EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling

Effective Thermal Conductivity in Bulk Materials at High Temperatures

Kristian Kiradjiev

Contents

1. Introduction

Background

In heavy industry, there is often the need to describe properties of composite materials. These composite materials could range from mixtures of materials being in the same phase (i.e. solid, liquid, or gas) to two-phase or even three-phase mixtures.

Calcination is used as a thermal treatment for materials to enhance, or reduce certain properties

The process of *calcination*, a form of thermal treatment of a material, enhances certain desirable propertie, and diminishes the effect of others. An example of this is the use of anthracite particles for the subsequent manufacture of electrodes for large furnaces. The aim is to create a material which resembles graphite, and thus has low electrical resistivity and can withstand high temperature and pressure. Anthracite is chosen due to its high carbon content, and it forms a particulate medium, which is a combination of solid particles and gas voids between them. There has been quite a lot of interest to this problem from Teknova, who aim to perform detailed simulations of the calcination process.

The Calciner

The calcination process takes place in a device called a Calciner. It is a large cylindrical furnace with a typical height of 8m and a diameter of 2m. As shown in Figure 1, at the top and the bottom of the Calciner, there are two electrodes, which produce a huge alternating current (of up to 15 000A) that is conducted through the anthracite particles. Due to their natural resistivity, this results in heating of the composite material, which is essential for the necessary chemical and physical reactions to occur. Anthracite particles are continuously fed from the top, and removed at the bottom via rotating *scrapers*. The flow is driven by gravity, and the speed is determined by the rate of removal by the scrapers. During the process, the anthracite undergoes three main transformations: *carbonisation*, *densification* and *graphitisation*. This is accompanied by release of volatile gases, shrinkage of the anthracite and, eventually, a reduction in the overall resistivity. The occurrence of these transformations is another reason why calcination is required since, when an electrode is assembled from this material, any further structural deformation while in use will be highly deleterious and unwanted. The threshold temperature for thermophysical stability of anthracite is quite high. Therefore, the temperatures that are developed in the Calciner can reach up to around 3000°C.

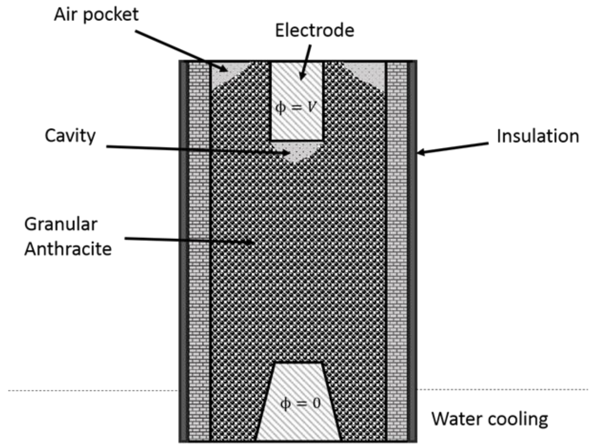

Figure 1: The Calciner is a large cylindrical furnace with two electrodes at the top and the bottom. Alternating current passes between them and is conducted through the particles in the furnace, causing heating of the material.

Accurate description of the heat transfer problem is necessary in order to perform cheaper computational simulations

In order to accurately describe the process of calcination, we have to consider the effect of the electrical current, heat transfer and mechanical flow of the particles. All these phenomena are coupled in a complex way, meaning that they depend on each other through complicated relationships. We will focus on the heat transfer problem due to its crucial influence on the whole process. This is very important when considering computational simulations since temperature distributions and heat fluxes need to be calculated in an accurate way, and experiments, on the other hand, are expensive and difficult to conduct. Our aim is to obtain an estimate of the effective thermal conductivity of the composite material, which could be used in subsequent computations by Teknova.

2. Modelling Effective Thermal Conductivity

Effective thermal conductivity refers to the conductivity that would result if the material were considered to be uniform

The thermal conductivity of a material is a measure of how well it conducts heat. Metals, for example, usually have high conductivities, whereas insulating materials, including air, have very low conductivities. When we talk about *effective thermal conductivity* of a composite material, we refer to the conductivity of the medium, treating it as it if were made of a uniform material. What makes this a difficult task is that each component has a different thermal property. Further, apart from ordinary conduction, there is a fundamentally different mode of heat transfer in the gas phase, namely, thermal radiation. Radiative heat transfer is highly dependent on temperature, so given the operating temperature regime of the Calciner, it is natural to ask how the temperature profile alters when we include radiation. Heat transfer can also occur by convection, which depends on the velocity of the material. We show a CT scan of a cross-section of a packed bed of the composite material in Figure 2. We see that the particles are angular in shape, whereas gas voids could be approximated by spherical holes if the 3D version of this picture is taken into account. The particles are relatively tightly packed and in contact between them.

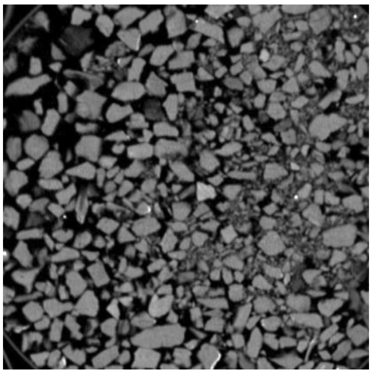

Figure 2: Picture of a packed bed of anthracite particles.

Glossary of terms

- Thermal conduction: Thermal conduction is a mode of heat transfer due to collisions of particles on atomic level in the material under consideration. The key parameter that measures this is the thermal conductivity.
- Thermal conductivity: Thermal conductivity is a property of a material that quantifies how well it conducts heat. It is measured in W m^{-1} K^{-1}. The reciprocal is called *resistivity*.
- Thermal radiation: This is the mode of heat transfer in which energy is emitted through electromagnetic waves. Therefore, matter is not required for it to occur. Thermal radiation is dependent on the fourth power of temperature through *Stefan-Boltzmann* law.
- Porosity: This refers to the volume fraction of gas in the material.
- Contact conductivity: This is the property which measures how well heat is conducted through contact points between two or more materials. Rough

boundaries have fewer contact points than smooth boundaries, and this reduces the total conductivity of the system.

We show a schematic of the various heat transfer mechanisms in Figure 3.

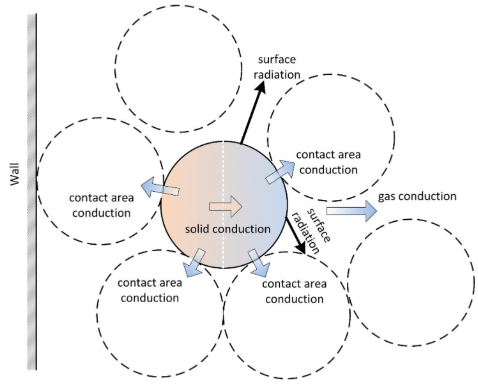

Figure 3: A schematic diagram of various heat transfer mechanisms in a particulate medium, taken from [2].

Mathematical model

We will derive an expression for the effective thermal conductivity of a composite solid-gas particulate material. We neglect heat transfer by convection due to the generally slow flow of the composite material. Further, we neglect thermal conduction in the gas due to its low conductivity. Thus, we only consider solid heat conduction in the particles and gas heat radiation in the voids between them.

We look at three different approaches: lumped parameter models, Maxwellian models and homogenisation

There are three main approaches that we take in modelling the effective thermal conductivity (see [1]). The first approach, used by Teknova, is based on a *Lumped Parameter* model. As the name suggests, in this approach the effects of various phenomena such as conduction, radiation, contact resistance, are combined into equivalent parameters in an appropriate way to obtain an effective conductivity.

We call the second approach *Maxwellian* due to the fact that Maxwell was one of the first to describe it. This is a more mathematically rigorous approach, in which we utilise solutions to the heat equation in the first material and examine their behaviour in the far-field to determine how the second material in the mixture contributes to the effective thermal conductivity. Originally, this model works for solid materials with heat conduction only. We derive an updated version, in which we take into account radiation. The drawback of this model is that, due to its assumptions, it works well for low porosities only. We also consider two other models, namely *Effective Medium Theory*, which closely resembles Maxwell's model, and *Differential Effective Medium Theory*, in which an equation for the effective conductivity is derived. It turns out that the latter performs better at higher porosities.

The third approach uses the method of homogenisation. In this approach, we aim to represent the porous medium as an assembly of periodic cells on a microscale, with the averaged effective properties varying on a macroscale. This method is useful, because it takes into account the geometry of the problem in the most detailed way.

At low temperatures contact resistance has a bigger effect

In all these models, contact resistance (or equivalently, contact conductivity) needs to be accounted for in order to achieve realistic predictions. We expect that contact resistance has a more pronounced effect at lower temperatures, since then solid conduction is the dominant mechanism of heat transfer. At higher temperatures, its effect is not expected to be dominant. We derive an expression for the effective conductivity, using all three approaches and, additionally, the contact conductivity.

Comments

- In the Lumped Parameter models, we make use of an effective radiative conductivity (see below) to account for heat transfer in the gas voids. We calculate a value for the contact resistance, which we use in these models.
- Maxwellian models work well for low porosities. We derive a novel version of them, incorporating radiation in a more realistic way, and justify the use of the effective radiative conductivity as the conductivity of the gas phase. A key step is to distinguish between gas particles in solid matrix and solid particles in gas matrix.
- Homogenisation works well for two different solid materials. Incorporating gas, we examine the effect of radiation given spherical gas pores inside a solid matrix.

3. Results

Teknova and Breitbach and Barthels' models

We present a comparison between the model Teknova uses and a model proposed by Breitbach and Barthels [2], which accounts for radiation in a more accurate way. Both of these models are examples of Lumped Parameter models. Teknova uses the following formula for the effective radiative conductivity

$$k_r = 4\varepsilon\sigma T^3 D_p,$$

where ε is the emissivity of the particles, σ is the Stefan-Boltzmann constant, T is the temperature, and D_p is the characteristic particle diameter. Breitbach and Barthels make use of the dimensionless parameter

Λ is a measure of the relative effect of solid conduction to radiation. For lower temperatures, it is big

$$\Lambda = \frac{k_p}{k_r},$$

which measures the relative effect of solid conduction to radiation, where k_p is the thermal conductivity of the solid particles. It turns out that, for temperatures up to 1000°C, Λ is very big meaning that radiation is not that important. We use the expressions for k_r and Λ in order to arrive at an expression for the effective thermal conductivity.

In Figure 4 (left), we show a plot of the effective thermal conductivity against temperature, as predicted by these two models. We see that there is good agreement between the two models until 2500°C. One implication of these models is that conductivity can grow unboundedly with temperature, which is a consequence of the assumption that we are considering a gas matrix with solid particles in it. Breitbach and Barthels also propose their own formula for contact conductivity, which depends on the elastic and geometric properties of the particles, which they use to calculate the effective thermal conductivity. In Figure 4 (right), we see a comparison of the results of Breitbach and Barthels' model with experimental results from [2]. In this low-temperature regime, we see an excellent agreement between their theory and the data. We conclude that simply model used by Teknova is likely to capture the temperature dependence of the effective thermal conductivity in the low-temperature regime.

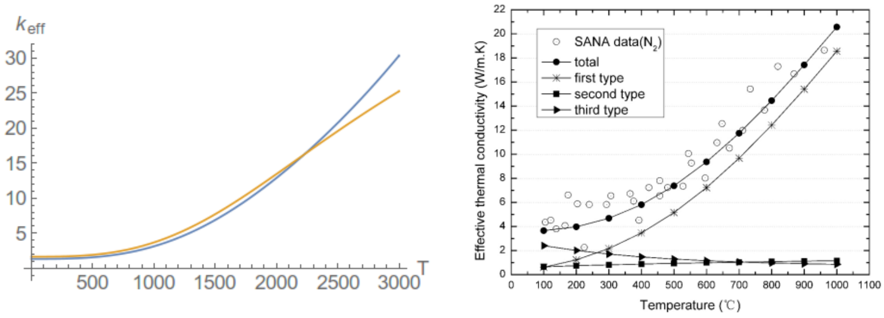

Figure 4 (left): Graph, showing a comparison between the effective conductivity, k_{eff}, predicted by the Teknova (blue) and Breitbach and Barthels' (orange) models. Figure 4 (right): Graph showing a comparison between experimental results and predictions from Breitbach and Barthels' model for solid particles with helium between them (taken from [2]). The relevant curve to look at is the one with solid black circles.

Maxwell's model, Effective Medium Theory model, and Differential Effective Medium Theory model

We generalise Maxwell's model, the Effective Medium Theory model, and the Differential Effective Medium Theory model to include radiation and we find that it is appropriate to use k_r as the effective radiative conductivity. In Figure 5, we see a comparison between these three models. We observe that they exhibit similar behaviour, but predict a higher value for k_{eff} at lower temperatures than the previous two models. This is a result of the fact that, in these models, we assume a solid matrix with gas voids in it. Furthermore, at higher temperatures, unlike the previous two models, these models predict saturation in the effective thermal conductivity, which should be the case in reality. This is because the solid part is the rate-limiting factor for the heat flow. This saturation can be partially seen in Figure 5 for Maxwell's model (blue curve), for example, and for the rest saturation is reached at higher temperatures.

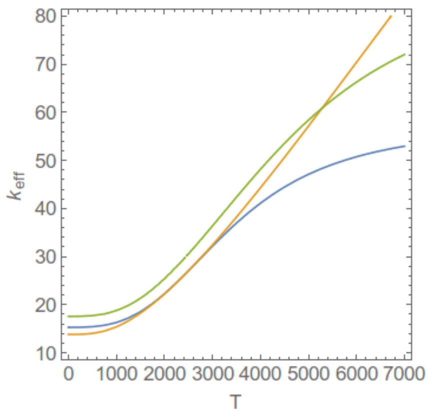

Figure 5: Graph showing a comparison between the k_{eff} predicted by the Maxwell's model (blue), the Effective Medium Theory model (orange), and the Differential Effective Medium Theory model (green).

Homogenisation

Our final approach, homogenisation, predicts that radiation does not have a significant effect on k_{eff} in low-temperature regimes. However, we expect radiation to be important at higher temperatures, and for this to enter the formula for k_{eff}.

4. Discussion, Conclusions & Recommendations

We have considered the problem of finding the effective thermal conductivity of a composite medium. We looked at three possible approaches. We found that the simple Lumped Parameter models, coupled with detailed descriptions of various effects, give results which compare well with experiments. The drawback of these models is that a separate formula needs to be determined for each geometry that is being considered. Maxwell's model and its counterparts are more complicated than Lumped Parameter models and we have generalised them to include radiation. These models assume a matrix of solid material containing gas voids, and predict saturation in the effective conductivity with temperature. This is an interesting result, which could be applied for various porous materials with gas voids inside. Homogenisation provides the most mathematically rigorous way of incorporating the geometry of the problem. However, in the low-temperature regime, we found that the effective thermal conductivity does not depend on radiation effects, although we anticipate that radiation will become important at higher temperatures.

More experimental data is required to validate the models

In general, we have looked at a wide range of models for effective thermal conductivity, ranging from more intuitive ones to mathematically rigorous results. We have obtained results in good agreement with available experimental data. Yet, more experiments are required in order to validate these models. There are several key extensions to be tackled in the future. Firstly, we should include heat transfer by convection of the gas. Secondly, we should take account of contact resistance more accurately in the Maxwellian models and should adapt the models to incorporate non-spherical voids.

5. Potential Impact

The results from this project are important because they give insight into the heat problem in the calcination and related processes. Our investigation forms part of the ElMET project, a multi-institution, multi-disciplinary investigation into the electrical behaviour of composite materials in furnaces at high temperatures.

Svenn Anton Halvorsen, Chief Scientist at Teknova, commented "*The goal of the ElMet project is to establish a detailed understanding of the operational conditions of electric furnaces by means of computational modelling. To this end, it is necessary to obtain accurate descriptions of the temperature distributions and heat fluxes. These, in turn, depend on the thermal conductivities of all parts of the system.*"

"*Kristian Kiradjiev's work has focused on establishing novel protocols and approximations to estimate effective thermal conductivities for granular material over a large range of temperatures. His work has been meticulous and it is giving us new tools and insights upon which we will base the reliability of future simulations.*"

References

1. Carol Pietrak et al (2015) *A Review of Models for Effective Thermal Conductivity of Composite Materials*. Journal of Power Technologies. **95**, 14-24.

2. C. Ren et al (2017) *Theoretical Analysis of Effective Thermal Conductivity for the Chinese HTR-PM Heat Transfer Test Facility*. Applied Sciences. **7**, 76.