EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling
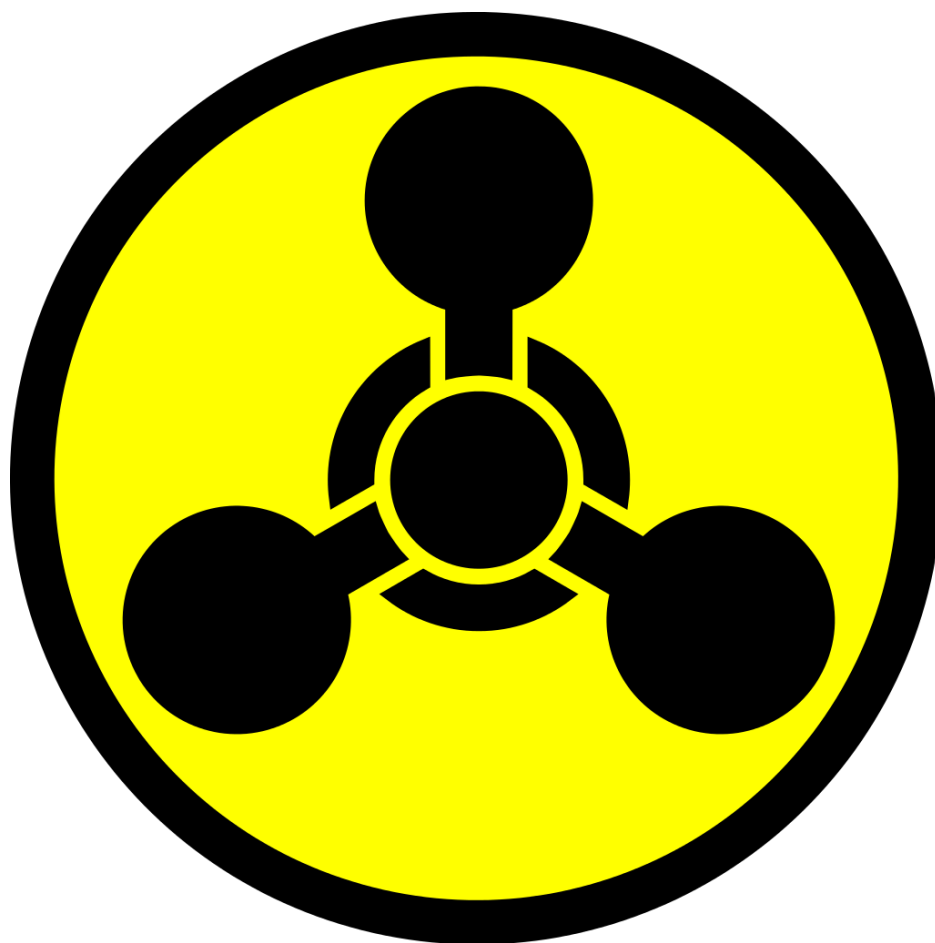
Homogenisation of agents and cleansers interacting on the microscale

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1. Introduction

Background information

DEFRA, the UK Government Department for the Environment, Food and Rural Affairs, has responsibility for the decontamination of hazardous chemicals, dispersed, for instance, as part of a chemical attack. Amongst other things, this may involve the decontamination of porous building materials (such as concrete, tarmac etc), into which the hazardous chemical fluid (the "agent") has seeped.

One possible decontamination procedure involves applying a cleaning solution (the "cleanser") on top of the porous material and letting it react into the agent trapped within the porous structure. It is crucial for public safety that all the agent is reacted away, but it is difficult to tell from surface measurements whether or not any agent remains unreacted inside the medium. It is also difficult to predict the time it takes for all the agent to be reacted away: while reaction times may (or may not) be known for the cleanser-agent pair in the lab, it is unclear how the porous material and shape of the spill within the porous medium affects the process. It is therefore relevant to study the process mathematically, to make predictions about how the cleanser reacts away the agent, and the timescale over which all of the agent is consumed.

> Understanding how a hazardous chemical and a cleaning solution interact within the porous material is important for effective and efficient decontamination.

Modelling the decontamination process

There have been many previous studies of fluid motion, solute diffusion, and chemical reactions in porous media, in the context, for example, of oil extraction or filtration systems. The unusual aspect in decontamination is that we are concerned with a situation where the agent and cleanser are immiscible fluids (typically we consider an oily agent and aqueous cleanser), so that the chemical reaction takes place on the boundaries between the two fluids. The diffusion of chemicals and motion of fluid–fluid boundaries is driven by the chemical reaction on these interfaces. Previous mathematical research into such situations, notably by Dalwadi et al. ([1], [2]) is built on a simple mathematical model and assumes that the diffusion and reaction processes occur only in one spatial dimension. The results are extended by Whitehead [3] to 2D agent spill geometries.

We are interested in investigating the validity of the underpinning models used in [1–3] and, in particular, whether they correctly account for the porous structure in which the process occurs. In effect, these models are valid in the fluid–filled pores of the material, but are not necessarily accurate over the porous structure as a whole. However, it is infeasible to keep track of the diffusion and reaction within a porous structure explicitly: such a model would be analytically and computationally intractable, with meshes required that cover material over the area of a spill (tens of centimetres) but that are detailed enough to track the fluid in the pores (on the order of microns for concrete). What is required is a simple model that applies to the whole of the spill, yet takes into account the effect of the fine-scale structure of the problem.

> Current models do not take the effects of the porous structure into account. The aim of this project is to derive new models that do.

Our aim is to investigate two such pore-scale models. We will derive "averaged" equations, valid over the entire large-scale domain, in which the pore-scale structure is correctly accounted for. The technique that we will use is mathematical homogenisation.

2. Mathematical model

We consider the situation in which agent has penetrated into a porous medium, and cleanser is applied to remove it. We assume that the fluids are stationary (i.e: there is no flow), and the chemicals diffuse through their solutions. We assume that the agent is neat, and so we do not have to explicitly track its concentration. Wherever there is an interface between the two fluids, the chemical reaction takes place, which we model using the Law of Mass Action, which states that the rate of the reaction is proportional to the product of the concentrations of the reactants. We assume the simplest stoichiometry, i.e.: that one molecule of agent reacts with

one molecule of cleanser to form one molecule of product and, since the agent has constant concentration, the rate of reaction is simply proportional to the concentration of cleanser at that point. The chemical reaction causes the motion of any boundary between the two fluids. By assuming that the total amount of cleanser and agent only decreases due to the chemical reaction, we derive two conditions that hold at the interface between the fluids.

The mathematical model, which is a differential-equation model for the concentration of cleanser and the position of any agent–cleanser interface (and based on [2]), is summarised as follows:

Mathematical models for the decontamination process incorporate the diffusion of chemicals through solution, and the chemical reaction wherever the cleanser and agent meet.
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1. The cleanser molecules diffuse through the cleanser solution;
2. On the cleanser–agent boundaries, the chemical reaction eats away the agent causing the boundary to move;
3. Where the cleanser solution meets the solid structure of the porous medium, there is no flux of cleanser into the solid.

A schematic of the process is shown in Figure 1. Our model holds in a complicated geometry: the diffusion of cleanser only happens in the pores of the material filled with the cleanser solution. Our aim is to average these equations using homogenisation theory to develop simple and accurate models that hold over the whole domain, taking the porous structure into account.
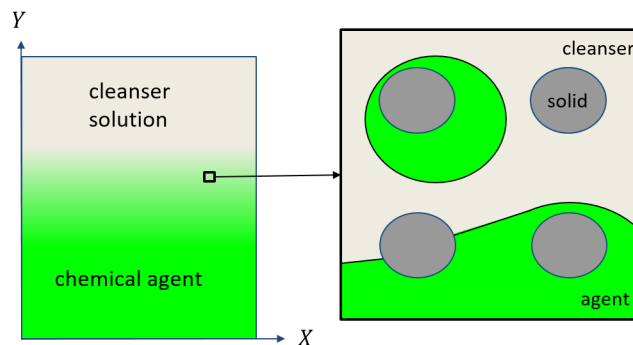

Figure 1 – The overall, and fine-scale problems. In the cleanser fluid, the diffusion equation describes the cleanser concentration. There is no flux of cleanser into the solid. At boundaries between cleanser and agent, two boundary conditions describe the movement of the boundary due to the chemical reaction

3. Mathematical homogenisation

Mathematical homogenisation is a systematic method for averaging the microscale behaviour in a mathematical model. It is applicable in a wide variety of different mathematical problems. For instance, we can rigorously derive the often empirically determined Darcy's Law for pressure-driven flow through a porous medium with this method.

It is necessary that the problem has two very different lengthscales. This allows us to separate out the pore-scale fluctuations from the overall behaviour.
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For homogenisation to be possible, the problem must involve multiple, well separated lengthscales. For our problem these are the scale of the porous structure (microns for concrete, for instance), and the scale of the agent spill (perhaps tens of centimetres). We denote the ratio between these lengthscales by ϵ, which is always a very small number. For problems concerning agent decontamination in concrete,

$$\epsilon = \frac{\text{scale of porous structure}}{\text{scale of the overall spill}} \approx 10^{-5}. \qquad (1)$$

The homogenisation procedure for problems of this type is outlined below:

1. Define spatial variables describing both the macroscale and the microscale. We use capitals (X, Y) for macroscale variables, and lower case (x, y) for microscale. These are assumed to be independent of one another.

2. Assume that dependent variables (such as the concentration of cleanser) depend on both the microscale and macroscale variables, and on time.

3. Alter the model equations to take into account variation over both the microscale and the macroscale. This requires changing any derivatives to take into account the variation over both the micro and macroscales.

4. Seek solutions in which we first study the overall behaviour due to the most dominant physical effects, and then study increasingly small corrections to this general behaviour. This technique allows us to separate out the different physical processes and eventually obtain simpler equations to describe the overall behaviour.

5. Assume that the problem is locally periodic on the microscale. For the decontamination of agent in concrete, this means assuming that the idealised microstructure of the porous medium is periodic. We find that, while we can have variation in cleanser concentration (and the other dependent variables) over the macroscale, the concentration doesn't change between neighbouring cells.

6. Analyse the problem at each level of accuracy, continuing until we have enough information to describe the macroscale behaviour fully. This process is fairly technical, and can be quite different for different homogenisation problems.

> Assuming local periodicity is crucial: it means we can average the equations locally, over a pore-scale cell.

4. Homogenisation approaches for this problem

We will consider two microscopic distributions of the agent; each will require a different homogenisation approach. First we look at the case in which the agent has coated the solid structure within each of the pores, but is then surrounded by water (or the aqueous cleanser solution). For instance, this could describe the situation in which agent has seeped into concrete that has been rained on before the decontamination procedure begins. Secondly, we consider the case where a region of the porous medium is completely saturated by agent, and cleanser is present in a layer above. Although this set–up is perhaps more intuitive, the homogenisation procedure in this case is rather more complicated, since the chemical reaction – which is the driver of all the processes – only occurs at the macroscale fluid–fluid interface, rather than in each microscale cell of the region.

We look at each of these scenarios in turn, and then compare the resulting macroscale models.

Case 1: agent layer on solid microstructure

First, we look at the case where agent coats the solid structure and is surrounded by the cleanser. As a simple model for this, we suppose the solid structure is composed of a square lattice of circular solid obstacle, with constant radius throughout (this models a constant porosity material). On each of these solid circles, we suppose there is a layer of the agent, forming an annulus around the solid. The thickness of the agent layer varies slowly in space, over the macroscale, due to the reaction with the cleanser over time. A schematic for this set–up is given in Figure 2. One microscale "cell" consists of the square with a single solid circle surrounded by agent.

Working through the stages of the homogenisation process as described in Section 3 we derive a set of simple equations that describe the cleanser concentration and local thickness of the agent layer, which hold over the whole region, but take the pore-scale structure and processes
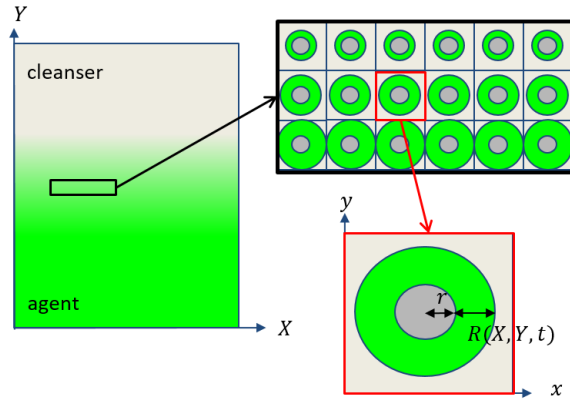
Figure 2 – **Schematic of the solid stucture and the agent layer.** r **is the radius of the solid material that makes up the porous medium, which we assume is constant everwhere, and** R **is the thickness of the agent layer, which varies over the macroscale domain.**

into account. This model is split into two cases: the situation where there is no agent, so the thickness R of the agent layer is zero, and the region where there is agent.

In the region where there is no agent ($R = 0$) we regain a diffusion equation for the cleanser concentration although, crucially, this now holds over the whole porous medium, not just in the pores. The effect of the solid structure is taken into account through the new diffusivity D_0^*. This is a constant between zero and the original diffusivity, D, of the cleanser in solution, and depends on the size of the solid circles: if the solid takes up very little space then the diffusivity is barely changed by the porous structure, but if the circles are large and leave little room for the cleanser, the average diffusion over the whole medium becomes very low.

In areas where there is agent, $R > 0$, the cleanser still satisfies a reaction–diffusion equation, with an extra sink-term due to the fact that cleanser is used up in the chemical reaction. We also obtain an equation that describes how the agent layer thickness decreases due to the chemical reaction. There are three new parameters D^*, A and L in our averaged equations, which are a result of the homogenisation procedure, and describe how the microscale effects enter the problem. The new diffusivity of cleanser D^* depends on the thickness of the agent layer, R, in exactly the same way as described above: if there is a thick agent layer the diffusion of cleanser is severely restricted, and so D^* is small, whereas if the layer of agent is very thin, the agent restricts cleanser diffusion barely more than the solid structure, and the diffusivity is close to D_0^*. The other parameters, A and L are the area occupied by cleanser solution in the cell, and the length of the cleanser–agent interface in the cell respectively. For our circular geometry,

$$A = 1 - \pi(r + R)^2, \qquad\qquad L = 2\pi(r + R). \qquad\qquad (2)$$

> The chemistry in the averaged model comes into the diffusion equation, which holds over the whole porous medium.
> The pore-scale geometry is encoded in the parameters D^*, A and L.

Case 2: sharp interface on the macroscale

Now we discuss the sharp interface model. A schematic for the procedure is given in Figure 3. In the diagram, the macroscale interface between the cleanser and the agent is given by $Y = H(T)$, and on the microscale it is given by $y = h(x, t)$.

We go through a similar homogenisation procedure to that in the previous case, and as described in Section 3. However, there are a number of extra complications in this scenario:

- The original model tells us how the microscale interface moves due to the chemistry and diffusion, but it is not obvious how to relate h and H. We do this by changing variables so that we are centred about the interface, and move with its average speed. This is called a "travelling-wave" change of coordinates.
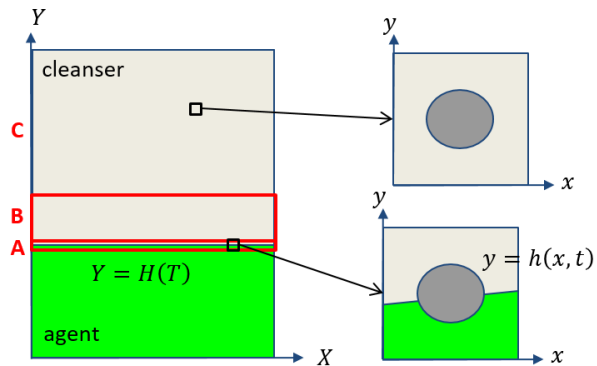
Figure 3 – Schematic of the sharp–interface model. We consider a flat macroscale interface for simplicity, although the microscale interface may not be flat in general.

> This homogenisation problem is more difficult because the chemical reaction only happens in region A of Figure 3, at the spill-scale cleanser–agent interface.

- Another complication of the fact that the chemical reaction only happens at the interface is that we have multiple regions in the problem in which different physics occurs, and we have to perform a "boundary-layer" analysis. Referring to Figure 3, in region A at the interface the chemical reaction is the most important effect. In the thicker region B, changes in the concentration of cleanser due to the chemical reaction are smoothed out as the cleanser diffuses, so that it can be matched to the diffusion processes occurring far from the interface, in region C.

- As well as two lengthscales, we also have two different timescales associated with this problem: the timescale of the microscale interface motion, t, and the timescale of the macroscale interface motion T. We have to homogenise in time as well as in space.

While the process is very complicated, the resulting model is very similar to the original microscale model except that we have a new diffusivity constant D_0^* (which takes into account the microstructure of the problem exactly as in the previous case) and a new parameter μ. This parameter μ takes into account the proportion of the macroscale interface which is actually a true interface between cleanser and agent (parts of the interface run "through" the solid structure, where no chemical reaction happens, and so the average speed of the interface is reduced). Although we perform the homogenisation for a flat macroscale interface, we would expect the result to be similar if we allowed the macroscale interface to vary spatially.

> The averaged equations have the same structure as the pore-scale equations, but with extra parameters D_0^* and μ which describe the pore-scale geometry.

Comparison of resulting models

Both the homogenisation procedures result in the same diffusion equation (and diffusivity) in the region where there is no agent, and so no chemical reaction. Otherwise, the two models we have derived are quite different in terms of the structure of the equations: in the first case, the chemical reaction happens anywhere where there is both cleanser and agent, reflecting the fact that the chemical reaction happens in all cells whereas, in the second case, the chemistry appears as a boundary condition at the fluid–fluid interface, as it does in the original pore-scale model.

For both cases, the structure of the homogenised equations remains unchanged if the microscale geometry is altered (if the solid was no longer a circle, for instance), but the parameters D^*, A, L and μ change to reflect the new microstructure.

In the first case, there is an interesting situation when the radius r of the solid particles is much larger than the agent layer thickness R. In this case, the parameters D^*, A and L are approximately constant, and the homogenised equations decouple, becoming much easier to solve.

A final point to highlight is that the form of the derived model for the sharp interface is similar to that used in [1] and [2], and also to that used by Whitehead [3], in which the parameters D_0^*

and μ are fixed. These results could easily be extended to accurately take the porous structure into account.

5. Discussion, conclusion & recommendations

We have derived two different models for the transport of a cleanser and its reaction with an immiscible hazardous agent inside a porous medium. Using the mathematical technique of homogenisation on two microscale models, we have generated average equations, valid on the spill scale, which describe the concentration of cleanser and the effect of the chemical reaction with the agent. The models include the microscale processes and the structure of the porous medium through new diffusivity parameters and parameters related to the surface area over which the reaction occurs.

It would be interesting to look next at some simple solutions of both of our models, and compare our results with those obtained from the simpler models that do not account for the fine-scale structure. It would also be worth studying, given a particular reaction rate, whether or not the two models predict the same qualitative behaviour, or how they are different. A detailed analysis of the sharp–interface model has been carried out simultaneously to this work by Whitehead [3]. Finally, an analysis of how the fine–scale geometry affects the macroscale behaviour, by finding the parameters D^*, A, L and μ for various different microstructures, could give an idea of the extent to which the medium itself affects the decontamination process taking place within it.

6. Potential impact

The models we have derived can be used to answer questions about the efficiency and speed of decontamination for particular types of spills in a more accurate way, since we know that the fine–scale structure and processes have been taken into account.

Ross Heatlie-Branson, Senior Scientific Officer – CBRN Recovery, DEFRA, said:

"Decontamination of a chemical warfare agent (CWA) after it has been dispersed is important as it ultimately protects the public from the negative health effects that will be experienced should they come into contact with the agent. Defra has a responsibility to ensure areas that have been contaminated with a CWA are returned to the public in a completely safe condition and decontamination is a major part of that recovery process. Ellen's project has accounted for various microscale effects and their bearing on the macroscopic scale, incorporating them into the overall model. These preliminary models have enhanced our understanding of contaminants and cleansers and their interactions and behaviour in porous media. It is a logical progression to build upon these models in order to further our understanding which could lead to positive changes to our decontamination protocols when faced with these situations in a real environment."

7. References

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[2] MP Dalwadi, D O'Kiely, SJ Thomson, TS Khaleque, and CL Hall. Mathematical modeling of chemical agent removal by reaction with an immiscible cleanser. *SIAM J. Appl. Math.*, 77(6):1937–1961, 2017.
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