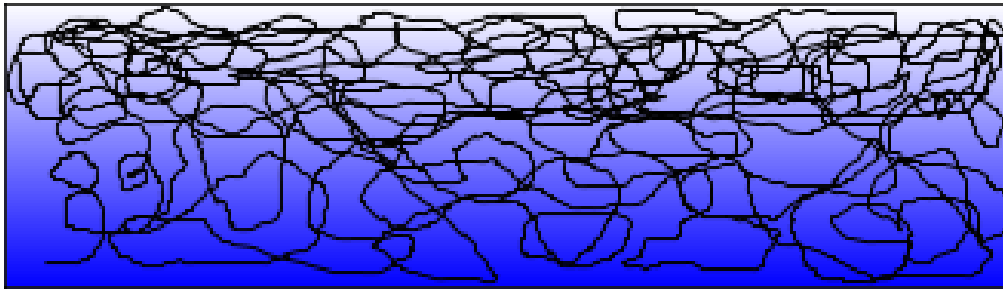


# EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling



Penetration of a liquid agent  
into a polymer

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# 1. Introduction

## Background

The UK Government Decontamination Service (GDS) plans and prepares for recovery following the deliberate or accidental release of hazardous materials (chemical, biological, radiological or nuclear). One major challenge in chemical decontamination is dealing with the possibility that hazardous agents will absorb into permeable building materials. When this happens, the building material can act as a reservoir that releases the agent into the air slowly, presenting a possible long-term hazard to human health. In order to assess these hazards, and in order to achieve effective decontamination, it is important to understand the processes by which agents are absorbed into, and released from, permeable materials, and how they may be extracted or otherwise eliminated. Since polymers have the capacity to absorb large amounts of agent, GDS are particularly interested in the dynamics of agent transport in common polymeric building materials, such as silicone sealants.

A hazardous agent can act as a solvent that leads to polymer swelling. Once the source of the agent is removed, the swollen polymer will dry and release the agent.

When a polymer comes into contact with a chemical agent, the agent can act as a solvent. The infiltration of a solvent will cause a polymer to swell, potentially allowing large amounts of solvent to be absorbed. After a solvent has been absorbed into a polymer, it will be released once the concentration of solvent in the outside environment is sufficiently low. This means that one method of decontaminating a polymeric material is simply to remove the source of contamination and wait for the agent to be expelled, possibly accelerating the process by blowing hot air over the polymer. This is very different from the usual decontamination approach for permeable building materials, which involves stripping out and disposing of any material that might be contaminated. While stripping out contaminated materials is effective, it is also expensive and time consuming, and GDS are interested in exploring the conditions under which alternative decontamination methods (such as the use of hot air) may be effective.

In order to assess the risks associated with contaminated polymers and to explore the effectiveness of different decontamination methods, GDS are interested in understanding:

1. The extent to which polymers in building materials swell when exposed to agents;
2. What parameters control the timescales for swelling and drying;
3. Whether any agent remains in a polymer when it has finished drying. If so, how much and where?


Mathematical modelling is a valuable tool for addressing these questions, since it is descriptive, predictive, and applicable over all relevant distance and time scales; in contrast, experiments can be costly and time consuming. In this report, we describe mathematical models that can be used to examine the swelling and drying of polymers, and we present an analysis of how these models might inform further work on decontamination.

## Modelling approach

The swelling of polymers has been studied in a range of contexts; applications of polymer swelling include controlled drug delivery, magma/mantle dynamics, and hydrogeology. However, describing these phenomena remains difficult, since the mechanical deformation of the swelling polymer, the flow of the solvent, and the thermodynamic properties of the entire system all need to be taken into account.

Several models exist for swelling of hydrogels, but they have never been adapted to the context of decontamination.

We base our work on recent models developed by Bertrand *et al.* [1] to describe the swelling and drying of spherical hydrogels. While these models underpin our work, there are two major challenges associated with adapting them to describe the infiltration of agents into polymers. The first challenge arises from the fact that hydrogels are never truly dry. Since a small amount of water is always present, hydrogels will always be in equilibrium with atmospheric moisture. As a result, the Bertrand *et al.* [1] model does not address the mathematical difficulties associated with the completely dry state. Since hazardous agents are not present in significant quantities in the natural environment, the completely dry state is physically relevant, and needs to be accounted for in models of decontamination. A second challenge is that the emphasis of previous work has mostly



been on modelling the swelling process. Since we are concerned with decontamination as well as contamination, we also need models that describe drying.

We concentrate on implementing our models in some simple geometries of practical significance. Specifically, we will consider slab-like geometries, representing polymeric floor or ceiling tiles; and hollow cylinders, representing polymeric cable coatings.

## 2. Mathematical Model

We first present a glossary of the key terms we use throughout the rest of this report.

### Glossary of terms

- Displacement of the polymer: The difference between the current and initial position of a point in the polymer lattice.
- Solvent volume fraction: The amount of space (as a ratio of solvent volume to total volume) occupied by the solvent. This will vary throughout the polymer.
- Stress: A mechanical quantity expressing the force per unit area that neighbouring particles exert on each other.
- Chemical potential: The work required to add an additional solvent molecule to the system. Solvent will move down gradients in chemical potential in order to minimise the total energy of the system.
- Equilibrium: A state of the system where there is no net flow of solvent because the chemical potential of the solvent is constant throughout. If the polymer is in contact with a reservoir of solvent, the polymer will be swollen at equilibrium; if the external environment contains no solvent, the equilibrium state will be unswollen.
- Darcy's law: A constitutive law that describes fluid flow in a saturated material. In our case, we use Darcy's law to describe the relationship between the solvent velocity and gradients in chemical potential.
- Swelling size: For the purposes of this report, we define swelling size as the ratio between the polymer size in its swollen equilibrium state, and the polymer size when dry. Since 'swelling size' is a ratio, the physical size of a swollen material can be obtained by multiplying the original size of a material by its 'swelling size'.
- Swelling/drying time: When a completely dry polymer is exposed to solvent, it will swell until equilibrium is reached. It will take an infinite amount of time to reach equilibrium, and so we define the swelling time as the time taken for the size of the polymer (expressed as a ratio of current size to initial size) to be within  $10^{-6}$  of the swelling size. Drying time is defined similarly, but we start at the swollen. We define swelling/drying times as dimensionless quantities by rescaling the physical times with respect to the diffusion timescale of the solvent.

### Mathematical model

We assume that (i) there is no reaction between the polymer and the solvent; (ii) gravity is a much less important driving force than chemical potential; (iii) the temperature is constant throughout the system. As a result of these assumptions, the main driver for solvent flow will be gradients in chemical potential. Our model combines solid mechanics, fluid dynamics, and thermodynamics. We assume that both the polymer lattice and the solvent are incompressible, and that there is no empty space or air in the system, so that every point is occupied by either polymer or solvent. This allows us to relate the displacement of the polymer directly to the local volume fraction of solvent.

We assume that the polymer lattice is always in mechanical equilibrium; this imposes a constraint on how the stress varies through space. We also assume that the solvent moves according to Darcy's law; this prescribes a relationship between the solvent velocity and gradients in chemical potential.

The theory of ideal elastomeric gels uses classical thermodynamic principles to obtain expressions for mechanical stress and chemical potential.

In order to close the system, we need to relate the stress in the polymer and the solvent chemical potential to the volume fraction of solvent. This is achieved using the theory of ideal elastomeric gels. This theory describes polymer-solvent interactions based on a thermodynamic competition between the chemical affinity between polymer and solvent (which favours swelling), and elastic forces (which favour the dry state). Using this theory, we can obtain thermodynamically-consistent expressions for both the stress and the solvent chemical potential as functions of the local volume fraction of solvent.

Swelling and drying can be described by using different initial conditions and boundary conditions. For swelling, we start with an initially dry polymer, and we assume the flux of solvent across the boundaries depends on the difference between the chemical potential of solvent at the boundary and some imposed (high) external chemical potential. This leads to a gradient in chemical potential (high at the boundary and low inside the polymer), which drives solvent into the polymer.

To describe drying, we begin with the polymer at its swollen state, and use a similar boundary condition to before, but where the external chemical potential is very low. We also impose a maximum evaporation rate that limits the flux of solvent out of the polymer. This maximum evaporation rate used in the drying problem means that there is an additional timescale to be considered that does not appear in the swelling problem; often, this timescale is long, meaning that drying is much slower than swelling.

## Comments

- By imposing the ‘swollen state’ boundary conditions and assuming that an equilibrium has been reached, we can solve a steady state problem to find the state of the polymer when it has finished swelling. This enables us to determine the swelling size without having to consider the dynamics of solvent flow.
- If we assume that both the solid displacement and the solvent volume fraction are small (i.e. the dry state), the model reduces significantly and we simply have to solve a diffusion equation for the solvent volume fraction.
- Although we develop the model in a general three-dimensional geometry, we will solve it in two simplified one-dimensional geometries: a ‘slab-like’ geometry, and a cylindrical geometry.

## 3. Parameters and Timescales

### Dimensionless parameters governing swelling size

In the case of a slab-like geometry, our model is governed by five dimensionless parameters. Only two of these are required to determine the swelling size of the polymer; the other three are only relevant to the dynamics of swelling and drying. From numerical experiments, we also find that these two parameters are also the main parameters that control the dynamics of swelling.

There two parameters that govern the swelling size are the ‘Flory-Huggins interaction parameter’,  $\chi$ , and the molecule size ratio,  $\Omega$ . Both of these depend on both the solvent and the polymer. The Flory-Huggins parameter is a dimensionless measure of the enthalpy of mixing, with small values corresponding to greater affinity between the solvent and polymer. For most polymer/solvent combinations this has values between 0.2 and 2. The molecule size ratio is the ratio of the volume of a solvent molecule to the average volume of a polymer molecule. This is typically small (between  $10^{-2}$  and  $10^{-4}$ ) since polymer molecules are much larger than solvent molecules.

### Timescales

Describing the dynamics of swelling and drying is more complicated than determining the swelling size of the polymer. In order to determine what parameters control the timescale of swelling and drying, we analysed a dimensionless form of our model, and then

$\chi$  is the Flory-Huggins parameter, which is a dimensionless measure of the enthalpy of polymer-solvent mixing, and  $\Omega$  is the ratio of solvent molecule volume to polymer molecule volume.

converted the results back into dimensional form. We find that there are two timescales that are particularly important for the dynamics:

- The **diffusion timescale** is the characteristic time that it takes for solvent to diffuse across the length of the polymer. This is directly proportional to the viscosity of the solvent, directly proportional to the square of the dry size of the polymer, and inversely proportional to the temperature of the system. Due to the wide range of polymer-solvent combinations that we are considering, this timescale can be anywhere from minutes to centuries.
- The **evaporation timescale** is the characteristic time that it takes for solvent to evaporate from the polymer if evaporation happens at the maximum rate. This is equal to the dry size of the polymer divided by the evaporation rate. The evaporation timescale also has a large range, between milliseconds and years.

Quasi-static drying occurs when evaporation is much slower than diffusion.

The swelling process depends on the diffusion timescale only, while the drying process can depend on both timescales. One important case is where the evaporation timescale is much longer than the diffusion timescale. We refer to this case as ‘quasi-static drying’.

## 4. Results

### Swelling size

We can determine the swelling size by considering only two parameters ( $\chi$  and  $\Omega$ ).

As noted above, the swelling size depends only on  $\chi$  and  $\Omega$ . As illustrated in Figure 1, the swelling size decreases with both increasing  $\chi$  and with increasing  $\Omega$ , and the dependence on  $\chi$  is slightly stronger than the dependence on  $\Omega$ . For the same values of  $\chi$  and  $\Omega$ , we find that the polymer swells more in a slab-like geometry than in a tubular geometry. For polymer-solvent combinations in a decontamination context, we expect  $\chi$  to be greater than one. Based on the results shown in Figure 1, this means that we would expect the polymer to increase in size by no more than a factor of two in unconstrained swelling. This amount of swelling would be reduced further in a confined geometry (such as a thin strip).

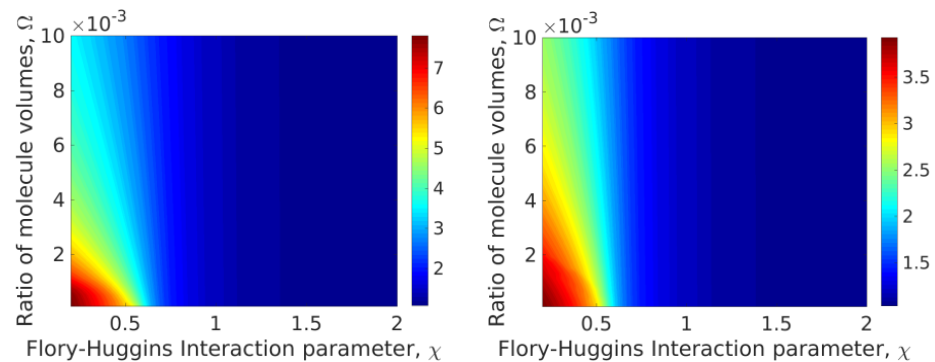
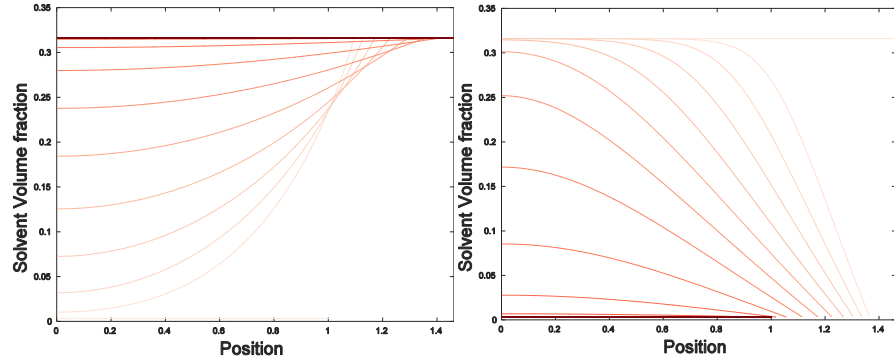


Figure 1: Dependence of equilibrium swelling size on  $\chi$  and  $\Omega$ , comparing slab-like (left) and cylindrical (right) geometries. The colour indicates the amount of swelling.

### Dynamics of swelling and drying

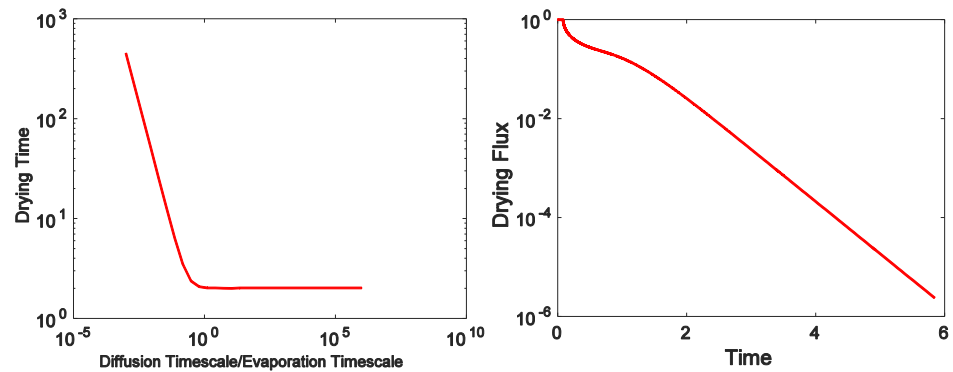
In Figure 2, we compare the dynamics of swelling with the dynamics of drying for the slab-like geometry. In both cases, we assume that one boundary of the polymer is fixed, so that there is no displacement and no flow of solvent through this boundary, while the other boundary is free to move. As shown in Figure 2, the dynamics of drying is qualitatively different from the dynamics of swelling.

For parameter-solvent combinations that are relevant in the context of decontamination, we find that the dimensionless swelling time is between 1 and 100, and we find that swelling time decreases with increasing  $\chi$  and  $\Omega$ . With all other parameters held fixed, swelling time is also longer in a slab-like geometry than it is in a cylindrical geometry.



**Figure 2: Dynamics of swelling (left; boundary initially at 1) and drying (right; boundary initially at swelling size), using the same parameters. The plots show solvent volume fraction against position in the polymer, with time increasing as the line darkens.**

The drying time depends on  $\chi$  and  $\Omega$ , but also on the ratio of the diffusion timescale to the evaporation timescale, as shown in Figure 3 (left). If the ratio is greater than 1, diffusion dominates and the drying time is independent of the evaporation timescale. If this ratio is between 0.1 and 1, then we find that the drying time depends strongly on the exact value of the ratio between the diffusion and evaporation timescales. If this ratio is very small, we can analyse the system further by exploiting the quasi-static drying approximation.



**Figure 3: (left) Drying time shown as a function of the ratio of diffusion timescale to evaporation timescale. (right) The flux of agent vapour leaving the polymer material (m/s) as a function of time, in the case of equal diffusion and evaporation timescales.**

When drying is quasi-static, we find that solvent and polymer are always in spatial equilibrium with an effective external chemical potential, which decreases over time. We find that the dimensional drying time (s) is equal to the swelling size, multiplied by the initial size (m) divided by the evaporation rate (m/s). We see this inverse dependence of drying time on evaporation rate for sufficiently small evaporation rates in Figure 3 (left). The drying model can also be used to estimate the rate of off-gassing from polymers. In Figure 3 (right), we show the flux of agent vapour leaving the polymer as a function of time. As time advances, the flux associated with off-gassing decreases exponentially to zero. These results could be used to estimate the time required in order for the rate of off-gassing to reduce to a safe level.

## Extending the model

We have concentrated on the case where temperature is held constant. A natural extension would be to consider a variable external temperature, in order to model hot air decontamination. The thermodynamics of the model already accounts for the temperature-dependence of swelling size, but further work is needed to describe the effects of variable temperature on the dynamics of decontamination.

The model can also be extended to the case where two different, miscible solvents are involved. This two-solvent model may be useful for studying the possibility of extracting an agent using a non-hazardous solvent.

## 5. Discussion, Conclusions and Recommendations

### Swelling size

We can use Figure 1 to predict swelling size on the basis of knowing both  $\chi$  and  $\Omega$ . Conversely, experimental measurements of swelling size can be used to estimate  $\chi$  or  $\Omega$  if the other parameter is known. In practical problems, it will be relatively straight forward to estimate  $\Omega$ , but much harder to estimate  $\chi$ . Hence, the results that led to Figure 1 are valuable for interpreting experimental results.

For general, physically realistic parameters, swelling and drying can take between a few minutes and a few centuries.

### Swelling and drying times

We found that the swelling time depends on the viscosity of solvent, the dry size of the polymer, and the temperature of the system. Depending on the exact value of the parameters, swelling can take between a few minutes and a few centuries. By first determining  $\chi$  or  $\Omega$  on the basis of experimental observations, and then applying our model, it is possible to estimate the swelling time.

For drying, there are qualitatively different behaviours depending on the ratio of the diffusion and evaporation timescales. If the diffusion timescale dominates, then the drying time will be similar to the swelling time. If the evaporation timescale dominates, then drying is quasi-static. In this case, the drying time can be much longer than the swelling time, and is inversely proportional to the rate of evaporation from the surface.

If the swelling timescale is long, then the system may not be at equilibrium by the time decontamination starts. Alternatively, there may not be enough agent present for the polymer to fully swell to equilibrium. This can be taken into account when considering the drying dynamics, and is another possible direction for future work.

The amount of solvent in the polymer and the drying flux both tend asymptotically to zero during drying, so the polymer is never completely dry.

### Solvent remaining in the polymer

The amount of agent remaining in the polymer is an exponentially decreasing function of time. Therefore, the polymer can dry out fully but this takes infinite time. To determine at which point the polymer is dry enough, we recommend that GDS take into account the level at which the rate of off-gassing is low enough to be safe. The necessary drying time can then be determined by referring to Figure 3 (right) or similar results.

## 6. Potential Impact

Emma Hellewell, Higher Scientific Offices at GDS, commented “*In the short term GDS need to understand the interactions of different chemicals on typical building surfaces to better inform the hazards and therefore the recovery options. This piece of work has started to explore one particular surface type and helped us to understand the material dynamics that dominate. By understanding the parameters that dominate we can determine whether the hazard still present, what remedial action we can undertake and how long will it be present if left untouched. It would help us to have an indication of how the different parameters over a certain range impact the absorption and drying times. Therefore if we know these values for a certain chemical we can roughly determine its impact on the polymer. This will help us to establish how we might tackle contamination on this surface and begin to consider how we decontaminate a hazardous chemical in the environment.*

*This has a wider impact on the UK recovery capability. If we can understand the impacts of chemicals and how they interact with different surfaces, a decontamination strategy can be better focussed and targeted. We will understand the hazard to individuals that remains from the chemical and how long this will persist for. In the longer term it will allow us to focus our areas of research more effectively. By utilising mathematical modelling we are able to explore the problem before conducting expensive and time consuming laboratory experiments and trials.”*

## References

1. Bertrand T., Peixinho J, Mukhopadhyay S, and MacMinn C. (2016). *Dynamics of Swelling and Drying in a Spherical Gel*. arXiv preprint, arXiv:1605.00599