

INFLUENCE OF ASH DEPOSIT CHEMISTRY AND STRUCTURE ON PHYSICAL AND TRANSPORT PROPERTIES

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Abstract

Boiler ash deposits generated during combustion of coal, biomass, black liquor, and energetic materials affect both the net plant efficiency and operating strategy of essentially all boilers. Such deposits decrease convective and radiative heat exchange with boiler heat transfer surfaces. In many cases, even a small amount of ash on a surface decreases local heat transfer rates by factors of three or more. Apart from their impact on heat transfer, ash deposits in boilers represent potential operational problems and boiler maintenance issues, including plugging, tube wastage (erosion and corrosion), and structural damage.

This report relates the chemistry and microstructural properties of ash deposits to their physical and transport properties. Deposit emissivity, thermal conductivity, tenacity, and strength relate quantitatively to deposit microstructure and chemistry. This paper presents data and algorithms illustrating the accuracy and limitations of such relationships.

Introduction

Ash deposit properties in boilers depend on both deposit structure and composition. Thermal conductivity and emissivity, the two properties with the greatest impact on heat transfer, demonstrate strong and complex dependencies on both deposit structure and composition. The effects of deposit structure relate largely to the phases present in the deposit and the extent of sintering or contact between individual particles. This paper focuses on the effects of emissivity and porosity variations on heat transfer through boiler deposits.

Heat and mass transfer through porous media depend on macroscopic and microscopic structural properties of the media. Upper and sometimes lower bounds for transfer coefficients can be established based on easily measured structural properties, but precise expressions for transfer rates depend on a high level of structural detail, commonly beyond what could reasonably be expected to be available in practical applications. Our approach is to identify the limits and increase the level of sophistication of our models up to the point that we make the best use of available information.

Results

A useful idealization for illustrating the major effects of deposit structure on thermal conductivity is a solid of known porosity and thermal conductivity and with no conduction in the gas phase. Quanta of vibrational energy (heat) move randomly through this solid. A temperature gradient in the solid is represented by spatial differences in the population of phonons. We seek an expression relating the efficiency at which phonons can move through the porous material to its physical structure. In this simple model, heat transfer proceeds through the solid phase at its customary rate but stops when it encounters the void phase.

Spatial autocorrelation functions relate the probability of two locations being the same phase (solid or void) as a function of distance between them. Generally, autocorrelation functions are bounded by ± 1 and are identically unity at displacements of 0. Characteristically for real materials, they also decay to a limiting value in a smooth but not necessarily monotonic fashion. For isotropic material, the limiting value is the volume fraction of the phase present at a displacement of 0. If the presence of void vs. solid phase is represented as a random event, there are fairly general conditions under which the autocorrelation becomes an exponential decay, with the spatial constant of the exponent a measure of average grain size.

In addition to the amount of solid vs. void volume in the material, the connectedness of the solid phase plays a large role in determining the heat transfer rate. There are higher order correlation functions and connected correlation functions that statistically give clues to the connectedness of a phase. The concept of tortuosity is the approach we have taken, where the tortuosity is defined as the shortest average path length through the solid phase between two points divided by the straight-line distance between the same points. As the solid phase becomes less connected, the tortuosity increases. Using these three most readily available characteristics of the solid phase, the solid volume fraction, the mean particle size, and the tortuosity, we have developed a model for the dependence of the average thermal conductivity on structural properties. We are currently pursuing means of extending the model to nonisotropic conditions more sophisticated descriptions of deposit structure. In its current state, the heat transfer model depends on material porosity and tortuosity

of both the condensed and gaseous phases, in addition to the thermal conductivity of the two phases.

Aside from the anisotropies of the material, this approach largely ignores the efficiency of the connections between particles. Particles that connect at a single point or over a very small area typically conduct heat far worse than those that are connected over large fractions of their projected areas. In some analyses, the connection points dominate the heat transfer process. This connectedness is captured somewhat, but not entirely, in the concept of the tortuosity. We will examine this aspect of our model in the future. In its current state, it may somewhat over-predict the heat transfer rate in porous media.

The over-prediction is partially compensated by the effect of our initial assumptions. In the original model, the void space was assumed to be non-conducting and radiative heat transfer through the material is ignored. In reality, both intra-media radiative heat transfer and conduction through the gas phase occur. At present, we allow these two simplifications in the model and recognize that they are somewhat balanced by the incomplete descriptions of connectedness of particles in the condensed phase.

In its current state, the heat transfer model reveals some useful insights. These will be illustrated by models of heat transfer through artificially conceived by realistic deposits under boiler-like conditions. The deposits are assumed to exist on cylindrical surfaces and the analysis at this point is limited to one dimension, i.e., the radial dimension.

One dimensional, transient heat transfer through a cylindrical surface is described by

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = k \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial r^2} \right] \quad (1)$$

Where traditional symbols are used for density, heat capacity, temperature, time, and radial direction and the effective thermal conductivity is represented by k . If the transient term is ignored, the partial differential equation becomes an ordinary, second-order differential equation of the form

$$0 = k \frac{1}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) \quad (2)$$

which can be solved directly. Two constants, a and b , are involved in the solution as constants of integration in the first and second steps of the solution as follows

$$a = r \frac{dT}{dr} \quad (3)$$

and

$$T = a \ln(r) + b \quad (4)$$

By equating the surface heat flux at the fireside of the deposit with the heat flux conducted through that deposit at that location,

$$-k \left. \frac{dT}{dr} \right|_{r=r_s} = q \quad (5)$$

the first constant can be evaluated as

$$a = \frac{-qr_s}{k} \quad (6)$$

The second constant is evaluated by equating the temperature at the inner surface of the deposit to the boiler tube surface temperature

$$T(r_i) = T_1 = \frac{-qr_1}{k} \ln(r_i) + b \quad (7)$$

which yields

$$b = T_1 + \frac{qr_1}{k} \ln(r_i) \quad (8)$$

rendering a final solution of the form

$$T(r) = T_1 - \frac{qr_1}{k} \ln\left(\frac{r}{r_i}\right) \quad (9)$$

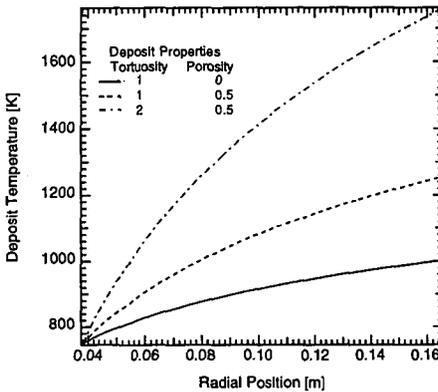


Figure 1 Parametric variation of deposit temperature as a function of position for various values of the solid volume fraction and tortuosity. See text for details of incident heat flux, etc.

This form reduces to a linear dependence of deposit temperature on distance in the limit of small deposit thickness relative to the radius of curvature. An example temperature profile is illustrated in Fig. 1 for the case of a five-inch deposit resting on a three-inch, outside-diameter steam tube with a 750 K surface temperature exposed to a heat flux of 10 kW/m² and with a thermal conductivity of 2.22 W/(m K). Both the porosity and tortuosity are considered to be unity in the base case, with both parameters being varied by a factor of two to illustrate the effects of deposit properties on the temperature profile. The temperature range depends linearly on the tortuosity and inversely on the porosity such that a change in either quantity changes the difference between deposit surface temperature and tube surface temperature by the same factor. The extent of curvature in the prediction is determined by ge-

ometry, not deposit physical properties. Deposits with solid volume fractions lower than (more porous than) 0.5 and tortuosities higher than 2 are common in many systems.

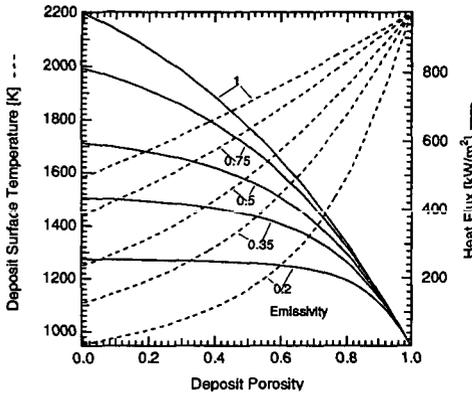


Figure 2 Deposit surface temperature and heat flux as a function of porosity and emissivity assuming no intra-deposit radiative heat transfer and a non-conducting gas phase. Tortuosity is assumed to be unity.

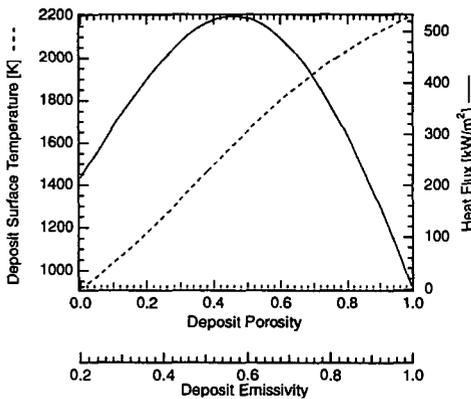


Figure 3 Deposit surface temperature and heat flux under the same assumptions as in Figure 2 but assuming a linear relationship between emissivity and porosity.

The previous predictions assumed that the incident heat flux, whether from radiation or convection, does not change as deposit surface temperature changes. In practice, incident heat flux is strongly coupled to deposit surface temperature. As an illustration, the heat transfer model predictions for the furnace section of a typical boiler are illustrated below. Only radiative heat transfer is considered, with an assumed black body radiative temperature of 2200 K, deposit thickness of 2 mm, deposit solid phase thermal conductivity of 2.22 W/(m K), and a waterwall composed of 750 K walls made of four inch OD tubes. Predictions of deposit surface temperature and heat flux are illustrated for a range of porosity and deposit emissivity values. Intra-deposit radiative heat transfer and intra-deposit conductive heat transfer through the gas phase are neglected and deposit tortuosity is assumed to be unity. None of these assumptions is generally accurate. They are made here to allow illustration of the impact of porosity and emissivity on heat transfer.

The parametric graph indicated in Fig. 2 belies the potential complexity of the relationships between deposit physical properties and heat transfer rates. While the trends in Fig. 2 indicate relatively smoothly varying and monotonic relationships between emissivity or porosity and heat flux, in practice the relationship may not be monotonic. In many cases of practical interest porosity and emissivity are correlated. Heat fluxes under such conditions may not vary monotonically with physical properties. Figure 3 illustrates the trends with an assumed linear relationship between porosity and emissivity, as read by the dual abscissae. As the relationships become more complex, and as factors such as intra-deposit radiative heat transfer and tortuosity are included, the relationships can become increasingly complex.

Structural properties of ash vary temporally, effecting changes in both porosity and tortuosity. A common example is sintering or melting of deposits, accompanied by increases in particle-to-particle contacting area and decreases in tortuosity and porosity. A simple example is illustrated in Fig. 4. In an idealized case of uniform spheres, a change in linear dimension of less than 15 % is accompanied by a change in contacting efficiency of theoretically zero in the initial case to 50 % in the slightly sintered case. This gives rise to proportional changes in tortuosity and the porosity changes from 0.48 to 0.17. Such changes lend themselves to mathematical treatments in predicting heat transfer through ash deposits. Similar treatments describe the effect of condensation or sulfation on deposit microstructure. These have been used in the past to explain the development of deposit properties ranging from tenacity to strength.

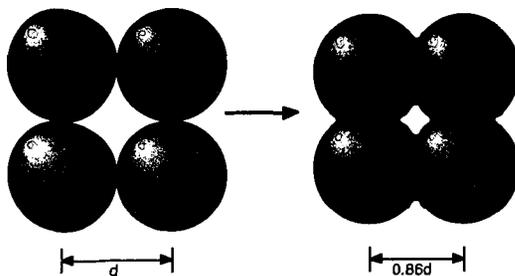


Figure 4 Conceptual illustration of the changes in contacting efficiency and tortuosity with sintering/melting.

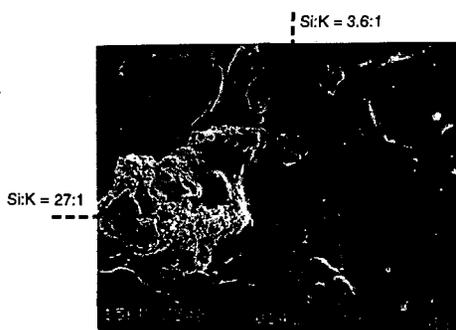


Figure 5 Scanning electron micrograph of a portion of a rice straw deposit collected from a ceramic surface in the MFC. The porous, silica based material was exposed by fracturing the deposit though one of the nodules evident in many locations on the smooth, glassy surface.

As a practical example, Figure 5 is a scanning electron micrograph of a deposit produced during combustion of rice straw in Sandia's Multifuel Combustor. The deposit was generated on the wall of the MFC combustor and accumulated over a 3 hour test period. The wall temperature was 900 °C, the gas temperature was 1000 °C, and the gas composition is estimated to contain 6 % oxygen. Most of the deposit has a glassy appearance, with occasional nodules under the otherwise smooth surface.

The deposit composition is determined as a function of location on the surface using electron dispersive spectroscopy in a scanning electron microscope. Both phases are composed principally of silicon. By comparison with the nodules, the glassy phase contains more nonsiliceous material. More than half of the nonsiliceous fraction is potassium.

For example, the melting point of silica decreases from about 1700 °C to less than 750 °C as potassium is introduced to form potassium silicates. Incorporation of additional materials, in particular other alkalis and alkaline earth materials, usually lowers the melting point further still. The silicon to potassium ratio observed in the glassy portions of the deposit illustrated in Figure 5 is about 3.4 on a mass basis, or about 81 % SiO₂ to 19 % K₂O. An equilibrium mixture of such material becomes completely molten at approximately 1300 °C. This is slightly above the temperature of deposit, but the addition of calcium and other heteroatoms to this mixture reduces the melting point significantly. The nodular material, on the other hand, has a much higher melting point. These changes in phase have obvious effects on the microstructure of the deposit and hence on its physical and transport properties.

Conclusions

Ash deposit microstructure influences the mechanical and transport properties by impacting the degree of connectedness between particles and the tortuosity of heat transport through the deposit. Mathematical models are used to predict the impact of microstructural features on bulk deposit properties and on resulting boiler performance. Deposit surface temperatures can change many hundreds of degrees, depending on deposit thermal and structural properties. Heat fluxes are also dominantly influenced by similar structural properties. Two properties that encapsulate much of the deposit microstructure effect are the porosity and tortuosity. Rational models of the dependence of thermal conductivity on these parameters are presented with predicted results. Experimental examples of how tortuosity and porosity develop in deposits, depending on deposit phase, are also presented.