

MODEL BASED TUNING OF THE RELEASE OF SELF HEALING AGENTS FROM ORGANIC COATINGS: FROM FICKIAN TO CONTROLLED RELEASE KINETICS

E. Javierre^{1,2}, S.J. García³, J.M.C. Mol⁴, F.J. Vermolen⁵, C. Vuik⁵, S. van der Zwaag³

¹Centro Universitario de la Defensa - AGM, Ctra. Huesca s/n, 50090 Zaragoza. Spain.

²Aragón Institute of Engineering Research (I3A), Universidad de Zaragoza. Spain.

Email: etelvina.javierre@unizar.es

³Faculty of Aerospace Engineering, Delft University of Technology.

Kluyverweg 1, 2629 HS Delft. The Netherlands.

Email: S.J.GarciaEspallargas@tudelft.nl, S.vanderZwaag@tudelft.nl

⁴Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology.

Mekelweg 2, 2628 CD Delft. The Netherlands.

Email: J.M.C.Mol@tudelft.nl

⁵Delft Institute of Applied Mathematics, Delft University of Technology.

Mekelweg 4, 2628 CD Delft. The Netherlands.

Email: F.J.Vermolen@tudelft.nl, c.vuik@tudelft.nl

Keywords: Self-healing, Pigment release, Corrosion inhibition, Fickian, Non-Fickian, Modelling

ABSTRACT

Coatings are a cheap and efficient solution to protect underlying metallic substrates against electrochemical corrosion. High performance coatings do not only provide this protection of the substrate in the undamaged state but also when they are scratched. This enhanced protection can be achieved in many different ways (ranging from primers based on expansive phases which seal the crack upon scratch [1] to encapsulated healing agents which polymerize when disrupted by the crack [2]). This work focuses on the behaviour of self healing organic coatings carrying corrosion inhibitors that are stored in one of the coating layers, usually the primer [3]. These inhibitor particles will not restore the coating surface topology, but will prevent oxidation at the exposed substrate.

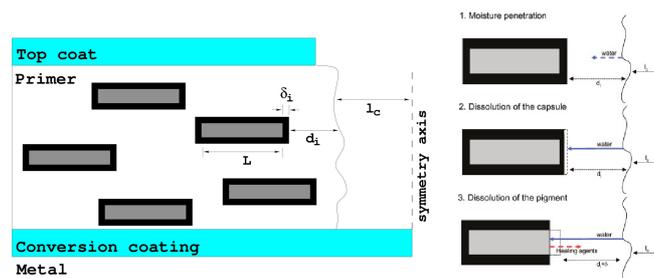


Figure 1: Left: schematic of a fractured organic coating that contains several encapsulated pigments dispersed through the primer. Right: response in a fractured coating -water uptake (top), capsule disruption (center), and leaching of corrosion inhibitors (bottom)- modelled in this study.

In this type of coatings, regardless of the inhibitor type, the corrosion protection mechanism is activated by the ingress of moisture via the crack towards the dispersed corrosion inhibitor particles (see schematic diagram in Figure 1). Moisture in the primer makes these particles dissolve and serves as a transport medium for the inhibitor pigments towards the exposed metallic substrate in the crack. Once in the crack, these compounds react with the electrolyte and thereby a passivation zone, which inhibits corrosion appears. Clearly, the corrosion inhibitors act as functional healing agents. The leaching rate of these compounds determines the system corrosion protection: a very fast initial release

could lead to the waste of pigments, whereas too slow a release may not provide enough inhibitors to the exposed substrate to fight corrosion.

A large number of experimental studies have addressed the leaching kinetics for several coating-inhibitor systems, and the obtained largely differing kinetics range from release behaviour proportional to $t^{0.25}$ to that to logarithmic time scales [3-4]. However, the experimental studies do not offer any clues as how to obtain a desired more constant release rate over longer exposure times.

In this work we use a mathematical-analytical model that combines the moisture absorption, corrosion inhibitor particle dissolution and pigment transport to the crack of each individual particle in the coating to predict the overall leaching kinetics. These stages are approached as phase transformations under equilibrium conditions using Fickian diffusion models, which allow a full characterization of the inhibitor leaching history as a function of the particle position within the primer and its diffusion rate. After this, the leaching history of all particles is assembled to find the needed physico-chemical properties of the coating that yield the prescribed leaching rate. Despite the release rate of each individual particle is Fickian, the overall release may show different trends. Figure 2 shows the results for a configuration with four particles located at 10, 12.5, 15 and 17.5mm from the crack. For this configuration, three different release kinetics ($t^{0.5}$, $t^{0.75}$ and t) are obtained by changing the times at which the particles become activated, which depend on the coating moisture absorption and capsule dissolution kinetics.

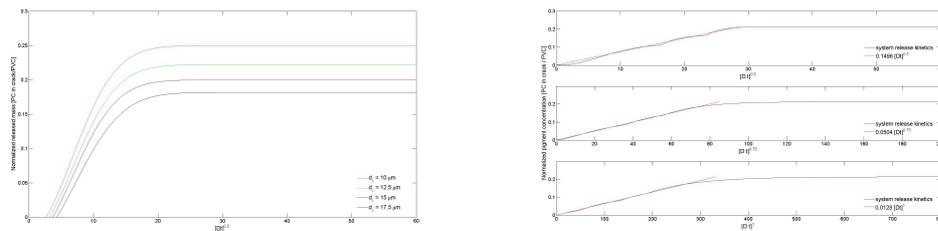


Figure 2: Left: release kinetics of each single particle in the configuration (d_c denotes the distance from the particles to the crack). Right: overall configuration release kinetics for specific particle activation times.

The current model depends on the corrosion inhibitor particle dissolution kinetics only, though, it allows a first qualitative prediction of the optimal particle distribution density that gives the desired healing kinetics. The model will be expanded with features dealing with moisture absorption kinetics and with particle capsule dissolution kinetics, in order to complete the optimization of the coating-inhibitor particle distribution, which is needed to obtain ideal self healing kinetics.

REFERENCES

- [1] F. Micciche, H. Fischer, R.J. Varley and S. van der Zwaag, Moisture induced crack filling in barrier coatings containing montmorillonite as an expandable phase, *Surface & Coatings Technology*, **202**, 2008, pp. 3346-3353.
- [2] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown and S. Viswanathan, Autonomic healing of polymer composites, *Nature*, **409**, 2001, pp. 794-797.
- [3] S.A. Furman, F.H. Scholes, A.E. Hughes, D.N. Jamieson, C.M. Macrae, A.M. Glenn, Corrosion in artificial defects. II. Chromate reactions, *Corrosion Science*, **48**, 2006, pp. 1827-1847.
- [4] A. Nazarov, D. Thierry, T. Prosek, N. Le Bozec, Protective Action of Vanadate at Defected Areas of Organic Coatings on Zinc, *Journal of The Electrochemical Society*, **152**, 2006, pp. B220-B227.