

EFFICIENT AND CLEAN POWER PRODUCTION: MINIMIZING IMPACTS OF INORGANIC COMPONENTS IN COAL AND OTHER FUELS

Steven A. Benson, Christopher J. Zygarlicke, and Everett A. Sondreal

Energy & Environmental Research Center, University of North Dakota

PO Box 9018, Grand Forks, ND 58502-9018

KEYWORDS: solid fuels, combustion, gasification, environmental issues

ABSTRACT

The inorganic components associated with coal and other solid fuels influence the design and operation of power systems. The problems associated with inorganic species include abrasion, corrosion, and erosion of system parts; slag flow in wet-bottom systems; fouling and slagging of heat-transfer surfaces; formation of fine particulate and vapor-phase species that are difficult to collect and can cause adverse environmental effects; plugging of gas-filtering systems; and disposal and utilization of ash residuals. The inorganic components associated with solid fuels consist of major, minor, and trace elements, which occur in a wide range of forms. For example, the association of inorganic components in coal depends on rank and depositional environment. Firing solid fuels for power production transforms the inorganic species to gases, liquids, and solids and carries them through the system with the bulk gas flow. The interaction and behavior of the inorganic gases, liquids, and solids in the system are dependent upon system design and operating conditions. Research and development over the past 20 years have provided key insights into the fundamental behavior of major, minor, and trace elements in combustion and gasification systems as well as associated pollution control systems, leading to improvements in the performance and design of conventional and advanced power systems.

INTRODUCTION

The current and future use of solid fuels such as coal, biomass, petroleum coke, municipal solid waste, and paper products is greatly dependent on solving problems related to the combustion behavior of the high-temperature, noncombustible inorganic fraction, or the ash-forming constituents. The abundance and forms of inorganic components associated with these fuels vary widely and can have significant impact on the economic and environmental performance of the power system. The inorganic components are the root cause of many operational and environmental problems in conventional and advanced power systems, which may include abrasion and erosion of equipment; ash deposition and corrosion on heat-transfer and refractory surfaces in boilers and gasifiers; poor slag flow in slagging combustors and gasifiers; emissions of acid rain-forming species; hazardous air pollutant emissions, including precursors to secondary particulate matter formation; and increased requirements for air pollution controls. The literature on ash-related issues is immense. Overviews of ash-related issues and compilations of work by many investigators can be found in the work of Benson (1, 2), Baxter and Desollar (3), Couch (4), Williamson and Wigley (5), Benson and others (6), Benson (7), Bryers and Vorres (8), and Raask (9, 10). Overviews of the environmental issues such as mercury, trace elements, and particulate matter have been summarized in two special issues (11, 12). In addition, a review of mercury transformation; behavior, and control was conducted recently (13).

Current and future trends in the use of solid fuels are being and will be driven by economic and environmental factors. Environmental factors have had significant impact on the type of coal utilized by the power industry. The Clean Air Act Amendments (CAAA) of 1990, Toxic Release Inventory (TRI), and an increased awareness of global warming have made a significant impact on the diversity of use of solid fuels in the future. The 1990 CAAA identified 189 hazardous air pollutants that are subject to control. Eleven trace elements including antimony, cadmium, lead, nickel, chromium, manganese, selenium, beryllium, cobalt, and mercury are among the 189 toxic substances. Currently, a significant effort is being conducted on mercury measurement and control for coal-fired utility boilers. The TRI now requires electric utility companies to report their annual releases of toxic chemicals. The TRI is a national compilation of releases of more than 600 chemicals designated as toxic by the Environmental Protection Agency (14). As a result of increased environmental pressure, many utilities have switched to low-sulfur coals for compliance with SO₂ regulations. In addition, the utilization of biomass-derived fuels appears to be on the rise because of concerns over global warming, which may in part be caused by an increase in CO₂ in the earth's atmosphere. The combustion of biomass does not increase the overall CO₂ inventory in the atmosphere. Finally,

deregulation of the utility industry is increasing incentives to fire the cheapest fuels available such as spot-market coals, petroleum coke, waste materials, and biomass.

INORGANIC COMPOSITION OF SOLID FUELS

Coal

The association and abundance of major, minor, and trace elements in coal is dependent upon coal rank and depositional environment. The inorganic components in lower-rank subbituminous and lignitic coals are associated with the organic and mineral portions of the coal matrix. The lower-rank coals contain high levels of oxygen, some of which are in the form of carboxylic acid groups that can act as sites for cations such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+} , and Ba^{2+} . The inorganic components associated with bituminous and anthracite are primarily in the form of discrete minerals. The major mineral groups include quartz, clay minerals, pyrite, and carbonates. The abundance and association of minerals in coal have been reviewed and published in *Fundamentals of Coal Combustion for Clean and Efficient Use* (15). The sulfur oxide emissions from power plants are derived from organic sulfur and mineral forms such as pyrite, gypsum, barite, and others. Air toxic metals can be associated both with organic functional groups and with minerals in coal. Commonly, trace elements in coal are included in the list of 189 toxic substances called out by the 1990 CAAA, for example, antimony, cadmium, lead, nickel, chromium, manganese, selenium, beryllium, cobalt, and mercury. The associations of trace elements in coals are summarized by Swaine (16), Finkelman (17), and Benson and others (18).

Petroleum Coke

The inorganic components associated with petroleum coke materials have been summarized by Bryers (19). Petroleum contains a low level of ash-forming species ranging from 0.5 up to 2.5 wt%. The inorganic components consist mainly of nickel, vanadium, sulfur, silicon, aluminum, and minor amounts of iron, sodium, and potassium. The key elements S, V, Fe, and Ni are organically associated as porphyrin complexes.

Biomass

The inorganic composition of biomass fuels has been reviewed by Jenkins and others (20). The inorganic components associated with biomass coals include Si, Al, K, Na, S, Cl, P, Ca, Mg, and Fe. These elements occur at different levels in various types of biomass fuel, including agricultural products (manure, hulls, pits), wood, herbaceous materials (grasses, straws, leaves), and a wide range of waste materials (e.g., municipal solid waste, sewage sludge, and plastics). Most of the inorganic components in plants are associated with the organic matrix, as in some lignitic and subbituminous coals. Biomass-type fuels also cause slagging and fouling problems that are similar to those produced from low-rank coals (6, 21–23). For example, in low-rank coals, alkali and alkaline-earth elements interact and combine with silicates to form low-temperature melt phases that melt at temperatures as low as 700°C, as well as sulfate phases that can have melting points as low as 650°C. Baxter and others (24) reported the formation of sulfate-, silicate-, chloride-, and carbonate-type deposits when biomass-type fuels were fired.

Trace elements are also of concern in biomass utilization. In Austria, Obermberger (25) reported concerns regarding the levels of Mn, Cu, An, Co, Mo, Ni, Cr, Pb, V, and Hg. The ash produced from biomass combustion systems is used as fertilizer, and the levels of selected trace elements must be below regulatory limits. Researchers in Austria have developed a method to fractionate the heavy metals.

BEHAVIOR IN CONVERSION AND ENVIRONMENTAL CONTROL SYSTEMS

Major, minor, and trace inorganic components associated with fossil and biomass fuels undergo a complex series of chemical and physical transformations in combustion and conversion devices, air pollution control systems, and in the ecosystem (26). These transformations are illustrated in Figure 1. The primary factors that influence the fate of the inorganic species include:

- The important operating conditions within the conversion system, such as oxygen stoichiometries and gas composition in general, flame and subsequent flue gas temperatures, particle residence times, and heating and cooling rates.
- The chemical composition and physical characteristics of inorganic components in the fuel that influence their reactivity and volatility during combustion or gasification.

- The transformations of inorganic components occurring during combustion/gasification and gas cooling that result in the formation of various inorganic vapor, liquid, and solid phases, depending on fuel composition and conversion conditions. These transformations typically result in the formation of a bimodal (modes at ~ 0.1 and $\sim 12 \mu\text{m}$) particle-size distribution of ash particles over a wide range of chemical compositions. Some mineral species in fuels may remain in their original form through the conversion and environmental control system. Other elements such as mercury may be released in their vapor state and tend to remain in the gas phase as an emission.
- The state (vapor, liquid, and solid) and physical properties (size, density, viscosity, and surface tension) of the intermediate ash species as a function of temperature, atmosphere, and residence time. The more volatile elements—which include the alkali metals (Na and K) and certain trace elements such as As, Se, Pb, Cd, Sb, Hg, and others—are enriched in the smaller size fractions of ash and in the vapor-phase portion of the flue gas stream. This distribution directly impacts fate of the inorganic intermediate species in the conversion and environmental control system.
- Ash deposition, corrosion, and erosion on heat-transfer surfaces depending on gas composition; condensed melt phases; ash particle size; and aerodynamics/fluid dynamic behavior.
- The progressive accumulation of intermediate ash materials that decrease heat transfer and increase fireside temperatures in the system. The characteristics of the liquid-phase components in deposits, as determined by their chemical composition are critical to deposit strength and growth development.

The capture of the inorganic intermediate material in air pollution control devices is dependent upon the form of the material and the mode of collection. In electrostatic precipitation, the collection efficiency of the particles is related to the resistivity of the ash and the particle size. Collection of ash in a baghouse is related to the size of the ash particles and the cohesive properties of the ash dust cake. The ash dust cake can capture both particulate and gas-phase components. Scrubbers are designed to capture vapor-phase species such as SO_2 , utilizing CaO or other reagents. The speciation of the inorganic elements, system conditions, sorbent composition and size, and residence time all influence the reaction of vapor-phase inorganic materials with dry and wet sorbents.

Hot-gas cleanup systems for advanced combustion and gasification systems utilize metal and ceramic-type filters. These filters must remove the particulate material to levels that can be tolerated by a turbine or fuel cell. Ceramic candle filters that are just beginning to be used in full-scale demonstration projects experience failures from a combination of adverse factors, including cyclic thermal stress, ash deposition and surface blinding, and corrosion of ceramic materials by alkalis, chlorides, trace elements, and molten slag phases.

DIRECTIONS FOR THE FUTURE

Future high-performance power systems that utilize coal, biomass, and oil and petroleum coke feedstocks must consider all of the forgoing impacts of inorganic components on system performance and emissions. The key is to match fuel quality with system design and operating conditions. Environmental drivers such as global warming, hazardous air pollutants, regional haze, and particle matter will have a major influence on future fuel sources, power system design, and operating conditions. In order to minimize environmental impact, control cost, and improve efficiency, it will be necessary to identify synergistic relationships for a variety of fuel blends, such as coal and biomass, under a wide range of design and operating conditions.

A vision for power systems for the next century is being developed by the U.S. Department of Energy Office of Fossil Energy (27). The Vision 21 power system is designed to coproduce electricity, heat, transportation fuels, and chemicals with little or no air pollution, solid wastes, or carbon dioxide emissions. The system would be fuel-flexible, thereby allowing for firing of a single fuel or a combination of fuels consisting of coal, natural gas, petroleum coke, and biomass. The energy plant comprises several modules, including combustion/gasification, separation/conversion, gas cleanup, CO_2 sequestration, power, fuels/ products, and steam and cogeneration. This scenario of how next-generation power systems will evolve must account for the effects of the noncombustible or inorganic fractions of the fuel, which greatly impact conversion and environmental control system components.

REFERENCES

1. Ash Chemistry: Phase Relationships in Ashes and Slags. Special Issue of *Fuel Processing Technology*; Benson, S.A., Ed.; Elsevier Science Publishers, July 1998, Vol. 56, Nos. 1-2, 168 p.
2. Ash Chemistry in Fossil Fuel Processes. Special Issue of *Fuel Processing Technology*; Benson, S.A.; Ed.; Elsevier Science Publishers, Sept. 1995, Vol. 44, Nos. 1-3, 288 p.
3. Baxter, L.; DeSollar, R., Eds. *Applications of Advanced Technology to Ash-Related Problems in Boilers*; Plenum Press: New York, 1996.
4. Couch, G. *Understanding Slagging and Fouling During Combustion*; IEA Coal Research Report, 1994.
5. Williamson, J.; Wigley, F., Eds. *The Impact of Ash Deposition on Coal Fired Plants: Proceedings of the Engineering Foundation Conference*; Taylor & Francis: London, 1994.
6. Benson, S.A.; Jones, M.L.; Harb, J.N. Ash Formation and Deposition—Chapter 4. In: *Fundamentals of Coal Combustion for Clean and Efficient Use*; Smoot, L.D., Ed.; Elsevier: Amsterdam, 1993, pp 299-373.
7. Benson, S.A., Ed. *Inorganic Transformations and Ash Deposition During Combustion*. American Society of Mechanical Engineers for the Engineering Foundation: New York, 1992.
8. Bryers, R.W.; Vorres, K.S., Eds. *Proceedings of the Engineering Foundation Conference on Mineral Matter and Ash Deposition from Coal*; Feb 22-26, 1988, Santa Barbara, CA; Unit Engineering Trustees Inc., 1990.
9. Raask, E. *Erosion Wear in Coal Utility Boilers*; Hemisphere: Washington, 1988.
10. Raask, E. *Mineral Impurities in Coal Combustion*; Hemisphere: Washington, 1985.
11. Trace Element Transformations in Coal Fired Power Systems. Special Issue of *Fuel Processing Technology*; Benson, S.A., Steadman, E.N., Mehta, A., Schmidt, C., Eds.; Elsevier Science Publishers: Amsterdam, Aug 1994; Vol. 39, Nos. 1-3, 492 p.
12. Air Quality: Mercury, Trace Elements, and Particulate Matter. Special Issue of *Fuel Processing Technology*; Benson, S.A., Brown, T.D., Eds.; Elsevier Science Publishers, in preparation, publish date in 1999.
13. Brown, T.D.; Smith, D.N.; Hargis, R.A.; O'Dowd, W.J. Critical Review: Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate. *J. Air & Waste Manage. Assoc.*, June 1999, pp 1-97.
14. Rubin, E.S.; Berkenpas, M.B. A National Analysis of Toxic Releases from Electric Power Plants. EM, *Air and Waste Management*, Oct 1999, pp 31-37.
15. Smoot, D.L. *Fundamentals of Coal Combustion for Clean and Efficient Use*; Elsevier: Amsterdam, 1993.
16. Swaine, D.J. *Trace Elements in Coal*; Butterworths: Boston, 1990.
17. Finkelman, R.B. Modes of Occurrence of Potentially Hazardous Elements in Coal: Levels of Confidence. *Fuel Processing Technology* 1994 39, 21-34.
18. Benson, S.A.; Pavlish, J.P.; Zygarlicke, C.J. Trace Elements in Low-Rank Coals. In *Proceedings of the 15th Annual International Pittsburgh Coal Conference*; Pittsburgh, PA, Sept 14-18, 1998.
19. Bryers, R.W. Utilization of Petroleum Coke and Petroleum Coke/Coal Blends as a Means of Steam Raising. In *Coal Blending and Switching of Low-Sulfur Western Coals*; Bryers, R.W., Harding, N.S., Eds.; American Society of Mechanical Engineers: New York, 1994.
20. Jenkins, B.M.; Baxter, L.L.; Miles, T.R. Jr; Miles, T.R. Combustion of Biomass. *Fuel Processing Technology*, 1998 54, 17-46.

21. Jones, M.L.; Benson, S.A. An Overview of Fouling/Slagging with Western Coals. Presented at the EPRI-Sponsored Conference on Effects of Coal Quality on Power Plants, Atlanta, GA, Oct 13–15, 1987; 22 p.
22. Erickson, T.A.; Ludlow, D.K.; Benson, S.A. Interaction of Sodium, Sulfur, and Silica During Coal Combustion. *Energy & Fuels* **1991**, 5 (4), 539–547.
23. McCollor, D.P.; Zygarlicke, C.J.; Oakley, R. Assessment of Cofiring Paper Sludge–Plastic Pellets with Bituminous Coal. In *Proceedings of the 16th Annual International Pittsburgh Coal Conference*; Pittsburgh, PA, Oct 11–15, 1999, 15 p.
24. Baxter, L.L.; Miles, T.R. Jr; Miles, T.R.; Jenkins, B.M.; Milne, T.; Dayton, D.; Bryers, R.W.; Oden, L.L. The Behavior of Inorganic Material in Biomass-Fired Power Boilers: Field and Laboratory Experience. *Fuel Processing Technology* **1998** 54, 47–78.
25. Obernberger, I., Ed. *Ashes and Particulate Emissions from Biomass Combustion*; Series Thermal Biomass Utilization, Vol. 3, Technical University of Graz, Institute of Chemical Engineering, Oct 1998.
26. Benson, S.A.; Sondreal, E.A. Ash-Related Issues During Combustion and Gasification. Presented as Keynote Address to the Engineering Foundation Conference on Impact of Mineral Impurities in Solid Fuel Combustion, Keauhou-Kona, HI, Nov 2–7, 1997.
27. *Coal and Power Systems, Strategic Plan and Multiyear Plans*; Office of Fossil Energy, U.S. Department of Energy, Washington, DC, Jan 1999.

FIGURES

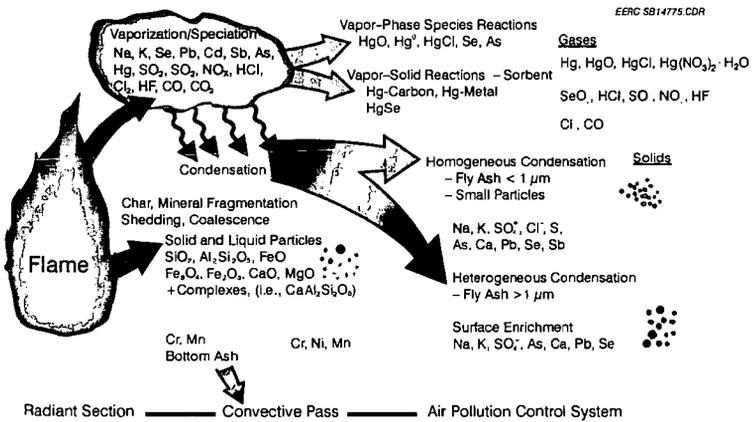


Figure 1. Examples of possible inorganic transformations during conversion.