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Modelling Removal of Sulphur Dioxide from Flue Gas

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Creative Technologies
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Contents

1. Introduction

Background

A major task in many industries is to reduce the concentrations of mercury and sulphur dioxide in flue gas they produce

Sulphur dioxide and gas-phase mercury are major components in flue gas used in a range of industries in which raw materials are processed. Due to their harmful effects on living organisms and the environment, their concentrations need to be sufficiently reduced before they can be released into the atmosphere. The solution W. L. Gore and Associates have developed, called GORE Mercury Control System (GMCS), is a unique chemical filtering device, which captures the mercury and also converts sulphur dioxide (SO_2) into liquid sulphuric acid (H_2SO_4). The device itself consists of multiple stackable *modules* of typical size 2 ft x 2 ft x 1 ft high, each having numerous open channels, through which the flue gas flows (see Figure 1). The open channels mean that the system operates with a very low pressure drop, avoiding the need for an additional fan that convects the gas. More importantly, the device can be directly installed wherever the gas is released without the need for construction of a specifically fitted building for this purpose (see [1] for a detailed description of the device and how it works).

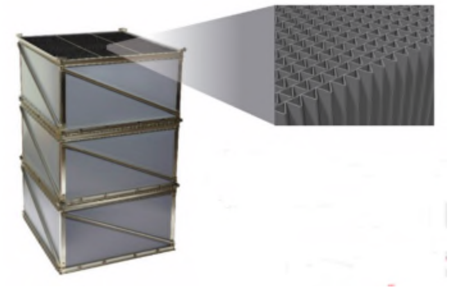

Figure 1: Three modules of Gore Mercury Control System, stacked on top of each other. To the right we see a zoomed in version of a single module (taken from [1]).

Operational mechanism

The GMCS device operates as a chemical filter, adsorbing mercury and converting sulphur dioxide into liquid sulphuric acid

The key parts of the GMCS device are the millimetre-thick sheets that surround each channel. As the gas flows through a module, it diffuses into these sheets, which have a highly porous structure. Each of them is made of a *Sorbent Polymer Catalyst* (SPC) composite, which consists of a *fluoropolymer* (ePTFE) fibrous matrix and activated carbon pellets (see Figure 2) [1]. When sulphur dioxide molecules come into contact with the pellets, chemical reactions are catalysed which convert the sulphur dioxide into liquid sulphuric acid. Mercury, on the other hand is chemically adsorbed into the pellets, and thereby removed from the gas.

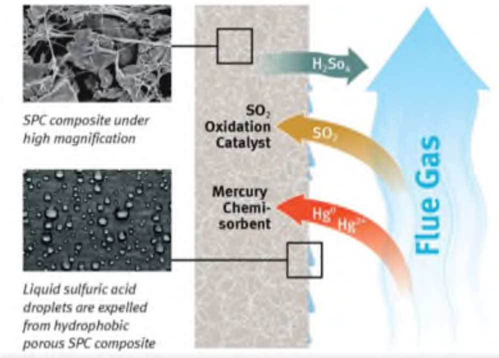

Figure 2: Operation mechanism of GMCS and scan micrographs of SPC and liquid sulphuric acid droplets on the surface of the filter (taken from [1]).

Challenges

The problem that Gore face lies in the production of sulphuric acid as part of the filtration process. Over time, drops of sulphuric acid gradually appear on the surface of the filter sheets (see Figure 2). When they become sufficiently large, these drops run down the surface under the influence of gravity. While this process looks like a natural cleansing mechanism of the filter itself, washing away any solid obstructions, it presents another issue: the liquid slowly fills the void space in the porous sheets, thus blocking incoming flue gas, which ultimately reduces the filter's efficiency. A key issue is to understand the driving mechanisms behind the accumulation of sulphuric acid, how the liquid evolves, and the timescales over which this happens. This will enable us to predict the filter's efficiency and suggest various improvements.

Over time, sulphuric acid seeps out from the surface of the filter's sheets. The key issue is to understand how, why and over what timescales this happens.

Other advantages of using this type of filtration include the huge storage capacity of SPC for mercury, being measured in years, rather than hours [1], and production of sulphuric acid "for free", which can be subsequently collected and used. This makes finding the solution to the filter blockage problem of great interest to W. L. Gore and Associates.

Our aim is to develop a microscale model to describe the build-up of sulphuric acid within the microstructure of the sheet, and to assess how local performance alters as sulphuric acid builds up.

2. Single Pellet Microscale Model

In order to gain insight into the problem, we will develop a *multi-scale* mathematical model in which we describe the spatial and temporal evolution of liquid sulphuric acid. The first building block is a microscale model which captures the behaviour of the chemical reactions on a single carbon particle. Our ultimate aim is to connect this with a device-scale model, which we will use to predict global properties of the filter such as its overall efficiency. The reason for this approach is that a single model that accounts for both local and global scales is analytically and computationally intractable due to the great range of length scales involved and the complexity of the underlying porous structure.

We study a microscale model first, focusing on a single carbon catalyst pellet, in order to understand the effects of the processes that occur at this scale

Glossary of terms

- Flue gas: This refers to exhaust gases, usually released from factories, produced during the processing of raw materials or a combustion process.
- SPC composite: Sorbent polymer catalyst (SPC) composite is a material which consists of fibres made from a specific fluoropolymer (ePTFE) and activated carbon particles (pellets), which act as chemical catalysts to speed up certain reactions.
- Reaction rate: This is the speed at which reacting chemicals are consumed by the reaction. A key measure is the chemical rate constant, which is usually experimentally determined.
- Stoichiometry: This is the relationship between relative quantities of various chemicals that participate in a reaction. It is usually measured in whole numbers or fractions that appear in front of the chemicals in a chemical equation.
- Diffusion: This is a natural transport mechanism in which a substance spreads out from regions of higher concentration to regions of lower concentration.

Mathematical model

We start by assuming that we have a spherical carbon pellet with a liquid sulphuric acid film growing uniformly on its surface. This is a reasonable initial assumption, because at the length scale of a single pellet (approx. 10μm in radius), the effect of gravity is not sufficient to skew the radial symmetry. All phenomena involving multiple particles, such as capillary effects, are ignored at this stage.

Instead of modelling multiple intermediate reactions, we assume an effective reaction takes place on the surface of the catalyst

The catalytic reactions take place throughout the whole carbon pellet, which is a porous material itself and provides a high surface area. In our model, we assume that the reaction happens on the surface of the pellet with an *effective* chemical rate constant. Thus we assume that the overall chemical reaction that describes the conversion of sulphur dioxide (SO_2) into sulphuric acid (H_2SO_4) is

$$2\,SO_{2\,(g)} + 2\,H_2O_{(g)} + O_{2\,(g)} \xrightarrow{\text{Cat.}} 2\,H_2SO_{4\,(l)}.$$

We do not track the water vapour concentration, since it is abundant in the surrounding air. We assume that the sulphur dioxide and oxygen move by diffusion through the air and then through the liquid sulphuric acid film until they reach the surface of the pellet, where they react under its influence (see Figure 3). As a result, we set up a system of equations that govern this diffusion process and an additional equation for the growth of the film. An interesting feature of this model is the need to prescribe a specific condition on the gas–liquid interface, called Henry's law, which gives the relationship between the concentration of SO_2 (and O_2) in the gas and in the liquid. We account for the reaction kinetics by imposing a condition on the surface of the carbon pellet that states that the rate at which sulphur dioxide is removed is given by the rate at which it is consumed by the reaction. In order to describe this rate, we use the law of mass action, which states that the reaction rate is proportional to the product of concentrations of the various reactants, raised to a power, determined by the *stoichiometric* coefficients in the chemical reaction.

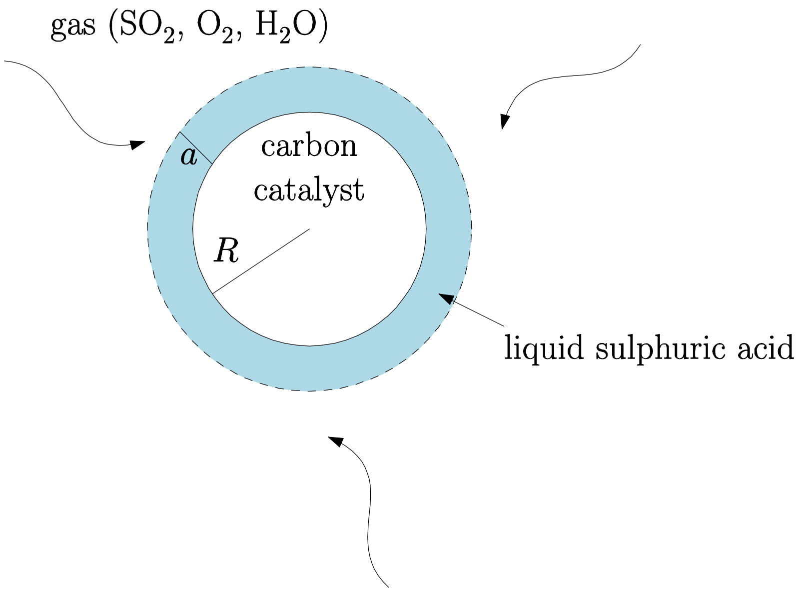

Figure 3: A schematic diagram of the single pellet model.

Comments

- We obtain a system of equations governing the concentration of sulphur dioxide and oxygen in the gas and in the liquid sulphuric acid layer. We couple this with an equation for the thickness of the film, which we ultimately aim to determine.
- We work out the sizes of the governing parameters and then make systematic approximations based on these.
- We aim to understand the dominant behaviour of the model through a simplified system of equations and eventually compare this with a numerical solution of the full system.

3. Results

Non-dimensionalisation

We simplify our system of equations by making approximations on the relative sizes of the contributions. This is systematically achieved through *non-dimensionalisation*, scaling variables with typical values. This process has two advantages: first, it makes all equations easier to be numerically manipulated, and, second, it gives a way of quantifying the relative effects of various factors in the model through the use of dimensionless parameter groupings.

We are presented with several natural possibilities for the timescale over which we can study the problem: the diffusive timescale of SO_2 in the gas; the diffusive timescale of SO_2 in the liquid; and the timescale over which the film grows. Since we are mostly interested in the evolution of the liquid film, we choose the third timescale. After using sample values for the various parameters in the model, we see that this timescale is also the longest.

The key dimensionless parameters governing the evolution are thus k_s, k_c which represent the relative rates of the chemical reaction to the rate of diffusion of SO_2 and O_2 in liquid sulphuric acid, respectively, and σ_s, σ_c which represent a ratio between the solubility in liquid sulphuric acid and the relative magnitude of diffusion coefficients in gas and sulphuric acid of SO_2 and O_2, respectively.

> Key dimensionless parameters measure the relative rate of the chemical reaction to diffusion, and the ratio between solubility and relative magnitude of diffusion coefficients in the gas and the liquid sulphuric acid

A simplified system

On the film-growth timescale, the system of equations describing the problem simplifies and we obtain an explicit formula for the thickness of the film. We validate our analytical solution by solving the full system numerically, which agrees very closely, as shown in Figure 4. We also show plots of the spatially varying concentrations of SO_2 (denoted s) and of O_2 (denoted c) in the liquid sulphuric acid for different times.

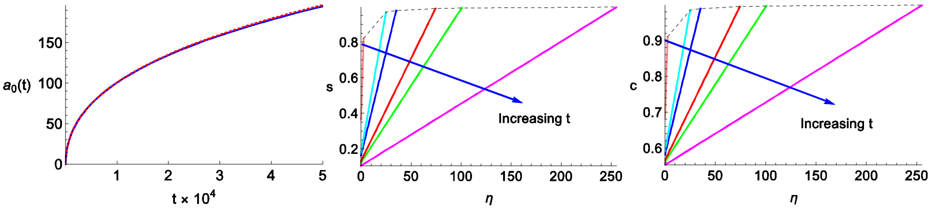

Figure 4: Graphs showing (left) the evolution of the thickness $a_0(t)$ of the liquid sulphuric acid film versus time, where the explicit solution to the simplified system is shown in blue and the numerical solution to the full system is shown in red; (middle) the spatial evolution of the concentration of SO_2 in the liquid sulphuric acid for different times (solid lines); and (right) the spatial evolution of the concentration of O_2 in the liquid sulphuric acid for different times (solid lines). The dashed curve shows the evolution of the concentration at the gas-solid interface with time (parameters: $k_s = k_c = \sigma_s = \sigma_c = 1$).

We find that the film grows linearly in time to begin with, slows to a square-root growth when it thickens, and, finally, grows like the cube-root of time when the film thickness becomes comparable with the pellet's radius. Thus, we see that

$$a_0(t) \sim C_1 t \qquad \text{for } t \text{ small,}$$

$$a_0(t) \sim C_2 \sqrt[3]{t} \qquad \text{for } t \text{ large,}$$

where C_1 and C_2 are constants, which depend on the dimensionless parameters, mentioned in the previous section. We show an excellent match between the explicit solution, and these predicted behaviours, in Figure 5.

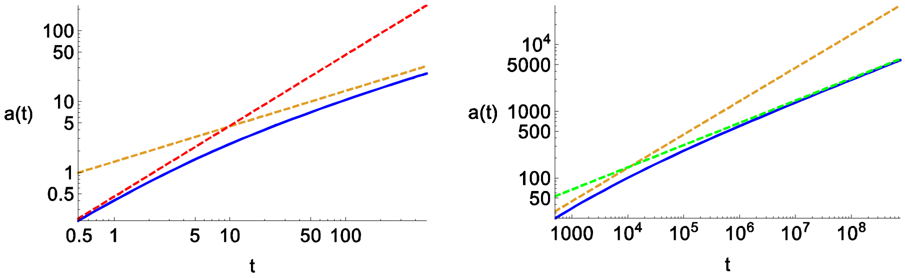

Figure 5: Graphs showing (left) the exact solution to the simplified system for the film thickness $a(t)$ (blue curve) on a log-log scale, where the dashed lines correspond to the predicted linear (red) and square-root (orange) behaviour for small and medium film thickness, respectively; (right) the exact solution to the simplified system for the film thickness $a(t)$ (blue curve) on a log-log scale. The dashed lines correspond to the predicted square-root (orange) and cubic-root (green) behaviour for medium and large film thickness, respectively (parameters: $k_s = k_c = \sigma_s = \sigma_c = 1$).

Some generalisations

If we generalise the reaction kinetics on the surface of the pellet to incorporate a more general power law dependence, we find that the small and large time behaviours are not altered and that the film thickness grows in a similar way as in the simple case.

Furthermore, we examine the effect of geometry by comparing rectangular, cylindrical and spherical pellets. For non-spherical geometries, the simplified system has some limitations in the way it is set up to mimic the model for spherical ones. We find that there are differences in the growth rate of the film for large times, with spherical pellets showing slowest growth.

Absorption of water by sulphuric acid from the surrounding air is an important effect to be considered due to its contribution to the growth of the film

Expanding the model

- Accounting for the hygroscopic nature (ability to absorb water) of sulphuric acid is an important effect we need to include in a future model. This provides another mechanism for film growth apart from the production of sulphuric acid at the surface of the pellets, and we expect it to become more important as the film grows, given that the humidity in typical applications is high.
- Despite our analysis about general reaction kinetics, it is important to represent the exact reactions that take place in order to have a more realistic model. It would be useful to obtain accurate estimates of the various chemical parameters, such as chemical rate constants, in order to justify our approximations.
- Our ultimate goal is to model the global-scale behaviour of the filtering device to predict its efficiency. For this purpose, it will be necessary to move from a single particle to many particles and model any interactions.

4. Discussion, Conclusions & Recommendations

We have developed a model describing the microscale problem for the removal of sulphur dioxide from flue gas. We have obtained solutions for the growth of the liquid sulphuric acid film in a simplified system, which agrees with the full numerical solution, and have analysed its behaviour for various time domains.

Simplified single pellet model

Our solutions for the evolution of the thickness of the liquid sulphuric acid layer reveal a complex transition from linear to sublinear growth. We observe similar behaviour for more general reaction kinetics which suggests that this is a generic behaviour, characteristic to our diffusion-limited process.

Generalisations

Introducing more complicated reaction kinetics, we found that, if we still use a single effective reaction, our analysis shows that the actual kinetics do not play a significant role on the general behaviour of the film growth. This means that our assumptions regarding the reaction appear sensible. Regarding the comparison between different geometries, although we conclude that spherical pellets provide slowest growth at large times, a more careful treatment of the full problem is required to be able to make more quantitative comparisons.

Looking forward, we will refine this model to include other effects such as adsorption of water, the growth rate of the film will be a key output, which will serve as an input to the device-scale model. Our aim is to link local properties to global ones such as the filter's efficiency.

5. Potential Impact

Uwe Beuscher, Technical Leader of Gore Mercury Control System Team at W. L. Gore and Associates, commented

"The goal of this project is to gain an understanding of the underlying mechanisms that cause the accumulation of sulphuric acid inside and on the surface of the filter, the timescales over which this happens, and how this affects the global efficiency of the device. The concentration and distribution of liquid inside the pore space of the filter and the influence on its growth rate by filter structural parameters will give design guidance for better and longer performing filters. The approach that has been taken can also give valuable insight into other problems where similar filtration and transport mechanisms are utilised. In particular, we can extend the results of this project to the removal of other chemicals such as mercury and its interaction with the liquid accumulation due to the SO_2 *reaction."*

"Kris's work has established the foundation for exploring the various physical phenomena that influence the performance of our products in relation to relevant filter properties. The single particle description will help us understand the limiting parameter and time scales to expand the model to understand the effect of structural filter properties and the proximity of multiple particles. We are very excited about the progress in this brief project period and are looking forward to employing this and improved versions of the model for our product development."

Vasudevan Venkateshwaran, an applied mathematician from the Modelling and Simulation Team at W. L. Gore and Associates, also commented

"Kris's work has focused on establishing a multi-scale modelling approach to estimate the effective sulphuric acid accumulation rate in the filter. He is an exceptionally talented mathematician and his work is giving us new insights into the connections between microscale phenomena and macroscale performance metrics of our filters. His work also will be applicable to other systems where similar physics are involved."

References

1. J Knotts et al (2017) *A Complete Mercury Control System*. World Cement. IEEE-IAS/PCA Conference.