

# HIGH-TEMPERATURE CORROSION IN POWER-GENERATING SYSTEMS

K. Natesan<sup>1</sup>

<sup>1</sup> *Energy Technology division,  
Argonne National Laboratory, 9700 S Cass Avenue, Argonne, IL 60439*

*key words: coal-fired systems, combustion, gasification, corrosion, materials*

**Abstract:** Several technologies are being developed to convert coal into clean fuel for use in power generation. From the standpoint of component materials in these technologies, the environments created by coal conversion and their interactions with materials are of interest. Coal is a complex and relatively dirty fuel that contains varying amounts of sulfur and a substantial fraction of noncombustible mineral constituents, commonly called ash. Corrosion of metallic and ceramic structural materials is a potential problem at elevated temperatures in the presence of complex gas environments and coal-derived solid/liquid deposits. This paper discusses the coal-fired systems currently under development, identifies several modes of corrosion degradation that occur in many of these systems, and suggests possible mechanisms of metal wastage. Available data on the performance of materials in some of the environments are highlighted, and the research needed to improve the corrosion resistance of various materials is presented.

## 1. Background

Poland has a significant coal reserve, which is mined for both domestic consumption and export to European countries and Russia. Furthermore,  $\approx 70\%$  of the electricity in Poland is generated by combustion of domestic coals. However, the power plants in Poland are of older vintage and current emission compliance requirements in Europe and improved process efficiency to mitigate CO<sub>2</sub> release necessitate the retrofit of existing power plants and use of advanced technology in construction of future power plants. Coal is a complex and relatively dirty fuel that contains varying amounts of sulfur and a substantial fraction of noncombustible mineral constituents, commonly called ash. Over the last 30 years, significant progress has been made toward the conversion of coal into synthetic fuels and toward the generation of electric power through coal combustion. For example, an examination of the use of fossil fuels to generate electric power in the U.S. shows that coal use in this sector grew dramatically from 1978 to 1986, after which it stabilized at  $\approx 80\%$  [1]. During the same period, consumption of natural gas and crude oil in the power sector declined to  $\approx 14$  and  $6\%$ , respectively. Even if the relative percentage of coal consumption does not change significantly, the tonnage use of coal is expected to increase as demand for electricity increases.

In recent years, global warming, CO<sub>2</sub> generation, acid rain, more stringent New-Source Performance Standards, environmental compliance, and the role of coal-fired power plant effluents in all of these areas have been discussed extensively. It is evident that electric utilities are concerned about these deliberations and the effects they will have on the selection of coal-fired processes by utilities and on the use of various coal feedstocks. Especially vulnerable are utilities that use high-ash coals and coals with high sulfur and chlorine content. Because of current and future legislation and anticipated stricter standards, it is obvious that systems with higher thermal efficiency and lower impact on the environment must be the norm of the future, irrespective of the location of the plant in the world.

Some of the advanced technologies under development for effective utilization of coal are

- Pulverized-coal-fired boilers with advanced steam cycles (PC)
- Low-emission boiler systems (LEBSs)
- Integrated gasification combined-cycle (IGCC) systems
- Fluidized-bed-combustion (FBC) cogeneration
- High-performance power systems (HIPPS).

Table 1 shows a comparative analysis of various technologies from the standpoint of efficiency, unit size, and capital cost [2]. Based on the cost of generating power and on the industry trends, power plants can be classified in terms of relative output of steam and gas turbines [2,3]. In PC systems with supercritical boilers, the output is 100% from steam turbines. In pressurized FBC systems, the split is 80% from steam turbines and 20% from gas turbines. In IGCC systems, the split is 45% from steam turbines and 55% from gas turbines. A comparative analysis of capital cost (\$/kw) and efficiency showed that gas turbine/simple-cycle systems are the cheapest, at \$175/kw with an efficiency of 35%. For the gas-fired combined-

Table 1. Efficiency, unit size, and capital cost of selected coal utilization technologies

Technology	Unit size (Mwe)	Net efficiency (%)	Capital cost (US \$/Kw)
Subcritical PC	50-1000	36-38	950-1300
Supercritical PC	50-1000	40-46	950-1600
PFBC	70-350	42-45	1000-1500
IGCC	100-320	43-45	1500-1600

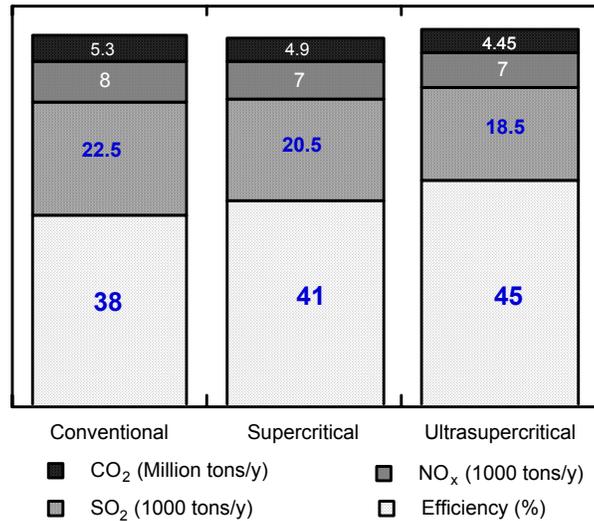


Figure 1. Efficiency, CO<sub>2</sub>, NO<sub>x</sub>, and SO<sub>2</sub> emissions in several 600-Mw coal-fired systems

cycle systems, capital cost and efficiency are \$450/kw and 55%, respectively. For the conventional PC boilers, these values are \$950-1300/kw and 36-38%, whereas for supercritical boilers the values are \$950-1600/kw and 40-46%. For both pressurized FBC and IGCC systems, they are \$1000-1600/kwh and 42-45%.

The use of various coals under differing combustion conditions, ranging from wide variations in the coal combustion/conversion gas chemistry to wide variations in the nucleation, growth, and condensation of particulates, can have a direct effect on material degradation in these systems. Contaminants such as alkali, chlorine, and sulfur vaporize during gasification and combustion and eventually condense on metal surfaces and the remove the protective layer from those surfaces by chemical reaction, fluxing, or fracture. Because processing conditions (temperature, pressure, air/fuel ratio, etc.) involved in the conversion of coal to gas are diverse, we need a thorough understanding of the influence of various gaseous species and particulates on material degradation to enable the selection of corrosion-resistant materials for a reliable system. Table 2 lists the service conditions and modes of degradation of key components (e.g., heat exchangers and gas turbines) of several systems that use coal as a feedstock [4]. It is evident from this table that the gas environment in these systems can vary widely in terms of oxygen activity, temperature range, types of deposits and particulates, and particulate velocity range. Furthermore, we can identify the key variables and possible rate-limiting steps (Table 3) for the corrosion, corrosion/erosion, and hot-corrosion/erosion phenomena that are operative in the degradation of materials in coal-fed energy-producing systems [4].

The development of the several advanced technologies, all of which emphasize high conversion efficiency and stringent environmental compliance, requires much higher temperatures than are presently in vogue and necessitates development of approaches to protect the structural materials/components from the hostile environments prevalent in these systems. In addition, the process changes involve air-deficient combustion, conditions of which also leads to an environment that is significantly more reducing and to deposits that are more corrosive than those prevalent in current combustion systems. Viability of the advanced technologies necessitates either the use of alternate “advanced” materials with inherently superior corrosion and strength properties (and significant added expense and less reliability) or modification of the surface regions of the current materials to accommodate the service requirements.

## 2. Pulverized-Coal-Fired Boilers

Over the past few years, extensive effort has been expended on the development of PC boilers with advanced steam-cycle conditions to improve the thermal efficiency of the PC systems [3]. Figure 1 shows comparative data on the efficiency and

Table 2. Service conditions and modes of degradation for component materials in coal-fired systems

Component System	Gas Env.	Gas Temp. Range (°C)	Metal Temp. Range (°C)	Deposit Type	Particulate and/or Part. Velocity	Mode of Degradation
<i>Heat Exchangers</i>						
PC boilers	Oxidizing	1300-1600	400-700	Alkali Sulfates Ash	Fly ash, <20 m/s	Alkali corrosion Fouling
FBC	Oxidizing, locally reducing	850	400-850	CaSO <sub>4</sub> , CaO Carbon, Fly ash Fly ash	Sorbent bed, fly ash 3-? m/s	Oxidation/Sulfidation Erosion
IGCC	Reducing, moderate to high H <sub>2</sub> S	900-1100	400-650	Fly ash Alkalis Chlorides	Fly ash, <20 m/s	Sulfidation/erosion? Fouling
HIPPS	Oxidizing	1300-1600	400-1300	Fly ash, Slag Alkali sulfates	Fly ash	Ceramic fracture Alkali corrosion Fouling
LEBS	Reducing, Sulfidizing	1300-1600	400-600	Sulfides Slag	Fly ash	Sulfidation Deposit corrosion Fouling
<i>Turbines</i>						
IGCC	Oxidizing	850-900	850-950	Fly ash/slag Alkali	Slag, 200-500 m/s	Hot corrosion/erosion
FBC Effluent	Oxidizing	850-900	600-900	Alkali sulfates Silicates Sorbent	Fly ash, sorbent, 200-500 m/s	Hot corrosion/erosion
HIPPS	Oxidizing	1300	1000	Alkalis	200-500 m/s	Oxidation/erosion

Table 3. Materials degradation in coal-fired systems

Phenomenon	Key Variables	Possible Rate-Limiting Step
Boiler tube corrosion	Alkali and chlorine contents Fly ash, temperature	Alkali condensation Oxide-sulfate reaction
Substoichiometric combustion (also gasification)	O and S partial pressures, temperature Downtime condensate Alkali/slag deposit	Fracture of oxide scale Oxidation/sulfidation Pitting and crevice corrosion
FBC in-bed corrosion	Bed chemistry Local particle velocity Particle size and loading	Oxidation/sulfidation Arrival rate of particles Fracture of surface scales
Low-temperature hot corrosion	Temperature, temperature gradient Salt-film thickness, S and alkali level	Sulfidation of transient oxides Transport of base metal (e.g., Ni and Co)
Hot corrosion/erosion	Alkali level Temperature Particle size, loading, and velocity	Fracture of scale Sulfidation of transient oxides Transport of base metals

CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub> emissions of a 600-Mw conventional, supercritical, and ultrasupercritical plants. The ultimate goal of the staged development of these systems is to change steam pressure and temperature from the current values of 16.5-24 MPa (2400-3500 psig) and 540°C (1000°F), respectively, to 34.5 MPa (5000 psig) and 650°C (1200°F). Fireside metal wastage in conventional 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 the 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) that are present in the coal feedstock.

The effect of boiler deposits on the corrosion of structural materials has been fairly well established by Reid [5]. The temperature regimes in which this corrosion occurs are summarized in Figure 2. The data generally show that K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> will form from K<sub>2</sub>SO<sub>4</sub> and SO<sub>3</sub> at 400°C when SO<sub>3</sub> concentration is at least 150 ppm; as the temperature increases, the SO<sub>3</sub> requirement increases, so that, at ≈500°C, at least 2000 ppm SO<sub>3</sub> will be required to form liquid K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>. Sodium pyrosulfate can form at ≈390°C with ≈2500 ppm SO<sub>3</sub>, but, at 485°C, ≈2 vol.% SO<sub>3</sub> will be required. Based on these results and the anticipated maximum level of ≈3500 ppm SO<sub>3</sub> in a pulverized-coal boiler, Reid concluded that pyrosulfates can contribute to metal loss in the water-wall and economizer tubes but may not be a cause of corrosion in superheaters and reheaters in conventional systems.

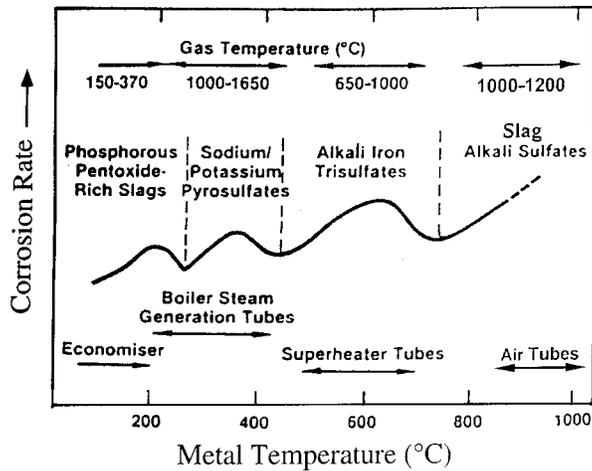


Figure 2. Regimes of fireside corrosion in coal-fired boilers.

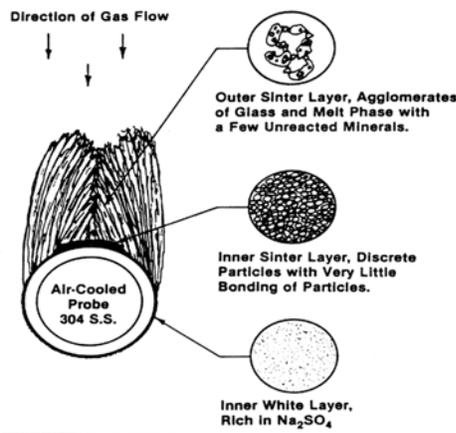


Figure 3. Structure of deposit on superheater tubes in pulverized-coal-burning boilers

Because most of the materials for application in boiler tubes are iron-based alloys, and because the mobility of iron from the alloy substrate to the scale/gas interface is fairly rapid, considerable attention has been given to understanding the formation of alkali-iron trisulfates and their role in the corrosion of steam superheaters in conventional boiler systems [5-7]. Figure 3 shows the characteristics of deposits in superheater sections that can lead to fouling and corrosion of the underlying metal. A general mechanism and a sequence of events for alkali-iron-trisulfate induced corrosion of iron-based materials is as follows. Initially, an oxide film forms on the metal surface; also, pyrite in the coal can oxidize during combustion to form iron oxide and sulfur dioxide/sulfur trioxide gases. Alkali sulfates that originate from alkalis in the coal and sulfur oxides in the furnace atmosphere, are deposited over the oxide scale on the superheater material. Eventually, because of the increasing temperature gradient, the outer surface of the alkali sulfate layer becomes sticky so particles of fly ash are captured. With further increase in temperature, thermal dissociation of sulfur compounds in the ash releases  $\text{SO}_3$  that migrates toward the cooler metal surface, while a layer of slag forms on the outer surface. With more ash in the outer layer, the temperature of the sulfate layer falls and reaction occurs between the oxide scale and  $\text{SO}_3$ , to form alkali-iron trisulfate. With this removal of the oxide scale, the metal oxidizes further. Deslagging due to temperature excursions or soot blowing to remove the deposits exposes the alkali-iron trisulfates to higher temperatures and leads to dissociation of sulfate and generation of  $\text{SO}_3$  for further attack of the metal.

As the steam temperature increases further in advanced combustion systems, the metals in the superheater regions will be subjected to much higher temperatures, and alkali sulfate and coal ash will be the predominant deposits. Several factors, including sulfur, alkali, chlorine in the 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 results for several candidate alloys are shown in Figure 4 [8]. It is evident that, at steam temperatures of  $\approx 540\text{-}565^\circ\text{C}$  ( $1000\text{-}1050^\circ\text{F}$ ), the metal temperature will be in the range of  $600\text{-}630^\circ\text{C}$  ( $1112\text{-}1165^\circ\text{F}$ ) and the corrosion rates will be acceptable for long-term service. In advanced steam cycles with anticipated steam temperatures and pressures of  $650^\circ\text{C}$  ( $1200^\circ\text{F}$ ) and 34.5 MPa, metal can attain temperatures of  $700^\circ\text{C}$  or higher, which lead to increased corrosion rates. Figure 5 shows relative corrosion loss data, and the relationship between chromium content and corrosion loss for various alloys tested at  $700^\circ\text{C}$  in the presence of synthetic coal ash and alkali sulfate [9].

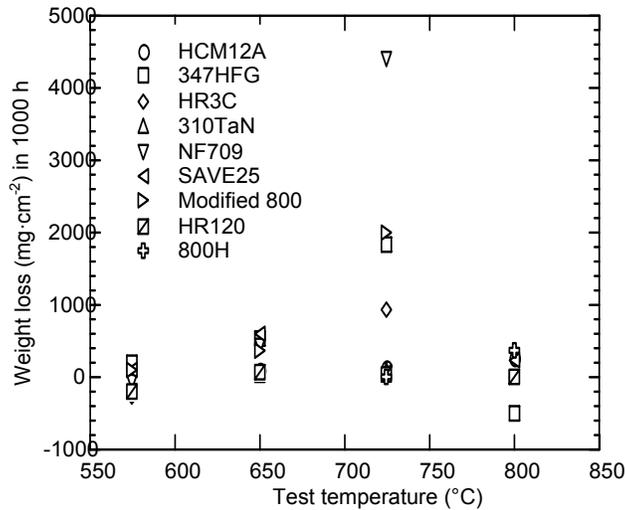


Figure 4. Corrosion test data for several alloys exposed to coal-fired-boiler environments.

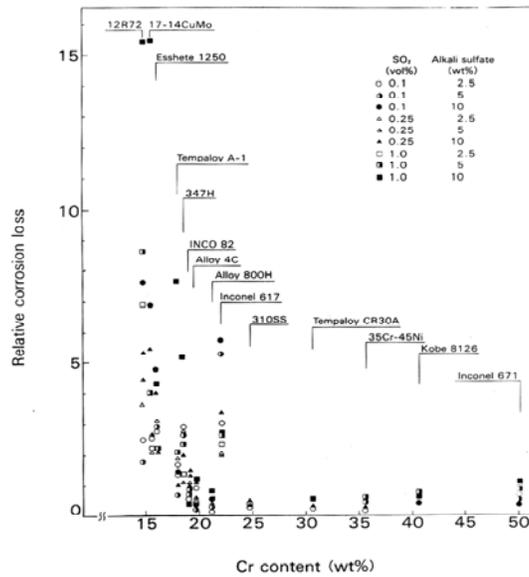


Figure 5. Relationship between chromium content of alloys and relative corrosion loss for alloys tested at 700°C in presence of coal ash, SO<sub>2</sub>, and alkali sulfate.

### 3. Low Emission Boiler Systems

This system would utilize staged combustion to develop a power plant that will drastically reduce SO<sub>2</sub>, NO<sub>x</sub>, and particulate emissions from current levels. Even though LEBSs are an extension of current boiler technology, the conditions during the first stage of combustion will be fuel-rich or air-lean, with a resultant gas chemistry that will be reducing for the internal structural components, and the deposit characteristics will be sulfides of various elements rather than the sulfates/oxides that are prevalent in conventional coal-fired boilers. The materials used for the boiler water wall and low-NO<sub>x</sub> burners are particularly susceptible to sulfidation attack by both H<sub>2</sub>S in the gas phase and sulfides (such as pyrite) in the deposits. The presence of sulfide deposit low-NO<sub>x</sub> systems can establish a locally much more reducing environment for the tube materials and alter the corrosion resistance of the materials. In the presence of a combination of S, Cl, and deposits, metallic materials can develop nonprotective oxide scales, undergo sulfidation degradation, lose structural elements as volatile chlorides, exhibit carburization and eventual attack of carbides by chlorine, and show alkali- and carbon-induced degradation, depending on the composition and exposure conditions.

Increases in superheater corrosion have been reported after the use of staged low-NO<sub>x</sub> combustion [10]. For example, corrosion rates for austenitic alloys, with Cr content of 18-30 wt.%, ranged from 0.3 to 0.8 mm/y after 26,500-35,135 h of exposure in TVA's Gallatin station, whereas nominal corrosion rates before staged combustion were 0.01-0.17 mm/y.

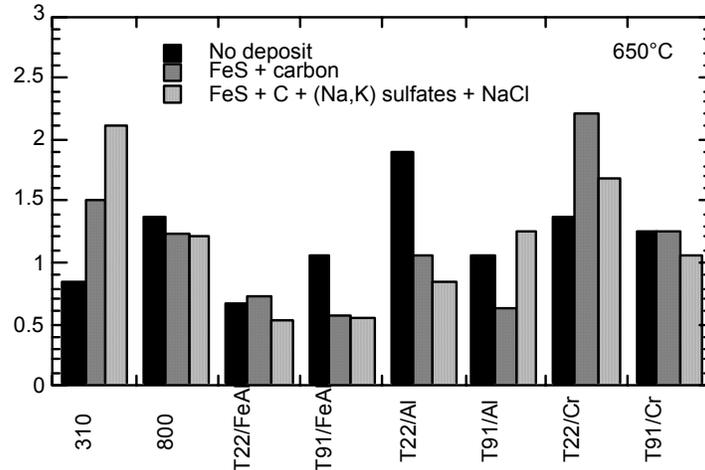


Figure 6. Effect of deposit chemistry on scaling and penetration data for several alloys and coatings

The reported potential causes for the increased corrosion rates are unburnt carbon and FeS in the deposits, locally reducing environment (a higher CO content), and S as H<sub>2</sub>S in the gas phase. In addition, alkali sulfates and alkali chlorides may exacerbate the corrosion process. A substantial body of information on a wide range of materials has been developed to identify candidates with adequate performance and enhanced reliability [10,11]. Figure 6 shows the effects of deposit chemistry on the corrosion performance of several austenitic alloys and coatings that are pertinent to low-NO<sub>x</sub> systems.

#### 4. Fluidized Bed Combustion Systems

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 for the cogeneration of electricity and useful thermal energy. Figure 7 shows schematic diagrams of typical bubbling- and circulating-fluid-bed systems. The key components of relevance are

- In-bed air-tube heat exchangers
- Steam-tube heat exchangers
- Gas turbines.

The FBC of coal produces principally O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, and N<sub>2</sub>, with minor amounts of SO<sub>3</sub>, nitrogen oxides, chlorides, and other volatilized salts. The gas composition depends significantly on the air/coal stoichiometric ratio. The concentration of SO<sub>2</sub> in the gas phase is 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 when compared with the bulk gas composition.

In general, the information available on the oxidation/sulfidation of structural alloys exposed to FBC environments indicates that the alloys develop predominantly oxide scales [12]. The high-chromium alloys develop thin chromium-rich oxide scales, but the scale thickness and depth of sulfur penetration increase as metal temperature increases. However, the sulfated sorbent deposit and the oxide scales are porous, and the scales generally contain a sulfide phase from the reaction between the constituents of the base metal and the sulfur released from the reaction of chromium or aluminum (in chromia- or alumina-forming alloys, respectively) with SO<sub>2</sub>. The porosity of the deposit and scale enables SO<sub>2</sub> gas molecules to permeate to the scale/substrate interface and cause internal sulfidation. Generally, acceptable lifetimes for alloys exposed to these environments are determined by the depth of internal sulfidation, which is largely determined by the alloy chemistry, temperature, and SO<sub>2</sub> content of the gas phase. The alumina-forming alloys, in general, are much more resistant to corrosion in these environments, but the scales are susceptible to spallation. When this occurs, the exposed alloy surface is denuded of aluminum; hence, re-formation of a protective oxide scale is impeded and accelerated sulfidation of the base metal ensues. Extensive reviews have been published on materials performance in FBC environments [12,13].

For air-tube heat exchanger applications at temperatures near those of the bed, corrosion is the dominant mechanism of materials degradation. 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 an atmospheric fluidized-bed combustion (AFBC) facility, test under gas-cycling conditions, and in a more severe laboratory test under low oxygen partial pressure. A 3000-h laboratory test showed that alloys such as HS 188, HS 556, HK 40, and 800H exhibited catastrophic corrosion in the presence of deposit material and sustained low pO<sub>2</sub>.



Figure 7. Schematic diagrams of bubbling- and circulating-bed systems. AFBAH in bubbling-bed concept = atmospheric fluidized-bed air heater.

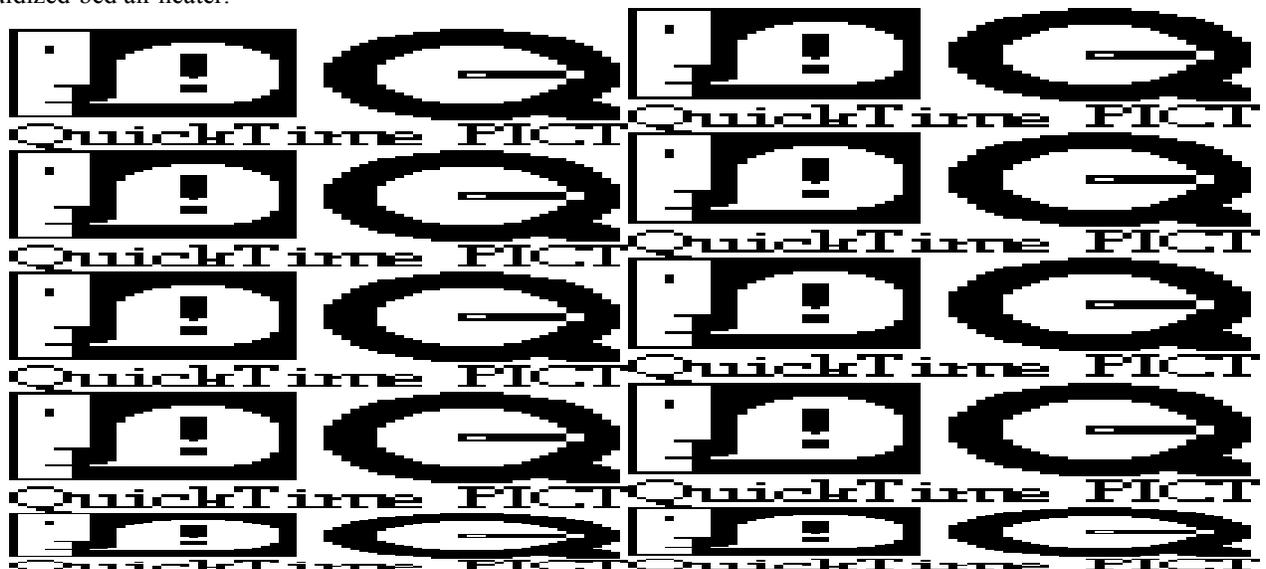


Figure 8. Corrosion penetration of alloys exposed in (a) absence and (b) presence of sulfated sorbent deposits in FBC environments.

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. Figure 8 shows corrosion penetration in alloys exposed to FBC environments with and without sulfated sorbent deposits [14].

For steam-tube heat exchanger applications at temperatures in the range of 500-650°C, both corrosion and erosion processes must be considered in the assessment of materials performance. Furthermore, tube bank geometry, tube bank distance from the air distributor, coal and limestone feedstock chemistries, and bed operating conditions all influence materials performance. Over the years, extensive data on metal wastage have been developed for several materials exposed in FBC facilities. Data from 13 sources, generated in 16 experimental FBC systems, have been compiled. Moreover, data are tabulated for exposures up to 10,000 h at temperatures between 600 and 900°C, and the extent of corrosion is evaluated in terms of scale thickness and depth of penetration of the alloys. Scale thickness is generally negligible and increases to a constant value after 2,000 h of exposure. Penetration depth is approximately three times scale thickness and tends to increase with exposure time [12].

## 5. Integrated Gasification Combined-Cycle Systems

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 rate of steam and water consumption.

Moreover, 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 9 shows a schematic diagram of an entrained slagging gasifier with syngas coolers. From the corrosion/materials standpoint, the components of interest in these systems are

- Syngas coolers
- Refractory-lined vessels
- Hot-gas cleanup systems
- Gas turbines.

Syngas coolers are generally used to recover the sensible heat from raw gas; they are very large (especially when compared with the gasifier) and are fabricated from metallic materials. The temperature of the metal in the syngas system is 300-500°C and the metal is exposed to a highly reducing atmosphere in the presence of hydrogen sulfide, the concentration of which is determined by the sulfur content of the coal feedstock. In addition, the environment contains hydrogen chloride. The gas temperature in the cooler is 1100-1300°C and the cooler experiences on/off service, which results in a contribution to corrosion during downtime. Experimental studies conducted in both laboratory and pilot-plant facilities have clearly established that alloy sulfidation is the major mode of material degradation and that a viable alloy should develop protective oxide scales on exposure to sulfur-containing, low-oxygen-partial-pressure atmospheres in coal gasification systems [15,16].

Figure 10 is a schematic representation of corrosion scale development and morphological changes in chromia-forming alloys exposed to a simulated coal gasification atmosphere. In the early stages of exposure, the alloy develops oxide and sulfide nuclei. Eventually, thermodynamic conditions establish a continuous chromia scale via reoxidation of sulfide particles, while the released sulfur is driven into the substrate along grain boundaries. Oxide growth occurs via chromium transport across the scale to the scale/gas interface, where it is oxidized, leading to increased thickness. At the same time, sulfur in the gas phase is adsorbed onto the scale/gas interface, and channels, through which transport of base-metal cations to the scale/gas interface is accentuated, are established in the fine-grained oxide scale.

If the sulfur pressure in the gas phase exceeds the metal/metal sulfide equilibria of the base-metal elements, sulfides of these elements are formed at the oxide scale/gas interface. As the sulfide grows, stresses develop in the oxide scale, which eventually is breached and sulfidation occurs at the oxide scale/substrate interface. Because the transport rates of cations and sulfur through the sulfide phase are orders of magnitude higher than the transport rates through the oxide scale, the sulfidation attack continues in an accelerated manner. At longer exposure times, the oxide is virtually destroyed and a massive sulfide scale develops, a condition that represents breakaway corrosion of the alloy. The same sequence of steps is operative in alumina-forming alloys, probably at a much slower rate than in chromia-forming materials. An extensive data base has been developed on the corrosion performance of various commercial and experimental alloys in a wide range of coal gasification environments [15-17].

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 approximately the past 20 years. It has been shown that refractories that contain mainly chromia-alumina solid solutions

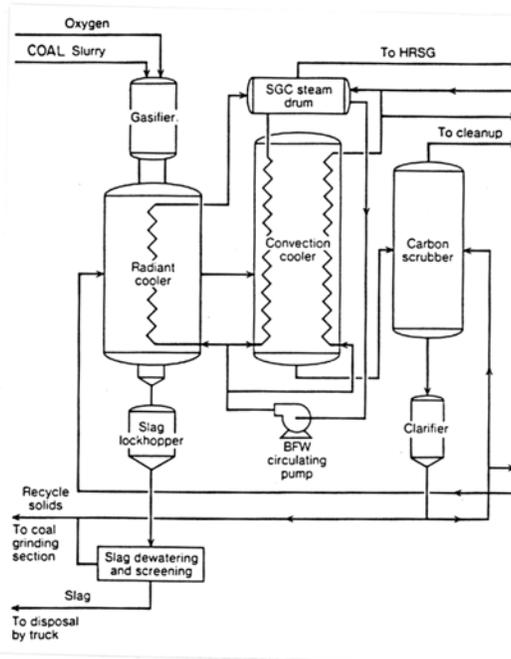


Figure 9. Schematic diagram of entrained slagging gasifier and syngas coolers.

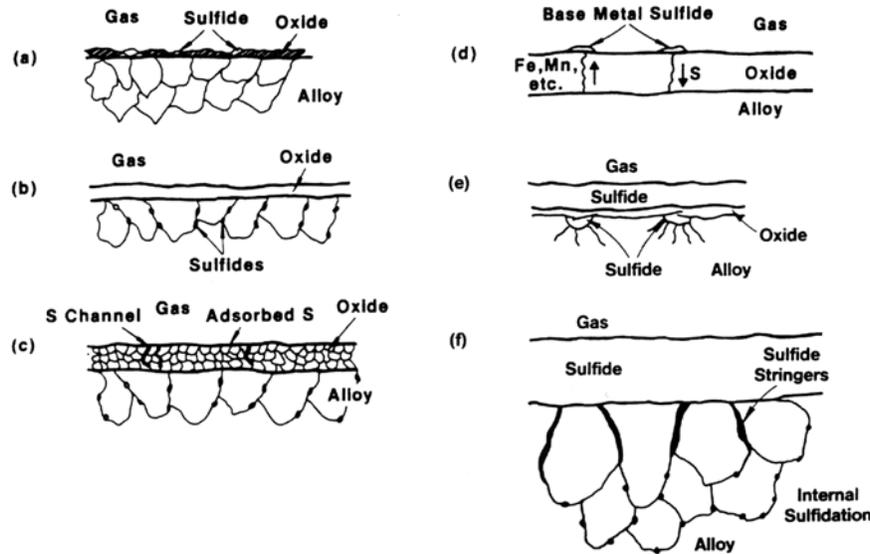


Figure 10. Schematic representation of reaction sequence, (a) through (f) for chromia-forming alloys exposed to a simulated gasification environment.

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. Correlations of refractory wastage data with operating conditions have shown corrosion/wear rates of  $<0.01$  mm/h during periods of steady-state operation.

A hot-gas cleanup system involves passing the raw gas from the gasifier into a porous ceramic filter that allows gases to pass through while particulates are trapped. The filters are periodically pulsed with a gas flow in the reverse direction to clean them of particulate material. The operating temperatures for cleaning hot gasifier fuel gases ranges from 250 to 700°C, depending on the gasifier technology and the contaminants being removed. The filter designs that have been considered include fabrics made from ceramic fibers, candles made of ceramic fibers or powders, and cross-flow type monolithic structures. The materials considered are cordierite, silicon carbide, quartz, zirconia, alumina, and mullite, and a combination of these. In addition, Fe aluminide intermetallics are being evaluated for application as filter material. Long-term (10,000-h) exposures of ceramic materials at temperatures of 500-550°C have not led to degradation of materials; however, the potential for the fuel gases to cause sulfidation of the downstream metallic components is a serious concern [18].

## 6. Corrosion in Gas Turbines

Gas turbine materials in FBC cogeneration systems that use air as the working fluid are exposed predominantly to heated air, with supplemental heat from burning of clean fuel such as natural gas. Corrosion of materials has been observed over a much wider temperature range (600-950°C) in the FBC effluent than in conventional gas turbines (800-950°C). Corrosion test data obtained from the effluent of a pressurized FBC system showed that both nickel- and cobalt-based alloys were equally susceptible to accelerated Type II hot corrosion. This form of corrosion, also known as low-temperature hot corrosion, involves eutectics of base metal sulfates and sodium sulfate, and, therefore, occurs predominantly at lower temperatures, especially in the effluent of the FBC environment [19]. For example, the eutectic temperature for sodium sulfate-cobalt sulfate is 565°C. In this case, the transient oxides of cobalt or nickel (which nucleate in the early stage of oxidation in chromium- and aluminum-containing superalloys) react with sodium sulfate to form eutectic salts that prevent formation of protective chromia or alumina. The corrosion process is strongly dependent on the partial pressure of sulfur trioxide at the melt/scale interface, but the process occurs at much lower temperatures than the melting point of sodium sulfate. This susceptibility to accelerated corrosion at lower temperatures was attributed to the presence of potassium in the FBC effluent.

## 7. Summary

Poland has an extensive reserve of high-ranking coals which is mined for both domestic consumption and export to European countries and Russia. The coal has been widely used in power generation but the limits on emission and efficiency improvements in coal utilization processes necessitate the retrofit of existing plants and use of advanced technology in future plants. This paper discusses several technologies that are available for application in the future and

elaborates on the required materials and their corrosion performance in several of the advanced processes. The major modes of material degradation in advanced fossil technologies that use coal as a feedstock are deposition/fouling, erosion, corrosion, and combined erosion/corrosion. The extent to which these degradation mechanisms are operative in several of the technologies, the key variables responsible for degradation, and the possible rate-limiting steps for some of the phenomena are identified. Typical data on the performance of materials in several of the environments are presented and sources for detailed data bases are listed. The paper presents information on PC boiler systems with higher steam temperature capability, FBC systems with the capability to capture sulfur, IGCC for production of syngas, and utilization of the gas in combined-cycle plants. In addition, advanced staged-combustion systems with a higher thermal efficiency and/or improved environmental compliance are discussed. The success of these systems depends on the development/identification of viable materials for heat transfer from the fireside to the working fluid and a better understanding of the performance of metallic materials in environments that are specific to various systems.

#### Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research Materials Program, under Contract W-31-109-Eng-38.

#### References

1. DOE, Annual Energy Review, DOE/EIA-0834, Energy Information Administration, U.S. Department of Energy, 1990.
2. Global Climate Committee of the International Energy Agency's Coal Industry Advisory Board Report, published by IEA, France, 1998.
3. Proceedings 2<sup>nd</sup> Int. Workshop on Corrosion in Advanced Power Plants, Tampa, FL, March 3-5, 1997, *Materials at High Temperatures*, 14, No.2, 1997.
4. K. Natesan, *J. Met.*, 43(11), p. 61-67, 1991.
5. W. T. Reid, *External Corrosion and Deposits*, American Elsevier, New York, 1971.
6. E. A. Sondreal, G. H. Gronhovd, P. H. Tufte, and W. Beckering, *Ash Deposits and Corrosion Due to Impurities in Combustion Gases*, R. W. Bryers, ed., Hemisphere Publishing Corp., Washington DC, p. 85, 1978.
7. R. W. Borio, A. L. Plumley, and W. R. Sylvester, *ibid*, p. 163.
8. K. Natesan, Proc. 16<sup>th</sup> Annual Conf. Fossil Energy Materials, Baltimore, MD, in press.
9. S. Kihara, T. Isozaki, and A. Ohtomo, Proc. JIMIS-3 High-Temperature Corrosion, Tokyo, Japan, p. 655, 1983.
10. W. T. Bakker, J. L. Blough, and W. W. Seitz, "Low NO<sub>x</sub> Combustion Systems and Superheater Corrosion," Paper 01168, NACE Corrosion/2001, Houston, TX, March 11-16, 2001.
11. K. Natesan and C. Kraus, Proc. 15<sup>th</sup> Annual Conf. Fossil Energy Materials, Knoxville, TN, Oak Ridge National Laboratory, 2001.
12. K. Natesan, S. A. Miller, and W. F. Podolski, Argonne National Laboratory Report ANL-86-42, 1987.
13. A. J. Minchener, P. T. Sutcliffe, I. S. Scott, R. S. Courtney, D. M. Lloyd, D. C. Read, T. Golesworthy, and J. E. Oakey, Electric Power Research Institute Report EPRI-CS-3511, 1984.
14. K. Natesan and W. F. Podolski, Proc. First Int. Conf. on Heat Resistant Materials, K. Natesan and D. J. Tillack, eds., ASM International, Materials Park, OH, p. 549, 1991.
15. K. Natesan, *Corrosion and Mechanical Behavior of Materials for Coal Gasification Applications*, Argonne National Laboratory Report ANL-80-5, 1980.
16. K. Natesan, *Corrosion (Houston)*, 41, p. 646, 1985.
17. V. L. Hill and B. A. Humphreys, *Metals Properties Council Reports FE-1784-45, -48, -51, and -54*, A. O. Schaefer, ed., 1978 and 1979.
18. J. E. Oakey and I. R. Fantom, *Hot Gas Cleaning-Materials and Performance*, presented at 2<sup>nd</sup> Int. Workshop on Corrosion in Advanced Power Plants, Tampa, FL, March 3-6, 1997, *Materials at High Temperatures*, 14, No.2, 337, 1997.
19. K. L. Luthra and D. A. Shores, *J. Electrochem. Soc.*, 127, p. 2202, 1980.