern of the fluidized bed and also decreased the nominal residence time of the coal particles by an unknown amount. However, all the O₂ had been consumed, i.e., 20% preoxidation had been achieved.

Run 2P1

Since coke had formed at 700°F in Run 1P, the next preoxidation run was made at 600°F to guarantee a preoxidized coal feedstock with a known retention time which could be fed to the gasifier.

In Run 2P1, a large temperature gradient developed soon after coal feeding was started. After two hours, the temperature increased suddenly to 800°F at which time the run was ended. Upon disassembly, there was no evidence of agglomeration, yet the temperature effects indicated that agglomerates had formed.

Laboratory tests showed that although the coal would not agglomerate at atmospheric pressure at 600-650°F, agglomeration could occur at pressure. This behavior was attributed to small amounts of waxy and resinous material which are present in nearly all bituminous coals. This material melts at relatively low temperatures and evaporates at atmospheric pressure before agglomerates can form. At elevated pressure, evaporation is hindered sufficiently so that the particles can stick to each other. The agglomerates so formed must have been very fragile and were broken up during manipulation of the reactor on disassembly after Run 2P1. In Run 1P the start-up procedure involved heating the coal through the 600-650°F range and agglomerates probably formed at that time.

Run 2P2

The start-up procedure was changed to ensure that the bed temperature always remained above 725°F. The run was carried out successfully at 750°F. Run data, some properties of the preoxidized coal product, the distribution of reacted O₂, and a material balance are presented in Tables 6 through 9.

Both Runs 1P and 2P2 products were fed to the gasifier at conditions described in Table 5. The Run 1P material melted and coal feeding had to be stopped after 13 minutes. The Run 2P2 material produced numerous small agglomerates.

It was apparent that, at the pressure used in the process, even 20% preoxidation was ineffective in preventing caking in the gasifier. Pretreatment by preoxidation involves dehydrogenation and devolatilization. Elevated system pressure inhibits these processes while increased preoxidation and temperature enhance these same processes. Since a higher preoxidation temperature can compensate for the suppressing effect of elevated pressure on dehydrogenation and devolatilization, preoxidation runs at 800°F were scheduled.

Runs 3P and 3P1

Runs 3P and 3P1 were made at 800°F. In both cases, soon after 800°F was reached in the bed, there was evidence of poor mixing or blockages in the bed. The beds were found to contain large amounts of agglomerates.

Runs 4P and 4P1

To establish a benchmark as to the severity of preoxidation for Ireland Mine coal which would assuredly provide an operable feedstock for the gasifier, the Run 2P2 product was subjected to a second stage of preoxidation in Run 4P at 750°F in which an additional 10% preoxidation occurred. Run data, some properties of the preoxidized coal product, the distribution of reacted O₂, and a material balance are presented in Tables 6 through 9.

Run 4P product was fed to the gasifier at conditions shown in Table 5. There was no evidence of agglomeration or ash slugging in the gasifier.

In order to obtain a gasifier feedstock which was more highly devolatilized, at the end of the 750°F operating period of Run 4P, the bed temperature was raised to 800°F while holding all input flows constant.

Increased particle swelling was apparent immediately. After about one hour at 800°F, the very low density material would not flow reliably through the overflow weir, and the run was shutdown. Inspection of the vessel after disassembly showed that no caking or agglomeration had occurred.

However, such a low density material, particle density less than 30 lb/ft³, would be impractical as a gasifier feedstock from the standpoint of maintaining an adequate carbon inventory and gas throughput.

Reference to Tables 2 and 7 shows that the density of the preoxidized coal product increased with decreasing particle size. This is illustrated in Figure 5 using the data from Runs 1P and 2P2. Results of Gieseler plastometer tests on the various fractions showed that the smaller particles also displayed less fluidity. It was concluded that a smaller size consist would be more operable in the gasifier than a larger particle which had experienced the same degree of preoxidation.

Staged Preoxidation Run

A series of runs were then made in which a finer size consist, nominally 48 x 150 mesh, of the raw coal feed was used in conjunction with two stages of preoxidation. From prior work both expedients are in the direction of reducing the excessive preoxidation required in single-stage treatment of relatively coarse coal.

a. First Stage - Run PR1

Programmed conditions called for the adiabatic level of 6.3% preoxidation. The actual coal feed rate was somewhat higher than the programmed value, with the result that 5.7% preoxidation was achieved. The run was completely operable and scheduled shutdown was made after making 143 pounds of steady-state product.

b. Second Stage at 775°F - Run PR1B

After steady-state conditions at 750°F had been reached in Run PR1A in which complete operability was demonstrated, the bed temperature was raised to 775°F for Run PR1B. The preoxidation level was increased slightly to compensate for lower level achieved in the first stage run such that the total level for both stages was 11.3% preoxidation, which is 50% greater than the adiabatic level at 775°F. This run was also completely operable with no caking or agglomeration occurring.

The Run PR1 product and all the air were fed into the configuration D draft tube shown in Figure 4. In a bench-scale preoxidation run, the draft tube probably makes little contribution to the process. In the tube, the incoming first-stage coal product and air were immediately diluted with a large amount of external bed material.

The draft tube was used to assure a smooth transition from start-up conditions involving an initial bed of inert char and to prevent localized hot spots caused by the highly exothermic preoxidation reactions. Axial traverses across the entire bed showed that the temperature was constant to within 4°F.

c. Second Stage Preoxidation Attempt at 800°F

In an effort to obtain a more highly devolatilized, and therefore a more thoroughly decaked product, the bed temperature was raised to 800°F via the electrical heaters at the end of the material balance period of Run PR1B. After about one-half hour, the pressure drop across the bed had increased and a large temperature gradient had developed. Inspection of the reactor after shut down showed that it was full of large chunks of agglomerates.

Detailed results of Runs PR1 and PR1B are given in Tables 6 through 9. Inspections of the preoxidized coal product from Run PR1B show that the material was considerably swollen and had a particle density of 49 lb/ft³, compared with the raw coal value of 82 lb/ft³. This result was not anticipated because our prior work had indicated that the smaller size fractions of the preoxidized coal products had suffered relatively little swelling. Some comparisons are shown below with data from two runs made during the earlier work.

<u>Run Number</u>	<u>1P</u>	<u>2P2</u>	<u>PR1B</u>
Raw Coal Size Consist	← 24 x 100 M →		48 x 150 M
Temperature, °F	700	750	775
Percent Preoxidation	19.5	18.6	11.3
<u>Particle Density, lb/ft³</u>			
Mean of Entire Product	61.6	53.1	48.6
65 x 100 mesh Fraction	76.8	73.1	54.4

The lower density of 65 x 100 mesh product produced in PR1B as compared with previous work may be because of the lower level of preoxidation and/or the higher temperature used.

The laboratory shock-heating test showed that the Run PR1B product would have been inoperable at gasifier conditions. The amount of agglomerates formed in the test was greater than that for the Run 2P2 product which actually was fed to the gasifier at process conditions and which was shown to be inoperable.

DISCUSSION OF PREOXIDATION RESULTS

The results obtained in this study are qualitatively in agreement with the results of previous investigators as discussed above. Particularly noteworthy is the adverse effect of the process pressure on the severity of pretreatment required to establish operability.^(5,6,8,9,10,12)

Staged preoxidation with a rising temperature regime between stages also appears moderately helpful in reducing the severity of pretreatment as shown by others.^(7,11) However, as noted above, for each coal, and each given size consist, there is a maximum pretreatment temperature at which the first pretreatment step itself remains operable. For the highly fluid Pittsburgh Seam coals, the maximum first-stage pretreater temperature at 15 atm pressure for 28 x 100 mesh feed is about 750°F.

Fine coal requires less severe pretreatment to achieve the same degree of decaking, which again is in agreement with other investigators.⁽¹³⁾

The level of preoxidation required to achieve operability with Pittsburgh Seam coals, as reported here, is substantially in excess of that indicated for the Synthane Process.⁽¹⁵⁾ A possible explanation is the added pretreatment received by

the coal in the Synthane Process by precarbonization in the free falling zone above the bed. Such added pretreatment is avoided in the Consol process to eliminate complications due to tar formation. The same result could possibly be achieved in the Consol process by addition of an extra preoxidation stage in the form of a transfer line reactor. This would be done by conveying the pretreated coal with air from the preoxidizer to the gasifier.

Another factor which is brought out in this study is that more severe pretreatment is required to decake the coal when the pretreatment step itself is conducted under pressure. This is illustrated by the results shown in Table 10, where the caking properties of Ireland Mine coal preoxidized at 1 and 15 atmospheres pressure are compared. The data of Table 10 also again illustrate the favorable effect of higher pretreatment temperatures in decaking, i.e., comparison of Runs 1P and 2P2.

The problem of pretreatment is also compounded by the need, as discussed above, to process a relatively coarse feed without a concomitant large decrease in particle density.

Noteworthy also is the excellent kinetics of the preoxidation step. Substantially complete oxygen consumption was observed in all of the preoxidation runs reported here. Supporting laboratory data on preoxidation kinetics are also given in reference (2). These data⁽²⁾ also point out an interesting finding that higher oxygen partial pressures cause a higher degree of decaking at the same preoxidation level.

PRETREATMENT VIA "SEEDED COAL PROCESS"

The principle of the preoxidation method of pretreatment is to convert the coal to a more rigid structure via oxidation such that the fluidity is severely reduced when the coal undergoes pyrolysis. The Seeded Coal Process would operate on just the reverse principle and actually utilize the natural fluidity of the coal. Unfortunately, we were severely handicapped by the small scale of the equipment available since the draft tube principle had to be adapted to the existing 4-inch diameter vessel.

The potential advantages of the process are that it will supply a feedstock that is assuredly operable with respect to agglomeration at gasifier conditions. In addition, it has the capability to produce a dense, closely sized feedstock substantially free of fines. This will permit a higher gasifier throughput than otherwise.

A series of exploratory tests were carried out with the configurations A, B and C as indicated in Figure 3. Best results were obtained with configuration C, but even here two basic deficiencies were noted. From the appearance of the agglomerates obtained, it was apparent that insufficient mixing was being achieved in the draft tube between the injected coal and the circulating char. Part of the difficulty is associated with the small scale of the equipment, since calculations show that the particle Reynolds number in the draft tube is barely above the Stokes Law range. Also, it was apparent that most of the fluidizing gas was bypassing the main bed in favor of the draft tube. The result was that a fluidized bed was not maintained external to the draft tube.

To overcome these limitations, the configuration C of Figure 3 was modified as follows:

To allow installation of an external baffle which would maintain fluidization of the external bed, the draft tube was raised 2 inches and the inlet lines were lengthened accordingly. An elliptical baffle 3-5/8" x 1-3/4" x 1/16" thick was welded to the accelerating gas line below the mouth of the tube at a slope of 60° from the horizontal. To help promote mixing a conical baffle was installed inside the tube with the apex of the cone positioned 1/2 inch above the end of the coal inlet tube. The configuration D obtained is shown in Figure 4.

Tests with an inert bed of 48 x 100 mesh char at 1500°F and 15 atm. system pressure showed that the external baffle was effective. The solids circulation rate upward through the tube was measured by substituting a known amount of air for some of the N₂ entering the solids feed line. From the measured temperature rise, the solids flow rate was calculated as 900 lb/hr by heat balance. Calculations involving the pneumatic transfer line⁽¹⁷⁾ model devised in the course of development of the CO₂ acceptor project showed that without the external baffle about 270 of the 340 SCFH of N₂ fed to the bottom of the external bed had entered the draft tube whereas with the baffle, the flow was reduced to about 60 SCFH.

Seven tests were made with the modified draft tube, using an external bed of 48 x 100 mesh char at 15 atm. system pressure. Common conditions for the runs are listed below:

Ireland Mine coal: sized to 100 x 200 mesh
 Coal Feed Rate: 2.0 lb/hr
 Duration of Feeding: 3.3 minutes
 Air to Coal Feed Line - Equivalent to 100% of adiabatic
 preoxidation level at the temperature used.

Gas Flows, SCFH

Air + N ₂ to Coal Feed Line	65
N ₂ to Accelerating Line	85
N ₂ to Bottom of External Bed	340

Tests were made at temperatures from 900 to 1500°F, in 100° increments. Temperature limits of operability were established as follows: (1) at 900°F little or no smearing occurs as was shown by presence of coal-derived material in the form of hollow spheres in the bed after the run, and (2) at 1500°F, caking occurred in the draft tube.

The products from the runs at 1000 to 1400°F all showed more uniform smearing than in any of the previous runs without the internal baffle. At the end of each run, the system was depressured and the bed was drained by removing the coal inlet line. The hot bed material was quenched rapidly by contact with dry ice in the catchpot. The entire bed material then was screened at 28 and 48 mesh. A characteristic of all the run products is that all contained some +48 mesh agglomerates which were external bed particles cemented together by a thin film of coal-derived material. No agglomerates larger than 28 mesh were found. The fewest agglomerates occurred at 1300°F, indicating that this may be the optimum temperature with respect to uniformity of smearing. The amounts of +48 mesh agglomerates which formed are listed below:

Temperature, °F	+48 Mesh Agglomerates/Wt. % of Bed Inventory
1000	18.0
1100	16.0
1200	15.5
1300	8.0
1400	10.7

The particle density, measured in mercury, for the +48 mesh agglomerates formed at 1300°F had a high value of 85 lb/ft³.

An attempt was made to run for a prolonged period at 1300°F and 15 atm. system pressure to determine the size distribution of the "equilibrium" product. To simulate the seed char in the commercial embodiment (fines from the internal cyclones in the gasifier) an initial external bed of -100 mesh precarbonized char was established.

Then, 100 x 200 mesh Ireland Mine coal and additional -100 mesh char were fed to the draft tube at rates of 2 and 4 lb/hr, respectively. The fine char contained a considerable amount of -325 mesh material which was elutriated from the reactor. The outlet piping system of the present equipment was not designed to handle large amounts of solids. The run had to be terminated after 35 minutes of feeding coal because the outlet system began to plug. Thus, an equilibrium bed was not established. However, analysis of the bed showed that it contained 50 wt % of +100 mesh agglomerates, with a top size of 24 mesh.

The high particle density achieved is favorable, in that "smearing" of liquid coal over the seed particles apparently is occurring as desired.

The small size of the existing equipment precludes any further meaningful studies of the Seeded Coal Process. The radial clearance between the inlet line and the wall of the draft tube is only 0.15 inch. The mouth of the tube eventually would become choked by the larger agglomerates which inevitably would be formed.

The results of the exploratory studies strongly indicate that future studies should be made.

Several essential factors are required to achieve success in such an operation. Intensive mixing in the draft tube is required to achieve smearing of the "liquid" coal over both the seed and recirculating char. A sufficient residence time in one pass through the unit of the recirculating burden is needed to complete the "drying out" or carbonization of the coal. Finally, the draft tube must be large enough to handle without choking, the largest size particles made in the process. All these factors point to a need for a larger unit in which the draft tube would be at least 2 inches in diameter as opposed to the present 0.680 inch. Such a unit, of course, would have a much higher capacity for coal feed which would lie approximately in the range of 30-300 lb/hr.

CONCLUSIONS

1. Encouraging results have been obtained in an exploratory study of the Seeded Coal Process. Future studies should be made with a larger reactor unit in which the draft tube diameter would be at least 2 inches (vs. 0.680 inch at present). The potential advantages of the process are that it will supply a feedstock which assuredly is operable with respect to caking/agglomeration at gasifier conditions, and that it can produce a dense, closely sized feedstock substantially free of fines which will allow a high gasifier throughput.
2. Preoxidation is an acceptable pretreatment technique for Illinois No.6 coals. A feedstock was produced at adiabatic preoxidizing conditions which was fed to a pressure gasifier with complete freedom from agglomeration.
3. Successful pretreatment within the framework of an adiabatic preoxidation process was not achieved with highly fluid Pittsburgh Seam coals using a size consist sufficiently coarse to be practical for fluidized bed processing when pretreatment was carried out under full system pressure. The minimum preoxidation level found is between 19 to 28 wt %. A three-stage process in which the third stage preoxidation is carried out in a transfer line reactor is a possibility which has not been explored.

Acknowledgment

Appreciation is expressed to the Environmental Protection Agency, Department of Health, Education and Welfare for financial support of the work presented in this paper and for permission to publish the results given.

REFERENCES

1. Curran, G.P., Fink, C.E., and Gorin, E., Proceedings of the Second International Conference on Fluidized Bed Combustion, Oct. 4-7, 1970. EPA Publication No. AP-109, Paper No. III-1-1.
2. Curran, G.P., et al., Annual Report by Consolidation Coal Co. to Control Systems Division, Office of Air Programs, OAP Contract No. EHSD 71-15, Period: Sept. 1, 1970 to Nov. 1, 1971, U.S. Dept. of Commerce, National Technical Information Service PB-210-840.
3. Curran, G.P.; Pasek, B.; Pell, M.; and Gorin, E., "Low-Sulfur Producer Gas via an Improved Fluid Bed Gasification Process." Paper presented before Third International Conference on Fluidized Bed Combustion, Oct. 29-Nov. 1, 1972.
4. Curran, G.P. and Gorin, E., "The CO₂ Acceptor Gasification Process - A Status Report - Application to Bituminous Coal." Ibid
5. Unpublished Work Carried Out Jointly by Consolidation Coal Co. and Esso Research in 1949.
6. Consolidation Coal Co., Research and Development Report No. 16 to the Office of Coal Research, U.S. Dept. of the Interior, Under Contract No. 14-01-0001-415 Interim Report No. 3, "Phase II - Bench-Scale Research on CSG Process" (January, 1970).
Book 3, "Operation of the Bench-Scale Continuous Gasification Unit." Gov't. Printing Office Catalog, No. 163.10:16/INT3/
Book 3.
7. Forney, A.J.; Kenny, R.F.; Gasior, S.J.; and Field, J.H., Adv. in Chem. Series No. 69, 128-136, ACS (1967).
8. Kavlick, V.J. and Lee, B.S., Adv. in Chem. Series No. 69, 8-17, ACS (1967).
9. Lee, B.S.; Pyrcioch, E.J.; and Schora, F.C., Jr., Ibid - 104-127 (1967).
10. Tsaros, C.L.; Knabel, S.J.; and Sheridan, L.A., Institute of Gas Technology, R&D Report No. 22, Interim Report No. 1 to the Office of Coal Research Under Contract No. 14-01-0001-381.
11. Sylvander, N.E., U.S. Patent 3,070,515, Dec. 25, 1962. Assigned to Consolidation Coal Co.
12. Curran, G.P.; Fink, C.E.; and Gorin, E., Proceedings of the Second International Conference on Fluidized Bed Combustion, Oct. 4-7, 1970, EPA Publication No. AP-107, Paper No. II-5-1.

13. Forney, A.J.; Kenny, R.F.; Gasior, S.J.; and Field, J.H.,
USEM - Report of Investigations 6797 (1966).
14. Forney, A.J.; Kenny, R.F.; and Field, J.H., ACS Preprints 11, 4,
322-332 (1967).
15. Forney, A.J., USEM, Private Communication.
16. "Pilot Scale Development of the CSF Process," Period: July 1, 1968
to Dec. 31, 1970, R&D Report No. 39, Vol. IV, Book 3.
Prepared for the Office of Coal Research by Consolidation Coal
Co. Under Contract No. 14-01-0001-310.
17. Consolidation Coal Co., Research and Development Report No. 16 to the
Office of Coal Research, U.S. Dept. of the Interior, Under
Contract No. 14-01-0001-415.
Interim Report No. 3, "Phase II - Bench-Scale Research on CSG
Process." (January, 1970).
Book 1, "Studies on Mechanics of Fluo-Solids Systems."
Gov't. Printing Office Catalog No. 163.10:16/INT3/Book 1.

TABLE I

Preoxidation Conditions and Results for Illinois No. 6 Coal
 System Pressure: 15 atmospheres (206 psig)
 Size Consist: 24 x 100 Tyler Mesh

Run Number	5P1	5P2	6P
Feed Coal	Illinois No. 6		
Temperature, °F	750	800	810
Inlet O ₂ Partial Pressure, atm	0.31	0.32	0.25
Fluidizing Velocity (top of bed), ft/sec	0.29	0.29	0.29
Moisture in Coal, Wt %, as fed	6.80	6.80	6.58
<u>Input</u>			
Coal Feed Rate, lb/hr (dry basis)	7.89	8.13	8.71
<u>Lift Gas, SCFH</u>			
Air	54.0	54.0	43.5
N ₂	97	99	110
<u>Fluidizing Gas, SCFH</u>			
Recycle	396	380	382
N ₂	0	0	0
Purges (N ₂), SCFH to bed	5	5	5
Purges (N ₂), SCFH above bed	10	9	6
<u>Output</u>			
Exit Gas Rate, SCFH ⁽¹⁾ (dry basis)	161	164	161
Exit Gas Composition, Mol % (dry basis)			
O ₂	<.01	<.01	<.01
CO ₂	3.03	3.36	2.54
CO	.40	.46	.25
CH ₄	.25	.38	.45
C ₂ H ₆	.08	.14	↕ (2) ↕
C ₂ H ₄	.01	.02	
C ₃ H ₈	.01	.06	
C ₃ H ₆	.01	.01	
COS	.02	.05	
SO ₂	.16	.18	.09
H ₂ S	<.003	<.003	--
H ₂	<.01	<.01	--
N ₂ (by difference)	96.03	95.34	96.39
Flow Rate, SCFH, at top of bed	572	563	569
<u>Water, lb/hr (corrected for coal moisture)</u>			
Condensate	.590	.722	.824
Moisture in Exit Gas	.006	.006	.006
Tar, lb/hr	.0934	.155	.292
Preoxidized Coal, lb/hr	7.20	6.81	6.76
Percent Preoxidation	11.9	11.5	8.7
Nominal Solids Retention Time, min	59	46	39
Duration of Steady-State Period, hr	10.0	6.0	5.5
Total Product, Pounds	72	41	37

(1) Standard conditions are 29.92 in Hg and 70°F.

(2) Not measured. Assumed to be the same as in Run 5P2.

TABLE 2

Properties of Illinois No. 6 Coal and Products

Hillsboro Mine Illinois No. 6 Feed Coal		5P1		5P2		6P	
	(1)	(2)					
Hydrogen, Wt % (dry basis)	4.19	4.18	3.18				3.44
Carbon	60.44	60.14	61.72	3.29	67.02		70.61
Nitrogen	1.17	1.22	1.34	1.44	1.44		1.36
Oxygen (by diff.)	8.81	7.67	7.81	7.98	7.98		5.80
Sulfur	4.46	4.93	4.07	3.72	3.72		3.40
Ash	20.93	21.86	21.88	16.55	16.55		15.39
Volatile Matter	37.2	36.4	23.4	21.6	21.6		22.0
Pyritic Sulfur	2.20	2.26	1.51	1.11	1.11		1.37
Sulfate Sulfur	.07	.30	.33	.27	.27		.07
Size, Tyler Mesh	Wt %	Wt %	Density, lb/ft ³	Wt %	Density, lb/ft ³	Wt %	Density, lb/ft ³
+24	0	0	0.4	1.4	37.9	2.0	44
24 x 28	9.6	15.8	7.9	14.0	40.1	17.0	50.0
28 x 35	39.3	41.1	33.3	35.5	44.1	34.5	50.5
35 x 48	34.2	29.0	34.7	32.0	58.8	29.4	49.2
48 x 65	15.0	12.7	20.2	15.0	61.5	14.3	64.3
65 x 100	1.3	1.0	3.0	1.8	72.9	2.2	58.9
-100	0.6	0.4	0.5	0.4		0.5	
Mean Diameter, inch (3)	.0166	.0176	.0158	.0171		.0175	
Mean Density, lb/ft ³ (4)	80.0	80.0	61.7	49.8		51.8	
Maximum Fluidity, DDPM (5)	2.8	--	< 1	--		--	

(1) Batch No. 1, used in Runs 5 P1 and 5P2.
 (2) Batch No. 2, used in Run 6P.
 (3) Arithmetic mean.
 (4) Measured in mercury at 1 atmosphere. Reciprocal mean.
 (5) Measured in Gieseler plastometer (ASTM Method D-2639-67T).

TABLE 3

Material Balances for Preoxidation Runs - Illinois No. 6 Coal

Basis: 100 lb Dry Coal Fed

<u>Run Number</u>	<u>5P1</u>	<u>5P2</u>	<u>6P</u>
Preoxidized Coal	91.25	83.76	77.60
Overhead Fines	.70	.50	.91
Tar	1.18	1.91	3.35
Carbon in CO + CO ₂	2.16	2.39	1.60
Hydrogen in H ₂ O	.84	1.00	1.06
Hydrocarbons (C ₁ -C ₃)	.40	.72	.72
Sulfur in SO ₂ and COS	.30	.38	.22
Coal Oxygen to Products	.61	2.88	4.25
Accumulation in Bed, Ash and S as FeS ₂	<u>2.56⁽¹⁾</u>	<u>6.46⁽¹⁾</u>	<u>10.29^(1,2)</u>
Total	100.00	100.00	100.00

(1) By difference.

(2) Ash and sulfur balances on product and bed materials gave 10.55 lb accumulation.

TABLE 4

Distribution of Oxygen in Products of Preoxidation - Illinois No. 6 Coal

Run Number	5P1		5P2		6P	
	Lb/hr	Percent	Lb/hr	Percent	Lb/hr	Percent
Output						
To Water						
Condensate	.524	53.2	.641	54.7	.732	65.0
Moisture in Gas	.005	0.5	.005	0.4	.005	0.4
To CO ₂	.402	40.8	.456	38.9	.338	30.1
To CO	.027	2.7	.031	2.7	.017	1.5
To SO ₂	.021	2.1	.024	2.1	.012	1.1
To COS	.001	0.1	.003	0.3	.003	0.3
In Tar	.006	0.6	.011	0.9	.018	1.6
On Coal (by diff.)	0	0	0	0	0	0
Total	.986	100.0	1.172	100.0	1.125	100.0
INPUT						
From Coal (by diff.)	.048		.234		.370	
Lb/hr O ₂ from Air	.938		.938		.755	
Total	.986		1.172		1.125	

TABLE 5

Typical Gasifier Conditions for
Testing Preoxidized Coals

Temperature	1700°F
Pressure	15 atm (206 psig)
Fluidizing Velocity	0.34 ft/sec
Feed Rate	4.15-4.85 lb/hr

<u>Compound</u>	<u>Feed, Mole %</u>	<u>Top of Bed, Mole %</u>
H ₂ O	23.6	15.3
H ₂	0.0	10.0
CH ₄	0.0	0.8
CO	0.0	12.0
O ₂ (from air)	6.8	0.0
CO ₂	11.8	12.8
N ₂	57.8	49.0
Inlet Oxygen Pressure, atm.		1.0

TABLE 6
 Oxidation Conditions and Results - Pittsburgh Seam Coal
 System Pressure: 15 atmospheres (206 psig)

Run Number	IP	ZP	FP	RI	RIIB
Feed Coal			2P2 Product	Ireland Mine	RI Product
Size Control, Tyler Mesh			50 x 100	48 x 150	775
Temperature, °F	700	750	750	875	40(*)
Inlet O ₂ Partial Pressure, atm	.49	.40	.32	.18	0.30
Fluidizing Velocity (top of bed), ft/sec	.24	.34	.29	0.30	0.71
Moisture in Coal, Wt % as Fed	1.58	1.58	1.03	1.83	5.64
INLET	6.5	7.46	9.34	10.44	18.4
Coal Feed Rate, lb/hr (dry basis)	73	80	98	35	126
Air	84	70	98	170	417
N ₂				0	0
Fluidizing Gas, SCFH	310	390	380	417	417
Recycle	0	92	0	0	0
Purges (N ₂), SCFH to bed	5	5	5	5	5
Purges (N ₂), SCFH above bed	15.5	15.5	15.5	7	11
OUTLET	169	256	159	212	159
Exit Gas Rate, SCFH (dry basis)	<.02	<.02	<.02	.14	<.01
Exit Gas Composition, Mol % (dry basis)	3.53	2.56	3.33	.76	.89
O ₂	1.20	.95	.89	.80	.44
CO		.82	.21	.03	.16
CH ₄	(*)	(*)	(*)	<.01	.01
C ₂ H ₆				<.02	.03
C ₃ H ₈				<.01	.01
C ₄ H ₁₀				<.02	.03
COS				<.01	.01
SO ₂				<.01	.01
N ₂ (b, difference)	95.3	96.4	95.6	98.64	98.04
Flow Rate, SCFH at top of bed	500	669	552	643	595
HAZELTINE (corrected for coal moisture)	.665	.728	.265	.677	.258
Moisture in Exit Gas	.008	.010	.008	.008	.008
Tar, lb/hr	0	.0148	0	.106	.092
Preoxidized Coal, lb/hr	(*)	6.96	9.14	9.89	5.31
Percent Preoxidation	19.5	18.6	10.0(*)	5.71	5.67
Meanal Solids Retention Time, min	(*)	5	5	5	5
Duration of Steady-State Period, hr	11	15	3.75	14.1	2.0
Total Product, Pounds	70	132	34	143	10.4

(*) Standard conditions are 29.92 in Hg and 70°F.
 (*) Uncertain because of agglomerate in reactor.
 (*) Not measured.
 (*) 9.5% based on original raw coal.
 (*) In draft tube.

TABLE I

Properties of Pittsburgh Seam Coal and Products

Run Number	Pittsburgh Seam		IP		2P2		-3P	
	Temperature, °F	Hydrogen, Wt % (dry basis)	Wt %	Density (t)	Wt %	Density	Wt %	Density
Carbon	72.24	70.51	16.3	50.6	16.1	42.4	13.8	47.7
Nitrogen	1.35	1.45	31.0	57.5	27.3	51.5	24.2	51.5
Oxygen	3.55	4.05	31.1	71.2	31.0	56.5	29.2	58.8
Sulfur	11.36	11.12	1.8	73.9	15.2	62.8	16.9	61.9
Volatiles Matter	40.1	32.7	0.5	76.8	2.1	74.0	5.5	70.2
Pyritic Sulfur	2.53	1.76						
Sulfate Sulfur	.07	.08						
Size, Tyler Mesh								
+84			0	81.0	3.4	42.0	4.0	41.2
24 x 28	11.2	11.2	16.3	50.6	16.1	42.4	13.8	47.7
28 x 35	35.4	35.4	31.0	57.5	27.3	51.5	24.2	51.5
35 x 48	34.8	34.8	31.1	71.2	31.0	56.5	29.2	58.8
48 x 65	16.9	16.9	1.8	73.9	15.2	62.8	16.9	61.9
65 x 100	1.2	1.2	0.5	76.8	2.1	74.0	5.5	70.2
-100	0.5	0.5						
Mean Diameter, in (s)		.0165		.0174		.0169		.0156
Mean Density, lb/ft ³ (s)		81.0		81.6		83.1		86.4
Maximum Fluidity DM (s)		> 37,000		16		1.0		

Run Number	Ireland Mine		PR1		PR1A		PR1R	
	Temperature, °F	Hydrogen, Wt % (dry basis)	Wt %	Density	Wt %	Density	Wt %	Density
Carbon	69.88	70.37	675	4.64	750	3.52	775	3.52
Nitrogen	1.25	1.08	70.37	10.2	70.44	9.7	70.60	10.2
Oxygen (by difference)	6.69	6.29	1.24	73.9	4.23	76.8	1.35	73.9
Sulfur	12.66	13.02	6.29	43.2	4.23	43.2	4.92	43.2
Volatiles Matter	41.3	35.5	13.02	15.02	15.02	16.10	16.10	16.10
Size, Tyler Mesh								
+28								
28 x 35								
35 x 48								
48 x 65								
65 x 100								
100 x 150								
-150								
Mean Diameter, in (s)		.00717		.00774		.00914		.00923
Mean Particle Density, lb/ft ³ (s)		82		82		82		82

(t) Measured in mercury at 1 atmosphere.

(s) Arithmetic mean.

(s) Reciprocal mean.
(s) As measured in Glassler Plastometer
(ASTM Method D-2639-67T).

TABLE 8

Material Balances for Pittsburgh Seam Coal Preoxidation Runs

Basis: 100 lb Dry Coal Fed

Run Number	2PZ	4P	PR1	PR1B
Preoxidized Coal	93.30	97.85	94.05	92.23
Overhead Fines	.58	1.21	.72	1.95
Tar	.20	0	1.01	1.63
Carbon in CO + CO ₂	3.65	2.23	.67	1.17
Hydrogen in H ₂ O	1.10	.33	.73	.52
Hydrocarbons (C ₁ -C ₃)	.34(1)	.15(1)	.17	.88
Sulfur in SO ₂ and COS	.75(2)	.26(2)	.03	.09
Coal Oxygen to Products	0	0	1.70	1.39
Carbon and Sulfur in Condensate	N.D.	N.D.	.10	.10
Total	99.92	102.03	99.18	99.96

(1) Only CH₄ was determined.

(2) By sulfur balance on coal feed and preoxidized coal product.

TABLE 9

Distribution of Oxygen in Products of Preoxidation of Pittsburgh Seam Coal

Run Number	2P2		4P		PR7		PR1B	
	Lb/hr	Percent	Lb/hr	Percent	Lb/hr	Percent	Lb/hr	Percent
Output								
To Water	.648	46.6	.235	25.1	.602	76.7	.229	57.5
Condensate	.009	.6	.006	.6	.008	1.0	.006	1.5
Moisture in Gas	.546	39.3	.437	46.7	.133	16.9	.118	29.5
To CO ₂	.080	6.5	.058	6.2	.026	3.4	.029	7.3
To SO ₂	.056	4.0	.024	2.5	0	0	.001	.3
To COS	(1)	-	(1)	-	.002	.2	.002	.5
In Tar	0.0	-	0.0	-	.002	.2	.013	3.4
Unreacted O ₂	.040	3.0	.178	18.9	.012	1.6	.0	.0
On Coal (by diff.)					0.0	0.0	0.0	0.0
Total	1.389	100.0	.937	100.0	.785	100.0	.398	100.0
Input								
From Coal (by diff.)	0		0		.177		.078	
Lb/hr O ₂ from Air	1.389		.937		.608		.320	
Total	1.389		.937		.785		.398	

(1) Not determined.

TABLE 10

Effect of Pretreatment Pressure on
Decaking of 28 x 200 M Ireland Mine Coal

<u>Pretreatment Pressure, atm</u>	<u>Run No.</u>	<u>Pretreatment Temperature, °F</u>	<u>Wt. % Preoxidation</u>	<u>Pretreated Coal⁽¹⁾ Max. Fluidity, DDPM</u>
1.5	1A	700	5.5	9
1.5	2A	700	13.8	0
15	1P	700	19.5	16
15	2P2	750	18.6	1.0

(1) Via Gieseler plastometer (ASTM Method D-2639-67T).

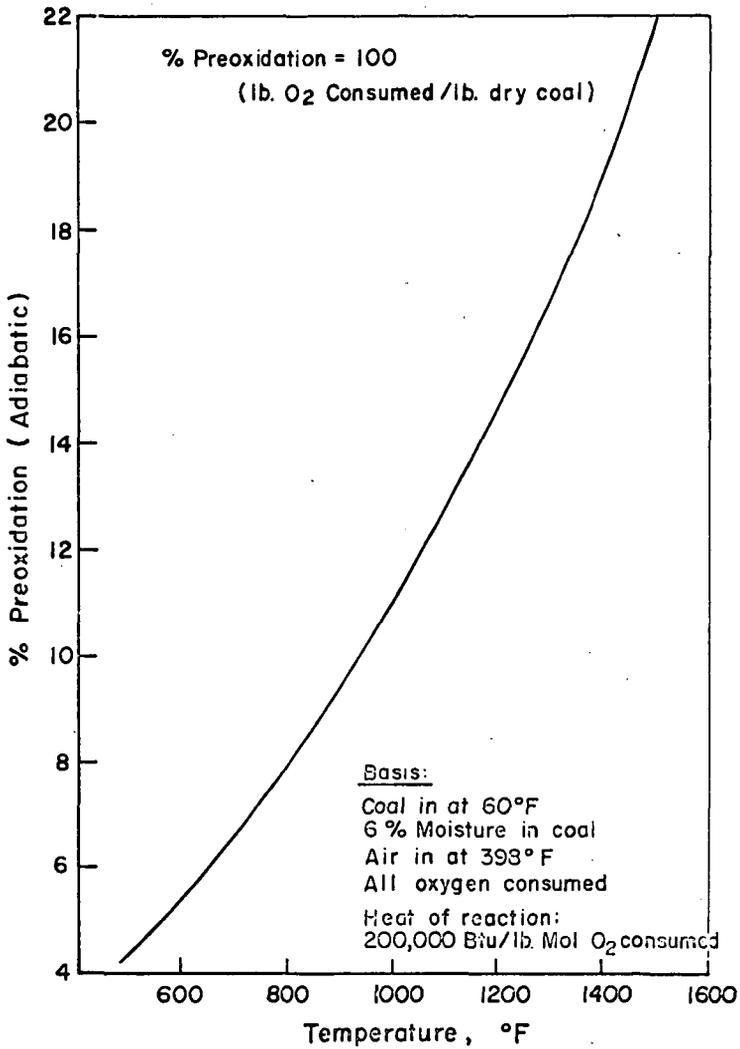


Figure 1 - % Preoxidation vs Temperature
For Adiabatic Constraint.

FIGURE 3
CONFIGURATION OF DRAFT TUBES USED IN SEEDED COAL TESTS

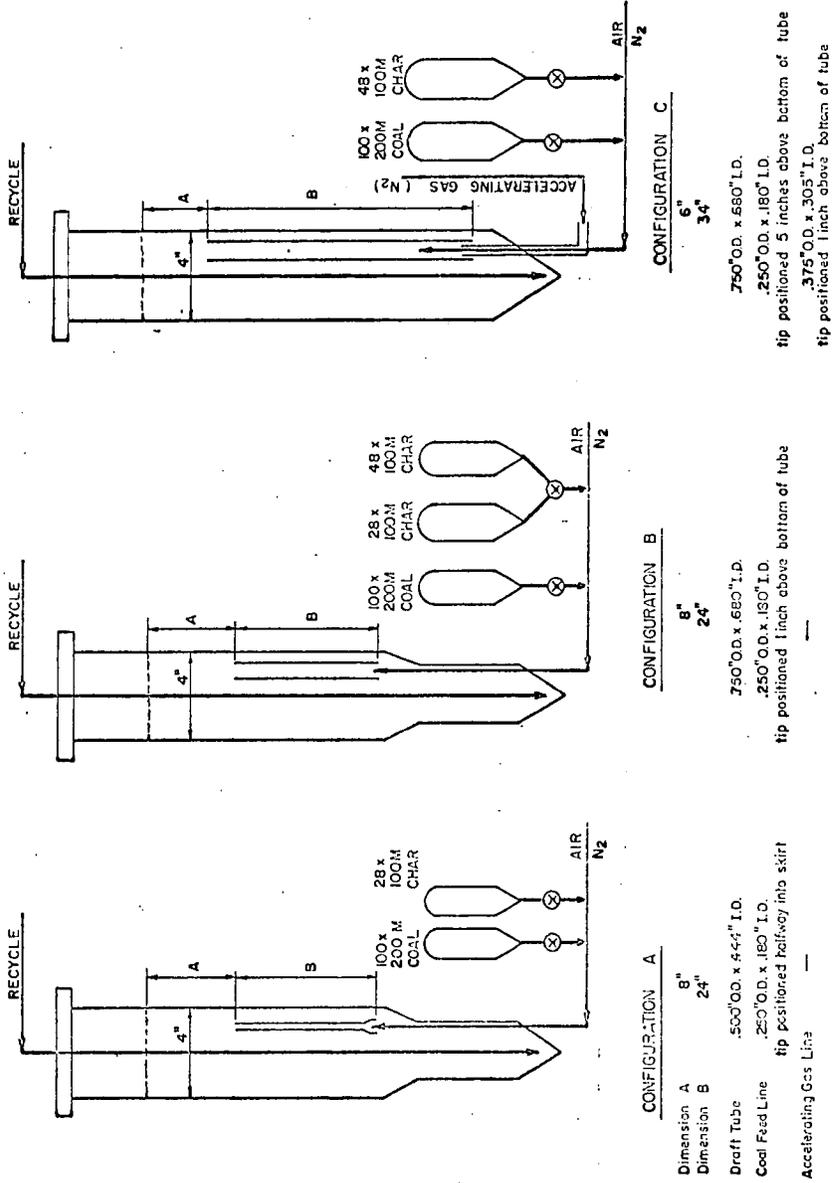
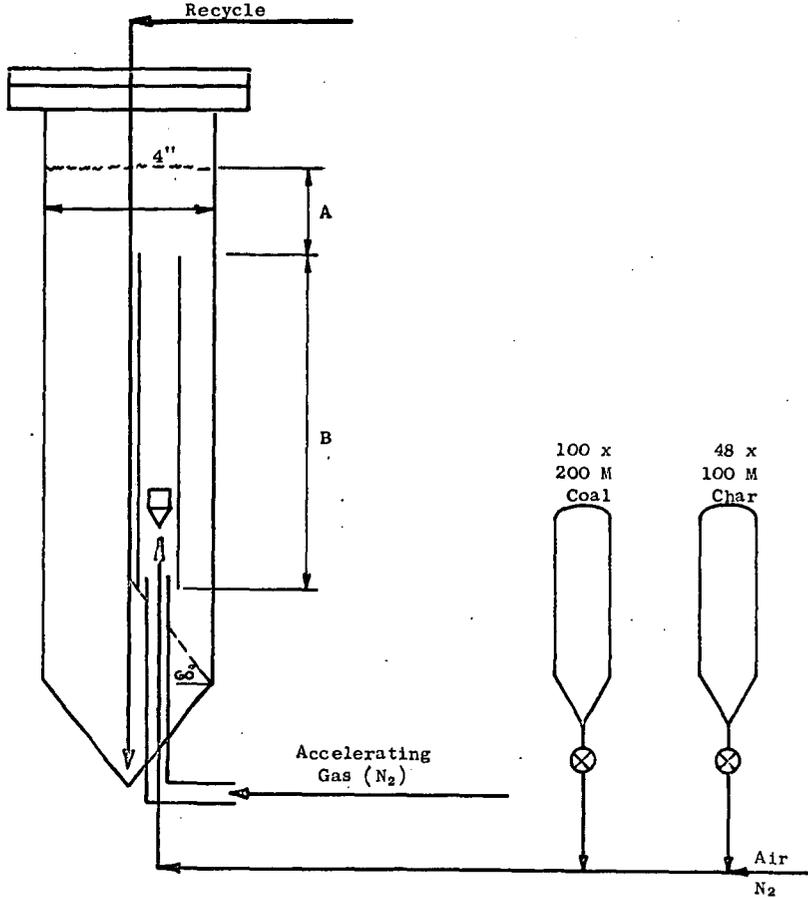


FIGURE 4

Configuration of Draft Tube Used in Seeded Coal TestsCONFIGURATION D

Dimension A	4"
Dimension B	34"
Draft Tube	.750" O.D. x .630" I.D.
Coal Feed Line	.250" O.D. x .180" I.D.
	Tip positioned 5-inches above bottom of tube
Accelerating Gas Line	.375" O.D. x .305" I.D.
	Tip positioned 1-inch above bottom of tube
External Baffle	3-5/8" x 1-3/4"
	Elliptical, 60° from the horizontal
Internal Baffle	3/8" D x 60° Cone
	Tip positioned 1/2" above coal feed line

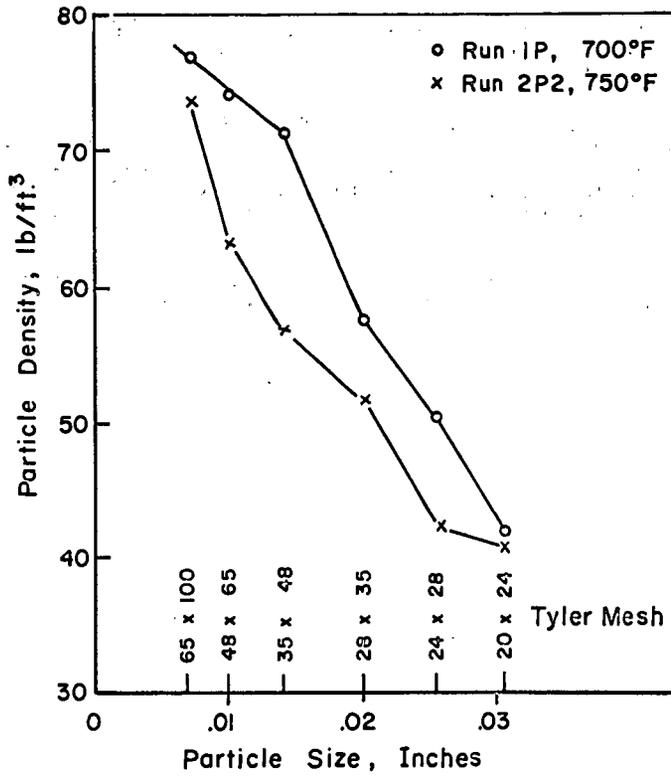


Figure 5 - Particle Densities For Preoxidized Ireland Mine Coal.

Movies of High-Velocity Fluidized Beds, Joseph Yerushalmi, The City College of The City University of New York, Department of Chemical Engineering, New York, N. Y. 10031

Movies will be shown (courtesy of Albert Godel and Babcock-Atlantique) of both experimental and commercial fluidized beds gasifying coal for the Ignifluid boiler. The movies elucidate the "Godel phenomenon" -- i. e., the accumulation of ash matter in agglomerates of golf-ball size from a bed of coke undergoing gasification by air at temperatures between about 1100° and 1300°C and fluidized at velocities of about 40 ft/sec.

Movies will also be shown of models at The City College of the "fast fluidized bed," in which fine solid is recirculated at velocities between 10 and 20 ft/sec.

TRACE ELEMENT ANALYSIS OF COAL BY NEUTRON ACTIVATION

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INTRODUCTION

This report presents the technology methods used at the NASA Plum Brook reactor (PBR) to analyze coal by neutron activation analysis. The work was performed for the Environmental Protection Agency (EPA) Division of Air Surveillance at Research Triangle Park, North Carolina, by the NASA Plum Brook reactor at Sandusky, Ohio, under an interagency agreement. Unfortunately, the work was terminated in January 1973 when the Plum Brook reactor was closed.

The general scheme of analysis - sample preparation, irradiation, and sample counting - is described. The discussion of data reduction includes the computerized method, interference corrections, and the precision and accuracy of the method. Some typical trace element results are given for coal, fly ash, and bottom ash. The manpower requirement for the analysis of 1000 samples per year is stated.

THE ANALYSIS SCHEME

Figure 1 shows the overall analysis scheme used at PBRF to analyze coal and fly ash samples by neutron activation analysis (NAA). (These same techniques and methods, with only slight modification, were used for the NAA of kerosene, jet fuel, gasoline, fuel oil, residual oil, ore, air particulates on filters, bottom ash, sand, clam tissue, corn, cement, limestone, stack scrubber water, crab shells, and river water.)

The basic procedure used two aliquots of the sample. One aliquot was encapsulated in a polyethylene vial, the other in a synthetic quartz (Suprasil) vial. The polyethylene vial, containing 50 to 100 milligrams of coal (10 mg or less of fly ash), was irradiated for 5 minutes in a thermal neutron flux of $1.5 \cdot 10^{14}$ n/cm²/sec. Then the irradiated sample was counted at decay times of ~5 minutes, ~30 minutes, and 24 hours. The quartz vial was irradiated for 12 hours in the same flux and counted at about 3 weeks decay.

Samples were counted on a 4096 channel gamma ray spectrometer using a Ge (Li) detector with a crystal diameter of 35 mm and length of 27 mm. Acceptable counting distances ranged from 3 to 40 cm, with detector dead time restricted to <20% whenever possible. The detector resolution was 3 keV with linearity adjusted to 1 keV/channel and maintained at ± 1 channel or less.

DATA REDUCTION

Altogether there were two irradiations associated with each pollution sample, and four counts - 5 minutes, 30 minutes, 24 hours, and 3 weeks decay. Each count of each aliquot produced a paper tape. Each tape, along with information regarding decay time, count time, flux level, sample weight, counting distance, and other parameters was processed through the data reduction code "SPECTRA."⁽¹⁾ Computing time on an IBM 360 Mod 67 was under 1 minute for all four tapes associated with one sample. Data were reported to EPA as parts per million of each trace element in the sample.

INTERFERENCE CORRECTIONS

EPA designates the elements Hg, Se, As, as "very hazardous." As a result, we devoted much attention to the accurate determination of these four elements by NAA. We found that, in coal, both selenium and ytterbium interfered with the detection of mercury; ytterbium interfered with selenium; and bromine and antimony interfered with arsenic.

The appendix to this paper describes how factorial experiment design techniques were used to derive empirical correction factors needed for the accurate determination of Hg, Se, and As.

PRECISION AND ACCURACY

Table 1 shows the standard deviation and the range of counting precision associated with the determination of trace elements in coal. The standard deviation is based on five aliquots.

Table 2 provides information on the accuracy of the NAA methods. Results of NAA of NBS standard reference materials (trace elements in a glass matrix) are compared with certified and interim NBS values. Other elements reported to EPA were frequently checked with homemade standards and with standards submitted by EPA.

TYPICAL TRACE ELEMENT RESULTS

Tables 3.1 to 3.4 show the form of computer outputs typically obtained, one for each of the four spectra associated with one sample. The data include the PBR sample number, the EPA identification number, and the input data required for the computerized data reduction. The third column shows the 56 elements that were routinely reported. Column four gives the results in ppm, and column 5 gives the standard deviation at 1 σ in ppm.

Typical results are tabulated in table 4 for seven coal samples, bottom ash, and fly ash. The results are given in ppm. The elements are listed along with the isotopes actually detected. Examination of the data shows that calcium, cerium, iron, aluminum, barium, potassium, manganese, sodium, rubidium, tin, titanium, thorium, uranium, vanadium, and zirconium are concentrated in fly ash. An additional comment regarding uranium and thorium: these elements are naturally radioactive and are α -emitters. For each ton of coal burned, the potential hazard exists of emitting 0.3 curies of α -activity, based on 1 ppm of uranium in coal.

No element in table 4 shows a higher concentration in the bottom ash than in the fly ash.

THE ANALYSIS CAPABILITY

The analysis capability developed at the Plum Brook reactor was geared to analyze 1000 samples per year as a part time effort. The program was also geared to developing the technology to handle and irradiate a large variety of pollution related samples with a minimum of manpower. During a typical work week, 24 samples were irradiated, counted, and reported. Total manpower expended averaged 3.0 to 3.5 hours per sample. Computer running time amounted to approximately 1 minute per sample with 56 elements reported.

CONCLUDING REMARKS

The trace element analysis of coal using NAA has been shown to be an accurate, reliable, and instrumental method of analysis. The associated technology was also developed to permit the analysis of up to 56 trace elements in each of 1000 samples

per year as a part-time effort. Computerized data reduction reduced the total manpower required to 3.0 to 3.5 hours per sample.

APPENDIX - INTERFERENCE CORRECTIONS FOR MERCURY, SELENIUM, AND ARSENIC

by Anne Bodnar

The elements Hg, Se, As, and Cd are designated as "very hazardous" by EPA. This appendix describes the method used to derive the complex correction factors required to achieve an accurate determination of Hg, Se, and As by NAA. Cadmium did not require any special interference corrections.

We detected an accuracy problem with the determination of Hg in coal. A count at 5 to 6 weeks decay time produced a Hg result ranging from 2 to 10 times smaller than the value obtained at 3 weeks decay. A correction for Se interference on Hg was being made, but, because of the similarity in the half-lives of Hg²⁰³ and Se⁷⁵, the low Hg results at 6 weeks decay could not be explained.

A search of the Nuclear Data Tables⁽²⁾ produced another interference: 4.2-day Yb¹⁷⁵. Not only did the 282-keV peak of Yb¹⁷⁵ interfere with Hg²⁰³, but also the 400.7-keV peak of Se⁷⁵ interfered with the 396-keV peak area of Yb¹⁷⁵, which was used for the Yb correction on Hg²⁰³. In addition, another Yb isotope, 32-day Yb¹⁶⁹ interfered with the 264-keV peak area of Se⁷⁵, which is used in the correction on Hg²⁰³ (peak area at 279 keV). These discrepancies were not eliminated by using theoretical corrections.

Finally, the problem was resolved by irradiating standards and mixtures of standards in a factorial experiment. The experiment design was a full factorial experiment with three variables (Hg, Se, Yb) at two levels, with replication, and with a center point added to test higher order effects. The high level was selected as 100 micrograms (µg), the low level as 10 µg. Table A-1 shows the treatments that were used.

Regression analysis on the data was used to estimate the coefficients in a predictive model equation. The dependent variable was chosen as the difference between the computer calculated value for Hg (or Se or Yb) and the true value. Independent variables were the other two elements plus plausible interactions (e.g., the interaction of Se-Yb on Hg). The coefficients derived for the predictive equations served as the basis for the empirical correction of Yb on Se and vice versa, and Yb-Se on Hg. Table A-2 compares the theoretical correction factors with the final form of the corrections based on the empirical data. A special subroutine was added to the SPECTRA computer program. The program was then tested by irradiating and analyzing other known samples. The calculated values agreed with the known sample contents. The method now allows us to determine Se and Hg in the presence of interferences which may be ten times greater in quantity.

This same technique has been used to determine arsenic in the presence of bromine and antimony.

REFERENCES

1. G. A. Borchardt, G. E. Hoagland, and R. A. Schmitt, J. Radioanalyt. Chem., **6**, 241 (1970).
2. Anon., "Nuclear Data Tables," Academic Press, New York, N.Y.

TABLE A-1

Treatment	Se	Hg	Yb	
1	-1	-1	-1	(-1) indicates low level, 10 μ g
2	+1	-1	-1	
3	-1	+1	-1	(+1) indicates high level, 100 μ g
4	-1	-1	+1	
5	+1	+1	-1	CP indicates $\left(\frac{\text{High level} + \text{low level}}{2}\right)$
6	-1	+1	+1	
7	+1	+1	+1	
8	+1	-1	+1	
Replicates				
4	-1	-1	+1	
7	+1	+1	+1	
8	+1	-1	+1	
Center point	CP	CP	CP	

TABLE A-2

1. Theoretical corrections for Se and Yb interferences on Hg

$$1. A_c = A_u - 0.0369 X$$

$$2. B_c = B_u - 0.118 A_c$$

$$3. D_c = D_u - 0.959 B_c - 0.387 A_c$$

2. Empirical form of Se and Yb correction factors for interference on Hg

$$1. A_c = A_u - 0.0433 X$$

$$2. B_c = 0.443(B_u - 0.118 A_c)$$

$$3. D_c = D_u - 1.65 B_c - 0.387 A_c$$

where A_c = selenium 264.6 KeV area corrected for Yb¹⁶⁹

A_u = net area of selenium (264.6 KeV), uncorrected

X = net area of Yb¹⁶⁹ at 177.2 KeV

B_c = ytterbium 396.1 KeV area corrected for selenium (264.6 KeV)

B_u = net area of ytterbium (396.1 KeV) uncorrected

D_c = mercury 279.1 KeV area corrected for selenium and ytterbium

D_u = net area of mercury (279.1 KeV) uncorrected

TABLE 1. - PRECISION OF EPA ROUND ROBIN COAL SAMPLE

Element	ppm	% std dev (1 σ)	Range of counting precision at 1 std dev, %
Ti	1 312	12	10-20
V	36	11	5-10
Al	15 700	9	0.6-1
S	<30 500	50	-----
U	0.98	8	8-12
Ba	340	12	5-8
Sr	93	10	8-11
I	2.8	14	12-30
Mn	38	7	0.5
Mg	890	28	12-33
Na	370	9	2-3
Cl	750	10	2
Ca	4 070	14	8-15
Cu	14	6	3-5
As	5.9	9	10-12
Br	20.	15	9-12
K	3 500.	10	3-4
Cd	<55	23	-----
Ce	17.3	5	1-2
Se	3.8	13	25-33
Hg	0.95	10	7-40
Cr	19	4	3-5
Cs	2.6	3	8-10
Ag	<0.4	25	-----
Zr	<70	55	-----
Zn	7.5	--	33
Fe	7 520	2	1
Co	5.5	15	1-13
Sb	6.4	24	8-15
Ni	<65	31	-----

TABLE 2. - COMPARISON OF NBS STANDARD REFERENCE MATERIALS WITH PBR RESULTS

	NBS 610*/PBR	NBS 612/PBR	NBS 614/PBR	NBS 616/PBR
Antimony	---	---	(1.06)/1.1 \pm .1	0.078 \pm .007/0.12 \pm .02
Cerium	---	(39)/37 \pm 2	---	---
Cobalt	(390)/135 \pm 14	(35)/31 \pm 1	0.73 \pm 0.02/0.59 \pm .006	---
Europium	---	(36)/26 \pm 1	0.99 \pm .04/1.1 \pm .6	---
Gold	(25)/20 \pm 2	(5)/4.7 \pm 1	(0.5)/1.0 \pm .8	---
Lanthanum	---	(36)/35 \pm 15	0.53 \pm .02/<2	---
Thorium	---	37.6 \pm .09/31.2 \pm 1	0.746 \pm .007/0.58 \pm .15	0.025 \pm .004/0.018 \pm .002
Scandium	---	---	0.59 \pm .04/0.68 \pm .23	0.026 \pm .012/0.020 \pm .004
Silver	(254)/180 \pm 80	22.0 \pm .8/31 \pm 7	0.46 \pm .02/0.57 \pm .07	---

* NBS values in parentheses are interim values for various reasons. Others are certified values.

TABLE 3.1 - TYPICAL INPUT AND OUTPUT DATA

SAMPLE NUMBER 2685
 ---EPAFA1280

DECAY TIME	810.	SEC.						
COUNT TIME	200.	SEC.						
SAMPLE MASS	0.4400F-01	GRAMS						
READ TIME	32.00	?						
LENGTH OF IRRADIATION TIME	300.0	SEC.						
FLUX LEVEL	0.1720F 15	NT. DEP SQ.CM. DEP SEC.						
DISTANCE	10.0CM.							
AREA OF FILTER IRRADIATED	0.000	SQ.CM.						
TOTAL AREA OF FILTER	0.000	SQ.CM.						
VOLUME OF AIR FILTERED	0.00000000	CURIC METERS						
KSIDPEA	4							
PG 2685	---	EPAFA1280	;	RH	;	0.58628274E-01	;	0.68124980E-02
PG 2685	---	EPAFA1280	;	YI	;	0.32399634E 03	;	0.43813904E 02
PG 2685	---	EPAFA1280	;	V	;	0.12669642E 02	;	0.68239159E 00
PG 2685	---	EPAFA1280	;	AL	;	0.34132515E 04	;	0.44224457E 02
PG 2685	---	EPAFA1280	;	S	;	0.74391514E 04	;	0.49796404E 04

TABLE 3.2 - TYPICAL INPUT AND OUTPUT DATA

SAMPLE NUMBER 2687
 ---EPAFA1280

DECAY TIME	2775.	SEC.				
COUNT TIME	1000.	SEC.				
SAMPLE MASS	0.44005-01	GRAMS				
DEAD TIME	20.00	%				
LENGTH OF IRRADIATION TIME	300.0	SEC.				
FLUX LEVEL	0.1720F 15	NT. DEP	50.0CM.	DEP	SEC.	
DISTANCE	10.0CM.					
AREA OF FILTER IRRADIATED	0.000	SQ. CM.				
TOTAL AREA OF FILTER	0.000	SQ. CM.				
VOLUME OF AIR FILTERED	0.00000000	CUBIC METERS				
KSIUPRA	4					
ROC 2687	---	EPAFA1280	U	0.57538927E	00	0.76593624E-01
ROC 2687	---	EPAFA1280	NY	0.57757538E	00	0.11211038E-01
ROC 2687	---	EPAFA1280	SA	0.58960208E	02	0.60001298E 01
ROC 2687	---	EPAFA1280	SP	0.39513138E	02	0.71572109E 01
ROC 2687	---	EPAFA1280	T	0.25780185E	01	0.50809118E 00
ROC 2687	---	EPAFA1280	MN	0.31050940E	01	0.68131624E-01
ROC 2687	---	EPAFA1280	NA	0.24354018F	03	0.64190508E 01
ROC 2687	---	EPAFA1280	CL	0.11268865E	04	0.20264618E 02
ROC 2687	---	EPAFA1280	TF	0.12514082F	02	0.45227633E 01
ROC 2687	---	EPAFA1280	GF	0.42372340F	02	0.27317642E 02
ROC 2687	---	EPAFA1280	IN	0.1403172E-	01	0.82265325E-02
ROC 2687	---	EPAFA1280	MG	0.2216431F	04	0.10726028E 04
ROC 2687	---	EPAFA1280	CA	0.13337019F	04	0.299888428E 03

TABLE 4. - ENVIRONMENTAL PROTECTION AGENCY SAMPLES* - COAL, FLY ASH, AND BOTTOM ASH

Element/ isotope	Coal L-14	Coal L-15	Coal L-16	Coal L-17	Coal L-18	Coal L-19	Coal L-20	Bottom ash L-21	Fly ash L-22	Fly ash L-23
Ag ^{110M}	<0.9	<0.7	<0.6	<0.6	<0.2	<0.2	<0.3	<0.2	<0.4	<0.2
Al ²⁸	17 200	8 080	13 300	12 100	10 800	6.170	27 600	67 500	89 600	99 700
As ⁷⁶	7.00	<1.2	4.8	<5	2.44	1.6	<6	<5	<7	<6
Au ¹⁹⁸	0.003	C.10	0.07	0.15	0.06	0.02	<0.4	<0.5	<2	<2
Be ¹³⁹	92	34	48	53	45	29	565	1500	1641	2370
Br ⁸²	20	3	22	19	9.0	16	<20	<15	<50	<30
Ca ⁴⁹	7 740	3 640	5640	<5 000	3290	1910	5960	14 300	23 200	26 200
Cd ¹¹⁵	<300	<110	<110	<90	<200	<30	<100	<900	<1200	<2000
Ce ¹⁴¹	21.1	8.83	16.2	13.0	10.6	8.97	28.0	71.8	104	103
Cj ³⁸	2820	1220	2760	1450	1250	2350	189	94	<200	168
Ni(Co ⁵⁸)	<90	<30	<80	<70	<60	<30	<20	<50	<80	<50
Co ⁶⁰	5.98	3.07	5.22	4.40	3.84	4.02	1.92	4.72	6.6	6.8
Cr ⁵¹	24.2	18.0	21.4	19.4	19.3	12.2	5.26	14.8	22	21
Cs ¹³⁴	3.32	1.56	2.58	2.35	2.03	1.13	0.92	2.81	4.4	4.1
Cu ⁶⁴	<30	29	<20	<20	<20	<20	<50	37	57	70
Dy ¹⁶⁵	1.2	0.58	0.76	0.77	0.67	0.42	0.90	2.0	2.8	3.50
Eu ^{152m1}	0.56	0.2	0.32	0.31	.30	.18	.36	0.91	1.2	1.5
Fe ⁵⁹	8970	13 700	9500	10 900	11 600	4550	6150	20 000	24 400	23 600
Ga ⁷²	7.2	<2	4.0	4.2	5.5	2.9	<6	<2	<30	<30
Ge ⁷⁵	<70	<4	<120	<40	<150	<200	<20	<200	<300	<400
Hf ¹⁸¹	1.05	0.50	0.81	0.65	0.60	0.42	2.28	6.50	8.5	8.7
Hg ²⁰³	<0.7	<0.5	<0.6	1.91	0.16	<0.3	<0.5	<0.7	<0.9	<0.9
Gd ¹⁵⁹	<70	<60	<40	<30	<40	<20	<80	<120	<140	<400
I ¹²⁸	<0.2	<1	<0.5	1.8	<2	0.65	<2	<1	<2	<20
In ^{116m1}	<0.05	<0.03	<0.02	0.073	0.029	<0.01	<0.05	<0.07	<0.02	<0.07

*The EPA could not reveal the source of these samples.

TABLE 4. - Continued. ENVIRONMENTAL PROTECTIVE AGENCY SAMPLES - COAL, FLY ASH, AND BOTTOM ASH

Element/ isotope	Coal L-14	Coal L-15	Coal L-16	Coal L-17	Coal L-18	Coal L-19	Coal L-20	Bottom ash L-21	Fly ash L-22	Fly ash L-23
Ir ¹⁹²	5.3	1.9	2.2	6.7	1.6	1.8	7	11	9.8	13
K ⁴²	7130	2464	3932	3748	3420	1690	1810	7170	9064	9800
La ¹⁴⁰	17.2	5.7	7.2	26	7.3	5.4	20	29	25	57
Lu ¹⁷⁷	0.58	0.36	0.42	0.32	0.35	0.22	0.51	1.23	1.6	1.8
Mg ²⁷	<450	<850	<1200	<4000	585	<600	1320	<11 000	2400	<9000
Mn ⁵⁶	95	53	62	49	38	25	93	300	371	422
Mo ⁹⁹	<600	<700	<260	<350	<300	<200	<3100	<2200	<13 000	<6000
Na ²⁴	1250	882	1070	833	757	487	2850	6080	8430	14 000
Nd ¹⁴⁷	<7	<2	<2	<5	<7	<3	<7	<10	<40	<30
Pt ¹⁹⁷	<300	<170	<160	<230	<200	<100	<1000	<700	<1400	<3200
Rb ⁸⁶	25.6	12.3	20.7	21.4	16.8	7.98	8.66	15.9	45	41
Re ¹⁸⁸	<0.3	<0.2	<0.2	<0.3	<0.4	<0.3	<0.5	<2	<1	<0.4
Rh ¹⁰⁴	<0.03	<0.09	<0.04	<0.2	<0.06	<0.06	<0.07	<0.3	<4	<0.3
S ³⁷	*	37 500	<53 000	<7 000	<9000	<30 000	<200 000	168 000	<200 000	<300 000
Sc ⁴⁶	4.56	2.67	3.84	3.42	3.17	2.07	3.02	7.42	11.4	11.7
Sb ¹²⁴	1.39	0.84	1.12	0.93	0.62	0.86	0.80	0.50	2.1	1.8
Se ⁷⁵	4.15	3.12	2.99	3.19	2.86	1.77	3.07	2.10	5.98	5.72
Sm ¹⁵³	2.23	0.82	1.2	1.2	1.1	0.81	1.5	3.5	4.4	4.9
Sr ^{87m}	56	<30	36	<20	<40	<20	106	<100	223	<200
Sn ^{117m}	76.5	<40	74.2	66	50	34	86	428	555	422
Ta ¹⁸²	0.35	0.12	0.27	0.25	0.18	0.17	0.65	1.66	2.4	2.4
Tb ¹⁶⁰	0.036	0.018	0.027	0.025	0.022	0.015	0.048	0.12	0.18	0.18
Th(Pa ¹³³)	4.19	2.16	3.23	2.84	2.84	1.73	7.49	19.1	25	25

* Data missing.

TABLE 4. - Concluded. ENVIRONMENTAL PROTECTIVE AGENCY SAMPLES - COAL, FLY ASH, AND BOTTOM ASH

Element/ isotope	Coal L-14	Coal L-15	Coal L-16	Coal L-17	Coal L-18	Coal L-19	Coal L-20	Bottom ash L-21	Fly ash L-22	Fly ash L-23
Ti51	1680	912	608	980	908	529	893	3820	4280	3428
U239	1.5	0.96	0.82	1.14	0.82	0.68	1.3	3.7	4.7	4.9
V52	34	23	26	27	23	15	18	29	65	64
W187	<4	<0.3	<0.4	<2	<2	<2	<20	<15	<20	<30
Yb175	3.68	1.88	4.06	1.83	0.46	0.91	0.84	2.36	3.8	2.9
Zn65	264	<3000	220	148	118	<400	<2000	187	299	341
Zr95	<50	<50	<50	<40	<50	<30	107	261	400	556

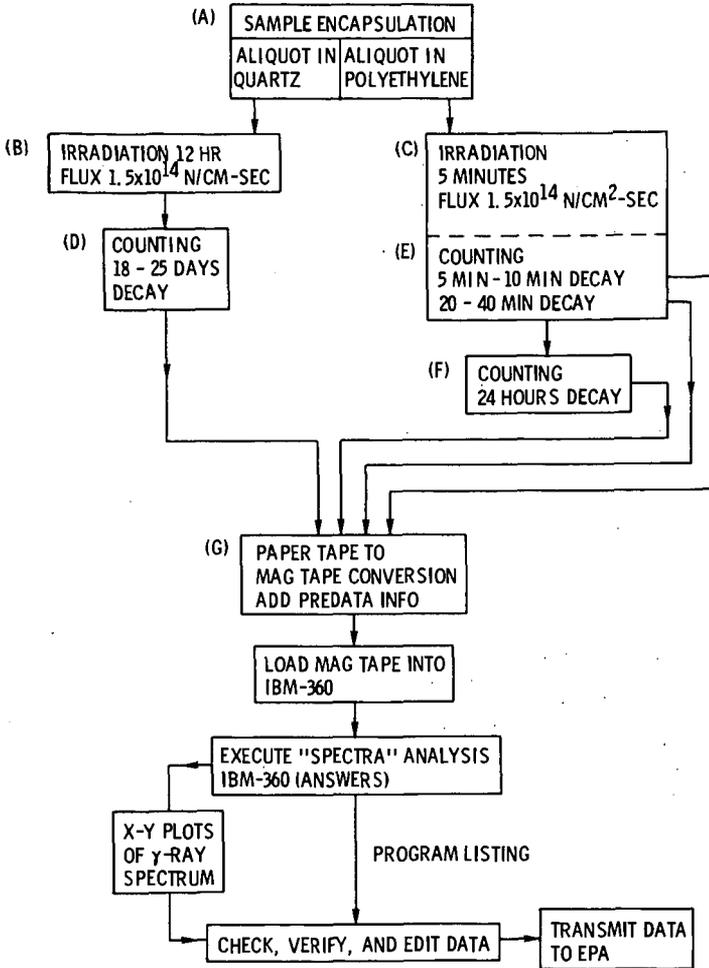


Figure 1. - Flow chart showing scheme for sample irradiation, counting, and data reduction of coal samples.

X-RAY FLUORESCENCE ANALYSIS OF WHOLE COAL

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Illinois State Geological Survey

Introduction

Recent interest in the trace element content of coal has led to the need for development of rapid, accurate analytical methods for their determination. Because X-ray fluorescence analysis has demonstrated its usefulness in the determination of major, minor, and trace elements in numerous types of materials, it was felt that this method could be extended to trace element determinations in whole coal. In the past such analyses have been seriously hampered by the lack of standard samples. However, U. S. Environmental Protection Agency sponsored research, which is being conducted in our laboratories, has generated a large number of coal samples for which trace elements have been determined by two or more independent analytical procedures (viz. optical emission, neutron activation, atomic absorption and wet chemical methods). Using these coals as standards, a X-ray fluorescence method has been developed for the determination of a number of trace and minor elements in pressed whole coal samples.

The instrument used in this project was a Phillips manual vacuum X-ray fluorescence spectrometer. All analyses for this study were made in the Analytical Chemistry Laboratories of the Illinois State Geological Survey. The work upon which this report is based was partially supported by U. S. Environmental Protection Agency Contract 68-02-0246.

Preliminary Investigation of Major and Minor Elements
in Whole Coal and Coal Ash

Two different types of materials - coal ash and whole coal - were analyzed in this project, and sample preparation was varied accordingly.

Whole coal was ground with 10 per cent by weight of a binder and pressed into a disc, which was used as the analytical sample without further treatment. Sample preparation techniques are given in detail in Illinois State Geological Survey Environmental Geology Note 61.

It was found that two grams of coal gave a disc that was infinitely thick with respect to soft X-rays emitted by "light" elements such as Mg, Si, Al, and Ca; however, for elements "heavier" than Br, it was necessary to increase the sample weight to attain infinite sample thickness, i.e., no X-rays penetrated through the pressed coal sample.

Our use of X-ray fluorescence was originally intended for the purpose of establishing major element matrix information on coal ashes to be analyzed for trace elements by optical emission spectroscopy. Both low temperature (<150° C) and high temperature (450° C) coal ashes, prepared as described by Kuch, Gluskoter, and Shimp (1973), were used for this purpose, and the method of Rose, Adler and Flannigan (1961) was adapted for the determination of major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, and V). The instrumental parameters used for these elements are given in Table 1. To assess the validity of this procedure, a series of analyzed coal ashes obtained from the British Coal Utilization Research Association (BCURA) were analyzed along with the two types of ash prepared in our laboratories. Calibrations for these analyses were prepared from National Bureau of Standards rock standards (1B, 1C, 1D, No. 78, No. 79, No. 88). The values determined for the BCURA coal ashes were in excellent agreement with published results of Dixon, Edwards, Flint, and James (1964). Standard deviations were calculated for duplicate coal ash determinations. They were: Si - .0715%, Ti - .0066%, Al - .0567%, Fe - .0493%, Mg - .0178%, Ca - .0282%, K - .0123%, P - .0074%, and V - 1.3 ppm. These deviations are comparable to "Class A" wet silicate analyses and are indicative of a high degree of accuracy.

Because of these encouraging results and previous work on brown coals by Sweatman, Norrish, and Durie (1963) and Kiss (1966), which indicated that major and

minor elements could be determined in whole coal, a series of 25 coals were prepared for analysis. For each coal, a low temperature ash, a high temperature ash and the whole coal itself were prepared for X-ray fluorescence analysis sample preparation procedures. When all values were converted to the whole coal basis, the agreement among the three types of coal materials was excellent (Table 2) indicating that the simpler and more rapid whole coal technique is acceptable for the determination of major and minor elements.

Determination of Trace Elements in Whole Coal

Trace element determinations on whole coal have been severely handicapped by the lack of analyzed standards. Because of this it has been necessary to prepare calibration curves from samples analyzed in our laboratories by other independent methods. The accuracy of the X-ray fluorescence method is, therefore, limited by the accuracy of the methods used for obtaining the trace element concentrations that were employed in preparing the calibrations. The difficulties encountered in uniformly adding known quantities of trace elements to ground whole coal prohibited the preparation of calibrations in that fashion.

The "light" coal matrix of carbon, hydrogen and oxygen and the relatively small variation of "heavier" trace elements permits their determination with a minimum of interferences. Using the same whole coal procedures as previously described for the determination of major and minor elements, P, V, Cr, Mn, Co, Ni, Cu, Zn, As, Br, Mo, and Pb have been determined directly in 50 whole coals.

The relative errors for all* elements determined are given in Table 4. These data indicate the precision obtained for the X-ray fluorescence analysis on duplicates of 15 samples of whole coal ground to -325 mesh. Accuracy of the X-ray fluorescence method was evaluated by calculating, from the 50 whole coals analyzed, the mean variation of each element* from its mean concentration as determined by the other independent methods previously mentioned (Table 5). Detection limits (three standard deviations above background) for each element are also given in Table 5.

X-Ray Matrix Corrections for Analysis of Whole Coal

Due to the lack of standards, variations in analyses made by other methods, and errors caused by coal sampling problems; it has been difficult to evaluate the need for X-ray matrix corrections and to select the best method for applying them. However, corrections were necessary because some elements in whole coal such as Fe, Si, and S may vary considerably. For these elements, corrections were applied indiscriminately to all samples because it was impossible to determine the point at which matrix variations required a correction greater than the accuracy limits of the method. We elected to use the minimum number of corrections compatible with reasonably accurate results. As a result the elements Mg, Al, Si, P, S, Cl, K, and Mo were left uncorrected. While these determinations probably could be improved (Berman and Ergun, 1968) they were shown to be adequate for our purposes (Table 2). The Ti and V values were corrected by using the variations in whole coal iron content.

The method of correcting the other elements for matrix variations was that of Sweatman, Norrish and Durie (1963). A total mass absorption was determined by measuring the attenuation of the radiation in question by a thin layer of the sample to be analyzed. The mass absorption coefficient M was calculated by
$$M = \frac{A}{W} \ln \frac{C_s}{C_x}$$

where A = area of sample (cm^2); W = weight of sample in grams; C_s = intensity in counts per second of the standard; and C_x = intensity in counts per second of the standard attenuated by the coal sample. Using these coefficients, a corrected value was obtained for the elements determined even when matrix variations were considerable. It should be noted that great care was taken to press the coals to a uniform thickness so that the mass absorption coefficient was affected only by density (for which compensation was made) and matrix considerations.

* For completeness, whole coal minor element data are also included in the trace element tables.

Effect of Coal Particle Size Upon Trace Element Analytical Precision

Our results indicated that coals ground to -60 mesh did not yield a consistently acceptable precision for most trace element determinations. Therefore, it was necessary to evaluate the errors associated with the determination of trace elements in coals ground to different particle sizes.

Nine coals, representing a range of trace element concentrations, were carefully ground to pass screens of various mesh sizes (Table 6). Duplicate two gram coal samples for each mesh size were weighed and, then, all were further reduced in size by grinding for 3 minutes in a No. 6 Wig-L-Bug. The final grinding of analysis samples eliminated, as nearly as possible, any variation in the pressed coal discs, which were subsequently prepared for analysis according to Ruch, Gluskoter, and Shimp (1973). In all, over 1000 individual determinations were made in this study.

Table 6 gives the combined means of the differences between duplicate trace element determinations for each coal particle size analyzed. Both the means of the absolute differences (ppm) and the means of the relative differences (absolute difference expressed as a percentage of the concentration) are given. The results show that there is a progressive improvement in precision with decreasing coal particle size.

The ranges of relative differences between duplicate analyses for a number of trace elements at three coal mesh sizes are given in Table 3. With the exception of Br, the ranges are narrower for the -200 and -325 mesh sizes than they are for the -60 mesh coal.

Progressive reduction in coal particle size from -60 to -400 mesh resulted in the improvement of precision for all elements except Br. The combined mean for all elements was reduced below 5% for coal ground to pass a -200 mesh sieve.

These data indicate that for most purposes acceptable precision can be obtained on -200 mesh coal. Further improvement is achieved on grinding to -325 mesh, but this will usually be unnecessary except for analyses to be used as standard values or other special purposes. Variations in the original field sampling of coal would probably negate any improvements in precision that might be gained from grinding below the -325 mesh size.

While this study applied directly to X-ray fluorescence analysis of whole coal, it is felt that it should also apply to any method in which a limited sample (~ 3 grams or less) is taken for analysis.

Discussion and Conclusions

Good agreement of whole coal results, as determined by X-ray fluorescence, was obtained with those values determined by several other independent methods (Table 5). Some variations among the methods were found to occur at the higher trace element concentrations, especially for the more coarsely ground coals. Because this was true not only of the X-ray fluorescence method, but also of the other methods investigated, it was felt that the variations were due to sampling errors caused by the occurrence of discrete mineral particles such as pyrite and sphalerite in whole coal. This has now been demonstrated to be true by geologists at the Illinois State Geological Survey using the scanning electron microscope.

It is apparent from Table 5 that trace elements determined by the X-ray fluorescence method described in this report are limited to those elements occurring in whole coals at concentrations of a few parts per million or greater. Elements such as Se, Hg, and Sb, which are usually present in whole coal at levels below one ppm, are not capable of being determined by this method.

Our results indicate that X-ray fluorescence provides a highly useful tool for rapid and reasonably accurate analysis of whole coal for trace elements. Because of the speed and simplicity of the method, it is highly adaptable to large scale surveys of coal resources. While the limitations of this simple procedure may preclude the determination of certain elements, the time-saving factor over other methods (40 or 50 to 1 in the case of Br by neutron activation) without loss of accuracy may well make X-ray fluorescence the method of choice for many elements. The availability of improved equipment, such as nondispersive systems and automation, could extend the application of X-ray analysis to a dominant position for the determination of trace elements in whole coal.

TABLE 1 - SPECTROMETER PARAMETERS

Element	X-Ray	2 θ Angle	Background 2 θ	Crystal	X-Ray Tube	PHA Volts	
						Base	Window
Si	KL ₃ & KL ₂	108.01 ^o	111.01 ^o	EDDT	Cr	7	17
Al	KL ₃ & KL ₂	142.42	145.95	EDDT	Cr	5	17
Ti	KL ₃ & KL ₂	86.12	89.12	LiF	Cr	5	18
Fe	KL ₃ & KL ₂	57.51	60.51	LiF	Cr	5	25
Ca	KL ₃	44.85	47.95	EDDT	Cr	14	30
K	KL ₃ & KL ₂	50.32	53.90	EDDT	Cr	14	21
Mg	KL ₂₃	136.69	139.69	ADP	Cr	4	8
V	KL ₃ & KL ₂	76.93	80.93	LiF	Cr	5	16
S	KL ₃ & KL ₂	75.24	78.38	EDDT	Cr	12	18
Cl	KL ₃	64.94	67.94	EDDT	Cr	11	19
P	KL ₃ & KL ₂	110.99	113.99	Ge	Cr	9	15
Ni	KL ₃ & KL ₂	48.66	50.36	LiF	Cr	10	27
Cu	KL ₃ & KL ₂	45.02	49.67	LiF	Cr	11	28
Zn	KL ₃ & KL ₂	41.79	44.25	LiF	Cr	10	22
Pb	L ₃ N ₅ & L ₂ M ₄	28.24	31.24	LiF	Cr	22	28
Br	KL ₃ & KL ₂	29.97	35.12	LiF	Cr	25	23
As	KL ₃ & KL ₂	34.00	37.00	LiF	Cr	24	23
Co	KL ₃ & KL ₂	52.79	53.79	LiF	W	13	16
Mn	KL ₃ & KL ₂	62.97	63.97	LiF	W	8	12
Mo	KL ₃ & KL ₂	20.33	19.83	LiF	W	36	40
			20.83				
Cr	KL ₃ & KL ₂	69.35	68.35	LiF	W	7	15

TABLE 2 - MEAN ABSOLUTE VARIATION
BETWEEN RAW COAL AND ASH

Element	(%) Average Difference	(%) Maximum Difference
Si	.10	.24
Al	.08	.12
Ti	.012	.030
Fe	.10	.17
Ca	.04	.12
K	.02	.04
P	.002	.005
Mg	.010	.015

TABLE 3 - RANGE OF RELATIVE ERRORS IN
PERCENT AT THREE WHOLE COAL
PARTICLE SIZES

Element	-60 Mesh	-200 Mesh	-325 Mesh
V	0.0 - 10.0	.3 - 5.0	.3 - 4.0
P	2.0 - 18.0	2.0 - 10.0	1.5 - 7.5
Ni	1.5 - 25.0	.0 - 20.0	1.5 - 8.0
Cu	.8 - 20.0	.2 - 1.0	.2 - 1.0
Zn	1.2 - 25.0	1.2 - 12.0	.1 - 6.5
Pb	.4 - 23.0	1.2 - 9.5	.4 - 5.0
As	.1 - 6.0	.1 - 4.0	0.0 - 1.5
Br	0.0 - 4.0	0.0 - 3.5	0.0 - 3.0

TABLE 4 - DEVIATIONS ON -325 M
WHOLE COAL

<u>Element</u>	<u>Standard Deviation</u>	<u>Relative Deviation (%)</u>
	<u>per cent</u>	
Al	.021794	1.77
Si	.05319	1.96
S	.013038	.532
Cl	.0035496	1.13
K	.00370135	2.26
Ca	.005291	1.65
Mg	.002097	3.88
Fe	.021977	1.26
	<u>ppm</u>	
Ti	4.1580	.564
V	1.5801	3.84
Ni	1.11744	4.29
Cu	.74833	3.92
Zn	3.6105	1.37
As	.94291	2.49
Pb	1.5286	2.29
Br	.39047	2.11
P	3.4066	10.92
Co	.4300	4.79
Mn	4.1429	7.53
Cr	1.1402	4.35
Mo	3.1080	23.9

TABLE 5 - COMPARATIVE ACCURACY FOR WHOLE COAL
AND LIMITS OF DETECTION

<u>Element</u>	<u>Accuracy</u>	<u>Limit of Detection</u>
	<u>per cent</u>	<u>per cent</u>
Al	± .08	.012
Si	± .10	.016
S	± .04	.003
Cl	± .01	.0015
K	± .02	.003
Ca	± .04	.0005
Mg	± .010	.015
Fe	± .10	.005
	<u>ppm</u>	
Zi	± 6.3	7.5 ppm
V	± 3.1	2.5 ppm
Ni	± 1.9	3.5 ppm
Cu	± 2.5	1 ppm
Zn	± 23.	2 ppm
As	± 4.3	3.2 ppm
Pb	± 7.7	1.8
Br	± 1.0	.5
P	± 15.	15 ppm
Co	± 1.3	2.5
Mn	± 3.4	4.5
Cr	± 2.1	1.5 ppm
Mo	± 5.2	5 ppm

TABLE 6 - MEAN ERROR FOR ALL ELEMENTS AT
VARIOUS COAL PARTICLE SIZES

<u>Mesh size</u>	<u>ppm</u>	<u>(%) Error of Mean Element Concentration</u>
-60 M	± 3.05	8.47
-100 M	± 2.11	6.38
-200 M	± 1.26	4.28
-325 M	± 1.12	2.62
-400 M	± 1.02	1.56
<<400 M	± .93	1.40

References

- Berman, M. and S. Ergun, Bureau of Mines, R.I. 7124, 20(1968).
- Dixon, K., A. H. Edwards, D. Flint and R. G. James, Fuel, XLIII, 331-347 (1964).
- Kiss, L. T., Anal. Chem., 38, 1713-1715 (1966).
- Ruch, R. R., H. J. Gluskoter and N. F. Shimp, Ill. Geol. Survey, E.G.N. 61, 81 (1973).
- Sweatman, T. R., K. Norrish and R. A. Durie, C.S.I.R.O., M.R. 177, 30 (1963).

TRACE IMPURITIES IN FUELS BY ISOTOPE DILUTION MASS SPECTROMETRY

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INTRODUCTION

Elements considered toxic to living organisms are present from the low ppb to the high ppm concentration range in coal and other fuels used as energy sources. With over half of the consumption of coal being used by large central power stations, the concentrated quantities of such potentially harmful elements as Hg, Cd, Pb, U and others are appreciable. In the USA, for example, with an average annual coal consumption of over 500 million tons, any element present in coal at the 1 ppm level generates a waste problem of 500 tons. Many of the elements of interest are concentrated in the particulate fly ash or in the bottom slag. The use of efficient electrostatic precipitators, however, prevent most of the fly ash from being dispersed into the atmosphere. The fly ash and the bottom slag then become a storage and containment problem.

The major thrust of this research effort has been to demonstrate the capabilities of spark source and thermal emission mass spectrometry for determining the fate of trace elements in coal fired central power plants. Additionally, isotope dilution methods for the analyses of Pb, Cd and Hg in gasolines and other petroleum fuels have been developed and used for referee and evaluation purposes.

EXPERIMENTAL

Spark Source Mass Spectrometry

The spark source mass spectrometer (SSMS) in this research was a commercial Mattauch-Herzog double focusing instrument; a schematic representation is shown in Fig. 1. In a SSMS analysis, an ion beam of the substance being investigated is produced in a vacuum by igniting a spark between two conductors employing a pulsed high-frequency potential of 50 kV. During this process, the electrode substance is evaporated and ionized. The produced ions are accelerated through the source slits by a constant potential of 25 kV into an electrostatic radial field which functions as an energy filter. As the ions pass through the magnetic field, deflection occurs so that a splitting of the ion beam takes place according to the mass-to-charge ratio; these charged particles impinge in focus on an ion-detector (photographic plate or photo multiplier) to form the mass spectrum. From the position of the lines and the relative intensity, elemental identification and abundance measurements can be made when the total ion beam current is known; this total ion current is measured by a monitor located just ahead of the magnetic analyzer. The resolution of the AEI-702R instrument used was greater than 3000. Ilford Q-2 photographic emulsions were used to record the mass spectra.

*Operated for the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Conducting electrodes for general scan analyses were prepared by mixing the pulverized coal or fly ash with an equal amount of pure Ag powder (99.999% Ag). The homogenized mixture was then pressed in polyethylene slugs in an isostatic electrode die at 25,000 psi for 1 min. The nominal electrode size was 1 cm x 0.15 cm. Sets of graded exposures were made from these electrodes so that the concentration range from 0.03 ppm up to the percent range was covered. Photoplates were interpreted according to the techniques given by Kennicott.⁽¹⁾ In fly ash and coal samples, Fe was determined chemically so the isotopes of Fe could be used as an internal standard.⁽²⁾ Computerized sensitivity values were used.

Isotope Dilution By Spark Source Mass Spectrometry

A unique and quite different approach to the determination of trace elements in solids, liquids and gases involves the use of the isotope dilution technique. This method has been operational for some time with mass spectrometers, using thermal ionization sources for solids and electron bombardment sources for gases, giving accurate results with small samples; however, not until recently has it been used for analyzing environmental samples with spark source mass spectrometers.⁽³⁾ The general method of isotope dilution has been described by Hintenberger.⁽⁴⁾ For each element to be determined, an enriched isotope, usually of minor abundance, is mixed with the sample. The isotopic ratios, altered by spike additions, are then measured on a portion of the sample by mass spectrometry. Even though the method is limited to elements having two or more naturally occurring or long-lived isotopes, it possesses the great advantage over other analytical techniques of being very sensitive and accurate, and relatively free from interference effects. Thermal source and electron bombardment mass spectrometers are well suited for isotope dilution, but they display very different sensitivities for various elements; whereas spark source mass spectrometers have similar sensitivities for all elements and can therefore be used without deleterious effects from a complete matrix change.

Fig. 2 shows a mass spectrum of cadmium spiked with enriched ^{106}Cd . The solid line at position 106 represents the ^{106}Cd spike and the dashed lines represent the relative abundances for the other Cd isotopes. The dashed line at juxtaposition at 106 is the relative abundances of ^{106}Cd as it occurs in nature. Table I shows the IBM 1130 computer programmed output for a typical isotope dilution analysis. The program is flexible in that the spike size, sample size, spike composition, and percent transmittance can all be variables. The three sets of data under 106 and 114 are percent transmittance for three photoplate exposures taken, and the results are reported in nanograms per gram.

Isotope Dilution By Thermal Emission Mass Spectrometry

For the quantitative measurement of Pb and U in coal and fly ash and Pb in gasoline, a three-stage thermal emission mass spectrometer (TEMS) was used (Fig. 3). The basic design of the instrument is based on that developed by White and Collins 1954⁽⁵⁾ and modified at ORNL. The addition of an electrostatic third stage increased the abundance sensitivity to 10^8 as described by Smith et al.⁽⁶⁾

The two magnetic stages are 30-cm radius followed by an electrostatic analyzer with a radius of 43.25 cm. The vacuum system is of all-metal construction

and is bakeable to 300°C. The analyzer region of the instrument is pumped with ion pumps and is maintained at a pressure of 10^{-5} torr. A combination titanium sublimation-ion pump is used to obtain operating pressures in the source region in the 10^{-5} torr range. A Nier thick-lens source,⁽⁷⁾ used in conjunction with a sample wheel arrangement,⁽⁸⁾ makes it possible to analyze as many as ten samples per day.

Ions are detected by a secondary electron multiplier behind the receiver slit. The pulses from the multiplier are accumulated in a 400-channel analyzer used in the time base mode. This arrangement allows the maximum sensitivity with respect to sample size. Mass measurements are made by sweeping the accelerating voltage across the region of interest, 233 through 238 for U; 204 through 208 for Pb. The determinations of uranium and lead in coal and fly ash and Pb in gasoline, both quantitatively and isotopically, are done by isotope dilution with enriched spikes of ^{235}U and ^{204}Pb .

Pb Analysis by TEMS. Lead analyses are made utilizing the gel technique described by Cameron et al. 1969.⁽⁹⁾ Lead ions are thermally produced at rhenium filament temperatures ranging between 1100-1300°C depending somewhat on the sample size. A loading of 10 nanograms provides enough sample to allow an analysis consisting of 10 runs of 200 sweeps across the masses of interest.

U Analysis by TEMS. Uranium ions are thermally produced at rhenium filament temperatures ranging from 1700-1850°C. Small quantities (10-100 nanograms) of uranium in the form of $\text{UO}_2(\text{NO}_3)_2$ produce sufficient ions for a precise analysis. A benzene reduction procedure has been developed at ORNL which produces only metal ion signals. This procedure produces a very clean uranium spectrum and increases the sensitivity of the measurement. As in the analysis of lead, an analysis consists of at least 200 sweeps across the masses of interest.

Preparation of Coal and Fly Ash for Isotope Dilution Analysis. Separate aliquots of coal and fly ash are weighed out and spiked with ^{204}Pb and ^{235}U , respectively. The chemical treatment and extraction of Pb and U from coal and fly ash are identical except coal is ashed at 450°C before chemical treatment. The samples are dissolved with a mixture of $\text{HF}\cdot\text{HNO}_3\cdot\text{HClO}_4$ in Teflon beakers. The lead is separated by dithizone extraction, evaporated to dryness, redissolved in dilute HNO_3 and 10 ng loaded on filaments with silica gel for mass analysis.

The uranium is separated after dissolving the sample as described for lead by extraction with TBP from 4 M HNO_3 . After the organic phase is scrubbed with 4 M HNO_3 , the uranium is back extracted into distilled water and evaporated to dryness. The uranium is loaded on a rhenium filament by dissolving the purified sample in a small volume of 0.05 M HNO_3 for analysis.

Preparation of Gasoline for Isotope Dilution Analysis. Aliquots of gasoline are spiked with ^{204}Pb and treated by either a wet chemical method or the bromine oxidation method described by Griffing and Rozek.⁽¹⁰⁾

The wet chemical procedure consisted of refluxing first with HNO_3 until the initial reaction subsided, then HClO_4 was added to the flask and the reflux continued until the reaction was complete. The resulting solution containing the inorganic lead was finally evaporated to near dryness, diluted to a suitable Pb concentration with dilute HNO_3 and loaded onto Re filaments for M.S.

In the bromine method, Br_2 in CCl_4 was added to the gasolines in a test tube. Complete conversion to lead bromide was assured by heating. The resulting lead bromide precipitate was dissolved with dilute $\sim 1 \text{ M}$ HNO_3 . The mixture was centrifuged and the organic layer discarded; the aqueous solution was adjusted for M.S. analyses. Either of the procedures works satisfactorily, but the Br_2 method is much easier, faster and has less possibility for contamination.

RESULTS AND DISCUSSION

The bulk of the samples for this study came from TVA's Allen Steam Plant at Memphis, Tennessee. The sampling points (Fig. 4) included inlet air, coal, bottom ash, precipitator inlet and outlet at the 268-ft. stack level. During the two-week sampling period the unit was operated under steady state conditions at 240 MW⁽¹¹⁾ with a uniform coal supply so that a mass balance might be established for a number of elements. All the coal from southern Illinois was washed and crushed by TVA so that 90% was <4 mesh. Nominal coal analysis indicated the following composition: 9.5% moisture, 34% volatiles, 43% fixed carbon, 13% ash and 3.4% sulfur.

The isotope dilution results in Table II are on fuel source samples considered homogeneous; these samples were obtained from NBS. The results in Table III are from the sampling points as indicated in Fig. 4. These summarized results are mostly by the SSMS general scan technique; the general scan technique has an estimated accuracy of better than ± 50 percent, while the isotope dilution measurements are limited by the emulsion detector to ± 3 -5%. The results are in terms of grams of metal flow per minute. The mass balance for the various elements was computed by the following equations:

$$Q_c(m) = C_c(m) \times (\text{g coal/min}) \quad (1)$$

$$Q_{pi}(m) = C_{pi}(m) \times (\text{g fly ash/min}) \quad (2)$$

$$Q_{ba}(m) = C_{ba}(m) \times (\text{g ash in coal} - \text{g fly ash/min}) \quad (3)$$

$$\text{Imbalance, \%} = \frac{(Q_{pi} + Q_{ba} - Q_c)}{Q_c} 100 \quad (4)$$

where $Q_c(m)$, $Q_{pi}(m)$ & $Q_{ba}(m)$ are flow rates of metal (m) in g min^{-1} for coal, precipitator inlet and bottom ash, respectively, and $C(m)$ is concentration in weight fraction. Coal consumption during the sampling was at a rate of $82.5 \text{ tons hr}^{-1}$, or $1.25 \times 10^6 \text{ g min}^{-1}$, and the fly ash flow rate was measured at $4.9 \times 10^4 \text{ g min}^{-1}$.

The metal balance for all the elements analyzed by mass spectrometry is good, but on the average shows a negative imbalance of 20%. Metals showing high imbalance, i.e., Hg, As and Se probably were in the gaseous state at the sample points. An example of this was the case for Hg in which a precipitator outlet sample showed a flow of 0.02 g min^{-1} , and at a point of this sampling the particulates are much cooler than the fly ash at the precipitator inlet.

The average imbalance for the elements measured by isotope dilution mass spectrometry with lower volatility showed an imbalance range from -8% to +12%; these results indicate the usefulness of mass spectrometry in evaluating environmental impacts.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance and cooperation of the many personnel of the Tennessee Valley Authority. This work was supported by the National Science Foundation Interagency Agreement No. AEC 40-237-70 and NSF AG 398. The work was carried out at ORNL which is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

REFERENCES

1. P. R. Kennicott, "Interpretation of Mass Spectrograph Plates," in *Trace Analysis by Mass Spectrometry*, (A. J. Ahearn, ed.), pp. 136-210. Academic Press, N. Y. (1972).
2. J. A. Carter and J. R. Sites, unpublished relative sensitivity values, 1972.
3. J. A. Carter and J. R. Sites, "Environmental Spectrometry," *Ann. Chem. Div. Progr. Rep.*, Sept. 30, 1972, ORNL-4838, pp. 44-46.
4. H. Hintenberger, "A Survey of the Use of Stable Isotopes in Dilution Analyses," in *Electromagnetically Enriched Isotopes and Mass Spectrometry*, (M. L. Smith, ed.), pp. 177-189. Academic Press, N. Y. (1956).
5. F. A. White and T. L. Collins, *Appl. Spectry.* 8, 169 (1954).
6. David H. Smith, W. H. Christie, H. S. McKown, R. L. Walker, and G. R. Hertel, *Int. J. Mass Spectrom. Ion Phys.*, 10, 343 (1972/1973).
7. A. O. Nier, *Rev. Sci. Instr.* 18, 398 (1947).
8. W. H. Christie and A. E. Cameron, *Rev. Sci. Instr.* 37, 336 (1966).
9. A. E. Cameron, D. H. Smith and R. L. Walker, *Anal. Chem.* 41, 525 (1969).
10. Margaret E. Griffing, Adele Rozek, L. J. Snyder, and S. R. Henderson, *Anal. Chem. Vol. 29*, 190, Feb. 1957.
11. N. E. Bolton, R. I. Van Hook, W. Fulkerson, J. A. Carter, W. S. Lyon, A. W. Andren, J. F. Emery, *Trace Element Measurements at the Coal-Fired Allen Steam Plant Progress Report*, March 1973, ORNL-NSF-EP-43.

Table I

Sample Computer Output for Cadmium by Isotope
Dilution Spark-Source Mass Spectrometry

CD	106	114	VOL	CONCK
SPIKE	88.400	2.500	1.000	1.000
SAMPLE	1.220	28.900	1.000	

	SAMPLE	NANO-GM	106	114
5	SOIL 318R	4005.000	19.3	16.2
5	SOIL 318R	4032.000	46.9	41.3
5	SOIL 318R	3933.000	64.6	60.0

Table II

ISOTOPE DILUTION RESULTS

Sample Type	Concentration, wt ppm			
	U TEMS	Pb TEMS	Pb SSMS	Cd SSMS
Coal	1.22		28	0.28
	1.18		26	0.34
	1.22		28	0.32
	1.22		30	0.32
Fly Ash	11.9		79	1.8
	11.7		78	2.2
	11.6		79	1.9
	11.6		76	1.5
Gasoline (a)		285 (b)	284 (c)	<.01
		282	284	<.01
		284	285	-
		283	279	-
Fuel Oil (a)			0.27	0.022
			0.28	0.021
			0.26	0.018
			0.23	-

(a) Results in $\mu\text{g/ml}$;

(b) Wet oxidation;

(c) Br_2 oxidation with TEMS.

Table III

IMPURITY MASS FLOW IN A STEAM PLANT
(Flow rate in g min^{-1})

Element	Coal	Bottom Ash	Precipitator Inlet	Imbalance %
Al	13,000	5,500	7,300	- 1.5
Ca	6,000	3,300	1,500	-20
Fe	25,000	10,000	4,900	-40
K	700	550	340	+27
Mg	1,800	770	340	-38
Na	370	220	150	0.0
Ti	880	220	240	-48
Mn	130	110	34	+11
As	6.2	0.22	2	-64
Be	<5	<1.1	0.83	--
Cd ^a	0.63	0.30	0.28	- 7.9
Cu	63	22	19	-35
Pb ^a	9.3	0.45	10	+12
Ni	<100	55	24	-21
Sb		0.8	0.5	--
Se	7.5	2.2	1	-58
V	37	11	17	-24
Zn ^a	110	2.0	100	- 7.3
Hg ^a	0.08 ^b	0.007 ^b	0.007	*

^a Isotope dilution; ^b Atomic absorption; ^c Ppt outlet 0.02.

*Most Hg flow is in stack gas.

FIGURE CAPTIONS

Figure 1. Schematic diagram of a double focusing spark-source mass spectrometer.

Figure 2. Computer plot of a cadmium spectrum spiked with enriched ^{106}Cd .

Figure 3. Schematic diagram of the three-stage mass spectrometer.

Figure 4. Schematic diagram of a TVA coal-fired steam plant.

ORNL-DWG. 73-3117

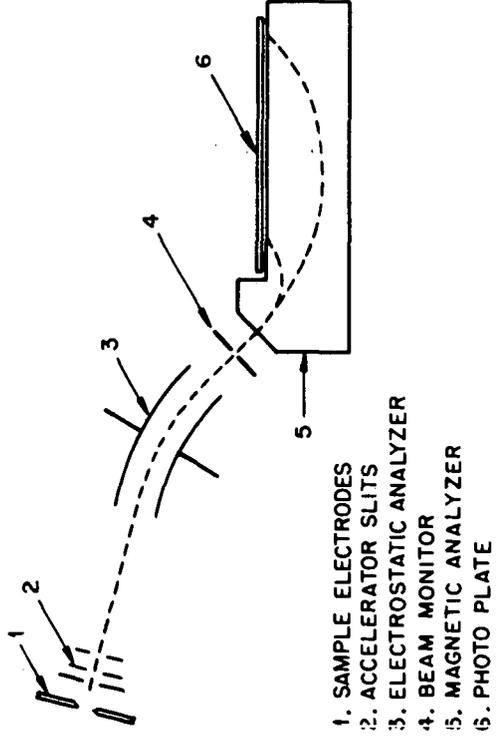
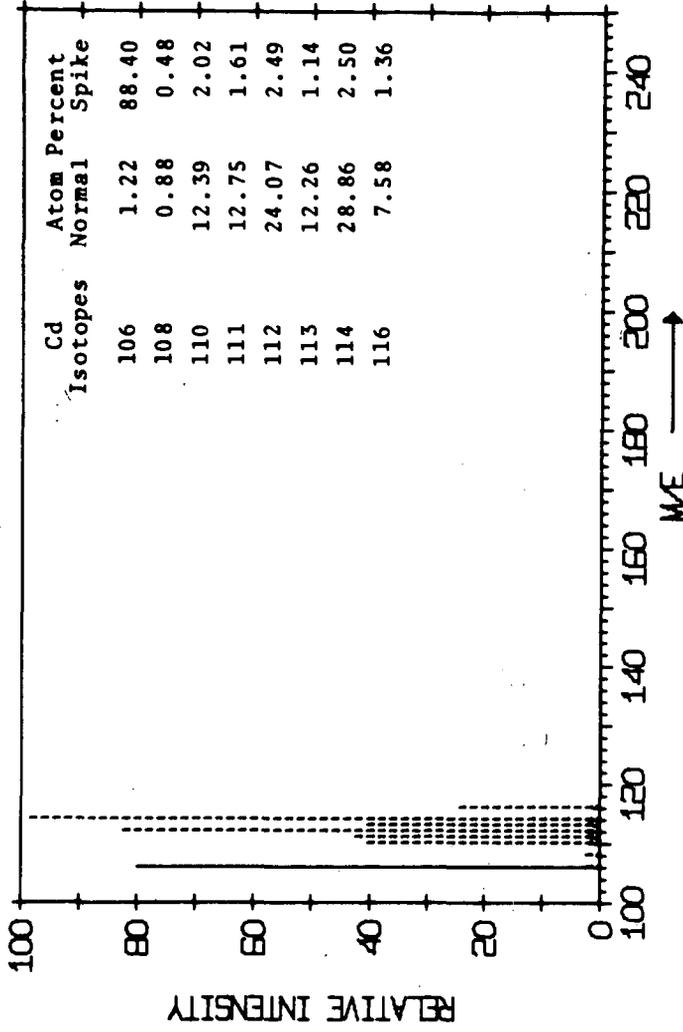


Figure 1. Schematic Diagram of a Double Focusing Spark-Source Mass Spectrometer

ORNL-DWG. 73-3116

Figure 2. Computer Plot of a Cadmium Spectrum Spiked with Enriched ¹⁰⁶Cd

ORNL-DWG. 70-9157

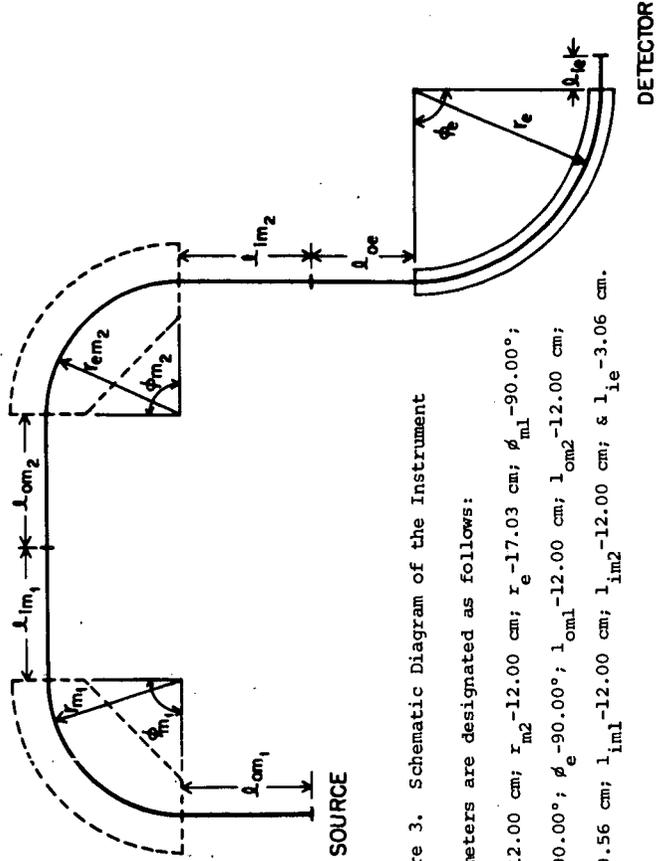


Figure 3. Schematic Diagram of the Instrument

Parameters are designated as follows:

- r_{m1} -12.00 cm; r_{m2} -12.00 cm; r_e -17.03 cm; ϕ_{m1} -90.00°;
 ϕ_{m2} -90.00°; ϕ_e -90.00°; l_{cm1} -12.00 cm; l_{om2} -12.00 cm;
 l_{im1} -12.00 cm; l_{im2} -12.00 cm; l_{ie} -3.06 cm.

ORNL - DWG. 73 - 3118

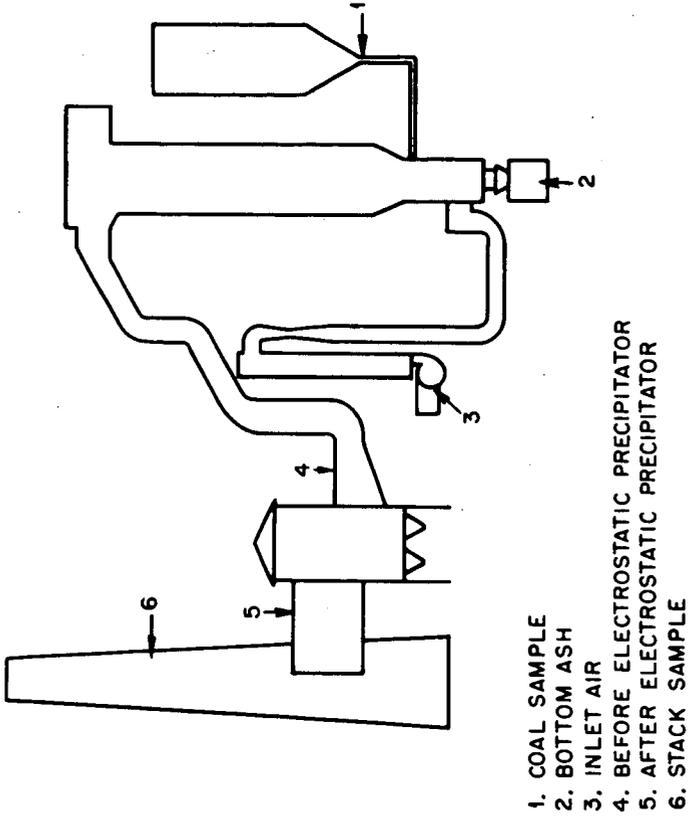


Figure 4. Schematic Diagram of a TVA Coal-Fired Steam Plant

TRACE IMPURITIES IN COAL

E. N. Pollock

Introduction

As trace impurities in the environment become of increasing concern, those materials that can have important impact on the environment are coming under careful scrutiny. Coal, along with the other sources of energy, is a material of major interest. The Federal Environmental Protection Agency is developing a growing list of environmental contaminants that will have to be monitored in the energy sources. These include mercury, beryllium and asbestos presently, but other elements that have undesirable physiological effects on plant and animal life such as cadmium, arsenic, lead and fluorine will receive increasing attention.

The determination of potentially toxic elements in coal has received little effort in the past. In many cases early information was unreliable because of poor methodology. Coal is a complex material containing both organic and inorganic phases and analyses in the past have suffered from both losses and contaminations in dissolution. Beyond the elemental analysis, the determination of elemental form, whether inorganic or organically bound, will condition the environmental impact. The investigators in the determination of mercury in coal have experienced all these problems in attempting to follow the mass balance of mercury in the combustion of coal.

This paper is still only concerned with elemental analyses. However, methods were investigated for most elements that could be potential environmental pollutants.

Two different general analytical techniques were employed: mass spectrometry and wet chemical methods. Six elements were determined by mass spectrometry and seventeen elements were determined by a variety of wet chemical methods.

Trace Elements by Spark Source Mass Spectrometry

The spark source mass spectrometric (SSMS) technique is one of the most sensitive instrumental methods for determining inorganic impurities in a variety of materials.¹ Since the advent of electrical detection, this method has become much more rapid and reliable². A method has been developed for the determination of six elements of toxicological interest and correlation between these impurities in the original coal and the coal ash will be shown. Since no primary standards are available at this time for coal, all mass spectrometric data is compared to atomic absorption spectrophotometry (AAS) values determined on the same samples. Relative standard deviations are on the order of 6 to 15% for the mass spectrometric data and 2 to 3% for the atomic absorption values.

Experimental

An AEI MS-7 spark source mass spectrometer equipped with electrical detection was used in this study. A description of this apparatus complete with manufacturer's accessories and modifications has been described previously and will not be detailed here². The instrument was used in the peak-switching mode only to provide more precise analyses. The instrument operating parameters are given in Table I. The integrated multiplier current for each preset position on the peak switches (each position corresponding to a different isotope to be determined) was displayed on a digital voltmeter. These intensity values were then used to calculate the actual concentration.

Standard and Sample Preparation

Since no primary standards were available at the time of this investigation, AAS was used to provide analyses on several different coals so that they could be used as secondary standards. Representative portions of

each sample and standard were obtained by grinding and splitting. The samples thus obtained (< 100 mesh) were then weighed into porcelain crucibles and placed into a vented cold furnace and the temperature is elevated to 300°C in one-half hour. The temperature was then raised to 550°C for one-half hour and then to 850°C for an additional hour. The crucibles were then removed from the furnace and the ash dry mixed with a glass stirring rod. The crucibles were then returned to the furnace at 850°C without venting until ashing was completed (usually one additional hour). Samples for SSMS were reground with a boron carbide mortar and pestle and diluted with two parts of high purity graphite. The samples with graphite were placed in polystyrene vials with two or three 1/8" diameter polystyrene beads and mixed in a spex mill for twenty minutes. Electrodes were prepared from the powders using the AEI briquetting die and polyethylene slugs.

Once the electrodes had been prepared, they were placed in the source of the instrument using a standardized mounting procedure. Repetitive exposures were then recorded for each element of interest in the standards and unknowns. The concentrations were calculated from the following relationship:

$$\frac{C_x}{C_s} = \frac{I_x}{I_s}$$

where C_s and C_x are the concentrations, the subscripts s and x refer to the standard and unknown, respectively:

I_s and I_x are the intensities (integrated multiplier currents).

Results and Discussions

One of the questions posed by the dry ashing of coal is whether or not some of the elements may be lost through volatilization during the combustion process. A comparison of wet ashing and dry ashing of some of the elements analyzed in this study is given in Table II. This data is based

solely on atomic absorption analyses. As can be seen from the table, the agreement between the two sets of data is generally very good. This would seem to indicate that none of these particular elements are lost during the dry ashing of coal. This data does not, however, allow one to make this same generalization for all elements since these are the only elements determined by both ashing techniques during this investigation. Kometani, et. al.³ have indicated that the presence of sulfates prevents the loss of many elements during dry ashing; and since coal contains appreciable amounts of sulfates, this may help to explain the agreement between the two methods of ashing. Vapor pressure data also imply that these metals could possibly be present as oxides or silicates. Since ash contents of the coals studied varied from 5 to 25% according to the geographical location, the standards for the SSMS analysis were chosen so as to coincide with the approximate area from which the actual samples were taken. Table III is a comparison of the AAS and SSMS data obtained on ten different coal samples from three or four different geographical areas. These values are based upon the metal concentration in the whole coal whereas the analysis was performed on the ash. Again, there is generally very good agreement between the two different methods used. This data also shows that hydrocarbon interference is not a problem at these concentration levels. A very volatile element such as mercury could not be analyzed using this method as it has been postulated that it is pumped away during heating caused by the excitation process, depending upon the parameters selected. The validity of SSMS with electrical detection has proven to be an acceptable method of analysis. Another important aspect of this study was the time involved per sample. Sample and standard preparation (including ashing), electrode preparation, instrument preparation (setting peaks), running of ten samples and four standards, data reduction and conversion to concentration in the whole coal required only fifteen hours. This represents 84 separate analyses. This fifteen

hours also includes sample turn-around time and five separate 0.3nC monitor exposures for each element in each sample and standard. The precision data for the SSMS technique is 6 to 15% relative. The detection limits for the elements studied are on the order of 1 to 2 ppmw in the whole coal using the previously mentioned parameters. This is not necessarily the lower limits as such items as exposure (nC), multiplier gain and sample dilution may increase or decrease this level. From the intensity values obtained during this investigation, absolute detection limits ranging between 0.1 and 0.3 ppm by weight with whole coal would be a realistic estimate. These lower values were not actually determined. The average deviation from the AAS results is 29.2%.

Trace Elements by Wet Chemical Methods

The determination of trace impurities by wet chemical methods can immediately be separated into two major divisions. First, those elements that can be dry ashed, leached in acid and the analysis completed by conventional AAS. These elements are Li, Be, V, Cr, Mn, Ni, Cu, Zn, Ag, Cd and Pb. Second, those that require specialized techniques.

1. Hg-O₂ bomb combustion followed by flameless AAS.
2. As, Bi and Sb - dry ashing and acid dissolution followed by determination of their hydrides using AAS.^{5, 6}
3. Se-combustion and cold trapping⁷ followed by determination as its hydride using AAS.
4. F - O₂ bomb combustion⁸ followed by specific ion analysis⁹.
5. B - dry ashing followed by Na₂CO₃ fusion, dissolution in dilute H₂SO₄, then followed by colorimetric determination with carminic acid.¹⁰

Determination of Li, Be, V, Cr, Mn, Ni, Co, Cu, Zn, Ag, Cd and Pb

Coal samples are prepared and ashed as described in the procedure employed for SSMS. Five gram samples of coal are used. The ash is placed in 100 ml teflon beaker containing 5 ml of HF (conc.) and 15 ml of HNO_3 (conc). Warm to dissolve the ash, then evaporate the solution just to dryness. Add water and a few drops of HNO_3 , then transfer to a 100 ml volumetric flask. Make to volume with water and mix. Immediately transfer to a plastic bottle to preserve as a stock solution for the conventional AAS determinations of Li, Be, V, Cr, Mn, Ni, Co, Cu, Ag, Cd and Pb.

Samples were also prepared for conventional AAS determination by wet ashing approximately 5.0 grams of coal in a mixture of HNO_3 , H_2SO_4 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

The Determination of Mercury

A coal sample is decomposed by burning a combustion bomb containing a dilute nitric acid solution under 24 atmospheres of oxygen pressure. After combustion, the bomb washings are diluted to a known volume and mercury is determined by atomic absorption spectrophotometry using a flameless cold vapor technique.

Procedure

Transfer approximately 1 gram of 60 mesh X O coal to a clean combustion crucible and weigh to the nearest 0.1 milligram. Transfer 10 ml of 10% nitric acid to the bomb, place the crucible in the electrode support of the bomb, and attach the fuse wire. Assemble the bomb and add oxygen to a pressure of 24 atmospheres (gauge). Place the bomb in the calorimeter (a cold water bath in a large stainless steel beaker is also satisfactory) and ignite the sample using appropriate safety precautions ordinarily employed in bomb calorimetry work.

After combustion, the bomb should be left undisturbed for 10 minutes to allow temperature equilibration and the absorption of soluble vapors. Release the pressure slowly and transfer the contents of the bomb (and crucible) to the mercury reduction vessel by washing with 10% nitric acid. Rinse the bomb, electrodes, and crucible thoroughly with several small washings of 10% nitric acid, then dilute the contents of the reduction vessel with 10% nitric acid to a total volume of 50 ml. Proceed with the determination as described under Standardization. Determine the amount of mercury in micrograms and divide by the sample weight in grams to obtain the mercury value in parts per million.

Standardization

Add an aliquot of a standard mercury solution to contain 0.1 micrograms of mercury to the mercury reduction flask. Add KMnO_4 (3%) dropwise until the pink color persists. Adjust the volume to 100 ml, then add in order 5 ml of HNO_3 (1:2), H_2SO_4 (1:1) and hydroxylamine hydrochloride. When the pink color fades, add 5 ml of the SnCl_2 (10%) and immediately connect into the system. Start the pump which circulates the mercury in the vapor phase through the optical cell in the atomic absorption spectrophotometer with the mercury lamp optimized at 253.7 nm and normal operating conditions as established by the AA instrument manufacturer. Samples are run by taking all or an aliquot from the O_2 bomb combustion stock solution.

The Determination of Arsenic, Antimony and Bismuth

As, Sb and Bi can be determined by AAS after generation and evolution of their hydrides. The hydrides are formed by the reaction of nascent hydrogen generated by magnesium metal in a $\text{TiCl}_3\text{-HCl}$ solution. A modified Perkin-Elmer High Sensitivity Arsenic-Selenium Sampling System can be used with any atomic absorption spectrophotometer.

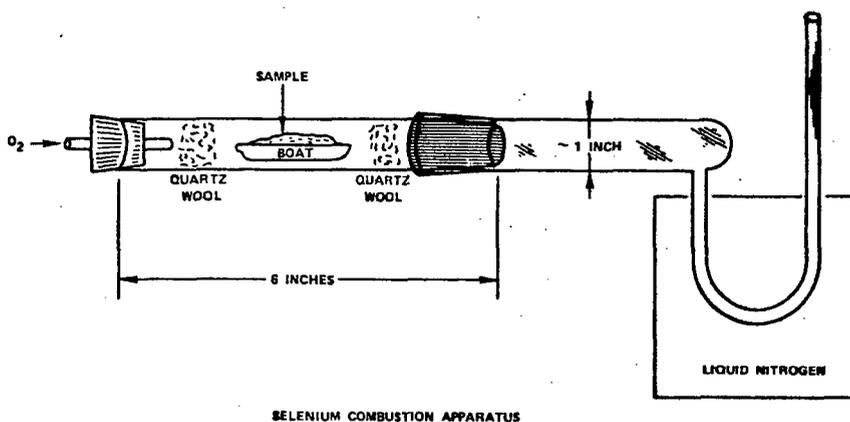
Coal samples for the determination of As, Sb and Bi can be ashed by the method previously described for Li, Be, etc. However, the ash should be leached in HF and HCl. Care must be taken in warming not to lose volatile chlorides. If HNO_3 is used in place of HCl, a mixed KI and SnCl_2 must be used in place of TiCl_3 to generate nascent hydrogen; however, the HCl system is preferred.

A separate aliquot of HCl-HF sample containing up to 0.3 micrograms of As or up to 0.6 micrograms of Sb or Bi is placed in the hydride generation flask. Add 10 ml of TiCl_3 (1% in HCl) and adjust the volume to 25 ml with water. After flushing the system with argon for fifteen seconds, add a one inch length of 1/8 inch diameter magnesium rod to the flask through the pinch damp. Allow one minute for collection time in the expansion vessel. Then release gases into the argon-hydrogen entrained air flame using a triple slot-type burner and the AAS manufacturer's standard practices. Blank and appropriate standards are run for each of the elements.

The Determination of Selenium

The prior separation of selenium from the bulk of the coal sample uses the combustion technique as described by H. L. Rook⁷. It was originally used in a neutron activation analysis. The equipment was modified to use a quartz combustion tube 5 1/2 inches long connected by a ground glass joint to a second section 3 1/2 inches long. The section ends with a U-tube which can be immersed in a Dewar Flask containing liquid N_2 or some other suitable coolant. For analyses, an 0.5 gram sample is weighed into a porcelain boat and inserted into the combustion tube with an O_2 flow of ~ 30 cc/min. With the cold trap in place, the sample is ignited by heating the combustion tube with a meker burner. The coal sample is allowed to burn freely, the temperature is then raised to the maximum of the burner for five minutes. The combustion tube is cooled for five minutes and separated from the condenser section. The condenser is removed from the cold trap and allowed to warm to ambient

temperature. Add 10 ml of HCl to the condenser and flush into a 50 ml volumetric flask. Wash condenser with water and add rinsings to the volumetric flask. Make to volume with water and mix. Take an aliquot of 15 ml or less containing up to 0.3 micrograms of Se and proceed as in the method for As, Sb, and Bi by AAS as previously described.



The Determination of Fluorine

A coal sample is decomposed by ignition in a combustion bomb containing Na_3CO_3 solution under 24 atmospheres of oxygen pressure. After combustion, the bomb washings are diluted to a known volume and an aliquot is taken to determine F by the standard Orion specific ion procedure.

Transfer approximately 1 gram of coal to a combustion crucible and weigh to nearest 1.0 mg. Transfer 5 ml of Na_2CO_3 solution (5%) to the bomb, place crucible in the electrode support and attach the fuse wire. Assemble the bomb and add oxygen to a pressure of 24 atmos. Place the bomb in a cold water

bath and ignite the sample using appropriate safety precautions.

After combustion, the bomb should be left undisturbed for ten minutes to allow temperature equilibration and absorption of the soluble vapors. Release the pressure slowly and transfer contents of the bomb (and crucible) into a 25 ml volumetric flask. Make several small washings with water and add rinsings to the volumetric flask. Make to volume with water and reserve the stock solution in a plastic bottle.

Using an expanded scale pH meter, such as the Orion 801, pipet 10 ml of the stock solution into a small beaker and add 10 ml of Tisab (Orion Cat. No. 94-09-09), determine the electrode potential using a fluoride electrode Orion 94-09. Comparison is made by bracketing with fluoride standards prepared similarly.

The Determination of Boron

After dry ashing in the manner used in the Li, Be, etc. procedure, the ash is fused with Na_2CO_3 , leached in water and acidified with H_2SO_4 . The colorimetric carminic acid method⁶ is then used for the determination of boron.

Weigh approximately 1 gram of coal into a platinum crucible and carefully ignite in a vented oven. Gradually increase the temperature to 850°C and maintain for one hour. Remove from oven and add 2 grams of Na_2CO_3 and fuse for ten minutes. Leach in 25 ml of warm water in a teflon beaker. When dissolution is complete, add 10 ml of H_2SO_4 carefully. Transfer to a 50 ml volumetric flask. Make to volume with water and reserve in a plastic bottle. Place a 5 ml aliquot or less in a 50 ml volumetric flask, make to 5 ml volume with H_2SO_4 (3.6M) if less than 5 ml aliquot was used. Aliquot should contain 0 to 100 micrograms of B. Then add 20 ml of chilled H_2SO_4 (18M) and swirl. Then add by pipet 20 ml of carminic acid (0.92 grams in H_2SO_4 18M). Make to volume with H_2SO_4 (18M) and determine absorbance in 1 cm cells in a spectrophotometer at 605 nm with a reagent blank in the reference cell. Compare to a standard curve containing 0 to 100 micrograms.

TABLE I

Operating Parameters

Spark Variac	35%
Pulse Repetition Rate (pps)	100
Pulse Length (μ sec)	100
Source Slit	0.002"
Multiplier Slit	.002"
Moniter Exposure	0.3nC
Multiplier and Amplifier Gains	Variable according to sample elements and concentration
Electrodes Vibrated	

Cu	
ASH	LEACH
1	17 16
2	12 15
3	50 50
4	13 14
5	9 9

Mn	
ASH	LEACH
1	67 64
2	179 169
3	122 128
4	12 15
5	8 7

Ni	
ASH	LEACH
1	19 15
2	4 6
3	84 85
4	13 12
5	7 5

Zn	
ASH	LEACH
1	121 110
2	7 9
3	1420 1450
4	16 23
5	17 19

Cd	
ASH	LEACH
1	2.8 2.8
2	0.6 0.6
3	13.1 12.8
4	0.6 <0.5
5	<0.5 0.5

Pb	
ASH	LEACH
1	13 15
2	8 16
3	105 111
4	13 18
5	8 8

Be	
ASH	LEACH
1	2.2 2.4
2	0.4 0.7
3	2.3 2.6
4	1.6 2.2
5	0.3 0.8

Li	
ASH	LEACH
1	6.8 8.0
2	9.5 11.2
3	17.1 20.8
4	11.8 12.8
5	3.1 3.6

V	
ASH	LEACH
1	55 41
2	10 10
3	43 43
4	18 22
5	7 10

DRY ASHING
VS
ACID LEACHING OF COAL

Cu	
MS	AAS
14	17
23	16
22	18
33	29
11	13
32	29
12	24
38	61
13	14
18	18

Zn	
MS	AAS
13	9
41	45
17	12
22	24
41	39
84	12
8	13
660	852
18	20
50	36

As	
MS	AAS
7.7	7.5
3.2	1.5
6.0	4.5
7.7	4.5
2.4	1.0
9.0	4.0
1.8	3.0
3.8	6.5
8.0	5.0
5.6	1.5

Mn	
MS	AAS
33	37
7200	193
90	65
101	93
62	52
124	96
11	19
143	117
22	21
73	49

Ni	
MS	AAS
14	23
23	30
21	31
14	21
14	22
28	28
7	15
41	81
7	22
15	18

Cr	
MS	AAS
26	24
20	12
21	17
12	16
18	19
19	12
13	13
36	31
15	20
37	16

V	
MS	AAS
25	32
21	21
35	23
43	24
24	25
24	21
15	24
20	40
61	37
27	30

TRACE
ELEMENTS
IN
COAL

REFERENCES

1. A. J. Ahearn, Ed., Trace Analysis by Mass Spectrometry, Academic (1972).
2. C. A. Evans, Jr., R. J. Guidoboni, and F. D. Leipziger, Apply Spect. 24, 85 (1970).
3. T. Y. Kometani, et. al. Environmental Science Technology, 6, 617 (1972).
4. W. W. Harrison and D. L. Donohue, Twentieth Annual Conference on Mass Spectrometry and Allied Topics, Dallas (1972).
5. E. N. Pollock and S. J. West, At. Abs. Newsletter, Vol. 11, No. 5, September-October, 1972.
6. E. N. Pollock and S. J. West, At. Abs. Newsletter, 1973.
7. H. L. Rook, Anal. Chem. Vol. 44, No. 7, June 1972, p. 1276.
8. ASTM D808 Part 17.
9. Orion Bulletin, No. 5 (1968).
10. E. N. Pollock and L. P. Zopatti, Talanta, Vol. 10, 118 (1963).

"EPA'S NATIONAL FUELS SURVEILLANCE NETWORK" - Robert H. Jungers, Robert E. Lee, Jr. and Darryl J. von Lehmden, Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 27711.

Implementing the Clean Air Act as amended in 1970 may require manufacturers of fuel and fuel additives to register their products with the Environmental Protection Agency. As an integral part of this program, a Fuels Surveillance Network was established in 1972 for the nationwide collection of fuel samples through the EPA regional offices. These samples are submitted to the National Environmental Research Center, Research Triangle Park, North Carolina, for extensive trace element analysis and for major fuel additive component analysis. The analytical data derived from the network samples will be used in a multiplicity of ways. The information will be used to verify manufacturer-registered data and to provide research input to studies on combustion emissions and health effects since trace elements in fuels can be emitted into the atmosphere during combustion. The information will also be used to develop emission factors to detect potentially toxic components introduced through contamination, and to provide a mechanism for enforcing Federal fuel additive standards (such as lead and phosphorous limits in gasoline). Samples collected in the 1972 operation were predominantly gasoline, although a limited number of samples of other types of fuels and fuel additives was collected. Trace analytical methods used included neutron activation, spark source mass spectrometry, isotope dilution, atomic absorption including carbon rod atomizer, anodic stripping voltammetry, isotope separation techniques, and lead screening techniques. Impact on the environment is discussed.

DO NOT
USE →

INTERLABORATORY EVALUATION OF STANDARD REFERENCE MATERIALS FOR TRACE ELEMENTS IN COAL, FLY ASH, FUEL OIL, AND GASOLINE - Darryl J. von Lehmden (1), Philip D. La Fleur (2), and Gerald G. Akland (1), (1) Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 27711, and (2) U. S. Department of Commerce, National Bureau of Standards, Washington, D. C. 20234

The Environmental Protection Agency and the National Bureau of Standards have jointly conducted an interlaboratory comparison program for trace elements in four standard reference materials. The concentration of fifteen chemical elements was certified by the National Bureau of Standards concurrent with the interlaboratory comparison program. The standard reference materials include coal, fly ash, residual fuel oil and gasoline. The concentrations were certified in these materials for the following elements; mercury, beryllium, lead, cadmium, vanadium, manganese, nickel, chromium, arsenic, selenium, zinc, sulfur, phosphorous, fluorine, and uranium. Over fifty laboratories participated in the interlaboratory comparison program. Chemical element concentrations are reported using neutron activation analysis (radio chemical and instrumental), atomic absorption spectrometry, spark source mass spectrometry (isotope dilution and general scan), X-ray fluorescence, optical emission spectroscopy, and a variety of colorimetric and gravimetric methods. Precision results are reported based on replicate analysis. Accuracy results are reported based on the certified values. Preliminary grouping of the "best" analytical methods for each chemical element in each samples matrix will be described.

THE FATE OF SOME TRACE ELEMENTS DURING COAL PRETREATMENT AND COMBUSTION

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4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213INTRODUCTION

Why should we interest ourselves in trace metals in coals? Fact #1: There are a number of elements known to be of high toxicity in coal, most of them present in trace amounts. Fact #2: Over 300 million tons of coal was burned in the United States last year for the generation of electric power. When we put the two facts together, we realize that we are talking of a total of tons; hundreds of tons or even thousands of tons of toxic elements present in the coal we burn for power generation. How much of these toxic elements are present in the coal we burn for power generation? How much of these toxic trace elements enters the environment via the smoke stacks of powerplants?

Today I would like to discuss two trace-element studies being carried out at the Pittsburgh Energy Research Center of the Federal Bureau of Mines. The first program, which is funded by the Bureau, is involved in elucidating the fate of the various toxic trace elements present in coal when the coal is burned in powerplants. The second program is funded by the Environmental Protection Agency and is concerned with investigating the distribution of the trace elements in coal using specific gravity separations to divide the coal into discreet fractions.

The two programs taken together can give us a picture of what happens to the trace elements in coal from the coal bed to the powerplant stack. Both investigations are still in progress, so today's talk is really an interim report. I would like to cover the problems we have encountered, the results we have obtained, and any conclusions we have drawn from the results.

The elements that we are currently studying in the EPA program are mercury, copper, chromium, manganese, nickel, and fluorine. In the Bureau program, studies so far have been limited to mercury, cadmium, and lead.

Let us elucidate some of the general problems one encounters in analyzing coal for its trace element content. Except for the special case of mercury, there is no standard coal presently available for use in trace-element analysis. Because the precision and accuracy of the analytical procedures used are in many cases affected by the matrix one is dealing with, the lack of a standard coal is a serious problem.

Contamination is another problem one encounters in trace analysis. Mercury is ubiquitous in many laboratories as is fluoride. Lead is present in dust particularly if your laboratory is close to automobile traffic.

EXPERIMENTAL APPROACH

A. Coal pretreatment study. Selected coals were crushed and separated in organic fluids of known specific gravity. The head (i.e., starting) coal and each specific gravity fraction were analyzed for the trace element or elements being studied and their distribution noted.

B. Combustion study. Coal was combusted in a 100-g/hr combustor, and the ash and flue gases were collected and analyzed for the trace element being studied. After completion of the initial study with the 100-g/hr combustor, coal and ash were obtained from a 500-lb/hr furnace and finally from commercial powerplants. The samples were analyzed

for the trace elements being studied, and the maximum amount of the element that could be released was calculated.

ANALYTICAL METHODS

A. Mercury. Mercury is determined in coal by means of a double gold amalgamation-flameless atomic absorption procedure. Because mercury is volatile and can thus be quantitatively separated from the coal matrix, calibration can be accomplished with mercury-saturated air. Mercury is the only trace element for which there is presently an NBS certified standard coal. We normally use mercury-saturated air for calibration purposes on a day-to-day basis and periodically analyze the NBS standard coal in order to check our procedure. Table 1 shows some of the results we have obtained with the NBS standard coal.

Table 1
Analysis of NBS SRM No. 1630
NBS certified mercury value = 0.126 ± 0.006 ppm Hg

<u>Dates</u>	<u>Number of replicates</u>	<u>Bureau value</u>
2/24/72	5	0.12 \pm 0.02
4/19/72	5	.12 \pm .01
7/5/72	6	.14 \pm .02
9/24/72 through 12/13/72	39	.13 \pm .03
2/1/73 through 3/2/73	37	.13 \pm .02

As you can see, agreement is very good.

B. Fluorine. Fluorine in coal is determined by combusting the coal in the presence of calcium oxide, fusing the residue with Na_2CO_3 , leaching the melt with phosphoric acid, distilling the solution with H_2SO_4 , concentrating the fluoride by passing the solution through an anion exchange resin (Amberlite IRA 410), and determining the fluoride content of the solution with a fluoride specific ion electrode. An NBS opal glass standard is frequently carried through the entire procedure to check fluorine recovery.

C. Copper, chromium, manganese, and nickel. The analytical method for the determination of copper, chromium, manganese, and nickel involves digestion of the coal with HNO_3 and HClO_4 , fusion of the residue with lithium metaborate, and determination of the combined digestion and leach solutions by atomic absorption spectrophotometry. Since there is no standard material to analyze for the construction of calibration curves, the method of standard additions is employed for the assay. While the method of standard additions does increase the time required for the analysis, it eliminates the effect of the matrix.

D. Cadmium and lead. Cadmium and lead are determined in coal by ashing the coal at 500°C , treating with HF and HCl, fusing the residue with K_2CO_3 , evaporating to near dryness, dissolving in HCl, adding KI and ascorbic acid, extracting into MIBK, and analyzing for Pb and Cd by means of atomic absorption. Blanks are carried through the entire procedure, and the method of standard additions is used for calibration.

RESULTS

A. Mercury. An Indiana V strip coal from Indiana and a Lower Kittanning strip coal from Pennsylvania were separated into four specific-gravity fractions and analyzed for their trace mercury content. The results are shown in tables 2 and 3. It is clear that mercury tends to concentrate in the mineral matter and probably exists in coal as an inorganic compound.

Table 2
Coal - Lower Kittanning Bed, Pennsylvania, strip coal
Mercury content of coal = 0.26 ppm

<u>Specific gravity</u>	<u>Weight-percent</u>	<u>Mercury content, ppm</u>	<u>Percent of total mercury in fraction</u>
Float - 1.30	20.0	0.16	12
1.30 - 1.40	28.1	.23	25
1.40 - 1.60	24.8	.19	18
Sink - 1.60	27.1	.43	45

Table 3
Coal - Indiana V Bed, Indiana, strip coal
Mercury content of coal = 0.13 ppm

<u>Specific gravity</u>	<u>Weight-percent</u>	<u>Mercury content, ppm</u>	<u>Percent of total mercury in fraction</u>
Float - 1.30	42.6	0.08 ±0.03	29 ±11
1.30 - 1.40	36.3	.07 ±.03	22 ±9
1.40 - 1.60	13.7	.15 ±.03	15 ±3
Sink - 1.60	7.4	.59 ±.05	34 ±3

Table 4
100-g/hr combustor: Summary of results

<u>Coal</u> ^{4/}	<u>Run</u>	<u>Combustion feed rate, g/hr</u>	<u>Efficiency, percent</u>	<u>Fly ash production rate, g/hr</u>	<u>Mercury content (±1 standard deviation)</u>			<u>Total mercury in fly ash, percent</u>	<u>Total mercury accounted for, percent</u>
					<u>Coal, $\mu\text{g/g}$</u>	<u>Fly ash, $\mu\text{g/g}$</u>	<u>Flue gas, $\mu\text{g}/\text{m}^3$</u> ^{3/}		
DRB-E	1	98.1	97.6	9.1	1/ 0.15±0.02	0.97±0.05	2.2	60	77
DRB-E	2	105.1	97.0	10.4		.83±.13	6.5	55	101
DRB-E	3	108.1	96.4	11.3		.95±.09	1.7	66	78
P-3	1	98.9	97.5	23.8	2/ .24±.05	.31±.04	7.4	31	62
P-3	2	135.7	96.3	34.3		.35±.06	(3/)	37	(3/)
P-3	3	117.2	98.3	27.1		.37±.04	14.4	36	94

^{1/} Average value of 12 replicates for DRB-E.

^{2/} Average value of 21 replicates for P-3.

^{3/} No flue gas sampling on this run.

^{4/} DRB-E is a washed deep-mined Pittsburgh seam coal originating in Washington County, Pa. P-3 is a mixture of Tebo seam and Weir seam coals from Henry County, Mo.

Table 4 shows the results obtained with the 100-g/hr combustor. Table 5 shows the results obtained with the 500-lb/hr combustor. Table 6 shows the analyses of the coals used in the combustion experiments with the 100-g/hr and 500-lb/hr combustors. Table 7 shows the results obtained with power plant samples. The terms MR, DRB-E, and P-3 are those employed by the engineers running the combustors to identify series of runs under slightly different conditions but using the same coal.

Table 5
500-lb/hr combustor: Summary of results

Mercury in coal (MR) ^{1/}	μg Hg/g coal	0.18 [±] 0.04
Number of replicates		23
Mercury in fly ash	μg Hg/g ash	0.22 [±] 0.04
Number of replicates		17
Percent of total mercury found in fly ash		12 [±] 3

^{1/} MR is a Pittsburgh seam coal from Pennsylvania.

Table 6
Analysis of coals combusted (mf basis)

	<u>DRB-E</u>	<u>P-3</u>	<u>MR</u>
Proximate analysis, weight-percent:			
Volatile matter	35.8	37.8	37.7
Fixed carbon	57.3	40.6	52.2
Ash	6.9	21.6	10.1
Ultimate analysis, weight-percent:			
Hydrogen	5.1	4.4	5.0
Carbon	78.1	61.9	74.2
Nitrogen	1.6	1.0	1.5
Oxygen	7.1	5.9	7.1
Sulfur	1.2	5.2	2.1
Ash	6.9	21.6	10.1
Calorific value, Btu	13,970	11,190	13,310
Free swelling index	8	2.5	1.5

Table 7
Summary of powerplant data

<u>Type of firing</u>	<u>Steam conditions</u>			<u>Coal fired</u>	<u>Fly ash sample collection conditions</u>	<u>Mercury content of the fly ash, μg Hg/g</u>
	<u>Rate, 10³ lb/hr</u>	<u>Pressure, psig</u>	<u>Temperature, ° F</u>			
Slag top	702	1,268	899	Illinois No. 6 hvcb.	Mechanical collector hopper	0.10 [±] 0.02
Slag top	723	1,293	799	Illinois No. 6, hvcb.	Electrostatic precipitator hopper	.26 [±] .04
Dry bottom	461	1,450	928	Kentucky No. 6, hvbb.	Mechanical dusty collector hopper	.22 [±] .02

Based on mercury analyses for Illinois No. 6 coal published by the Illinois Geological Survey, the average percentage of the mercury in the original coal accounted for in the ash is 13 percent.

The results seem to indicate that as only 10 to 15 percent of the mercury is retained by the fly ash, 85 to 90 percent of the mercury in the coal could be emitted via the powerplant smoke stacks.

B. Lead and cadmium. The results obtained for cadmium and lead are limited and of a preliminary nature. The longer time required for each analysis and the problems of contamination resulted in less replication. As the result of insufficient replication, most of the results reported do not have statistical errors attached (however, each is the average of at least two values).

Table 8 gives the lead and cadmium assays for Pittsburgh seam coal; table 9 gives the concentration of lead and cadmium found in the ashes from combustion experiments. Table 9 also shows the percentage of the lead and cadmium in the coal that was retained by the ash. The conditions under which the coal was burnt varied with each run, particularly with the 500-lb/hr combustor so that the results of individual runs cannot be compared. It should be noted that cadmium and lead are retained to a greater degree in the ash from the 500-lb/hr combustor than was mercury. This of course could be predicted from relative volatilities.

Table 8
Lead and cadmium content of a
Pittsburgh seam coal (± 1 S.E.)

<u>Lead content,</u> <u>ppm</u>	<u>Number of</u> <u>samples</u>	<u>Cadmium</u> <u>content, ppm</u>	<u>Number of</u> <u>samples</u>
7.7 \pm 0.5	9	0.14 \pm 0.05	9

Table 9
Lead and cadmium in fly ash

<u>Combustor</u>	<u>Cadmium in</u> <u>ash, ppm</u>	<u>Cadmium accounted</u> <u>for, percent</u>	<u>Lead in</u> <u>ash, ppm</u>	<u>Lead accounted</u> <u>for, percent</u>
100 g/hr	1.0	68	--	--
100 g/hr	.74	54	71	92
100 g/hr	.99	76	68	93
500 lb/hr	1.22	101	49	72
500 lb/hr	.78	65	44	64
500 lb/hr	.36	37	25	46

C. Copper, chromium, manganese, and nickel. Efforts aimed at defining the behavior of Cu, Cr, Mn, and Ni during specific gravity separation and combustion of coal are in a very preliminary stage. Efforts to date have been aimed at optimizing the analytical procedures and locating and eliminating sources of contamination. One interesting preliminary result presented in table 10 seems to indicate that crushing coal adds significant amounts of manganese to the coal. The jaws of the crushing apparatus were made of a manganese steel. The coal used was a strip coal from the Lennox Bed in Colorado.

Table 10
Analysis of coal before and after crushing, ppm

<u>Element</u>	<u>Concentration before crushing</u>	<u>Concentration after crushing</u>
Cr	3.4	4.3
Cu	3.2	5.4
Mn	4.1	10.3

D. Fluorine. Efforts aimed at analyzing coals for fluorine have been stymied by contamination problems. Sources of fluorine contamination have been located in phosphoric acid, calcium oxide, boiling chips, and teflon-covered stirring bars. Extreme care must be taken in the selection of storage containers, and the history of the distillation apparatus should be known. We believe that we have now located the sources of error in the fluoride analysis and are in the process of analyzing series of float-sink samples for their fluoride content.

SUMMARY AND CONCLUSIONS

Our efforts with trace elements in coal have to date met with varying degrees of success, but certain important conclusions can be drawn from our findings.

First, it would appear that as much as 40 percent of the mercury in the coal is associated with the high specific gravity fraction of the coal. Thus if the pyrite is removed from coal to lower sulfur emissions, a substantial part of the mercury in the coal is also removed at no extra cost. Second, about 10 to 15 percent of the mercury from the coal may remain with the fly ash in coal-burning powerplants. Taking both factors into account could reduce the maximum emission of mercury to about 50 percent of that present in the coal.

Cadmium and lead are less volatile elements than mercury. As one would expect, the experimental evidence indicates that they are retained in the fly ash to a greater extent than is the mercury. As the program continues, other elements that are even less volatile than lead and cadmium will be investigated, and one would expect them to be retained in the fly ash to an even greater extent than are lead and cadmium.

Our experience with fluorine, copper, manganese, chromium, and nickel emphasizes the difficulties inherent in doing trace analyses in matrices as complex as coal. While care must be exercised in performing any chemical analysis, trace analysis requires extreme vigilance. In addition to the care required in trace analyses, our studies have shown that the coal handling procedures themselves may add trace elements to the coal.

TRACE ELEMENT MASS BALANCE
AROUND A COAL-FIRED STEAM PLANT*N. E. Bolton, J. A. Carter, J. F. Emery, C. Feldman,
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1. Introduction

Toxic elements are present in trace quantities in coal and other fossil fuels. Since the quantities of these fuels consumed each year are enormous, the associated quantities of potentially harmful toxic elements are also appreciable. For example, assuming 600 million tons of coal burned per year in the United States, with average concentrations*** for Hg of 0.10 ppm, Pb-20, Cd-0.4, As-5, Se-5, Sb-4, V-25, Zn-200, Ni-100, Cr-20, and Be-2, the corresponding tonnages of the elements are: Hg-60, Pb-12,000, Cd-240, As-3000, Se-3000, Sb-2400, V-15,000, Zn-120,000, Ni-60,000, Cr-12,000, and Be-1200.

An appreciable fraction (62%) of the coal consumed is burned at central power stations, so it is important to know the fate of potentially hazardous trace elements at such plants. The purpose of this work is to determine the fate of trace elements in coal associated with generation of electricity at a large central power station. The study involves two complementary activities: (1) a mass balance for trace elements through the plant as obtained by in-plant sampling, and (2) measurements of the elements in the surroundings to estimate the effect of emissions on the concentration of toxic elements in air, soil, plant life, and in the water, sediment, and biota of the stream receiving the ash pond runoff. This paper deals with the in-plant portion of the work, which is a collaborative effort between ORNL and TVA.

The power station at which the study was made is the Thomas A. Allen Steam Plant in Memphis, Tennessee, which has an 870 MW(e) peak capacity from three similar cyclone fed boilers. The plant is part of the TVA power system, and it was chosen because the Number 2 Unit was being renovated with addition of a new Lodge Cottrell electrostatic precipitator so the TVA Power Production Division test sampling crew were available to help sample during compliance testing of the precipitator.

2. Sampling and Methods of Analysis

Figure 1 shows the sampling points on a schematic of the Number 2 Unit. Samples taken at locations Number 1 and 2 were composite samples of the coal entering the boiler, and of the slag material leaving the boiler, respectively. At location Number 3 the inlet air being supplied to the boiler was sampled. At locations 4 and 5 a series of samples were taken isokinetically at various locations in the ducts before and after the electrostatic precipitator, respectively; and at location 6 a series of samples were taken isokinetically in the stack at approximately 82 m above ground level.

The large size of the ducts being sampled required specially fabricated sampling

* Work supported by the National Science Foundation RANN Program under NSF Interagency Agreement No. AG-398 with the U.S. Atomic Energy Commission.

** Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission, Contract No. W-7405-eng-26.

*** These concentrations are representative of values measured for coal burned at the Allen Steam Plant.

probes and special probes equipped with forward-reverse pitot tubes for determining isokinetic sampling rates. Figure 2 shows how the sampling probe was constructed. The sample is drawn through an alundum thimble at a predetermined isokinetic sampling rate. This thimble is followed by a Gelman fiberglass filter paper holder which collects particles as small as 0.1μ . This is essentially the standard ASTM method for sampling gases for particulates.¹ These filters are then followed by the cold trap to bring the flue gas through the dew point very quickly and collect all materials which will condense in a dry trap. Because of the very high concentration of moisture in the flue gas it was necessary to add a dropout glass jar following this cold trap to prevent loss of the condensate. The cold trap and condensate dropout jar were used in an attempt to trap mercury and other condensable vapors from the flue gas sample.

Two probes were fabricated for sampling the precipitator inlet, one for the precipitator outlet and one for the stack. By limiting the number of test points at each plane in the precipitator outlet the average sampling time required to complete a test was about 280 to 300 minutes. The types and numbers of samples collected for each complete run are shown in Table 1. The total number is 24 distinct samples for each complete test run.

Table 1. Types and numbers of samples

Composite Coal Sample - 1
Composite Slag Tank Sample - 1
Precipitator Inlet - 6 thimbles, 2 cold traps, 2 glass papers
Precipitator Outlet - 4 thimbles, 1 cold trap, 1 filter paper
Stack Sample - 2 thimbles, 1 trap, 1 glass paper
Inlet Air - 1 thimble and 1 glass paper

Although the plant is designed to operate at 290 MW per unit, a 240 MW load was chosen for these tests because it was felt that this load could be maintained without interruption during the 5-hour sampling time required to secure our samples. The consumption of coal at this power level is 82.5 tons per hour on a dry weight basis. Sampling of the coal and slag was performed by compositing samples obtained periodically during the course of the test. From the weight of fly ash material collected in the ASTM filter system, the total air volume passed through the thimble, and the velocity of air passing through the system, the total particulate flow rate was calculated. In all, four runs were made, 1 reference test, and 3 for mass balance (runs 5, 7, and 9). A gas velocity traverse was made in the precipitator inlet and outlet ducts just prior to each mass balance run to determine isokinetic sampling rates for each sampling position.

The reference test was performed using the standard ASTM method for determining grain loadings to electrostatic precipitators. This test was used to verify the adequacy of the number of samples secured for mass balance calculations. Comparison of grain loading calculations using TVA standard probes and ORNL fabricated probes show the mass balance samples are, indeed, representative.

Analysis of the samples for elemental constituents was performed using instrumented neutron activation analysis (NAA) and spark-source mass spectrometry (SSMS)² In addition, the many Hg determinations were made by flameless atomic absorption (AA).

The NAA technique involved irradiating each dry homogenized sample (0.01 to 0.2 g) in a sealed plastic vial. This vial was placed in a "rabbit" together with

Au and Mn flux monitors and irradiated in the Oak Ridge Research Reactor for a period varying from a few seconds (for short lived radioactive products), to 20 minutes. After irradiation the samples were removed and counted at various set decay times using a Ge(Li) detector and a nuclear-data PDP-15 analyzer computer system. Using programs developed at ORNL, these counting data were processed, and x-ray peaks identified, absolute activities calculated, and from the flux measurement and known nuclear parameters, the $\mu\text{g/g}$ of each element found was calculated. Results in all cases have a 5-10% uncertainty assignment. The entire process is nondestructive in that no chemical treatment is performed, so there is only a minimal chance of sample contamination or loss.

The flameless atomic absorption method has a reproducibility of about 2% or better for homogeneous specimens. Checks³ between AA and NAA (with radiochemical separation after irradiation) and isotope dilution spark source mass spectroscopy on thoroughly homogenized tuna fish and Bureau of Mines round-robin coal specimens indicate good agreement between the methods. ($0.425 \pm 0.9\%$, $0.45 \pm 3.5\%$, and $0.45 \pm 4.4\%$ for tuna by AA, NAA, and SSMS, respectively, and 1.004 is the average ratio of NAA to AA results for 5 coal samples.) These results indicate that the technique used in sample preparation for AA did not result in mercury losses since the NAA method is not subject to losses of this type.

Spark-source mass spectrometry (SSMS) is also a multi-element technique; conventionally the data obtained are semi-quantitative and the results have an uncertainty of $\pm 50\%$ or less. If the stable isotope dilution technique is performed, the SSMS can be $\pm 3\%$. This latter technique was used for a few elements: Pb, Cd, and Zn as noted in the tabulations of results. NAA and SSMS complement each other quite well, and those elements for which one technique has poor sensitivity can usually be measured by the other.

3. Mass Balance Results

A mass balance for the various elements was calculated using the following equations:

$$Q_C(A) = C_C(A) \times (\text{g coal/min}) \quad (1)$$

$$Q_{P.I.}(A) = C_{P.I.}(A) \times (\text{g fly ash/min}) \quad (2)$$

$$Q_{S.T.}(A) = C_{S.T.}(A) \times (\text{g ash in coal/min} - \text{g fly ash to precipitator/min}) \quad (3)$$

for balance:

$$Q_C(A) = Q_{P.I.}(A) + Q_{S.T.}(A) \quad (4)$$

$$\text{percent imbalance} = \frac{Q_{P.I.} + Q_{S.T.} - Q_C}{Q_C} \times 100 \quad (5)$$

$Q_C(A)$, $Q_{P.I.}(A)$ and $Q_{S.T.}(A)$ are the flow rates of element A in g/min associated with the coal, precipitator inlet fly ash, and slag tank solids, respectively, and $C_C(A)$, $C_{P.I.}(A)$ and $C_{S.T.}(A)$ are the corresponding concentrations of element A in the coal, the fly ash collected in the precipitator inlet, and the slag tank solids. The flow of trace elements into the plant with suspended particulates in inlet air was negligible. We were unable to measure the total solids flow from the slag tank because of the nature of this discharge. (Every four hours the slag tank residue is washed out to the ash pond with 2-4 hundred thousand gallons of water.) For this reason we estimated the slag tank discharge as the difference between ash flow rate in the coal and the total fly ash flow rate. Presuming that this assumption is valid, that the sampling was complete and representative, and that

the analyses are correct, the condition for balance is given by equation 4. To test this we have calculated a percent imbalance from experimental results by equation 5. Also, the precipitator efficiency for an element was calculated by

$$\text{Precipitator efficiency} = \frac{Q_{P.I.}(A) - Q_{P.O.}(A)}{Q_{P.I.}(A)} \times 100 \quad (6)$$

The results of the mass balance calculations for 8 major elements and 22 minor elements for run 9 are given in Tables 2 and 3, together with the corresponding concentrations in the coal, precipitator inlet and outlet fly ash, and in the slag tank solids. A complete tabulation of results for all three runs is given in a progress report of the project⁴ and this includes some data for 57 elements.

In general, agreement between the two analytical methods is reasonable. There is a consistent negative imbalance, the average of which was -26% and -16% for NAA and SSMS results, respectively, for the major elements and -1% and -18% for the minor elements. In the averages for minor elements we have excluded the results for Hg and As. In view of the assumptions necessary and the difficulty of obtaining truly representative samples the balance is satisfactory for most elements. Notable exceptions are elements which can be present in a gaseous form. One may be arsenic (Table 3) and another is mercury which is discussed below. One reason for the consistent negative imbalance could be that fly ash samples were taken under steady state conditions. Two operations were not investigated and these might account for this imbalance. The air heaters are cleaned pneumatically once per 8-hour shift, and soot is blown from the boiler tubes about two times per shift. If this material were measured it would increase the average fly ash flow rate ($Q_{P.I.}$). It is not known whether or not these operations can account for a significant percentage of the trace elements. Future in-plant sampling will include these two operations.

As in the case of the slag tank there was no way to quantitatively measure the precipitator residue flow rate. These residues are slurried with water and flushed continuously to the ash pond. However, for all of the elements except selenium the precipitator was extremely efficient (> 95%) as calculated from the inlet and outlet fly ash concentrations using equation 6. The reason that selenium fails to be scavenged effectively is not known and certainly warrants investigation. One possibility is that part of the selenium is in a volatile state but is readily adsorbed on particulates trapped by the alundum thimbles.

Mercury has been determined on virtually every sample (the filters, cold trap and slag tank water and residue). We are unable, however, to find the bulk of the Hg that we know is entering the system via the coal. From this we conclude that Hg is present in the stack gas as a vapor which we were unable to trap.

Table 4 gives all of the values obtained for Hg in coal which range from .057 to .198 ppm, but most values are in the range of 0.07 ppm. Our attempt at a Hg balance for runs 5 and 9 is shown in Table 5. From these numbers it is clear that very little mercury (~ 12%) remains with the slag and fly ash particles. The cold trap was not effective in trapping Hg vapor (~ 11%). The results are in qualitative agreement with those of Billings and Matson,⁵ except that these authors were able to collect the Hg in the gas phase. Their data shows that most of the Hg is in the gas phase which can also be implied from our results.

Recently, we returned to the Allen plant and sampled the flue gas using a four impinger train with a pre-scrubber of sodium carbonate to remove the acid gases, followed by three impingers charged with iodine monochloride solution. Preliminary results show that mercury was collected and quantities detected were of the expected magnitude based on Hg concentrations in the coal which we had measured previously. This technique will be used for the Hg balance at the next in-plant sampling.

Table 2. Elemental concentrations and mass balance results for a number of major elements measured for run 9

Element	Method	Concentration (ppm unless otherwise indicated)			Mass Flow (g/min)			Precipitator Efficiency (%)
		Coal	S.T. ^a	P.I. ^a	Coal	S.T. ^a	P.I. ^a	
Al	NAA	1.06%	6.6%	6.9%	1.3×10^4	7.2×10^3	3.4×10^3	68
	SSMS	1%	5%	10%	1.3×10^4	5.5×10^3	7.3×10^3	-1
Ca	NAA	0.38%	2.7%	1.4%	0.47×10^4	3.0×10^3	6.8×10^2	-22
	SSMS	0.5%	3%	1%	0.6×10^4	3.3×10^3	1.5×10^3	-20
Fe	NAA	1.3%	10.1%	9.3%	1.6×10^4	1.1×10^4	4.5×10^3	-3.1
	SSMS	2%	10%	10%	2.5×10^4	1×10^4	5×10^3	-40
K	NAA	0.22%	0.95%	1.65%	0.27×10^4	1.0×10^3	8.0×10^2	-33
	SSMS	0.06%	0.5%	0.7%	0.07×10^4	5×10^2	3×10^2	+14
Mg	NAA	0.17%	0.41%	0.53%	0.21×10^4	4.5×10^2	2.7×10^2	-66
	SSMS	0.15%	0.7%	0.4%	0.18×10^4	8×10^2	3×10^2	-39
Mn	NAA	54	418	323	67	46	16	-7.5
	SSMS	100	1000	700	130	110	34	11
Na	NAA	0.069%	0.32%	0.7%	860	350	340	-20
	SSMS	0.03%	0.2%	0.3%	370	220	150	0
S	NAA	5.1%	30%	10.5%	6.4×10^4	3.3×10^4	1.5×10^4	-24
	SSMS	5%	3000	3700	890	330	180	-43
Ti	NAA	710	3000	2500	880	220	240	-48
	SSMS	700	2000	1000	880	220	240	-48

^aS.T., P.I., and P.O. are abbreviations for slag tank solids, precipitator inlet, and precipitator outlet, respectively.

Table 3. Elemental concentration and mass balance results for a number of minor elements measured for run 9

Element	Method	Concentration (ppm)			Mass Flows (g/min)					Precipitator Efficiency (%)	
		Coal	S.T. ^a	P.I. ^a	P.O. ^a	Coal	S.T. ^a	P.I. ^a	Imbalance (%)		P.O. ^a
As	NAA	3.8	0.5	46	50	4.7	0.05	2.2	-52	0.1	95
	SSMS	5	2	40	20	6.2	0.2	2	-64	0.04	98
Ba	NAA	79	600	1700	100	130	33	83	-11	0.2	99+
	SSMS	<5	<10	17	<10	<6.3	<1.1	0.83	+8.5	<0.02	98
Be	ID ^b	0.47	-3	5.8	0.31	0.59	0.31	0.33			
	SSMS	0.5	2	<10	7	0.63	0.22	<0.5	-1.0	0.014	<96 ^c
Co	NAA	3.3	19	25	58	4.1	2.1	4.4	-19	0.11	91
	SSMS	7	40	70	40	9	4.4	3.4	-13	0.08	96
Cr	NAA	21	180	356	300	26	20	17	42	0.6	96
	SSMS	30	<200	70	40	37	<22	3.4		0.08	98
Cs	NAA	1.5	8	21	4	1.9	0.88	1.02	0	0.008	99+
	SSMS	50	200	400	400	63	22	19	-35	0.8	96
Eu	NAA	0.17	1.4	1.8		0.21	0.15	0.09	14		
	SSMS	~1				~1					
Hg	AA	0.063	0.09	0.043		0.079	0.0099	0.0021	-85		
	NAA	5.0	42	32		6.3	4.6	1.5	-3		
La	SSMS	~10				~10					
	SSMS	25	200	300	200	31	22	15	19	0.4	97
Mo	NAA	20				25					
	SSMS	20	80	200	20	25	8.8	9.7	-26	0.04	99+
Ni	SSMS	<100	500	500	1000	<130	55	24		2	92
	ID ^b	7.4	-4	149		9.25	0.42	8.60	-3		
Pb	SSMS	<20	3	250	100	<25	0.3	12		0.2	98 ^c
	NAA	<1	<0.2	3.2		<0.75	<0.02	0.2			
Sb ^d	SSMS	8	7	10	10	0.8	0.5	0.5		0.02	96
	NAA	3.2	22	25	10	4.0	2.4	1.2	-10	0.02	98
Sc	NAA	3.2	14	<32-48	760	4.0	1.5	<1.5-2.3	<-25 to -5	1.4	7 to 39
	SSMS	6	20	200	7.5	2.2	1.0		-58	0.4	60
Sr ^e	SSMS	20	200	20	20	25	20	1.4	-14	0.04	97
	NAA	3	20	18	3	3.7	2.2	0.87	-17		
Tl	SSMS	<2	2	40	30	<2.5	0.2	1.9			
	NAA	1.67	14	17	7	2.1	1.5	0.83	11	0.014	98
U	NAA	21	125	200	63	26	14	9.7	-9	0.12	99
	SSMS	30	100	350	100	37	11	17	-24	0.2	99
Zn	ID ^b	94	~20	1500		117	2.1	86	-24		
	SSMS	85	100	3000	900	110	11	150		1.7	98 ^c

^aS.T., P.I., and P.O. stand for slag tank solids, precipitator inlet, and precipitator outlet, respectively.^bData obtained by isotope dilution mass spectrometry for composite samples from runs 5 and 9.^cPrecipitator efficiencies calculated on the basis of P.O. by SSMS for run 9 and P.I. by ID from the composite sample runs 5 and 9.^dRun 5 data.^eRun 7 data.

Table 4. Hg in coal as determined by atomic absorption

Sample	Date	Hg($\mu\text{g/g}$)		
2 ECS 24	26 Jan	0.057		
5 CS 24 AM	28 Jan	0.064	0.063	
5 CS 24 PM	28 Jan	0.069	0.058	
7E CS 26 AM	31 Jan	0.198		
7E CS 26 PM	31 Jan	0.169	0.148	0.136
9E CS 16 AM	1 Feb	0.076	0.060	
9E CS 16 PM	1 Feb	0.060	0.058	
10E CS 19 AM	2 Feb	0.068		
10E CS 19 PM	2 Feb	0.073		
11E CS	3 Feb	0.060		

Table 5. Hg balance

Material	Average Flow g/day	Hg $\mu\text{g/g}$	Hg Flow g/day
Run 5			
Coal	1.8×10^9	0.064	115
Ash (Slag)	1.43×10^8	0.07	10
Precipitator Inlet	0.96×10^8	0.04	4
H ₂ O to Ash Pond	2.9×10^9	0.003	9
Gas (Cold Trap)	4.3×10^{10}	0.0003	13
Run 9			
Coal	1.8×10^9	0.064	115
Ash (Slag)	1.58×10^8	0.09	14
Precipitator Inlet	0.70×10^8	0.043	3
H ₂ O to Ash Pond	2.9×10^9	0.001	3
Gas (Cold Trap)	4.4×10^{10}	0.0003	13

4. Fly Ash Particle Characterization

Figure 3 shows scanning electron photomicrographs of fly ash particles from the precipitator inlet and outlet and from the stack. The particles are predominantly spherical and there is considerable agglomeration of small particles (submicron size) to large ones. Also, there appears to be a fuzzy material present which might be a sulfur compound. Preliminary evidence for this is scanning electron microscope fluorescence analyses of some of the larger particles deposited from the precipitator inlet flue gas on the first stage of a Cassella cascade impactor. Figure 4 shows such an analysis. All of the fluorescence lines, except aluminum, can be attributed to the particles. Since the particles were collected on an aluminum foil the aluminum peak is due primarily to the foil. Upon ion etching by bombardment with argon ions, the sulfur peak decreased substantially indicating sulfur was present primarily on the surface of the particles. As one would expect, the preliminary evidence is that the fly ash particles are a complicated mixture of the elements.

Work is still in progress on determining the particle size distribution in the flue gases before and after the precipitator, and in the stack. Also, composition of fly ash as a function of particle size is in progress.

5. Conclusions

Trace element mass balance measurements around the Number 2 Unit of the coal-fired Allen Steam Plant in Memphis yielded a respectable balance for many elements. However, the results showed a consistent negative imbalance. This might be due to the fact that soot blowing and air heater cleaning operations were not taken into account in the sampling. Because the method of flue gas sampling was designed primarily to collect particulates efficiently, good balances were not obtained for elements forming volatile compounds. For example, more than 80% of the mercury entering with the coal is emitted with the flue gas as a vapor. The large imbalance for arsenic (-58%, Table 3) indicates that a substantial portion of this element is also in the vapor phase of the flue gas.

The electrostatic precipitator was very efficient ($\sim 98\%$) for most trace elements based on analyses of the fly ash particulate specimens collected from the precipitator inlet and outlet. An exception was selenium. Although a reasonable mass balance was obtained for this element (see NAA results, Table 3), it was not removed efficiently by the precipitator. This may indicate that a significant fraction of the material is in the vapor phase in the flue gas, and that it is being adsorbed in

passing through the alundum thimble filter used to sample the fly ash. Accounting more completely for the volatile trace elements such as Hg, Se, and As remains the most significant question still to be answered in future mass balance work.

6. Acknowledgements

The authors wish to express their appreciation to the following personnel of the Tennessee Valley Authority without whose assistance this study could not have been accomplished: Mr. Joseph Greco, Chief Plant Engineering Branch, Division of Power Production; Mr. John H. Lytle, Plant Engineering Branch, who supervised the field test crew during the mass balance runs; and, Dr. Lucy E. Scroggie, Supervisor of the Industrial Hygiene Laboratory, who coordinated TVA's contribution in this joint study for Dr. F. E. Gartrell, Director of Environmental Planning.

7. References

1. Standard Method for Sampling Stacks for Particulate Matter, ASTM Designation, D-2928-71, Jan. 8, 1971.
2. J. A. Carter and J. R. Sites, "Analysis of Radioactive Samples by Spark Source Mass Spectrometry," p. 347 in Trace Analysis by Mass Spectrometry, A. H. Abern (ed.), Academic Press, New York, N.Y., 1972.
3. C. Feldman, J. A. Carter, and L. C. Bate, "Measuring Mercury," Environment **14**, (6) 48 (1972).
4. N. E. Bolton et al., Trace Element Measurements at the Coal-Fired Allen Steam Plant, Progress Report, June 1971 - January 1973, Oak Ridge National Laboratory report, ORNL-NSF-EP-43, March 1973.
5. C. E. Billings and W. R. Matson, "Mercury Emissions from Coal Combustion," Science **176**, 1232 (1972).

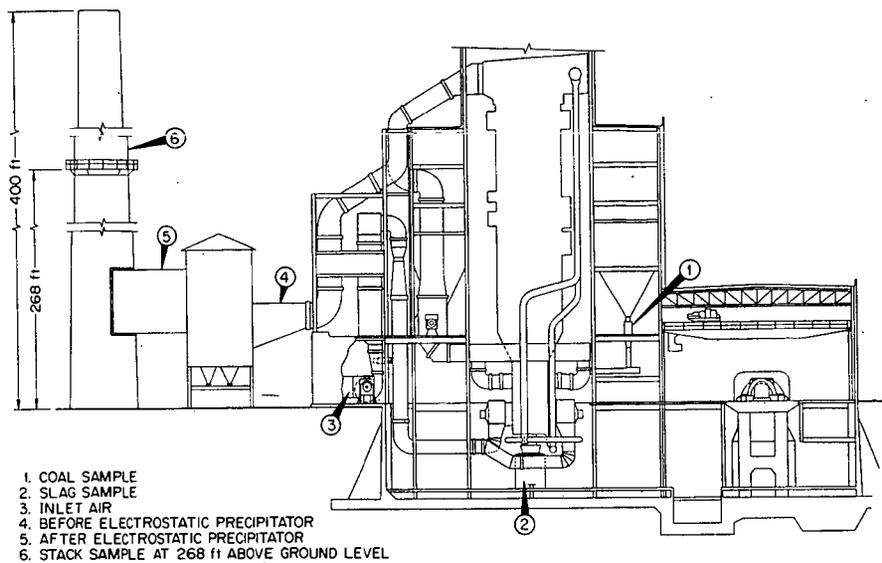


Fig. 1. Schematic of Number 2 Unit, Allen Steam Plant, Memphis.

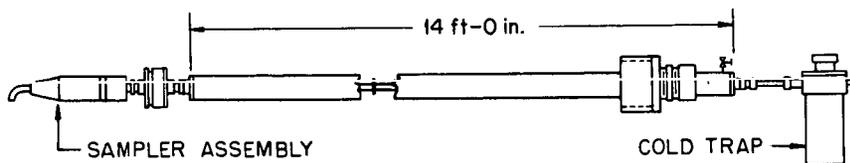


Fig. 2. Schematic of Sampling Probe Used for Mass Balance Study.

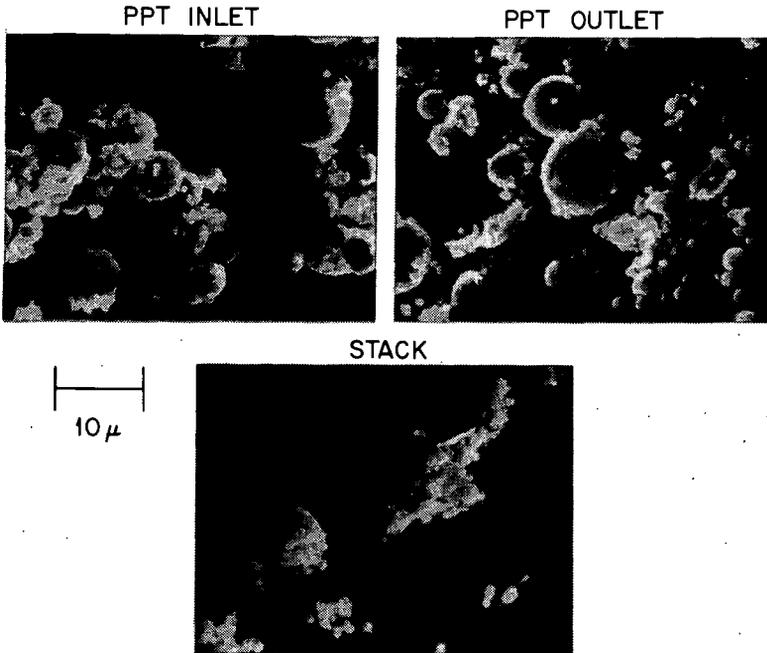


Fig. 3. Scanning Electron Photomicrographs of Fly Ash Particulates Collected on Alundum Thimbles Used to Sample the Precipitator Inlet and Outlet and the Stack.

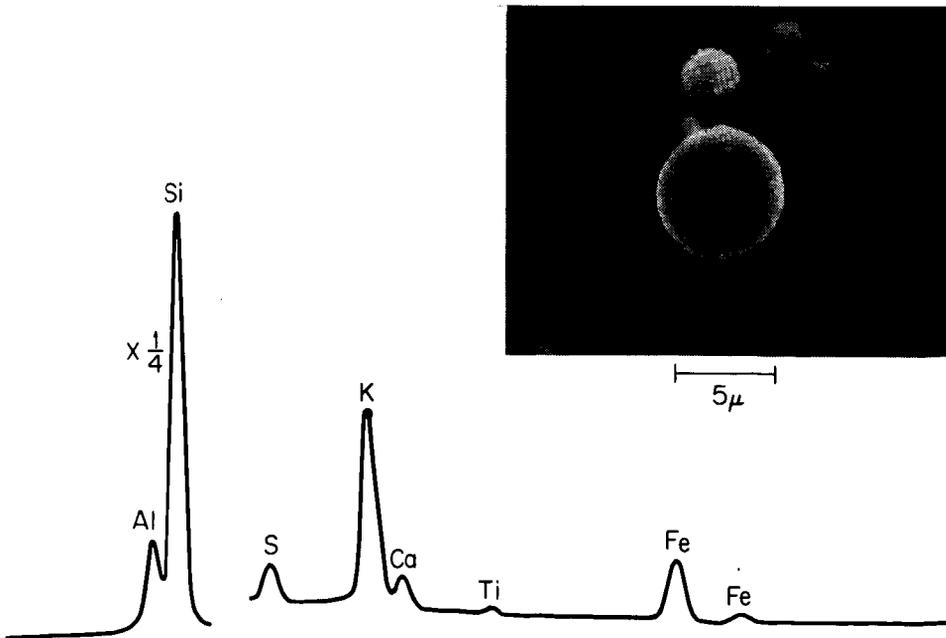


Fig. 4. Qualitative Fluorescence Analysis of a 5 μ Fly Ash Particle Trapped on the First Stage of the Cassella Cascade Impactor Used to Sample the Precipitator Inlet.

REACTIONS OF ALKALI METAL COMPOUNDS DURING COAL GASIFICATION FOR ELECTRIC POWER GENERATION.* Sven A. Jansson, Westinghouse Research Laboratories, Pittsburgh, Pa., 15235.

Alkali metal compounds cause hot corrosion and fouling in gas turbines. The extent of alkali release during gasification of coal depends largely on the chemical composition of alkali compounds in coal and on the chemical reactions of these compounds in the coal gas environment. This paper describes results from a study of alkali metal reactions during different steps of the gasification process. Thermochemical calculations and diagrams are used to determine the probable reaction processes, the nature of any volatile alkali metal species, and the composition of solid or liquid reaction product ash components. The calculations show that chlorine promotes alkali release through the formation of highly volatile alkali chlorides. Hydrogen chloride is another important reaction product. As the coal gas is burned with air and expanded through a gas turbine, the alkali chlorides react with sulfur compounds in the gas to form sulfate deposits.

Calculations have been made to determine the effects of different levels of alkali metal, sulfur, and chlorine on condensation temperature and the nature of turbine deposits.

*Work partially supported under contract with the Office of Coal Research.

State of Trace Elements of Coal During Gasification, A. Attari and J. C. Pau,
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A preliminary study has been initiated (under EPA sponsorship) to determine the concentration of some 35 trace elements in coal with particular emphasis on their fate and distribution among the various solid, liquid, and gaseous effluents of HYGAS pilot plant, now under operation at the Institute of Gas Technology. Coal and solid residue samples were obtained from the pretreatment, hydrogasification, and electrothermal stages of bench-scale development unit of the HYGAS plant. The samples were dry ashed in an oxygen plasma low-temperature asher and the resulting ash samples were decomposed with HF, then dissolved in perchloric acid for subsequent analysis by various atomic absorption methods, except for mercury, which was determined by a combustion-nonflame-AA method. Thus far, Sb, As, Be, Cd, Cr, Pb, Hg, Ni, Se, Te, and V levels have been measured in feed and solid residues of a bituminous coal and the results show substantial removal of elements such as As, Cd, Pb, Hg, Se, and Te during gasification. These results, however, are based on a limited number of samples and further work is in progress to analyze a larger number of samples before any firm conclusions can be drawn.

Coal Gasification for Electric Power Generation - Process Conditions Effecting Contaminant, D. H. Archer, J. L. P. Chen, E. F. Sverdrup, R. W. Hornbeck, Westinghouse Research Labs, Beulah Road - Churchill Boro, Pittsburgh, Pa. 15235.

A coal gasification process has been proposed to provide fuel for electric power generation in a gas and steam turbine combined cycle power plant. The process uses multistaged fluid beds with countercurrent gas and solids flow to produce a low cost plant capable of economically gasifying a wide range of coals. The plant is being designed to meet stringent air pollution standards. It employs a high temperature dolomite sorbent bed for desulfurization. Both coal and dolomite particles are followed through the gasification process to establish the gas compositions, residence times, and temperatures that will effect the release of contaminants. Using these process conditions, a companion paper estimates the release of the alkali metal compounds which are potentially harmful to the turbine.

EVALUATION OF MORDENITE CATALYSTS FOR PHENANTHRENE HYDROCRACKING

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INTRODUCTION

H-mordenite, in combination with hydrogenation catalysts, has been used in hydrocracking of different types of hydrocarbons. Voorhies and Hatcher¹ and Beecher et al.² used pd-H-mordenite in the study of kinetics of hydrocracking of C₆, C₈ and C₁₀ paraffinic and naphthenic hydrocarbons. The hydrogen mordenite used had a SiO₂/Al₂O₃ of about 10. The reactions were found to be of first order with respect to hydrocarbon concentration and the activation energies of hexane, cyclohexane, n-decane and Decalin were found to be 48, 31, 33 and 25 kcal./mole respectively. Beecher et al.² also used hydrogen mordenite having a SiO₂/Al₂O₃ of greater than 50 in combination with palladium in the hydrocracking of n-decane and Decalin. The aluminum deficient catalyst combination was found to be over 4 times as active as pd-H-mordenite combination. Aluminum deficient H-mordenite (SiO₂/Al₂O₃ = 64) was also found to be more active in cumene cracking by Eberly and Kimberlin³. Qader et al.^{4,5} studied the hydrocracking of naphthalene and anthracene over catalysts containing H-mordenite (SiO₂/Al₂O₃:10) and oxides and sulfides of Co, Mo, Ni and W. The reactions were found to be of first order with respect to hydrocarbon concentration and the activation energies of naphthalene and anthracene hydrocracking were found to be 30.5 and 28.6 kcal./mole respectively. The anthracene hydrocracking data was also found to be compatible with the dualsite mechanism according to the Langmuir-Hinshelwood model. The hydrocracking of phenanthrene over catalyst combinations containing H-mordenites of 10, 50 and 100 silica-alumina ratios is presented in this paper.

EXPERIMENTAL

Phenanthrene of over 99.8 percent purity was hydrocracked in a batch stirred tank reactor of 1-litre capacity, shown in Figure 1. Twenty grams of phenanthrene, 7.5 grams of H-mordenite or silica-(low) alumina and 2.5 grams of WS₂ were used in each experiment. Hydrocracking was carried out in the temperature range 400°-500°C at a constant initial (cold) pressure of 1800 psi. The final (hot) pressures varied between 3000 and 3500 psi. The reactants and catalysts were heated to the experimental temperature in 25-35 minutes and the time when the temperature reached the experimental temperature was taken as zero reaction time as shown in Figure 2. The conversions at zero reaction times were determined by cooling the products immediately after the temperature reached the experimental temperature. It took 1-2 minutes to cool the products to below 300°C in all experiments. It was assumed that no reaction took place during the cooling cycle. Zero reaction time hydrocracking conversions varied between 1 and 5 weight percent of phenanthrene under the experimental conditions employed. Experiments were conducted at reaction times of zero time (as defined above), zero time + 20, zero time + 30 and zero time + 60 minutes. The conversions obtained in between zero reaction time and zero time + 60 minutes were used for evaluation of mechanisms and kinetics. The volume of initial hydrogen used in the reaction and the product gases were measured by a wet gas meter. The liquid product and the spent catalyst were recovered by washing all the reactor parts with acetone.

In experiments designed for calculating weight balances, a weighed quantity of Tetralin was used for recovering the liquid product and catalyst. Catalyst was then separated from the liquid by filtration, washed with acetone and dried at 110°C. The weight of the liquid product was then obtained by difference.

$$\text{Weight of liquid product} = (\text{weight of Tetralin} + \text{Liquid Product} + \text{Catalyst as recovered from the reactor}) - (\text{Weight of initial Tetralin used for washing} + \text{weight of dried spent catalyst}).$$

The weight of C₁-C₄ gases formed was obtained from total volume of gaseous product and gas composition. The difference between initial hydrogen used in the reaction and hydrogen present in product gas was taken as hydrogen consumed in the reaction. The analyses of liquid and gaseous products were done by gas chromatographic techniques. Since phenanthrene molecule contains 14 carbon atoms, all compounds in the product containing 13 carbon atoms or less were taken as cracked products for calculating hydrocracking conversions. The mole percent hydrocracking conversions were obtained from liquid product analyses.

$$\text{Mole percent hydrocracking conversion} = (\text{Sum of mole percentages of all components of the liquid product which is equal to 100}) - (\text{Sum of mole percentages of all components of the liquid product containing 14 carbon atoms}).$$

This was done on the assumption that there will be no change in the liquid moles during the reaction since each mole of phenanthrene can yield only one mole of each component of the liquid product. The higher compounds reported include liquid product components which come out in the chromatographic analysis after phenanthrene and coke.

COKE DETERMINATION

The fresh and spent catalysts were heated in a muffle furnace at 600°C for 3 hours and the weight losses were determined. The difference between the weight losses of each used catalyst and the fresh catalyst was taken as coke formed during the reaction.

RESULTS AND DISCUSSION

Reaction Mechanism:

Hydrocracking of phenanthrene involves three main reaction steps of hydrogenation, isomerization and cracking as indicated by the product distribution data given in Table I. Phenanthrene first gets hydrogenated to di-, tetra- and octa-hydrophenanthrenes. The hydrophenanthrenes, then get isomerized to C₁₄ isomers. C₁₄-isomers contain the same number of carbon atoms (14) as hydrophenanthrenes and they are formed from tetra- and octahydrophenanthrenes by the skeletal rearrangement of saturated six member rings of the latter to saturated five member rings with methyl groups attached to them. The C₁₄-isomers contain one or two saturated five member rings. This skeletal rearrangement is analogous to the isomerizat-

ion of hydroanthracenes to C₁₄-isomers as reported by Qader et al.⁵. The third reaction step is the hydrocracking of hydrophenanthrenes and C₁₄-isomers to lower molecular weight compounds. The product distribution data given in Table I indicates that the initial products of hydrocracking are C₁₃-isomers and naphthalenes. C₁₃-isomers contain 13 carbon atoms and one five member saturated ring in the molecule and they are formed from C₁₄-isomers by demethylation of the latter. The alkylnaphthalenes and naphthalene are formed by the hydrocracking of hydrophenanthrenes, and C₁₄- and C₁₃-isomers. The formation of naphthalenes and tetralins as the initial products of hydrocracking suggests that cracking is taking place in one of the side benzene rings of the hydrophenanthrenes, and C₁₄- and C₁₃-isomers. As cracking proceeds further, indans and alkylbenzenes are formed in the product. This suggests that indans and alkyl benzenes are formed from naphthalenes and tetralins by the occurrence of hydrogenation, isomerization and cracking reactions as reported earlier by Qader et al.⁴. The product distribution data obtained in this work suggest that phenanthrene hydrocracking takes place through the occurrence of a multistep mechanism of hydrogenation, isomerization and cracking as shown in Figure 3. The reaction is a very complex one and the mechanism presented in Figure 2 represents only the gross hydrocracking pattern. Somewhat similar mechanisms were earlier reported by Sullivan et al.⁶ and Rumohr and Kölling⁷. Sullivan et al.⁶ hydrocracked phenanthrene over a nickel sulphide on silica-alumina catalyst and found that the reaction took place partly by a similar mechanism as shown in Figure 3 and partly by two other mechanisms. Rumohr and Kölling hydrocracked phenanthrene over a nickel on alumina catalyst and reported that the reaction took place by a mechanism somewhat similar to the one shown in Figure 3.

KINETICS OF HYDROCRACKING

During hydrocracking, phenanthrene gets hydrogenated to hydrophenanthrenes which subsequently get isomerized to C₁₄-isomers. The hydrophenanthrenes and C₁₄-isomers will then crack to lower molecular weight compounds. All compounds of the product containing less than 14 carbon atoms are taken as cracked products in the calculation of hydrocracking conversions. The conversion data were evaluated by a simple first order rate equation (1) where "x" is mole fraction conversion of phenanthrene

$$\ln (1-x) = -KT + Q \quad (1)$$

(mixture of phenanthrene, hydrophenanthrenes and C₁₄-isomers) and Q is a constant. The plots of equation (1) shown in Figures 4 and 5 indicate that the order of hydrocracking reaction is one with respect to phenanthrene concentration at constant hydrogen pressure. The first order rate constants were used in calculating Arrhenius activation energies as shown in Figure 6. Activation energies of 20.8 and 35.3 kcal./mole were obtained in the hydrocracking of phenanthrene over H-mordenite (10) + WS₂ and Silica-(low) alumina + WS₂ catalysts respectively. The activation energies indicate that the hydrocracking reaction is predominantly controlled by chemical processes. The first order rate constants of phenanthrene obtained over Mordenite and Silica-alumina catalyst systems were found to be represented by equations (2) and (3) respectively.

$$K_m = 2.6 \times 10^2 e^{-20,800/RT} \text{ min.}^{-1} \quad (2)$$

$$K_{SA} = 7.3 \times 10^6 e^{-35,300/RT} \text{ min.}^{-1} \quad (3)$$

ACTIVITIES OF CATALYSTS

Activities of catalysts depend upon reaction conditions and nature of reactants. Activities of catalysts can be evaluated and compared by reaction rates calculated from conversion data. The rate of a chemical reaction is very much influenced by the catalyst activity and it is necessary to keep the catalyst activity same throughout the reaction. In hydrocracking coke deposition takes place on the catalyst and reduces the available active sites which in turn reduces the activity. A large excess of catalyst is used in this work to insure availability of sufficient number of active sites during the reaction. Conversion data obtained on four different catalysts are shown in Figure 7 and the first order rate constants are used to represent catalyst activities. The activities of the catalysts varied in the order H-M-50 + WS₂ \approx H-M-100+WS₂ > Silica-(low) alumina + WS₂ > H-M-10 + WS₂ as shown in Table II. The activity of mordenite + WS₂ catalyst system almost doubled when the silica-alumina ratio of mordenite increased from 10 to 50. The activities of mordenites with silica-alumina ratios of 50 and 100 were found to be same. The aluminum deficient mordenites were earlier found to be more active in the hydrocracking of n-decane and Decalin². Though activity increased with silica-alumina ratio, the phenanthrene hydrocracking mechanism remained same as indicated by the product distribution data given in Table III.

COKE FORMATION

Conversion data shown in Figure 2 indicate that most of the coke was formed during initial stages of the reaction. After the deposition of initial coke, the activity of the catalyst probably gets equilibrated. This appears to be happening at the zero reaction time and the increase in coke deposition after the zero time is not very high. The coke data shown in Figure 8 indicate that the mordenite based catalysts produce less coke when compared to silica-alumina based catalyst. The silica-alumina ratio of the mordenite appear to be having some influence on coke yield. Catalysts with silica-alumina ratios of 50 and 100 yielded more coke when compared to catalyst with silica-alumina ratio of 10.

REACTIVITIES OF HYDROCARBONS

The reactivities of different polynuclear aromatic hydrocarbons are compared by their first order rate constants as shown in Figure 9 and Table IV. The data show that phenanthrene is less reactive when compared to naphthalene and anthracene and more reactive than pyrene. The reactivities varied in the order anthracene > naphthalene > phenanthrene > pyrene.

ACKNOWLEDGMENT

This work is supported by the Office of Coal Research and the University of Utah.

LITERATURE CITED

1. Voorhies, Jr., A., Hatcher, Jr., W. J., Ind. Eng. Chem. Prod. Res. Develop., 8, 361 (1969).
2. Beecher, R., Voorhies, Jr., A., Eberly, Jr., P., Ind. Eng. Chem. Prod. Res. Develop., 7, 203 (1969).
3. Eberly, P. E. and Kimberlin, Jr., C. N., Ind. Eng. Chem. Prod. Res. Develop., 9, 335 (1970).
4. Qader, S. A., Sridharan, R., Hill, G. R., Abstracts, The Second North American Meeting of Catalysis Society, Houston, Texas, p. 75 (1971).
5. Qader, S. A., Chun Chen, L. and Mcomber, D. B., 165th National Meeting, American Chemical Society, Division of Petroleum Chemistry, preprints, 18, No. 1, 60 (1973).
6. Sullivan, R. F., Egan, C. J., Langlois, G. E., J. Catalysis, 3, 183 (1964).
7. Rumohr, V. C. and Kölling, G., Erdol und Kohle-Erdgas-Petrochemie Vereinigt mit Brennstoff-Chemie, 25, No. 6, 309 (1972).

TABLE I. HYDROCRACKING PRODUCT DISTRIBUTION OF PHENANTHRENE
PRESSURE: 1800 PSI (COLD)

Catalyst	WS ₂ (2.5 gram)	H-Mordenite (7.5 gram)	WS ₂ (2.5 gm) +H-Mordenite (7.5 gram)	
			400 0+5	450 0+10
Temperature, °C	400	500	400	450
Reaction Time, Mins.	0+5	0+30	0+5	0+10
<u>LIQUID PRODUCT</u>				
<u>COMPOSITION, WT. %</u>				
Phenanthrene	66.89	82.04	40.37	64.00
Hydrophenanthrenes (Di-, Tetra-, and Octa-)	29.17	10.54	51.70	25.64
Hydrophenanthrene isomers (C ₁₄)	2.68	3.01	4.21	5.22
Hydrophenanthrene isomers (C ₁₃)	0.70	0.50	0.41	0.76
Naphthalenes and Tetralins	0.56	3.13	2.99	3.00
Indans	nil	0.78	0.32	0.11
Alkylbenzenes and benzene	nil	nil	nil	1.27

TABLE II. ACTIVITIES OF CATALYSTS
TEMPERATURE = 450°C
PRESSURE = 1800 psi (cold)

<u>Catalyst</u>	<u>First Order Rate Constant, Sec.⁻¹</u>
H-M-10+WS ₂	12.8 x 10 ⁻⁵
H-M-50+WS ₂	21 x 10 ⁻⁵
H-M-100+WS ₂	21 x 10 ⁻⁵
Silica-(low) Alumina + WS ₂	17 x 10 ⁻⁵

TABLE III. HYDROCRACKING PRODUCT DISTRIBUTION OF PHENANTHRENE
PRESSURE = 1800 psi (cold)

Catalyst	H-M-10+WS ₂	H-M-50+WS ₂	H-M-100+WS ₂
Temperature, °C	400	425	400
Reaction Time, Mins.	0+5	0+5	0+5
<u>LIQUID PRODUCT COMPOSITION, WT. %</u>			
Phenanthrene	40.37	81.95	74.90
Hydrophenanthrenes (Di-, Tetra-, and Octa-)	51.70	15.36	20.19
Hydrophenanthrene isomers (C ₁₄)	4.21	1.31	0.97
Hydrophenanthrene isomers (C ₁₃)	0.41	0.11	0.48
Naphthalenes and Tetralins	2.99	1.27	2.74
Indans	0.32	nil	0.72
Alkylbenzenes and Benzene	nil	nil	nil

TABLE IV. REACTIVITIES OF HYDROCARBONS

Hydrocarbon	TEMPERATURE: 450°C	First Order Rate Constant, Sec. ⁻¹
	PRESSURE: 1800 PSI (COLD)	
Anthracene		16.5 x 10 ⁻⁵
Naphthalene		14.3 x 10 ⁻⁵
Phenanthrene		12.8 x 10 ⁻⁵
Pyrene		5 x 10 ⁻⁵

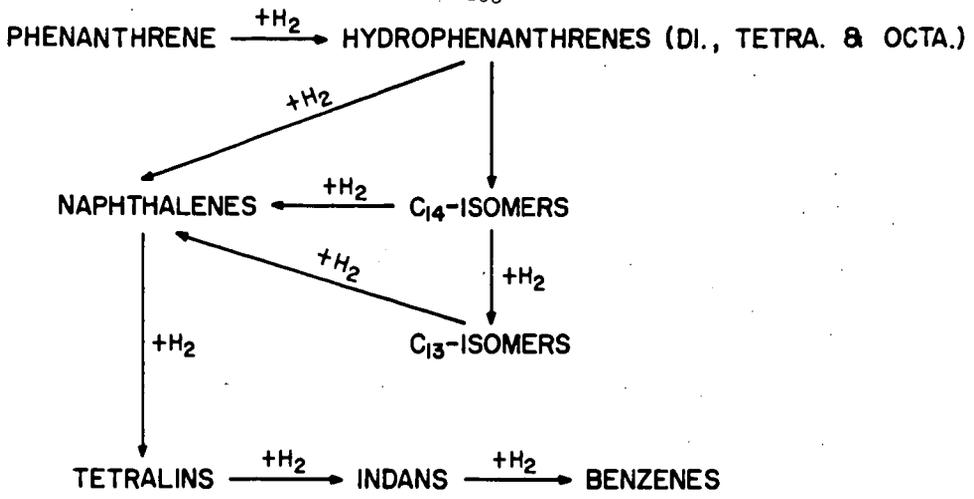
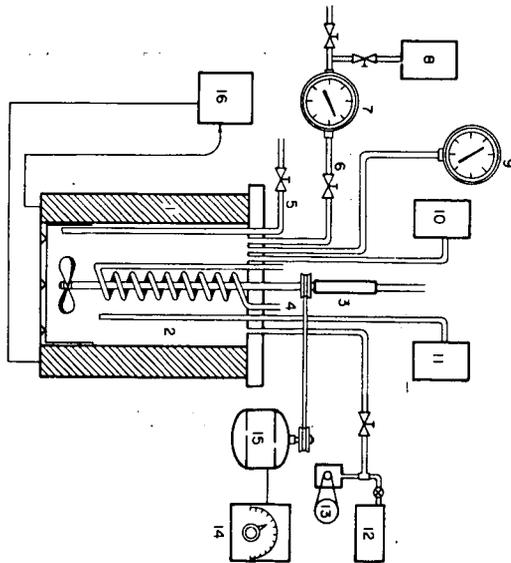


FIGURE 3. HYDROCRACKING MECHANISM OF PHENANTHRENE

FIGURE 1. BATCH STIRRED TANK REACTOR ASSEMBLY.



1. Heating jacket;
2. Thermowell.
3. Magnetic drive assembly.
4. Cooling coil.
5. Liquid sampling line.
6. Gas sampling line.
7. Flow meter.
8. Gas chromatograph.
9. Pressure gage.
10. Pressure recorder.
11. Temperature recorder.
12. Hydrogen tank.
13. Vacuum pump.
14. Stirrer controller.
15. Motor.
16. Temperature controller.

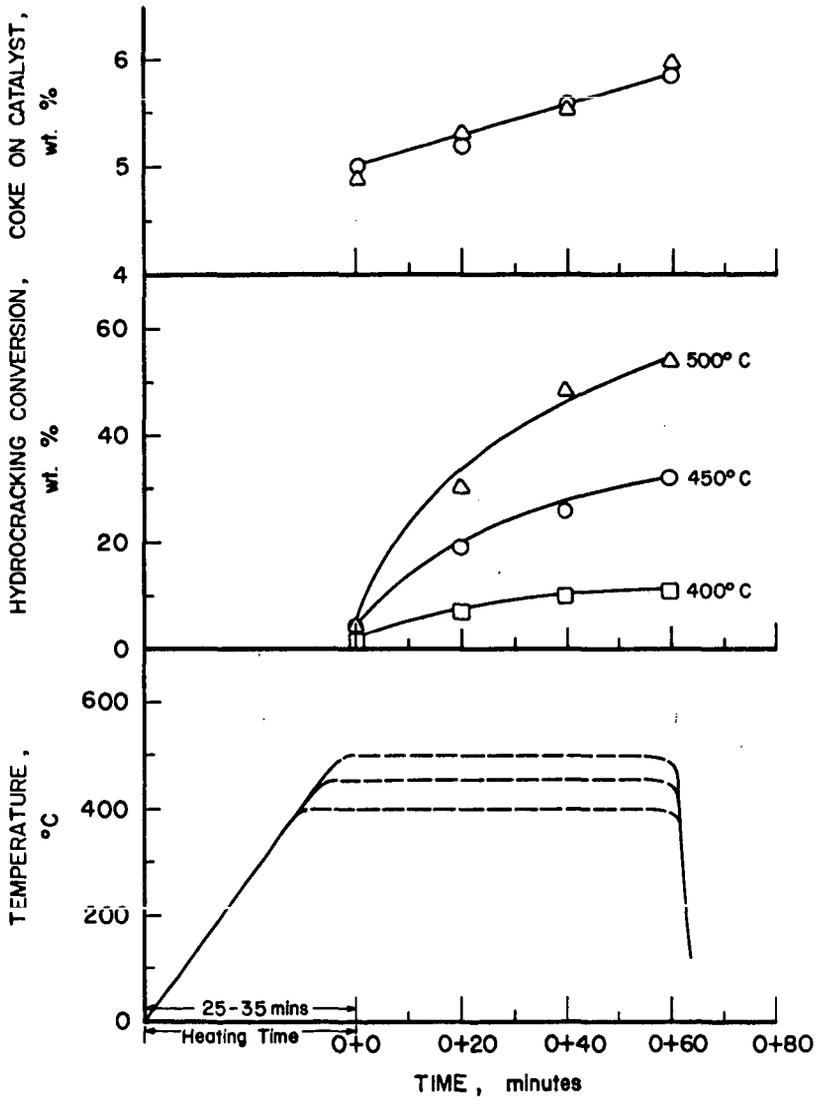


FIGURE 2. HEATING TIME - REACTION TIME - CONVERSION - COKE DEPOSITION

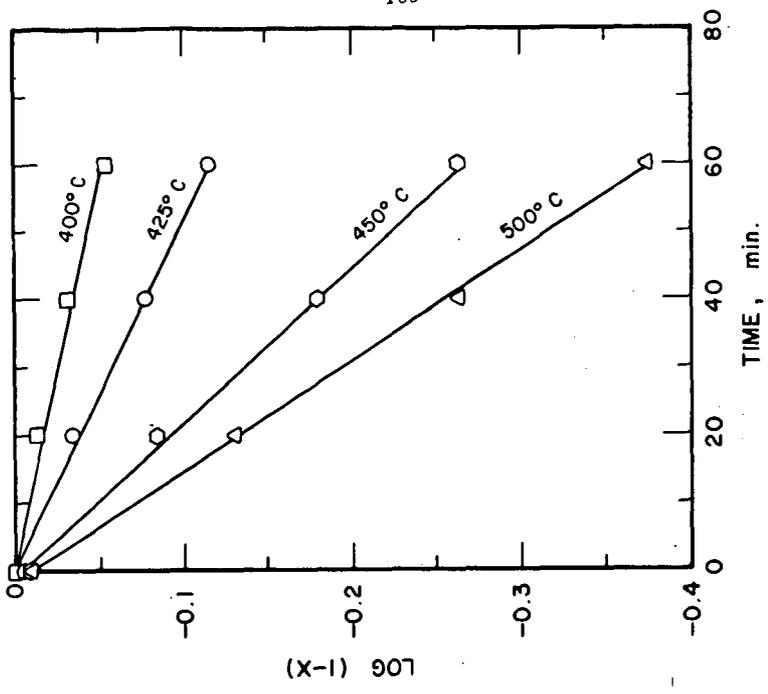


FIGURE 5. FIRST ORDER PLOTS-SILICA-(LOW) ALUMINA + WS₂

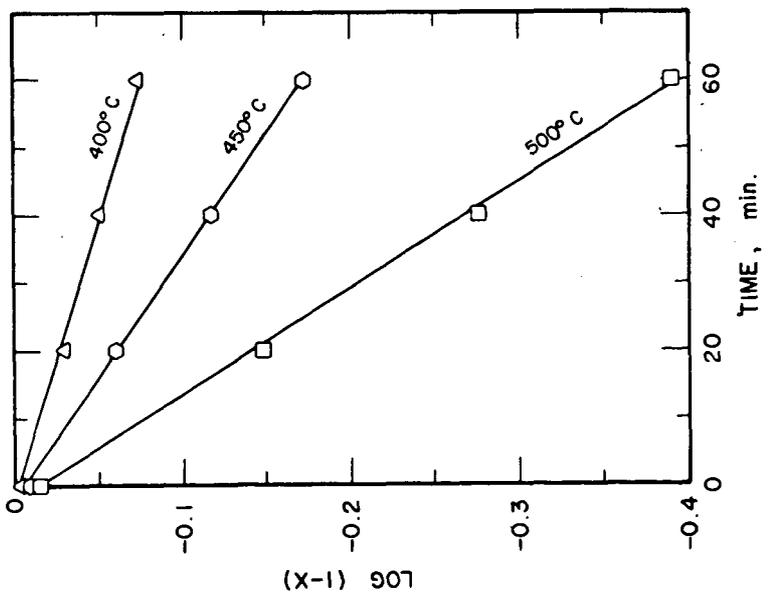


FIGURE 4. FIRST ORDER PLOTS-H-M-10+WS₂

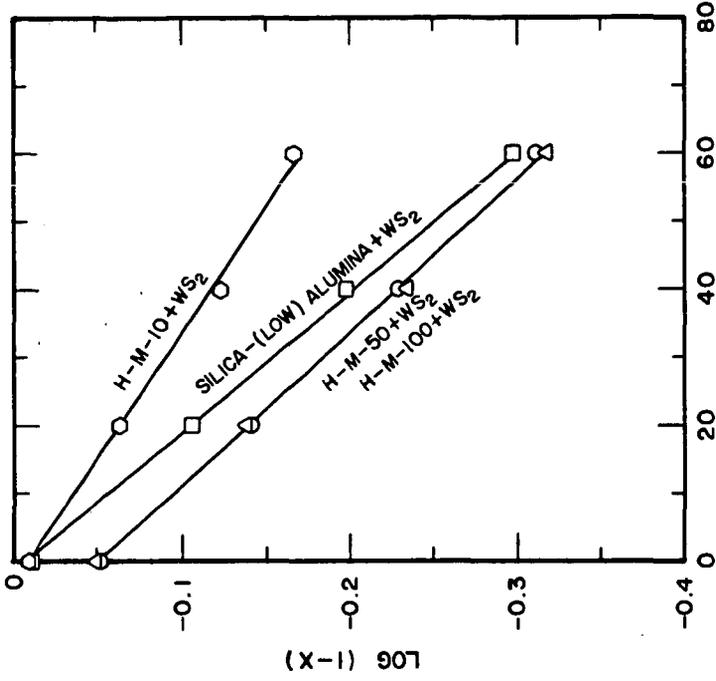


FIGURE 7. ACTIVITIES OF CATALYSTS
 TEMPERATURE: 450°C
 PRESSURE: 1800 PSI (COLD)

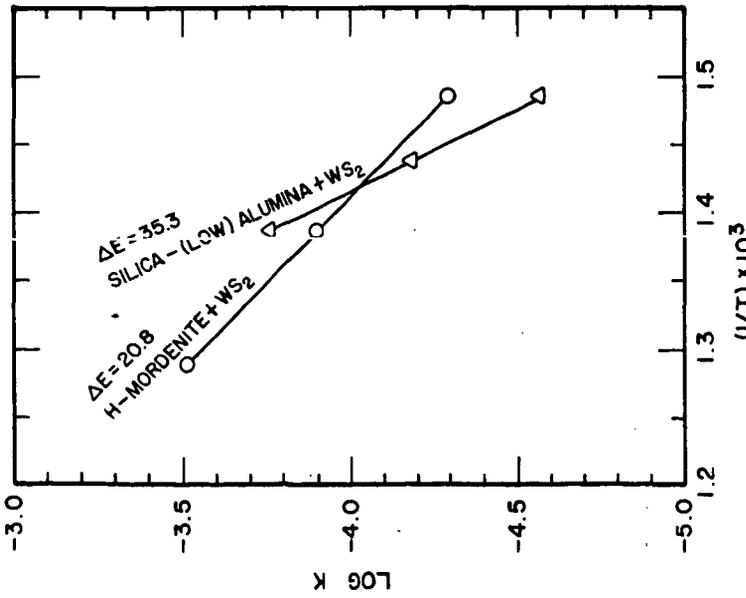


FIGURE 6. ARRHENIUS PLOT

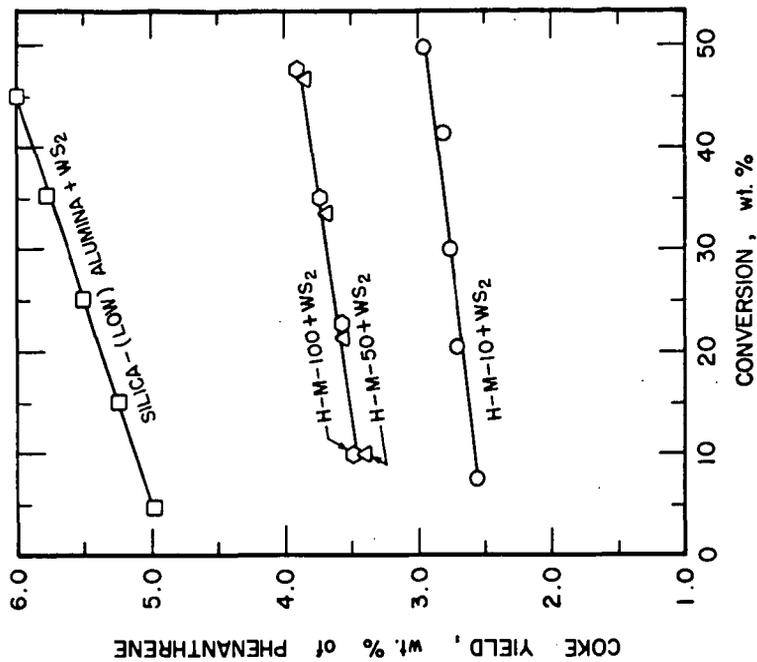


FIGURE 8. COKE YIELD DATA
 TEMPERATURE: 450°C
 PRESSURE: 1800 PSI (COLD)

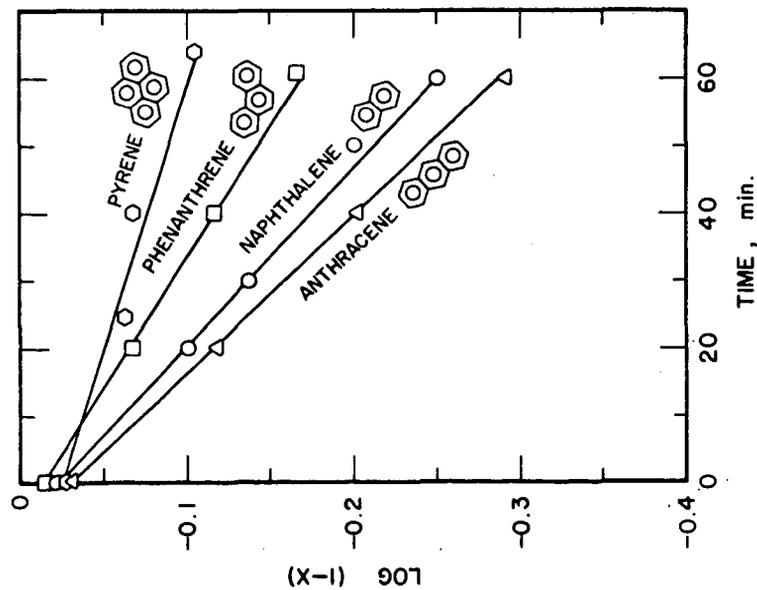


FIGURE 9. REACTIVITIES OF HYDROCARBONS
 TEMPERATURE: 450°C
 PRESSURE: 1800 PSI (COLD)

COAL TAR AND PETROLEUM PITCHES AS BINDERS
FOR PREBAKED ELECTRODES

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INTRODUCTION

It has been shown that improved binders for Soderberg electrodes can be made by incorporating a rubber reinforcing grade of carbon black in low grade coal tar pitch or a residue from catalytic cracking of petroleum. At the concentration used (1-1.5% of the paste) carbon blacks cannot function merely as a partial replacement for coke fines. The high surface area, small particle size reinforcing blacks improve the homogeneity and mechanical stability of the binder-coke mixture by preventing the separation of oily components at high temperatures and apparently have a catalytic effect on polymerization and condensation reactions associated with coking of the binder.

A cracked petroleum pitch containing carbon black has also been compared to coal tar pitch in a prebaked electrode formulation. In the manufacture of prebaked electrodes, sized calcined coke and/or anthracite aggregate is mixed with 20 to 25% of coal tar pitch at 100-150°C using a hydraulic ram press. A small amount of paraffinic mineral oil is added to the mix to act as a lubricant during extrusion. Extruded electrodes are cooled in a water bath, then packed in sand and baked in a gas-fired pit furnace. The temperature in the furnace is increased gradually over a period of about 30 days to a maximum of 950-1000°C. After baking, the electrodes are cooled, repacked in calcined coke, and graphitized by heating to 1500-3000°C.

The coking characteristics needed in a binder for prebaked electrodes are generally similar to those for Soderberg paste, though lower paste fluidity is adequate for prebaked electrodes: while the paste must be fluid enough to permit forming by extrusion, it is not necessary or desirable that it flow under its own weight.

EXPERIMENTAL

The properties of a coal tar pitch (K) suitable for the manufacture of prebaked electrodes are given in Table 1 along with those of three petroleum binders. Binder H was prepared by dispersing 2.5% of fluffy (unpelletized) ISAF black in the pitch by mechanical stirring. Pitches G and J were made via a colloidal dispersion of commercial pelletized SRF carbon black in an aromatic oil, followed by distillation in vacuo, as previously described.

Thermogravimetric Analyses

Many electrode manufacturers use thermogravimetric analysis (TGA) of the binder to establish the temperature cycle for baking electrodes so that the rate of evolution of hydrocarbon vapours can be controlled. Too rapid emission of gases may cause electrodes to crack during the baking operation. Since the vapours are burned in the furnace

pit and contribute heat to the baking process, a moderate rate of volatilization is required to provide good temperature control. According to a common laboratory procedure, a weighed sample of pitch is placed on a balance pan enclosed in a furnace, the temperature of which is increased to 650°C over a period of 10 hours under nitrogen, and the loss in weight is determined at several temperatures.

The results of coking tests carried out by this procedure (TGA No. 1) on coal tar pitch K and petroleum binder H are shown in Figure 1. Although the initial temperature for evolution of volatiles was about 100°C higher for H than for K, the maximum rate of volatilization (slope of the linear part of the thermogram) of H was greater, and above 600°C it lost weight at a faster rate than K. Rapid loss in weight and a low carbon residue by TGA are generally considered to indicate a tendency to form a porous electrode. However, some doubt remained about the validity of this accelerated TGA test; as noted above, when electrodes are baked commercially, the temperature is raised much more slowly.

A TGA test (No. 2) was carried out at a much lower heating rate. Samples of binder in crucibles were heated for 22 hours in a nitrogen atmosphere at each of seven temperatures from 250 to 800°C, total heating time: 154 hours. After each period, the crucibles were removed from the furnace, cooled in a desiccator, and weighed. The results (Figure 2) differed markedly from those obtained by rapid heating. The coal tar pitch still began to vaporize at a lower temperature than the petroleum pitches G and H, but the maximum rate of volatilization was about the same for all. The different shape of the initial part of the curve for pitch K was shown previously by vacuum distillation analysis to be due to its higher content of non-coke forming light ends as compared to cracked petroleum pitch binders⁽¹⁾.

After slow heating to 800°C, the weight of residue was virtually the same for all pitches. The amount of coke was 69-72% of the binder, as compared to 52-60% by the conventional isothermal coking value test (2.5 hours at 550°C) and the rapid heating TGA method. This is in agreement with Charette and Girolami⁽²⁾ and Martin and Nelson⁽³⁾, who observed that the amount of coke from some coal tar pitches varied inversely as the rate of heating, since slow heating favours condensation and polymerization over cracking and volatilization. Heating rate has a greater effect on cracked petroleum pitch containing carbon black than on coal tar pitch: the difference in the amount of coke from slow and fast heating TGA tests was larger for H (72 vs 52%) than for K (69 vs 60%). This can undoubtedly be explained by the higher proportion of distillable coke forming components in a cracked petroleum residuum as determined by vacuum distillation and analysis of narrow cuts⁽¹⁾.

A third series of TGA tests were carried out to determine the effect of the presence of petroleum coke aggregate. Girolami⁽⁴⁾ reported that coal tar pitch has a higher apparent coking value when heated in the presence of calcined coke particles than when heated alone. In our test, (TGA No. 3) mixtures containing 23% binder and 77% calcined coke flour* were heated for 22 hours at each of six temperatures

* Coke I, Figure 4

between 300 and 800°C. As indicated in the next section, the proportions of binder and coke used were about optimum for prebaked electrodes made from this aggregate.

The results of the tests, shown in Figure 3, were quite different from those observed for the binders alone at the same heating rate. The initial evolution of volatiles from all of the mixtures occurred at the same temperature (300°C) but at about double the rate observed for the pure binders at 300-450°C, indicating interaction between the pitch and coke. At the same final temperature (800°C) the weight loss was higher than when the binders were heated alone, a result in disagreement with the observations of Girolami, and of Martin and Nelson above. The cracked pitch H containing only 2.5% carbon black had an extremely low effective coking value (29), whereas the one with 5% carbon black and the coal tar pitch both had about 50. Conclusions are that the additional 2.5% carbon black in G is of benefit during the baking procedure and this is borne out by the electrode test data presented in the following section.

Evaluation of Test Electrodes

The three petroleum binders and coal tar pitch, inspections of which are given in Table 1, were compared in several prebaked electrode formulations containing 21 to 27% binder. Two calcined coke aggregates were used, with particle size distributions as shown in Figure 4. About 2% extrusion oil based on the coke was added to the mixture. The coke and binder were stirred in a sigma bladed mixer at about 160°C and molded at 130°C under a pressure of 5,000 psig. After cooling to 95°C, the samples were removed from the molds, measured and weighed. The binders all gave similar molded green mix densities. The green electrodes were packed in calcined coke in stainless steel molds for baking, which was carried out in a 48 hour controlled temperature cycle. The electrodes were held at the maximum temperature of 1000°C for 2 hours. After cooling in the furnace, they were removed from the molds, brushed free of coke scale, measured and weighed, then machined to obtain specimens 2.5 inches in diameter and 3 inches long which were evaluated for density, electrical resistivity, and compressive strength. Experimental data for the mixes containing the optimum amount of binder (22-23 wt %) are summarized in Tables 2 and 3. The average loss of volatiles from cracked pitch (5.0% SRF black) using the two coke aggregates was the same as for the coal tar pitch (33-34%), but the others containing only 2.5% black lost 37 and 40% in weight respectively.

Table 4 gives a comparison of effective coking values obtained by five procedures: the isothermal coking test, three laboratory TGA tests and during baking of electrodes. The isothermal test, which agrees with the Norske method⁽²⁾, and the rapid heating TGA procedure (No. 1) both gave less coke than when electrodes were baked. This result confirms results reported by Martin and Nelson⁽³⁾. The slow heating TGA procedure (No. 2) on the binders alone gave a coke yield somewhat higher than that found in the baking tests. However, TGA test No. 3 on the binder/coke mixture produced substantially less coke than by electrode baking, a result that is not susceptible to a plausible explanation.

It appears that thermogravimetric analysis of the binder alone at a very slow heating rate can be used to predict the approximate yield of coke from coal tar pitch binders and possibly from cracked petroleum binders containing the optimum amount (about 5%) of carbon black. However, it must be concluded that in other cases a reliable indication of performance is obtainable only by preparing and baking test electrodes.

Figure 5 shows the density of baked test electrodes as a function of the amount of coked binder (coke residue, wt %, x binder content). Each curve has a maximum corresponding to the optimum amount of coked binder. An electrode made using pitch G with the optimum carbon black content had a maximum baked electrode density at least as high as coal tar pitch binder.

As expected, the compressive strength of baked test electrodes varied directly with electrode density, and for the same coke aggregate the relationship is independent of the origin of composition of the binder (Figure 6). The indicated higher average strength of electrodes made from coke I may be due to the denser grading of this aggregate in the coarse fractions.

The electrical resistivity of baked electrodes decreased with increasing electrode density as shown in Figure 7. Because coke II is more densely graded in the fine fractions, electrodes made from this aggregate had lower electrical resistivity than those made from coke I, especially at low electrode densities.

ACKNOWLEDGEMENT

The assistance of W. D. Horley in the laboratory evaluations and of Esso Research Laboratories, Baton Rouge, Louisiana, personnel in baking and testing of electrodes is gratefully acknowledged.

LITERATURE CITED

- (1) King, L. F. and Robertson, W. D., Fuel, Lond. 1968 47, 197
- (2) Charette, L. P. and Girolami, L., Fuel, Lond. 1958 37, 382
- (3) Martin, S. W. and Nelson, H. W., Ind. Eng. Chem. 1958 50, 33
- (4) Girolami, L., "Effect of Aggregate on the Coking of Binder in Petroleum Coke-Pitch Mixtures;" paper presented at symposium on Non-Fuel Uses of Coal, American Chemical Society, Cincinnati, Ohio, meeting, January 13-18, 1963.

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

PROPERTIES OF BINDERS FOR PREBAKED ELECTRODES

COMPOSITION WT %	Coal Tar		Cracked Petroleum Pitch	
	Pitch K	G	H	J
VACUUM REDUCED				
CAT CRACKING RESIDUE	85	97.5	97.5	
SRF CARBON BLACK	5		2.5	
ISAF CARBON BLACK				2.5
PROPERTIES				
SOFTENING POINT (C/A) °C	100	97	102	100
DENSITY AT 15°C g/cm ³	1.31	1.23	1.22	1.22
CONING VALUE, WT %	58	52	54	53
BENZENE INSOLUBLE, WT %	31	8	3.5	3.5
DINDLINE INSOLUBLE, WT %	8	5	2.5	2.5
C/H (ATOMIC) RATIO	1.7	1.3	1.3	1.3

Table 1

THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.1

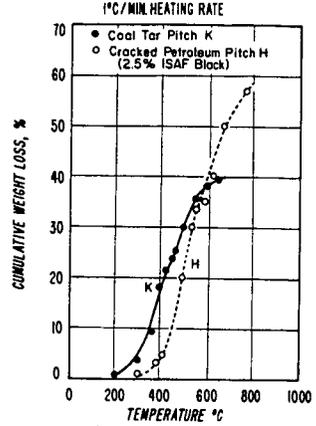


Figure 1

THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.2

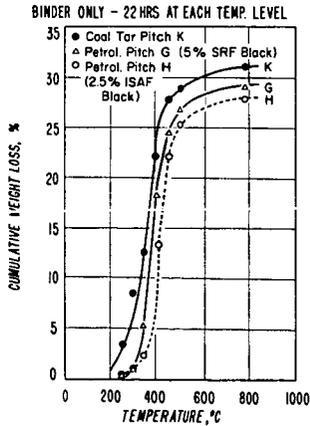


Figure 2

THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.3

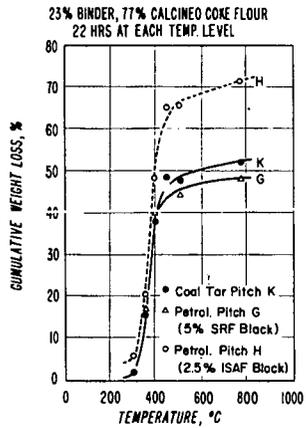


Figure 3

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

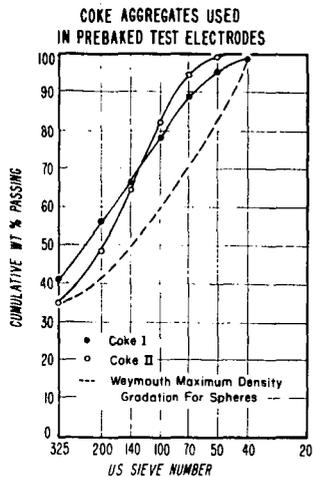


Figure 4

PERFORMANCE OF BINDERS IN PREBAKED ELECTRODES

BINDER	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
BINDER CONTENT, WT %	23.0	23.0	23.0	23.0
BAKED ELECTRODES				
DENSITY, g/cm ³	1.49	1.50	1.45	1.43
ELECTRICAL RESISTIVITY, 10 ³ ohm cm	1.09	1.08	1.13	1.16
COMPRESSIVE STRENGTH, kg/cm ²	508	543	329	326

*OPTIMUM 2, PARAFFINIC EXTRUSION OIL ADDED IN ADDITION TO BINDER

Table 2

PERFORMANCE OF BINDERS IN PREBAKED ELECTRODES

BINDERS	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
BINDER CONTENT, WT %	23.0	23.0	22.0	22.0
BAKED ELECTRODES				
DENSITY, g/cm ³	1.50	1.46	1.46	1.45
ELECTRICAL RESISTIVITY 10 ³ ohm cm	1.06	1.08	1.08	1.15
COMPRESSIVE STRENGTH, kg/cm ²	467	357	378	221

*OPTIMUM 2, PARAFFINIC EXTRUSION OIL ADDED IN ADDITION TO BINDER

Table 3

EFFECTIVE COKING VALUE OF BINDER PITCHES

BINDER	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
COKING PROCEDURE				
ISOTHERMAL, 25HR AT 550°C	-	58	52	54
TGA 1 - 10 HR TO 850°C (binder only)	-	60	-	52
TGA 2 - 154HR TO 800°C (binder only)	-	69	71	71
TGA 3 - 132HR TO 800°C (23 binder, 77% coke)	-	48	51	129
ELECTRODE BAKING 48HR TO 1000°C (23 binder, 77% coke)	-	67	66	63

Table 4

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

RELATIONSHIP BETWEEN BAKED ELECTRODE DENSITY & COKED BINDER CONTENT

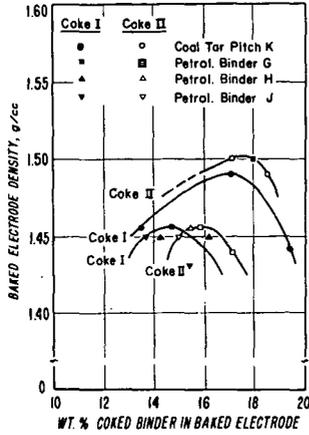


Figure 5

RELATIONSHIP BETWEEN COMPRESSIVE STRENGTH & DENSITY OF BAKED TEST ELECTRODES

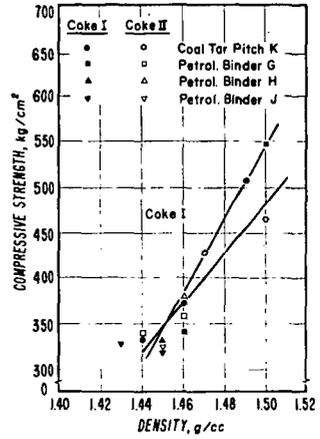


Figure 6

RELATIONSHIP BETWEEN ELECTRICAL RESISTIVITY & DENSITY OF BAKED TEST ELECTRODES

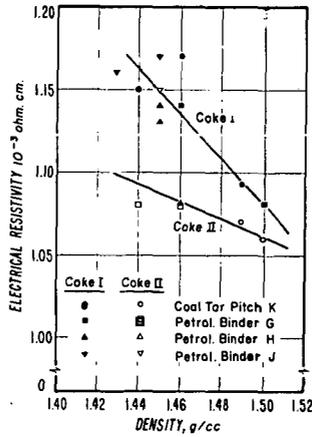


Figure 7

COAL TAR AND PETROLEUM PITCHES AS
BINDERS FOR SODERBERG ELECTRODES

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INTRODUCTION

It was concluded from a previous study⁽¹⁾ that the efficacy of coal tar and petroleum pitches as binders for coke in carbon electrodes is governed mainly by their aromaticity and content of distillable coke precursors. A thermal petroleum pitch containing about the same amount of resins insoluble in quinoline and benzene as coal tar pitch, but no volatile coke formers, was unsatisfactory as an electrode binder⁽²⁾. On the other hand, a vacuum reduced residue from a petroleum catalytic cracking process, though having no C₁ (quinoline insoluble) or C₂ (quinoline soluble, benzene insoluble) resins and few of the other characteristics of coal tar pitch, generally gave laboratory test electrodes having high density and compressive strength.

Parameters affecting the yield of binder pitch from the petroleum catalytic cracking process have been identified. Data obtained by vacuum reduction of catalytically cracked residues are shown in Figure 1. The yield of pitch having a softening point of 95°C is a function of aromaticity, as indicated by the U.S. Bureau of Mines Correlation Index (BMCI), the yield increasing from 6% of an 80 BMCI residue to 30% of a 120 BMCI residue. Figure 2 shows the relationship between aromaticity of the material boiling above 370°C and cracking severity as indicated by feed conversion to gas and naphtha boiling below 221°C.

In aluminum manufacture, inorganic contaminants in either the binder or coke aggregate components of the electrodes in the reduction furnace may show up as impurities in the product, or may accumulate in the molten electrolyte and reduce the current efficiency of the cell. Typical specifications for electrode binder pitches allow a maximum of 0.3% ash. To meet this requirement, it is necessary to remove at least 95% of the catalyst fines (corresponding to all particles larger than about 10 microns) from catalytically cracked residue. Semi-commercial studies showed that this can be accomplished by allowing the solids to settle in tankage at 65°-110°C for 5-10 days per foot of liquid depth.

EXPERIMENTAL

Some Soderberg pastes made with cracked petroleum pitch are mechanically unstable at high temperatures: at 255°C oil components are exuded from the green mix of pitch and petroleum coke aggregate. This was found to be a function of binder content, separation of oil being observed only at the pitch level required to impart adequate flow properties to the paste. Oil bleeding is an undesirable property because of the possibility of leakage from the anode casing in commercial operation. A related phenomenon is a tendency for the green mix to decrease in consistency soon after preparation. Mechanical instability is not normally observed when paste is prepared with coal tar pitch as binder.

Earlier work had indicated that a pitch suitable as an electrode binder could be made by heat soaking a catalytically cracked petroleum residue at about 375°C in the presence of an active carbon catalyst (type CAL, 12-40 mesh, Pittsburgh Coal and Chemical Co. Inc.)⁽³⁾ and the yield also was increased from 25% to 42%. Though it was well known that coarse (thermal) carbon blacks, when added in large quantities to Soderberg paste, may act as a replacement for some of the coke fines⁽⁴⁾, the use of catalytic amounts of high surface area, non-pelletized blacks pre-dispersed in the pitch had not been reported.

The type of carbon black is critical⁽⁵⁾. The most suitable ones are the super abrasion (SAF) furnace blacks, intermediate super abrasion (ISAF), semi-reinforcing (SRF) furnace blacks made by G. L. Cabot Inc. and fast extruding furnace black (FEF) of Columbian Carbon Co. Because of their high surface area, structural characteristics and surface adsorption properties, these rubber reinforcing grade blacks are also effective as stabilizers for Soderberg paste (Table 1). At a concentration of 5% in catalytically cracked petroleum binder (1.5% of the paste) the furnace blacks prevented bleeding of oil and change in consistency of the green mix, whereas the large particle size MT (thermal) black provided no significant improvement in these properties. It is probable that there is also a catalytic effect involving the formation of C₁ and C₂ resins in situ during the carbonization (baking) process. It is important to note that, to be effective, aggregates in commercial pelletized carbon blacks must be broken down into discrete particles. A concentrated suspension of the black in an aromatic distillate (from thermal cracking of gas oil), prepared by mixing in a tank, was passed through a colloid mill, and a quantity sufficient to give the desired carbon black content in the finished binder was blended with the vacuum reduced pitch or with the feedstock to distillation. The blending oil was removed later in vacuo.

When proper dispersion is attained, there is little or no tendency for solids to settle out of pitches containing furnace blacks during hot storage. Frequent circulation of coal tar electrode binder pitch is commonly practiced in the industry to minimize the deposition of benzene and quinoline insoluble components in storage tanks. One micron is reported as the average diameter of quinoline insolubles⁽⁶⁾. Our laboratory data showed that two representative coal tar pitches deposited about half of their C₁ and C₂ resins in 5 to 20 days at 205°C. A cracked petroleum pitch, in which 5% of pelletized SRF black (80 µ particle diameter) had been dispersed by colloid milling, required 330 days at 225°C for settling of 25% of the black.

Flow Properties of Soderberg Pastes

In addition to its other functions, the binder in Soderberg paste must impart the fluidity necessary for flow to all parts of the anode casing. This depends on the gradation of the coke aggregate (which in practice is fixed), the amount of binder and its viscosity.

The flow properties of Soderberg paste are commonly evaluated by an empirical "elongation" test^(3,5). Four samples of paste, pressed into a cylindrical mold and cooled rapidly, are placed on an aluminum test plate - made so that the surface is sloped at an angle of 10° to

the horizontal - and heated in an oven at 255°C for 15 minutes. The plate is then removed from the oven, shock chilled, and the elongation of the samples as a percentage of the original length is calculated. For commercial electrodes, the value desired is approximately 100%, and it varies more or less logarithmically with the binder content. With coal tar pitches, 30 to 35% binder is needed⁽⁷⁾.

Although the addition of a small amount of furnace black to a binder substantially improves the stability of Soderberg paste, it also reduces fluidity. Typical results for two such carbon blacks in catalytically cracked petroleum pitch are shown in Figure 3. Elongation also depends on the particle size of the black (Figure 4). Thermal blacks have a negligible effect on paste fluidity at low concentrations; this is undoubtedly related to their inability to modify the oil bleeding and aging characteristics of the paste.

A study was made of the flow properties of catalytically cracked petroleum pitches containing SRF carbon black and of Soderberg paste made with them. An experimental sample, designated as "Cracked Pitch D" was prepared on a small commercial scale as described above. Another pitch (Blended Pitch E) was prepared in the laboratory. Vacuum reduced (480°C+) bottoms from catalytic cracking, blended with 5 wt % of a 150°C softening point vacuum reduced tar from thermal cracking of gas oil, and a dispersion of SRF carbon black in oil were redistilled in vacuo to remove the oil. These two petroleum pitches are compared in Table 2 with a coal tar pitch binder (F) typical of that used at about 30% concentration in Soderberg paste.

The viscosity of electrode binder pitch is normally measured with a Brookfield viscosimeter at various temperatures and spindle rotation speeds. The rate of shear is high, but not precisely known. This is not important in the case of coal tar pitches which are reported to be Newtonian⁽⁸⁾. Since cracked petroleum pitches were suspected of being pseudoplastic, it was decided to determine viscosity at known shear rates.

Flow properties of binders D, E and F were evaluated in Koppers vacuum capillary viscometers at three temperatures: 107, 135 and 163°C. Data obtained at various shear rates are shown in Figures 5, 6 and 7. While coal tar pitch F was confirmed as being Newtonian throughout, the petroleum pitches were shear sensitive. At the lowest temperature and shear rate D had the lowest viscosity, at 135°C it was intermediate and at 163°C and high shear rate it had the lowest viscosity. Flow indices calculated for D and E were 0.7 and 0.9 (1.0 for F).

In commercial practice, Soderberg paste is cast into blocks about 3.5 x 13 x 1 ft in size and weighing over 5000 lb. The anodes are replenished by placing a block of solidified paste on top, where the temperature is 100-150°C. The paste should flow to all corners of the anode casing under these conditions. The pressure at the bottom of a block of paste due to its own weight is approximately 10^4 dynes/cm². The laboratory elongation test previously described was developed to control the fluidity of Soderberg pastes made with coal tar pitch under average commercial operating conditions. In the laboratory test, the stress causing the paste to flow is about 10^3 dynes/cm² but the

temperature (225°C) seemed much too high. Additional elongation tests done at 205° and 150°C gave the results shown in Figure 8. The binder requirements of the three pitches were as indicated, being based on 80-100% elongation at 255°C. The effect of too little binder on the elongation of the paste is shown by the lowest curve.

To simulate the very low shear rates of commercial operation, a laboratory spreading test was developed. A block of Soderberg paste, 1.5 x 6 x 0.5 inches in size and loaded with steel weights as required, is placed in a shallow steel container (2.5 x 6 x 0.25 inches) and heated in an oven at 150°C. Since the volume of the container was made equal to the volume of the semi-molten block of paste, spreading of the block is complete when the container is filled. Tests were carried out using pastes containing the "optimum" amount of coal tar pitch F, cracked pitch D, and blended pitch E, for periods of 1, 8 and 16 hours: (a) under a load of 0.5 psi which produces a stress of about 10^4 dynes/cm², and (b) under no applied load. The results are shown in Figure 9.

Correlations between Soderberg paste elongation, spreading tests and the apparent viscosity of the binder under similar conditions of temperature and stress are complex. At 255°C and a shearing stress of 10^3 dynes/cm², the apparent viscosities of all three binders tested are so low (0.01 poise) that the binder viscosity probably has little effect on the flow properties of the paste. Under these conditions, it is the amount of binder that has the greatest effect on the fluidity of the paste by controlling the packing of the coke aggregate particles.

In the elongation test at 150°C, there is some indication that the flow of the paste increases as the apparent viscosity of the binder increases, and the same result was observed in the spreading test at 150°C under a load of 0.5 psi (upper curve, Figure 10). It is possible that in this viscosity range (about 1 to 10 poises) the film of binder on the coke aggregate particles is not of sufficient thickness to lubricate them under a stress of 10^3 to 10^4 dynes/cm²; and as the viscosity of the binder is increased, friction between the particles decreases due to the thicker lubricant film.

In the spreading test at 150°C with no applied load (lower curve, Figure 10) flow varies directly as the apparent viscosity of the binder, indicating that at extremely low stress levels, the viscous resistance of the binder has a significant retarding effect on the flow of the paste.

Electrode Performance

The performance of the binders in laboratory scale baked electrodes is summarized in Table 3. The procedure of Jones et al was used⁽⁹⁾. All test data appear satisfactory. For cracked pitch D, the optimum binder content, the elongation at 225°C immediately after preparation and again after aging the paste for 24 hr at 225°C, and the properties of baked test electrodes made from aged and unaged paste are given.

L. Girolami⁽¹⁰⁾ has reported a "saturation" test which involves heating coal tar Soderberg paste in two stages (at 200°C and at 300°C) prior to laboratory coking at the normal temperature of 550°C. The yield of coke was increased by the preheating steps, depending on the fineness of the coke, the soaking temperature and the binder/aggregate ratio. Girolami ascribed this behaviour to displacement of air or other gases adsorbed on the coke aggregate, thus permitting more intimate contact between binder and coke. Our results appear to confirm this finding: the density and compressive strength of electrodes increased significantly after heat soaking of the paste. This has been observed in our laboratory with many petroleum pitches.

A small scale trial of cracked petroleum pitch D was carried out in a commercial Soderberg anode. In spite of the fact that less than the indicated optimum amount of binder was inadvertently used in the paste (26 vs 31%) the performance was satisfactory, the rate of anode consumption being low. The paste on the top of the cell required manual spreading since it would not spread to fill the casing completely by virtue of its own weight. The petroleum binder exhibited extremely low volatility at the ambient temperature, so the amount of vapour above the cell was almost negligible compared to that evolved by coal tar binders.

Upgrading Coal Tar Pitch

Coal tar pitches from different sources are variable in quality. Low grade binders can be improved for Soderberg electrode use by addition of furnace blacks in much the same way as petroleum residua. The improvement is evidenced by increased density and compressive strength of baked test electrodes. Coal tar pitches which are most readily upgraded are those having a relatively low coking value (about 50%) and a quinoline insolubles content of less than 10%. Literature data⁽⁶⁾ indicate that the best coal tar binders contain 10 to 15 wt % of quinoline insoluble resins.

Laboratory inspections and performance data are summarized in Table 4. Addition of 2.5 wt % of a reinforcing black to poor quality coal tar pitches effected a marked improvement in performance. In one case, (A), the elongation of the paste was below the desired value for Soderberg electrodes, but this could be overcome by increasing slightly the amount of binder used. This is shown in B, where the retarding effect of the carbon black on paste flow was compensated for by increasing the binder content from 30.5 to 32%.

ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of W. D. Horley who carried out the laboratory evaluations and A. J. Hellwig, who assisted in plant production of samples for commercial trial.

LITERATURE CITED

1. King, L. F. and Robertson, W. D., Fuel, Lond. 1968, 47, 197.
2. King, L. F. and Steele, C. T., U.S. Patent 3,173,851, March 16, 1965.
3. King, L. F., U.S. Patent 3,355,377, November 28, 1967.
4. Swallen, L. C. and Nelson, H. W., U.S. Patent 2,527,595, October 31, 1950.
5. King, L. F., Robertson, W. D. and Steele, C. T., U.S. Patent 3,316,183 April 25, 1967.
6. Charette, L. P. and Girolami, L., Fuel, Lond. 1961, 40, 89.
7. Darney, A. "Pitch Binder for Carbon Electrodes" pp 152-161 in Industrial Carbon and Graphite, Society of Chemical Industry: London, 1958.
8. McNeil, D. and Wood, L. J. "The Use of Coal Tar Pitch as Electrode Binder" *ibid.* pp. 162-172.
9. Jones, H. L., Simon, K. W., Wilt, M. H. "An Improved Evaluation of Electrode Binder Pitches Using the Compressive Strength of Electrodes". Paper presented at the Division of Gas and Fuel Chemistry, American Chemical Society, Boston, Mass. meeting April 5-10, 1959.
10. Girolami, L. "Effect of Aggregate on the Coking of Binder in Petroleum Coke - Pitch Mixtures"; paper presented at symposium on non-fuel uses of coals, American Chemical Society, Cincinnati, Ohio, meeting January 13-18, 1963.

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

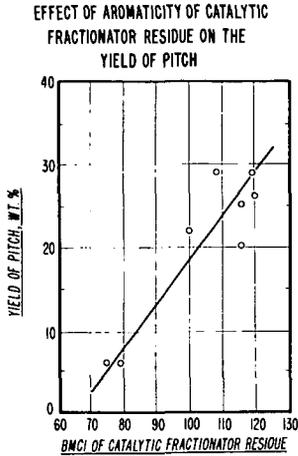


Figure 1

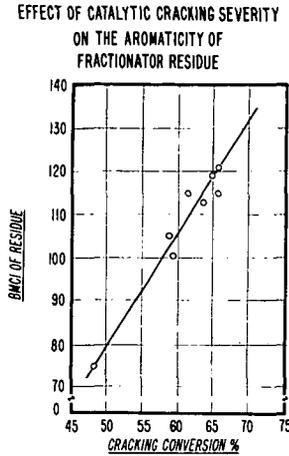


Figure 2

PROPERTIES OF SODERBERG PASTES

BINDER	Coal Tar Pitch (Typical)		Catalytically Cracked Petroleum Pitch			
	None	None	ISAF	SRF	SRF	Thermal
CARBON BLACK IN BINDER						
TYPE			ISAF	SRF	SRF	BIT
GRADE			23	88	80	470
AVER. PARTICLE SIZE, μ			2.5	5.0	7.5	5.0
WT.						
OPTIMUM BINDER CONTENT, WT. %	28-33	27	31	32	33	30
STABILITY	Good	Poor	Good	Good	Good	Poor
AGEING CHARACTERISTICS	Good	Poor	Poor	Good	Good	Poor
BAKED TEST ELECTRODE COMPRESSIVE STRENGTH, Kg/cm^2	750-450	270-405	400	380	410	370

Table 1

EFFECT OF CARBON BLACK CONCENTRATION IN CRACKED PETROLEUM PITCH ON FLOW PROPERTIES OF SODERBERG PASTE

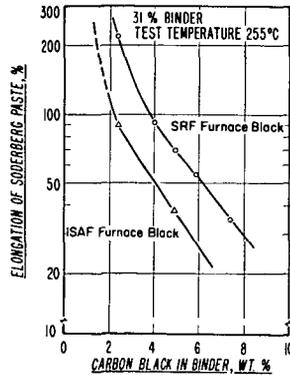


Figure 3

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

EFFECT OF PARTICLE SIZE OF CARBON BLACK IN CRACKED PETROLEUM PITCH BINDER ON THE FLOW PROPERTIES OF SODERBERG PASTE

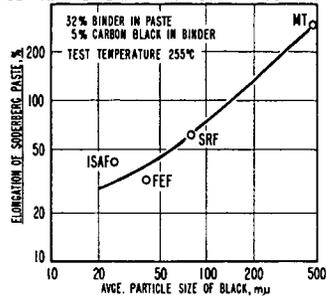


Figure 4

PROPERTIES OF BINDERS FOR SODERBERG ELECTRODES

	Coal Tar Pitch		Petroleum Pitch	
	F	D	E	
COMPOSITION, WT. %				
VACUUM REDUCED				
CAT CRACKING RESIDUE		85	80	
VAC REDUCED THERMAL CRACKING RESIDUE		-	5	
SRF CARBON BLACK		5	5	
PROPERTIES				
SOFTENING POINT (A) °C	82	80	82	
DENSITY AT 15°C, g/cm ³	1.31	1.23	1.24	
COKING VALUE, WT. %	58	54	57	
BENZENE INSOLUBLE, WT. %	22	8	10	
QUINOLINE INSOLUBLE, WT. %	18	6	7	

Table 2

APPARENT VISCOSITY OF ELECTRODE BINDER PITCHES AT 107°C
KOPPERS TYPE VACUUM CAPILLARY VISCOMETER

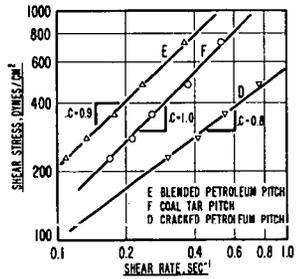


Figure 5

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

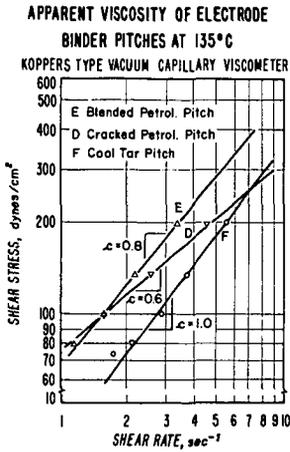


Figure 6

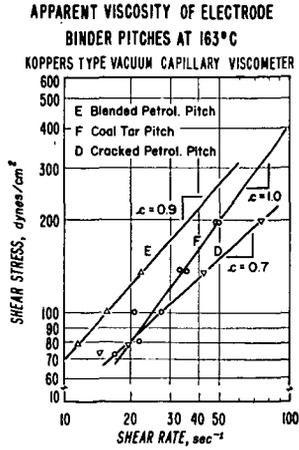


Figure 7

EFFECT OF TEMPERATURE ON THE ELONGATION OF SODERBERG PASTES

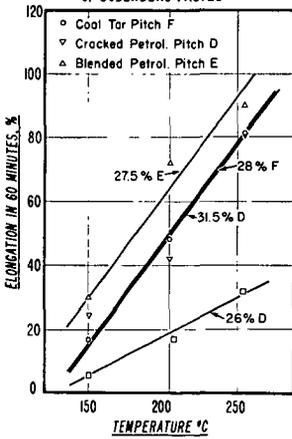


Figure 8

SPREADING OF SODERBERG PASTES AT 150°C

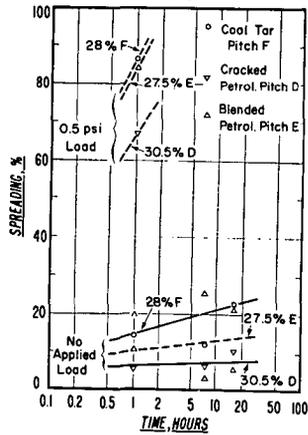


Figure 9

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

RELATIONSHIP BETWEEN SPREADING OF SODERBERG PASTE
& BINDER VISCOSITY

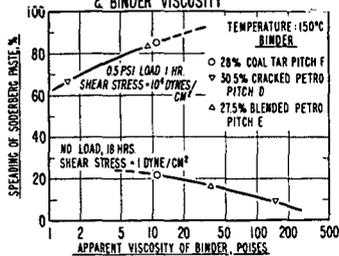


Figure 10

PERFORMANCE OF SODERBERG ELECTRODE BINDERS

Binder	Coal Tar	Petroleum			
	Pitch F	Cracked Pitch D	Blended Pitch E		
SODERBERG PASTE					
BINDER CONTENT, WT. %	28	28	31	33	27.5
ELONGATION AT 255°C, %	82	40	84	181	72
AFTER AGEING	-	52	82	174	-
BAKED ELECTRODES					
DENSITY, g/cc					
FROM UNAGED PASTE	1.42	1.44	1.43	1.40	1.38
FROM AGED PASTE ⁽¹⁾	-	-	1.47	1.45	-
COMPRESSIVE STRENGTH, Kg/cm ²					
FROM UNAGED PASTE	354	372	381	286	313
FROM AGED PASTE ⁽¹⁾	-	-	426	408	-

(1) 24 HR. AT 225°C.

Table 3

UPGRADING COAL TAR BINDERS BY ADDITION OF CARBON BLACK

PITCH	A		B	
	2.5%	5%	2.5%	5%
CARBON BLACK	NONE	ISAF	NONE	SAF
SOFTENING POINT, °C	...	52	...	110
COKING VALUE, %	50	53	51	53
BENZENE INSOLUBLES, %	25	28	26	28
QUINOLINE INSOLUBLES, %	8	9	2	5
SODERBERG PASTE				
BINDER, %	30.5	38.5	30.5	32
ELONGATION, % (255°C)	78	32	88	59
BAKED ELECTRODES				
APPARENT DENSITY, g/cm ³	1.38	1.45	1.38	1.41
COMPRESSIVE STRENGTH, Kg/cm ²	295	434	274	388

Table 4

CONVERSION OF MANURE TO OIL BY HYDROTREATING

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INTRODUCTION

In an effort to utilize a significant potential energy source and at the same time reduce pollution, the Bureau of Mines has been experimentally converting organic wastes to oil. The original process (1,2) uses carbon monoxide and water to treat the organic material at temperatures of 350°-400°C and pressures near 4000 psi. Even though this reaction proceeds well and produces a good yield of oil, there are some technical problems that have to be resolved before the process would be economical. The major problems include the high operating pressure, the large amounts of energy necessary for heating the water reactant, and the purification of the process water containing organic solubles.

In our previous study (3) on bovine manure conversion, we reported that significant improvements in reducing operating pressure and energy requirement for heating were achieved by replacing large percentages of water with a suitable high boiling vehicle. It was also shown that synthesis gas can be used in place of carbon monoxide to convert manure to oil in reasonably good yield. The present work deals with further attempts to use manure-derived oil as a recycle vehicle in place of water. We have found that manure oil is an unsuitable vehicle, giving poor conversion and oil yield in the absence of a suitable catalyst. However, bovine manure, like coal, can be hydrogenated and liquefied at elevated temperatures and pressures in the presence of a vehicle and a cobalt molybdate catalyst. This process may be uneconomical because it requires fairly large amounts of expensive hydrogen in the reaction. A promising method for hydrotreating organic wastes using synthesis gas and a combination of cobalt molybdate-sodium carbonate catalyst is presented in this report. The proposed process requires no process water and results in the effective hydrogenation and deoxygenation of organic wastes without a significant consumption of hydrogen.

EXPERIMENTAL

The conversion of manure to oil was studied in a 500-ml magnetically-stirred, stainless steel autoclave. Bovine manure from Beltsville, Maryland, was used. Chemical analyses of two samples used are given in Table 1. A high boiling alkylnaphthalene-based oil (boiling above 235°C) and manure-derived oils were used as vehicles. A manure oil produced from the reaction of manure with CO and H₂O at 380° and 4500 psi was used as the starting vehicle. In several series of experiments using different gas reactants or catalytic conditions, each succeeding run within a series utilized the oil product recovered from the preceding run as the vehicle. The catalyst was a commercial cobalt molybdate supported on silica alumina used either in the presence or absence of sodium carbonate.

TABLE 1. Analyses of bovine manure (as used), percent

Sample	C	H	N	S	O (by diff.)	Ash	Moisture
1	44.2	6.2	2.5	0.35	39.9	6.9	3.8
2	42.5	5.7	2.3	0.35	34.7	14.5	4.2

For most of these experiments, hydrogen and synthesis gas (approximately equal parts of hydrogen and carbon monoxide) were used as gas reactants at initial pressures of 1000 to 1500 psi. Operating pressures ranged from 2000 to 3000 psi at reaction temperatures of 330° to 425°C, and the reaction was maintained for 15 to 60 minutes at the reaction temperature. After the experiment, rapid internal cooling of autoclave to ambient temperature was achieved. Total products were centrifuged at ambient temperature to obtain centrifuged liquid oils. Centrifuge cakes containing residue and water were extracted by benzene. The water was removed by azeotropic distillation and the remaining oil was recovered by removing the benzene with a rotary vacuum evaporator. Gaseous products were analyzed by mass spectrometry. Data on conversion, oil yield, hydrogen consumption, and carbon dioxide formation, etc., are given as weight percent based on moisture- and ash-free manure.

RESULTS AND DISCUSSION

Effects of Catalyst and Vehicle

The conversion of bovine manure to oil by reaction with synthesis gas is greatly influenced by the presence or absence of catalyst and vehicle. Initial experiments showed that bovine manure could be converted to oil by a mild hydrotreating with hydrogen or synthesis gas in the presence of alkylnaphthalene oil as vehicle. When a manure oil was used as vehicle, however, manure conversion and oil yield were poor, and the oil product became more viscous after each successive run. The use of sodium carbonate as catalyst (1) did not improve the oil quality. After being hydrotreated in the presence of a CoMo catalyst, manure oil became a good vehicle, and successive runs using the manure oil product as vehicle in the presence of CoMo catalyst gave good results. The fluidity of vehicle oil could be maintained throughout many successive runs, suggesting the feasibility of using manure oil product as a recycling vehicle. Analyses of vehicles are given in Table 2. Note that properties of manure oil are improved after hydrotreating with either hydrogen or synthesis gas in the presence of a CoMo catalyst. The oxygen content and oil viscosity are reduced. Effects of vehicle and catalyst on the conversion of manure to oil by hydrotreating with synthesis gas are shown in Table 3. At temperatures of 380° and 425°C and an operating pressure of about 3000 psi, both alkylnaphthalene oil and manure oil used as vehicle gave high conversion and good oil yield when the CoMo catalyst was present.

TABLE 2. Analyses of vehicles, percent

	C	H	N	S	O (by diff.)	Kinematic viscosity, centistoke at 60°C
Alkylnaphthalene oil	90.6	8.7	0.06	0.37	0.3	1.7
Manure oil ^a	80.7	9.6	4.0	0.20	5.5	550
Treated manure oil ^b	80.9	10.3	4.5	0.21	4.1	120
Treated manure oil ^c	83.8	10.2	4.6	0.11	1.3	17

^a Prepared by reaction of manure with CO and H₂O at 380°C and 4500 psi.

^b Manure oil was hydrogenated with H₂ at 380°C and 2200 psi in the presence of a CoMo catalyst.

^c Manure oil was hydrotreated with synthesis gas at 425°C and 2600 psi in the presence of a CoMo catalyst.

TABLE 3. Effects of vehicle and catalyst on conversion of manure

(vehicle:manure = 2.3:1, 1500 psi initial synthesis gas pressure)

Vehicle	Alkylnaphthalene oil				Manure oil	
Temperature, °C	380	380	425	425	380	425
Catalyst ^a	-	CoMo	-	CoMo	CoMo	CoMo
Operating pressure, psi	3200	3000	3200	3100	3000	3000
Time, min.	30	30	15	15	30	15
Conversion, percent ^b	86	92	88	95	93	93
Oil yield, percent ^b	34	47	35	45	45	40

^a Two parts catalyst per 100 parts feed of manure plus vehicle.^b Weight percent of maf manure.Effects of Gas Reactants

To determine the effects of various gas reactants on the conversion of manure, hydrogen, carbon monoxide, and synthesis gas were compared. Vehicle oils for different runs were conditioned by pretreating with the different gases at desired experimental conditions. At an initial pressure of 1500 psi, operating pressures at 380°C reaction temperature ranged from 2600 to 3500 psi, depending on the extent of hydrogen consumption or hydrogen formation during the reaction. Data are given in Table 4.

Experiments with hydrogen indicate that cobalt molybdate catalyzes the hydrogenation reaction under the operating conditions. The conversion, oil yield, and hydrogen consumption were increased by the use of the catalyst. When carbon monoxide or carbon monoxide and water were used to react with manure, both conversion and oil yield were low, and the oil product behaved poorly as a vehicle. But synthesis gas could be used in place of hydrogen without adverse effects on manure conversion, oil yield, and oil quality. In this comparison, hydrogen consumption decreased from 3.0 to 2.3 percent, water yield decreased from about 23 to 13 percent, but carbon dioxide formation increased considerably. The oxygen content in manure was removed in the form of water and carbon dioxide in both cases.

TABLE 4. Effects of gas reactants on conversion^a

(manure oil:manure = 2.3:1, 30 minutes at 380°C)

Gas reactant	H ₂		CO		H ₂ + CO (1:1)	
Catalyst ^b	-	CoMo	-	CoMo	-	CoMo
Initial pressure, psi	1500	1500	1500	1000 ^c	1500	1500
Operating pressure, psi	2900	2700	3500	2900	3200	3000
Conversion, percent	78	97	72	84	81	93
Oil yield, percent	23	47	19	34	23	45
H ₂ consumption, percent	2.2	3.0	(1.2) ^d	(1.6) ^d	1.4	2.3
CO ₂ formation, percent	17	16	78	86	60	42

^a Data are given in weight percent of maf manure.^b Two parts of catalyst per 100 parts feed of manure plus manure oil.^c Water (33 parts per 100 parts manure) was also added as the reactant.^d Hydrogen formation.

Effects of Reaction Variables

Pressure. The effect of operating pressure on the conversion of manure was studied for both hydrogen and synthesis gas. The reactions were carried out at 380°C for 30 minutes. Starting at the same initial pressures, the hydrogen runs did not reach as high operating pressures as the synthesis gas runs, probably because of the greater hydrogen consumption. As shown in Figure 1, the conversion and the oil yield increase slightly with pressure in the range of 1500 to 3000 psi, but there are very little differences between hydrogen and synthesis gas.

Temperature. Of all the variables investigated, temperature has the most dramatic effect on the properties of the oil product. Experiments were conducted at an initial pressure of 1500 psi but at different operating pressures, ranging from 2600 to 3100 psi, depending on the reaction temperature and gas reactant. The reaction was maintained for different periods at different temperatures: 60 minutes at 330°C, 30 minutes at 380°C, and 15 minutes at 425°C. The results in Table 5 indicate, for both hydrogen and synthesis gas runs, that the hydrogen consumption increased with temperature without improvements in the conversion or oil yield. However, significant improvements in oil product quality were observed with increasing temperature; carbon content increased, oxygen content decreased, and viscosity was reduced. The change in the properties of oil product is accompanied by some decrease in the oil yield, mainly because the oxygen-containing groups are further reduced and the product oil is subjected to cracking. The amount of low molecular weight hydrocarbon gases produced was small but increased with temperature. Again, in comparison with the hydrogen runs, the synthesis gas runs yielded greater amounts of carbon dioxide but smaller amounts of water. In the hydrogen runs, the constant amount of carbon dioxide formed (average 16 percent) is probably all that could be produced from the thermal decomposition of the manure.

TABLE 5. Hydrotreating of manure at various temperatures^a

(manure oil:manure = 2.3:1, CoMo catalyst, 1500 psi initial pressure)

	H ₂			H ₂ + CO (1:1)		
	330	380	425	330	380	425
Temperature, °C	330	380	425	330	380	425
Operating pressure, psi	2600	2700	2700	3100	3000	3000
Time, minutes	60	30	15	60	30	15
Conversion, percent	95	97	94	94	93	93
Oil yield, percent	49	47	39	47	45	40
CH ₄ formation, percent	0.3	0.9	2.7	0.5	1.3	3.5
CO ₂ formation, percent	17	16	16	31	42	47
H ₂ O yield, ^b percent	20	23	25	16	13	10
H ₂ consumption, percent	2.3	3.0	4.5	2.0	2.3	2.6
Oil analysis, percent						
C		81.9		77.5	81.5	83.4
H		9.7		9.8	9.9	10.2
N		4.2		4.3	4.4	4.6
S		0.18		0.19	0.10	0.11
O (by diff.)		4.0		8.2	4.1	1.7
Kinematic viscosity of oil at 60°C, centistoke		118		563	129	17

^a Data are given in weight percent of maf manure.

^b Excluding moisture content in manure.

Reaction Time. Figure 2 shows the effect of time on the conversion of manure by hydrogen at 380°C. The time required to reach 380°C in the autoclave was about 60 minutes, and the reaction was then maintained at this temperature from 0 to 60 minutes. Nearly 85 percent of conversion occurred before the system reached 380°C, and the conversion approached a limit of about 97 percent after the reaction was in progress at 380°C for 30 minutes. All carbon dioxide was produced before the reaction mixture reached 380°C (before zero time). The progress of the hydrogenation, and probably the upgrading of the oil properties, can be better measured by the hydrogen consumption which increased from 1.4 percent at zero time to 3.6 percent at 60 minutes.

Effect of Sodium Carbonate

Two comparative series of experiments were carried out hydrotreating bovine manure. In the first series, manure was hydrotreated with synthesis gas at an initial pressure of 1000 psi and 380°C reaction temperature for 30 minutes in the presence of a CoMo catalyst and a manure oil vehicle. Various amounts of water (0 to 50 parts per 100 parts of manure) were added in different runs to determine the effect of moisture content of manure. In each succeeding run, the oil product recovered from the preceding run was used as vehicle. In the second series, experiments were carried out in the similar manner except that 2 percent Na₂CO₃ (based on feed of manure plus vehicle) was added in addition to the CoMo catalyst.

Results are shown in Table 6. Operating pressures were higher in Series 2 than in Series 1 at equal water levels. The average oil yield in the presence of Na₂CO₃ increased and the kinematic viscosity of the product decreased. In addition, hydrogen consumption was reduced as shown in Figure 3. Less hydrogen was consumed with increasing moisture content of manure, without any effect on the conversion of manure to oil. Other noticeable effects of the Na₂CO₃ addition were increased carbon dioxide formation and decreased water yield. It is apparent that in the presence of Na₂CO₃, hydrogen consumed is partly replenished by the reaction of carbon monoxide with water during hydrotreating. As a result, effective hydrogenation and deoxygenation of manure are accomplished without significant consumption of hydrogen.

CONCLUSIONS

Bovine manure is hydrogenated and liquefied by hydrogen or synthesis gas (equal amounts of hydrogen and carbon monoxide) at temperatures of 330° to 425°C and operating pressures of 1500 to 3000 psi in the presence of a recycle manure oil and a cobalt molybdate catalyst. With an increase in temperature, oxygen content and viscosity of oil product decrease, but hydrogen consumption increases. Synthesis gas can be used in place of hydrogen to reduce hydrogen consumption without adverse effects. A significant improvement on this process, when using synthesis gas, is achieved by adding sodium carbonate to the reaction mixture; hydrogen consumption is reduced markedly, oil yield improved, and oil viscosity reduced. Manure with moisture contents up to about 35 weight percent was evaluated and found acceptable as feedstocks. The other feature of the process is that it requires no process water, and this eliminates the problem of heating or purifying large amounts of the process water.

REFERENCES

1. H. R. Appell, Y. C. Fu, S. Friedman, P. M. Yavorsky, and I. Wender. BuMines RI 7560, 1971, 5 pp.; Agr. Eng., March 1972, pp. 17-19.
2. S. Friedman, H. H. Ginsberg, I. Wender, and P. M. Yavorsky. Third Mineral Wastes Utilization Symp., IIT, March 1972.
3. Y. C. Fu, S. J. Metlin, E. G. Illig, and I. Wender. Preprints, Div. Fuel Chem., Am. Chem. Soc., vol. 17, No. 1, 37 (1972).

TABLE 6. Effect of Na₂CO₃ on hydrotreating of bovine manure by synthesis gas
 (manure oil:manure:water = 2.3:1:0-0.5, 1000 psi initial pressure, 380°C, 30 minutes)

Series	Catalyst	Operating pressure, ^a psi	Conversion, percent	Oil		H ₂ consumption, percent	CO ₂ formation, percent	Kinematic viscosity, ^b cs at 60°C
				yield, percent	42-44			
1	CoMo	2100-2700	95-98	42-44	46-48	1.0-2.1	34-45	138
2	CoMo-Na ₂ CO ₃	2200-3000	95-98	46-48		(0.75) ^c -0.4	67-86	65

^a Operating pressure increased with the amount of water added.

^b Kinematic viscosity of the oil product obtained at the end of the series.

^c Hydrogen formation.

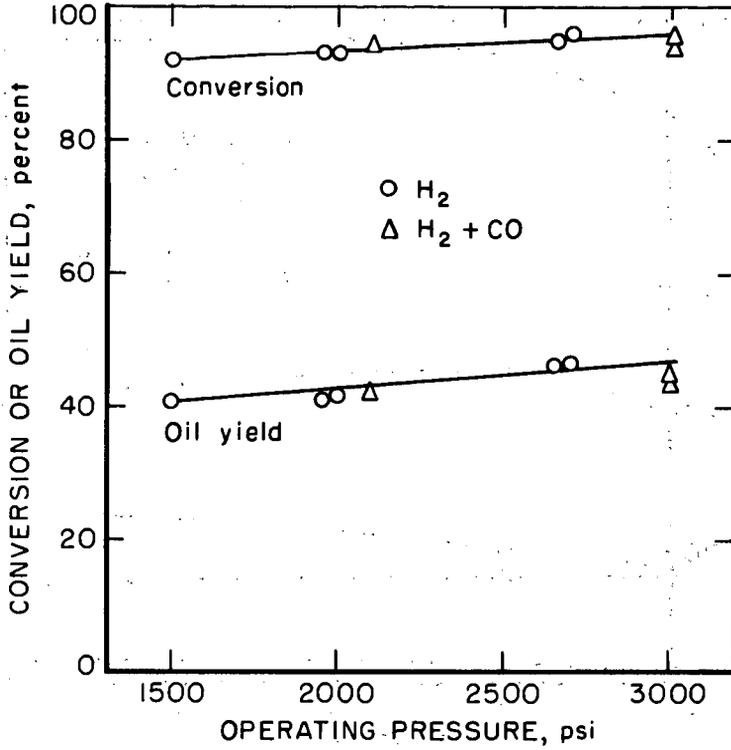


Figure 1- Effect of operating pressure on conversion of manure at 380°C

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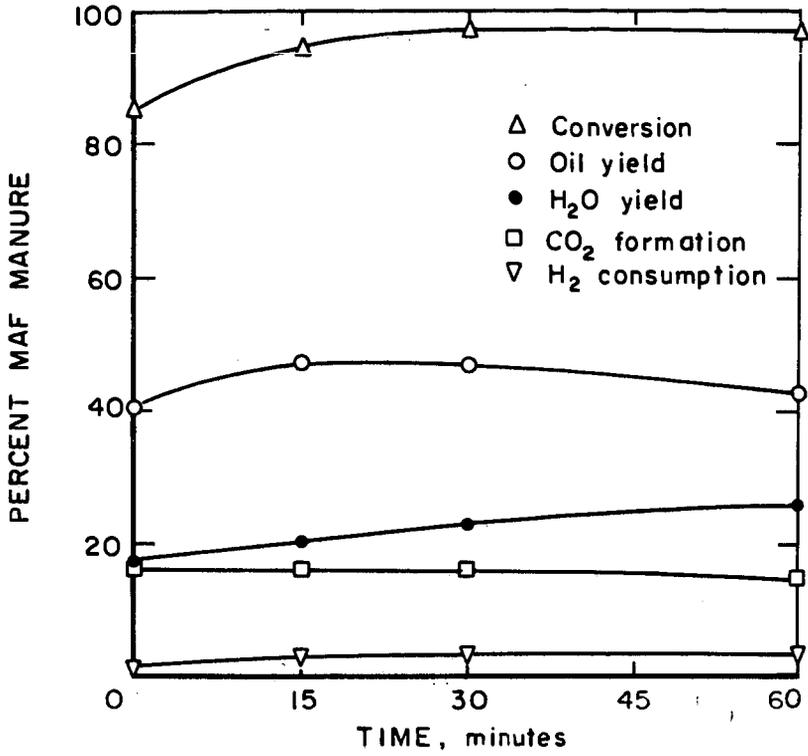


Figure 2-Effect of time on conversion of manure by H₂ at 380°C.

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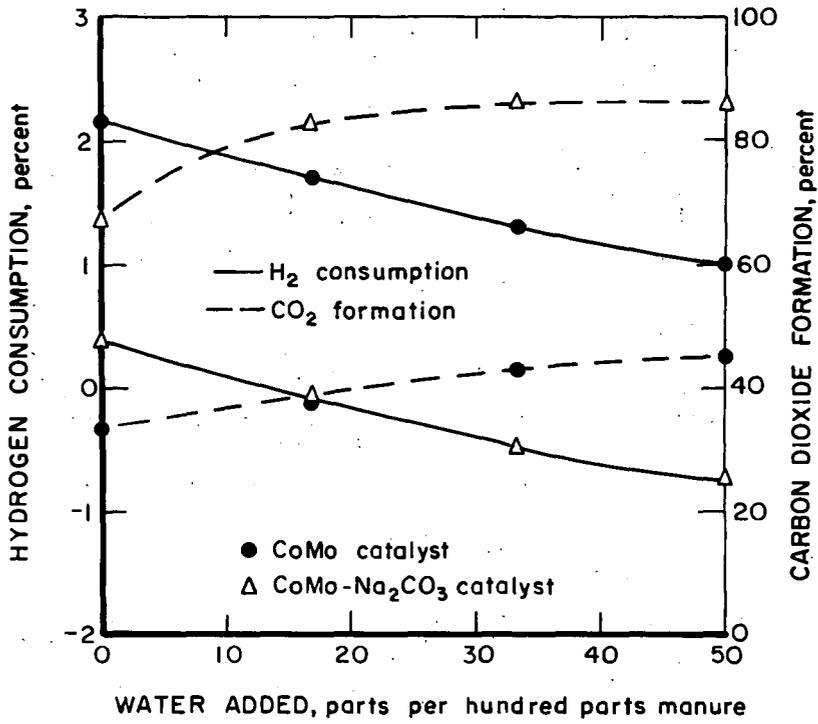


Figure 3—Effect of moisture content of manure at 380°C.