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Jelena Zaninović

`jelena.zaninovic@itwm.fraunhofer.de`

Fraunhofer Institute for Industrial Mathematics

Sebastian Osterroth

Fraunhofer Institute for Industrial Mathematics

Claudia Redenbach

Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau

Katja Schladitz

Fraunhofer Institute for Industrial Mathematics

Peter Visser

AkzoNobel (Netherlands)

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Stochastic geometry models for inhibitor particles in active-reactive coatings and their impact on leaching simulations on the micro-scale

Jelena Zaninović^{1,2*}, Sebastian Osterroth², Claudia Redenbach¹,
Katja Schladitz², Peter Visser³

¹Department of Mathematics, Rheinland-Pfälzische Technische
Universität Kaiserslautern-Landau (RPTU), Gottlieb-Daimler-Straße
48, Kaiserslautern, 67663, Germany.

²Division Processes and Materials, Fraunhofer-Institut für Techno- und
Wirtschaftsmathematik, Fraunhofer-Platz 1, Kaiserslautern, 67663,
Germany.

³AkzoNobel, Rijksstraatweg 31, 2171 AJ Sassenheim, The Netherlands.

*Corresponding author(s). E-mail(s):

jelena.zaninovic@itwm.fraunhofer.de;

Contributing authors: sebastian.osterroth@itwm.fraunhofer.de;
claudia.redenbach@rptu.de; katja.schladitz@itwm.fraunhofer.de;
peter.visser@akzonobel.com;

Abstract

Active-reactive coatings are indispensable in protecting metal appliances in maritime and aerospace applications. Safety standards in aerospace industry require extensive testing before introducing new chemical formulations. These are however needed to replace toxic ones. Virtual design of new formulations is challenging as leaching on the micro-structural scale is not yet fully understood. Recently, the formation of an interconnected pore system allowing for ion transport could be directly observed for the first time. Here, we report on the first attempt to simulate this phenomenon numerically within realizations of stochastic geometry models fitted to the observed model coating samples.

Keywords: nano computed tomography, Gibbs Laguerre tessellations, random sequential adsorption

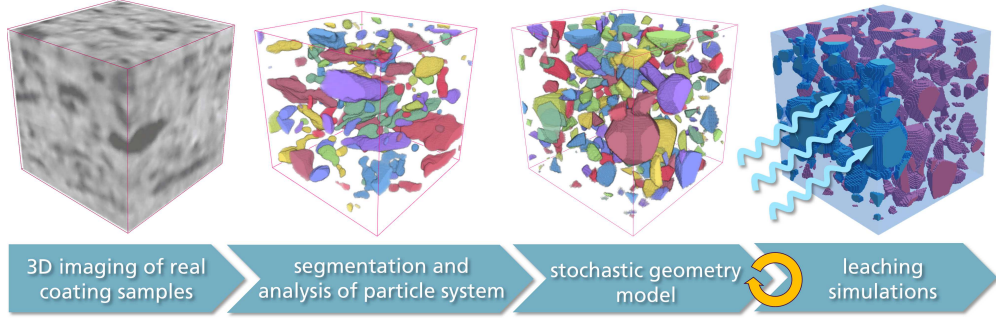


Fig. 1: A schematic of our modelling approach. First, we image model coating samples – non-destructively and 3D. Second, we segment the inhibitor particles in the resulting volume images and extract morphological characteristics. Third, a stochastic geometry model is fitted to these characteristics, generating synthetic coatings. Finally, leaching is numerically simulated within these synthetic coatings. Based on the simulation result, the stochastic geometry model can be altered until the target behavior is reached.

1 Introduction

Active-reactive coatings are a commonly applied means to counteract the ubiquitous corrosion of metallic appliances. The idea is to "pacify" surface defects by ions set free from salt particles by exactly the substance causing the corrosion, in most applications water. These salt particles, called inhibitors, are mixed in a sophisticated way to ensure the right amount of ions being transported to the defect region in the needed time. The inhibitors are accompanied by a dozen of other particle types guaranteeing processability and longevity of the coating. Traditionally, hexavalent chromium salts have been used as main inhibitors in active-reactive coatings. Alternatives are needed, as these are toxic [1]. However, the search for new formulations for active-reactive coatings is tedious, as it is still mainly driven by expert's intuition. This is because a systematic exploration of all possibilities is prohibitive due to the number of parameters that can be varied.

The VIPCOAT project, funded by the European Union within the Horizon 2020 program, aimed at providing corrosion scientists tools for accelerating the development of new active-reactive coatings in many ways: By training machine learning models to predict promising candidates [2, 3] based on electrochemical data of inhibitor candidates [4], by predicting the leaching on the meso-scale by FEM simulations [5, 6] or by a surrogate model [7].

We follow the idea of (micro-)structure optimization based on stochastic geometry modelling as publicized e.g. in [8–14]. That is, we observe the micro-structure of active-reactive coatings, capture its main geometric features by a stochastic geometry model, and numerically simulate the process of dissolution of the inhibitor particles and transport of the ions to the defect region – the leaching process. Figure 1 summarizes the main idea of micro-structural optimization for active-reactive coatings in a scheme. Completing this program would allow to first design new coating formulations and

to evaluate and optimize their leaching behavior virtually. Only promising candidates identified that way would later be produced and costly experimentally tested.

For active-reactive coatings, this micro-structure optimization turns out to be challenging in every step involved starting with imaging the micro-structure. Micro-computed tomography (CT) allows to quantify the leaching front advancement in ex-situ leaching experiments [15], but it is too coarse to follow individual particles. The dissolution of individual inhibitor particles and formation of pores can be observed by sub-micron or nano CT exploiting the phase contrast [16–21]. This requires however simplified coating formulations [20, 21] or additional information from destructive electron microscopy based techniques (FIB-SEM, SBF-SEM, EDX) [16–19]. Bradley et al. observed dissolution of strontium rich particles by ex-situ nano CT, supported by EDX [16]. They also showed particles inside the sample, not directly exposed to the solvent, to dissolve, and that way indirectly proved the formation of pathways during leaching. Hughes et al. measured the size of strontium-chromate clusters in a coating sample imaged by sub- μ CT using synchrotron radiation and SBF-SEM [19]. Recently, we succeeded in observing the growth of interconnected pore clusters in an in-situ leaching experiment imaged by synchrotron radiation nano CT [21]. However, the obtained sequences of 3D images at nano-scale resolution still do not reveal completely, how exactly the leaching progresses into the material.

For the geometric modeling step, to the best of our knowledge, the work [20] is the only attempt so far to fit a stochastic geometry model to inhibitor particles based on particle characteristics observed in image data. All inhibitor particle species we considered so far – barium sulfate, lithium sulfate, calcium sulfate, and zinc phosphate – as well as the strontium rich particles imaged in [16] and [19] feature a polyhedral shape. We observed very wide size distributions with a strong size-shape correlation. The larger the particles the less spherical they are. This strong correlation induced a very sophisticated and computationally demanding geometry model, namely Gibbs Laguerre polyhedra [20].

The spatial arrangement of inhibitor particles has not yet been analyzed. So for the moment, random sequential adsorption (RSA, e. g. [22]) ensuring placement without overlap is the most reasonable modeling approach. Consequently, the Gibbs Laguerre polyhedra do not form large connected components. This is a major flaw as successive dissolution of touching inhibitor particles is currently believed to be the major way how the leaching progresses deeper into the coating [18, 21]. Much stronger connectivity could be enforced e. g. as in [23], where particles are placed in cells of a Laguerre tessellation to model the micro-structure of battery electrodes, but here this approach seems neither backed by data nor otherwise justified.

The only previous attempt to simulate leaching on the scale of the inhibitor particles is Bonetti’s cellular automaton [24, 25]. Without any model fitting in the strict sense, Bonetti et al. [25] generate random particle shapes by cutting spheres with random planes, mix them with deterministic cylindrical shapes if needed, and place them by RSA, too. In [25], the formation of connected particle clusters is observed at a particle volume fraction of 22.5 %. It is however, not clear, whether this is due to the particle shape and size distributions or rather an effect of the coarse discretization by voxels with edge lengths of 0.25 (in [24] only), 0.5, and 1.0 μm [24, 25].

Here, we simulate the dissolution of inhibitor particles within realizations of the geometry models numerically in order to learn how variations of particle size and shape distribution as well as their spatial arrangement alter the leaching behavior of the virtual model coating. More precisely, for the lithium sulfate and the calcium sulfate model coatings investigated in [21], we compare the Gibbs Laguerre polyhedra RSA model fitted as described in [20] with an RSA model with a cuboidal typical grain with the same size and aspect ratio distributions. Additionally, we study the impact of mechanisms of enforcing stronger connectivity of the particles.

2 Methods

The onset of the leaching process is easily explained: The inhibitor salt particles at the interface with the defect are in direct contact with water and thus directly dissolved. The dissolution generates ions that are able to pacify the defect. That is, ions prevent the defect from growing and eventually reach the metal surface to be protected. The yet to be fully revealed question is: How exactly does this process of dissolution and transport of ions to the defect region progress further into the coating?

2.1 Continuum percolation in germ-grain models

The most commonly accepted answer to the above question is: Via interconnected pathways of pores that form exactly by successive dissolution of connected inhibitor particles. This moves our leaching problem close to the classical continuum percolation problem: Given a stochastic germ-grain model, for which parameters, in particular for which intensity, do connected components of infinite volume occur at a certain probability?

Note that continuum percolation is a vast research topic within the even vaster general field of percolation theory. Alternative settings are cells of a tessellation [26] and random graph based models – obviously closely related. For an overview and further references, we refer to Torquato [26, Chapter 9]. Here, we stick to the germ-grain model setting as thoroughly reviewed by Jeulin [27].

Analytical, and even many simulation based results are available for the Boolean model. Typically, the distribution of the typical grain Ξ_0 is fixed. Hence, the intensity $\lambda > 0$ remains the only free parameter. Hall [28] derived analytical results for the classical Boolean model of spherical grains in $\mathbb{R}^d$, $d \geq 2$. We follow the summary and notation in [22, Section 3.3.4]: Let p_∞ denote the probability that the typical grain is part of a cluster formed by infinitely many grains and o_∞ the expected number of grains in the cluster containing the typical grain. Then it holds [28] that

$$\begin{aligned} \mathbb{E}(\text{vol}_d(\Xi_0)^2) < \infty \text{ if and only if } \exists_{0 < \lambda'_c < \infty} \begin{cases} \lambda < \lambda'_c & \text{then } o_\infty(\lambda) < \infty \\ \lambda > \lambda'_c & \text{then } o_\infty(\lambda) = \infty \end{cases} \\ \text{and } \mathbb{E}(\text{vol}_d(\Xi_0)^{2-1/d}) < \infty \quad \text{then} \quad \exists_{0 < \lambda_c < \infty} \begin{cases} \lambda < \lambda_c & \text{then } p_\infty(\lambda) = 0 \\ \lambda > \lambda_c & \text{then } p_\infty(\lambda) > 0 \end{cases}. \end{aligned}$$

Clearly, $0 \leq \lambda'_c \leq \lambda_c \leq \infty$. In general, it is an open question, whether $\lambda'_c = \lambda_c$. For spherical grains with bounded radii distribution, $\lambda'_c = \lambda_c$ [29, 30]. Physicists derive a lower bound for the critical intensity from the mean number of grains intersecting the typical grain $\lambda \mathbb{E}(\text{vol}_d(\Xi_0 \oplus \tilde{\Xi}_0))$ [22, (3.106)]. The so-called excluded volume $\text{vol}_d(\Xi_0 \oplus \tilde{\Xi}_0)$ is the mean volume surrounding the typical grain that can not be occupied by another grain without penetrating it. The approximation thrives on $\lambda'_c \mathbb{E}(\text{vol}_d(\Xi_0 \oplus \tilde{\Xi}_0)) = 1$ as – on average – each grain should be connected to one other grain, if the system percolates. Let $\bar{V}, \bar{S}, \bar{M}$ be the mean volume, surface area, and integral of mean curvature of the typical grain. For isotropic germ-grain models in $\mathbb{R}^3$, Steiner's formula yields

$$\mathbb{E}(\text{vol}_3(\Xi_0 \oplus \tilde{\Xi}_0)) = 2\bar{V} + (\bar{S}\bar{M})/2\pi \quad \text{and thus} \quad \hat{\lambda}'_c = 1/(2\bar{V} + (\bar{S}\bar{M})/2\pi). \quad (1)$$

A more precise approximation arises from a topological argument [22, 27]: Consider the specific Euler number (or specific connectivity number)

$$\chi_V(\lambda) = \lambda \exp(-\lambda \bar{V}) \left(1 - \frac{\lambda}{4\pi} \bar{M}\bar{S} + \frac{\pi\lambda^2}{384} \bar{S}^3 \right).$$

Remember that the Euler number in 3D is roughly the alternating sum of the numbers of connected components, tunnels, and holes. Consequently, χ_V is positive for small intensities with many isolated grains and eventually turns negative when the Boolean model features less connected components but a lot more tunnels. Thus, the intensity at which the specific Euler number turns zero first, is taken as estimate for λ'_c :

$$\hat{\lambda}'_c = \frac{48\bar{M}}{\pi^2\bar{S}^2} \left(1 - \left(1 - \frac{\pi^3\bar{S}}{6\bar{M}^2} \right)^{1/2} \right). \quad (2)$$

The second zero yields the critical intensity for the complement [31].

The first application of continuum percolation was described by Gilbert [32] who modeled wireless networks by the connected components of a random graph formed by connecting all R -close points of a 2D Poisson point field. Applications to materials structures and properties are plenty, see [26, Chapter 9] for a wide overview. In applications, usually, the *percolation threshold* of the volume fraction is used instead of the critical intensity. For Boolean models, it is just the volume fraction reached at the critical intensity $0 \leq V_{V,c} = 1 - \exp(-\lambda'_c \bar{V}) \leq 1$. Examples with percolation thresholds arbitrarily close to the minimum 0 as well as approaching the maximum at 1 can be constructed by nesting and iteration [26].

For Boolean models of equal sized disks and spheres and equal sized and oriented rectangles and cubes [33], and for cylinders [34], percolation thresholds have been estimated by (1). Both estimators, (1) and (2), indicate, that the critical intensity depends strongly on the size and the shape of the typical grain with particular emphasis on the shape. And indeed, extremely low thresholds are e. g. reached for prolate cylinders with high aspect ratios modeling carbon nano-tubes. As a consequence, carbon nano-tubes can make a composite electrically conducting at very low volume fractions. Jeulin [27] cites the impressive example of the isotropic Boolean model of spherocylinders with

aspect ratio 100 having a percolation threshold $< 2\%$ whereas the percolation threshold for a Boolean model of spherical grains is $> 28\%$. A second example of percolation at extremely low volume fractions are Boolean models of 2D geometric shapes like rectangles or ellipses modeling 3D fracture systems in soil or rocks [35–37]. Xu and coauthors find in their simulation studies percolation thresholds varying strongly with changing aspect ratio for isotropic Boolean models of spherocylinders, congruent regular polyhedra, and prolate and oblate spheroids, too [38–40]. For the finite systems we are interested in here, particle size polydispersity has a strong influence as well, as e. g. shown for cylinders [41].

Simulation is the only option as soon as the germ-grain model features attractive or repulsive interaction of the grains, a complex grain shape distribution, or a grain orientation distribution different from constant or isotropic. Obviously, simulation studies are rather difficult, too, in particular for wide spread grain size distributions and grain shapes deviating strongly from spherical. For interacting grains, there are some percolation results for attractively or repulsively interacting spheres [26] and for cherry pit models of cylinders [41]. Jeulin and Moreaud [42] describe and fit Cox-Boolean models of spheres and spherocylinders featuring 2-3 scales in a sequence of papers [43]. The percolation behavior of cylinders or spherocylinders explains the extreme variety in electrical conductivity that can be achieved by them, in particular for the cherry pit cylinder model [41] and [27]. The use case maybe the closest to ours is the plasma spray modeling by flat cylinders mimicking the droplets. Shape and orientation of all droplets are the same, all lie in the coating plane. Jeulin and Moreaud [43] find percolation thresholds close to 15% both in the coating plane and orthogonal to it, with the threshold in the latter case varying slightly stronger with the cylinders’ aspect ratio.

Our setting is not a percolation problem in the strict sense as we are not interested in the occurrence of truly infinite pore systems. The question is rather, how many of the pacifying ions will be transported to the defect in which time. So maybe, the tortuosities measured by Xu and Jiao [38] are more revealing at the end. Nevertheless, we learned that the particle volume concentrations of 20-30 % that are typical for active-protective coatings can very well allow for percolation already and that we have to expect strong particle shape dependence. Emad et al. [44] derived from measurements supported by microscopic imaging the hypothesis of a change in the leaching behavior at the critical particle volume fraction (particle volume concentration, PVC). Bonetti [24] simulated the leaching process during the first 216 hours for the coating formulation from [45] featuring lithium carbonate as active component accompanied by magnesium dioxide, barium sulfate, and titanium dioxide, originally treated as pure fillers but later allowed to dissolve, too. Volume ratios of chemical constituents were kept constant, while the PVC varied between 7.5 and 37.5 %. Bonetti’s findings [24] are well in line with the purely geometric results summarized in this section: The amount of reachable inhibitor particles changes significantly close to the critical PVC which varies according to the exact settings. More elongated or smaller particles as well as the introduction of local small defects in the polymer matrix by switching 5 % of the matrix voxels to be ”pores” decrease the critical PVC.

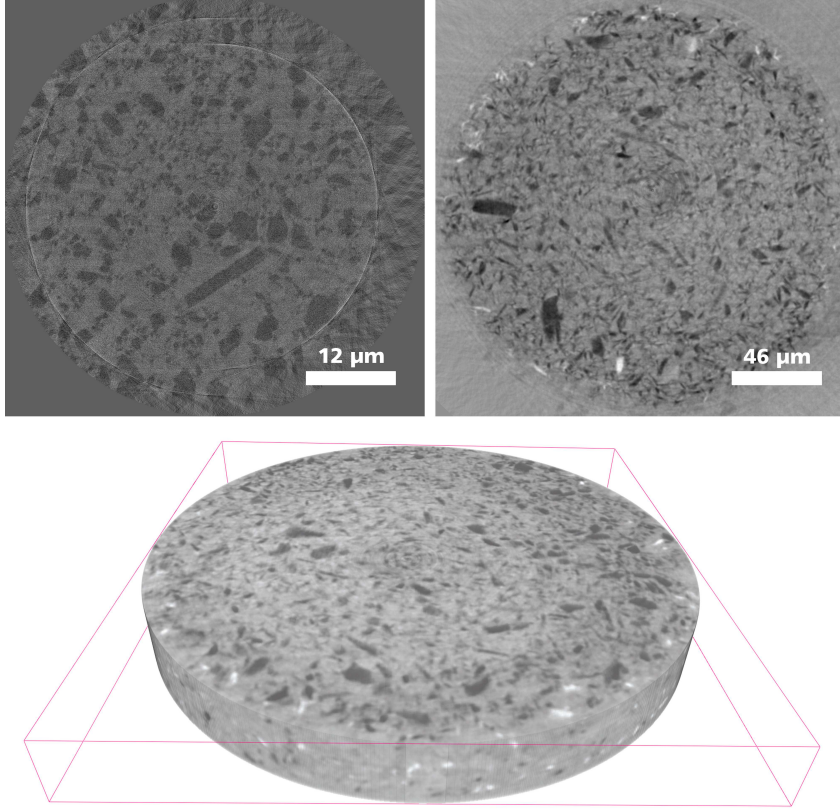


Fig. 2: Top: slices through the original, reconstructed SR nano CT images of model coatings. Left: calcium sulfate. Right: lithium sulfate. Bottom: Rendering of the calcium sulfate example. Diameter $\approx 160\ \mu\text{m}$, thickness $\approx 30\ \mu\text{m}$. Inhibitor particles appear dark.

2.2 Stochastic geometry models for inhibitor pigments

We consider two different coating configurations in terms of pigments and PVC: a lithium sulfate coating with PVC 20%, and a more sparsely packed calcium sulfate coating with PVC 11%. These two pigments have very different shape-size distributions, which we study and explain in more detail in [20]. One of the original images used is visualized in Figure 2. Briefly, lithium sulfate particles are on average smaller, while calcium sulfate features several very large, elongated particles.

A Gibbs Laguerre model [46] was fitted to the shape-size distribution retrieved from 3D images of coatings loaded with these inhibitors. In a nutshell, we start with a 3D Laguerre tessellation where the number of cells fits the number of particles observed in the real coatings. The target joint shape-size distribution of the particles is given as a 2D histogram. More precisely, we capture size by the mean width roughly estimated by the mean of the diameters measured in the 13 discrete direction given by the image

[47] while shape is described by the aspect ratio derived from length and thickness of the minimal volume bounding cuboid [48, 49]. These choices are motivated by the demand to compare particles segmented from the images with very rough surfaces to simulated polyhedra.

The polyhedral cells in the tessellation are our particle sample. Iteratively, generator points are added, moved or removed, and the change is accepted only if it brings us closer to the target distribution. The final cells provide us with a collection of particles that are subsequently placed in space by RSA. That is, particles are placed sequentially. The location for the current particle is drawn uniformly randomly within the field of view, and discarded if it would cause collision with previously placed particles. In the latter case, a new location is drawn for the same particle. For more details about the Gibbs Laguerre model, we refer to [20].

The choice to model inhibitor particles by polyhedra fits the observed shapes [16, 19–21] and using cells of a tessellation yields a large sample at once without the need to fit excessively many parameters. Particle systems fitting an observed size distribution can be generated in seconds that way [50]. However, our particle size distributions are very wide and – more importantly – due to the strong size-shape correlation, both quantities must be fitted jointly [20]. As a consequence of fitting to the 2D size-shape histogram, currently, our Gibbs Laguerre modelling is too slow for interactive use. Yet, this is a prerequisite for rendering it a viable tool for coating design.

One way to cut the computational costs is to replace the polyhedral particles by simple cuboids that can be generated one by one, still according to the observed empirical size-shape distribution. Switching to a cuboid model reduces the runtime from the scale of days to just minutes, depending on the size of the synthetic sample. So far, it is not known how this simplification affects the connectivity, and thus the leaching process. Hence, we investigate this question here.

We generate coatings according to the Gibbs Laguerre models fit to the pure lithium sulfate and calcium sulfate model coatings observed by SR-nano-CT in [20]. For each synthetic coating with polyhedral particles, a "twin" cuboid sample is created. To preserve shape, the minimal volume bounding cuboid of each polyhedron is used. To preserve particle size, this bounding cuboid is scaled such that its volume matches the one of the polyhedron. The RSA process is run independently for polyhedra and cuboids. The resulting discrete samples are finally represented as cubic 550^3 voxel images with voxel size 45 nm and thus side length of 25 μm . This size was chosen because typical active-reactive primers are applied in layers of 15 – 25 μm , with airplane coatings typically at the thicker end of this range. Unless explicitly noted otherwise, we stick to this sample size throughout. Figure 3 shows one realization of each model – Gibbs Laguerre and cuboids, for lithium sulfate and calcium sulfate.

2.3 Leaching on the micro-scale

Leaching is understood as a three-stage process, comprising first direct dissolution of the exposed particles, followed by so-called Fickian diffusion [51] where water travels to particles in contact with the exposed ones, and finally diffusion through interconnected pathways that have developed during the first two stages [19, 24, 52, 53].

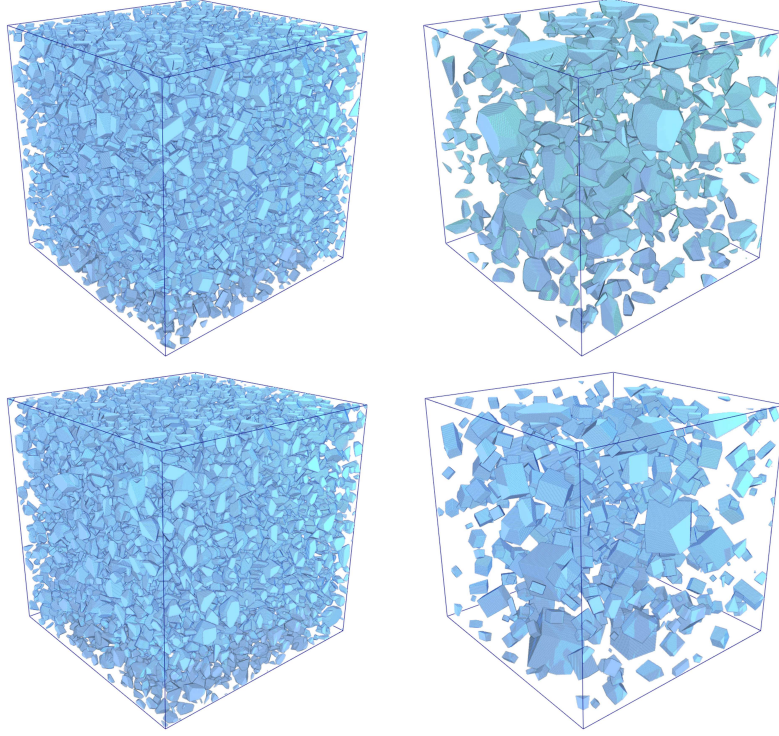


Fig. 3: Examples of synthetic coatings. Left: lithium sulfate. Right: calcium sulfate. Top row: polyhedral particles. Bottom row: cuboid particles. The cubic observation window has side length $25\text{ }\mu\text{m}$.

The main transport paths for water are cavities left by dissolving particles. It has been speculated [19], and finally demonstrated [21], that these cavities get connected by tunnels and coalesce into pore clusters over time. Thus, modeling the particle contact correctly is crucial when attempting to simulate leaching.

There are several concurrent theories about possible modes of ion transport in the literature. Here, we briefly summarize them, a more comprehensive overview of the different theories is given in [21] and [15]. First, the particle-matrix interface has been shown to permit water and ion transport [54, 55]. It is however not yet known how permeable the interface is and up to which size ions can pass through.

Second, large particles account for most of the inhibitor volume fraction, but are by far outnumbered by the small particles. Tiny particles that are below the observation range of both SR-nano-CT and FIB-SEM are spread throughout the polymer matrix. The particles are milled to the desired size distribution. Therefore, it would not be surprising if the dust was concentrated close to the larger particles, as it consists of fragments of them. It is possible that these very small particles are responsible for the formation of the tunnels.

Third, the epoxy binder that encases the particles is made of polymer chains which, in theory, are not permeable. However, the epoxy is not always homogeneous and can have areas of lower density [56]. These areas may be permeable and therefore offer another transport path. This is, however, the hypothesis that is least supported in the literature.

2.4 Geometric model alterations

As explained above, connectivity of the particle system is crucial. Nevertheless, we have neither reliable information of the initial connectivity before the exposure to water, nor do corrosion experts fully agree on how the interconnected pore system observed later on forms. We can therefore only try to capture these effects phenomenologically.

Clearly, if there is little to no contact, as is likely to result from particle placement by RSA, leaching will stop right after the direct dissolution stage. We will therefore investigate the connectivity of the discretized particle systems before attempting to simulate any leaching. Interpreting voxels as small cubes, we consider discrete connectivity via voxel faces only (6-neighborhood) as well as via faces, edges, and corners (26-neighborhood).

Several geometric alterations would enhance connectivity of the original RSA particle system, the most intuitive being to relax the criterion for two particles to be connected to R -closeness for a suitable distance R . Sub-resolution particles, shrinkage cracks, or pores as well as the particle interfaces could be integrated explicitly into the geometric models. To limit the experimental effort and due to lacking evidence, we subsume these effects into an additional phase to capture not finally disclosed ways to "connect" particles. Details of these alterations are explained in the following.

2.4.1 Connecting particles by morphological closure

A morphological closure is a dilation followed by an erosion [47]. Space between objects in the foreground is closed; we have control over how close objects have to be for this to happen. We can use a closure to introduce anything from very thin tunnels to entire interstitial zones. In Figure 4, we see how a closure can be used to imitate tunnels between particles. The cavities in the images are left by dissolved particles. While the leaching continues, they grow together into a small pore cluster. We can gain more control over how delicate the tunnels are by implementing the morphological closure with a Euclidean distance transform (EDT) as illustrated in Figure 5. The threshold t determines how strongly we close the particle system. We can think of it as the distance (in voxels) at which we consider the particles to be touching. We start by applying the EDT on the background yielding for each background voxel its distance to the foreground. Thresholding by t returns the dilated particle system as foreground. Applying the EDT once more, but now on the foreground, then thresholding again, we erode the dilated particle system resulting in the closed image.

2.4.2 An additional synthetic phase

Figure 6 shows a sub-volume of a model realization of the calcium sulfate with polyhedral particles, with multiple alterations introduced to increase connectivity: dissolving

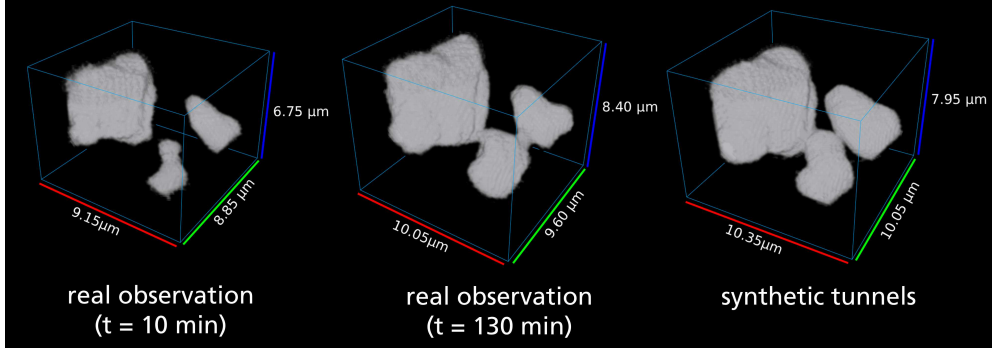


Fig. 4: Real observations of tunnels forming between cavities from our in-situ imaging campaign [21] next to artificial tunnels created via a morphological closure. The coating considered here was loaded with lithium sulfate particles.

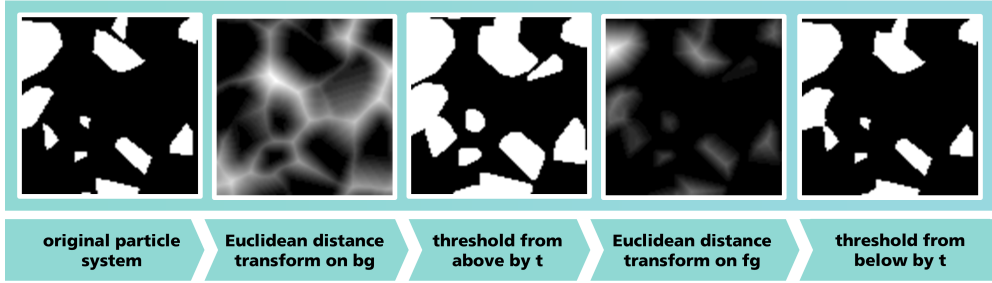


Fig. 5: Morphological closure via EDT. The transformations are applied on the full size 3D image. 2D cutouts are shown for illustration, only. bg refers to background, fg to foreground.

tunnels, particle dust, permeable interface. For the particle polymer interface, erring on the side of caution, we introduce a one-voxel-thin layer around the particles using a dilation via EDT. This very thin layer acts as the interface and permits fluid flow.

Very fine dust (< 50 nm) can just be added by independently sprinkling in tiny, i. e. one voxel particles. Note that coarser dust (500 nm–1 μ m), could be incorporated by generating a second sample of small particles and placing them together with the already drawn particle sample by RSA.

2.5 Dissolution simulation

Leaching in active-reactive coatings boils down to two key physicochemical phenomena: dissolution of soluble pigments, and diffusion of the water/solvent. Dissolution is more or less straightforward - when pigments come in direct contact with water, they release ions at a rate determined by the material's solubility and the concentration of

the solution. When modeling diffusion, complexity arises from the transport paths, not from chemical processes. As discussed in Section 2.3, transport seems to be possible along the particle-polymer interface and through lower density epoxy. In-situ observations of a model coating have demonstrated the emergence of tunnels, connecting cavities into pore clusters, the process generating these tunnels still being not fully understood.

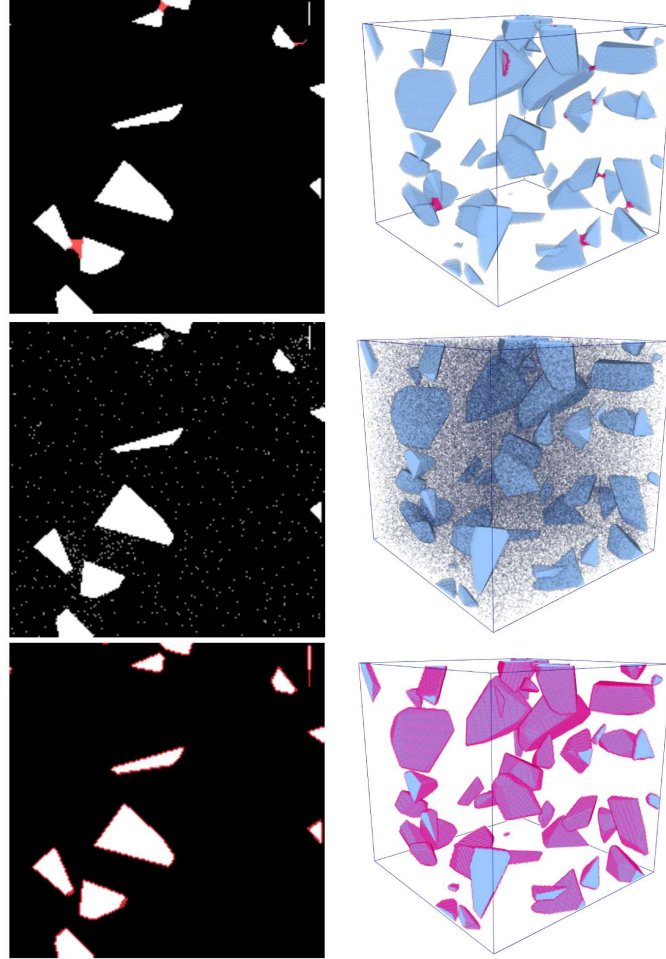


Fig. 6: Sub-volume (side length $9.12\ \mu\text{m}$) of a simulated calcium sulfate sample with polyhedral particles featuring several alterations. First column: a central slice. Second column: 3D volume renderings of the changes – tunnels (reddish, first row), dust distributed throughout the entire sample, a bit more concentrated in interstitial areas (second row), and finally, the particle-polymer interface – particles (blue) wrapped with a very thin interface layer (magenta, third row).

2.5.1 Bonetti’s cellular automaton

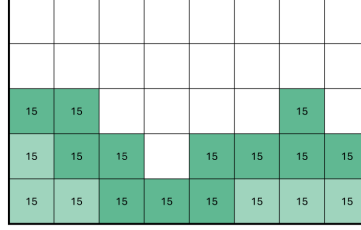
So far, the only model of leaching in active-reactive coatings using a 3D digital twin of a coating is Bonetti’s [25] cellular automaton. He models coating samples of the size $200\text{ }\mu\text{m}\times 200\text{ }\mu\text{m}\times 30\text{ }\mu\text{m}$, with cell sizes of 0.25, 0.5, or 1 μm . Each cell is assigned one of five different states: salt, polymer, liquid, dissolved, pore. The chemical composition of the coating is a realistic one containing four different salts – one corrosion inhibitor and three fillers. Salts behave according to their chemical properties – the inhibitor dissolves quickly, whereas only the cells on the surface of filler particles dissolve sufficiently fast to generate a path. The polymer is in general impermeable to water, but pore cells are scattered throughout to mimic defects.

To model leaching, Bonetti applies two automaton rules alternately, namely dissolution of soluble pigments and diffusion of the resulting solution. Two main parameters are introduced: C_{solid} and C_{diss} . Roughly speaking, C_{solid} controls the dissolution rate of a salt cell, while C_{diss} controls the diffusion rate of a dissolved cell. Figure 7 sketches this model’s mechanism.

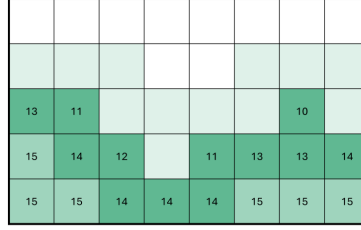
Salt cells are initially assigned an integer value C_{solid} , effectively a counter of liquid neighbors the cell needs to interact with to fully dissolve. Different species are assigned different values – the soluble lithium carbonate was assigned a C_{solid} orders of magnitude lower than the filler salts. In every dissolution step, the rate of release is determined by the number of liquid neighbors. The adjacent liquid cells are flipped to state ”dissolved” and the cell’s counter C_{solid} is reduced by the number of liquid neighbors. When C_{solid} of the salt cell hits 0, the cell is considered fully dissolved and its state is flipped to ”liquid”.

Every dissolution step is followed by C_{diss} diffusion steps. In each diffusion step, every dissolved cell chooses a neighbor at random. If it selects a liquid neighbor, the two cells swap states. If it selects a solid neighbor, nothing happens. This way, the dissolved cells travel deeper into the coating or exit the coating. Only dissolved cells that leave the coating are counted as ”leached”.

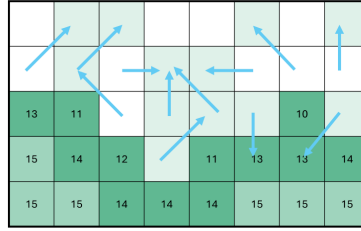
1x dissolution



1x diffusion



4x diffusion



1x dissolution

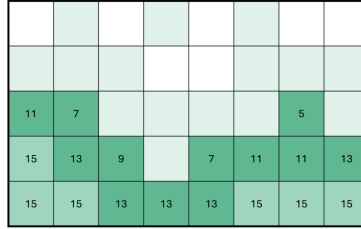
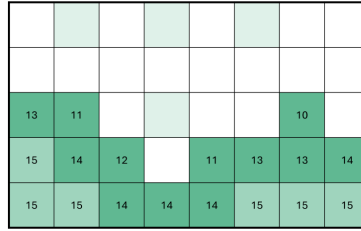


Fig. 7: Bonetti's cellular automaton for leaching for parameters $C_{\text{diss}} = 5$ and $C_{\text{solid}} = 15$, with the latter enforcing a salt cell to interact with a total of 15 liquid/water cells to fully dissolve. Salt cells are marked green, and dissolving and dissolved cells by lighter shades of green. The amount that dissolves in each step is determined by the cell's number of liquid neighbors. As the cell dissolves, it releases a concentrated solution into the adjacent liquid cells, which then travels through the material by a random walk. With this parameter configuration, there are 5 diffusion steps for every dissolution step. Some dissolved cells will exit the coating and should – provided proper calibration – coincide with the leached mass captured by measurements.

2.5.2 Our dissolution model

We choose to model dissolution only for the moment. Rather than trying to match the complete physicochemical process as closely as possible, our main aim at present is to use a phenomenological model and to understand how geometric micro-structural differences affect the leaching behavior. Diffusion is of course indispensable to model realistic leaching kinetics. However, for simulating the opening of pathways and water-salt contact, dissolution suffices.

The dissolution of inhibitor particles is simulated similarly to the dissolution of crystals in rock physics. The change in concentration, or, more generally, a material indicator, is described by the distribution of the surrounding fluid and the identification of the surface itself. The model presented in [57] is adjusted to the setup at hand. In contrast to [25], the model uses a time-continuous description instead of the discrete cellular automaton model. More precisely, the dissolution is described by an ordinary differential equation and therefore modeled continuous in time. It is based on the identification of dissolution rates, which are parametrized to specific surface sites of the inhibitor particles. In general, a complete rate spectrum describes the dissolution process [58]. Additionally, the dissolving fluid needs to be present at the specific surface sites, i.e., its concentration needs to be larger than zero.

We simulate in the voxel image representation of our geometric model realizations. That means, our voxels play the same role as Bonetti’s cells. Each voxel is assigned an ID specifying whether it belongs to the fluid (water), a solid component, or the pore phase. Over the course of leaching, the ID can change. The salt particles, dust, and tunnels are treated as solid material components that can turn into a pore. The particle-polymer interface and lower-density epoxy are treated as another solid component which allows for limited water flow. Each component is assigned a set of reaction rates based on the desired behavior.

First, we focus on the solid components. Let ϕ denote the solid volume fraction of a voxel. That is, the ratio of the volume of the solid component in that voxel to the volume of the voxel. At the beginning, all salt voxels are supposed to be completely filled, thus $\phi = 1$. As salt dissolves, the voxel’s solid volume fraction decreases and finally the voxel is labeled porous. The change of the volume fraction is described by $\frac{d\phi}{dt} = -r$, where r denotes the reaction rate. When ϕ hits 0, the formerly solid salt voxel turns into fluid.

For each component and phase, we specify three reaction rates based on the number of liquid neighbors (see Table 1). Based on their 6-neighbors, voxels are divided into three categories: a face voxel has one liquid neighbor, an edge voxel has two, and a corner voxel has three or more. We introduce corresponding reaction rates (face, edge, corner), proportional to the number of liquid neighbors ($r_f < r_e < r_c$). Note that these rates are not intended to account for the chemical properties and reactions of the components. The aim here is rather to match their relationships.

Figure 8 illustrates several iterations for a set of example parameters. The voxels are color-coded according to their category in the next iteration. The update rule for each voxel is obtained by considering an explicit Euler discretization of the underlying

	salt	tunnels	interface
r_f	1	0.5	0.1
r_e	2	1	0.2
r_c	5	2.5	0.5

Table 1: Leaching rates for different phases. The salt is assumed to dissolve at the highest rate. Therefore, in each category, the highest value is assigned to salt. The tunnels are assumed to give more resistance to fluid movement, as we cannot know how much soluble matter there is. The effective difference in solubility (lithium sulfate dissolves two orders of magnitude faster than calcium sulfate) is accounted for by selecting different time scales for the two salts (1/time for lithium sulfate and 2/time for calcium sulfate) - although they have the same numerical value, their reaction speeds will be different.

differential equation. Choosing a time step Δt , the n -th time step reads

$$\phi^{n+1} = \phi^n + \Delta t(-r_n), \quad (3)$$

where r_n is determined by the category of the voxel at time step n . The initial value ϕ^0 is given by the initial distribution described above. As the dissolution plays out, the surroundings of a salt voxel will change, and its category will adjust accordingly. Once a voxel is fully dissolved ($\phi = 0$), it flips into a fluid state. Diffusion is not modeled, so the reaction rate is not affected by the concentration of the fluid. It is also not possible to track directly how much mass exited the coating; we therefore treat everything dissolved as leached. The total leached mass m_{leached} is the difference between the initial (time step 0) and the final (time step N) mass of salt. It is computed as

$$m_{\text{leached}} = \rho_{\text{salt}} V_{\text{voxel}} \sum_{i=1}^{N_{\text{voxel}}} (\phi_i^0 - \phi_i^N), \quad (4)$$

where ϕ_i denotes the solid volume fraction in voxel i , V_{voxel} the volume of a single voxel, and ρ_{salt} the density of the salt. Since we consider the dimensionless solid volume fraction for describing the status of the voxel, the reaction rate r has the unit 1/time. It can be converted to a classical dissolution rate, with mass per time as a unit, by multiplying with the voxel volume and the density of the component the voxel belongs to.

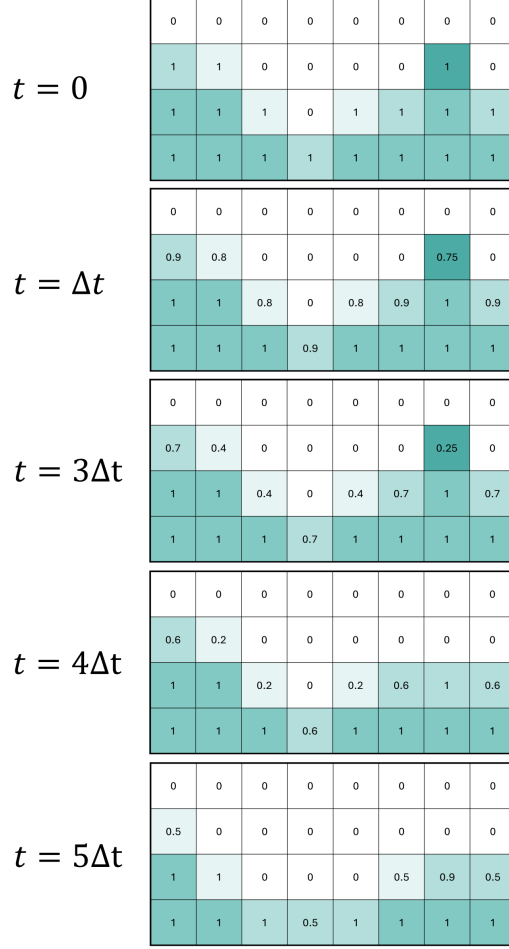


Fig. 8: A demonstration of our leaching model for the following dissolution rates: $r_c = 0.25$, $r_e = 0.2$, and $r_f = 0.1$. Only dissolution is modeled. In each iteration, salt voxels dissolve at a rate determined by the number of faces in contact with water. The color-coding of each voxel indicates its category in the next step.

3 Results

3.1 Connectivity

The point of altering our initial particle systems was to introduce and study contact between particles. Some of the questions we are trying to study are the following: How does particle shape influence contact behavior? What volume and depth do the emerging particle clusters have? How do the alterations suggested in Section 2.4 influence the simulation results? When analyzing the connectivity, we look for percolating

inhibitor type	particle shape	# particles	N6/ N26	# clusters	maximal cluster			mean cluster	
					vol [μm^3]	frac vol [%]	diam [μm]	vol [μm^3]	diam [μm]
Li_2SO_4	polyh	7 395	6	6 805	9.15	0.30	4.76	0.46	1.27
			26	5 866	10.97	0.35	5.94	0.53	1.36
	cuboidal	7 329	6	6 816	8.04	0.26	4.49	0.45	1.14
			26	5 909	8.84	0.29	5.61	0.52	1.22
CaSO_4	polyh	572	6	573	80.46	5.32	6.60	2.65	2.12
			26	551	86.18	5.68	7.09	2.76	2.17
	cuboidal	551	6	543	74.77	4.78	7.09	2.86	1.90
			26	533	77.55	4.94	7.78	2.92	1.91

Table 2: Initial connectivity of model coatings. "Frac vol" is the fraction of the total particle system volume comprised by the maximal cluster. The number of clusters exceeding the number of particles for the calcium sulfate Gibbs Laguerre polyhedra system is an artifact of the 6-connectivity.

clusters (in our case, clusters spanning the entire observation window) or any large clusters of particles. The shape of the clusters is interesting, too: Are they compact and concentrated in one place, or do they stretch deeply into the sample? We also want to track changes in the number of connected components.

3.1.1 Initial connectivity

Table 2 summarizes the connectivity of the initial model particle systems. For the lithium sulfate model with PVC 20 %, a couple of smaller clusters are present right from the beginning while the calcium sulfate with PVC 11 % is essentially disconnected. All values reported are averages over 10 realizations of the respective model.

3.1.2 Connectivity after morphological closure

In Figures 9 and 10, we show how the maximal cluster develops when increasing particle connectivity by morphological closure as described in Section 2.4.1. We observe the fraction of the total particle system volume comprised by the maximal volume cluster as well as the maximal diameter of the maximal volume cluster as a function of the distance at which two particles are connected. Note that the cluster of maximal volume is not necessarily the one featuring the maximal diameter. This explains the non-monotonicity of some of the curves in Figures 9 and 10. Figures 13 yields examples of percolating clusters in synthetic lithium and calcium sulfate samples.

3.1.3 Leaching simulation

Results of the leaching simulation are summarized in Table 3. Figure 14 yields a visual comparison of the simulated leaching behavior of the two inhibitor species. Finally, Figures 15 and 16 depict some special cases of pore cluster growth.

The alterations suggested have surprisingly little impact on the connectivity/the simulated leaching behavior.

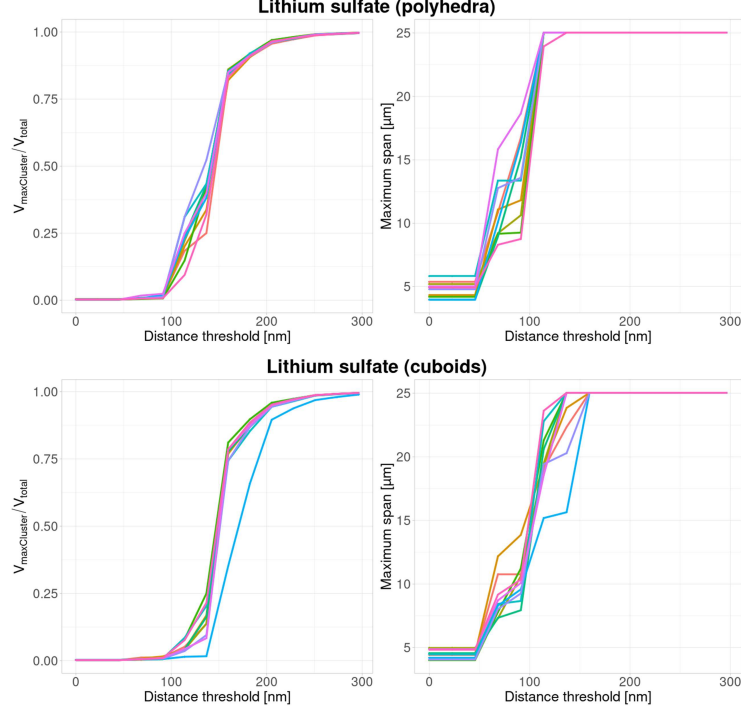


Fig. 9: Connectivity in the simulated lithium sulfate samples induced by morphological closure. Left: fraction of the total particle system volume comprised by the maximal cluster. Right: maximal diameter of the cluster of maximal volume.

4 Discussion

We follow up on our recent breakthroughs in 3D imaging, analyzing, and geometrically modeling the micro-structure of active-reactive coatings. Here, we report on the next step towards micro-structural optimization: A study on the connectivity and the dissolution behavior of synthetic coating models fitted to two of the previously

inhibitor type	particle shape	depth of leaching front			fraction of inhibitor volume		
		min	mean	max	min	mean	max
Li ₂ SO ₄	polyh	11.30	13.40	15.00	20.85	34.40	54.32
	cuboidal	12.81	14.45	15.00	34.51	53.90	71.61
CaSO ₄	polyh	2.70	2.70	2.70	5.88	15.89	30.16
	cuboidal	2.70	2.70	2.70	6.40	12.67	25.39

Table 3: Results of the dissolution simulation. Depth of ingress into the material in flow direction (x). All experiments done on (15 μm)³ subvolumes.

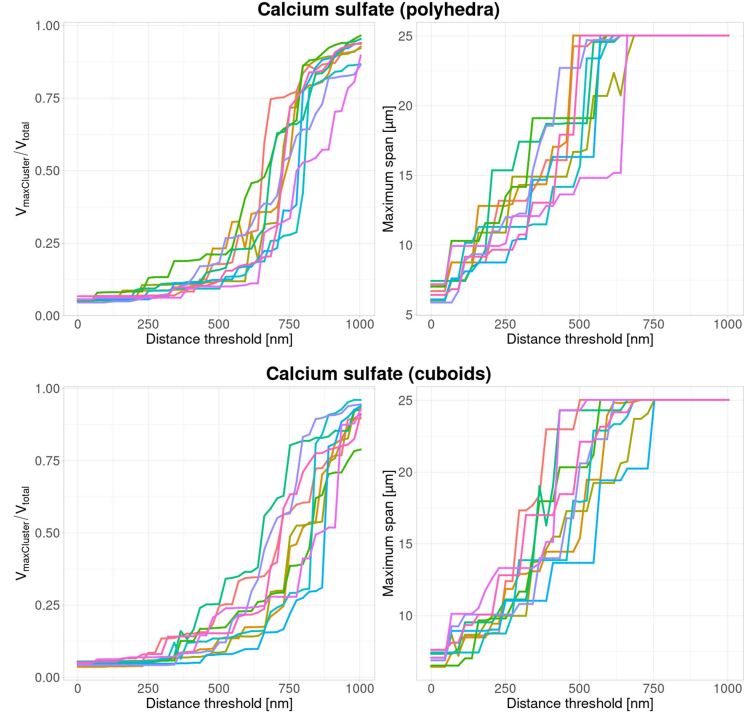


Fig. 10: Connectivity in the simulated calcium sulfate samples induced by morphological closure. Left: fraction of the total particle system volume comprised by the maximal cluster. Right: maximal diameter of the cluster of maximal volume.

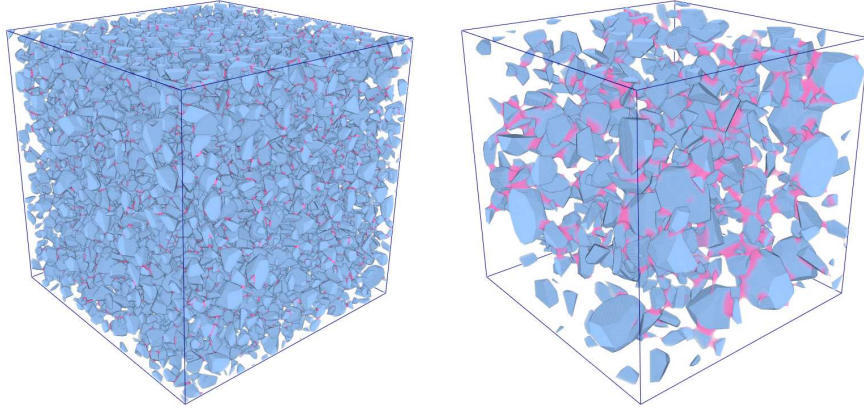


Fig. 11: A closed lithium sulfate (left) and closed calcium sulfate (right) sample. Both observation windows have a side length of $25\mu\text{m}$. Particles systems light blue, tunnels generated by morphological closure pink. Due to the different volume fraction and particle size distribution, the two species require vastly different tunnel sizes to connect them.

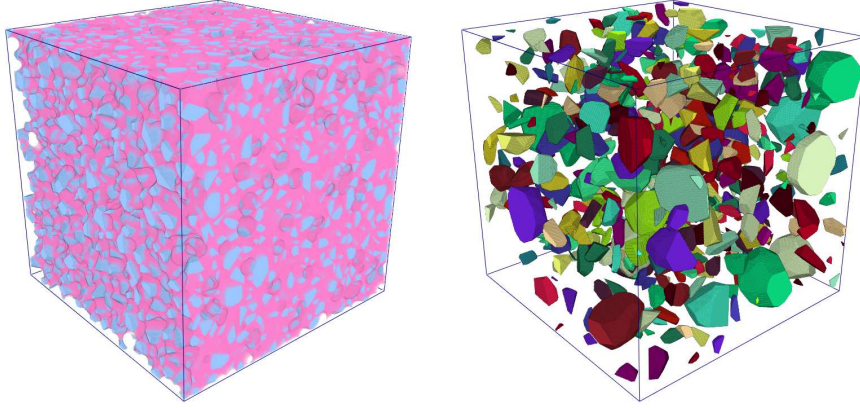


Fig. 12: The samples from Figure 11 with swapped thresholds for generating the tunnels by morphological closure (rendered pink). The generous threshold needed for calcium sulfate will completely encase the lithium sulfate particles in the new phase. The low threshold that suffices to connect lithium sulfate leads to a calcium sulfate coating with little-to-no connections (colors indicate connected components). The corresponding samples with cuboid particles behave similarly.

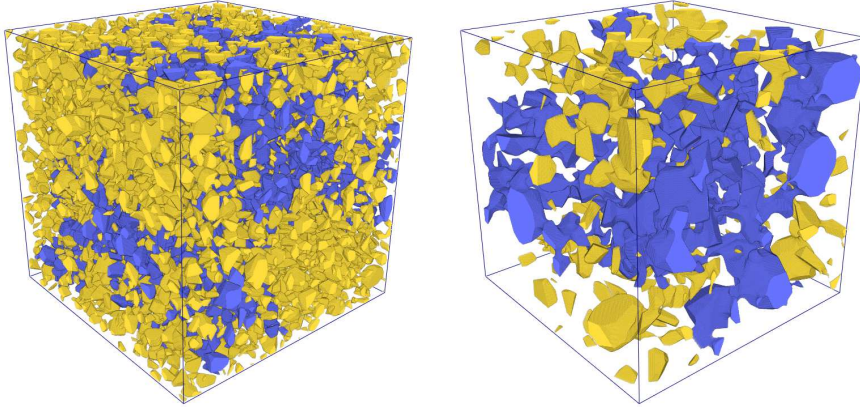


Fig. 13: Examples of percolating clusters (purple) in a closed lithium sulfate (left) and calcium sulfate (right) sample. Lithium sulfate was closed with a threshold of $t = 2.5$ voxels (114 nm); calcium sulfate with $t = 15$ (684 nm). Both observation windows have a side length of 25 μm .

investigated inhibitor particle types – lithium sulfate and calcium sulfate. The vivid research field of continuum percolation deals with very similar problems, does however not cover our case: Polyhedral grains of widely varying sizes and with shapes strongly correlated with the sizes.

We observe strong differences for 6- and 26-connectivity underlining that the scale/resolution critically impacts connectivity. This is an additional strong argument

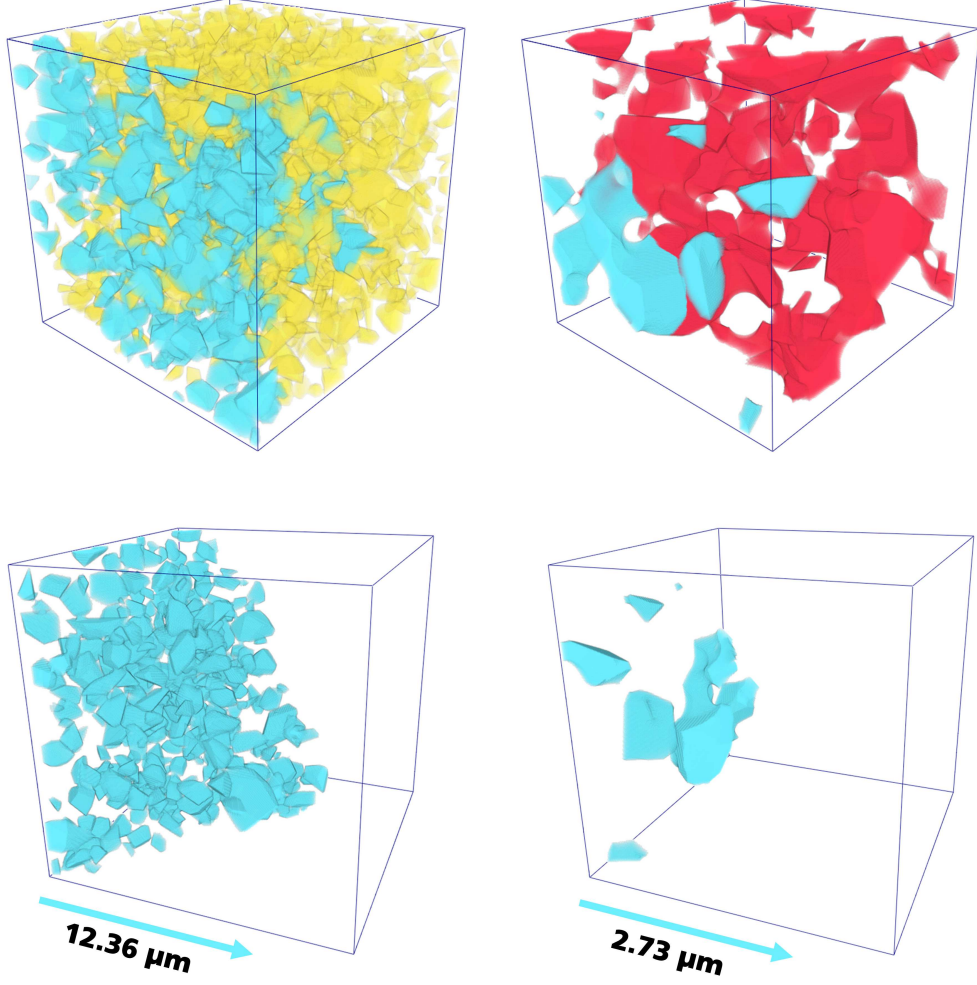


Fig. 14: Front and side view of effects of leaching on two synthetic coatings with polyhedral particles. Left: lithium sulfate (yellow) reacts rapidly and the leaching front reaches deep into the structure. Right: calcium sulfate (red) dissolves slowly – in the same time frame, only surface particles manage to dissolve. The pore networks (blue) are highlighted in the bottom row.

for introducing tunnels by morphological closure as this allows to control the distance at which particles are treated as being connected independently of the chosen voxel size. On the other hand, our two examples show interesting behavior only at rather different distance thresholds t as illustrated in Figures 11 and 12. How to choose the distance at which particles should be treated as being connected should thus be investigated in the future. Beyond distance, the spatial arrangement of the particles could

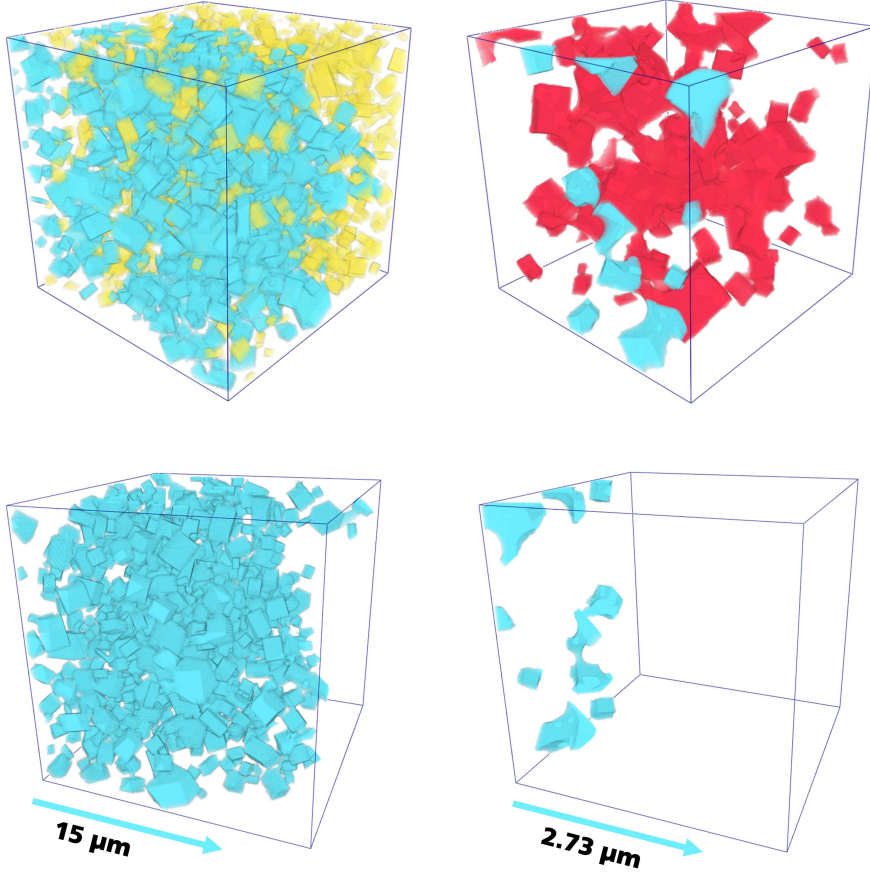


Fig. 15: In general, the trends observed in samples with polyhedral particles apply to samples with cuboids as well. Here, we highlight an example of a synthetic lithium sulfate coating where the cluster reaches the other end of the volume, eating up 50% of total particles. The color coding is the same as in Figure 14.

of course be altered, too. Incorporating the approach from [59] is subject of further research, too.

As suggested by the continuum percolation literature, shape matters. Even the cuboids with same volume and aspect ratio as the polyhedra do behave differently wrt cluster formation.

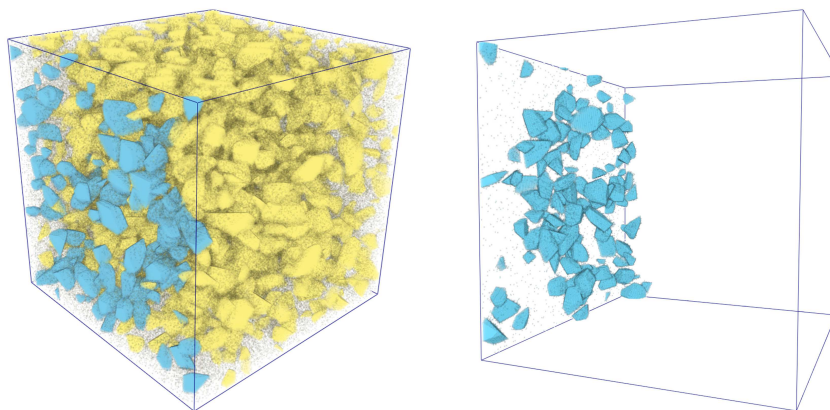


Fig. 16: The alterations discussed in 2.4, i.e. the interface layer and dust, were added to a lithium sulfate particle system. The leaching front did not progress deeper into the sample due to a lack of 6-connectivity.

5 Conclusion

This is just a very first step towards simulating micro-scale leaching. The effects of varying size or shape distributions of the same inhibitor particle species could nevertheless be studied this way already. The biggest challenges to overcome before getting closer to realistic active-reactive coatings are proper calibration by choosing experimentally determined values for the leaching rates in Table 1 and to migrate to model coatings featuring multiple particle types.

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Declarations

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Data availability

Raw and processed image data as well as model realizations will be published after thorough editing. Meanwhile, they are available on request.

Author contributions

JZ processed images and data and designed and conducted the simulation study, SO developed, adapted, and described the dissolution simulation. JZ, PV, and KS conceptualized the study. PV provided domain background and data. JZ and KS wrote the manuscript. CR revised it critically. All authors read and approved the final manuscript.

References

- [1] Gharbi, O., Thomas, S., Smith, C., Birbilis, N.: Chromate replacement: what does the future hold? *npj Mater Degrad* **2**(12) (2018) <https://doi.org/10.1038/s41529-018-0034-5>
- [2] Winkler, D.A., Hughes, A.E., Özkan, C., Mol, A., Würger, T., Feiler, C., Zhang, D., Lamaka, S.V.: Impact of inhibition mechanisms, automation, and computational models on the discovery of organic corrosion inhibitors. *Progress in Materials Science* **149**, 101392 (2025) <https://doi.org/10.1016/j.pmatsci.2024.10139>
- [3] Özkan, C., Sahlmann, L., Würger, T., Feiler, C., Lamaka, S., Zheludkevich, M., Taheri, P., Mol, A.: Gaining scientific understanding with small data machine learning: explainable molecule representations and their consensus. *npj Mater Degrad* **9**(157) (2025) <https://doi.org/10.1038/s41529-025-00713->
- [4] Özkan, C., Sahlmann, L., Feiler, C., Zheludkevich, M., Lamaka, S., Sewlikar, P., Kooijman, A., Taheri, P., Mol, A.: Laying the experimental foundation for corrosion inhibitor discovery through machine learning. *npj Mater Degrad* **8**(21) (2024) <https://doi.org/10.1038/s41529-024-00435->
- [5] Abdelrahman, N., Van den Steen, N., Özkan, C., Wang, C., Song, C., Visser, P., Lamaka, S.V., Kallip, S., Böttcher, R., Mol, J.M.C., Zheludkevich, M.L., Terryn, H., Hauffman, T., Meeusen, M.: Corrosion protection in a coating defect on AA2024-T3 by lithium carbonate inhibitor leaching: An experimentally validated FEM approach. *Corrosion Science* **250**, 112861 (2025) <https://doi.org/10.1016/j.corsci.2025.11286>
- [6] Abdelrahman, N., Delaere, K., Meuris, P., Visser, P., Van den Bossche, B., Terryn, H., Haile Mamme, M., Meeusen, M.: An empirically based finite element method approach for modelling the leaching of lithium carbonate from an active primer system. *Progress in Organic Coatings* **211**, 109770 (2026) <https://doi.org/10.1016/j.porgcoat.2025.10977>

- [7] Sahlmann, L., Abdelrahman, N., Meeusen, M., Delaere, K., Meuris, P., Bossche, B.V., Konchakova, N., Terryn, H., Mamme, M.H., Feiler, C., Zheludkevich, M.L.: Surrogate modelling of corrosion inhibition finite element simulations using machine learning. *npj Mater Degrad* **10**(38) (2026) <https://doi.org/10.1038/s41529-026-00760-5>
- [8] Schladitz, K., Peters, S., Reinel-Bitzer, D., Wiegmann, A., Ohser, J.: Design of acoustic trim based on geometric modeling and flow simulation for non-woven. *Computational Materials Science* **38**(1), 56–66 (2006)
- [9] Redenbach, C., Schladitz, K., Vecchio, I., Wirjadi, O.: Image analysis for microstructures based on stochastic models. *GAMM-Mitteilungen* **37**(2), 281–305 (2014)
- [10] Zhang, J.F., Andrä, H., Zhang, X.X., Wang, Q.Z., Xiao, B.L., Ma, Z.Y.: An enhanced finite element model considering multi strengthening and damage mechanisms in particle reinforced metal matrix composites. *Composite Structures* **226**, 111281 (2019) <https://doi.org/10.1016/j.compstruct.2019.111281>
- [11] Andrä, H., Dobrovolskij, D., Schladitz, K., Staub, S., Müller, R.: Modelling of geometrical microstructures and mechanical behaviour of constituents. In: Diebels, S., Rjasanow, S. (eds.) *Multi-scale Simulation of Composite Materials: Results from the Project MuSiKo*, pp. 31–56. Springer, Berlin Heidelberg (2019). https://doi.org/10.1007/978-3-662-57957-2_3
- [12] Hofmann, T., Westhoff, D., Feinauer, J., Andrä, H., Zausch, J., Schmidt, V., Müller, R.: Electro-chemo-mechanical simulation for lithium ion batteries across the scales. *International Journal of Solids and Structures* **184**, 24–39 (2020) <https://doi.org/10.1016/j.ijsolstr.2019.05.002>. Physics and Mechanics of Random Structures: From Morphology to Material Properties
- [13] Marr, J., Zartmann, L., Reinel-Bitzer, D., Andrä, H., Müller, R.: Parametric optimization of the effective thermal conductivity for a three-phase particle-filled composite. *Computational Materials Science* **205**, 111214 (2022) <https://doi.org/10.1016/j.commatsci.2022.111214>
- [14] Marr, J., Zartmann, L., Reinel-Bitzer, D., Andrä, H., Müller, R.: Multi-scale optimization of the viscoelastic behavior of short fiber reinforced composites. *Int J Mech Mater Des* **19**, 501–519 (2023) <https://doi.org/10.1007/s10999-023-09645-w>
- [15] Müller, O., Klein, P., Konchakova, N., Schladitz, K., Visser, P., Zaninović, J.: Following the leaching fronts: synchrotron (sub)micro-computed tomography for active protective coatings (2026). Submitted.
- [16] Bradley, R.S., Liu, Y., Burnett, T.L., Zhou, X., Lyon, S.B., Withers, P.J.,

- Gholinia, A., Hashimoto, T., Graham, D., Gibbon, S.R., Hornberger, B.: Time-lapse lab-based x-ray nano-CT study of corrosion damage. *Journal of Microscopy* **267**(1), 98–106 (2017) <https://doi.org/10.1111/jmi.12551>
- [17] Hughes, A.E., Mayo, S., Yang, Y.S., Markley, T., Smith, S.V., Sellaiyan, S., Uedono, A., Hardin, S.G., Muster, T.H.: Using X-ray tomography, PALS and Raman spectroscopy for characterization of inhibitors in epoxy coatings. *Progress in Organic Coatings* **74**(4), 726–733 (2012) <https://doi.org/10.1016/j.porgcoat.2011.06.023>. Coatings Science International 2011
- [18] Hughes, A.E., Trinchi, A., Chen, F.F., Yang, Y., Sellaiyan, S., Carr, J., Lee, P.D., Thompson, G.E., Xiao, T.Q.: Structure and transport in coatings from multiscale computed tomography of coatings—new perspectives for electrochemical impedance spectroscopy modeling? *Electrochimica Acta* **202**, 243–252 (2016) <https://doi.org/10.1016/j.electacta.2015.10.183>
- [19] Hughes, A.E., Trinchi, A., Chen, F.F., Yang, Y.S., Cole, I.S., Sellaiyan, S., Carr, J., Lee, P.D., Thompson, G.E., Xiao, T.Q.: The application of multiscale quasi 4D CT to the study of SrCrO₄ distributions and the development of porous networks in epoxy-based primer coatings. *Progress in Organic Coatings* **77**(11), 1946–1956 (2014) <https://doi.org/10.1016/j.porgcoat.2014.07.001>
- [20] Schladitz, K., Jung, C., Flenner, S., Godehardt, M., Grevelhörster, B., Greving, I., Klein, P., Konchakova, N., Redenbach, C., Visser, P., Zaninović, J.: Geometric modelling of corrosion inhibitor pigments in active protective coatings based on SR-nano-CT images. *Progress in Organic Coatings* **197**, 108762 (2024) <https://doi.org/10.1016/j.porgcoat.2024.108762>
- [21] Zaninović, J., Nogatz, T., Schladitz, K., Flenner, S., Greving, I., Klein, P., Konchakova, N., Redenbach, C., Visser, P.: Leaching in active protective coatings observed in-situ by nano-CT using synchrotron radiation. *Corrosion science* **263**, 113631 (2026) <https://doi.org/10.2139/ssrn.5674456>
- [22] Chiu, S.N., Stoyan, D., Kendall, W.S., Mecke, J.: *Stochastic Geometry and Its Applications*, 3rd edn. Wiley, Chichester (2013)
- [23] Feinauer, J., Westhoff, D., Kuchler, K., Schmidt, V.: 3d microstructure modeling and simulation of materials in lithium-ion battery cells. In: Baum, M., Brenner, G., Grabowski, J., Hanschke, T., Hartmann, S., Schöbel, A. (eds.) *Simulation Science*, pp. 128–144. Springer, Cham (2018)
- [24] Bonetti, E.: A modelling approach to study the microstructure and leaching behaviour of active protective coatings. PhD thesis, University of Manchester (2021)
- [25] Bonetti, E., Visser, P., Siperstein, F.R., Gibbon, S.R.: A cellular automaton paint to study the leaching of active corrosion inhibitors from primers. In: Féron, D.,

- di Caprio, D. (eds.) Corrosion Modelling with Cellular Automata. European Federation of Corrosion (EFC) Series, vol. 71, pp. 89–107. Woodhead Publishing, Sawston (2024). <https://doi.org/10.1016/B978-0-443-13786-0.00002-2>
- [26] Torquato, S.: Random Heterogeneous Materials: Microstructure and Macroscopic Properties. Springer, New York (2002)
 - [27] Jeulin, D.: Morphology and effective properties of multi-scale random sets: A review. *Comptes Rendus Mécanique* **340**(4), 219–229 (2012) <https://doi.org/10.1016/j.crme.2012.02.004>
 - [28] Hall, P.: On Continuum Percolation. *The Annals of Probability* **13**(4), 1250–1266 (1985) <https://doi.org/10.1214/aop/1176992809>
 - [29] Zuev, S.A., Sidorenko, A.F.: Continuous models of percolation theory I. *Theor Math Phys* **62**, 51–58 (1985) <https://doi.org/10.1007/BF01034824>
 - [30] Penrose, M.D.: On a continuum percolation model. *Advances in Applied Probability* **23**(3), 536–556 (1991) <https://doi.org/10.2307/1427621>
 - [31] Jeulin, D.: Morphological Models of Random Structures. *Interdisciplinary Applied Mathematics*, vol. 53. Springer, Cham (2021). <https://doi.org/10.1007/978-3-030-75452-5>
 - [32] Gilbert, E.N.: Random plane networks. *Journal of the Society for Industrial and Applied Mathematics* **9**(4), 533–543 (1961) <https://doi.org/10.1137/0109045>
 - [33] Haan, S.W., Zwanzig, R.: Series expansions in a continuum percolation problem. *Journal of Physics A: Mathematical and General* **10**(9), 1547 (1977) <https://doi.org/10.1088/0305-4470/10/9/013>
 - [34] Balberg, I.: Universal percolation-threshold limits in the continuum. *Phys. Rev. B* **31**, 4053–4055 (1985) <https://doi.org/10.1103/PhysRevB.31.4053>
 - [35] Jeulin, D.: Random structure models for homogenization and fracture statistics. In: Jeulin, D., Ostoj-Starzewski, M. (eds.) *Mechanics of Random and Multiscale Microstructures*, pp. 33–91. Springer, Vienna (2001). https://doi.org/10.1007/978-3-7091-2780-3_2
 - [36] Mourzenko, V.V., Thovert, J.-F., Adler, P.M.: Percolation of three-dimensional fracture networks with power-law size distribution. *Phys. Rev. E* **72**, 036103 (2005) <https://doi.org/10.1103/PhysRevE.72.036103>
 - [37] Khamforoush, M., Shams, K.: Percolation thresholds of a group of anisotropic three-dimensional fracture networks. *Physica A: Statistical Mechanics and its Applications* **385**(2), 407–420 (2007) <https://doi.org/10.1016/j.physa.2007.07.037>

- [38] Xu, W., Jiao, Y.: Theoretical framework for percolation threshold, tortuosity and transport properties of porous materials containing 3d non-spherical pores. *International Journal of Engineering Science* **134**, 31–46 (2019) <https://doi.org/10.1016/j.ijengsci.2018.10.004>
- [39] Xu, W., Zhu, Z., Jiang, Y., Jiao, Y.: Continuum percolation of congruent overlapping polyhedral particles: Finite-size-scaling analysis and renormalization-group method. *Phys. Rev. E* **99**, 032107 (2019) <https://doi.org/10.1103/PhysRevE.99.032107>
- [40] Xu, W., Zhang, Y., Jiang, J., Liu, Z., Jiao, Y.: Thermal conductivity and elastic modulus of 3d porous/fractured media considering percolation. *International Journal of Engineering Science* **161**, 103456 (2021) <https://doi.org/10.1016/j.ijengsci.2021.103456>
- [41] Otten, R.H.J., Schoot, P.: Continuum percolation of polydisperse nanofillers. *Phys. Rev. Lett.* **103**, 225704 (2009) <https://doi.org/10.1103/PhysRevLett.103.225704>
- [42] Jeulin, D., Moreaud, M.: Multi-scale simulation of random spheres aggregates-application to nanocomposites. In: 9th European Congress on Stereology and Image Analysis, Zakopane, Poland, vol. 1, pp. 341–348 (2005)
- [43] Jeulin, D., Moreaud, M.: Percolation of random cylinder aggregates. *Image Analysis and Stereology* **26**(3), 121–127 (2007) <https://doi.org/10.5566/ias.v26.p121-127>
- [44] Emad, S.G.R., Zhou, X., Morsch, S., Lyon, S.B., Liu, Y., Graham, D., Gibbon, S.R.: How pigment volume concentration (PVC) and particle connectivity affect leaching of corrosion inhibitive species from coatings. *Progress in Organic Coatings* **134**, 360–372 (2019) <https://doi.org/10.1016/j.porgcoat.2019.05.008>
- [45] Visser, P., Liu, Y., Zhou, X., Hashimoto, T., Thompson, G.E., Lyon, S.B., Ven, L.G.J., Mol, A.J.M.C., Terry, H.A.: The corrosion protection of AA2024-T3 aluminium alloy by leaching of lithium-containing salts from organic coatings. *Faraday Discussions* **180**, 511–526 (2015) <https://doi.org/10.1039/c4fd00237g>
- [46] Seitz, F., Petrich, L., Staněk, J., Krill, C., Schmidt, V., Benes, V.: Exploration of Gibbs-Laguerre tessellations for three-dimensional stochastic modeling. *Methodology and Computing in Applied Probability* **23**, 669–693 (2021) <https://doi.org/10.1007/s11009-019-09757-x>
- [47] Ohser, J., Schloditz, K.: 3d Images of Materials Structures – Processing and Analysis. Wiley VCH, Weinheim (2009)
- [48] Barequet, G., Har-Peled, S.: Efficiently approximating the minimum-volume bounding box of a point set in three dimensions. *J. Algorithms* **38**(1), 91–109

- (2001) <https://doi.org/10.1006/jagm.2000.1127>
- [49] Vecchio, I., Schladitz, K., Godehardt, M., Heneka, M.: 3d geometric characterization of particles applied to technical cleanliness. *Image Analysis and Stereology* **31**(3), 163–174 (2012)
 - [50] Buze, M., Feydy, J., Roper, S.M., Sedighiani, K., Bourne, D.P.: Anisotropic power diagrams for polycrystal modelling: Efficient generation of curved grains via optimal transport. *Computational Materials Science* **245**, 113317 (2024) <https://doi.org/10.1016/j.commatsci.2024.113317>
 - [51] Fick, A.: On liquid diffusion. *Journal of Membrane Science* **100**(1), 33–38 (1995) [https://doi.org/10.1016/0376-7388\(94\)00230-V](https://doi.org/10.1016/0376-7388(94)00230-V) . The early history of membrane science selected papers celebrating vol. 100
 - [52] Furman, S.A., Scholes, F.H., Hughes, A.E., Lau, D.: Chromate leaching from inhibited primers: Part ii: Modelling of leaching. *Progress in Organic Coatings* **56**(1), 33–38 (2006) <https://doi.org/10.1016/j.porgcoat.2006.01.016>
 - [53] Laird, J., Visser, P., Ranade, S., Hughes, A.E., Terryn, H., Mol, J.M.C.: Li leaching from lithium carbonate-primer: An emerging perspective of transport pathway development. *Progress in Organic Coatings* **134** (2019) <https://doi.org/10.1016/j.porgcoat.2019.04.062>
 - [54] Donkers, P.A.J., Huinink, H.P., Erich, S.J.F., Reuvers, N.J.W., Adan, O.C.G.: Water permeability of pigmented waterborne coatings. *Progress in Organic Coatings* **76**(1), 60–69 (2013) <https://doi.org/10.1016/j.porgcoat.2012.08.011>
 - [55] Kopeć, M., Rossenaar, B.D., Leerdam, K., Janssen, A., Davies, A.N., Lyon, S.B., Visser, P., Gibbon, S.R.: Influence of TiO₂ pigment particles on chromate ion transport in epoxy films. *npj Mater Degrad* **5**(9) (2021) <https://doi.org/10.1038/s41529-021-00156-7>
 - [56] Sellaiyan, S., Hughes, A.E., Smith, S.V., Uedono, A., Sullivan, J., Buckman, S.: Leaching properties of chromate-containing epoxy films using radiotracers, PALS and SEM. *Progress in Organic Coatings* **77**(1), 257–267 (2014) <https://doi.org/10.1016/j.porgcoat.2013.09.014>
 - [57] Prill, T., Fischer, C., Gavrilenko, P., Iliev, O.: Implementing the variability of crystal surface reactivity in reactive transport modeling. *Transport in Porous Media* **140**(2), 535–557 (2021)
 - [58] Winardhi, C.W., Godinho, J.R.d.A., Gutzmer, J.: The effect of macroscopic particle features on mineral dissolution. *Minerals* **13**(2), 253 (2023)
 - [59] Memmesheimer, M.A., Redenbach, C.: Fitting the topology of synthetic particle systems with a novel graph representation (2026). <https://doi.org/10.48550/>

