

MATHEMATICAL MODELLING OF CHEMICAL AGENT REMOVAL BY REACTION WITH AN IMMISCIBLE CLEANSER

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Abstract. When a hazardous chemical agent has soaked into a porous medium, such as concrete, it can be difficult to neutralise. One removal method is chemical decontamination, where a cleanser is applied to react with and neutralise the agent, forming less harmful reaction products. There are often several cleansers that could be used to neutralise the same agent, so it is important to identify the cleanser features associated with fast and effective decontamination. As many cleansers are aqueous solutions while many agents are immiscible with water, the decontamination reaction often takes place at the interface between two phases. In this paper, we develop and analyse a mathematical model of a decontamination reaction between a neat agent and an immiscible cleanser solution. We assume that the reaction product is soluble in both the cleanser phase and the agent phase. At the moving boundary between the two phases, we obtain coupling conditions from mass conservation arguments and the oil–water partition coefficient of the product. We analyse our model using both asymptotic and numerical methods, and investigate how different features of a cleanser affect the time taken to remove the agent. Our results reveal the existence of two regimes characterised by different rate-limiting transport processes, and we identify the key parameters that control the removal time in each regime. In particular, we find that the oil–water partition coefficient of the reaction product is significantly more important in determining the removal time than the effective reaction rate.

Key words. decontamination, surface reaction, moving boundary problem, Stefan problem, asymptotic analysis

AMS subject classifications. 80A32, 92E20, 35C20, 80A22

1. Introduction.

1.1. Decontamination in porous media. Chemical spills can be both environmentally and financially disastrous, and a clear understanding of the effectiveness of different clean-up methods is vital for quick and efficient decontamination. Chemical spills are typically neutralised by applying a cleanser solution to the spill which reacts with the contaminating agent to produce less harmful products. With a small number of exceptions, the cleansers used for decontamination are applied as aqueous solutions [17, 19]. However, many agents of concern are organic compounds with low solubility in water. This means that achieving good mixing of the aqueous decontaminant with the organic agent is often a critical rate-limiting step, and the speed of decontamination is greatly affected by the water-solubility of the contaminating agent [1, 9, 10, 17, 21].

The challenges of achieving good mixing of cleanser and agent are particularly pronounced when the agent has soaked into a porous material, such as concrete. In this case, the cleanser and agent cannot be mixed mechanically (*e.g.* by stirring), and the speed of decontamination is likely to be limited by cleanser and agent transport. Studying the decontamination of porous materials also presents experimental challenges. While some methods have been developed for investigating the behaviour of

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41 agents in porous media [20], it is extremely difficult to track the progress of a neu-
 42 tralisation reaction *in situ* and thus obtain reliable data about the effectiveness of a
 43 decontamination protocol [16].

44 In many cases, multiple different cleanser solutions could be used to neutralise
 45 the same agent; for a detailed description of cleanser solutions in current use, and
 46 different decontamination reactions and their products, see [19] and [14], respectively.
 47 However, only limited data are available about how quickly and how completely a
 48 contaminating agent in a porous medium is neutralised by a given cleanser.

49 Mathematical modelling of decontamination in porous media can give valuable
 50 insights into the effectiveness of cleanser solutions by analysing how different physical
 51 and chemical properties of agents and cleansers affect the speed and effectiveness of
 52 decontamination. This information can be used both to guide the choice of cleanser
 53 for a specific application and to inform the development of new cleansers.

54 **1.2. Reactions at phase boundaries.** In a general setting, the evolving dis-
 55 tributions of agent, cleanser, and reaction products in a porous medium are controlled
 56 by (i) the transport of chemical species by diffusion and advection, and (ii) the re-
 57 actions that occur. If the agent and the cleanser solution are completely immiscible,
 58 these reactions only occur at phase boundaries. Reactive transport of chemicals in
 59 multiphase systems is important in hydrology and geology, and various mathematical
 60 models have been developed to describe reactive transport [4, 5, 12, 13, 15, 18].

61 In many of these models, the reacting species are in different phases and reactions
 62 occur only at phase boundaries. To the best of our knowledge, apart from a study
 63 group report on preliminary work [6], the published literature deals only with reactions
 64 of this type where one of the reacting species is in a solid phase, within which diffusion
 65 and advection can be neglected. In contrast, we are concerned with the reaction
 66 between a water-phase cleanser solution and an oil-phase agent, where the important
 67 reacting species are in two distinct *fluid* phases and chemical transport in each phase
 68 occurs due to diffusion. In this context, simultaneous transport of the reactive species
 69 to the phase boundary is crucial.

70 As we describe below, our model of decontamination involves mass exchange
 71 between two phases (an oil phase and a water phase) at a free boundary. Mass
 72 exchange at phase boundaries has been extensively studied in the context of the
 73 Stefan problem, a famous model of melting and freezing (see, for example, [2, 3, 7,
 74 8]). While there are important differences between decontamination and the classical
 75 Stefan problem, we show that our model reduces to a Stefan problem with kinetic
 76 undercooling in certain limits.

77 **1.3. Outline of paper.** This paper describes the development and analysis of a
 78 model of decontamination in two immiscible phases, where chemical transport is due
 79 to diffusion in each phase and the decontamination reaction occurs at the boundary
 80 between the two immiscible fluid phases. While real decontamination systems can
 81 be very complicated, often involving multiple reactions with multiple products [14],
 82 we concentrate on an idealised scenario involving a bimolecular reaction between a
 83 neat agent and a cleanser solution to produce a single reaction product. The agent
 84 and cleanser solution are assumed to be immiscible, but the neutralisation reaction
 85 is assumed to yield a reaction product that gets distributed between the two phases
 86 according to a known partition coefficient.

87 The assumptions that we make in developing our model allow us to analyse how
 88 the salient features of the decontamination system (*e.g.* the reaction rate constant,
 89 the diffusion constants of different species, the partition coefficient for the distribution

of reaction product between phases) affect the overall speed of decontamination. As discussed above, since we can find no references in the present literature that discuss (let alone quantify) how such features affect decontamination speed, this paper represents a valuable first step in understanding the processes that control the effectiveness of decontamination.

In §2, we describe the development and nondimensionalisation of our model, paying particular attention to the boundary conditions that hold at the moving interface. This leads to equations (12)–(15), which give a dimensionless representation of our model, transformed to fixed spatial domains. In §3 we consider the early-time asymptotic behaviour of the model and present numerical solutions to the system. While not important for determining the overall speed of decontamination, the early-time analysis is essential for developing accurate and efficient numerical schemes for solving (12)–(15). We also introduce two measures of agent removal time that can be used to characterise decontamination.

We follow this in §4 with an asymptotic analysis of the governing equations for long time. Under the assumption that the initial agent layer is deep, we find that the long-time dynamics of the model fall into one of two regimes. We investigate the behaviour of the system in both of these regimes, providing asymptotic results where possible. These results allow us to gain deeper physical insight into the underlying system and predict the most important parameters for decontamination. We discuss the physical implications of our work in §5, where we present our results in dimensional form and thus identify some desirable features of cleansers.

2. Model development.

2.1. Model outline. Throughout this paper, we use SI units to indicate the dimensions of parameters and variables when they are first introduced. We consider a one-dimensional porous medium of length \bar{L} [m], with the \bar{x} -axis pointing into the medium, as shown in figure 1. Before the decontamination reaction begins, the neat agent has penetrated to the end of the porous medium, so that the agent entirely occupies the region $0 < \bar{x} < \bar{L}$. Then, at time $\bar{t} = 0$, an aqueous solution of cleanser with uniform concentration \bar{c}_0 [mol m⁻³] is introduced to the surface at $\bar{x} = 0$. The aqueous phase (containing the cleanser) and the oil phase (containing the agent) are assumed to be immiscible, but the position of the interface between them, $\bar{s}(\bar{t})$ [m], can change in time. We assume that the porous medium is homogeneous and fully saturated with fluid. As a result of this, the porosity of the medium does not play an explicit role in our analysis.

At the interface between the phases, the cleanser and the agent react irreversibly. This reaction consumes cleanser and agent and leads to the formation of a neutral product that is soluble in both the aqueous phase and the oil phase. In the aqueous phase, the evolving concentration of cleanser is given by $\bar{c}(\bar{x}, \bar{t})$ [mol m⁻³] and the evolving concentration of reaction product is given by $\bar{p}(\bar{x}, \bar{t})$ [mol m⁻³].

In the oil phase, we assume that the product and agent form an ideal mixture whose molar volume is independent of composition. We describe the evolving composition of the oil phase using the volume fraction of reaction product in the oil phase, $\bar{\phi}(\bar{x}, \bar{t})$ [dimensionless]. Since the oil phase contains only agent and product, the volume fraction of contaminant in the oil phase is $1 - \bar{\phi}$. Ideality of the agent-product mixture implies that the diffusion of product in agent is equivalent to the diffusion of agent in product, and hence we can represent diffusive transport in the oil phase using a single diffusion equation for $\bar{\phi}$.

We assume that all transport of cleanser, agent, and product within their re-

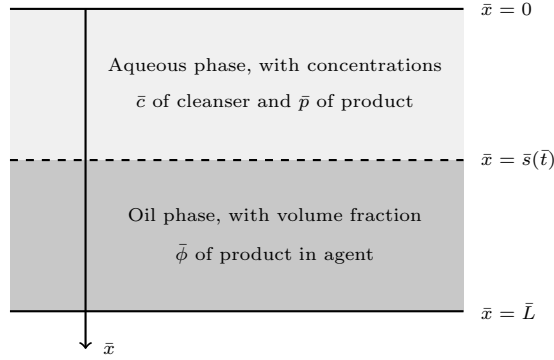


FIG. 1. Schematic diagram of the physical problem. Over time, the interface between the aqueous phase and the oil phase moves down (in the direction of increasing \bar{x}) as agent is consumed.

139 spectively phases is due to diffusion. Assuming Fickian diffusion and exploiting the
 140 assumption that the porous medium is saturated and uniformly porous, this gives the
 141 governing equations for the evolution of \bar{c} , \bar{p} and $\bar{\phi}$ to be

142 (1a) $\bar{c}_{\bar{t}} = \bar{D}_c \bar{c}_{\bar{x}\bar{x}},$ for $0 < \bar{x} < \bar{s}(\bar{t})$ and $\bar{t} > 0,$

143 (1b) $\bar{p}_{\bar{t}} = \bar{D}_p \bar{p}_{\bar{x}\bar{x}},$ for $0 < \bar{x} < \bar{s}(\bar{t})$ and $\bar{t} > 0,$

144 (1c) $\bar{\phi}_{\bar{t}} = \bar{D}_\phi \bar{\phi}_{\bar{x}\bar{x}},$ for $\bar{s}(\bar{t}) < \bar{x} < \bar{L}$ and $\bar{t} > 0,$

146 where \bar{D}_c [$\text{m}^2 \text{s}^{-1}$], \bar{D}_p [$\text{m}^2 \text{s}^{-1}$] and \bar{D}_ϕ [$\text{m}^2 \text{s}^{-1}$] are the effective diffusion coefficients
 147 within a porous medium of the cleanser in aqueous solution, the product in aqueous
 148 solution, and the agent/product in the oil phase respectively. Subscripts of \bar{t} or \bar{x}
 149 denote partial derivatives with respect to time and space respectively.

150 At $\bar{x} = 0$, we assume that the cleanser is continually being replenished at a
 151 constant concentration \bar{c}_0 [mol m^{-3}] while the reaction product is continually being
 152 removed from the system. At $\bar{x} = \bar{L}$, we assume that there is a fixed boundary that
 153 no species can pass through. This yields the boundary conditions

154 (2) $\bar{c} = \bar{c}_0, \quad \bar{p} = 0 \quad \text{for } \bar{x} = 0,$

155 (3) $\bar{\phi}_{\bar{x}} = 0 \quad \text{for } \bar{x} = \bar{L}.$

157 At $\bar{t} = 0$, the interface between the phases is located at $\bar{x} = 0$, and there is no
 158 oily product yet, so the initial conditions are

159 (4) $\bar{\phi} = 0, \quad \bar{s} = 0 \quad \text{for } \bar{t} = 0.$

161 **2.2. Interfacial conditions.** We assume that the agent and the cleanser react
 162 in an irreversible bimolecular reaction at the phase boundary to produce the reaction
 163 product. For simplicity, we assume that the rate of the decontamination reaction
 164 is proportional to the bulk concentrations of the two reagents in the neighbourhood
 165 of the phase boundary. While this approach means that we neglect the kinetics of
 166 absorption and desorption, Kumar *et al.* [11] have shown that it is consistent with
 167 more complicated kinetic schemes in appropriate limits.

168 Mathematically, we describe the kinetics of decontamination by introducing the
 169 total molar flux of reaction, \bar{R} [$\text{mol m}^{-2} \text{s}^{-1}$]. This represents the consumption rate
 170 of cleanser and agent (and, equivalently, the production rate of reaction product) per

171 unit area of the interface. Using our assumption that \bar{R} is proportional to the amounts
172 of cleanser and agent available at the oil-water interface, we obtain

$$173 \quad (5) \quad \bar{R} = \bar{k}\bar{c}[\bar{s}(\bar{t}), \bar{t}] \{1 - \bar{\phi}[\bar{s}(\bar{t}), \bar{t}]\},$$

174 where \bar{k} [m s^{-1}] is a constant of proportionality which we refer to as the *effective rate*
175 *constant*.

176 We use (5) to obtain interfacial conditions on \bar{c} , $\bar{\phi}$, and \bar{p} , noting that the total
177 amounts of cleanser, agent, and product in the system (in moles) are given by

$$178 \quad (6a) \quad \mathcal{C}(\bar{t}) = \bar{A} \int_0^{\bar{s}(\bar{t})} \bar{c}(\bar{x}, \bar{t}) \, \text{d}\bar{x},$$

$$179 \quad (6b) \quad \mathcal{A}(\bar{t}) = \frac{\bar{A}}{\bar{V}_m} \int_{\bar{s}(\bar{t})}^{\bar{L}} 1 - \bar{\phi}(\bar{x}, \bar{t}) \, \text{d}\bar{x},$$

$$180 \quad (6c) \quad \mathcal{P}(\bar{t}) = \bar{A} \int_0^{\bar{s}(\bar{t})} \bar{p}(\bar{x}, \bar{t}) \, \text{d}\bar{x} + \frac{\bar{A}}{\bar{V}_m} \int_{\bar{s}(\bar{t})}^{\bar{L}} \bar{\phi}(\bar{x}, \bar{t}) \, \text{d}\bar{x},$$

182 where \bar{A} [m^2] is the area of the spill, and \bar{V}_m [$\text{m}^3 \text{mol}^{-1}$] is the molar volume of the
183 agent/product mixture. Since we have assumed that the agent and product form an
184 ideal mixture, \bar{V}_m is a constant independent of $\bar{\phi}$.

185 Differentiating (6a) using Leibniz's rule, we recognise that the molar flux of
186 cleanser into the oil-water interface is given by $\bar{D}_c \bar{c}_{\bar{x}} + \bar{c} \bar{s}_{\bar{t}}$, evaluated at $\bar{x} = \bar{s}(\bar{t})$.
187 Since the removal of cleanser at the oil-water interface happens via the decontamina-
188 tion reaction, we use (5) to obtain

$$189 \quad (7a) \quad \bar{D}_c \bar{c}_{\bar{x}} + \bar{c} \bar{s}_{\bar{t}} = -\bar{k}\bar{c}(1 - \bar{\phi}) \quad \text{on } \bar{x} = \bar{s}(\bar{t}) \text{ for } \bar{t} > 0.$$

190 Repeating this process with equations (6b) and (6c), we obtain two further inter-
191 facial conditions,

$$192 \quad (7b) \quad -\frac{\bar{D}_\phi}{\bar{V}_m} \bar{\phi}_{\bar{x}} + \frac{1 - \bar{\phi}}{\bar{V}_m} \bar{s}_{\bar{t}} = \bar{k}\bar{c}(1 - \bar{\phi}) \quad \text{on } \bar{x} = \bar{s}(\bar{t}) \text{ for } \bar{t} > 0,$$

$$193 \quad (7c) \quad \bar{D}_p \bar{p}_{\bar{x}} + \bar{p} \bar{s}_{\bar{t}} = \frac{1}{\bar{V}_m} \bar{s}_{\bar{t}} \quad \text{on } \bar{x} = \bar{s}(\bar{t}) \text{ for } \bar{t} > 0,$$

195 where (7c) has been rearranged using (7b).

196 We obtain the final interfacial condition by assuming that the reaction product is
197 locally in equilibrium between the oil phase and the water phase. Thus, the concen-
198 trations of product on either side of the interface are related via a partition constant,
199 and the final interfacial condition is

$$200 \quad (7d) \quad \frac{\bar{\phi}}{\bar{V}_m} = \mathcal{K} \bar{p} \quad \text{on } \bar{x} = \bar{s}(\bar{t}) \text{ for } \bar{t} > 0,$$

201 where \mathcal{K} [dimensionless] is the oil-water partition constant of the reaction product.
202 In practice, \mathcal{K} can be estimated from octanol-water partition constants, which have
203 been measured for a range of relevant compounds [14].

204 We note that the interfacial conditions stated in (7) are similar to those considered
205 in Stefan problems with kinetic undercooling. To see this, consider the limit $\mathcal{K} \rightarrow 0$,
206 where no reaction product enters the oil phase. In this case, the interfacial conditions
207 for \bar{c} and \bar{s} can be reduced to

$$208 \quad (8a) \quad \bar{D}_c \bar{c}_{\bar{x}} = -\bar{k}\bar{c} - \bar{c} \bar{s}_{\bar{t}},$$

$$(8b) \quad \bar{s}_{\bar{t}} = \bar{k} \bar{V}_m \bar{c},$$

which are equivalent to the classic Stefan problem with kinetic undercooling [8].

2.3. Nondimensionalisation and transformation to a fixed domain. As part of our nondimensionalisation, we pre-empt the challenges associated with numerical solution on a domain with a moving boundary, and introduce a boundary-fixing transformation by defining ‘upper’ and ‘lower’ spatial variables, $\xi \in [0, 1]$ and $\eta \in [0, 1]$, respectively, so that

$$(9) \quad \xi := \frac{\bar{x}}{\bar{s}(\bar{t})}, \quad \eta := \frac{\bar{L} - \bar{x}}{\bar{L} - \bar{s}(\bar{t})}.$$

With these definitions, the boundary conditions applied at $\bar{x} = 0$ and $\bar{x} = \bar{L}$ are now applied at $\xi = 0$ and $\eta = 0$, respectively, while the interfacial conditions applied at the moving boundary $\bar{x} = \bar{s}(\bar{t})$ are now applied at the fixed boundaries $\xi = 1$ and $\eta = 1$.

We nondimensionalise our dependent variables by introducing

$$(10) \quad \bar{c}(\bar{x}, \bar{t}) := \frac{c(\xi, t)}{V_m}, \quad \bar{p}(\bar{x}, \bar{t}) := \frac{p(\xi, t)}{V_m}, \quad \bar{s}(\bar{t}) := \frac{\bar{D}_c}{k} s(t), \quad \bar{t} := \frac{\bar{D}_c}{k^2} t,$$

and, observing that $\bar{\phi}$ is already dimensionless, we also use $\bar{\phi}(\bar{x}, \bar{t}) = \phi(\eta, t)$.

Applying the nondimensionalisation and the boundary-fixing transformation described above, we identify the following set of five dimensionless parameters that prescribe the system:

$$(11) \quad \beta := \bar{c}_0 \bar{V}_m, \quad D_p := \frac{\bar{D}_p}{D_c}, \quad D_\phi := \frac{\bar{D}_\phi}{D_c}, \quad \mathcal{K}, \quad d := \frac{\bar{L}k}{D_c}.$$

We discuss the decontamination of sulfur mustard in §5.3, for which we obtain typical parameter values of $\beta \approx 0.03 - 8$ and $\mathcal{K} \approx 0.14 - 7.1$. However, diffusion and reaction coefficients are more difficult to obtain. In §4, we explore in detail the case where d is much larger than the other parameters in the system, modelling deep spills of agent.

In rescaled form, the governing equations (1) become

$$(12a) \quad c_{\xi\xi} + \dot{s}s\xi c_\xi = s^2 c_t \quad \text{for } 0 < \xi < 1 \text{ and } t > 0,$$

$$(12b) \quad D_p p_{\xi\xi} + \dot{s}s\xi p_\xi = s^2 p_t \quad \text{for } 0 < \xi < 1 \text{ and } t > 0,$$

$$(12c) \quad D_\phi \phi_{\eta\eta} - \dot{s}(d - s)\eta\phi_\eta = (d - s)^2 \phi_t \quad \text{for } 0 < \eta < 1 \text{ and } t > 0,$$

where $\dot{s} = ds/dt$ and subscripts of ξ , η , and t represent partial differentiation. We observe that $s(t) \in [0, d]$, and hence $(d - s)$ is always nonnegative.

The initial conditions (4) become

$$(13) \quad \phi(\eta, 0) = 0, \quad s(0) = 0,$$

while the boundary conditions (2) and (3) become

$$(14) \quad c(0, t) = \beta, \quad p(0, t) = 0, \quad \phi_\eta(0, t) = 0.$$

Additionally, the interfacial conditions (7) are now

$$(15a) \quad c_\xi + sc = sc(\phi - \dot{s}),$$

$$251 \quad (15b) \quad D_\phi \phi_\eta = -(d-s)(\dot{s}-c)(1-\phi),$$

$$252 \quad (15c) \quad D_p p_\xi = s\dot{s}(1-p),$$

$$253 \quad (15d) \quad \phi = \mathcal{K}p,$$

255 where all variables are evaluated for $t > 0$ and at $\xi = 1$ or $\eta = 1$, as appropriate. The
256 full dimensionless system is then described by (12)–(15).

257 3. Early-time asymptotics and numerical solutions.

258 **3.1. Early-time asymptotics.** Since the aqueous phase is initially absent from
259 the system, the boundary-fixing transformation described in §2.3 is singular at $t = 0$.
260 We circumvent the numerical difficulties created by this singularity by calculating
261 the early-time behaviour of the system as $t \rightarrow 0^+$. We use these results to start our
262 computations at a small but finite time.

263 We begin by using (12)–(15) to obtain consistent initial conditions for c and p .
264 For small s , assuming that all other terms are bounded, (12) yields $c_{\xi\xi} = p_{\xi\xi} = 0$ and
265 (15) yields $c_\xi(1, 0) = p_\xi(1, 0) = 0$. Applying the boundary conditions (14), we obtain

$$266 \quad (16) \quad c(\xi, 0) = \beta, \quad p(\xi, 0) = 0.$$

268 We can now obtain early-time results. Rescaling t with an arbitrary small param-
269 eter and seeking asymptotic balances in (12) and (15) where c , p , ϕ and s are close
270 to their initial values, we find that $s = O(t)$, $c = \beta + O(t)$, $\phi = O(t)$, and $p = O(t)$.
271 Solving for c , p , and s leads to the explicit results

$$272 \quad (17) \quad c \sim \beta - \beta^2(1+\beta)\xi t, \quad p \sim \frac{\beta^2 \xi t}{D_p}, \quad s \sim \beta t, \quad \text{as } t \rightarrow 0^+.$$

274 In order to obtain explicit early-time results for ϕ , we make the assumption that
275 d is large. This corresponds to a deep spill of chemical agent, and is the main focus
276 of our analysis in §4. In this case we seek a boundary layer solution for ϕ near $\eta = 1$;
277 we introduce the rescaled spatial variable $X = d(1-\eta)$ to obtain the leading-order
278 early-time system

$$279 \quad (18a) \quad D_\phi \phi_{XX} + \beta \phi_X = \phi_t \quad \text{for } X > 0 \text{ and } t > 0,$$

$$280 \quad (18b) \quad \phi = \frac{\beta \mathcal{K} t}{D_p} \quad \text{on } X = 0 \text{ for } t > 0,$$

$$281 \quad (18c) \quad \phi \rightarrow 0 \quad \text{as } X \rightarrow \infty \text{ for } t > 0,$$

$$282 \quad (18d) \quad \phi = 0 \quad \text{on } t = 0 \text{ for } X > 0.$$

284 This is solved by

$$285 \quad (19) \quad \phi = \frac{\beta \mathcal{K}}{2D_p} \left\{ (\beta t + X) \operatorname{erfc} \left(\frac{X + \beta t}{2\sqrt{D_\phi t}} \right) + e^{-\beta X/D_\phi} (\beta t - X) \operatorname{erfc} \left(\frac{X - \beta t}{2\sqrt{D_\phi t}} \right) \right\},$$

287 where $\operatorname{erfc}(z)$ is the complementary error function.

288 **3.2. Numerical solutions.** The full dimensionless problem (12)–(15) is solved
289 using the method of lines. We use a uniform mesh for ξ and, to resolve the boundary
290 layer observed in the previous section, we use a non-uniform mesh with logarithmically
291 spaced points for η . The logarithmic spacing is focused near $\eta = 1$ and is only used

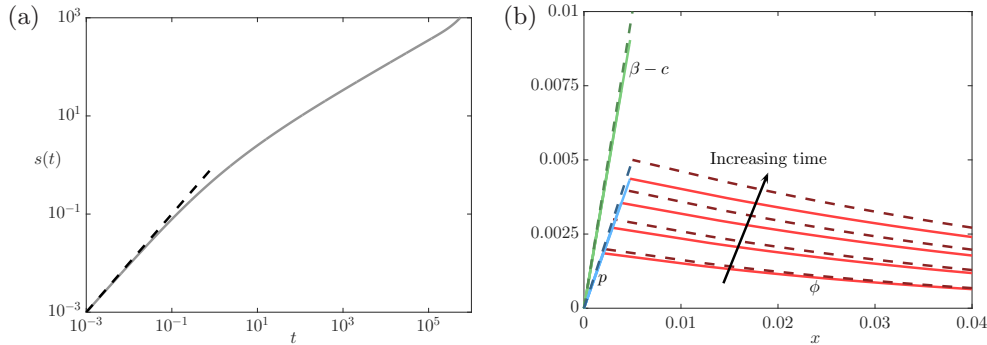


FIG. 2. (Colour online) Comparison of numerical solutions (solid) and asymptotic results (dashed) at early times for $\beta = \mathcal{K} = D_\phi = D_p = 1$, $d = 10^3$. (a) The position of the moving boundary. (b) The change from the initial conditions at early time. The decrease in cleanser concentration profile, $\beta - c$ (green), increase in product concentration in aqueous phase, p (blue), and increase in product concentration in oily phase, ϕ (red), at times $t = 2 \times 10^{-3}, 3 \times 10^{-3}, 4 \times 10^{-3}, 5 \times 10^{-3}$ with the arrow denoting an increase in time. The numerical solutions start from $t = 10^{-3}$ as described in the text.

292 while $s(t) < d/4$; after this point in time, we use a uniform mesh. We discretise (12)–
 293 (15) in space using second-order finite differences, and integrate in time with `ode15s`
 294 in MATLAB, using the early-time solutions (17) and (19) to provide consistent initial
 295 conditions. We use ‘ghost’ points just outside the domain to impose the boundary
 296 conditions, using (15c) for \dot{s} , (15a) for c , (15d) for p , and (15b) for ϕ at the free
 297 boundary. We verify the early-time solution by comparing full numerical solutions
 298 initiated at $t = 10^{-3}$ with the early-time asymptotic solutions (17) and (19) in figure 2,
 299 and we observe good agreement. The asymptotic predictions (17) for $\beta - c$ and p do
 300 not change in time when rescaled for the physical domain via (9), and the early-time
 301 numerical solutions exhibit the same behaviour.

302 In figures 3 and 4 we show the evolution of the cleanser–agent–product system
 303 for illustrative parameter values, namely $\beta = D_\phi = D_p = 1$, $d = 10^3$, with $\mathcal{K} = 10$ in
 304 figure 3 and $\mathcal{K} = 1$ in figure 4. As we discuss further in §5, values of \mathcal{K} within an order
 305 of magnitude of unity are realistic. Additionally, we expect all diffusion constants to
 306 be comparable. The choices of \mathcal{K} that we make in figures 3 and 4 enable us to
 307 demonstrate how different parameter choices lead to qualitatively different solution
 308 behaviours.

309 In both figure 3 and 4, we observe that the interface moves in the positive x -
 310 direction, consuming the agent. The interface reaches the lower boundary almost an
 311 order of magnitude faster for $\mathcal{K} = 1$ than for $\mathcal{K} = 10$. Additionally, we observe that
 312 the concentration profiles of cleanser, c , and product in the upper and lower regions,
 313 p and ϕ , respectively, are sensitive to the partition coefficient \mathcal{K} . For $\mathcal{K} = 10$, we
 314 observe that ϕ reaches values close to 1 (so agent concentration is close to 0) while
 315 the interface is still far from the lower boundary (figure 3) whereas, for $\mathcal{K} = 1$, $\phi < 1$
 316 throughout the reaction and c appears to vanish close to the interface (figure 4).
 317 There is a significant difference in the system behaviour between these two cases, and
 318 we can see this more clearly by considering the proportion of remaining agent in the
 319 system, defined by

$$320 \quad (20a) \quad \Phi(t) = \frac{d - s(t)}{d} \int_0^1 (1 - \phi(\eta, t)) \, d\eta.$$

321

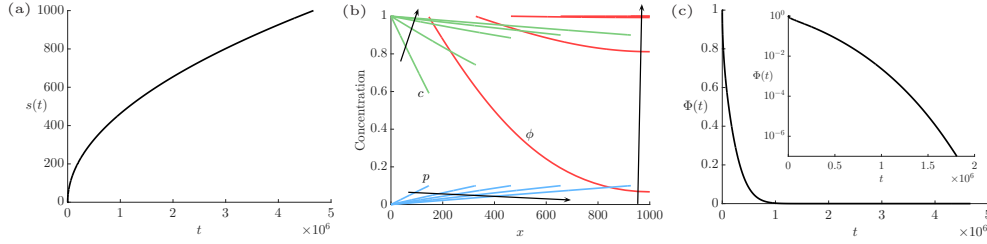


FIG. 3. (Colour online) Numerical results for the system (12)–(15) using the parameter values $\beta = D_\phi = D_p = 1$, $\mathcal{K} = 10$, and $d = 10^3$. (a) The position of the moving boundary, $s(t)$. (b) The concentrations of the cleanser, c (green), product in aqueous phase, p (blue), and product in oily phase, ϕ (red), at (non-uniform) times $t = 1 \times 10^5, 5 \times 10^5, 1 \times 10^6, 2 \times 10^6, 4 \times 10^6$, where the arrows denote increasing time. (c) The proportion of remaining contaminant in the system, $\Phi(t)$, defined in (20a). The inset shows a log-lin version of the same function.

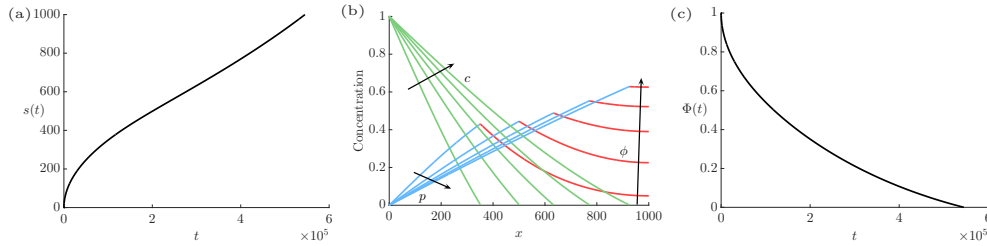


FIG. 4. (Colour online) Numerical results for the system (12)–(15) using the parameter values $\beta = D_\phi = D_p = \mathcal{K} = 1$, and $d = 10^3$. (a) The position of the moving boundary, $s(t)$. (b) The concentrations of the cleanser, c (green), product in aqueous phase, p (blue), and product in oily phase, ϕ (red), at times $t = 1 \times 10^5, 2 \times 10^5, 3 \times 10^5, 4 \times 10^5, 5 \times 10^5$, where the arrows denote increasing time. (c) The proportion of remaining contaminant in the system, $\Phi(t)$, defined in (20a).

322 For $\mathcal{K} = 10$, we see that most of the agent is consumed significantly before the
 323 moving interface reaches the lower boundary (figure 3c) and we see that, for example,
 324 $\Phi < 10^{-4}$ before the interface has reached a third of the way to the lower boundary.
 325 However, for $\mathcal{K} = 1$ the agent appears to be consumed more uniformly as the interface
 326 moves, and the remaining agent in the system is only small when the interface is close
 327 to the lower boundary (figure 4c).

328 In order to make quantitative comparisons of different decontamination simula-
 329 tions, we now introduce two different measures of the time taken to decontaminate
 330 the system. The first of these is a measure of the time until complete agent removal,
 331 t_f ; we refer to this as the *final time* and define it by

$$332 \quad (20b) \quad t_f := \min\{t > 0 : s(t) = d\}.$$

334 While t_f is the time taken for the interface to reach the lower boundary (and hence
 335 the time taken to completely remove all agent), it is possible that most of the agent
 336 reacts with the cleanser long before $t = t_f$, as illustrated in figure 3. To investigate
 337 this scenario, we introduce a second measure of removal time, t_e . We refer to t_e as the
 338 *effective removal time*, and it corresponds to the time taken until the total amount of
 339 remaining agent drops below some safe threshold. We define t_e by

$$340 \quad (20c) \quad t_e := \min\{t > 0 : \Phi(t) < \varepsilon\},$$

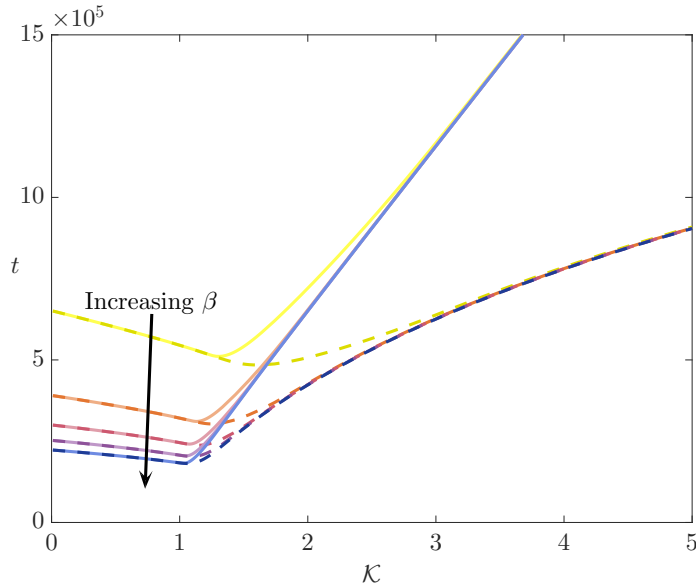


FIG. 5. (Colour online) The final time t_f (solid lines) and effective removal time t_e (dashed) as functions of \mathcal{K} , calculated using numerical solutions of (12)–(15). Each line denotes a different value of β , corresponding to $\beta = 1, 2, 3, 4,$ and 5 . We use parameter values $D_\phi = D_p = 1$, and $d = 10^3$.

342 where ε represents the proportion of the original agent that remains when the safe
 343 threshold is reached. We take $\varepsilon = 10^{-4}$ throughout this paper. The fact that $t_e < t_f$
 344 follows from the definitions in (20), from which we also expect the final and effective
 345 removal times to be close to one another, except for in scenarios where $\phi \approx 1$ before
 346 the interface reaches the lower boundary.

347 As \mathcal{K} increases, for a given β , we observe that the final times and the effective
 348 removal times are close to one another until \mathcal{K} reaches some threshold value, after
 349 which the two measures of removal time diverge (figure 5). Moreover, we observe
 350 that neither measure of removal time is a monotone function of \mathcal{K} ; instead, there are
 351 optimal \mathcal{K} values at which the final time or effective removal time are minimised, and
 352 these optimal values of \mathcal{K} depend weakly on β . Additionally, we observe that both
 353 measures of removal time depend strongly on β when \mathcal{K} is small, but are effectively
 354 independent of β when \mathcal{K} is large.

355 To further understand the dependence of t_f and t_e on β , \mathcal{K} , and the other model
 356 parameters, we proceed by analysing (12)–(15) using asymptotic methods in the phys-
 357 ically relevant limit of large d . This will enable us to make general deductions about
 358 the system and will provide physical insight into the parameters that control the
 359 decontamination process. Additionally, we investigate why the final and effective
 360 removal times diverge in certain parameter regimes.

361 4. Long-time asymptotic analysis.

362 **4.1. Large d assumption.** We now explore in detail the scenario where there
 363 is a deep spill of agent, so that $d \gg 1$. In particular, we investigate the case where d
 364 is much larger than the other parameters in the system. Within this limit, we find that
 365 different regimes arise for quantifiably different values of the remaining dimensionless
 366 parameters.

367 As we are interested in the removal times t_f and t_e , defined in (20), we consider
 368 the regime where $s = O(d)$. The scalings for this long-time regime are

$$369 \quad (21) \quad t = d^2 T, \quad s = dS,$$

370 and hence $S \in [0, 1]$. The time scaling explains the magnitude of the y -axis in figure
 371 5, and means that figure 5 will be valid for general large d with a suitable scaling of
 372 the y -axis. Expanding in inverse powers of d and retaining only leading-order terms,
 373 the governing equations (12) become

$$374 \quad (22a) \quad c_{\xi\xi} + SS_T \xi c_{\xi} = S^2 c_T \quad \text{for } T > 0 \text{ and } \xi \in (0, 1),$$

$$375 \quad (22b) \quad D_p p_{\xi\xi} + SS_T \xi p_{\xi} = S^2 p_T \quad \text{for } T > 0 \text{ and } \xi \in (0, 1),$$

$$376 \quad (22c) \quad D_{\phi} \phi_{\eta\eta} + S_T (S - 1) \eta \phi_{\eta} = (S - 1)^2 \phi_T \quad \text{for } T > 0 \text{ and } \eta \in (0, 1).$$

378 Similarly, the leading-order boundary conditions from (14) become

$$379 \quad (23) \quad c(0, T) = \beta, \quad p(0, T) = 0, \quad \phi_{\eta}(0, T) = 0 \quad \text{for } T > 0,$$

381 and the leading-order interfacial conditions from (15) become

$$382 \quad (24a) \quad (1 - \phi)c = 0,$$

$$383 \quad (24b) \quad \frac{S - 1}{S} c_{\xi} - D_{\phi} \phi_{\eta} = (1 - S) S_T (c + 1 - \phi),$$

$$384 \quad (24c) \quad D_p p_{\xi} = S S_T (1 - p),$$

$$385 \quad (24d) \quad \mathcal{K} p = \phi,$$

387 where all functions are evaluated for $T > 0$ and at $\xi = 1$ or $\eta = 1$, as appropriate.
 388 The full leading-order system for long time is then given by (22)–(24).

389 We see that (24a) offers two possibilities for the behaviour of this system, where
 390 either $\phi = 1$ or $c = 0$ at the interface. Both scenarios are observed numerically,
 391 as illustrated in figures 3b and 4b. These distinct scenarios arise due to different
 392 rate-limiting mechanisms which we describe in §4.2 and §4.3. Once we have derived
 393 asymptotic solutions within each of these regimes, we show that they are associated
 394 with different parameter regimes. This analysis is described in §4.4, where we ad-
 395 ditionally develop an *a priori* classification based on the system parameters. From
 396 figures 3 and 4, it appears that $c = 0$ is associated with larger \mathcal{K} , and $\phi = 1$ is
 397 associated with smaller \mathcal{K} ; we formalise this observation in §4.4.

398 In the case where $\phi = 1$ at the interface, which we refer to as Regime I, agent in the
 399 oil phase is consumed as soon as it reaches the interface and hence the rate-limiting
 400 step is the removal of oily-phase product from the neighbourhood of the interface,
 401 which is in turn controlled by the transport and removal of aqueous product to/at
 402 the upper boundary. In this regime, we will also show that the vast majority of
 403 agent is removed before the interface reaches the lower boundary, resulting in t_e being
 404 significantly shorter than t_f . In the case where $c = 0$ on the reaction interface, which
 405 we refer to as Regime II, cleanser in the aqueous phase is consumed as soon as it
 406 reaches the interface and hence the rate-limiting step is the transport of cleanser to
 407 the interface. We now consider Regime I.

408 **4.2. Regime I: Decontamination limited by product removal.** In this
 409 section, we consider the regime where $\phi = 1$ at the oil-water interface. We see from
 410 figure 3 that this case can lead to $\phi \approx 1$ throughout the oil phase before the interface

reaches the lower boundary, and thus can result in an effective removal time, t_e , that is significantly less than the final time, t_f . We therefore expect this regime to explain the disparity between t_e and t_f in figure 5.

In Regime I, the relevant interfacial conditions from (24) are

$$(25a) \quad \phi = 1,$$

$$(25b) \quad \frac{S-1}{S}c_\xi - D_\phi\phi_\eta = (1-S)S_Tc,$$

$$(25c) \quad D_p p_\xi = SS_T(1-p),$$

$$(25d) \quad p = 1/\mathcal{K}.$$

The leading-order system in this regime is thus given by (22), (23), and (25).

As the interfacial conditions (25c,d) only involve the dependent variables p and S , we can solve for these variables independently of c and ϕ , and hence the system decouples. Moreover, as p now satisfies a Dirichlet condition on the interface, p exhibits similar behaviour to the classic Stefan problem [3, 7]. Solving the system given by (22b), (23b), and (25c,d), we obtain

$$(26) \quad p(\xi) = \frac{\operatorname{erf} \lambda_p \xi}{\mathcal{K} \operatorname{erf} \lambda_p}, \quad S(T) = 2\lambda T^{1/2}.$$

Here, $\operatorname{erf}(z)$ is the error function, $\lambda_p = \lambda/D_p^{1/2}$, and λ_p satisfies the transcendental equation

$$(27) \quad \mathcal{K} = 1 + \frac{e^{-\lambda_p^2}}{\lambda_p \sqrt{\pi} \operatorname{erf} \lambda_p}.$$

We note that (27) only has solutions when $\mathcal{K} > 1$; we discuss this in more detail in §4.4. Inserting scaling (26) into definition (20b), we deduce that, in this regime, the final time

$$(28) \quad \frac{t_f}{d^2} = \frac{1}{4\lambda^2} + O(1/d) \quad \text{as } d \rightarrow \infty,$$

where λ is defined in (27). We note that the only dimensionless parameters that affect t_f are \mathcal{K} and D_p , so of the three diffusion processes occurring in the system the diffusion of product in aqueous solution is the most important.

Our task is now to solve for the remaining variables, c and ϕ . Using (26), the system decouples further, and we can first solve for ϕ from (22c), (23c), and (25a), then solve for c from (22a), (23a), and (25b). To solve this reduced system, we must obtain effective initial conditions, and this is carried out in a similar manner to the analysis in §3.1. That is, we now look for a small-time solution to the reduced problem, and we refer to this as the *intermediate-time* solution.

As $T \rightarrow 0^+$, we make the formal scalings $T = \delta \tilde{T}$ and $\eta = 1 - \delta^{1/2} \tilde{X}$, where $\delta \ll 1$ is an arbitrary small parameter. We look for solutions where $c = c(\xi)$ and $\phi = \phi(\tilde{X}, \tilde{T})$ in the system (22), (23), and (25), essentially seeking the long-time solution to the problem with an infinite lower domain. At leading order in δ , the governing equations (22a,c) are

$$(29a) \quad c_{\xi\xi} + 2\lambda^2 \xi c_\xi = 0 \quad \text{for } \xi \in (0, 1),$$

$$(29b) \quad D_\phi \phi_{\tilde{X}\tilde{X}} + \frac{\lambda}{\tilde{T}^{1/2}} \phi_{\tilde{X}} = \phi_{\tilde{T}} \quad \text{for } \tilde{X} > 0 \text{ and } \tilde{T} > 0;$$

453

454 the fixed boundary condition (23a) is

$$455 \quad (30) \quad c(0) = \beta;$$

457 and the interfacial conditions (25a,b) are

$$458 \quad (31a) \quad \phi(0, \tilde{T}) = 1,$$

$$459 \quad (31b) \quad c_\xi(1) + 2\lambda^2 c(1) = 2\lambda D_\phi \tilde{T}^{1/2} \phi_{\tilde{X}}(0, \tilde{T}).$$

461 Finally, the matching condition for ϕ is

$$462 \quad (32) \quad \phi \rightarrow 0 \quad \text{as } \tilde{X} \rightarrow \infty.$$

464 The system (29)–(32) is solved by

$$465 \quad (33a) \quad c \sim \beta - D_\phi \left(\frac{\beta \lambda_\phi \operatorname{erfc} \lambda_\phi + e^{-\lambda_\phi^2/\sqrt{\pi}}}{\lambda \operatorname{erf} \lambda + e^{-\lambda^2/\sqrt{\pi}}} \right) \frac{\operatorname{erf}(\lambda \xi)}{\operatorname{erfc} \lambda_\phi},$$

$$466 \quad (33b) \quad \phi \sim \frac{\operatorname{erfc}((1-\eta)/\sqrt{4D_\phi \tilde{T}} + \lambda_\phi)}{\operatorname{erfc} \lambda_\phi},$$

468 where $\lambda_\phi = \lambda/D_\phi^{1/2}$ and we have re-written the solution for ϕ in terms of η and T . We
 469 note that the long-time solutions to the modified problem with a semi-infinite lower
 470 domain in Regime I are given by (26) and (33), where λ is the solution to (27).

471 Thus, in Regime I, we have reduced the task of fully understanding our system
 472 to numerically solving the system (22a,c), (23a,c), and (25a,b) using initial conditions
 473 (33). We use the method of lines as described in §3.2, but now with a uniform
 474 mesh in both domains. This reduced model gives excellent agreement with the full
 475 problem (12)–(15) (see figure 6), and demonstrates that, in this regime, the important
 476 dimensionless parameters are \mathcal{K} , D_p , and D_ϕ .

477 **4.3. Regime II: Decontamination limited by supply of cleanser.** In the
 478 regime where $c = 0$ at $\xi = 1$, the long-time behaviour is limited by the supply of
 479 cleanser to the interface. In this regime, the interfacial conditions (24) become

$$480 \quad (34a) \quad c = 0,$$

$$481 \quad (34b) \quad \frac{S-1}{S} c_\xi - D_\phi \phi_\eta = (1-S) S_T (1-\phi),$$

$$482 \quad (34c) \quad D_p p_\xi = S S_T (1-p),$$

$$483 \quad (34d) \quad \mathcal{K} p = \phi.$$

485 The leading-order system for Regime II is given by (22), (23), and (34). To
 486 solve this system numerically, we must also calculate appropriate ‘initial’ conditions
 487 as $T \rightarrow 0^+$. Thus, just as we did with Regime I, we now look for a small-time solution
 488 to the reduced problem in Regime II, which we again refer to as the intermediate-time
 489 solution. The scalings are the same in this regime, and we seek solutions using the
 490 formal scalings $T = \delta \tilde{T}$, $\eta = 1 - \delta^{1/2} \tilde{X}$, and $S = 2\lambda(\delta \tilde{T})^{1/2}$, where $\delta \ll 1$ is an
 491 arbitrary small parameter, and λ is a constant which must be determined as part of
 492 the solution. We note that the interfacial position again scales with the square root of
 493 time in this intermediate-time solution, a scaling often seen in Stefan-type problems

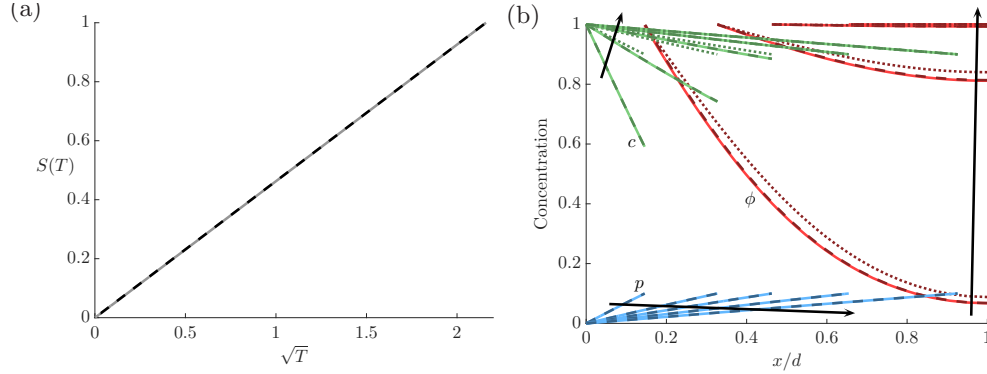


FIG. 6. (Colour online) Comparison of numerical solutions to the full problem (12)–(15) (solid lines) and the large d problem (22a,c), (23a,c), (25a,b), (26) and (27) (dashed lines) in Regime I, for $\beta = D_\phi = D_p = 1$, $\mathcal{K} = 10$, and $d = 10^3$. (a) The position of the moving boundary. (b) The concentrations of the cleanser, c (green), product in aqueous phase, p (blue), and product in oily phase, ϕ (red), at (non-uniform) times $t = 1 \times 10^5, 5 \times 10^5, 1 \times 10^6, 2 \times 10^6, 4 \times 10^6$, with arrows denoting increasing time. The dotted lines show asymptotic solutions c (green dotted) and ϕ (red dotted) in the large K limit, defined in (48) and (45), respectively.

494 [3, 7]. However, we shall see that the square-root scaling does not hold throughout
 495 this regime.

496 We look for solutions where $c = c(\xi)$, $p = p(\xi)$, and $\phi = \phi(\tilde{X}, \tilde{T})$ in the system
 497 (22), (23), and (34). At leading order in δ , the governing equations (22) are

498 (35a)
$$c_{\xi\xi} + 2\lambda^2 \xi c_\xi = 0,$$

499 (35b)
$$D_p p_{\xi\xi} + 2\lambda^2 \xi p_\xi = 0,$$

501 for $\xi \in (0, 1)$, and

502 (35c)
$$D_\phi \phi_{\tilde{X}\tilde{X}} + \frac{\lambda}{\tilde{T}^{1/2}} \phi_{\tilde{X}} = \phi_{\tilde{T}},$$

504 for $\tilde{X} > 0$ and $\tilde{T} > 0$; the fixed boundary conditions (23) are

505 (36)
$$c(0) = \beta, \quad p(0) = 0;$$

507 and the interfacial conditions (34) are

508 (37a)
$$c(1) = 0,$$

509 (37b)
$$2\lambda\tilde{T}^{1/2} D_\phi \phi_{\tilde{X}}(0, \tilde{T}) = c_\xi(1) + 2\lambda^2 (1 - \phi(0, \tilde{T})),$$

510 (37c)
$$D_p p_\xi(1) = 2\lambda^2 (1 - p(1)),$$

511 (37d)
$$\mathcal{K}p(1) = \phi(0, \tilde{T}).$$

513 Finally, the matching condition for ϕ is

514 (38)
$$\phi \rightarrow 0 \quad \text{as } \tilde{X} \rightarrow \infty.$$

516 The system (35)–(38) is solved by

517 (39a)
$$c(\xi) = \beta \left(1 - \frac{\text{erf}(\lambda\xi)}{\text{erf}\lambda} \right),$$

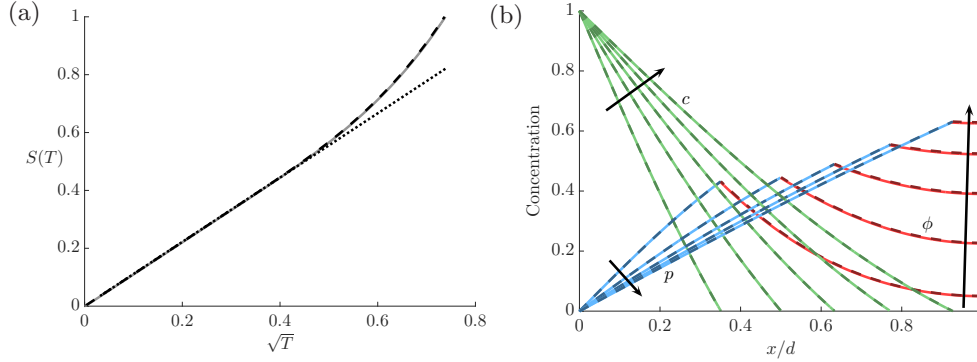


FIG. 7. (Colour online) Comparison of numerical solutions to the full problem (12)–(15) (solid lines) and the large d problem defined by (22), (23), (34), (39), (40) (dashed) in Regime II, for $\beta = D_\phi = D_p = \mathcal{K} = 1$, and $d = 10^3$. (a) The position of the moving boundary. The dotted black line is $s = 2\lambda t^{1/2}$, where λ is obtained from the solution to the transcendental equation (40). (b) The concentrations of cleanser, c (green), product in aqueous phase, p (blue), and product in oily phase, ϕ (red), at times $t = 1 \times 10^5, 2 \times 10^5, 3 \times 10^5, 4 \times 10^5, 5 \times 10^5$, with arrows denoting increasing time.

$$518 \quad (39b) \quad p(\xi) = \frac{\lambda_p \operatorname{erf}(\lambda_p \xi)}{\lambda_p \operatorname{erf} \lambda_p + e^{-\lambda_p^2/\sqrt{\pi}}},$$

$$519 \quad (39c) \quad \phi(\eta, T) = \frac{\mathcal{K} \lambda_p \operatorname{erf} \lambda_p \operatorname{erfc}((1 - \eta)/\sqrt{4D_\phi T} + \lambda_\phi)}{(\lambda_p \operatorname{erf} \lambda_p + e^{-\lambda_p^2/\sqrt{\pi}}) \operatorname{erfc} \lambda_\phi},$$

520
521 recalling that $\lambda_p = \lambda/D_p^{1/2}$ and $\lambda_\phi = \lambda/D_\phi^{1/2}$, and where λ satisfies the transcendental
522 equation

$$523 \quad (40) \quad \lambda_\phi - \frac{\beta e^{-\lambda^2}}{\sqrt{\pi D_\phi} \operatorname{erf} \lambda} = \mathcal{K} \left(\lambda_\phi - \frac{e^{-\lambda_\phi^2}}{\sqrt{\pi} \operatorname{erfc} \lambda_\phi} \right) \frac{\lambda_p \operatorname{erf}(\lambda_p)}{\lambda_p \operatorname{erf} \lambda_p + e^{-\lambda_p^2/\sqrt{\pi}}}.$$

525 We note that the long-time solutions to the modified problem with a semi-infinite
526 lower domain in Regime II are given by (39) with $S = 2\lambda T^{1/2}$, where λ is the solution
527 to (40).

528 Thus, in Regime II, we have reduced the task of fully understanding our system
529 to numerically solving the system (22), (23), and (34) using initial conditions (39)–
530 (40). We use the method of lines with a uniform mesh in both domains. We see
531 that these numerical solutions to the reduced problem (dashed lines) show superb
532 agreement with the solutions to the full problem (solid lines) in figure 7. Moreover,
533 the intermediate-time square root solution to the interfacial position (dotted line in
534 figure 7a) also provides excellent agreement until the lower boundary starts to affect
535 the system.

536 Although we have derived reduced systems for Regimes I and II in §4.2 and §4.3,
537 it is not yet apparent which regime holds for a given set of parameter values. In the
538 next section, we use the results we have derived from our reduced systems to *a priori*
539 classify the two regimes analytically, in terms of the system parameters.

540 **4.4. Classifying the long-time regime from parameter values.** As de-
541 scribed in §4.2 and §4.3, we find that the position of the moving interface can be
542 approximated by $S = 2\lambda T^{1/2}$ throughout Regime I and for early time in Regime II.

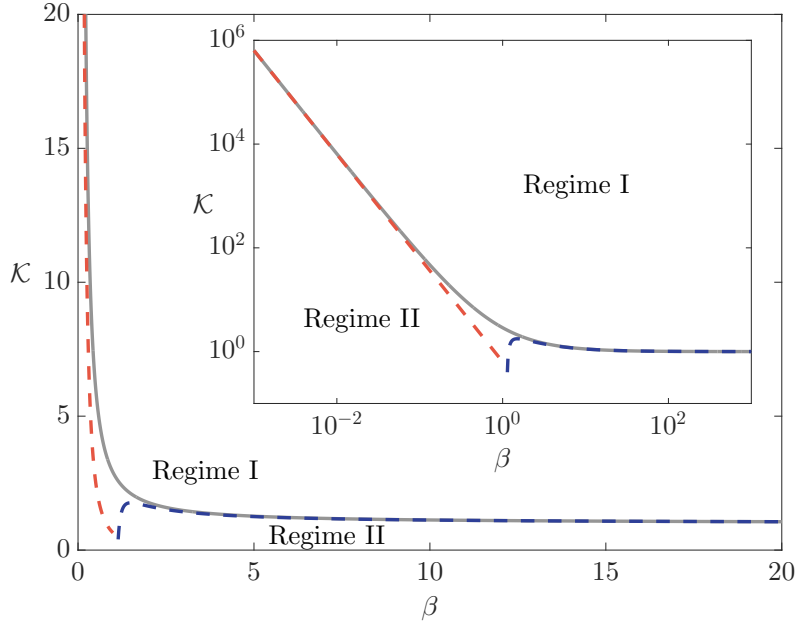


FIG. 8. (Colour online) The critical line described by (27) and (41) in a linear (main) and a log-log plot (inset). The solid grey lines are the numerically determined critical lines, the dashed red lines are from the small β /large \mathcal{K} asymptotics (42a), and the dashed blue lines are from the large β /small $(\mathcal{K} - 1)$ asymptotics given in (42b). We use $D_\phi = D_p = 1$ for both figures.

543 In each case, λ is the solution to a transcendental equation, given by (27) for Regime
 544 I and (40) for Regime II. The critical line in parameter space associated with the
 545 boundary between Regime I and Regime II occurs when both transcendental equa-
 546 tions are satisfied. Thus, re-writing (40) using (27) for simplicity, the critical line
 547 occurs when

$$548 \quad (41) \quad \frac{e^{-\lambda_p^2}}{\lambda_p \sqrt{\pi} \operatorname{erf} \lambda_p} = \mathcal{K} - 1 \quad \text{and} \quad \frac{\beta e^{-\lambda^2}}{\sqrt{D_\phi} \operatorname{erf} \lambda} = \frac{e^{-\lambda_\phi^2}}{\operatorname{erfc} \lambda_\phi},$$

550 are both satisfied, recalling that $\lambda_p = \lambda/D_p^{1/2}$ and $\lambda_\phi = \lambda/D_\phi^{1/2}$. This critical line
 551 may be obtained numerically using a standard root-finding method and we note that
 552 the critical line exists for all positive values of β , D_ϕ , and D_p , but is only defined for
 553 $\mathcal{K} > 1$. In (β, \mathcal{K}) -parameter space, $\mathcal{K} \rightarrow \infty$ as $\beta \rightarrow 0$, and \mathcal{K} monotonically decreases
 554 as β increases, with $\mathcal{K} \rightarrow 1^+$ as $\beta \rightarrow \infty$ (figure 8). Regime I occurs above the critical
 555 line in figure 8, and Regime II occurs below.

556 Finally, in the asymptotic limits of small and large β , we may simplify (41) to
 557 obtain

$$558 \quad (42a) \quad \mathcal{K} = \frac{2D_p D_\phi}{\pi \beta^2} + O(\beta^{-1}) \quad \text{for } \beta \ll 1,$$

$$559 \quad (42b) \quad \mathcal{K} \sim 1 + \frac{\left(D_p (\pi \log \beta)^{1/D_p - 1}\right)^{1/2}}{\beta^{1/D_p}} \left(1 + \frac{\log(\pi \log \beta)}{4 \log \beta}\right) \quad \text{for } \beta \gg 1,$$

561 and we see that these asymptotic approximations show excellent agreement with the
 562 numerical solutions to (41) in their respective limits (figure 8).

563 Now that we have classified each regime based on the system parameter values,
 564 we can explain when and why the final and effective removal times diverge. As \mathcal{K}
 565 increases, more of the product created at the interface goes into the lower oily phase
 566 compared to the upper aqueous phase. This dilutes the oily phase near the interface,
 567 creating a larger concentration gradient in the oily phase which pushes more agent
 568 towards the interface. Thus, significantly more agent is consumed at the interface, so
 569 that the proportion of agent remaining in the system drops close to zero before the
 570 interface is near the lower boundary.

571 For a given β , we can now associate Regime I with larger \mathcal{K} , and Regime II with
 572 smaller \mathcal{K} . We now present some asymptotic results for large and small \mathcal{K} .

573 **4.4.1. Large \mathcal{K} results for Regime I.** We now use asymptotic methods to
 574 approximate t_f and t_e in the limit of large \mathcal{K} in Regime I. In this limit, we can solve
 575 (27) to obtain an asymptotic result for λ , the coefficient governing the interfacial
 576 velocity, as follows

$$577 \quad (43) \quad \lambda = \sqrt{\frac{D_p}{2\mathcal{K}}} \left(1 + \frac{1}{3\mathcal{K}} + O(\mathcal{K}^{-2}) \right) \quad \text{as } \mathcal{K} \rightarrow \infty,$$

579 and thus we see that the interfacial velocity is slower when \mathcal{K} is large, and the leading-
 580 order velocity is inversely proportional to the square root of \mathcal{K} . Combining (28) and
 581 (43), we further deduce that

$$582 \quad (44) \quad \frac{t_f}{d^2} \sim \frac{1}{2D_p} \left(\mathcal{K} - \frac{2}{3} \right) \quad \text{for } \mathcal{K} \rightarrow \infty, d \rightarrow \infty,$$

584 and thus we see that the time taken for the interface to reach the lower boundary
 585 scales with \mathcal{K} in this limit.¹ The large \mathcal{K} asymptotic results for t_f in figure 9 (green
 586 line) show excellent agreement with the numerical solutions (black addition signs),
 587 even for lower values of \mathcal{K} .

588 Moreover, using the slow interfacial velocity result, we can also obtain an asymp-
 589 totic solution for ϕ when $\mathcal{K} \rightarrow \infty$, and hence for t_e . In this limit, the leading-order
 590 equation for ϕ becomes

$$591 \quad (45a) \quad D_\phi \phi_{\eta\eta} = \left(2\lambda T^{1/2} - 1 \right)^2 \phi_T,$$

592 valid when $0 < T < 1/(4\lambda^2)$, noting that λ is given by (43), and subject to the initial
 593 and boundary conditions

$$594 \quad (45b) \quad \phi(\eta, 0) = 0 \quad \phi_\eta(0, T) = 0 \quad \phi(1, T) = 1.$$

596 The system (45) is solved by

$$597 \quad (46) \quad \phi = 1 - \sum_{n=0}^{\infty} \frac{2(-1)^n}{w_n} \exp \left\{ -\frac{w_n^2 D_\phi}{2\lambda^2} \left[\frac{2\lambda T^{1/2}}{1 - 2\lambda T^{1/2}} + \log \left(1 - 2\lambda T^{1/2} \right) \right] \right\} \cos w_n \eta,$$

599 where $w_n = \pi(2n + 1)/2$.² We see that (46), the asymptotic solution for ϕ , shows
 600 good agreement with the full numerical solution (figure 6).

¹We could also have obtained (43) and (44) by directly considering the limit $\mathcal{K} \rightarrow \infty$ in (25).

²We note that the system (45) and solution (46) could also have been derived by investi-
 gating the asymptotic region where $T = O(1/\lambda^2)$ and looking for a solution of the form $\phi =$
 $1 + \exp(-g(\lambda^2 T)/\lambda^2) f(\eta)$.

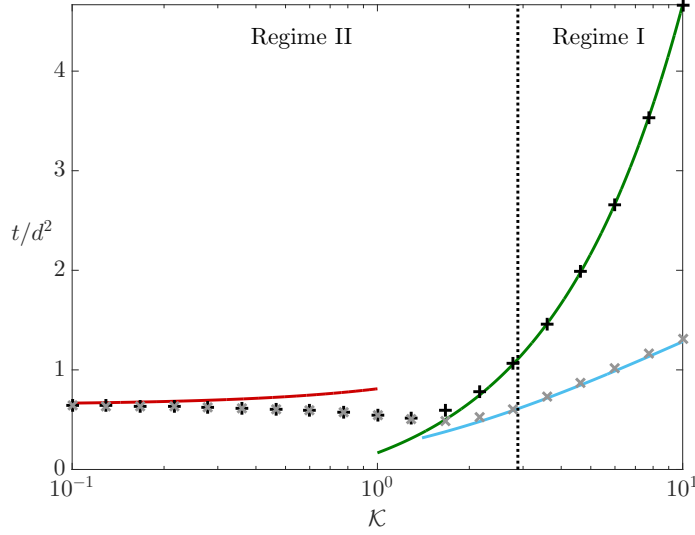


FIG. 9. (Colour online) The scaled final time t_f/d^2 and effective removal time t_e/d^2 as functions of \mathcal{K} for $\beta = D_\phi = D_p = 1$ and $d = 10^3$. The black addition signs are the numerically determined final times and the grey multiplication signs are the numerically determined effective removal times, both from the full problem defined in (12)–(15). For large \mathcal{K} , we plot asymptotic approximations of t_f/d^2 (green) and t_e/d^2 (blue), from (44) and (47), respectively. For small \mathcal{K} , the final and effective removal times coincide, and we approximate both with the red line using (28). The vertical black dotted line at $\mathcal{K} = 2.885$ denotes the position of the critical line between regimes, defined by (41).

601 The asymptotic solution (46) allows us to approximate t_e . From (20c) and (46),
 602 we see that t_e can be approximated by $t_e \sim d^2 T^*$, where T^* is a solution to $F(T^*) = \varepsilon$
 603 and $F(T)$ is defined by

(47)

$$604 \quad F(T) = \left(1 - 2\lambda T^{1/2}\right) \sum_{n=0}^{\infty} \frac{2}{w_n^2} \exp \left\{ -\frac{w_n^2 D_\phi}{2\lambda^2} \left[\frac{2\lambda T^{1/2}}{1 - 2\lambda T^{1/2}} + \log \left(1 - 2\lambda T^{1/2}\right) \right] \right\}.$$

605

606 Furthermore, as $\lambda = O(1/\sqrt{\mathcal{K}})$ is small in this limit, we can approximate $F(T)$ by the
 607 first term of the infinite sum in (47). Making all of these simplifications, estimating
 608 t_e reduces to the problem of numerically solving a transcendental equation. We see
 609 excellent agreement between the asymptotic approximation of t_e (blue line) and the
 610 full numerical results (grey multiplication signs), again even for only moderately large
 611 values of \mathcal{K} (figure 9).

612 We note that the interfacial condition (25b) is greatly simplified in this limit, if
 613 $\phi \approx 1$. In this scenario $c = c(\xi)$, and

$$614 \quad (48) \quad c(\xi) = \beta \left(1 - \frac{\lambda \operatorname{erf} \lambda \xi}{\lambda \operatorname{erf} \lambda + e^{-\lambda^2}/\sqrt{\pi}} \right),$$

615

616 towards the end of the decontamination in Regime I. In figure 6, we confirm that (48)
 617 only shows good agreement with the full numerical solution when $\phi \approx 1$.

618 Finally, our large \mathcal{K} analysis shows that t_e and t_f are independent of β in this
 619 regime. This is because the cleanser dynamics are not important in this regime; the
 620 important mechanism is product removal from the oily phase. In general, a large D_ϕ

621 results in quicker transport of agent to the interface, with the effect of decreasing t_e ,
 622 the effective removal time, and a large D_p results in quicker transport of product in
 623 the aqueous phase to the upper boundary, with the effect of decreasing t_f , the final
 624 time. We note that there is another distinguished asymptotic limit of this system
 625 when D_p is as large as d , but the analysis of this limit is beyond the scope of this
 626 paper.

627 **4.4.2. Small \mathcal{K} results for Regime II.** In contrast to Regime I, the final time
 628 and effective removal times almost coincide in Regime II (figures 5 and 9). Naively,
 629 one might hypothesise that the interfacial velocity $S = 2\lambda T^{1/2}$, with λ defined in (40)
 630 for the intermediate-time system, would be a good approximation of the interfacial
 631 velocity throughout the process. However, our numerical solutions show that this
 632 only gives a good estimate for the removal time in the limit $\mathcal{K} \rightarrow 0$ (red line in
 633 figure 9); the discrepancy between (39c) and (23c), the boundary condition at $\eta = 0$,
 634 when $1 - \eta = O(T^{\frac{1}{2}})$ is not small means that the intermediate-time system cannot
 635 generally be used to estimate removal time.

636 In light of this, and having briefly discussed the limit $\mathcal{K} \rightarrow 0$ at the end of §2.2,
 637 we now consider this limit in more detail. Our aim is to explain the accuracy of the
 638 removal time naively estimated by the intermediate-time solution when $\mathcal{K} \rightarrow 0$. In
 639 this limit, we find that $\phi = O(\mathcal{K})$, and hence the long-time interfacial conditions (24)
 640 become, to leading order in \mathcal{K} ,

$$641 \quad (49a) \quad c = 0,$$

$$642 \quad (49b) \quad c_\xi + SS_T = 0,$$

$$643 \quad (49c) \quad D_p p_\xi = SS_T(1 - p),$$

$$644 \quad (49d) \quad \mathcal{K}p = \phi,$$

646 for $\xi, \eta = 1$ with $T > 0$. Hence, the system decouples for c and S , which are now
 647 governed by the classical Stefan problem with interfacial conditions (49a,b); in this
 648 simplified system, β acts as the inverse Stefan number [3, 7]. Thus, the solutions for c
 649 and p in this limit are the same as for the intermediate-time problem, given by (39a)
 650 and (39b), with $S = 2\lambda T^{1/2}$, where λ satisfies the transcendental equation

$$651 \quad (50) \quad \lambda = \frac{\beta \exp(-\lambda^2)}{\sqrt{\pi} \operatorname{erf} \lambda}.$$

653 Although ϕ must be solved using the full equation (22c) with the interfacial condition
 654 (49d), the small \mathcal{K} result for the interfacial velocity over the long timescale, which we
 655 present above, agrees with the intermediate-time result for the interfacial velocity for
 656 small \mathcal{K} , presented in §4.3. This can be seen from the agreement between the small
 657 \mathcal{K} limit in (40) and (50). Thus, we have shown that the intermediate-time interfacial
 658 velocity becomes valid for all time in the limit of small \mathcal{K} , explaining why the naive
 659 intermediate-time result for the removal time becomes accurate in the same limit.

660 5. Discussion and conclusions.

661 **5.1. Dimensional results.** The asymptotic results in §4 are all obtained by
 662 considering a ‘deep’ spill of agent; that is, we assume throughout that $d := \bar{L}k/\bar{D}_c$
 663 is large. We find that this leads to two different regimes, one where the rate of
 664 decontamination is limited by the removal of product from the system (Regime I,
 665 described in §4.2), and another where the rate of decontamination is limited by the
 666 supply of cleanser to the interface between the phases (Regime II, described in §4.3).

667 Our asymptotic results are stated in terms of the dimensionless model developed
 668 in §2.3, but it is also valuable to examine them in dimensional form. We find that
 669 the leading order results for the dimensional removal time often depend on only some
 670 of the eight dimensional parameters introduced in §2.1 and §2.2 (\bar{L} , \bar{D}_c , \bar{D}_p , \bar{D}_ϕ ,
 671 \bar{c}_0 , \bar{V}_m , \bar{k} , and \mathcal{K}). Information about which dimensional parameters appear in the
 672 leading order expression for the removal time has the potential to be particularly
 673 valuable to experimental researchers, since it indicates the parameters that have the
 674 most influence on the time taken to remove a harmful agent.

675 In Regime I, reversing the nondimensionalisation of (28) gives the result that the
 676 dimensional time to complete removal, \bar{t}_f [s], is given to leading order by

$$677 \quad (51) \quad \bar{t}_f \sim \frac{\bar{L}^2}{4\bar{D}_p\lambda_p(\mathcal{K})},$$

678 where $\lambda_p(\mathcal{K})$ is implicitly defined by (27). Hence, if $d = \bar{L}\bar{k}/\bar{D}_c$ is large and we satisfy
 679 the conditions in §4.4 in order to be in Regime I, the leading order time to complete
 680 removal depends only on \bar{L} , \bar{D}_p , and \mathcal{K} .

681 Following the analysis that leads to (44), we further simplify this to obtain

$$682 \quad (52) \quad \bar{t}_f \sim \frac{\bar{L}^2}{2\bar{D}_p}\mathcal{K} - \frac{\bar{L}^2}{3\bar{D}_p}$$

683 as long as \mathcal{K} and $\bar{L}\bar{k}/\bar{D}_c$ are both large.

684 In Regime I, we recall from figures 5 and 9 that the effective removal time, t_e ,
 685 may be very different from the final time, t_f , and that t_e may be a better measure of
 686 the decontamination time than t_f . Starting from (47) and reversing the nondimen-
 687 sionalisation, we find that the dimensional effective removal time, \bar{t}_e [s], is given to
 688 leading order in large $\bar{L}\bar{k}/\bar{D}_c$ and large \mathcal{K} by

$$689 \quad (53) \quad \bar{t}_e \sim \frac{\bar{L}^2}{4\bar{D}_p\lambda_p(\mathcal{K})} \tau \left[\frac{\bar{D}_\phi}{\bar{D}_p\lambda_p(\mathcal{K})^2} \right],$$

690 where $\tau(R)$ is implicitly defined by

$$691 \quad (54) \quad \varepsilon = \frac{8(1 - \tau^{1/2})}{\pi^2} \exp \left\{ -\frac{\pi^2 R}{8} \left[\frac{\tau^{1/2}}{1 - \tau^{1/2}} + \log(1 - \tau^{1/2}) \right] \right\},$$

692 where ε is the threshold introduced in (20c), and $\lambda_p(\mathcal{K})$ is implicitly defined by (27) as
 693 before. The dimensional effective removal time is therefore (to leading order) a func-
 694 tion of \bar{L} , \bar{D}_p , \bar{D}_ϕ and \mathcal{K} only. This further illustrates the fact that, in Regime I, the
 695 removal of the agent is relatively insensitive to the cleanser dynamics. In particular,
 696 increasing the cleanser concentration, \bar{c}_0 , or using a cleanser with a higher diffusivity,
 697 \bar{D}_c , has very little effect on the agent removal time, provided the parameters already
 698 satisfy the conditions to be in Regime I.

699 In Regime II, we expect the cleanser dynamics to be more important, since the
 700 rate-limiting process is the supply of cleanser to the interface between the phases.
 701 While Regime II is more complicated than Regime I, we again find that the leading-
 702 order dimensional removal time is independent of some model parameters. We recall
 703 that we are able to obtain an ‘intermediate time’ solution in Regime II because (after
 704 an initial transient) the solution is insensitive to the initial conditions imposed. By

705 inspection of (22), (23), and (34), we note that the intermediate time problem is inde-
 706 pendent of $d = \bar{L}\bar{k}/\bar{D}_c$. Hence, by reversing the nondimensionalisation and applying
 707 the long time scaling from (21), we see that the dimensional removal time must take
 708 the form

$$709 \quad (55) \quad \bar{t}_f \sim \frac{\bar{L}^2}{\bar{D}_c} f \left[\bar{c}_0 \bar{V}_m, \frac{\bar{D}_p}{\bar{D}_c}, \frac{\bar{D}_\phi}{\bar{D}_c}, \mathcal{K} \right],$$

710 where f is some function. Thus, \bar{t}_f must be independent of \bar{k} to leading order; even in
 711 Regime II, changing the reaction rate constant has only a small effect on the removal
 712 time. Furthermore, when \mathcal{K} is small, we find that

$$713 \quad (56) \quad \bar{t}_f \sim \frac{\bar{L}^2}{4\bar{D}_c\lambda(\bar{c}_0\bar{V}_m)},$$

714 where $\lambda(\beta)$ is defined implicitly by (50). Hence, for sufficiently small \mathcal{K} we find that,
 715 to leading order, \bar{t}_f depends only on \bar{L} , \bar{D}_c , \bar{c}_0 and \bar{V}_m ; apart from the dependence
 716 on \bar{V}_m , the removal time is completely independent of the properties of the agent and
 717 the reaction product.

718 **5.2. The desirable features of a cleanser.** In many cases, a range of differ-
 719 ent cleanser solutions could be used against the same agent [14, 19]. Choosing an
 720 appropriate cleanser depends on a number of factors (for example, the possibility of
 721 chemical reactions between the cleanser and the substrate), but one important factor
 722 is the speed with which the cleanser will eliminate an agent. This has been the focus
 723 of our analysis, our results can be used to indicate how properties such as the cleanser
 724 concentration, the cleanser potency (as measured by the effective rate constant), and
 725 the cleanser reaction mechanism affect the speed of decontamination. Some cleanser
 726 properties that one might expect to be important turn out to have only a minor effect
 727 on the speed of decontamination. This insight is valuable in highlighting how to focus
 728 efforts and resources when choosing a cleanser for a given task.

729 We find that the leading-order dimensional removal time does not depend on the
 730 cleanser concentration applied at the surface, \bar{c}_0 , in Regime I, but does depend on
 731 \bar{c}_0 in Regime II. If the reaction product is more soluble in water than oil (and hence
 732 $\mathcal{K} < 1$), the relevant parameter regime will always be Regime II and increasing \bar{c}_0 will
 733 always decrease the removal time (albeit with diminishing returns). Moreover, when
 734 $\mathcal{K} \rightarrow 0$ we can use (50) and (56) to obtain asymptotic results for the removal time as
 735 a function of \bar{c}_0 .

736 If the reaction product is more soluble in oil than water (and hence $\mathcal{K} > 1$),
 737 we observe from figure 8 that increasing \bar{c}_0 (and hence β) will lead to a transition
 738 from Regime II to Regime I. Hence, increasing the cleanser concentration will only
 739 cause significant decreases in removal time up to the point where removal of reaction
 740 product (and hence availability of agent at the reaction interface) supersedes cleanser
 741 availability as the rate-limiting step of decontamination. Thereafter, further increases
 742 in cleanser concentration will not lead to significant improvements in decontamination
 743 speed.

744 Our analysis also shows that the leading-order removal time is independent of the
 745 effective rate constant \bar{k} in both Regime I and Regime II. If \bar{k} is sufficiently small
 746 that the ‘deep spill of agent’ assumption is no longer valid, then the decontamination
 747 behaviour may change significantly. However, as long as $\bar{k} \gg \bar{D}_c/\bar{L}$, changing the
 748 reactivity of a cleanser will only yield a small change in removal time. This suggests

TABLE 1

Reaction products and typical parameters for three cleansers that can be used to neutralise sulfur mustard. We estimate the molar volume of sulfur mustard $\bar{V}_m = 1.2 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ by combining density [14] and molar mass information.

Cleanser	DS2	5% Bleach sol.	Ca(OH) ₂ sol.	Ref.
Product	Divinyl sulfide	Mustard sulfoxide	Thiodiglycol	[14, 17]
\bar{c}_0 (mol m ⁻³)	6.7×10^3	6.7×10^2	2.5×10^1	[14, 17]
$\beta = \bar{V}_m \bar{c}_0$	8	8×10^{-1}	3×10^{-2}	
\mathcal{K}	7.1	1.4×10^{-1}	1.7×10^{-1}	[14]

749 that replacing an effective cleanser with an even more potent cleanser (where the
750 reaction products are the same but the reaction is faster) will not significantly improve
751 decontamination speed.

752 In contrast, the decontamination time depends strongly on the partition coeffi-
753 cient of the reaction product, \mathcal{K} . If all other parameters are kept fixed, we find that
754 there is an optimal value of \mathcal{K} for which the removal time is minimised, as illustrated
755 in figures 5 and 9. However, since there are typically only two or three reaction path-
756 ways that can be used to neutralise a given agent [14, 21], there is only limited scope
757 for tuning \mathcal{K} to be close to the optimal value.

758 That said, our analysis shows that the removal time increases linearly with large
759 \mathcal{K} , while it approaches a constant as $\mathcal{K} \rightarrow 0$. This suggests that, as a rule of thumb,
760 a cleanser that leads to a reaction product that is exclusively (or almost exclusively)
761 soluble in the water phase will lead to faster decontamination than a cleanser that
762 leads to a reaction product that is exclusively (or almost exclusively) soluble in the
763 oil phase. While an intermediate value of \mathcal{K} may lead to still faster decontamination,
764 we expect that small \mathcal{K} will be preferable to large \mathcal{K} in many situations.

765 **5.3. Decontamination of sulfur mustard.** We now consider a specific exam-
766 ple, the decontamination of sulfur mustard. Three examples of cleansers that could
767 be used to neutralise sulfur mustard are Decontamination Solution 2 (DS2), a 5%
768 bleach solution, or a saturated calcium hydroxide solution [14, 17]. In each case, the
769 mechanism of decontamination is different, leading to different reaction products.

770 From experimental results for each cleanser, we can estimate the concentrations
771 of active ingredient (\bar{c}_0), the key product formed, and estimated oil-water partition
772 coefficients (\mathcal{K}) based on octanol–water partition coefficients given in [14], and we
773 state these values in table 1. However, it is more difficult to obtain data on relevant
774 diffusivities and effective reaction coefficients. It should also be noted that the mecha-
775 nisms of decontamination of sulfur mustard are far more complicated than the simple
776 bimolecular reaction we propose in this paper; despite this, we hope to gain valuable
777 insights into the dominant kinetics of decontamination using our model analysis.

778 For each of the three cleansers, we determine whether the decontamination reac-
779 tion takes place in Regime I or Regime II, making the assumption $D_p = D_\phi = 1$. We
780 find that the reaction is in Regime II for each cleanser, so that increasing cleanser
781 concentration speeds up decontamination. With DS2, however, the decontamination
782 reaction will be close to the boundary between Regime I and Regime II, and it is
783 possible that increases in cleanser concentration will be less effective. Since diethylen-
784 etriamine, the active ingredient in DS2, is highly reactive and corrosive, this might
785 even suggest that reducing the concentration of diethylenetriamine in DS2, and hence
786 increasing the amount of time that it could be applied before the substrate becomes

787 damaged, might be an effective strategy for improving the efficiency of decontamina-
788 tion.

789 **5.4. Conclusions.** In this paper, we have presented and analysed a model of
790 chemical decontamination that reveals how different features of a cleanser affect the
791 speed of decontamination. We consider a one-dimensional porous medium of finite
792 depth, fully saturated with a chemical agent. Initially, a cleanser in aqueous solution
793 is applied at the top of the porous medium. To the best of our knowledge, this
794 together with a study group report on preliminary work [6] are the first models of
795 reactive decontamination where the reacting species are in different fluid phases; our
796 model could therefore form the foundation for a range of future modelling work on
797 chemical decontamination and similar processes. We note that, since the medium is
798 fully saturated and the porous medium is inert, the system under consideration is a
799 diffusion problem with a reaction at the moving interface between the two fluid phases.
800 Future extensions of this work might include the effects of advection within each fluid
801 phase, using Darcy’s law. One could model the effect of scrubbing at the surface
802 by pressure-driven forcing of the cleanser solution through the porous medium, and
803 scenarios where the medium is only partially saturated, in which the fluid dynamics
804 could be modelled using Richards’ equation.

805 The problem under consideration here is a moving-boundary problem with some
806 similarities to the classical Stefan problem with kinetic undercooling, but we find that
807 the precise behaviour is markedly different in different parameter regimes. In the limit
808 where the initial agent layer is deep compared to diffusive lengthscales, we identify
809 two distinct parameter regimes in which the rate of decontamination is limited by
810 either the transport of cleanser or the transport of reaction product. In each case we
811 determine the long-time behaviour and hence removal time in this asymptotic limit.
812 Our asymptotic analysis shows that, to leading order, the time required to remove the
813 agent only depends on some of the model parameters. Importantly, we find that the
814 removal time is independent of the effective rate constant in all parameter regimes
815 considered here. This indicates that using a more potent cleanser (one where the rate
816 of reaction between cleanser and agent is faster) may not lead to significant improve-
817 ments in removal time. Moreover, we find that changing cleanser concentration only
818 affects the removal time in certain parameter regimes. In fact, the oil–water partition
819 coefficient of the reaction product appears to be more significant in determining the
820 time taken to remove the agent; for given values of the remaining system parameters,
821 this partition coefficient has an optimal value that minimises the removal time.

822 The work in this paper was motivated by the extreme difficulty of performing
823 experiments using live agents, due to safety and visualisation challenges. By contrast,
824 mathematical modelling allows for the exploration of many hypothetical scenarios.
825 It is our hope that the model and analysis presented in this paper will guide the
826 development and improvement of methods used by the chemical decontamination
827 community, and provide inspiration for further study of this topic.

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839

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