EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling

Modelling decontamination of two-dimensional spills

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1. Introduction

Background

Following the release of harmful chemical substances, e.g. through industrial accident or chemical attacks, it is crucial that the harmful agent be removed and any materials decontaminated as quickly and as efficiently as possible. Any agent on an exposed surface can be removed relatively easily without the destruction of property. If, however, the exposed area consists of porous materials such as concrete, then the agent will seep into the pores inside the material and will become significantly more difficult to remove. In this case, the contaminated materials can be destroyed and removed entirely or, more preferably, the dangerous agent can be neutralised in situ by applying a decontaminating cleanser to the surface of the porous material. Some agents are organophosphorous compounds including, for example, insecticides and several nerve agents such as Sarin or VX. These compounds are typically insoluble in water but can be decontaminated by highly alkaline solutions. The decontamination reaction occurs whenever the agent and cleanser come into contact, and the key question is how to apply the cleanser to the surface of a porous medium in order to ensure that all the agent in the bulk is removed.

> Chemicals trapped in porous materials, such as concrete, are significantly harder to remove than when they reside on the surface.

There is considerable academic interest in the area of fluid dynamics of cleaning and decontamination but little has been done to address the situation of decontaminating porous media. Some progress has been made in modelling immiscible decontamination in one spatial dimension [1] and our aim is to extend this work to include two-dimensional effects, in order to determine the extent to which a reaction front spreads out horizontally. This will help inform decontamination experts at the Department for Environment, Farming and Rural Affairs (DEFRA) whether it is best to apply a large amount of cleanser in the centre of the contaminated region or to cover the whole area with a thinner layer of decontaminant.

2. Mathematical Model

Our aim is to model a decontamination protocol that involves gently applying a thin layer of decontaminating cleanser to the top of a porous medium containing a thin saturated region of dangerous agent trapped near the surface. We consider a finite volume of both the agent and cleanser and we assume that there is a sufficient amount of cleanser to decontaminate the agent fully. While, in practice, the agent can be in solution or can be miscible with the applied cleanser, for simplicity we assume the worst case scenario of a neat, saturated, agent layer immiscible with the cleanser. We assume that the decontamination reaction takes place at the interface between the two regions and will move through the agent layer as the agent is reacted away. For simplicity, we assume that any products given off by the reaction are hydrophilic and insoluble in the agent species. In this way, the agent layer will remain neat throughout the decontamination process.

> We model the case of a neat, saturated agent immiscible with the cleanser applied.
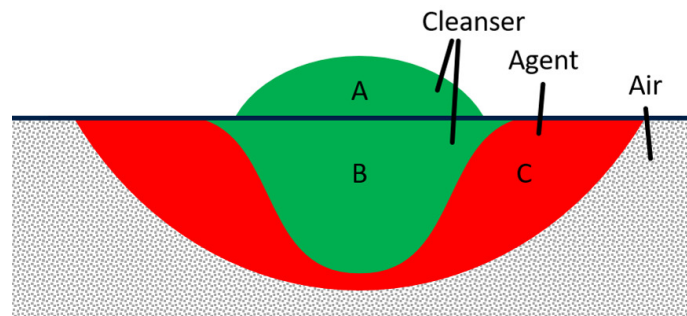

Figure 1 – **Characteristic decontamination set-up mid-cleanup with applied cleanser in region A, reacting into agent layer, region C, creating a decontaminated cleanser region, B.**

We also assume that the volume of the products given off by the reaction do not impede the diffusion of cleanser. Lastly, we assume that the region in the porous medium not initially saturated with agent contains only air into which no cleanser or agent is lost through evaporation ("off-gassing").

Under these assumptions, we depict a typical two-dimensional decontamination scenario in Figure 1. Our model for decontamination involves diffusion of the cleanser throughout the aqueous regions A and B, and a reaction at the interface between the cleanser and the agent layer contained in region C. One way to find the equations that hold on the spill scale is to pose the equations on the microscale and use a mathematical technique called homogenisation to accurately capture the effects of the pores on the spill-scale model, as undertaken in Luckins [2]. Here, we use the relevant form of these macroscale equations and we simplify the problem by exploiting the fact that the agent and cleanser form thin regions (width $\gg$ depth). In our model, we track the concentration of the cleanser in time and space, as well as the location of the agent–cleanser interface.

Glossary of terms

- **Neat:** A chemical substance is neat if it is present in a liquid phase without a solvent. That is, it is not dissolved in another chemical.

- **Porous medium:** A porous medium is a solid material with many connected holes, or pores.

- **Saturated:** A porous material is saturated if the pores contain only liquid.

3.   Results

Timescale Analysis

We use our model to predict that the dynamics of the decontamination occur over three distinct timescales. The relative sizes of these timescales determine the qualitative differences in the propagation of the reaction front that can occur. The timescales are

- The vertical diffusion timescale, over which the concentration of cleanser evens out vertically ($\approx$4 minutes for a droplet with an aspect ratio of 0.1).

- The horizontal diffusion timescale, over which the concentration of cleanser evens out horizontally ($\approx$7 hours).

- The reaction timescale, over which the cleanser and agent species react.

Depending on the specific agent and cleanser combination, the size of the reaction rate and associated timescale for complete cleanup can greatly vary in magnitude from under a minute to several hours. To this end, we consider several sizes of the reaction timescale relative to the diffusion timescales. In general, we consider the dynamics over the fastest possible timescale since we are interested in how to find the most efficient clean-up strategies.

We exploit the fact that the ratio of the height of the applied cleanser to its width is small. We ignore terms which are of a similar size to this small parameter, and solve the simplified equations. This gives us a solution which is a very good estimate for the true solution, providing the ratio is sufficiently small.

We use a technique called asymptotic analysis to simplify the model, exploiting the fact that the agent layer is thin.

High Reaction Rate Limit

In this limit, the reaction rate is much faster than the rate of either vertical or horizontal diffusion. We find that the cleanser at the reaction front reacts very quickly, and the reaction is limited by the diffusion of cleanser molecules to the reaction interface, which occurs over

the slower vertical diffusion timescale. We find that the cleanser concentration at the reaction front is equal to zero since the cleanser is reacted away as soon as it arrives there. This tells us that, even if we were to make our cleanser solution unrealistically reactive with the agent, the total clean-up time would still be limited to an order of minutes because of the vertical diffusion. We see in Figure 2 an example decontamination with a reaction timescale of a few seconds. The black line below zero shows the agent profile while the coloured lines show the shape of the reaction interface at various different times. We see that it takes ~ 100 minutes for complete decontamination to occur. In all of the plots, the vertical extent has been magnified by a factor of 10 compared to the horizontal since we have scaled by the applied cleanser width and height. Additionally, in all plots, the total amount of cleanser is chosen to be just enough to decontaminate the agent fully.
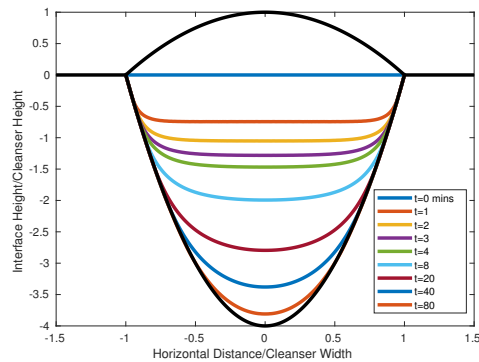

Figure 2 – Graph showing the interface height at various times for the case of a reaction that occurs faster than vertical diffusion and with the cleanser fully covering the agent. The black line above zero shows the applied cleanser profile and the black line below zero shows the agent profile.

> We find that we need to cover the whole contaminated region with cleanser to decontaminate as efficiently as possible.

In the decontamination scenario shown in figure 2, the entire width of the contaminated region is overlaid with cleanser. If we do not cover the whole contaminated region but instead put the same amount of cleanser in a smaller region in the centre, we see in Figure 3 that, over the same timescale, not all the cleanser has been reacted away. Instead we find that the cleanser reacts, primarily, downwards with little horizontal motion of the reaction front. This observation may seem counterintuitive, but it is because the agent is much thinner than it is wide.
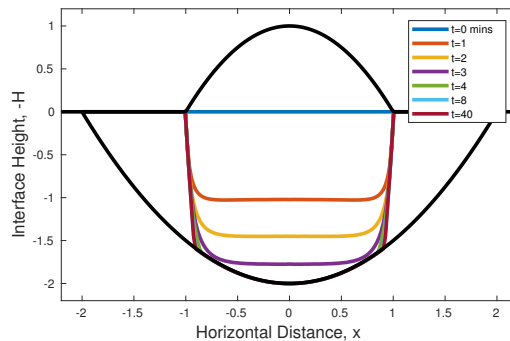

Figure 3 – Graph showing the interface height at various times for the case of a reaction that occurs faster than vertical diffusion and with the cleanser only covering half of the agent.

Vertical Diffusion-Reaction Balance

This limit corresponds to the chemical reaction occurring over the same timescale as vertical diffusion (an order of minutes). This case is very similar to the case of a faster reaction rate but now the cleanser at the reaction interface does not get completely reacted away. The reaction rate here can be as much as hundreds of times smaller than the previous case but, as we can see from Figure 4, there is a relatively small change to the velocity of the interface. On this
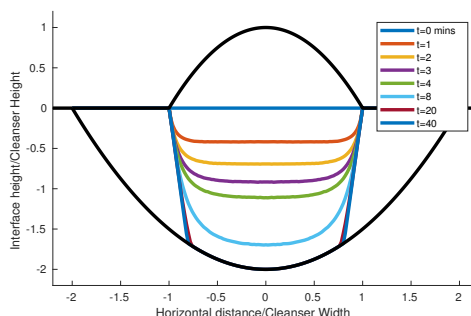

Figure 4 – Graph showing the interface height at various times for the case of a reaction that occurs on the same timescale as vertical diffusion.

timescale, there is no mixing laterally of the cleanser. This means that any column of cleanser only interacts with the cleanser and agent above and below it and does not move laterally at all. This is important since it means that covering the agent region completely may still not suffice to react away all of the agent if there are insufficient cleanser molecules directly above the agent, as can be seen near ±1 in Figure 4.

Intermediate Reaction Rate Limit

> We find qualitatively different clean-ups occur depending on how fast the reaction is compared to the diffusion rates.

This limit corresponds to the case where the reaction occurs much slower than vertical diffusion but much faster than horizontal diffusion. In this limit, we find that the vertical mixing has largely occurred and so the concentration in any vertical column of cleanser is approximately constant. Additionally, as with the previous limits, horizontal diffusion has not yet had an effect so very little mixing occurs over the course of a decontamination. As we can see from Figures 5 and 6, the region between the dotted lines runs out of cleanser. Since horizontal diffusion occurs on a much longer timescale, this surplus cleanser we can see remaining in the middle of the region does not mix horizontally. We conclude that there is a region directly under the droplet of cleanser which is not decontaminated on this timescale.
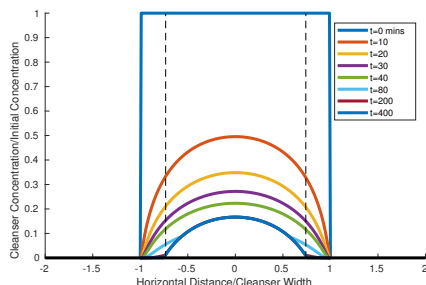

Figure 5 – Graph showing the cleanser concentration profile across the width of the cleanser region at various times for a reaction that occurs on a timescale between that of vertical diffusion and horizontal diffusion.
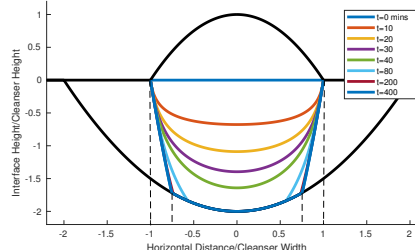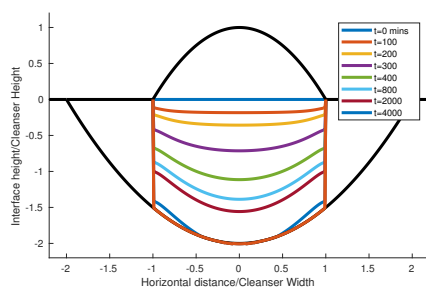

Figure 6 – Graph showing the interface height at various times for the case of a reaction that occurs on a timescale between that of vertical diffusion and horizontal diffusion.

Horizontal Diffusion-Reaction Balance

In this limit, the reaction occurs slowly enough that it takes place on the same timescale as the horizontal diffusion (i.e. over several hours). This means that vertical diffusion happens very quickly and the cleanser will be well mixed vertically. However, in contrast to all previous limits, horizontal diffusion will now play a role over the whole course of the reaction. As we can see from Figures 7 and 8, the reaction still moves mostly vertically downwards but nowhere does the concentration of cleanser go to zero. For a reaction this slow, cleanser can mix horizontally from regions of excess cleanser to regions of less cleanser. This means that everywhere underneath the applied cleanser region can be decontaminated. This can be seen in Figure 7, where the reaction front has vertical edges. Given this, it is important to note that the reaction front still does not spread very far horizontally. In reality, this front moves a similar distance both horizontally and vertically but since the depth can be hundreds of time smaller than the width, a small proportion of the total width of the spill is decontaminated of this timescale.

Figure 7 – Graph showing the interface height at various times for the case of a reaction that occurs on the same timescale as horizontal diffusion.
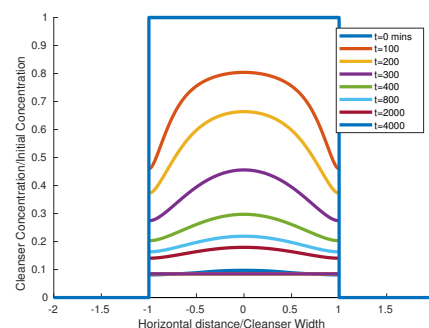
Figure 8 – Grpah showing the cleanser concentration profile across the width of the cleanser region at various times for the case of a reaction that occurs on the same timescale as horizontal diffusion.

> The cleanser mainly eats downwards into the agent but does spread horizontally over a much longer timescale.

Long Time Dynamics

Our results on the short timescale have shown us that, to decontaminate most efficiently, the contaminated region needs to be completely overlaid with cleanser. However, if we are prepared to wait much longer, the decontamination front will move laterally. We also model this long-time behaviour and present an example total decontamination in Figure 9. We see that the reaction front has reached the full depth of the agent layer and then moves outwards with a vertical front until the agent is all removed.

4.   Discussion, conclusions, & recommendations

We have explored the behaviour of a simple model for the decontamination of a two-dimensional spill of a nasty chemical agent. We exploited the fact that the agent, and cleanser applied to remove it, are present as thin layers. We find several different qualitative decontamination dynamics depending on the relative size of the diffusion and reaction rates. In all cases we find that the cleanser decontaminated the material beneath it, but did not spread laterally over short timescales, which suggests that the contaminated region should be completely covered with sufficient cleanser for the reaction to occur most efficiently. Even then, we find that the vertical diffusion timescale is a limit to the total clean-up time. Trying to increase the reaction rate beyond this limit yields no decrease in the clean-up time. Beyond this, we find different dynamics depending on whether horizontal diffusion is significant or
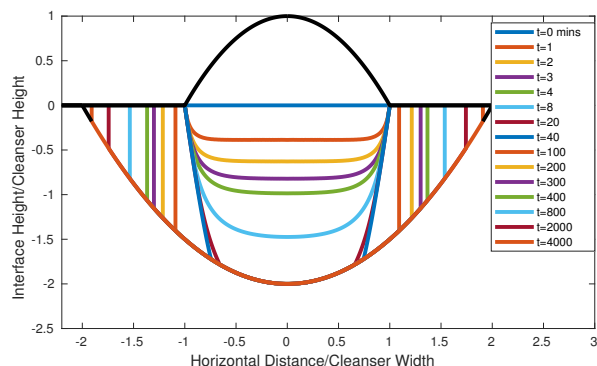
Figure 9 – Graph showing the interface height at various times for the case of a reaction that occurs on the same timescale vertical diffusion where we wait long enough for horizontal motion of the interface to occur.

not over the decontamination. If it is not significant, we find that, in certain regions, the cleanser runs out and does not decontaminate fully, while in others there is an excess of cleanser. Decontamination scenarios with faster reaction rates can also exhibit lateral mixing but waiting for this timescale can extend the total clean-up time severalfold.

There are numerous areas for future work. Firstly, a comparison of the simplified models to a full numerical simulation and to experiments would help confirm results. Additionally, there are multiple assumptions we have made to simplify the model which could be relaxed and examined. Some interesting next steps would be to include fluid flow within the agent and cleanser layers (allowing the chemicals to flow under gravity), dissolution of the reaction products into the agent layer, and more complicated underlying chemistry.

5. Potential Impact

The work of the report, the accompanying report by Luckins [2], and any further research into this area has the potential to make a lot of difference in how we go about dealing with chemical spills and attacks. A better understanding of the underlying dynamics will allow for more confidence in a decontamination strategy, ultimately reducing risk to life and saving time and money.

Ross Heatlie-Branson, Senior Scientific Officer of CBRN Recovery commented: *"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. Oliver's work is important as he has provided us with an understanding of the "decontamination dynamics" in a two-dimensional problem relevant to scenarios that we could find ourselves in a real incident. It is a logical progression to build upon this work 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."*

References

[1] M. Dalwadi, D. O'Kiely, S. Thomson, T. Khaleque, and C. Hall. Mathematical modeling of chemical agent removal by reaction with an immiscible cleanser. *SIAM Journal on Applied Mathematics*, 77(6): 1937–1961, 2017.

[2] E. Luckins. Homogenisation of agents and cleansers interacting on the microscale. *InFoMM Mini-Project Technical Report*, 2018.