MATERIALS PERFORMANCE IN ADVANCED COMBUSTION SYSTEMS

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ABSTRACT

A number of advanced technologies are being developed to convert coal into clean fuels for use as feedstock in chemical plants and for power generation. From the standpoint of component materials, the environments created by coal conversion and combustion in these technologies and their interactions with materials are of interest. The trend in the new or advanced systems is to improve thermal efficiency and reduce the environmental impact of the process effluents. This paper discusses several systems that are under development and identifies requirements for materials application in those systems. Available data on the performance of materials in several of the environments are used to examine the performance envelopes for materials for several of the systems and to identify needs for additional work in different areas.

BACKGROUND

The production of clean liquid and gaseous fuels from coal offers a means of reducing U.S. dependence on imported oil while using our vast coal reserves in an environmentally acceptable fashion. A significant reserve of high-sulfur coal is available for energy use, provided it can be cleaned before or during conversion to meet federal emission standards for effluents. Coal is a complex and relatively dirty fuel that contains varying amounts of sulfur and a substantial fraction of noncombustible ash constituents. Over the last 20 years, significant progress has been made toward the conversion of coal into synthetic fuels and toward the generation of electric power through coal combustion.

An examination of the use of fossil fuels in U.S. electric power generation (see Fig. 1) shows that coal use in this sector grew dramatically from 1978 to 1986, after which it stabilized at about 80% (DOE, 1990). Consumption of natural gas and crude oil in the power sector declined during the same period, to about 14 and 6%, respectively. Further gains for coal in this sector are considered unlikely in view of the more stringent environmental regulations for power plants and the logistics of those plants that must use gas or oil as fuel. Even though the relative percentage of coal consumption may not change significantly, the tonnage use of coal is expected to increase as demand for electricity increases.

In recent years, extensive discussions have been held in public forums and policy meetings on global warming, CO2 generation, acid rain, more stringent New Source Performance Standards, and environmental compliance, as well as on the role of fossil-fired power plant effluents in all of the above. It is evident that electric utilities are concerned with these deliberations and their effects on utility use of different coal feedstocks. Especially vulnerable are utilities that use eastern high-sulfur coal. Because of current and future legislation and anticipated stricter emission standards, it is obvious that systems with higher thermal efficiency and lower impact on the environment be the norm of the future.
The advanced systems of interest are

(a) Pulverized-coal-fired boilers with advanced steam cycles (PC)
(b) Integrated gasification combined cycle (IGCC)
(c) Fluidized-bed-combustion cogeneration (FBC)
(d) Magnetohydrodynamic topping cycles (MHD)
(e) High-performance power system (HIPPS) and
(f) Low-emission boiler system (LEBS)

**Pulverized-Coal-Fired Boilers**

Over the past few years, extensive studies have been conducted to develop PC boilers with advanced steam-cycle conditions to improve the thermal efficiency of these systems (Culler, 1985). The staged development of these systems has the ultimate goal of achieving steam pressure and temperature of 34.5 MPa (5000 psig) and 650°C (1200°F), respectively, from the current values of 540°C (1000°F) and 16.5–24 MPa (2400–3500 psig). Fireside metal wastage in coal-fired boilers can occur via gas-phase oxidation or deposit-induced liquid-phase corrosion. The former can be minimized by using materials that are oxidation-resistant at service temperatures of interest. On the other hand, deposit-induced corrosion of materials is an accelerated type of attack influenced by the vaporization and condensation of small amounts of impurities such as sodium, potassium, sulfur, chlorine, and vanadium, or their compounds, which are present in the coal feedstock. The effect of boiler deposits on the corrosion of structural materials has been fairly well established by Reid (1971) and Wright et al. (1978), and the temperature regimes in which this corrosion occurs are summarized in Fig. 2.

A number of factors, including sulfur, alkali, chlorine in coal feedstock, excess air level used in the combustion process, and metal temperature, determine the extent of corrosion of superheater materials in coal-fired boilers. Typical corrosion data, developed by Kihara et al. (1983), for several candidate alloys are shown in Fig. 3. It is evident that at steam temperatures of 540–565°C (1000–1050°F), the metal temperature will be in the range of 600-630°C (1112–1165°F) and the corrosion rates will be acceptable for long-term service. In advanced steam cycles with anticipated steam temperatures and pressures of 650°C (1200°F) and 34.5 MPa, metal temperature can attain 700°C or higher, resulting in increased corrosion rates. It is obvious that new materials or corrosion protection of existing materials are needed for reliable service of superheaters in advanced steam-cycle plants.

Several materials have been evaluated by Gold and Jaffee (1984) for advanced steam turbine applications from the standpoint of rotor size, rotor material strength, embrittlement characteristics, thermal cracking, bolting and transition joints. It has been concluded that available materials (developed over the last 10 years with “clean steel” technology) will be adequate for turbine applications in advanced steam-cycle systems.

**Figure 2. Regimes of fireside corrosion in coal-fired boilers**
Gasification Combined Cycle

The coal gasification technologies emphasize production of intermediate-energy syngas by using oxygen and steam to gasify the coal. Both dry ash and slagging gasifiers are being developed. Slagging gasifiers, into which finely ground coal is injected through a burner, have the advantages of rapid gasification rate and lower consumption rate of steam and water. Further, the process lends itself to lower emission of toxic materials because all potentially harmful organics are destroyed at the elevated temperature of the process. Figure 4 shows a schematic diagram of an entrained slagging gasifier with syngas coolers. From the materials standpoint, the components of interest in these systems are

(a) Syngas coolers
(b) Refractory lined vessels
(c) Hot gas cleanup system
(d) Gas turbines

Syngas coolers are generally used to recover the sensible heat from the raw gas; these components are very large (especially compared to the gasifier) and are fabricated with metallic materials. Syngas coolers are generally used as evaporators but generation of superheated steam is also a possibility. The metal temperature of the syngas system is at of 300–500°C and the metal will be exposed to a highly reducing atmosphere in the presence of hydrogen sulfide, the concentration of which will be determined by the sulfur content of the coal feedstock. In addition, the environment will contain hydrogen chloride. The gas temperature in the cooler will be 1100–1300°C (2000–2350°F) and the cooler will experience on/off service, resulting in corrosion contribution during downtime. Sulfidation is the major mode of material degradation and is accompanied by pitting/crevice corrosion of materials that are susceptible to aqueous corrosion during downtime. Extensive test programs have been conducted to evaluate the corrosion performance of several materials in
simulated syngas environments and in syngas coolers of large gasifier systems. These materials include low-alloy steels, aluminized and chromized steels, and several types of austenitic stainless steels. Corrosion rates have been established, but there is concern about extrapolating the relatively short time data to long-term predictions on life of the component, because the materials are susceptible to breakaway or accelerated corrosion when exposed to mixed-gas environments (Natesan, 1987; Perkins and Bakker, 1987).

Corrosion and wear performance of refractory materials largely determine the overall availability of plants in coal gasification schemes. Chemical compatibility of refractories with coal slags has been the subject of intense study for the past 10 years or so. It has been shown that refractories containing mainly chromia-alumina solid solutions formed thick scales of an \((\text{Mg,Fe})(\text{Cr,Al})_2\text{O}_4\) spinel that seemed to be the most stable phase in contact with coal slags (Kennedy, 1981). Correlations of refractory wear data with operating conditions have shown wear rates of <0.01 mm/h during periods of steady-state operation. Even though a two-year life for the refractory lining is currently possible and the gasifier can be relined on an established maintenance schedule, development of long-life refractory bricks with adequate corrosion resistance in molten coal-slag environments while maintaining adequate mechanical integrity, e.g., resistance to creep and thermal shock, is still needed.

The hot gas clean up system involves passing the raw gas from the gasifier in to a porous ceramic filter, which lets the gases pass through and while the particulate are trapped in the filter. The filters are periodically pulsed with a gas flow in the reverse direction to clean the filters of particulate material. The filter designs considered include fabrics made from ceramic fibers, candles made of ceramic fibers or powders, and monolithic cross flow type. The materials considered are cordierite, silicon carbide, quartz, zirconia, alumina, and mullite and a combination of them.

Corrosion of gas turbine materials in the presence of liquid sodium sulfate, either by itself or in combination with sodium chloride, has been a problem in gas turbines; this corrosion process has been termed "hot corrosion" to differentiate it from gas-phase sulfidation attack. In addition, the gas velocity in the turbine can range from 200-500 m/s which causes erosion degradation of blade material. The combination of hot corrosion/erosion is of serious concern in obtaining adequate life for land based turbines, especially those that utilize coal-derived products. Discussions on corrosion evaluation of gas turbine materials and coatings is beyond the scope of this paper. A comparative data for corrosion of simple aluminides, aluminides with rhodium and platinum bond coats, and \(\text{CoCrAlY}\) overlay coating after exposure to a hot corrosion environment at 982°C (1800°F) is shown in Fig. 5 (Kemp, 1980). The results show that the performance of a given coating is strongly influenced by the substrate alloy and a bond coat of precious metal platinum (rather than rhodium) is beneficial in reducing corrosion in nickel-base superalloys. The overlay CoCrAlY coating on a cobalt-base MarM-509 alloy exhibited the best performance among all the coatings examined in this study.

**Fluidized-Bed Cogeneration**

This approach employs the technology of coal-fired cogeneration in the form of a combined-cycle atmospheric or moderately pressurized fluidized bed in which an air heater heats the air in a gas-turbine cycle for the cogeneration of electric and thermal energy. The hot gas clean up system involves passing the raw gas from the gasifier in to a porous ceramic filter, which lets the gases pass through and while the particulate are trapped in the filter. The filters are periodically pulsed with a gas flow in the reverse direction to clean the filters of particulate material. The filter designs considered include fabrics made from ceramic fibers, candles made of ceramic fibers or powders, and monolithic cross flow type. The materials considered are cordierite, silicon carbide, quartz, zirconia, alumina, and mullite and a combination of them.
electricity and useful thermal energy. Figure 6 shows schematic diagrams of typical bubbling- and circulating fluid-bed systems. The key components of relevance in these systems are

(a) In-bed air-tube heat exchanger
(b) Steam-tube heat exchanger and
(c) Gas turbines

The fluidized-bed combustion of coal produces gas that principally contains O₂, CO₂, H₂O, SO₂, and N₂, together with minor amounts of SO₃, nitrogen oxides, chlorides, and other volatilized salts. The gas composition depends importantly on the air/coal stoichiometric ratio. In addition, SO₂ concentration in the gas phase will be determined by the type and amount of sulfur sorbent and the sulfur content of the coal used in the combustion process. However, the local chemistry beneath the deposit could be quite reducing relative to the bulk gas composition. This can have important implications for the initiation/propagation of sulfidation penetration of alloys and can lead to substantial reduction in component life.

Materials/environment interactions in FBC systems indicate that structural alloys develop predominantly oxide scales when exposed to O₂–SO₂ gas mixtures of combustion atmospheres at elevated temperatures (Natesan, 1990). Natesan et al. (1987) made a detailed evaluation of materials information developed from exposures of cooled and uncooled corrosion/erosion probes in 13 FBC facilities. In addition, materials tests were conducted for 3000 h in simulated combustion atmospheres at Argonne National Laboratory and for 2000–h in the DOE atmospheric fluidized-bed combustion facility in California (Natesan and Podolski, 1988; Natesan et al. 1991). Corrosion information, developed from these studies have been used to assess performance of several candidate materials as a function of specimen orientation, exposure location in the combustor, and time of exposure. Some of the conclusions drawn from these studies are discussed in the following paragraphs.

For air-tube heat exchanger applications at temperatures near that of the bed, corrosion is the dominant degrading mechanism for the materials; erosion is generally not of concern. Under these conditions, performance of austenitic stainless steels, e.g., Types 304, 310, and 330, and alloys such as HR 3C, FW 4C, and 8XX is adequate and these materials have exhibited low depths of penetration after exposure in (a) an AFBC facility, (b) a laboratory test under gas cycling conditions, and (c) a more severe laboratory test under low oxygen partial pressure (pO₂).

Alloys such as HS 188, HS 556, HK 40, and 800H exhibited catastrophic corrosion in the presence of deposit material and sustained low-pO₂, based on a 3000–h laboratory test. Although these test conditions are more severe than those the materials will be subjected to in a typically well-run FBC system, the data nevertheless suggest the susceptibility of these materials to accelerated...
corrosion. Alloys such as HH, HP 50, 253 MA, XM 19, Sanicro 33, HS 556, and HS 188 exhibited unacceptable corrosion behavior when the alloys were in contact with bed material. Figure 7 shows a comparison of corrosion penetration in alloys exposed to FBC environments with and without sulfated sorbent deposits.

Another aspect to materials selection for the air heater tubes in cogeneration systems is the mechanical properties of the materials at elevated temperatures. At the high temperatures of interest, time–dependent properties such as creep rate and creep rupture life will determine the adequacy of the material. Although the ASME code does not specify information for temperatures beyond 816°C, the criteria on maximum allowable stress can probably be extrapolated to higher temperatures. These criteria specify that the maximum allowable stress for the material shall not exceed the lowest of the following: 100% of the average stress for a creep rate of 0.01% in 1000 h, 67% of the average stress for rupture at the end of 100,000 h, or 80% of the minimum stress for rupture at the end of 100,000 h. A compilation has been made of the available data on the creep properties of candidate alloys to examine the effect of metal temperature on the creep strengths and creep rates (Natesan, 1992). Based on the criteria of 67% of the average stress for rupture at the end of 100,000 h, allowable stress values were computed (many of the alloys are not coded under ASME rules, but it is assumed that the criteria used for the coded materials will be applicable to noncoded alloys). The computed values are shown in Fig. 5. The allowable stress values are ≈6.9 MPa (1000 psi) at 871°C (1600°F), based on air test data without allowance for fireside corrosion effects.

For steam–tube heat exchanger applications at temperatures in the range of 500–650°C, both corrosion and erosion processes need to be considered in the assessment of materials performance. Further, tube bank geometry, tube bank distance from the air distributor, coal and limestone feedstock chemistries, and bed operating conditions all influence material performance. A number of materials have performed well as evidenced by the data developed over the years by exposure of corrosion/erosion probes in TVA–20MW and TVA–160MW atmospheric FBC facilities.

The gas turbine materials in cogeneration systems that use air as the working fluid will be exposed predominantly to heated air, with supplemental heat from the burning of clean fuel.

![Figure 7](http://proceedings.asmedigitalcollection.asme.org)
Magnetohydrodynamic (MHD) generation of power is based on the direct conversion of fuel energy into electrical energy by flowing a heated, electrically conducting fluid through a magnetic field. In coal-fired open-cycle MHD system, the working fluid is utilized on a once-through basis and consists of multiphase fossil fuel combustion products. Figure 9 shows a schematic of the open-cycle MHD system. The overall plant consists of a topping cycle, where the electrical energy is directly produced by the MHD generator, and a steam-bottoming plant, where additional heat energy and the seed material are recovered. Key components of interest in this system are

- Slagging combustor
- Channel electrodes and insulators
- Radiant boiler
- Downstream superheaters and evaporators

The MHD combustor system consists of an oil-fired heater, a precombustor, slagging first stage, and a second stage. The oil-fired unit produces an oxidant at ≈650°C (1200°F) for use by the precombustor. The precombustor further heats the oxidant to about ≈1600°C (2900°F), using a fraction of the total coal flow to the combustor. Within the first stage, the remainder of the coal is burned under fuel-rich conditions, and potassium compounds are injected near the exit of the first stage to make the increase the electrical conductivity of the gas. Oxygen is injected in the second stage to complete the combustion process. A test program was conducted at Argonne to evaluate candidate materials in slag-side and water-side environments that simulate those anticipated in a prototype MHD combustor (Natesan et al., 1989). Based on corrosion information from this study and code-allowable stress values for different materials, maximum permissible operating temperatures were estimated for candidate materials at various locations in an MHD combustor. The results are shown in Table 1.

The life of an MHD channel is determined chiefly by the design and material selection of the internal wall elements—electrodes, sidebars, and insulators—which are collectively called the gas-side design. Adequate performance of materials selected for the MHD channel construction is mandatory for successful application of this technology in retrofit and commercial coal-fired energy systems. In the high-temperature environment of the MHD channel, vaporization of several coal/seed components and subsequent deposition of these materials on the walls of the channel can occur. This hostile environment generally contains potassium compounds, sulfur compounds, and ash/slag constituents. In the proof-of-concept
design, the channel is made of oxygen–free high–conductivity copper (OFHC); the caps are W, Pt, and stainless steel at different locations, and BN is used as the insulating material.

The major functions of the radiant boiler are to produce steam, remove the slag from the high–temperature combustion gases leaving the combustor, and cool the gases in a controlled manner to minimize NOx concentration in the gas phase. At present, combustion in the primary combustor is optimized to achieve the maximum power from the MHD channel, which implies an air/coal stoichiometric ratio of 0.50–0.60. These reducing conditions also result in low nitric oxide concentration. When the combustion ratios are substoichiometric, the gases entering the radiant boiler will be predominantly reducing (having a low pO2), and the sulfur levels in the gas can be high because of the use of medium– to high–sulfur coal. Studies conducted at Argonne have shown that carbon steel and low–alloy steels will perform adequately up to 400°C and that these materials, if protected with a stainless steel cladding or a ramming refractory coating, will

<table>
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<th>Component</th>
<th>Low–carbon alloy</th>
<th>Glidcop</th>
<th>OFHC</th>
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<tbody>
<tr>
<td>Pre–combustor</td>
<td>355&lt;sup&gt;a&lt;/sup&gt;</td>
<td>465&lt;sup&gt;b&lt;/sup&gt;</td>
<td>315&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
<td>Slagging stage</td>
<td>345&lt;sup&gt;c&lt;/sup&gt;</td>
<td>370&lt;sup&gt;c&lt;/sup&gt;</td>
<td>315&lt;sup&gt;e&lt;/sup&gt;</td>
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<tr>
<td>Second stage</td>
<td>–</td>
<td>–</td>
<td>315&lt;sup&gt;e&lt;/sup&gt;</td>
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<sup>a</sup>Oxidation limit based on data from Natesan, (1986).
<sup>b</sup>ASME code allowable stress limit.
<sup>c</sup>Sulfur corrosion limit.
<sup>d</sup>Waterside corrosion at 12 m/s; 230°C and fouling on fireside may lower this value.
<sup>e</sup>Waterside corrosion at 7 m/s; 230°C may lower this value.
be suitable for application in radiant boilers up to 550°C.

The gases that enter the secondary superheater (SSH), reheater, intermediate temperature air heater (ITAH), and economizers will have PO2 values that correspond to an air/coal stoichiometric ratio of 0.95–1.05, the actual value dictated by the nitric oxide concentration in the exit gas. Extensive testing of materials, conducted by Natesan and Swift (1989) at Argonne, showed that austenitic alloys will be adequate for SSH application at a metal temperature of 593°C. However, the same alloys under ITAH conditions (at 762°C) exhibited substantial corrosion. Figure 6 is a plot of metal recession data developed for several alloys under the ITAH, SSH, and the ITAH transition conditions. Also indicated in the figure are the corrosion limits of 0.5 mm/yr calculated by either linear or parabolic kinetics for the corrosion process. When linear kinetics are used, the low-to medium-chromium steels under ITAH transition conditions and most of the austenitic alloys (except 310 steel) under ITAH conditions exhibit corrosion rates much higher than the limit. On the other hand, when parabolic kinetics were used, all the austenitic alloys exhibited metal recession rates of <0.5 mm/yr under ITAH conditions; however, once the scale cracks/spalls or erodes away in the exposure environment, the chromium-depleted zone underneath the original scale will result in fast-growing iron oxide, and accelerated/breakaway corrosion would occur.

High-Performance Power System

The high-performance power system has the ultimate goal of producing electricity from coal with an overall thermal efficiency of 47% or higher (compared with ~35% for current systems) and to reduce CO2 emissions by 25–30% (Ruth, 1991). The pulverized-coal high-temperature advanced furnace (HITAF) in the HIPPS concept will heat air to an intermediate temperature of ~980°C (1800°F), and will burn supplemental clean fuel to boost the temperature of air to the turbine inlet to 1260°C (2300°F) or higher. Use of supplemental fuel can be reduced as HITAF technology evolves to permit air to be heated to higher temperatures in the furnace.

HITAF represents a major departure from conventional pulverized-coal-fired boilers in which steam is raised to a maximum of 538–600°C (1000–1110°F). Important differences are seen in the chemical/physical characteristics of the ash deposit layers, which are likely to be dominated by alkali sulfates rather than pyrosulfates or alkali-iron-trisulfates; and in the increased mobility of corrosion-accelerating agents in the deposit layers due to the much higher temperature of the heat transfer surfaces. A major challenge is to develop methods to combat severe deposition, erosion, and corrosion (DEC) of heat transfer surfaces exposed to higher than normal temperatures. These methods could include fuel selection; cleaning of aggressive contaminants from coal; fine grinding of coal; use of sorbents/additives; mitigation of deposit accumulation; and selection of advanced corrosion-resistant alloys, coatings, and ceramic materials for vulnerable heat transfer sections. A substantial body of information on a wide range of materials (many of them new and some yet to be developed) will be required in order to achieve adequate performance of components and enhanced reliability.

Low-Emission Boiler System

This system would utilize staged combustion to develop a power plant that will drastically reduce SO2, NOX, and particulate emissions from current levels. Even though LEBS is an extension of current boiler technology, the first stage of combustion will have fuel-rich or air-lean conditions with a resultant gas chemistry that will be reducing for the internal structural components, and the deposit characteristics will be sulfides of different elements rather than the sulfates/oxides that are prevalent in conventional coal-fired boilers. In this case, a better evaluation of currently used structural alloys in the LEBS environment will be needed to establish performance envelopes/limitations for the materials.
Figure 10. Metal recession data for several alloys coated with MHD deposit and exposed to different conditions for up to 2000 h.

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