Mater. Res. 5, 83 (1971); Conference on in situ Composites (Publication NMAB-308-1, National Academy of Sciences, Washington, D.C., 1973),

- F. D. Lemkey and E. R. Thompson, in *Conference* on in situ Composites (Publication NMAB-308-1, National Academy of Sciences, Washington, D.C.,
- National Academy of Sciences, Washington, D.C., 1973), vol. 2, p. 105.
 13. J. L. Walter and H. E. Cline, *ibid.*, vol. 1, p. 61.
 14. T. Yamamoto, S. Taguchi, A. Sakakura, T. No-zawa, *IEEE Trans. Magn.* 8, 677 (1972); A. Sakakura, T. Wada, F. Matsumoto, K. Ueno, K. Takashima, K. Kawashima, *Magnetism and Magnetic Materials*—1974, C. D. Graham, Ed. (Conference Proceedings No. 24, American Institute of Physics, New York, 1975), p. 714.
 15. T. Yamamoto and T. Nozawa, *J. Appl. Phys.* 41, 2981 (1970).
- 2981 (1970).
- C. Cawthorne and E. J. Fulton, *Nature (London)* C. Cawthorne and E. J. Fulton, *Nature (London)* S75 (1967).
 W. G. Johnston, T. Lauritzen, J. H. Rosolowski, A. M. Turkalo, in *Radiation Damage in Metals* (American Society for Metals, Metals Park, Ohio, in press).
- E. Bloom, J. D. Stiegler, A. F. Rowcliffe, J. M. 18. E. E. E. Blohn, D. Streger, A. P. Kowenne, S. M. Leitnaker, in preparation. Y. Y. Yao and J. T. Kummer, J. Inorg. Nucl. Chem. 29, 2453 (1967). W. vanGool, Ed., Fast Ion Transport in Solids (North-Holland, Amsterdam, 1973).
- 20. W

- R. W. Powers and S. P. Mitoff, J. Electrochem. Soc. 122, 226 (1975).
 J. J. Burke, A. E. Gorum, R. N. Katz, Eds., Ce-
- ramics for High Performance Applications (Pro-ceedings of the 2nd Army Materials Technical Conference) (Brook Hill, Chestnut Hill, Mass., Since Si_3N_4 , and SiAlON.
- SiC, Si₁N₄, and SIAION.
 G. E. Gazza, J. Am. Ceram. Soc. 56, 662 (1973).
 S. Prochazka, Spec. Ceram. 6, 171 (1975).
 L. E. Hibbs, Jr., and R. H. Wentorf, Jr., High Temp.-High Pressures 6, 409 (1974); M. D. Horton, B. J. Pope, H. T. Hall, in Diamond-Partner in Productivity (Industrial Diamond Association of America, Moorestown, N.J., 1974), p. 19.
 W. G. French, A. D. Pearson, J. B. MacChesney, America, Bey MacChesney, April 202 (1975).
- W. G. French, A. D. Pearson, J. B. MacChesney, Annu. Rev. Mater. Sci. 5, 373 (1975).
 For comprehensive sources, see: J. Non-Cryst. Sol-ids Spec. Vol. 2 (1970); ibid., 4 (1970); ibid., 8–10 (1972). These volumes contain the collected papers on nonoxide glasses presented at three separate conferences. 28. P. I. Vincent, Proc. R. Soc. London Ser. A 282,
- 113 (1964).
 J. Preston, *Polym. Eng. Sci.* 15, 3 (1975).
 N. J. Capiati and R. S. Porter, *J. Polym. Polym.* 2010;
- N. J. Capiati and R. S. Porter, J. Polym. Sci. Polym. Phys. Ed. 13, 1177 (1975); J. Mater. Sci. 10, 1671 (1975).
 H. E. LaBelle, Jr., and A. I. Mlavsky, Mater. Res. Bull. 6, 571 (1971).

Materials for Advanced **Energy Technologies**

Richard S. Claassen

Materials and energy are inextricably linked. Industrial materials cannot be produced without energy, nor can energy be produced without specialized materials. For example, the recovery and processing of industrial materials required about 16 percent of the total U.S. energy consumption in 1974. The interdependence of the two has been increasing and will continue to increase with time as the more easily won raw materials are exhausted and as the energy conversion and utilization schemes become more sophisticated. Although research and development on ways to recover and process materials with less energy is a challenging opportunity for the materials community (1), I will focus on the materials technology that will be required in major developing systems for extracting, converting, distributing, and using energy.

Figure 1 is a schematic representation of the energy sources; methods of processing, conversion, transmission, and storage; and forms of fuel energy that may exist in the near term (about 1990). The boxes with hatching indicate the elements which I believe require significantly improved mate-20 FEBRUARY 1976

rials technology if meaningful contributions are to be made to the national energy balance. At a later time breeder reactors may be added as converters of uranium, and eventually some form of pure fusion may provide an entirely new source of energy. The successful development of these new nuclear energy technologies will be heavily dependent on achieving substantial improvements in the performance of materials.

The fact that most fuel sources must be processed in some way or converted to another form before they are suitable for consumption is emphasized in Fig. 1. With the exception of solar heating, all systems being considered in this country for replacement of petroleum and natural gas depend on processing and conversion; that is why materials will dominate the resolution of our energy problem. Diminishing supply of low-cost and easily obtained fuels, increased environmental protection measures, and fuel conservation through increased efficiency are all factors which combine to place higher performance demands on every part of the energy supply system. Development of higher-temper-

- J. Haggerty, in preparation.
 A. M. Houston, *Mater. Eng.* 81, 33 (1975).
 Because the literature on structural composites is Because the interature on structural composites is so extensive, no special references are cited. For further information, see L. J. Broutman and R. H. Krock, Eds., *Composite Materials* (Academic Press, New York, 1974), vols. 1–6. W. B. Hillig, R. L. Mehan, C. R. Morelock, V. J. DeCarlo, W. Laskow, *Am. Ceram. Soc. Bull.* 12, 1054 (1975). A. Hall Plact World 1974 34 (1974).
- A. Hall, Plast. World 1974, 34 (1974).
 W. J. Ward III, in Recent Developments in Separation Science, N. Li, Ed. (CRC Press, Cleveland,
- Ohio, 1972), pp. 153–161.
 B. N. Chapman and J. C. Anderson, Eds., Science and Technology of Surface Coating (Academic Press, New York, 1974).
 R. J. Russell, Mater. Eng. 81, 48 (1975).
 M. Schnoller, IEEE Trans. Electron Devices 21, 212 (1975). 38.
- 40 313 (1974).
- 41. G. Dearnaley, Nature (London) 256, 701 (1975).
 42. D. Maydan et al., in Technical Digest, 1974 International Electron Devices Meeting (Institute of Electrical and Electronics Engineers, New York, 1975).
- 43. G. J. Michon, H. K. Burke, D. M. Brown, M. Ghezzo, in *Proceedings of the 1975 International Conference on the Application of Charge Coupled* Devices (Naval Electronics Laboratory Center, San Diego, Calif., 1975).

ature or longer-wearing materials, for example, can yield improvements for every step in Fig. 1. For some elements in the newly evolving program, indicated by hatching in Fig. 1, a significant materials development or improvement is essential to economic operation or even technical feasibility. I will emphasize those elements after some observations on availability of materials

Supply of materials. Since the shortfall of domestic petroleum supplies was dramatized by the Arab boycott, it has been natural to ask whether there will also be shortages of the materials required to implement our new energy programs. I believe the answer is "No," but it is easy to point out a number of examples where careful attention and action are required (2).

1) High chrome alloys are needed for virtually every energy use-from oil refinery pipes to cryogenic structures in the magnets used in magnetic confinement fusion reactors. For chromium we are completely dependent on foreign sources of unknown future political stability.

2) Gallium arsenide cells are attractive for solar photovoltaic use, but a simple computation indicates that for even 8×10^9 watts, 10 percent of the estimated electric generation capacity in 1990, 105 tons (metric) of gallium would be required compared to an estimated world resource of 1.1×10^5 tons (3).

3) Through catalytic oxidation, fuel cells provide direct conversion of hydrogen-rich

The author is director of materials and processes at Sandia Laboratories, Albuquerque, New Mexico 87115. This article derives partly from deliberations of an ad hoc committee organized by the National Re-search Council's Commission on Sociotechnical Sys-tems and chaired by the author, which held a workshop with invited consultants at Airlie House, Virginia, in July 1974 to discuss the impact of critical materials in the near-term energy program.

fuels to electricity. They offer unique advantages for some applications. The most successful fuel cells, however, require an investment of 20 grams of platinum catalyst per kilowatt, and about one-fifth of that is consumed per year. Use of fuel cells to produce 10 percent of the nation's estimated electrical energy in 1990 would consume about 32 million grams per year, compared with the total world production of about 50 million to 70 million grams per year.

Problems like these, however, can be avoided by adequate forethought. Since the energy program, for example, requires only a few percent of this country's consumption of chromium, the heavy cosmetic use of chromium could presumably be diverted, if necessary. To satisfy needs for corrosion-resistant materials, alloys in which aluminum is used instead of chromium to form passive film could be further developed. Solar cells designed for large applications will be based on more abundant materials such as silicon or copper and sulfur. To avoid the platinum supply problem in fuel cells, molten carbonate cells are under development in which nickel-base electrodes perform the catalysis.

Although the materials supply problem in our energy program can be contained by early system studies and careful design, full development of suitable materials obviously takes many years. Careful thought must be given now to future requirements.

Bulk resource materials may be available in adequate supply to support the energy program, but there may still be shortages of special end products. Steel pipe for oil wells is in short supply. Thick steel plates of large dimensions are needed for steam pressure vessels and for coal gasification reactors at a rate twice that of the projected supply (2). The near-term energy program will create a heavy demand for large forgings for turbines, generators, and pressure vessels, probably beyond the present capacity of the industry. Coal cars, draglines, and mine trucks are items with long lead times for delivery. Considerably improved definition and forecast of the needs of particular types and forms of materials for the energy program will be required to enable industrial suppliers to expand capacity sufficiently to support the energy program.

In discussing the sequence of materials developments that will be required for new energy technologies, it is convenient to identify three time periods-the near term, midterm, and long term. I use these categories in the sense that some significant contribution could be made to the nation's energy flow during each period. Implied, in turn, is completion of development and design, followed by considerable investment in construction. Advocates of a particular energy scheme may quarrel with my assignments, but any general understanding of the materials-energy problem requires a realization that most new technologies will take considerable time to make a significant impact. On the other hand, the investment in specialized materials development must be made in the next few years or the new materials will not be available when needed.

Near Term-Now to 1990

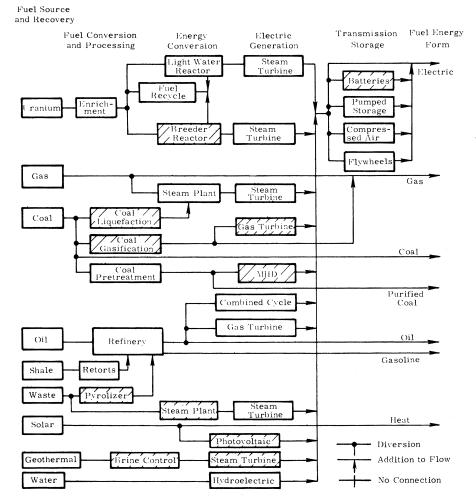
Coal must relieve the pressure on petroleum and natural gas supplies for the near term. By refining it or by adequate stack scrubbing, we can burn more coal. To directly offset petroleum consumption, coal must be processed to achieve two major objectives: (i) the reduction of sulfur and other undesirable pollutants, and (ii) conversion to a liquid or gaseous form. Many schemes and processes to achieve these objectives are under development (4). At the simplest conceptual level, it is just a matter of adding hydrogen in the proportion necessary for the end product desired. Figure 2 illustrates the ratio of hydrogen to carbon in various fuels. Fortunately, the process of adding hydrogen can be designed to remove most of the sulfur, since hydrogen sulfide is more thermodynamically stable than the organically bound sulfur or iron disulfide in coal.

Present commercial schemes for producing hydrogen gas use petroleum derivatives as feed materials, but in the future it will be necessary to recover hydrogen from water by using the combustion of carbon as the energy source. The reaction of separating water into O_2 and H_2 is energetically expensive, requiring 57 kilocalories per mole (0.24 megajoule per mole), although a high fraction of this energy will be recovered later from the hydrocarbon fuel.

Coal liquefaction. The coal conversion most appealing for the near future is therefore the one that adds the least hydrogen liquefaction; that is, coal is sufficiently hydrodesulfurized to produce a material that can be pumped through pipelines and fired in large boilers to produce electricity or

740

Fig. 1. Partial schematic representation of the energy flow as it may exist in the United States in 1990 when the first four fuel sources will probably still contribute more than 95 percent of the total. Note that the energy sources under development for the future depend on processing or conversion. Boxes with hatching show steps for which new materials are essential.



process heat. In 1974, the United States consumed 3.4 quads (5) of natural gas and 3.3 quads of oil in electric generating plants (6). Suitably liquefied and purified coal, 3.1×10^8 tons per year, could be substituted for these precious fuel forms.

The several coal liquefaction processes under active development transport mixtures of coal and liquid or gas at high temperatures (700° to 730°K or 800° to 850°F) and pressures of several thousand pounds per square inch (psi) gauge. The combination of sulfur and particulate matter makes these streams extremely destructive to the piping, valves, and containers, especially when the flow changes direction. The most frequently used erosion-resistant engineering materials (Stellite and cobaltbonded tungsten carbide) are subject to some corrosion in sulfidation environments, so new materials of longer life are needed.

It may be necessary to exploit surface protective techniques such as reactive vapor deposition of refractory carbides and nitrides, or fused salt electroplating of refractory alloys. Control of the microstructure and internal stress of protective coatings may be the key to eventual success.

Coal gasification. Coal gasification methods are categorized in three principal groups according to energy content in the product: (i) low Btu (obtained by reacting air and steam with coal), intended principally for on-site generation of electricity; (ii) medium Btu (obtained by reacting oxygen and steam with coal), intended primarily as feedstock for production of methane; and (iii) high Btu (methane), intended for direct replacement of natural gas in existing distribution systems. The many technical approaches within the categories share a number of serious materials problems. Those for the high-Btu process are most serious, yet representative (7).

The Lurgi process, developed decades ago in Germany, has been successfully operated for years to produce low- and medium-Btu gas. This process is limited technically because it can use only certain types of coal feed and economically because it is not readily scaled to large size. The newer processes for coal gasification use more universal schemes for introducing coal and promise lowered cost through larger size and higher pressure of operation. Highpressure reaction gives greater throughput and shifts the chemical equilibrium $2H_2 +$ $2CO \approx CH_4 + CO_2$ toward methane, so that less hydrogen must be added in the final methanation step. But it is this combination of high pressure and large volume that leads directly to the first major materials problem.

The heart of a coal gasification plant is 20 FEBRUARY 1976

the reactor vessel, wherein the coal is reacted with oxygen and steam to produce a gaseous mixture of methane, carbon monoxide, and hydrogen along with carbon dioxide, water, hydrogen sulfide, and other impurities. To maximize the methane content, the pressure may be 2000 psi and the temperature between 1150° and 1250°K (1600° and 1800°F) for high reaction rates. These temperatures are well above the working strength of steel-about 730°K (850°F)-so a thick ceramic liner like highdensity alumina must be provided to insulate the steel surface. The vessel will be subjected over long periods to extremely aggressive environments, and the problem will be aggravated by the thermal stresses accompanying any necessary shutdowns of the reactor. The normal method for increasing the resistance of ceramic material

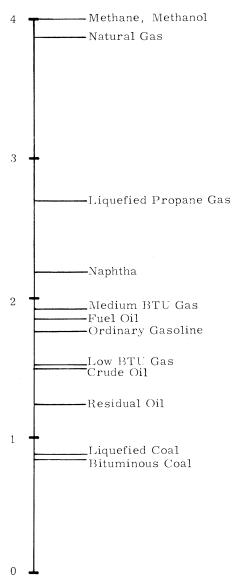


Fig. 2. Atomic hydrogen/carbon ratios for various fuels. Additional hydrogen, amounting to about 0.35 unit on this scale, is required for coal liquefaction. Most of it combines with sulfur and oxides in the coal to create hydrogen sulfide and water.

to chemical and mechanical degradation increasing the density—decreases the desired insulating property. A material satisfying both conflicting requirements must be developed and evaluated in the actual environment of the reactor.

The reactor vessel may reach 7.6 m in diameter and 76 m in height (25 by 250 feet), weighing as much as 1500 tons in the largest of these units (7). Even the "small" vessels in the high-pressure, high-temperature plants under consideration may be larger than the pressure vessels in a typical nuclear power plant. The high-strength steel exposed to 700° to 730°K (800° to 850°F) will be subjected to a high-pressure hydrogen environment for many years of operation. Should the reactor suddenly be shut down for some operational emergency, the temperature of the steel will drop rapidly, trapping the hydrogen at pressures far above its equilibrium value. Microcracks and voids may be introduced as the steel is again heated to operating temperature, providing potential nuclei for subsequent cracks or fractures. These phenomena must be much better understood so that any necessary modifications to steel alloys can be made before large reactor vessels are built.

The mood of the country is such that major engineering failures will no longer be tolerated. Since a reactor vessel may cost as much as a half-billion dollars. financial arguments also preclude the loss of a reactor through destructive failure. The need to virtually guarantee no failure during the operating lifetime puts great pressure on the design, evaluation, and testing of such reactors, including all aspects of the materials. The problem is challenging indeed, because the operating conditions threaten to be more severe than any experienced to date, yet at the same time the reactors are so big as to require field assembly. We have no procedures for automated welding of such large-volume vessels in the field and no proved techniques for nondestructive field testing of large-volume vessels with walls 30 cm (1 foot) thick. The difficulties we have experienced with the high-pressure tubing of the steam portion of pressurized water reactors should alert us to the magnitude of effort that will be required to satisfactorily develop large reactor vessels. A promising material for the pressure vessel is 21/4 percent chromium-1 percent molybdenum steel.

The second major materials problem in coal gasification is the erosion-corrosion of components that must contain or control moving fluids containing particulates. This problem is similar to that in coal liquefaction, but is possibly worse in gasification because of the higher temperatures and higher stream velocities involved. Because we have little experience in this area, considerable knowledge must be gained before we can understand the processes. New specifications must be developed and more definitive test and evaluation techniques proved before we can design adequate materials for long life and high reliability.

So little is known about the response of materials under these conditions that there is no obvious candidate. High-temperature alloys of chromium, iron, and nickel selected for resistance to scaling, sulfidation, and phase changes must be evaluated. Coating with refractory materials like alumina or zirconia may be required to protect the alloys from erosion.

Water-moderated reactors. An enormous amount of effort has been spent on materials for nuclear reactors: understanding radiation effects, evaluating materials in test reactors, and the like. The materials that form the neutronic system have performed satisfactorily; however, difficulties in the secondary steam system have led to excessive downtime. Stress corrosion has caused leakage in the tubes, particularly at positions where local geometry causes stagnation. One manufacturer has shown that this problem can be greatly reduced by controlling the alkalinity of the water to a narrow range by buffering with a mixture of disodium hydrogen phosphate and trisodium phosphate. Materials with greater resistance to stress corrosion should, nevertheless, be developed as one step toward demonstrating more reliable performance of power reactors.

Municipal waste. The energy content of recoverable organic waste produced in this country is now greater than 2 guads per year and is increasing in proportion to the population. Most of the recoverable energy is contained in municipal waste, which is a mixture of metals, glass, dirt, and combustibles (8). When the raw refuse is incinerated directly to recover the heat content, highly corrosive slags are produced, which attack the heat transfer surfaces. Incineration slags are very complex and contain nearly all the elements of the periodic table, the primary constituents being silica, alumina, iron oxides, and calcium oxides, with lesser amounts of titania and magnesia. The mixture is highly variable from incinerator to incinerator, so it will be particularly difficult to develop refractory materials that can universally withstand the particularly destructive environments in waste combustion units.

It will generally be desirable to separate the noncombustible materials before combustion or pyrolytic conversion to fuel for three reasons: (i) to recover the economic value of the metals and glasses, (ii) to recover the considerable energy investment in originally producing the metals and glasses in the waste (estimated to be 1 percent of the national energy consumption), and (iii) to minimize the slag corrosion problem in the combustor or reactor. The separation procedures involve shredding, screening, air classification, magnetic and eddy current separation, gravity separation, and flotation. The shredders used to comminute the municipal wastes are subject to considerable wear from the abrasive action of the refuse. Because of this gradual wear, the characteristics of the shredded product change, giving rise to difficulties in classifying, feeding, and burning the material. Therefore, development of better abrasion-resistant materials for shredders would accelerate exploitation of this important energy resource.

High-temperature turbines. The efficiency of a gas turbine in converting the energy content of the gas to mechanical motion is limited by the input temperature. Since ceramic materials are inherently tolerant to high temperatures, they could contribute to the development of turbines of higher efficiency. One problem lies in demonstrating long life of ceramic turbine blades when subjected to the repeated temperature shocks of start-ups and continuing centrifugal stress. Since a life of 30 years is the norm for large electric generating equipment, life predictions must be based on an understanding of pertinent degradation mechanisms and on accelerated tests that can be correlated to operating conditions.

Experimental work in a joint government-industry program has demonstrated that silicon nitride ceramic blades can operate at a temperature of 1650°K (2500°F) without cooling (9) so that, combined with a second stage of conventional steam, the overall combined cycle efficiency can be 49 percent. Developing the ceramic blades to a commercial level will, however, require considerable additional effort. We lack knowledge and experience in the design criteria for such applications of brittle materials. Designing with ceramics is in no respect similar to designing with metals. A whole new field of knowledge and practice must be developed to deal with problems such as failure mechanisms, creep, and fatigue over long periods at high temperatures and stresses. In addition, forming and rapid machining processes for the ceramics will require development.

In the meantime, metallic alloys are being pushed toward 1370° K (2000°F) by internal cooling and composite strengthening (10).

Geothermal. Present commercial production of electricity from geothermal

sources in the United States is limited to the Geysers field near San Francisco where dry steam (steam vapor containing no free water particles) is available (11). Such sources are limited, and any substantial contribution to the energy program must come from liquid-dominated geothermal fields, or from high-temperature dry rock or magma in which water is circulated from the surface. In either case, hot and extremely corrosive liquid must be dealt with. The largest proved resource in this country is near the Salton Sea in California, but the liquid-dominated fields there have a salinity content up to 25 percent by weight compared to 3.5 percent for seawater. The Salton Sea brine also contains chlorides of 13 other elements. When it is fed directly to a turbine, scale is deposited on iron surfaces of the well head, steam pipes, separators, and turbines; corrosion attacks turbine nozzles, blades, and shaft seals; turbine blades are eroded by fine rock dust blown from the well in quantities that exceed the collecting power of the separator; and on iron parts, coatings are formed composed of iron oxide silica and magnesia. Candidate materials that resist corrosion by brines are high-purity, lowglass ceramics, tantalum, titanium, and perhaps zirconium and plastics. Known for high-temperature resistance and hydrolytic stability are polytetrafluorethylene (Teflon), poly(phenylene sulfide), and poly(phenylene oxide). Other potentially useful plastics are polybenzimidazoles and polyquinoxalines, but few data are available on their hydrolytic stability. It is likely that considerable materials development will need to be accomplished along these lines before recovery of geothermal energy is practical on a large scale. The potential, however, is for as much as 5 quads per year from the Salton Sea area.

Midterm-1990 to 2005

During this period, additional technologies may start to make significant contributions to our energy program. Two represent essentially new resources; the others are concerned with processing of energy.

Fast breeder reactors. The liquid metal fast breeder reactors will operate at a much higher flux (10^{16} compared to 10^{13} neutrons per square centimeter per second in a thermal reactor). This high, fast flux produces many voids in metals, which in simulation experiments cause about 20 percent swelling (*12*). Such swelling would require the design of greater spacing between fuel pins to maintain coolant flow. But since high density of fuel is of first importance to the breeding ratio, to hold swelling to a few percent it will be necessary to develop ways to force recombination of the vacancies and interstitials formed by neutron knock-ons before the vacancies can migrate and cluster to form a void. This might be accomplished by alloying or doping with an element, such as a rare earth, which forms active sites for recombination through trapping of interstitial atoms. Considerably more fundamental understanding of the mechanisms will be needed to accomplish this goal.

Photovoltaic conversion of solar energy to electricity. The silicon solar cell, a derivative of the early transistor work at the Bell Telephone Laboratories, has proved its merit on many space flights, where it is the prime electrical power source. A fraction of the incident optical energy, typically 10 to 12 percent, is converted directly to electrical energy. For large-scale application in the U.S. energy economy, the problem is entirely one of cost (3). Solar cell arrays now cost \$20,000 to \$80,000 per peak kilowatt compared with approximately \$500 per kilowatt for conventional steam electric generators (which, of course, require fuel). Cost reduction of two orders of magnitude calls for revolutionary approaches to the system design, the materials, and the methods of manufacturing. One approach is to replace the silicon single-crystal cell with a material or materials that have the appropriate semiconducting properties and yet can be deposited as thin films with suitable properties. Materials of this type that have been actively studied incude CdS and CdTe. The most advanced thin-film solar cell is the $CdS: Cu_2S$ heterojunction. It can be fabricated in a manner amenable to large-scale production techniques. Neither this cell nor the variety of other homo- and heterojunction thin-film cells [such as GaAs, GaAlAs: GaAs, CdS: CdTe, and CdS (CuInSe₂)] is nearly as well understood as single-crystal silicon cells, so considerable work will be required before we can determine whether this is the most promising way to achieve direct solar electric power. Availability of materials such as cadmium and gallium must also be established.

Since silicon is so thoroughly understood, some feel that it represents the most promising route to success. New preparation and processing techniques (such as growing long ribbons of single-crystal silicon) may reduce the basic material cost by an order of magnitude. Other processing refinements and the economy of scale associated with very large production quantities can further reduce costs. With optical focusing systems to concentrate sunlight

20 FEBRUARY 1976

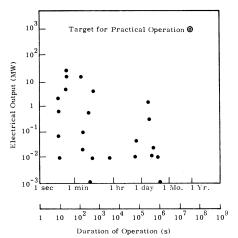


Fig. 3. Output electric power as a function of test duration for open-cycle MHD units using clean fuel (17). Operating time was limited principally by materials properties.

onto the cell so that it is, in effect, working harder, fewer cells will be needed to produce the same amount of electricity.

For any of the solar energy methods photovoltaic, wind, ocean thermal gradient, space heating, or water heating—systems with lifetimes of 25 years or more are required. It will be difficult to provide materials that operate that long in the natural environment.

Magnetohydrodynamic (MHD) conversion of coal. Magnetohydrodynamics offers a way to convert the energy in coal to electricity without rotating machinery (13). In principle, an easily ionized element such as potassium or cesium is seeded into the gaseous combustion products to provide good electrical conduction. The fastflowing, high-temperature gas is channeled into an intense (~ 5 tesla) magnetic field with electrodes at right angles to the field. The Lorentz force on the moving conductor generates a voltage on the electrode, allowing electric energy to be extracted. If the goals for an operating temperature of 2500°K can be met, an MHD system followed by a conventional steam cycle is estimated to achieve 50 percent efficiency.

No materials are known that can withstand the environment for very long. Figure 3 shows the limited operating times that had been achieved up to June 1975 with clean fuels in MHD test configurations. Economic operation will require at least 20 times the power levels and 20 times the duration of operation achieved in these tests. Moreover, coal combustion gas will coat all surfaces with slag, the uncombustible content present in all coal. Oxides of iron, aluminum, and silicon are the main components of slag; in combination with the seed they react with surfaces in ways that have not been measured, let alone understood.

Development of the electrode material alone will be a major task. The electrical resistivity should be less than 0.01 ohm meter and relatively independent of temperature. It must withstand mechanical and electrochemical erosion while sustaining heat fluxes of 1.5×10^6 to 3×10^6 watt/m² (0.5×10^6 to 1.0×10^6 Btu's per hour per square foot), comparable to the heat fluxes at the side of a reentry vehicle. The electrode material should have no phase change up to 2100°K and low chemical reactivity with oxygen or the seed-slag mixture.

In early work in this country metal electrodes (copper or Inconel) have been used at modest temperatures with resultant lower efficiencies. Russian workers have reported encouraging results with electrodes made of the borides of titanium, zirconium, niobium, and alloys of these (14). For the future, lanthanum chromic oxide or mixed chromates, or zirconia or zirconia-ceria mixtures, hold promise because of their high-temperature properties, chemical inertness, and low specific resistivity.

Storage. Effective and economic means of storing electric energy are desirable for several reasons. First, intermittent sources such as sunlight or wind become more attractive with good storage methods. Second, the large day-night fluctuation of energy use could be leveled so that the least efficient and most fuel-expensive generating equipment could be eliminated. And third, some energy consumption (such as for personal transportation) could be shifted from petroleum-based fuel to electricity, which could be supplied from coal or nuclear sources.

The only device under active consideration for storing electric energy in its own form is a superconducting solenoid (15). Since efficiency can only be achieved at large scale, experimental development costs have been large, and the program has not yet caught the imagination of any funding organization. Other methods of storing electric energy depend on first transforming it to some other form of energy. Most practical is the pumping of water uphill into a reservoir at night and recapturing the stored energy by having it flow downhill during the day. The number of reservoir sites near areas of large energy consumption is limited, however, and lakeside residents may not always accept a lake whose level changes several meters each day.

Electrical energy is traditionally stored as electrochemical energy. Lead acid batteries are in large production and are reasonably inexpensive, but they do not store sufficient energy per unit weight to be used

Table 1. Operating conditions envisaged for the first-wall components of fusion reactors, based on a wall loading of 1 Mw/m^2 . Data are from (16, p. S9).

Parameter	Value
Temperature (°K)	600 to 1300 (steady state) $\Delta T \approx 50$ to 300 (thermal pulse)
Neutron exposure (neutrons per square centimeter per year)	10^{21} (14.1 Mev) 10^{22} (total)
Damage rate (displacements per atom per second)	10 ⁻⁶ to 10 ⁻¹
Gas generation rates (atomic parts per million per year)	75 to 500 (hydrogen) 30 to 600 (helium)
Stress levels (megapascals)	10 to 100
Cycles per year, excluding mirror machines	$6 imes 10^3$ to $3 imes 10^8$

for personal vehicle propulsion. Nor do they attain the long life and large number of charge-discharge cycles needed for load leveling at central plants. Another disadvantage for either application is the inability of the lead storage battery to sustain repeated deep discharges. The nickeliron battery, developed by Thomas Edison in 1901, has excellent properties, including long life and many discharge cycles, but it is too expensive for large-scale application. The same is true of silver-zinc or nickelcadmium batteries.

A large impact on the overall national energy program will probably be achieved only through development of completely new battery systems, and those in turn are almost entirely dependent on materials developments. A number of electrochemical systems are under intensive investigation to satisfy stringent new requirements for batteries. These include a lithium-sulfur couple with a molten salt electrolyte, sodium-sulfur with a solid ceramic (beta eucryptite) electrolyte, and lithium chlorine with a molten salt electrolyte. For each of these not only is a whole new technology required, but serious materials problems arise in constructing the battery cells. The positive electrode and its attachment to the current collector suffer a high (oxidizing) potential, which is aggravated by elevated temperatures and any solid oxide electrolytes present. A new material is required that will adequately withstand this destructive environment. The terminals that carry the current through the cell wall must be insulated, and an impervious ceramic material must be developed which is sufficiently resistant to corrosion by the electrolyte.

The allowable cost of the raw material used to fabricate such a battery makes the materials development program truly formidable. A simple calculation shows that the materials can cost the manufacturer no more than 30 cents per pound if the specific energy density is 40 watt-hours per pound, a reasonable goal (2). Thus, any material used in quantity in the battery must be readily available at low cost.

Flywheeels provide an alternate method

for storing electric energy for load leveling or transportation. The critical material parameter is the ratio of strength to weight. Composite materials with fibers such as Kevlar in modified epoxy have strength-toweight ratios four times that of highstrength steel. The principal problem will be developing adequate two-dimensional strength for practical wheel configurations.

Long Term-2005 and Beyond

Great hope is being placed in controlled fusion-that is, the nuclear reaction of hydrogen isotopes-to furnish the largest portion of the energy that we will need in the long term. The three principal approaches, in order of funding support, are: magnetic confinement, laser fusion, and electron beam fusion. Each is incredibly difficult and beyond the level of technology yet achieved in any other program. Each depends in a critical way on the development of new materials, new concepts, and a deeper understanding of physical phenomena. Materials problems pervade all the programs, but the problem of the first-wall material in a controlled thermonuclear reaction will suffice to dramatically illustrate the challenge (16).

The reacting plasma at 100° to 500°MK must be contained in a vacuum envelope, the inner surface of which, closest to the plasma, is referred to as the first wall. The formidable environment at the wall is defined in Table 1. The first problem is to prevent material leaving the wall, which will poison the plasma. A surface element of low atomic number (such as beryllium) may be required. In addition, three points should be emphasized. (i) There is a high flux of 14.1-Mev neutrons from the deuterium-tritium reaction. The only available experimental results obtained at similar fluxes are from fission spectrum neutrons. High-intensity sources of 14-Mev neutrons have not yet been developed for test and evaluation purposes. (ii) At these fluxes every atom will theoretically be displaced more than ten times a year, yet the original mechanical properties must be maintained. (iii) Large amounts of soluble and insoluble gas will be generated in the bulk material, leading to a loss of ductility; this is further aggravated by the irradiation.

Several candidate materials are being investigated. More data are available on the austenitic stainless steels than on any other materials, including measurements of the influence of fission neutrons on their stress-rupture ductility. The stress-rupture life of steel is strongly reduced at temperatures above 550°C because of helium bubble formation and accumulation at internal surfaces such as grain boundaries (16, p. S8). The chromium in stainless steel has a high vapor pressure, and sputtering rates may be a problem under the intense bombardment of ions and neutral particles. Nevertheless, stainless steel is the likely candidate for first-wall designs, at least in the early development reactors.

The refractory metals-vanadium, niobium, and molybdenum-are promising first-wall candidates because of their structural strength and low vapor pressure at high temperatures. Because these three metals show loss of ductility due to helium gas bubble accumulation and neutron irradiation, alloys with titanium, zirconium, or chromium are more likely candidates. Whatever the alloy, it must withstand repeated stress cycling in the presence of intense irradiation, which produces voids, hydrogen, helium, and transmutation elements such as zirconium from niobium or chromium from vanadium. Experimental data will not be available until there is a new generation of neutron test facilities.

Magnitude of the Problem

This brief description of some of the materials problems in the energy program may leave some readers with the impression that each problem can be solved when necessary by a hard-hitting effort by one or two companies, perhaps with the support of a government laboratory. Don't believe it! These materials problems are as challenging as any we have ever faced, even allowing for the increased sophistication of materials science. A large, high-technology industry has increased the working temperature of the turbine blade 10°C per year, but for practical magnetohydrodynamics increases of hundreds of degrees are needed in the operating temperatures of materials. The transistor and its progeny did not dominate the electronics market until dozens of universities had formed solid-state research groups to understand silicon in exquisite detail, and if a different material such as CdS : Cu₂S is to be used for photovoltaics, a similar broad effort will be required. To prepare for the

era of nuclear power plants, this country has wisely supported for almost 20 years extensive studies on radiation effects in materials at universities and national laboratories. Since problems accompanying controlled thermonuclear reactions are far worse, a correspondingly greater understanding of and experience with the interaction of nuclear radiation with matter is needed before even demonstration models can exploit future successes in laboratory experiments.

To meet the diverse materials needs of the energy program, we will need substantial and sustained effort from universities, industrial organizations, and government laboratories, guided by close interplay with energy system designers.

References and Notes

- E. T. Hayes, Science 191, 661 (1976).
 For a brief discussion of nine elements that may be in short supply for the energy program, see Ad Hoc Committee on Critical Materials Technology in the Energy Program, Materials Technology in the Near-Term Energy Program (National Acad-emy of Sciences, Washington, D.C., 1974), pp. 115-125.
 B. Luwack, Natl Sci. Found, NSE DAN 74 677.
- 113-123.
 R. Lutwack, Natl. Sci. Found. NSF-RA-N-74-072 (15 October 1974).
 For a capsule description of 12 coal conversion programs, see Chem. Eng. Progr. 71 (No. 4), 61 (1975).
- (1975).
 Conversion factors for some units in this article are: 1 quad = 10¹⁵ British thermal unit (Btu) = 1.3 × 10¹⁸ joules; 1 pound per square inch (psi) = 7100 pascals. *Electron World* 184 (No. 2), 28 (15 July 1975).
 A. J. McNab, "Design and materials requirements for coal gasification," *Chem. Eng. Prog.* 71, (No. 11), 51 (1975).
 A. Abrie description of the technical as well as account of the technical as well as account.
- 8. A brief description of the technical as well as eco-
- Provide description of the technical as well as eco-nomic aspects is given in J. G. Abert, H. Alter, J. F. Bernheisel, *Science* 183, 1052 (1974).
 D. J. Lines (*10*, pp. 155–186).
 P. R. Sahm and M. O. Speidel, Eds., *High-Tem-*

perature Materials in Gas Turbines (Elsevier, Amsterdam, 1974).

- sterdam, 1974).
 See G. R. Robson [Science 184, 371 (1975)] for a broader perspective on geothermal energy.
 For a technical discussion of radiation damage in breeder reactor materials see G. L. Kulcinski, P. G. Doran, M. A. Abdou, Am. Soc. Test. Mater. Spec. Tech. Publ. STP-570 (1975).
 R. J. Rosa, Magnetohydrodynamic Energy Conversion (McGraw-Hill, New York, 1968); chapter 1 provides an engineering introduction to the basic principles.
- 14.
- 15.
- 16. H
- I provides an engineering introduction to the basic principles.
 G. V. Samsonov, E. P. Sprashinin, N. I. Mazur, V. V. Morozov, A. Kh. Achurin, Ur. A. Kunipskii, *High Temp. (USSR)* 12, 551 (1974).
 G. C. Gardner, A. B. Hart, R. B. Moffitt, J. K. Wright, *Energy Dig.* 4 (No. 3), 38 (May-June 1975).
 F. L. Vook et al., *Rev. Mod. Phys.* 47, Suppl. 3 (1975); see reference 2, p. S8, for technical background on the CTR first-wall problem.
 W. K. Jackson et al., in Sixth International Conference on Magnetohydrodynamics Electrical Power Generation, J. E. Kleteis, Ed. (National Technical Information Service, Springfield, Va., 1975), vol. 5, p. 40, figure 8; see also P. C. Strangeby, Univ. Toronto Inst. Aerosp. Stud. Rev. No. 39 (1974), p. 35, figure 7. 17. (1974), p. 35, figure 7.