EVOLUTION OF FLAME-BORNE MINERAL MATTER IN A 350 MW_e PULVERISED COAL-FIRED BOILER

Glenn P. Devir[a]
Co-operative Research Centre for Coal in Sustainable Development
School of Chemical Engineering
University of Queensland
Sir Fred Schonell Drive
St Lucia QLD 4072 AUSTRALIA

John H. Pohl
Alexandria Research Institute
Department of Mechanical Engineering
Virginia Tech
Suite 400, 206 N. Washington St
Alexandria VA 22314

Introduction

The mineral matter present in burning pulverised coal particles will experience rapid, high temperature transformations in the gas path of a utility boiler. These inorganic combustion residues may remain inert, melt, spheroidise, coalesce, vesiculate, fragment, freeze, crystallise, vapourise, and/or condense during transport from the bulk gas phase, across the cooler boundary layer, to heat transfer surfaces. The evolution of such flame-borne mineral matter will be dependent upon the size, composition and time-temperature history of each mineral inclusion in the parent coal particle.

The local gas environment is likely to be reducing for flame-transformed mineral matter on or beneath the surface of receding char particles. Conversely, mineral particles which have been liberated from the coal substance during milling will experience oxidising conditions in the gas path of a boiler, as will flame-transformed mineral matter which is released from the char during char burnout.

The evolution of flame-borne mineral matter during pulverised coal combustion is being studied as part of an investigation into the mechanisms of slagging in a 350 MW_e opposed-fired boiler. The observed transformation phenomena of mineral matter in the gas phase are described in terms of classical sintering theory. Possible explanations for the observed absence of various transformation phenomena are also proposed. It is hoped that the interpretation accompanying the images presented in this paper will contribute to a qualitative understanding of particulate transformations in pulverised coal-fired boilers. This paper concludes by identifying future research directions to hopefully resolve the uncertainties of such transformations.

Methodology

The mineralogy of the sub-bituminous coals fired in this minemouth power station typically consist of 60-70% kaolinite ($4SiO_2.2Al_2O_3.4H_2O$), 10-20% siderite ($FeCO_3$) and 5-15% quartz (SiO_2), with minor quantities (<2%) of other minerals present. The mineral matter transformations occurring in the hottest region of the furnace are assessed by using a water-cooled probe to quench and withdraw particulates through a port eight metres above the top row of burners. Particles are examined under the scanning electron microscope (SEM) to ascertain probable physical and chemical transformation mechanisms.

[a] Present address (and to where all correspondence should be addressed): Process Engineer, HRL Technology, 1 Acirl St, Riverview QLD 4303, AUSTRALIA, gdevir@acirl.com.au

Results and Discussion

The most predominant type of particle sampled was glassy sub-micron non-porous aluminosilicates. However, considerable evidence was found to support the notion that kaolinite-derived particles coalesced to various degrees with other kaolinite-derived particles.

An approximate solution for the rate of surface tension driven coalescence of two spheres with single point contact was first proposed by Frenkel[1]. The rate of neck growth, relative to the instantaneous radius a of one of the growing spheres, was shown to be proportional to $(\gamma/\eta)^{-}$, and inversely proportional to $(a\gamma)^{-}$, where γ and η are the surface tension and viscosity of the coalescing species. However, this approach, and many subsequent attempts to model coalescence, both empirically and theoretically, have been based on non-porous particles of like composition.

The time required for pore closure in a viscous body due to capillary forces was shown by Frenkel[1] to be proportional to $a_o\eta$ and inversely proportional to γ, where a_o is the initial pore radius. A kaolinite-derived particle in the furnace of a boiler may possess[2] a pore-free viscosity of 10 Pa.s and a surface tension of 0.4 Nm^{-1}. For a 5 μm initial pore radius, the time required for pore closure would therefore be anticipated to be less than one millisecond. However, it is evident from Figures 1 to 3 that pore closure is not complete in the residence time of the furnace, which is likely to be somewhere in the order of one second.

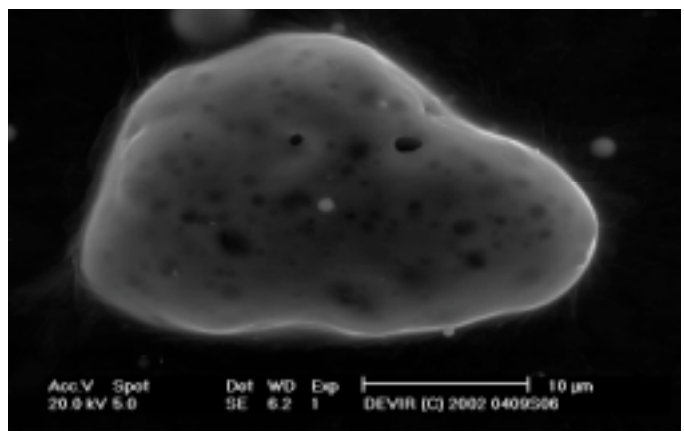

Figure 1. Partial coalescence of several large kaolinite-derived particles. Secondary electron image.

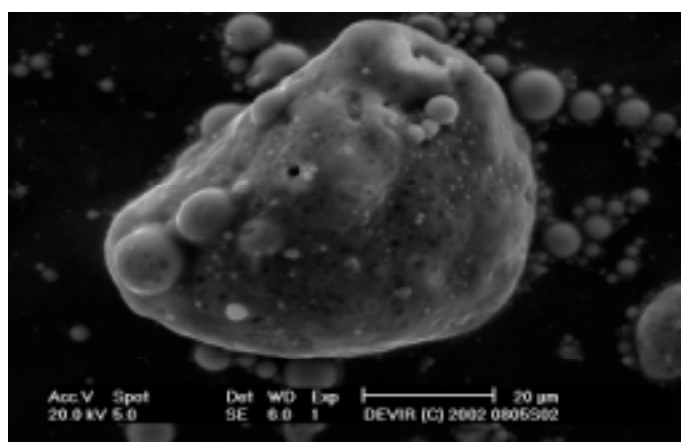

Figure 2. Partial coalescence of many various-sized kaolinite-derived particles. Secondary electron image.

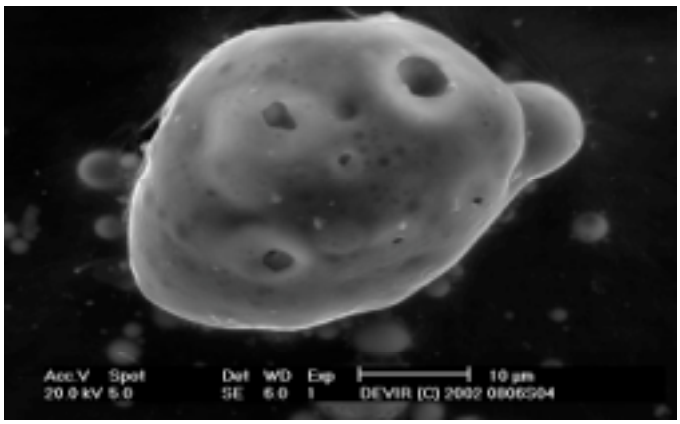

Figure 3. Large rounded kaolinite-derived particle with large pores. Secondary electron image.

The interfaces of real coalescing fluids possess complex rheological properties, and may exhibit viscous, viscoelastic or even elastic behaviour, with both spatial and temporal variations[3]. It is apparent from these images that the kinetics of pore closure in flame-borne kaolinite-derived particles are somewhat slower than that predicted by viscous sintering theory. The retardation of pore closure may explain the incomplete coalescence of large kaolinite-derived particles in the furnace, as evidenced in Figures 1 to 3.

The presence of pores may either increase or decrease the effective viscosity, depending upon the pore morphology. Spherical pores are thought to decrease the effective viscosity, due to the much lower viscosity of the gas phase. Non-spherical pores, however, may increase the effective viscosity of the particle due to their higher resistance to shearing stress, and hence viscous flow.

Many large irregularly-shaped, slightly rounded particles were observed, with varying degrees of surface porosity. Qualitative analysis of various points on each particle was performed using energy dispersive x-ray analysis (EDXRA). It was found that spot compositions ranged from almost pure silica (SiO_2) to the composition of metakaolinite ($4SiO_2.2Al_2O_3$), with regions of low surface porosity corresponding to high silica point concentrations. It was concluded that kaolinite-derived particles had wet the inert surface of large quartz particles, forming a molten porous layer. Figure 4 shows one of these particles.

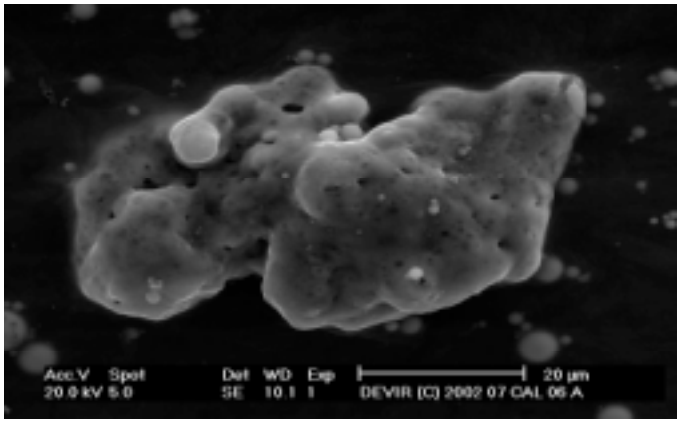

Figure 4. Wetting of inert quartz particle by mobile porous aluminosilicate layer. Secondary electron image.

There was no conclusive evidence to ascertain the primary transformation mechanism of siderite-derived ('FeO_n') particles in the boiler furnace. Iron oxide particles were predominantly less than 1 µm in diameter, suggesting that fragmentation may have been a dominant mechanism. Raask[4] documented the fragmentation of siderite-derived particles into sub-micron particulates, and attributed this phenomenon to the rapid evolution of carbon dioxide from a low viscosity liquid. Iron oxide particles between 5 and 10 µm were rarely observed, suggesting that coalescence of siderite-derived particles was not likely.

There was no evidence found to support the idea that kaolinite-derived particles coalesced with siderite-derived particles to form low melting temperature aluminosilicate particles. Sintering literature suggests that a broad range of responses are possible in mixed powder systems, depending upon the physical and chemical properties of each component[5]. Sintering and coalescence will occur readily where there is intersolubility between the mixed powders, thereby allowing chemical potential gradients to dominate the surface energy driving force for viscous flow. However, resistance to coalescence will occur when at least one of the species possesses a low solubility in the other, or indeed if one or more species is very porous.

SEM images of cross-sectioned boiler deposits suggest that siderite-derived particles are very soluble in aluminosilicate regions, but not vice versa[6]. This observation may provide a qualitative explanation as to why coalescence is observed in some coal mineralogical systems and not others.

Conclusions

This paper examined the evolution of flame-borne mineral matter during the combustion of sub-bituminous coals in a 350 MW_e pulverised coal-fired boiler. The observed transformation phenomena were documented and described in terms of viscous sintering theory. It was concluded that the thermodynamic data currently available in the literature to help describe the high temperature mineral matter transformations occurring in coal combustion is inadequate. This data is largely restricted to compositions and temperatures of interest to metallurgists and ceramists, and therefore is of limited use to combustion engineers. It is recommended that a database of thermodynamic properties (e.g., viscosity of solid-liquid and liquid-gas mixtures, solubility, diffusivity, activity coefficients, etc.) be generated for slag compositions and temperatures of interest to combustion engineers. The high temperature transformations of mineral matter occurring in the gas phase of the boiler may then be better understood.

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