INORGANICS IN FUEL: A CENTURY OF SCIENTIFIC AND ENGINEERING PROGRESS

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INTRODUCTION

Combustion of fossil fuels has been the backbone of the power generation, manufacturing and transportation industries in the twentieth century. Although the mix of fuels has changed, at the close of the century we find that combustion systems have not changed overmuch. Operational caused by inorganic elements in fossil fuels (corrosion, slagging, and fouling) continue to present problems in combustion systems, although substantial progress has been made in understanding and addressing such problems. In the latter half of the century, the impact of inorganic elements in fossil fuels on the environment was recognized as a potential problem. Considerable effort has therefore been directed at understanding the behavior of certain trace metals such as mercury, arsenic, nickel, chromium, and selenium during the combustion process. This paper briefly reviews the behavior of inorganic elements in practical combustion systems as well as the progress made in applying this knowledge to improvements in operational and environmental performance.

Most inorganic elements in the periodic table can be found in fossil fuels, although only a small number occur in significant concentrations to cause operational or environmental problems. Coal has by far the highest content of ash, although the chemical composition of lower ash fuels can make oil and biomass problematic in some instances. Table 1, drawn largely from Bryers,[1] summarizes the contributions of the elements in ash from various fuels to slagging, fouling, corrosion, and environmental problems. Slagging is defined as deposition of fly ash in the radiant section of the furnace, on both heat transfer surfaces and refractory surfaces. Fouling occurs in the convective heat transfer section and includes deposition of ash and volatiles as well as sulfidation reactions of ash. Fouling results in loss of heat transfer efficiency and blockage of the gas flow path. Corrosion occurs primarily on the water-wall tubes in the radiant section of the boiler and results in thinning of tubes with eventual leaks.

Table 1. Impact of Inorganic Elements in Fuel on Operational and Environmental Problems.

	Bituminous Coal	*Subbituminous Coal*	*Lignite*	*Oil and Coke*	*Biomass*
Wt% Ash	*5-20%*	*4-7%*	*5-20%*	*0.1-0.5%*	*1-3%*
Si	S		S		S
Al	S		S		
Fe	S		S		
Mg	S		S		
Ca	S	F, S	F, S		
Na	C, F	F	F	F,C	C, F
K	S				C, F
S	C, F	F	F	C,F	C,F
Cl	C				C
Ni				F	
V				C, F	
As	E	E	E	E	
Cr				E	
Hg	E	E	E	E	

Major elements are shown in **bold**
C – Corrosion
E – Environmental
F – Fouling
S - Slagging

Environmental problems include the impact of ash on the air pollution control devices (APCDs) and on the environment. Increasingly, the emission of toxic metals to the air and water from fossil fuel combustion is recognized as a problem. Mercury is the element of most concern, particularly for coal-fired power plants. Other metals (e.g., As, Cr, Ni, V) are also of concern when burning petroleum-derived fuels. There are other impacts of inorganic elements in the environmental performance of combustion systems, including operation of particulate collection devices and the poisoning of selective catalytic reduction catalysts by arsenic. In coal-fired power plants, the sodium and sulfur contents of the fuel both affect the resistivity of the fly ash. If an electrostatic precipitator (ESP) is used to collect the ash, resistivity is the key ash parameter which influences the collection efficiency.

CHARACTERIZATION OF INORGANIC ELEMENTS IN FUEL

Coal was the first fossil fuel to be used for generation of steam applied to transportation and manufacturing, and later to large-scale power generation. Heavy oils and coke, produced from refining of petroleum have been utilized for power generation and manufacturing in the latter half of the century. Wood and agricultural wastes (biomass) have been used at a low level throughout the century, and this may increase with concerns about the use of non-renewable resources. Most of the fossil fuels used for large scale industrial use have a substantial fraction of inorganic elements, the exceptions being natural gas and transportation fuels such as gasoline and diesel oil.

Early methods for characterizing inorganic elements in coal were indirect, for example, ash content or fusibility of the ash. It acknowledged early on that the composition of coal ash strongly influenced the tendency to form deposits in the combustion system. Beginning in the 1930's, the contribution of specific minerals to slagging and fouling problems was recognized using methods of density separation to isolate mineral-rich fractions of coal.[2] With the advent of cyclone boilers for pulverized coal, viscosity measurements were made on coal ash.[3] Mineralogical characterization of coal continued, resulting in a fairly comprehensive understanding of the occurrence and formation of the major minerals in coal by techniques such as physical separation, selective leaching, and x-ray diffraction analysis. Table 2 summarizes the important minerals in coal.[1] More recently, automated techniques such as computer controlled scanning electron microscopy (CCSEM)[4] and scanning electron microscopy point count (SEMPC)[5] have been developed to provide a more accurate picture of the minerals in coal.

Table 2. Minerals occurring in coal

Quartz
Shale group
Species: illite, montmorillonite, muscovite, bravaisite
General formula: $(K, Na, H_3O, Ca)_2 (Al, Mg, Fe, Ti)_4 (AlSiO_8O_{20}(OH,F)_4)$
Kaolin group
Species: kaolinte, livesite, metahalloysite
Formula: $Al_2(Si_2O_5)(OH)_4$
Sulphide group
Species: pyrites, marcasite
Formula: FeS_2
Carbonate group
Species: calcite, dolomite, ankerite
Formula: $(Ca,Mg,Fe,Mn) CO_3$
Chloride Group
Species: sylvite, hallite
Formula: KCl, NaCl

Since the 1960's, low rank coals have become more widely used for steam generation because of their low ash and sulfur contents. Low rank fuels have a major proportion of inorganic elements organically bound to the coal matrix instead of in discrete minerals. Selective leaching (or chemical fractionation) methods have been used to identify and characterize the organically bound elements, primarily Ca, Na, and Mg in subbituminous and lignite coals.[6] Recently, selective leaching and advanced analytical methods such as X-Ray absorption fine structure spectroscopy have been applied to the problem of determining the forms of occurrence of trace elements in coal.[7,8]

Oil and coke, as well as biomass, have much lower ash contents than coal and little, if any minerals (although the inorganic elements in these fuels can still cause problems in practical combustion systems). Generally the ash content and ash composition of these fuels is all that is measured, although the mineralogy and leaching behavior of elements of some biomass fuels have been reported.[1]

IMPACT OF INORGANIC ELEMENTS ON SYSTEM OPERATION

At the start of the twentieth century, coal burned in stoker-fired units was the most common for industrial applications. In the 1920's pulverized coal was introduced and this allowed the design and implementation of new combustion system designs, including wall-fired boilers, cyclone boilers, and fluidized bed combustors. Large scale refining of petroleum in the latter half of the twentieth century introduced new fuels, heavy oils and coke, which are often burned to produce steam and/or electricity in suspension-fired and fluidized bed combustion systems.

Figure 1 illustrates the transformation of inorganic elements during coal combustion. Petroleum-derived fuels and biomass transformations are similar, although these fuels have less discrete mineral matter than coal. During the combustion process, the carbon matrix is consumed resulting in very high particle temperatures. Most of the inorganic elements (either from discrete minerals or organically associated) coalesce into ash particles in the range of 1-20 microns in diameter. A small part of the inorganic elements vaporize during the combustion process (1-5 wt%) and recondense, forming a fine (0.1-0.5 micron) aerosol. Some inorganic vapors condense on the larger ash particles, but the high specific surface area of the submicron aerosol tends to bias condensation to the smaller particles.

These ash particles reside largely in the flue gas in pulverized coal- or oil-fired combustion systems. In cyclone-fired boilers and fluidized bed systems, the majority of the ash ends up as slag or spent bed material. This fly ash, in the flue gas, deposits on heat transfer surfaces in the boiler and ultimately, on modern coal-fired combustion systems, must be removed before the gas can be emitted to the atmosphere.

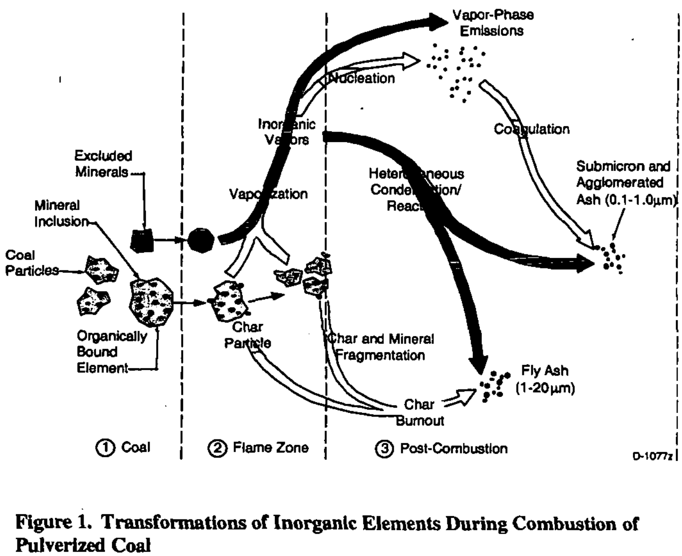

Figure 1. Transformations of Inorganic Elements During Combustion of Pulverized Coal

As discussed above, slagging, fouling and corrosion affect the operation of industrial combustion systems and are directly caused by inorganic elements in fossil fuels. Coal combustion systems are plagued by all these problems. Corrosion is the dominant problem in oil-fired boilers because of the formation of vanadium sulfate deposits which are quite corrosive. Corrosion can be a problem in some biomass combustion systems because some biomass fuels have a very high alkali content. The combination of silica and alkali can also result in slagging and fouling.

Initially, empirical indices were developed to evaluate the potential for operational problems due to the inorganics in fuels. There are many such indices,[1] but they are not specific to particular boiler designs or operating conditions. As discussed above, the realization that specific minerals in coal were responsible for slagging, fouling, and corrosion led to an explosion of research on mineralogical characterization of fuels. This was followed by attempts to create mechanistic (as opposed to empirical) models for the behavior of inorganic elements in practical combustion systems.[9,10,11] Such models are used to provide better indications of the potential effects of fuels on system operations.

IMPACT OF INORGANIC ELEMENTS ON THE ENVIRONMENT

The emission of toxic metals to the air and water from fossil fuel combustion is becoming of concern. In the United States, the potential for regulation of hazardous air pollutants, including metals, was specifically addressed in the 1990 Amendments to the Clean Air Act.

A recent report by the Environmental Protection Agency (EPA) on emission of hazardous air pollutants by electric utilities predicted that emissions of air toxics from coal-fired utilities would increase by 10 to 30% by the year 2010.[12] Mercury from coal-fired utilities was identified as the hazardous air pollutant of greatest potential public health concern. Anthropogenic emissions of mercury account for 10 to 30% of the world-wide emissions of mercury.[12] EPA has estimated that during the period 1994-1995 annual emissions of mercury from human activities in the United States were 159 tons.[12] Approximately 87% of these emissions were from combustion sources. Coal-fired utilities in the U.S. were estimated to emit 51 tons of mercury per year into the air during this period. Considerable work is in progress by the author,[13] and many other groups, which will lead to a more complete understanding of the behavior of mercury in coal-fired power plants.

Other metals (e.g., As, Cr, Ni, V) are also of concern when burning petroleum-derived fuels. Chromium and nickel are the metals of most concern for residual oil combustion. Certain compounds of Cr and Ni are highly carcinogenic. Advanced analytical methods such as XAFS have been used to identify compounds of these elements in residual oil fly ash in order to assess the potential health risks.[14] Cd and Zn in biomass fly ash have also been characterized by this technique. When considering the potential risk to human health or to the biosphere, the ability to identify specific compounds of these toxic metals becomes vitally important. Advanced analytical methods have proved useful in the past and are continually being improved.

SUMMARY

Inorganic elements are present in almost all industrially important fossil fuels and can have major impacts on operation and environmental performance of fossil fuel combustion systems. Improved analytical methods for measuring the composition and for characterizing the form of inorganic elements in fuels have been developed. These methods have led to a better understanding of the behavior of inorganic elements in combustion systems and have spurred the development of fundamentally based models which have been applied in practical systems. More recently, concerns have been raised over the impact of fossil fuel combustion systems on the environment. Advanced analytical methods are just now starting to be applied to characterization of trace metals in fossil fuel and in combustion byproducts. This will lead to an improved understanding of the behavior of trace metals in combustion systems and more effective methods to assess the potential risk to human health.

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