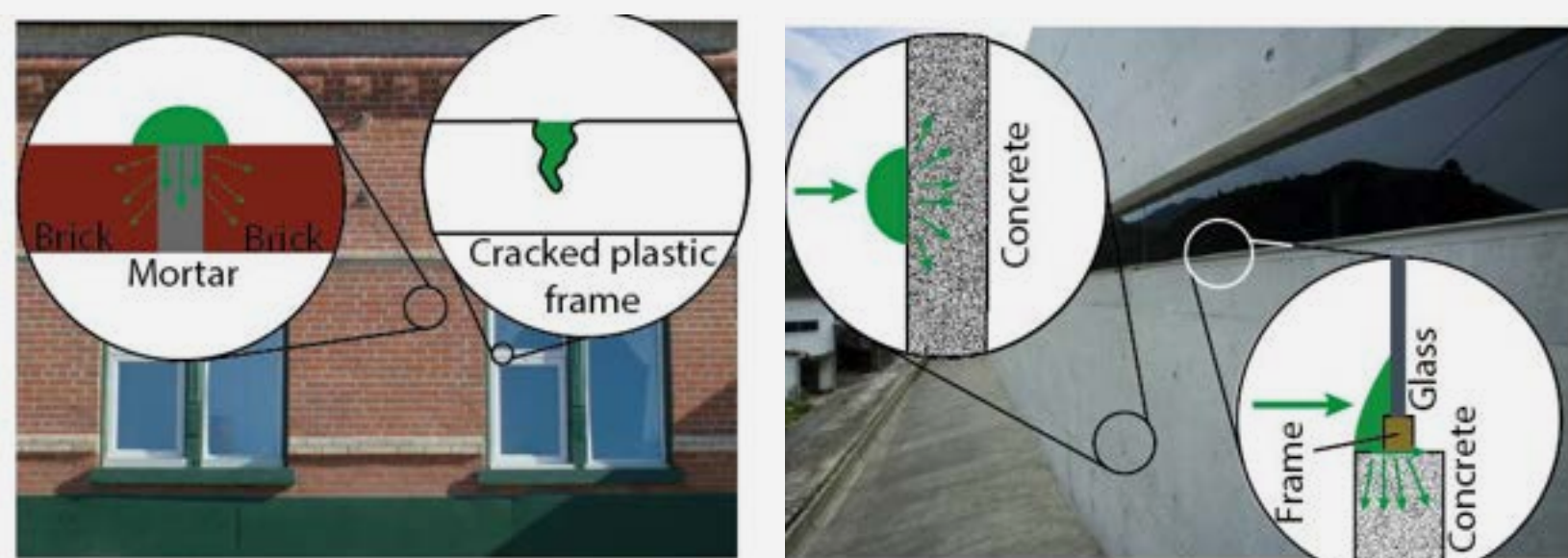


Hydrogel models to study contaminant trapping in polymers

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Decontamination problems in a civilian context

The problem

Hazard management, mitigation and removal of extremely toxic substances from absorbing surfaces in situations in which the contaminated surfaces **cannot** be disposed of.

Examples:

- Accidents with HazMat transporters
- Spills/decommissioning of chemical plants
- Terrorist attacks (e.g. Salisbury)
- Military operations in certain theaters.



Decontamination in a defence context

Introduction

Polymers are crucial substances in engineering and construction. Their interaction with fluids and thus hazardous chemicals depends on the chemical details of both: a given polymer may appear inert against one fluid and swell or dissolve in another.

Decontamination questions:

- How much is absorbed?
- How fast is it absorbed?
- Which hazard does it pose?
- How can it be removed?

Challenges:

- Diagnostics challenging due to small quantities
- Chemical variability
- Hard problem (chemically driven flows, swelling).

solvent	δ^a	S^b	μ (D)	ref ^c	rank ^d
perfluorotributylamine	5.6	1.00	0.0	10	32
perfluorodecalin	6.6	1.00	0.0	10	33
pentane	7.1	1.44	0.0	10	3
poly(dimethylsiloxane)	7.3	-	0.6-0.9	8, 14	-
diisopropylamine	7.3	2.13	1.2	10	1
xylene	8.9	1.41	0.3	10	4
toluene	8.9	1.31	0.4	10	13
ethyl acetate	9.0	1.18	1.8	8, 10	19
benzene	9.2	1.28	0.0	10	14
chloroform	9.2	1.39	1.0	10	5
2-butanone	9.3	1.21	2.8	10	18
tetrahydrofuran (THF)	9.3	1.38	1.7	10	7
dimethyl sulfoxide (DMSO)	13.0	1.00	4.0	10	35
propylene carbonate	13.3	1.01	4.8	10	30
methanol	14.5	1.02	1.7	8, 12	28
ethylene glycol	14.6	1.00	2.3	13, 15	37
glycerol	21.1	1.00	2.6	13, 15	37
water	23.4	1.00	1.9	8, 12	38

^a δ in units of cal^{1/2} cm^{-3/2}. ^b S denotes the swelling ratio that was measured experimentally; $S = D/D_0$, where D is the length of PDMS in the solvent and D_0 is the length of the dry PDMS. ^c References refer to literature values of δ and μ . ^d Rank refers to the order of the solvent in decreasing absorption ability (see Figure 1).

Example: absorption data for different solvents into PDMS

Approach: chose a highly swelling surrogate system (hydrogel/water) to investigate these questions.

Swelling in air: vapour phase transport



Initial state: hydrogel sheet is flat

A few minutes after droplet placement: the droplet no longer appears as a sessile droplet but the sides appear steeper.

Once the droplet is completely absorbed, a buckling instability becomes visible at the surface of the swollen region

After a while, the swollen region becomes smooth.

As time progresses, the droplet shape continues to evolve.

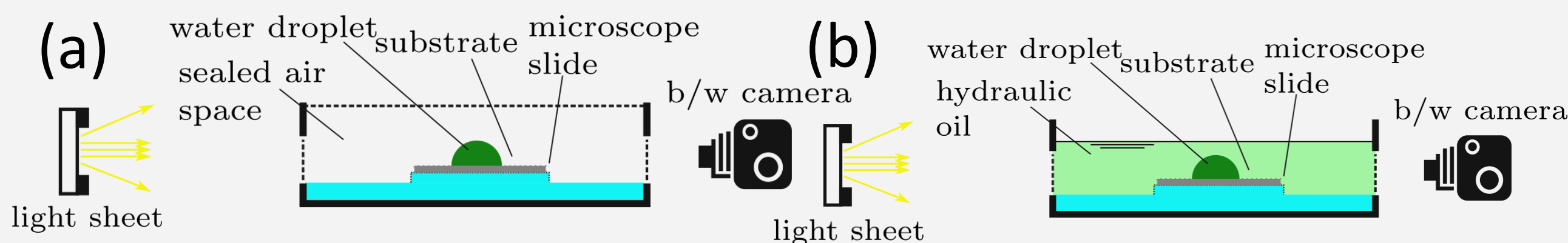
Interpretation

After the water droplet is placed on the hydrogel, it is absorbed rapidly. At the same time, some water evaporates and sets the chemical potential of water in the surrounding air to similar values as in the droplet. Within the polymer, the chemical potential of water is low. Therefore, water is absorbed both **directly from the droplet** as well as **from the vapour in the surrounding atmosphere** into the hydrogel. This demonstrates the vapour hazard from an absorbed hazardous material.

Conclusion

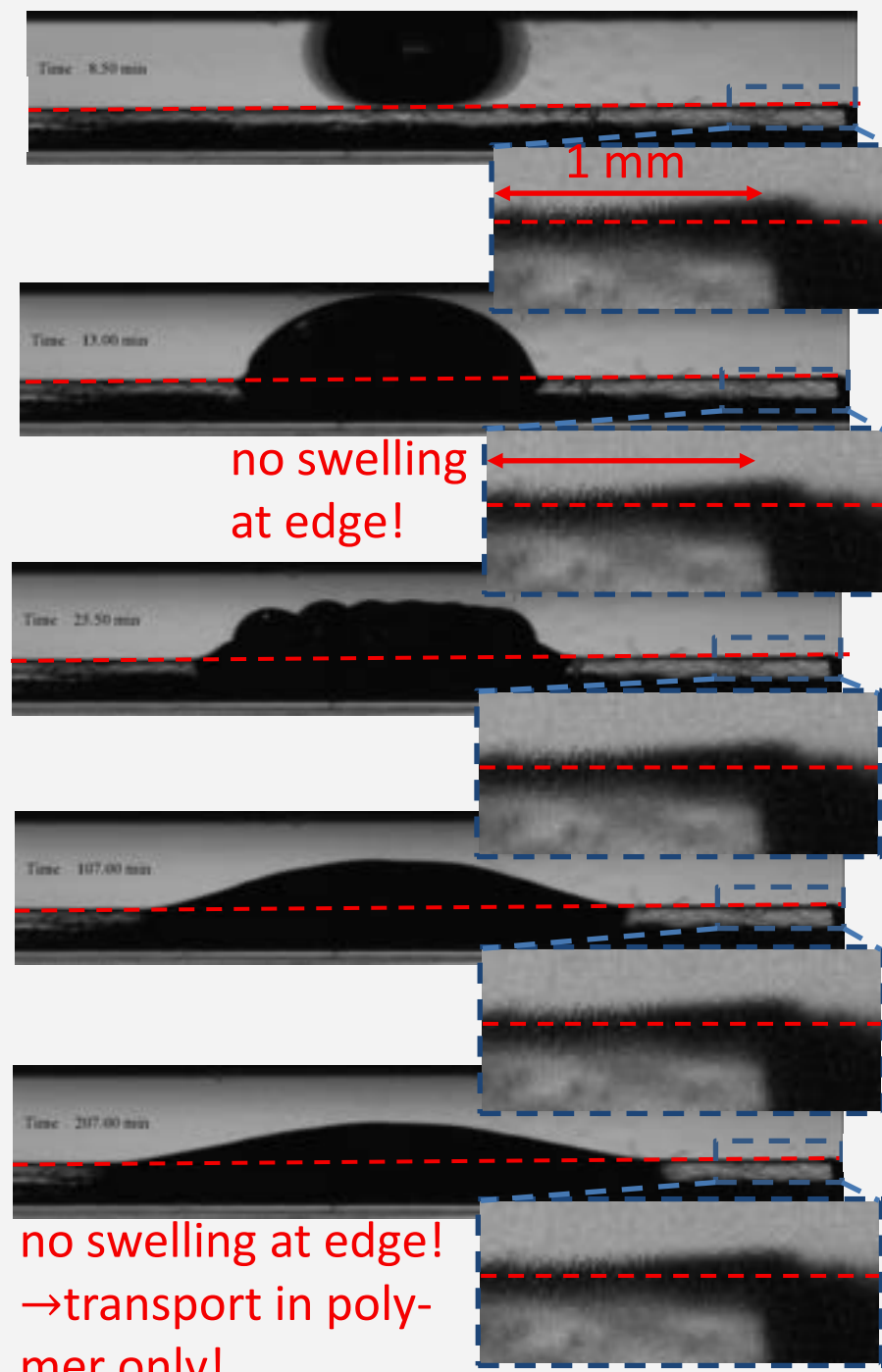
- Absorption of droplets into polymers occurs through vapour and liquid absorption
- (Linear) poroelasticity models are capable of capturing the essential features of the long-time absorption process
- Next: consider short-time absorption, extraction of contaminant.

Experimental



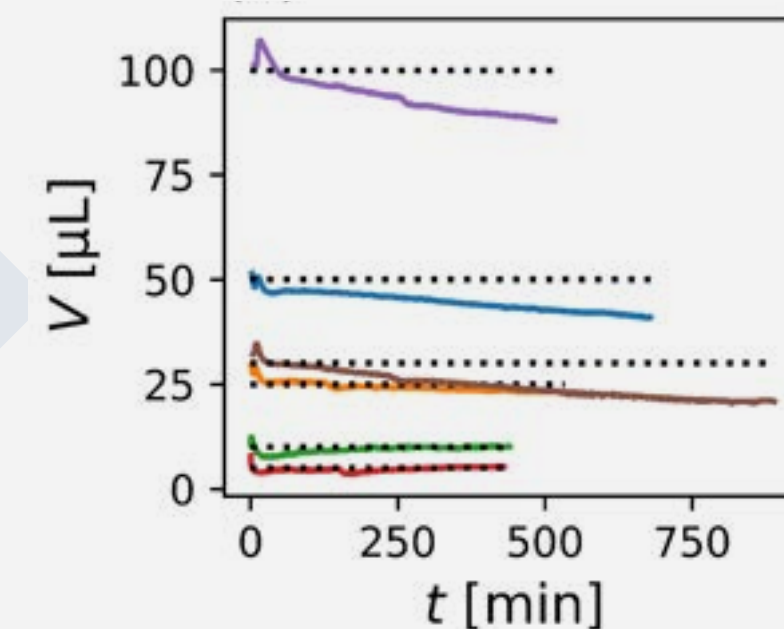
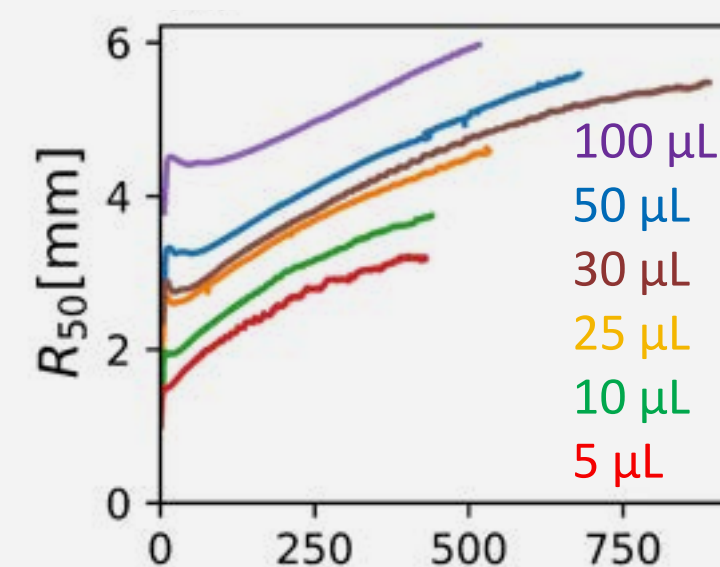
- Hydrogel substrates are manufactured from medical grade hydrogel (Medela Pads), which are glued on microscope slides
- Water is the environmentally friendly contaminant
- We observe swelling from the side with a telecentric lens to follow the swelling process.
- (a) Initial experiments were carried out under a cover, creating a sealed air space. This highlighted the role of vapour phase transport in the contamination process (see panel vapour phase transport)
- (b) We use a hydraulic oil to suppress vapour phase transport around the hydrogel (see panel polymer transport)

Swelling under oil: polymer transport only



Qualitatively, the polymer goes through the same stages as in air. The absence of swelling at the edge of the sheet confirms that transport occurs only within the polymer, not the surrounding medium.

Image analysis extracts measures the height profile $h(t)$ derived measures such as the volume V and the radius (defined via relative height, e.g. by $h(R_x(t)) = \frac{x}{100} \max(h(r, t))$)



Linear poroelasticity model (long-time limit)

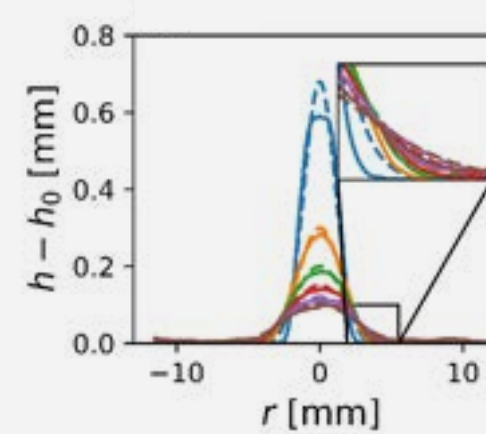
Polymer volume fraction ϕ , velocities of polymer and water $w_i = u_i e_r + w_i e_z$, polymer displacement $\xi = \xi e_r + \zeta e_z$, \mathcal{K}_0 permeability coefficient, K osmotic modulus, G shear modulus, t time. Ideal mixing (volume conservation). Assume a geometry with $h \ll R$, one finds:

$$\frac{\partial H}{\partial \tau} = \frac{A}{\rho} \frac{\partial}{\partial \rho} \left(\frac{\rho k}{H} \frac{\partial H}{\partial \rho} \right) \text{ with } k = \left(\frac{A}{H} \right)^\beta$$

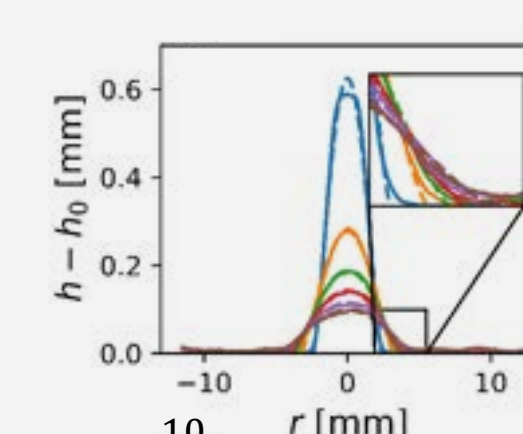
Small deformation: $\max(H) - A \ll 1$, Large deformation: $\max(H) \ll A$

$$R_s = \left(1 + \frac{2\tau}{V} \right)^{1/2}$$

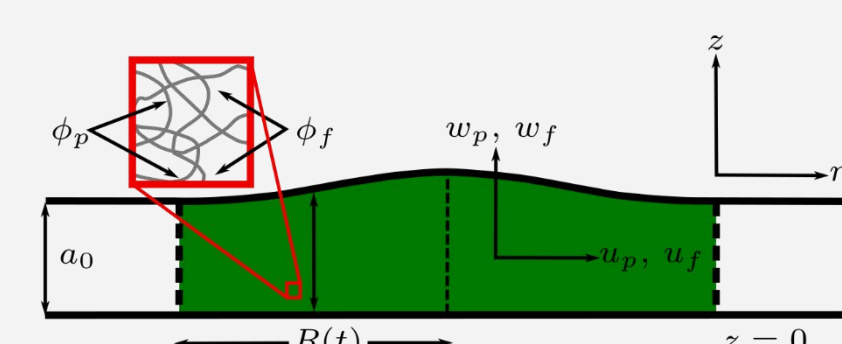
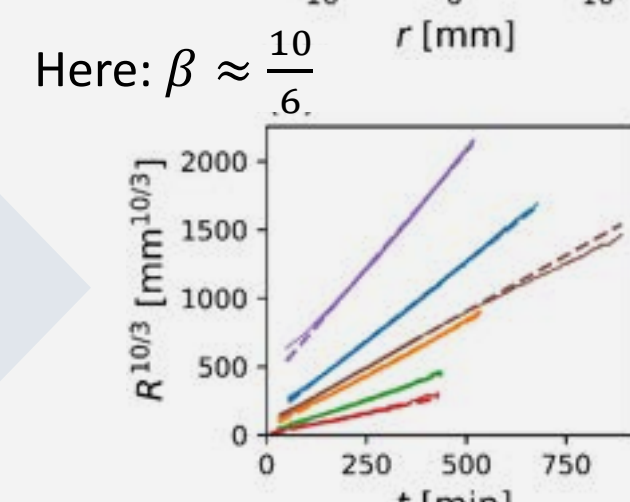
$$R_l = \left(1 + \frac{2\tau}{V} A^{\beta-1} \right)^{1/2\beta}$$



The model obtained in the small deformation model overpredicts the swollen region (inset). It cannot capture the spreading rate well.



The large deformation model gives a better apart from the leading edge (inset) of the swollen region. It also captures the radial spreading rate better.



Water transport

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (u_w (1 - \phi)) = 0$$

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (u_p \phi) = 0$$

$$(w_p - w_w) = - \frac{\mathcal{K}(\phi)}{(1 - \phi)\mu} \nabla p$$

$$\mathcal{K}(\phi) = \mathcal{K}_0 \left(\frac{\phi_0}{\phi} \right)^\beta$$

Polymer deformation

$$E = \frac{1}{2} (\nabla \xi + (\nabla \xi)^T)$$

$$\nabla \cdot \left(\left(K - \frac{2}{3} G \right) \text{tr}(E) I + GE - I p \right) = 0$$

Doi (2009), Yoon(2010), Bertrand (2016) Etzold (2020/21 submitted)

H, τ , \bar{V} , A, ρ are dimensionless quantities