

Research challenge: clean energy from coal

We must look to research to help us use
energy from coal without ripping up the Earth
and unduly polluting the atmosphere.

Bernard R. Cooper

The need for the use of coal as a source of energy presents an environmental problem of enormous scope and difficulty, and physicists can contribute much toward solving this problem. Both coal as a material and the technical processes employing coal present "dirty" problems. The fact is, however, that the complexities involved in this problem create possibilities and need for applied research of a high quality.¹ For example, to minimize the pollution, recent developments often resort to indirect or elaborate means for extracting the energy content of coal.

Because coal utilization presents "dirty" (that is, complex) problems to a physicist, many physicists probably feel a visceral aversion to research in this area. This is largely because of ignorance of the research needs of modern coal mining and utilization technology. Most physicists probably feel that a coal mine is the last place in the world where physics research would be useful. Yet, as discussed later in this article, the photograph on the cover of this issue of *PHYSICS TODAY* shows a computer-controlled mine ventilation monitoring system that could gain greatly in effectiveness from some basic surface-physics knowledge. Better yet would be to supersede coal mining through techniques such as underground gasification. Physics research is necessary to do this. For example, knowledge of electromagnetic properties of coal at microwave frequencies, obtained experimentally as shown in figure 1, is required to develop systems for remote monitoring of burn fronts in underground gasification.

The major areas for present and future use of coal are combustion for electrical power generation, pyrolysis (coking) to produce reducing carbon for the metal-

lurgical industries, gasification and liquefaction. At present the major use of coal as an energy source is in direct combustion, while gasification and liquefaction are two areas of potential major importance.

The technical and scientific work related to coal utilization falls into several basic categories, all of which are permeated by the environmental aspect. Among these is characterizing the coal itself as well as its impurities. Finding how to remove impurities is an important part of coal preparation. In the processing category, coal-fired magnetohydrodynamic power generation raises many problems of interest to the physicist. Materials problems seem to be a key bottleneck for all of the technology areas. And mining, an area from which physicists probably feel most remote, calls most demanding for genuinely revolutionary advances. The use of coal presents both demands and opportunities, and one of the challenges lies in understanding the ultimately limiting factor—the consequent increase of carbon dioxide in the atmosphere.

Characterizing coal

The use of coal basically involves two kinds of scientific questions, those helping to characterize coal as a material and those dealing with the technologies necessary for such use. In dealing with measurements characterizing coal as a material, one must recognize what is too often the ill-defined and qualitative nature of such measurements. So the first and most fundamental problem one encounters in developing new technologies to improve the use of coal as an energy source is to answer the question, "What is coal?"

Coal is a complex heterogeneous material, characterized by differences in the kinds of original plant materials (type); degree of metamorphism (rank), and the

amount and type of impurities present.

The classification of coals by rank is what most people have some familiarity with—coal can be anthracite, bituminous, subbituminous, lignite, and their subvariations. This classification is according to a fixed carbon and calorific value (BTU/lb), calculated for carbon free of minerals. Wood was the dominant plant material in typical peat swamps; therefore, typical coals consist predominantly of the wood-derived vitrinite (one of the organic components of coal). Identification of the rank of a coal provides a key, through established correlations, to many of the physical and chemical properties of the vitrinite.

However, coals contain, in different proportions, mineral matter and organic components other than vitrinite, which leads to the concept of characterizing coals according to type; that is, the content and distribution of such substances. The type thus reflects the heterogeneity inherited from the diverse source materials. Classification as to type is done by visual comparison and is highly subjective—for example, how shiny the organic material appears to the eye. The utility (grade) of coal for any use is specified by criteria for that particular use, which, in turn, depend on rank, type or both. The sulfur content, which is a critical and undesirable impurity for most applications, is a type-related property that is independent of the rank of a coal.

Reflectance measurements provide one of the most useful ways to characterize coal quantitatively. Indeed Alan Davis¹ has pointed out that reflectance has been judged to be the best single parameter of rank in coals of relatively high rank. The advantages of reflectance measurement for this purpose are that it is rapid, may be performed on relatively small samples, and, because a single, homogeneous vitrinite sample is used, it is independent of the mineralogical variability that can in-

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fluence the results of chemical testing.

The principal method used for determining reflectance employs a microscope photometer, which measures the intensities of reflected light with a photomultiplier by comparison against a glass or mineral standard. A stabilized polarized light source is usually used, and, because of the anisotropy of the coal, the polarization is rotated for maximum reflectance; this, when averaged for a series of readings, gives the mean maximum reflectance of vitrinite. Figure 2 shows the relationship of reflectance to carbon content and calorific value for a sampling typifying 390 US coals.

The flattening of the reflectance curve at low carbon content in figure 2a means that although reflectance is a useful parameter at high-rank levels, its use in distinguishing among lower-rank coals is limited. However, for the lower-rank coals (lignites and subbituminous) the shifts in peaks of the fluorescence spectra of the spore remains of the original plant material serve as the basis for a satisfactory means of rank differentiation.

An example of an important class of properties for which the current measuring techniques are basically qualitative and empirical is that of thermoplastic behavior. There are several indications that the potential for liquefaction of coals may be related to their plastic properties. The tendency of certain coals to soften and swell at elevated temperatures could aid their hydrogenation and solvation, or, under unfavorable conditions, lead to the production of inert coal.

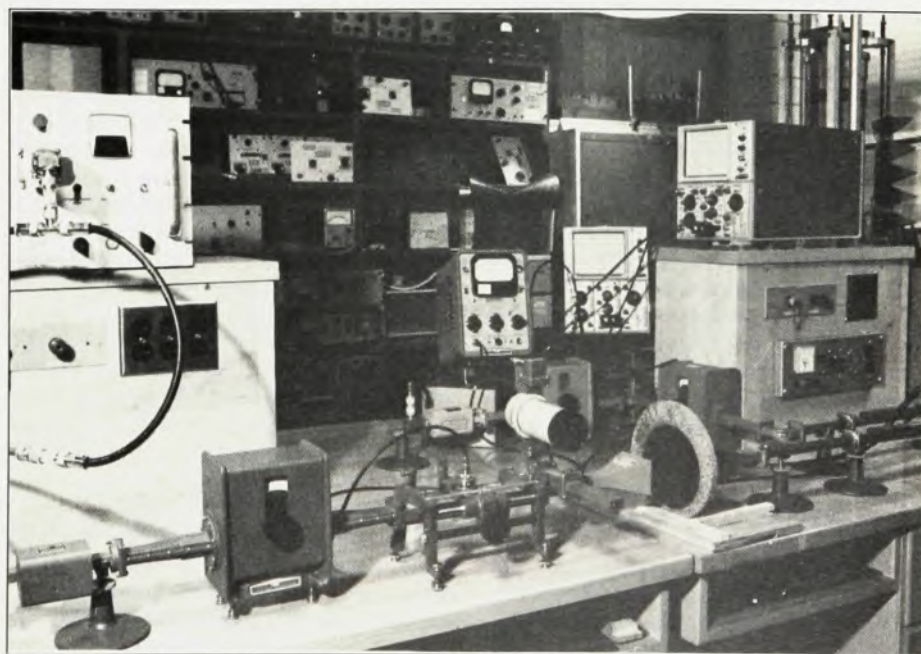
So quantitative measurement of the thermoplastic behavior of coal is important. By and large, however, the techniques used for this purpose, whether simple or ingeniously complicated, are typically highly empirical. For example, various plastometers have been developed that show the resistance to movement offered by powdered coke when it is

heated at standard heating rates. In the Gieseler plastometer, commonly used for measuring thermoplastic behavior, a stirrer is put into coal packed in a cylinder, and a constant torque is applied. As the coal softens when heated, the applied torque causes the stirrer to move, and the rate of movement, as well as several significant points in the movement, can be observed. As might be expected for such a highly empirical measuring technique, significant differences have been found among the results obtained from different designs of the Gieseler apparatus.

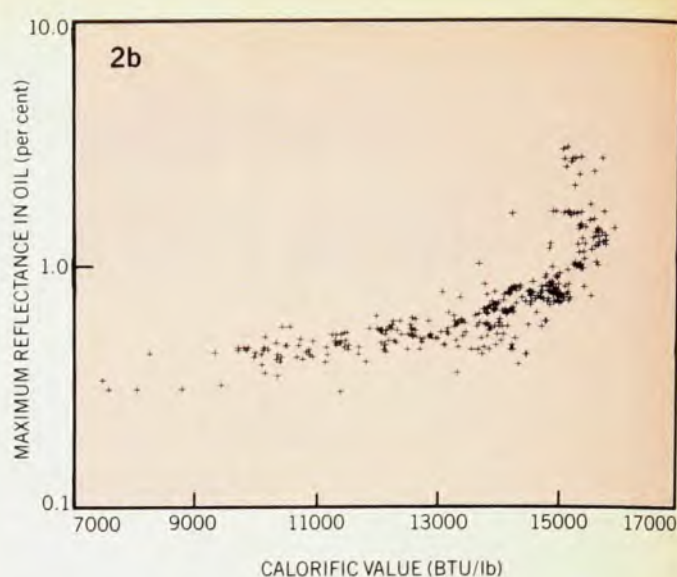
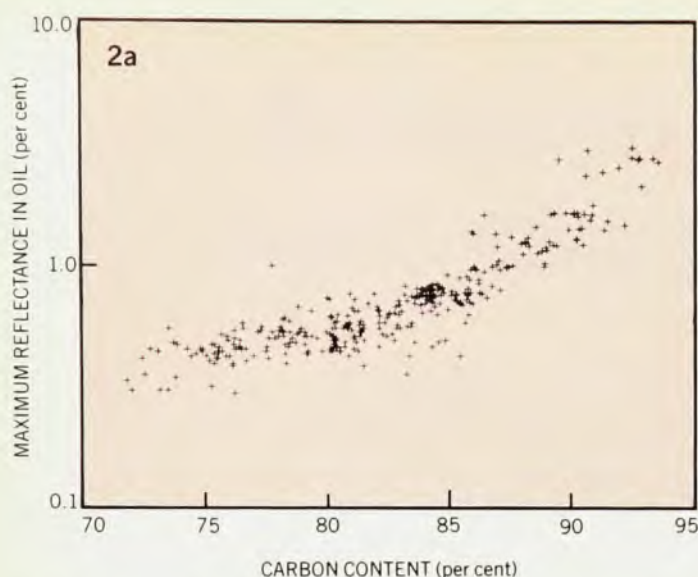
Besides the two examples given, it would be valuable to develop and improve techniques to measure a number of important physical coal parameters and properties. Among these are: density,

with pore volume being the key problem; hardness and grindability (and the associated question of the microstructure of coal and its relationship to pulverizing coal), and electromagnetic properties. Knowledge of the latter is important for remote monitoring and communication techniques. Both in improving existing techniques, as well as in developing new and direct techniques, it is important to develop a high-quality and convenient technique for routine characterization of large numbers of samples. In this regard, account must be taken of the influence of moisture, temperature, mineralogical heterogeneity, and the anisotropic effects of bedding—the coal's horizontal situation in the seam.

The most troublesome pollutants con-



Measuring electrical properties of coal at microwave frequencies. The sample in this two-path interferometer is the disc-shaped object between transmitting and receiving antennas. The data are required for underground-gasification technology. (Courtesy C. A. Balanis.) Figure 1



The reflectance of vitrinite as a function of (a) the carbon content of dry samples, free of minerals, and (b) the calorific value of moist samples,

free of minerals. Samples of 390 types of US coals are represented in the data shown here. (Courtesy A. Davis.)

Figure 2

nected with coal combustion are the sulfur oxides. In the coal itself, sulfur can be in either inorganic or organic compounds. The former, often called "pyritic" sulfur, seems to be more susceptible to removal, and the physical characterization and techniques for the removal of sulfur are aimed at these compounds.

Removing impurities

As far as removal technology goes, physicists have been giving the most attention to magnetic separation. This technique is based on the fact that the inorganic sulfur usually occurs in compounds with iron. It must be borne in mind, however, that to warrant large-scale use, this technique must compete economically with other, more mundane ones. Present commercial techniques depend basically on density differences; that is, they involve fracturing to "liberate" the pyrite, shaking, washing and/or flotation.

Because inorganic sulfur typically occurs compounded with iron, Mössbauer² and bulk-magnetic³ measurements have recently been introduced as valuable ways to characterize inorganic sulfur impurities. In pure pyrite the iron occurs in the low spin state,² and indeed the susceptibility of pure pyrite is very low.³ With regard to magnetic cleaning of coal, an important question in practice is the extent of transformation of the pyrite during storage or preparation into compounds with appreciable susceptibility.

Mössbauer spectroscopy is useful for both qualitative and quantitative analyses of the sulfur-iron compounds in coal. For qualitative analysis, the Mössbauer spectrum serves as a fingerprint technique by identifying the oxidation state and chemical environment of the iron. In contrast to x-ray diffraction, Mössbauer spectroscopy can be successfully applied to poorly crystallized materials. The use

of this technique for quantitative analysis is based on the fact that the intensity of an absorption spectrum depends on the number of Mössbauer atoms in the absorber. Since Mössbauer spectroscopy is a nondestructive method, a sample can be analyzed more than once to test for reproducibility. This technique also has other advantages² over standard chemical analysis.

Figure 3 shows the kind of information obtained from Mössbauer spectroscopy. The top panel shows typical results for a coal with a relatively high pyrite content. The spectra of iron in both FeS_2 and FeSO_4 can be identified. The middle panel shows the effect of low-temperature ashing on the sulfur-iron compounds in this sample. One detects the presence of a new phase, $\text{Fe}_2(\text{SO}_4)_3$, containing Fe^{3+} . The iron oxidation took place at the expense of the FeS_2 and FeSO_4 . The bottom panel shows behavior for a low pyrite coal. Here there is more FeSO_4 relative to FeS_2 . The Mössbauer technique promises to be particularly useful² in correlation with coal clean-up studies, and in conjunction with coal conversion processing, for example in studies of coal liquefaction residues.

Magnetic characterization, by measuring the bulk susceptibility and magnetization of the coal, is an important adjunct to cleaning coal by magnetically separating the pyritic sulfur from it. The success achieved in tests of magnetic separation⁴ depends on the fact that the ostensible "pyrite" in the coal at the time of magnetic separation has a much higher susceptibility, 100 or 1000 times greater, than that of pure pyrite. This is presumably due to partial oxidation of the pyrite to a sulfate, or to partial alteration to ferrimagnetic pyrrhotite, FeS_x (x approximately 1.14). An important practical question is whether it is necessary to induce pyrite conversion artificially to

higher susceptibility compounds, or whether the natural oxidation of the coal while being stored will serve this function.

No one has ever performed a magnetic separation of sulfur, in an iron-compound form, from coal at the mine's mouth. It should be borne in mind, however, that before its use, the coal is typically pulverized, a process that aids its oxidation. Magnetization experiments have shown that the pulverization of identical coal samples produces significant spontaneous magnetization superposed on the residual susceptibility. This provides clear evidence that normal handling of coal can influence the success of magnetic separation.

Besides magnetic studies, other work is valuable for characterizing pure pyrite and its state in coal. Studies of dielectric properties have been done to judge the possibility of converting pyrite by selective microwave heating, but this method probably involves unacceptable microwave power levels. Scanning electron microscopy and energy dispersive x-ray analysis has given valuable information⁵ on the microcrystalline nature of pyrite in coal.

In practice, magnetic cleaning of coal⁴ is most favorable in the case of liquified coals. For this situation, under the most favorable conditions of temperature and magnetic field, 95 to 99 percent of the inorganic sulfur and up to 40 percent of the mineral content entering into the ash has been removed. Temperatures in the neighborhood of 220°C appear to be optimum. Most tests have been run at magnetic flux densities of 2 tesla. High values (5–8 tesla) improve the performance; however, the improvement near 220°C is not large. The composition of the sulfides and the thermal history of the sample, presumably through converting the sulfides, have an important influence

on the degree of separation attained. Other impurities in coal include about sixty trace elements, which occur in concentrations from parts per million to parts per billion. Among these are selenium, potassium, barium, phosphorus, zinc, manganese, germanium, arsenic, nickel and strontium. Some of these (for example, arsenic) are environmentally harmful. Others, such as the transition metals, may have important catalytic effects in certain processes. For both these reasons, it is desirable to characterize these trace impurities, and, in some cases, to avoid or to remove them. Avoiding undesirable trace elements can be done partially through selection of the coal for a particular application, and partially by tying them up chemically in emissions and/or using electrostatic precipitation to remove particulate matter containing them. As reported by A. G. Sharkey, Jr.,¹ high-resolution mass spectrometry, magnetic resonance, infrared, ultraviolet, and Raman spectroscopy and ESCA (electron spectroscopy for chemical analysis) are all useful in analyzing for these trace elements. The scanning electron microscope, electron microprobe and proton induced x-ray emission all appear to offer considerable potential for such analysis. Another promising technique is opto-galvanic spectroscopy. This is based on the fact that if current from a constant voltage source is passed through a flame, the current is found to change when the flame is irradiated by intense laser radiation corresponding to an absorption of a species present in the flame.

Coal-fired MHD power generation

Magnetohydrodynamic power generation (perhaps better known as "MHD"), as discussed in reference 6 and by William D. Jackson in reference 1, involves direct conversion of the thermal energy in a gas or liquid into electrical power. This is done by expanding a heated, electrically conducting fluid through a magnetic field.

Figure 4 portrays the principles of MHD power generation. In the schematic MHD channel shown, the upper and lower walls are the electrodes, and the side walls are insulators. The magnetic field is transverse to the direction of gas flow and parallel to the electrodes. Energy is added to the gas at the left, by combustion; the flow is then accelerated in a nozzle and enters the duct. The Lorentz force gives rise to an induced electromotive force, and the current collected by the electrodes serves to supply power to an external load. The conductivity of the gas is obtained by a potassium seeding process yielding electrons and ions. The current in the gas is carried almost entirely by the electrons, which are coupled to the ions through coulomb interactions. The electrons and ions exchange momentum and energy with the neutral gas

molecules primarily through elastic collisions. The currents involved interact with the magnetic field. Through the energy exchange with the neutral molecules this interaction serves to exert a braking force on the fluid. The gas flow does work against this force, and energy is transferred from the fluid to the external load. Thus thermal energy is converted directly to electricity.

If we denote the electrical conductivity of the plasma by σ , the velocity of the plasma (which corresponds to the gas temperature) by v , and the magnetic induction by B , the maximum power density of the duct has a value of $\frac{1}{4}\sigma v^2 B^2$. To reduce both construction costs and heat losses, a high energy density is essential. Thus MHD power generation is practical only if all three quantities are high. For gases, at the highest temperatures attainable with fossil-fuel combustion products (2000–3000 K), the aforementioned seeding with an easily ionizable material, cesium or potassium, is necessary to obtain reasonable electrical conductivity (1–30 mho/m). Cost favors potassium. The high magnetic inductions required (approximately 5–6 tesla) over large volumes are practical only through the use of large superconducting magnets. In the MHD duct the electrical conductivity falls rapidly with decreasing gas temperature along the duct, and it becomes uneconomic to extract electrical power directly from the gas by the MHD process below gas temperatures of 2000–2300 K. The remaining heat in the combustion gas stream must be extracted elsewhere in an integrated power plant.

There are a number of problem areas in MHD power generation, and several of these call for basic physics-oriented research. First are questions related to the plasma dynamics. There has been much work, with considerable success, in this area; nevertheless, important questions remain. Here the essential question is whether the plasma flow is stable when significant power is extracted from the gas.

The need for very large superconducting magnets is clear. At present, the largest magnet for MHD application has been designed and built at Argonne National Laboratory for use in joint US-USSR studies on the U-25 power plant near Moscow. This magnet maintains a field of 5 tesla over a length of 4.2 meters

with a diameter varying between 40 and 60 cm. Commercial MHD generators may be from 15 to 25 meters long with diameters up to a few meters, the magnetic field required in this volume being up to 6 tesla.

The key problem area for practical development of coal-fired MHD power generation is that of materials. This is caused by the combination of high temperature and highly destructive environment. The presence of coal slag is an important part of this environment, and studies of coal slag as a material would be valuable. For example, further information about the electrical properties of this semiconductor would be useful.

Materials problems occur for both the electrode and insulating materials making up the duct walls. The electrodes must withstand high temperatures, and for this reason ceramics are the leading candidates. Because the duct combustion gases have an oxygen partial pressure of approximately 10^{-2} atmosphere, it is clear that only oxides are likely to be stable at suitably high temperatures.

The electrical conductivity required for the electrodes is greater than $0.1 (\text{ohm-cm})^{-1}$, a relatively high value for a ceramic. The conductivity must be essentially all electronic. Ionic conductivity through ion depletion can reduce the strength of the material. Although it might be possible to overcome the depletion problem for oxygen ion transport, conduction involving oxygen ions can oxidize metallic lead-outs, destroying proper operation. Furthermore, the conductivity must not drop much with temperature if one is to avoid severe joule heating at the electrode-lead-out interface.

Several candidates for electrode materials are receiving serious attention. Among these are $\text{CeO}_2\text{-ZrO}_2$, where one varies the concentration of CeO_2 from 18 to 80 percent between the plasma interface and the current lead-out. This is to compensate for the marked drop in electrical conductivity of stabilized zirconia with temperature toward the cold side of the electrode. A second class of materials receiving considerable attention are the oxides with perovskite structure based on LaCrO_3 , such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$. Another approach involves using an iron spinel electrode. The electrode is $\text{FeAl}_2\text{O}_4\text{-Fe}_3\text{O}_4$, the insulator Al_2O_3 , and the power

Sensors Used in Mine-wide Ventilation Monitoring System

Parameter	Sensor type
Air flow	Vortex/ultrasonic
Differential pressure	Diaphragm/magnetic balance
Methane concentration	Catalytic hotwire
Carbon-monoxide concentration	Solid state
Temperature	Thermistor
Relative humidity	Solid state

lead-out is stainless steel. This arrangement provides compatibility with the slag because it contains Al_2O_3 and Fe_3O_4 .

The cathode emissivity must be high enough to avoid arcing. Thus one wants a low work function with resultant high thermionic emission. The surface of the cathode will be covered by molten slag, which contains the potassium seed. An important area for research is the study of work functions under circumstances pertinent to actual operating conditions. It may be that the slag-seed composition and wall temperature can be adjusted to optimize the emissivity of the cathode area.

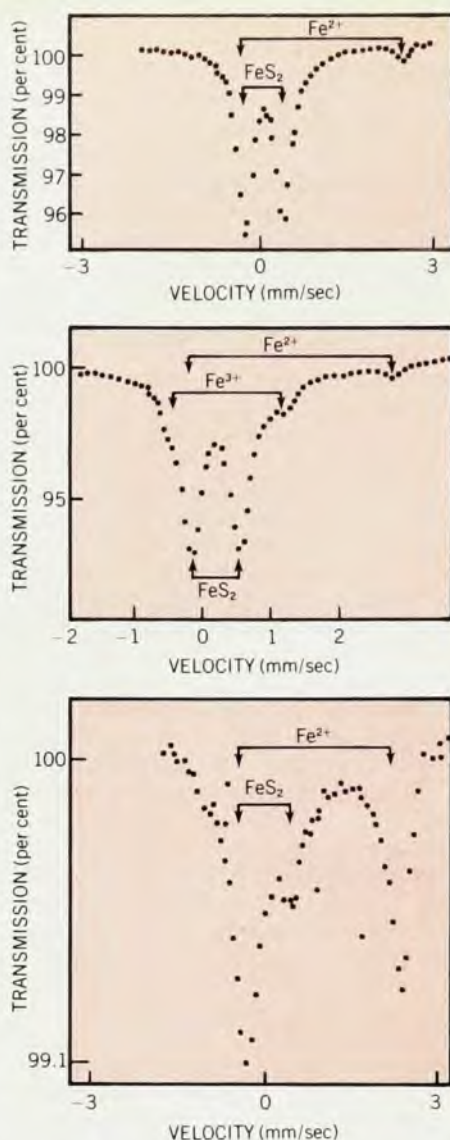
In practical electrode arrangements, which are segmented to reduce power losses due to currents along the electrode, there are high electric fields—about 5 kV/m—across the insulator used for segmentation. The required insulator properties are high electrical resistivity, adequate resistance to thermal shock, resistance to corrosion and seed penetration, adequate mechanical strength and low vaporization rate. Among materials considered for insulators have been alumina, boron nitride, beryllia, magnesia, silica, thoria and stabilized zirconia. Alumina (Al_2O_3) and magnesia (MgO) are used in electrode-insulator systems of current interest. Calcium and strontium zirconates have also received serious consideration.

Erosion and corrosion

Just as for MHD power generation, materials are a key bottleneck in the development of economically viable gasification and liquefaction technologies. These material problems relate to the behavior of surfaces of the pertinent solids. Thus erosion and corrosion, which involve the wear of surfaces due respectively to impingement of solid particles (N.P. Suh in reference 1), and to removal of structural material by chemical attack (Kenneth Natesan in reference 1), are the major causes of failure of components in pilot-plant operation.

Research problems in erosive wear include the experimental and theoretical understanding of erosion mechanisms and the use of this knowledge to develop erosion-resistant materials and components, as well as the monitoring of erosion effects *in situ* under operating circumstances, so as to gain knowledge of such effects and to be able to replace components before actual failure.

Basic erosive-wear mechanisms are not fully understood. They can differ, even with the same materials, depending on the conditions under which the wear occurs. Basically two types of mechanisms have been suggested for erosion in ductile materials: in one, the abrasive particle cuts the metal's surface, whereas the second mechanism suggests plastic deformation and fatigue effects as the causes for erosion. The relative importance of these



Mossbauer spectra of coal. Top: coal with a relatively high pyrite content. Middle: the same coal as above, but after ashing. Bottom: low-pyrite coal. (P. A. Montano.) Figure 3

two effects varies drastically with the angle of impingement. For angles up to about 40° from parallel to the surface, the cutting mechanism is dominant. However, such effects fall off strongly with increasing angle, and for angles from about 70° up to normal incidence, the cutter mechanism offers basic understanding. Which region of angular incidence is important in practice depends on the particular component and flow pattern.

Experimentally, in addition to the impingement angle of particles, a number of other parameters characterize erosive wear effects. These are the velocity, size, hardness, amount and concentration of the particles themselves, the prevailing temperature, and the hardness and melting temperature of the material being impacted.

The aim of theoretical work on erosion is to develop models and equations that can be used for predictive studies. Mi-

chael Momoun and William J. Shack at Argonne National Laboratory have done extensive analytical modeling aimed at predicting the erosive wear of materials used in coal gasification plants.

For brittle materials, such as refractory linings, the most important mechanism of erosive wear is probably impact fatigue, the generation of cracks, with the material eventually falling out. There is a threshold velocity below which there is no erosion for this mechanism. Such a threshold velocity also exists for erosive wear in ductile materials, but the threshold for brittle materials is higher, perhaps by a factor of six or so. For the latter type of material, grain size effects (depending on the size of impacting particles) are important. This is particularly true if the grain size is greater than that of the impacting particles.

Chung K. Hsieh and William A. Ellingson⁷ have developed a technique of infrared imaging to monitor the erosive wear in refractory ceramic linings inside steel transfer pipes. In figure 5, the infrared emission gives a temperature profile of the outside of the metal pipe. Then, using an analysis based on a three-dimensional heat-transfer model, one can calculate the degree of erosion on the inside necessary to get that temperature distribution. A "hot spot" associated with a cavity in the lining shows up clearly in figure 5.

George C. Stanton and Ellingson⁸ have developed an ultrasonic system to monitor the erosion of the wall of a metal pipe in coal-gasification processes at high temperatures. Convectively cooled acoustic waveguides are attached to the pipe at the points to be monitored, and longitudinal-wave transducers, at 5 MHz, are attached to the waveguides. The thickness of the wall is then obtained from the time difference between the signals reflected at the outside and inside walls of the metal pipe.

In an actual working environment there is a strong interaction between corrosion and erosion effects. Important parameters affecting corrosive action are temperature, pressure and the compositions of the corroding gas and of the alloy being attacked. Different coals also give rise to different corrosion problems. For example, many coals of the Western US have high alkali content and low sulfur content, while the situation is often the reverse for Eastern coals. Thus corrosion from alkali vapors is a problem with Western coals. In the fluidized-bed techniques for reducing sulfur impurities in Eastern and other coals through chemical reaction with limestone particles, alkali salts may be added to the limestone to aid the process. This also gives rise to alkali and chloride corrosion. Metallic-alloy selection for different high-temperature applications is based on the strength of the alloy as well as its resistance to a complex environment that is

both corrosive and erosive to the material.

Surface physicists can make an essential contribution to dealing with corrosion, through the study of the growth of protective oxide scales on alloys. For a judicious selection of an alloy for a given application, it is essential to understand the mechanisms of oxide and sulfide formation on alloys of different compositions. Another important question relates to the rates of transport of substitutional elements (minority elements in alloys, such as chromium and nickel) and reactive species (for example, oxygen and sulfur) through the oxide and sulfide phases. Another area of considerable importance is the role of minor alloying elements such as manganese and silicon in the oxidation and sulfidation behavior of materials.

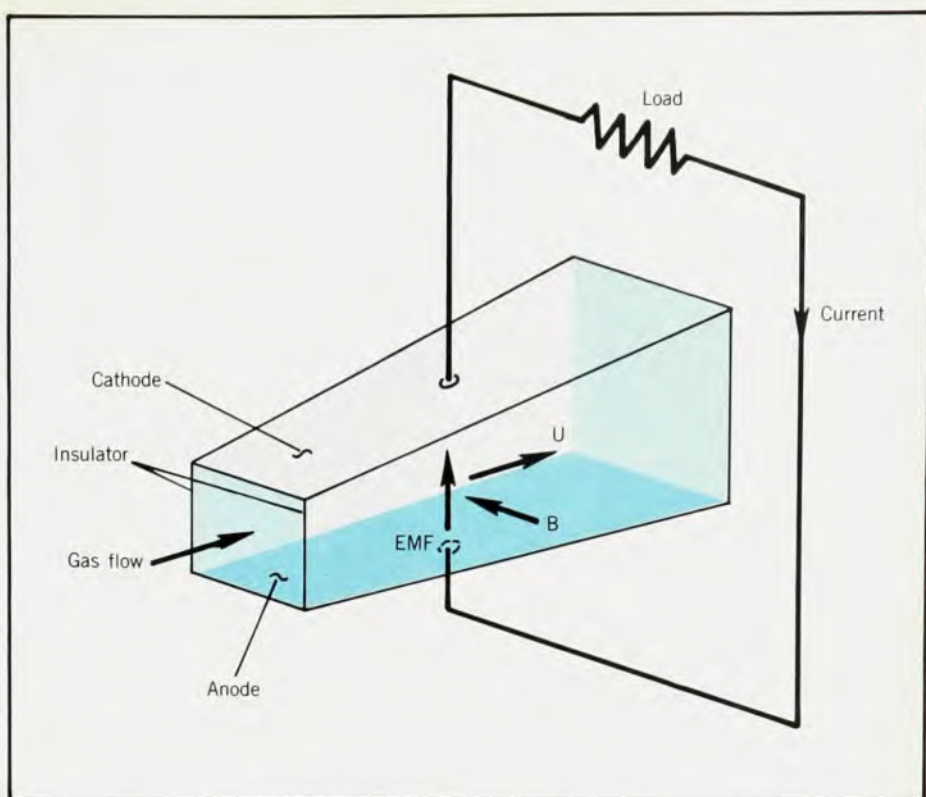
Hydrogen effects (Paul Shewmon in reference 1), degrading the properties of metals, are an important corrosive effect. These include embrittlement of higher-strength steels at room temperature and hydrogen attack that degrades the mechanical properties of pressure vessel steels at elevated temperatures (300–500°C).

Hydrogen embrittlement effects diminish rapidly with temperature, and are of concern only in shut-down and start-up procedures. Hydrogen attack is a much more serious problem. High-pressure hydrogen combines with carbon to form methane. The hydrogen permeates the steel and internally generates insoluble methane, which forms bubbles. The bubbles grow with increasing hydrogen pressure and link up to form fissures along internal boundaries, destroying much of the alloy's ductility and strength. It is important to understand the mechanisms of this effect, in order to counter it, and to monitor it in actual operating conditions, particularly in the very large steel pressure vessels (1000–2000 tons each) to be used in coal conversion systems.

Use of nuclear-reaction techniques to develop depth profiles of the hydrogen distribution⁹ should help in understanding hydrogen effects. Systematic implantation of hydrogen, coupled with such nuclear-reaction techniques, may be of particular benefit.

Catalysis

Improvements in catalysis offer the possibility of dramatic improvements in coal-utilization technology. For example, new catalysts to bring about coal liquefaction in reaction with hydrogen under mild conditions, producing the desired aromatic hydrocarbon distillates, with little or no production of gas by-products would be a revolutionary breakthrough. Another example would be the development of a catalyst system capable of bringing about the direct conversion of coal with steam under mild conditions into methane.



Magnetohydrodynamic conversion of the thermal energy of a coal-derived gas into electricity. The duct, shown very schematically in this diagram, consists of a cathode and anode, insulators and a lead-out to an external load. (Courtesy W. D. Jackson.)

Figure 4

Some key points with regard to catalysts in coal conversion processes are:

- Real catalysts are usually used in an extremely dispersed form. This is really a different state of matter than the surface of a bulk solid.

- Besides finding new and effective catalysts, it is important to try to understand effects altering the performance of existing catalysts. A crucial point is to understand the mechanism of catalyst "poisoning" by sulfur and by coal mineral matter. Catalyst-support effects (the interaction of a metallic catalyst with the semiconductor or insulator support material) is another mechanism affecting catalytic performance, about which little is known.

- It is important to understand the catalytic properties of mineral matter intrinsic to coal.

In practice, the likeliest route to produce fuels from coal involves gasification to produce a mixture of CO and H₂, followed by a catalytic synthesis reaction to give the final desired products. But such catalytic synthesis of organic compounds has many problems. Major problem areas are the undesired formation of metal carbonyls, the sensitivity of the process to sulfur, the "deactivation" of the catalysts, and the possibilities for selecting the final products (M.A. Vannice and R.C. Garten in reference 1).

Probably the greatest problem in catalysis is the latter one. Alloys offer much potential for the control of possibilities for selecting the final product. For example,

supported RuFe alloy clusters exhibit catalytic behavior markedly different from that of either metal by itself. This behavior is dependent upon the Ru/Fe atomic ratio, and a broad minimum in both the paraffin/olefin ratio and methane formation exists between Ru/Fe ratios of 0.5 and 2.

Information on the effects of the size of catalyst particles and of the catalyst-support relationship are limited as yet. Significant effects related to the crystallite size appear to occur with platinum particles, but minor effects, at most, exist with nickel catalysts. With palladium catalysts, the support appears to play a major role in the behavior of the catalyst. Further understanding of these effects is an area of opportunity for surface physicists.

Atmospheric CO₂; mining constraints

Finally, we come to the two areas of ultimate limitation on the use of coal. While the entire area of coal use is one gigantic environmental problem, the ultimate and unavoidable end effect is the production of carbon dioxide. Similarly, the beginning of coal utilization is getting coal out of the ground to utilize, or, more generally, getting the energy content of the coal out of the ground in a convenient form. This involves mining or some technique superseding mining as presently practiced.

The concern with CO₂ production is the buildup of this gas in the atmosphere,¹⁰ which, in turn, gives rise to the "green-

house" effect (CO_2 is transparent to incoming visible light, but absorbs the outgoing radiation of long wavelengths, thus raising temperatures near the Earth's surface). The consequence is thought to be an increase of 2–3°C in the Earth's surface temperature for each doubling of atmospheric CO_2 . However, the effect increases with increasing latitude, giving perhaps 8 to 10°C warming in the polar regions. The concentration of CO_2 in the atmosphere has grown about 14 percent in the past 125 years, with a quarter of that increase occurring in the last decade. Reasonable projections on the basis of present use and fossil-fuel reserves indicate a doubling of atmospheric CO_2 concentration in about 60 years.

In fact, the ultimate capacity of the ocean system is far in excess of that required to deal with all the fossil carbon that mankind may wish to use. On a time scale measured in thousands of years, the CO_2 content of the atmosphere may well be determined by the equilibrium established with the inorganic carbon of the deep ocean. The rate of exchange between the atmosphere and the ocean as a whole, however, is low. Present information indicates that the average residence time of water in the deep oceans is in the range of 500 to 2000 years.

So the problem of getting rid of excess atmospheric CO_2 appears to be largely one of a very large relaxation time associated with ocean turnover. Thus the accuracy of models that oceanographers have constructed for the mechanisms of mixing in the ocean are crucial in predictions of the buildup of atmospheric CO_2 . Carbon-14 and tritium produced in atomic-bomb tests have been used as tracers to study the rate at which the ocean water of the upper layer is exchanged with that of the depths. In current work, oceanographers are reviewing their assumptions to see if they have overlooked mechanisms that would be able to sequester additional amounts of carbon.

A possibly important man-made effect on atmospheric temperatures is that of airborne particulates. These might bring about a cooling by back-scattering solar radiation. Indeed, deliberately introducing appropriate particles into the upper atmosphere has been suggested as a means of counteracting a temperature increase due to CO_2 buildup. However, the magnitude of this effect, even whether it is one of cooling or warming, depends on many factors—the altitude, size, concentration, and reflectivity or refractive index of the particles.

Physicists may be able to contribute toward evaluating the CO_2 problem through development of improved theoretical models and more precise determination of the numerous measurements needed for accurate climatic predictions. One place where physicists can clearly contribute is in providing further and



Infrared image of eroded refractory lining of a steel pipe and the corresponding isometric temperature profiles. The image covers an area of 2500 mm² and the temperature range is approximately 30–100°C. (Courtesy W. A. Ellingson.)

Figure 5

more accurate information about the distribution of tritium and of the carbon isotopes, particularly C^{14} , which are used in understanding the carbon cycle.

In considering the CO_2 buildup problem, one should bear in mind that advanced coal utilization should be meant as a bridging energy technology, perhaps to be used extensively for 40 to 50 years, but certainly to be superseded by renewable and/or essentially inexhaustible resources such as nuclear breeder technology, nuclear fusion and solar energy.

All of the possibilities for increased coal utilization call for a very large increase in the amount of coal mined. This represents a great problem when viewed against the recent record of coal production. Even before the miners' strike of 1977–78, the Administration in the US had reduced its coal-production goal from a doubling of 1976 levels by 1985 to an increase by two thirds. In the period from 1969 to 1976, the productivity of miners decreased drastically, from 15.6 to 8.5 tons per miner day for underground mining, and from 35.7 to 26.0 tons per miner day for "strip" mining (James R. Garvey in reference 1). Moreover, environmental considerations argue against looking to greatly increased strip mining, the obvious way to increase coal production easily.¹¹

It is clearly vital to improve and perhaps supersede the present mining technology. Physicists can contribute to this through high-quality applied and, perhaps surprisingly, even basic research. Obvious possibilities are in the instru-

mentation-monitoring-control area. Some of the decrease in the productivity of miners can be attributed to improved safety regulations. A desirable goal is to develop remote monitoring techniques, thereby maintaining and even improving safety, while decreasing the amount of manpower not actually used in coal production. M. Dayne Aldridge and his colleagues¹² at West Virginia University have developed a system for mine-wide monitoring and control of ventilation, one of the key factors in safe operation in any coal mine (some mines cover areas of more than 100 square kilometers). This system (shown in the cover photograph) has been installed for testing purposes at the "Federal No. 2" mine of the Eastern Associated Coal Corp near Miracle Run, West Virginia. The production of this mine in 1975 was just under a million tons, and it employs a variety of mining techniques.

The system monitors the velocity of air, the differential pressure between incoming and nearest return air passages, concentrations of methane and carbon monoxide, temperature and relative humidity. The type of sensor for each of these parameters is listed in the table on page 35. The last four sensors are enclosed in a single steel housing (the steel box above the miner's head on the right in the cover photograph). The air-flow sensor is enclosed in a separate housing (top, left of center). Forty sets of sensors are installed in the mine, and each of them is connected to a telemetry unit (the large unit between the two miners). The telemetry units are connected to a central computer that scans all sensors once each minute and checks for possible alarms.

There is a need for research work to improve the sensors and find new ones. The carbon-monoxide sensor, in particular, calls for more research. This sensor is based on a solid-state surface effect. Carbon-monoxide absorption apparently causes a change in the surface electronic structure, and this is sensed as a resistance change. The composition of the present device was developed on a highly empirical basis, and suffers from a lack of selectivity toward CO. Fundamental research work is needed both for understanding the surface absorption mechanism of CO in the present sensors and for finding new, more selective CO sensors.

Clearly the ideal solution to the mining problem is to remove the energy content, or some more desirable material than the raw coal, from the ground. The one technology presently available that offers promise in this direction is underground gasification.¹³ This may prove to be the ideal way to exploit low-grade coal resources in the West, and, with more work to overcome the difficulties of using Eastern bituminous coals, may also be used in the deep mines of the East.

The method used at present in underground gasification is quite simple. Two

wells are drilled to the base of a coal seam, at a separation of 20 to 50 meters. The two wells are linked in some manner. The coal is ignited through one well, and air is injected through the second well. Via the linking channel, the air from the second well reaches the flame front and draws it toward the second well. This initial linking may occur either via the inherent permeability of the coal, as is possible for Western coals, or via a channel of coal fractured by hydrofracturing, directional drilling or detonation of shaped charges. Eventually, the fire expands and consumes all the coal between the wells. By controlling the flow of injected air, partial combustion of the coal is obtained so that low-BTU gas (100–170 BTU/ft³) is emitted from the first well. Such gas is then used in gas turbines near the well site to generate electricity.

Besides ensuring safety within existing mining technology, remote monitoring is also important to develop wholly new technology such as *in situ* underground gasification. Constantine A. Balanis and colleagues¹⁴ have been developing electromagnetic instrumentation to detect, monitor and map the burn front in an underground coal-gasification process. To design the system, the electrical properties of coal at microwave frequencies must be known. As shown in figure 1, the electrical properties of typical coal samples were measured with a two-path interferometer at microwave frequencies (around 9 GHz), as a function of the temperature of the sample, and the direction and polarization of the electromagnetic wave. Variations with frequency in the ultra-high frequency range (0.5–100 MHz) were examined using an impedance bridge.

Associated with a coal sample are three distinct physical planes, related to its situation in the seam, prior to mining; namely, the "bedding" or horizontal plane parallel to the Earth's surface, and the "face" and "butt" cleats—the planes across and along the seam, respectively. The conductivity of a given sample varies by as much as a factor of six, depending on the direction of propagation and the polarization axis, relative to these planes. Knowledge of these propagation phenomena allows the improvement of the efficiency of an underground electromagnetic system by appropriately orienting the transmitting and receiving elements.

Finally, let me point out one interesting possibility that could bring about a true revolution in coal mining. This would couple underground gasification with nearby generating plants, using MHD—"topped," gas-turbine power generation. The system would combine the most advanced generating technique with the most advanced technique for getting coal energy out of the ground. Such a scheme would offer great advantages environmentally, by reducing the need for cooling

water, a very important feature for the Western US, economically, by reducing the capital investment compared with that required for a "conventional" gasification plant, and from an efficiency viewpoint, by increasing the efficiency of use of the coal's energy content.

* * *

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