EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling

Modelling of Carbon Paste Baking

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1. Introduction

Ramming paste is used as an impermeable lining for metallurgical furnaces. It consists of grains of anthracite (a type of coal) held together with a binder.

Carbon pastes are industrial products which are used in different areas of industrial metallurgy, such as components of electrodes in silicon furnaces. In particular, ramming paste is a type of carbon paste used as a lining for furnaces. The paste forms an impenetrable layer around the main furnace vessel, preventing liquid metal and other substances from leaking into the surrounding work environment. Ramming paste is also used for Hall-Héroult cells in aluminium refining, where it is both used as cell lining and to bind together many small rectangular electrodes in the base of the cell.

In both situations, safety and economic considerations mean that high quality ramming paste –which does not have gaps for furnace material to seep through – is crucial. Lower quality pastes need to be replaced more frequently, potentially after less than one year of operation, compared to 5-10 years for high quality paste. Replacing ramming paste is expensive, both due to the costs of the replacement and the loss of production during the replacement period.

The process of installing ramming paste in a furnace begins with an empty, unheated furnace. The paste, which has a rubbery consistency at this stage, is poured around the edges of the furnace. Workers then go into the furnace and use mechanical equipment to compress the paste. The furnace is then slowly heated over several hours to high temperatures, causing the paste to harden and form an impermeable layer around the furnace. This heating process is called baking.

Most binders are made from coal tar pitch, which is a carcinogen. New non-toxic binders are being developed.

Typical ramming pastes contain granular particles of anthracite (a type of coal with similar properties to graphite), held together with a binder. The most common binders are made from coal tar pitch. However, exposure to coal tar pitch, which can occur during the compression stage, is associated with increased risk of bone, liver, and kidney cancer, among other illnesses. Elkem, a large Norwegian producer of carbon and silicon products, has been developing alternative ramming pastes using safer, non-toxic, binders. To assist with this development, Elkem are working with Teknova, a small Norwegian industrial research institute, to make models for these new ramming pastes.

Our goal is to build a mathematical model describing the baking of ramming paste. This will assist Elkem and Teknova in the development of non-toxic binders for ramming paste, by enabling them to run computational simulations of the baking process, which can be performed more quickly and at a lower cost than laboratory experiments. Such a model could also provide useful information not available from laboratory experiments, such as an understanding of which physical processes are most important in the baking process. In particular, we aim to provide:

- A mathematical model describing the key physical processes which occur during the baking of ramming paste;
- An analysis of this model, showing the relative importance of each physical process;
- Numerical simulations of a simplified model, including validation against experimental results and an analysis of its sensitivity to input parameters; and
- Recommendations of changes to the paste baking process which would reduce the likelihood of the paste cracking and therefore improve the quality of the paste.

The layout of this report is as follows. The next section contains a description of the alternative ramming pastes, and a description of the mathematical model for the baking process. We then examine how the model solutions agree with experimental data, and suggest changes to the baking process to reduce the risk of cracking of the ramming paste.

2. Baking Process for Ramming Paste

Once ramming paste has been installed in a furnace, the furnace is slowly heated. This allows the paste to 'bake', when it hardens and forms an impermeable layer around the furnace edges. During baking, several physical processes take place:

- Evaporation of volatile chemicals;
- Gas movement within the paste, leading to mass loss as gases escape;
- Heat transfer within the paste;
- Deformation and hardening of the paste.

Ramming paste is mostly (80-90% by mass) comprised of grains of anthracite. The remainder of the paste is a binder, which holds the grains of anthracite together. The paste is a porous medium – it is not completely solid, containing a network of air-filled pores.

During baking, the binder undergoes chemical reactions, and forms a seal between the anthracite pieces. These chemical reactions produce gases, which cause an increase in pressure within the paste. These pressure differences cause the gas to escape the paste into the external environment. However, the build-up of pressure can lead to internal forces, and excessive pressure can cause the paste to crack. Paste which cracks during baking no longer forms an impermeable layer around the furnace, and must be replaced at great cost.

Elkem's non-toxic binders contain water which evaporates during baking. The fast evaporation rate leads to a build-up of pressure, increasing the risk of the paste cracking.

Although most binders are made of highly toxic coal tar pitch, Elkem's non-toxic binders are made of organic compounds dissolved in water. Elkem has observed that, during the baking process, the paste loses mass quickly as the baking temperature passes 100°C. Elkem believes that this increased rate of mass loss is due to the evaporation of the water from the binder. The speed of this mass loss is faster than typically seen for coal tar pitch binders, and Elkem believes that this can lead to cracking.

In the development of a mathematical model for the baking process, we place particular emphasis on heating, pressure changes due to water evaporation, and how this causes the paste to deform and crack.

The experimental setup we consider is a small cylindrical sample of paste, which is heated slowly from room temperature to several hundred degrees Celsius over several hours. The external pressure is held constant throughout the experiment.

Mathematical model

To construct a mathematical model of the baking process, we make several simplifying assumptions. The most important is that the binder is only comprised of water, all of which can evaporate. That is, we ignored the organic compounds in the binder, and instead increased the relative proportion of anthracite – which does not undergo any reactions – so that the proportion of 'binder' in the paste actually refers to the proportion of water in the paste.

We ignore all reactions except the evaporation of water, which is the fastest and most significant reaction.

This assumption means that the only reaction occurring is the evaporation of water, which we assume to depend on temperature and the proportion of binder (i.e. water) and gas in the paste. This dependency is important, since evaporation occurs at the interface between the water and the pores in the paste – if either were absent, no evaporation could occur.

We also treat the entire paste – both anthracite and binder – as a single porous structure. This means that any deformations in the paste, such as from pressure build-up or thermal expansion, occur in both the anthracite and binder simultaneously.

Under these assumptions, our model for the baking of paste describes the evolution of temperature, gas pressure, and the mass and deformation of anthracite and binder in the paste, due to the following processes:

- Heat transfer through the paste via convection and conduction;
- Evaporation of water;
- Movement of gas through the pores in the paste (due to pressure gradients);
- Deformation (including cracking) and hardening of the paste.

We scale the model, enabling us to identify certain physical processes as having negligible effect in this particular situation. These processes are the changes in thermal energy of the gas (including the convection of heat by the flow of gas) and gravity. A similar analysis also provides an understanding of the time scales over which some of the key processes occur. We find that the fastest physical process is evaporation, the second fastest is the movement of gas through the paste, and the slowest is the external temperature increase controlling the baking.

In the following sections, we present results for a simplified version of our model, which ignores the deformation and hardening of the paste. Although the actual formation of cracks and changes in porosity are captured in the deformation part of the model, this simplified model still provides a useful description of the pressure changes within the paste, and therefore gives us an understanding of the circumstances under which cracking is likely to occur.

3. Model Validation and Predictions

In this section, we discuss how the simplified model – which includes heat transfer, evaporation, and gas movement – predicts the likelihood of cracks forming in the paste.

A simplified model, incorporating heat and mass transfer, predicts mass loss from evaporation which agrees with experimental data.

In Figure 1a, we show a comparison between the mass loss profile predicted by our simplified mathematical model and experimental data provided by Elkem. The model predicts that the majority of the mass loss will occur within a small temperature range, after which no further mass loss is observed. At this point, all the binder has evaporated, and the gas has flowed out sufficiently so that the pressure is constant throughout the sample. The experimentally-observed mass loss beyond this point, at about 200°C, is from reactions involving the organic compounds in the binder, which the model does not capture. As the rate of mass loss observed at these temperatures is low, it is less relevant for understanding the formation of cracks.

The model predicts the mass loss observed in experiments. In particular, it provides an excellent prediction of the overall mass loss over the temperature range when the largest structural changes are observed experimentally, and when the pressure is highest. Since we expect the risk of cracking to be highest at this point, we would expect information provided by this model to be useful for predicting cracking. As this model does not capture deformations of the paste, we cannot measure the formation of cracks directly. However, we can use the size of the pressure peak within the sample as an indicator of cracking likelihood, since the higher the maximum pressure in the sample, the greater the risk of cracking.

In Figure 1b, we show how the pressure changes over time at different points between the centre and boundary of the sample. We see that the pressure increases quickly towards a maximum value, which occurs at about the same time as the largest rate of evaporation and of mass loss within the sample, then returns to its original equilibrium level as the reaction completes.

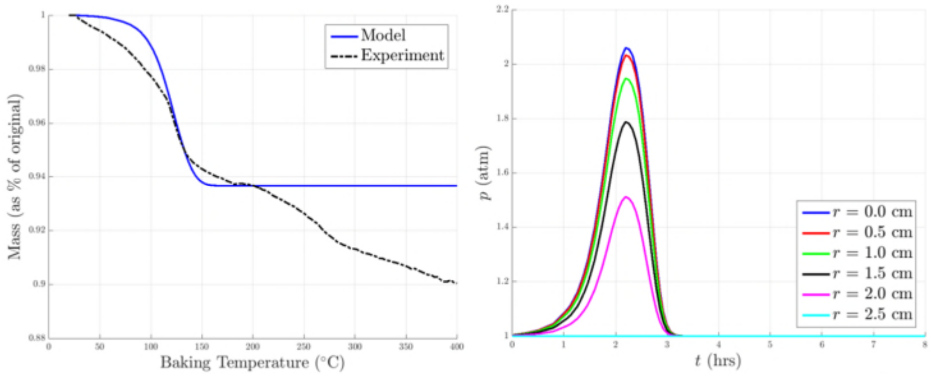

Figure 1. In (a; left), a comparison of mass loss in the sample observed experimentally and predicted by the simplified model. In (b; right), a plot of the predicted pressure through time at different radii within the sample ($r = 0$ cm is the centre of the sample, 2.5 cm is the external surface of the sample). Experimental data source: Elkem Carbon.

For our simplified model, we use the maximum gas pressure attained during baking as a proxy for the likelihood of the paste cracking.

In the following sections, we consider a number of factors which can be measured or changed experimentally, and how they may affect the likelihood of cracking. To do this, we will consider the maximum pressure attained in the sample, and attempt to understand how to reduce it.

Impact of total baking time

In the experiments, the paste is heated to several hundred degrees over several hours. Elkem has observed that increasing the temperature to the same maximum level more slowly – that is, having a longer total baking time – decreases the risk of cracking. In Figure 2a, we show the maximum pressure attained anywhere in the sample, at any point during the baking process, for different total baking times. The model matches Elkem's observation – lower pressures are attained when the total baking time is longer.

Slowing the rate of baking temperature increase, particularly around 100°C, reduces the risk of cracking.

However, as we saw in Figure 1a, most of the evaporation and mass loss occurs within a small temperature range around 100°C. Therefore, we might expect that a slower rate of temperature increase near 100°C would reduce the maximum pressure, but without as large an increase in the total baking time required to reach the same maximum temperature. This is what our model predicts – by reducing the temporal gradient of temperature over the range 80-120°C, we can reduce the maximum pressure. For example, by halving the temperature gradient in the range 80-120°C, we can reduce the total baking time from 8 hours to 6 hours, while simultaneously reducing the maximum pressure attained.

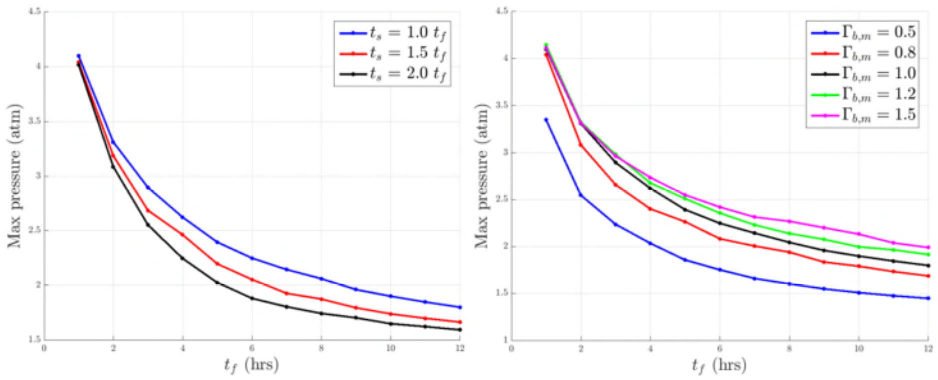

Figure 2. In (a; left), the maximum pressure attained anywhere in the sample at any point during baking, for different total baking times t_f. The different lines represent how much slower the temperature range 80-120°C was heated (blue is the same speed throughout, black is twice as slow, etc.). In (b; right), the same plot, but the curves represent different mass fractions of binder (black is the original mass fraction, blue is half as much binder, etc.).

Impact of anthracite/binder ratio

Decreasing the proportion of water in the paste reduces the likelihood of cracking.

Another quantity of interest is the amount of water in the sample; in our model, this corresponds to the proportion of binder in the paste, since we treat the mass from organic compounds as (non-reactive) anthracite. In Figure 2b, we show that the maximum pressure decreases as the initial proportion of binder in the paste $\Gamma_{b,m}$ is reduced.

Interestingly, the model also predicts that reducing the proportion of binder causes the (lower) maximum pressure to be attained later in the baking process. A lower binder proportion means the maximum pressure is reached at a higher baking temperature. Since the paste hardens as the baking progresses, reaching the maximum pressure later during baking is desirable, since harder paste is less likely to crack.

4. Discussion, Conclusions, and Recommendations

We have developed a model which captures all of the important physics which take place during baking, in order to gain a better understanding of the underlying physical processes. We have presented results of a simplified version of this model, where we use pressure changes to understand the likelihood of cracks forming in the baked paste. This simplified model shows a good fit to experimental mass loss data, particularly during times when the internal gas pressure is largest, and hence the risk of cracking is greatest.

By considering the model parameters which can be controlled experimentally, the simplified model predicts different ways the risk of cracking could be reduced. Firstly, the temporal gradient of the temperature profile can be reduced. In particular, decreasing the gradient near 100°C can reduce the risk of cracking without substantially increasing the total time needed to reach the required maximum temperature. Also, by reducing the proportion of water in the paste, a lower pressure may be attained later in the baking process when the paste is harder.

Our model could be improved by further validation against experimental data. In particular, for the simplified heat and mass transfer model, further experiments could provide greater clarity on what maximum pressures correspond to cracking. This would improve the model's usefulness, by improving the connection between model predictions (a pressure profile) and the presence of cracking (the actual phenomenon of interest).

The underlying mathematical model could be improved by including a more sophisticated description of the evaporation rate, or incorporating the weakening of the paste porous structure during baking, using 'damage models'. A better fit to experimental data, particularly for high baking temperatures, could be achieved by extending the model to include the chemical reactions which the organic compounds undergo during heating.

5. Potential Impact

The mathematical model can be used as an initial predictor of paste cracking during baking, improving the efficiency of the product development process.

The mathematical model developed in this project will be used by Teknova and Elkem to assist in the continued development of binders for ramming paste. By improving the operational performance of non-toxic binders, the metallurgical industry will be able to more quickly move away from highly toxic coal tar pitch binders, with a corresponding improvement in worker safety. The results presented here demonstrate that the model can predict the impact of changing different baking parameters, such as the external temperature profile, on the likelihood of cracking occurring. By using this model as an initial tool during development, Elkem may be able to reduce the time and financial costs associated with laboratory experiments.

Ellen Nordgård-Hansen, Senior Researcher at Teknova, and Øyvind Mikkelsen, Senior R&D Engineer at Elkem, said: "*The results from the mini-project help the development of new non-hazardous binders for carbon products in the metallurgical industry. Specifically, it gives an increased understanding of the phenomena of importance during the baking of carbon paste. The results are clearly presented and the sensitivities to the different variables are shown in figures and tables. This makes it possible to efficiently optimise the paste for different applications. The well-documented project results enable further development of the mathematical models internally in order to implement more of the relevant physics.*"

Cover image source: Elkem Carbon.