The University of Manchester

H2020-MSCA-ITN-2016/721451

# PARTICLE LEACHING FROM POLYMERIC COATINGS
# A Combined Experimental and Simulation Study


*Eugenio Bonetti –AkzoNobel, Malmö, SE and CEAS, The University of Manchester, UK*

*Ander Cervellera-Dominguez – AkzoNobel, Sassenheim, NED and School of Materials, The University of Manchester, UK*

*Peter Visser – AkzoNobel, Sassenheim, NED*

*Simon Gibbon – AkzoNobel, Felling, UK*

*Professor Xiaorong Zhou – School o Materials, The University of Manchester, UK*

*Flor R. Siperstein – CEAS, The University of Manchester, UK*


**FORMULA X**

**Manchester, UK**

# Introduction

## Active corrosion protection by organic coatings in Aerospace

### Corrosion in modern world

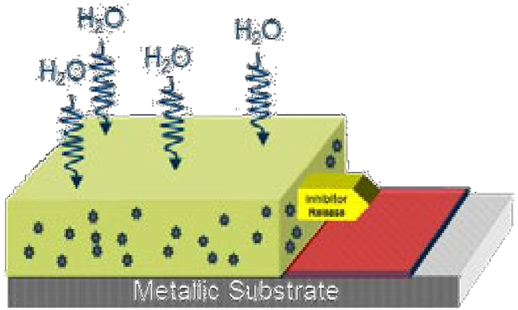
- Corrosion cost: 2.5 trillion US$ - 4% percent of the global Gross Domestic Product (GDP)
- 20-35% of this loss could have been saved by implementing better corrosion preventing practices. German, T. & Section, N. Corrosion news. 140 146 (2018).

**In the aerospace industry corrosion impacts**

- Cost
- Aircraft availability
- **Safety**
- **Social**

<u>October 1992, The Netherlands:</u>
Fatigue corrosion cracking
https://aviation-safety.net/database/record.php?id=19921004-2

### Organic coatings provide corrosion protection




**Key steps for corrosion inhibition via leaching**

1. Water uptake
2. Dissolution of active pigment
3. Transport and delivery of active species through the polymeric matrix to de defect area
4. Fast, effective, and irreversible passivation

O Gharbi et al. *Npj Materials Degradation*, **2**, 12 (2018)

<u>April 1988, Hawaii:</u> Fatigue corrosion cracking
https://faculty.up.edu/lulay/me401/aloha_flight_243_a_new_direction.pdf

# Introduction

## Active corrosion protection by organic coatings in Aerospace

### Challenge

**Develop coatings that are:**

- **Environmentally friendly**
- **Sustainable**
- **Efficient**
- **Cost effective**

### Approach

- **Replacing toxic chemicals (chromates)**
- **Use renewable materials**
- **Understand and optimise performance**
- **Minimise use of expensive materials**

UNDERSTAND LEACHING OF INHIBITORS FROM ORGANIC COATINGS

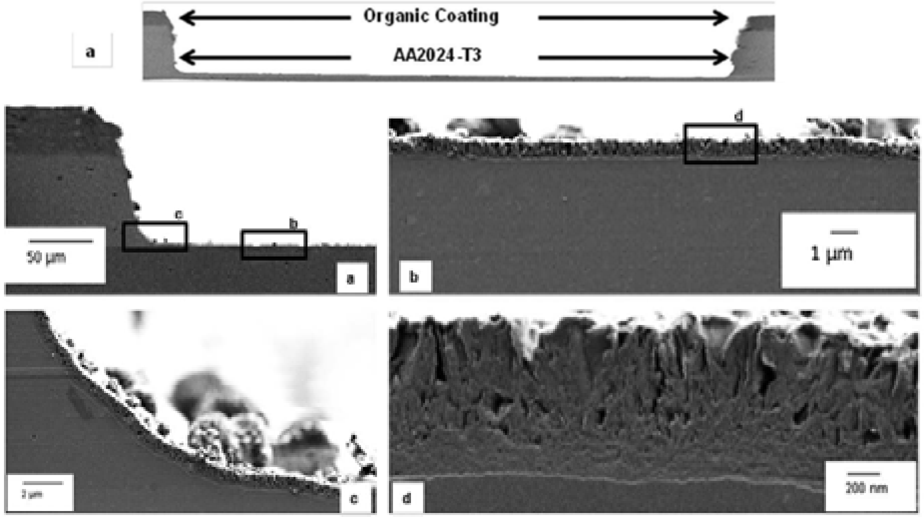
UNDERSTAND THE RELATIONSHIP BETWEEN LEACHING AND PERFORMANCE

# Introduction

## Lithium leaching technology protection concept

Provide fast, **effective**, and **irreversible** corrosion inhibition

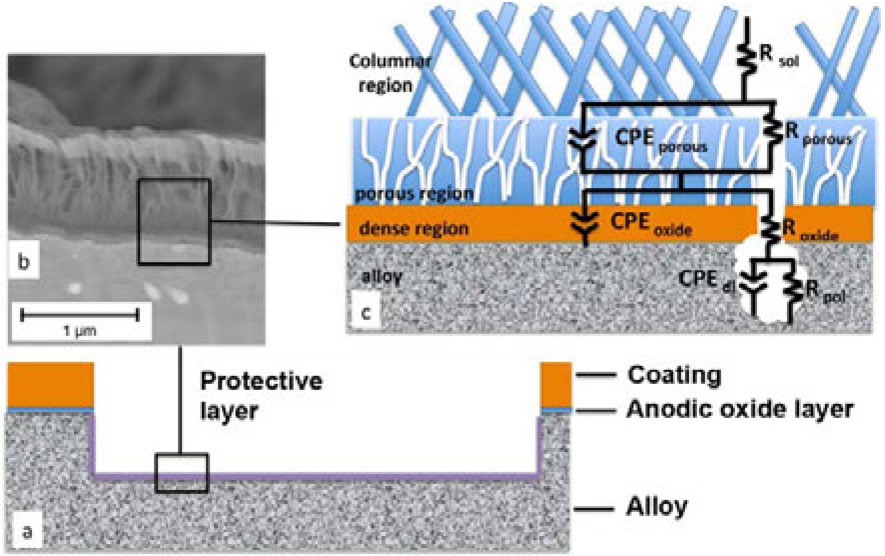
1. Leaching of lithium ions
2. Lithium ion transport to defect area
3. Formation of a protective layer on the aluminium substrate




Visser et al. *Faraday Discuss.* **180**, 511-526 (2015)

Fitting with physical model

- Oxide layer provides corrosion protective properties




Visser et al. *Journal ofThe Electrochemical Society*, **164** (7) C396-C406 (2017)

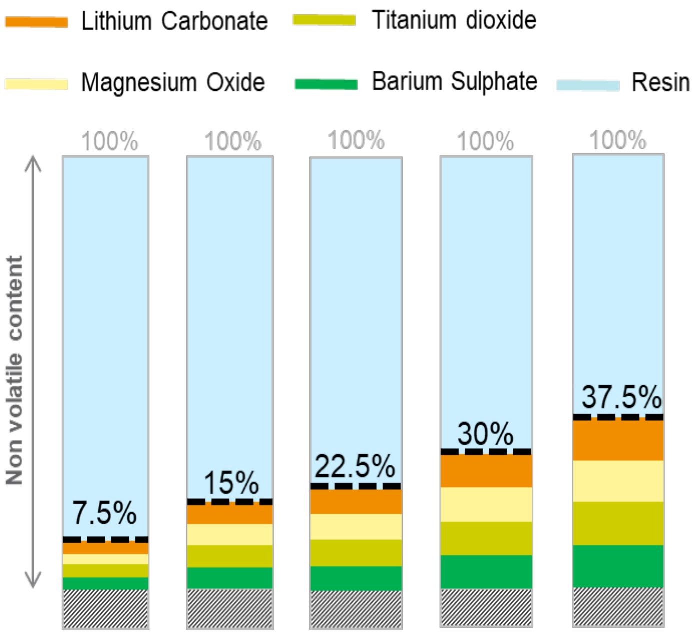


H2020-MSCA-ITN-2016/721451

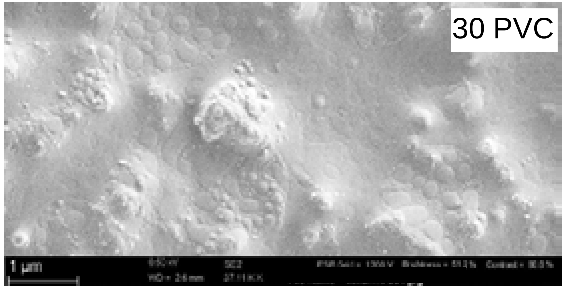
# The effect of the PVC

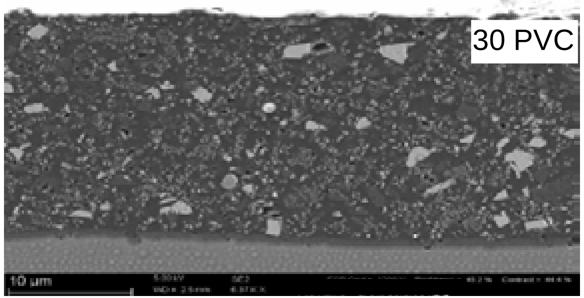
## Systems of study and microstructure analysis

**Epoxy model system with PVCs between 7.5 – 37.5%**
Pigment ratios constant

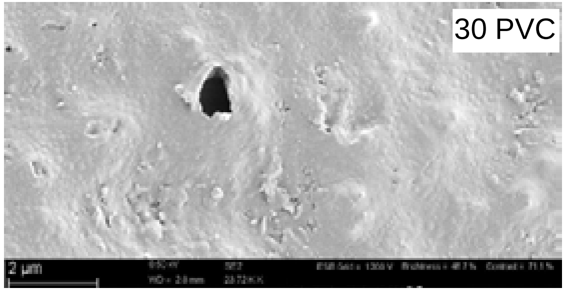


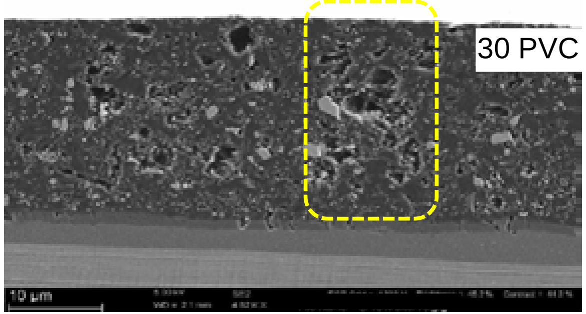

**Before exposure**




**After 2 weeks exposure to 3.5% NaCl solution**



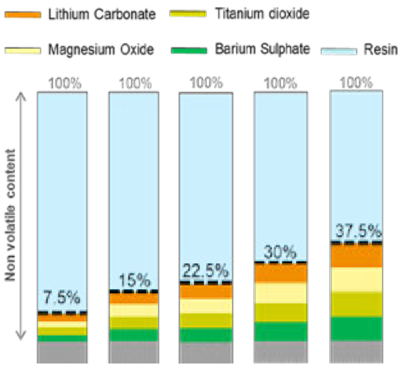



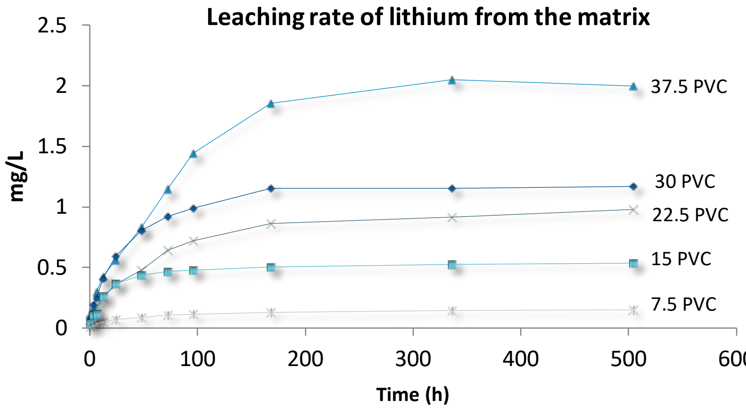
# The effect of the PVC

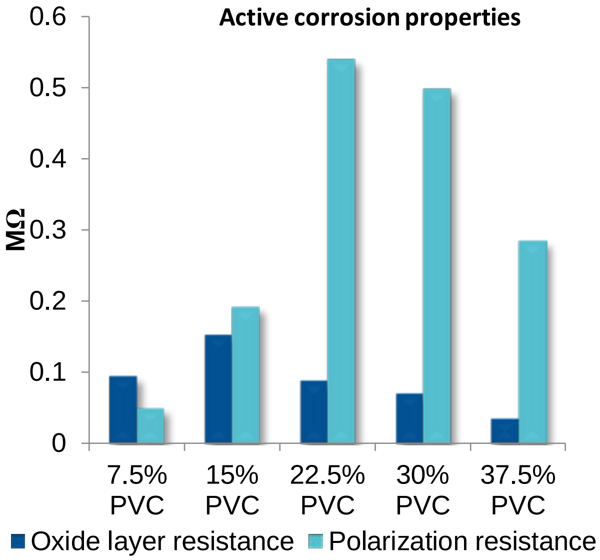
## Lithium leaching and corrosion protection properties

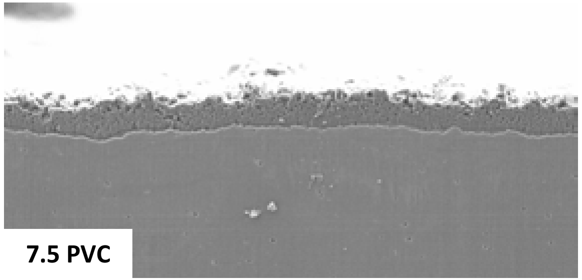
**Epoxy model system with PVCs between 7.5 – 37.5%**

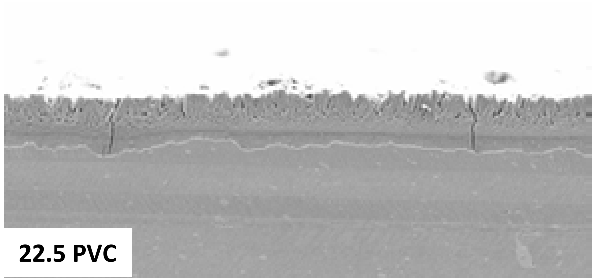
Pigment ratios constant

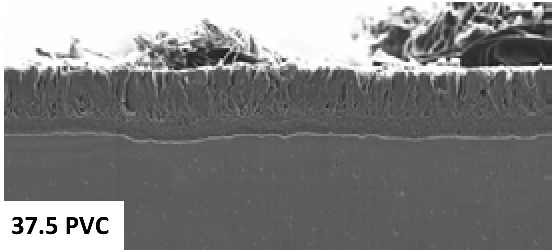





H2020-MSCA-ITN-2016/721451

# The effect of the PVC

**Higher pigment volume concentration result in higher leaching rates and faster exhaustion of the system**

- Larger network of interconnected pigment clusters

**Increase of pigment volume concentration decrease the barrier properties of the coating**

- Formation of defects through the polymeric matrix which enhance water permeation

**Slower dissolution rate leads to higher $R_{oxid}$ and $R_{pol}$** – Better active corrosion protection

**Can we control the rate of release?**

**Can we control the amount released?**

**Develop a model that describes the leaching of inhibitors with sufficient accuracy to explore the formulation space and inform what are the desirable features or properties of the coating and inhibitor**

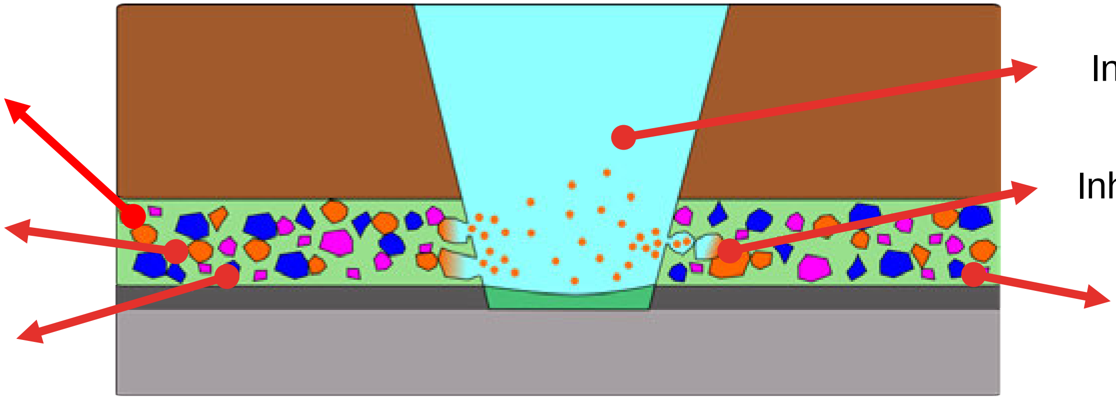

H2020-MSCA-ITN-2016/721451

# Release of corrosion inhibitors

Binder properties

Particles microstructure

Pigment volume concentration



Inhibitor solubility

Inhibitor dissolution rate

Fillers

**Cellular Automata Model is a good compromise to model the release of inhibitors:**

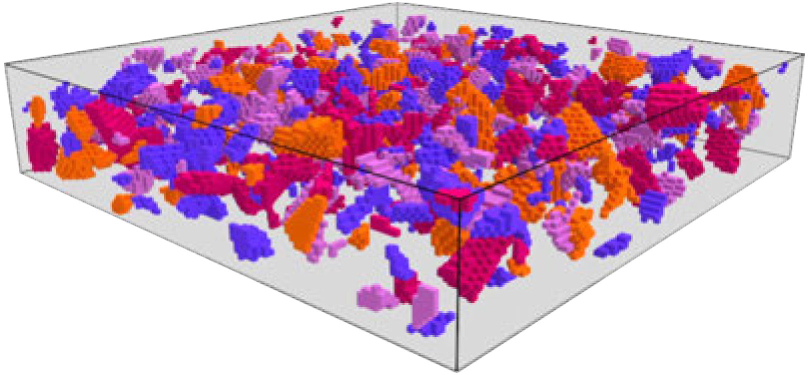
- ✓ Can capture different physical phenomena
- ✓ Can be related to real physical properties of the system
- ✓ Computationally efficient



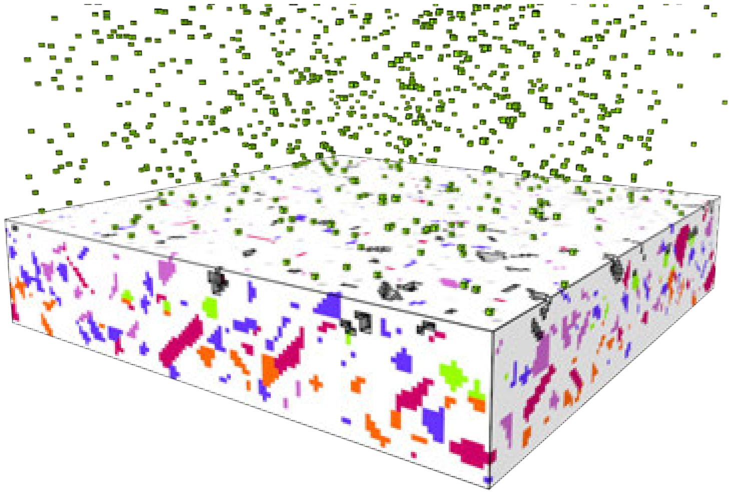
H2020-MSCA-ITN-2016/721451

# Approach

**Microstructure generation**



**Release simulation**

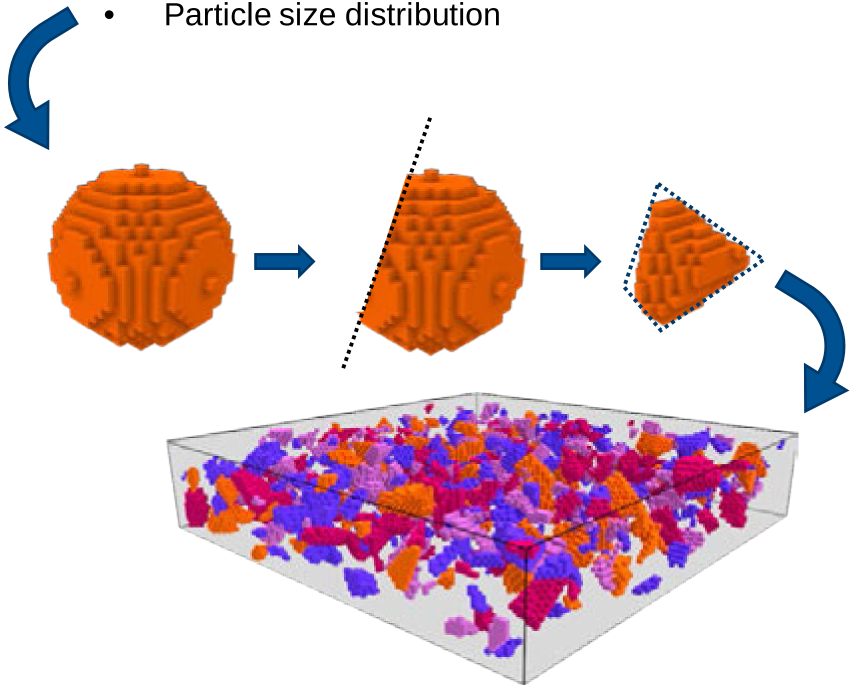




H2020-MSCA-ITN-2016/721451

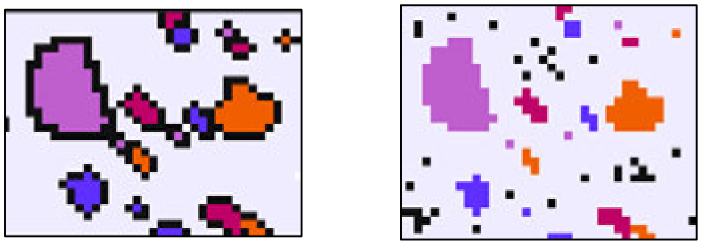
# Microstructure generation

- Pigment volume concentration
- Particle size distribution



Clusters formation

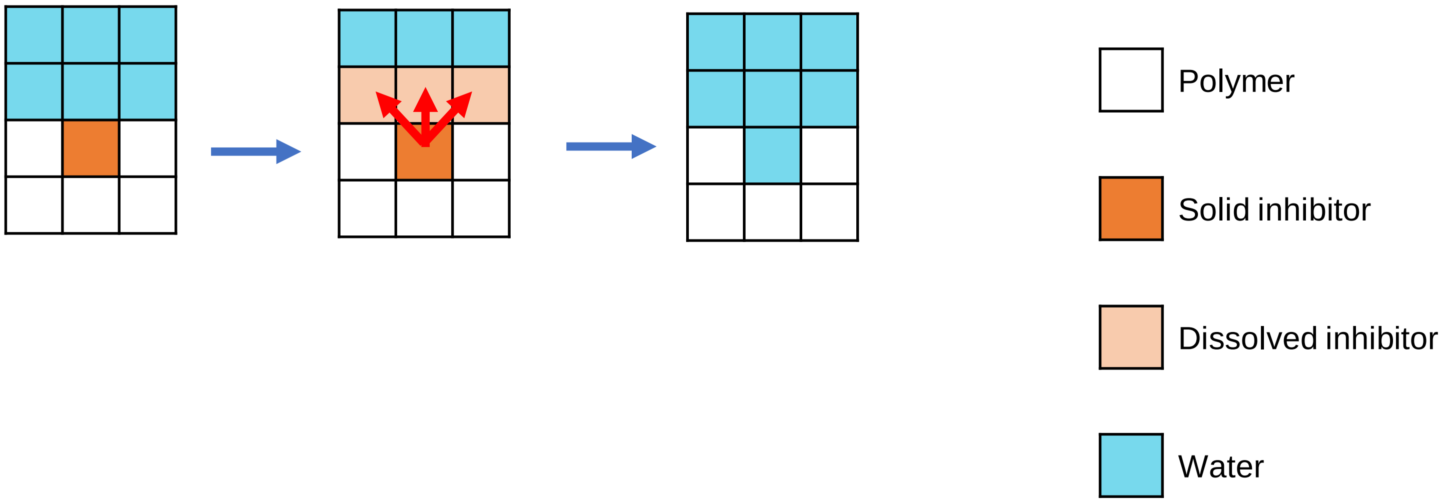
Permeable heterogeneities



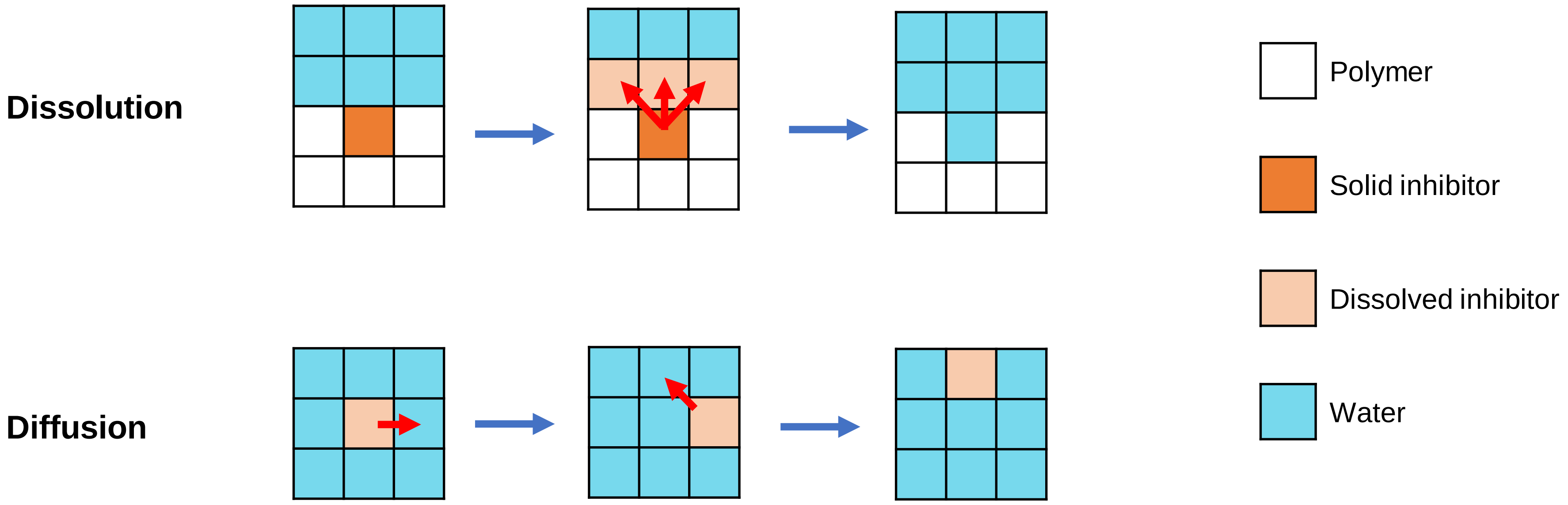

H2020-MSCA-ITN-2016/721451

# Release simulation

**Dissolution**

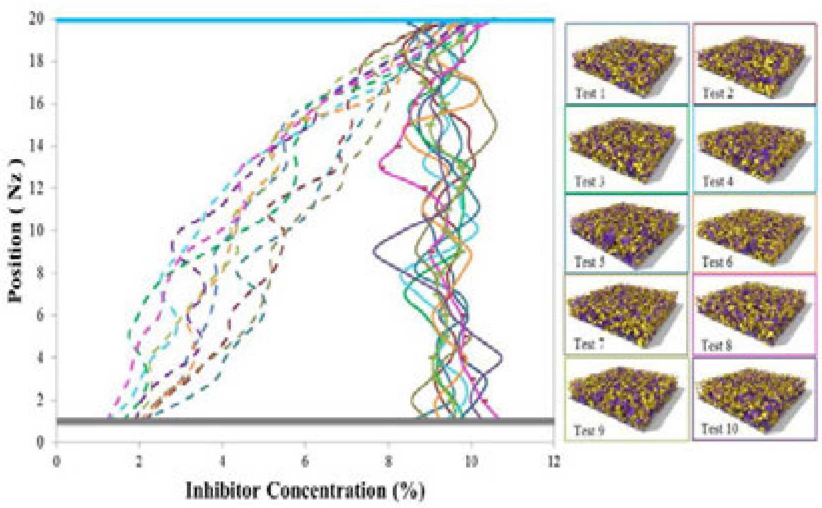


# Release simulation

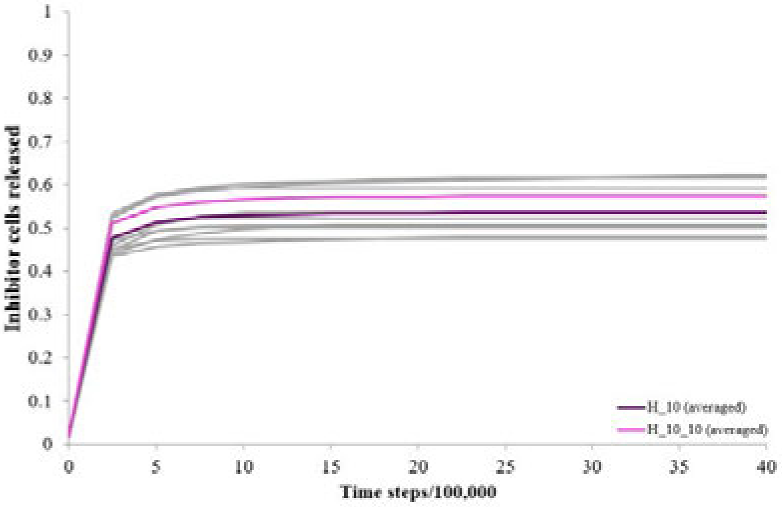


# Results

## Total and connected inhibitor concentration




## Release curves

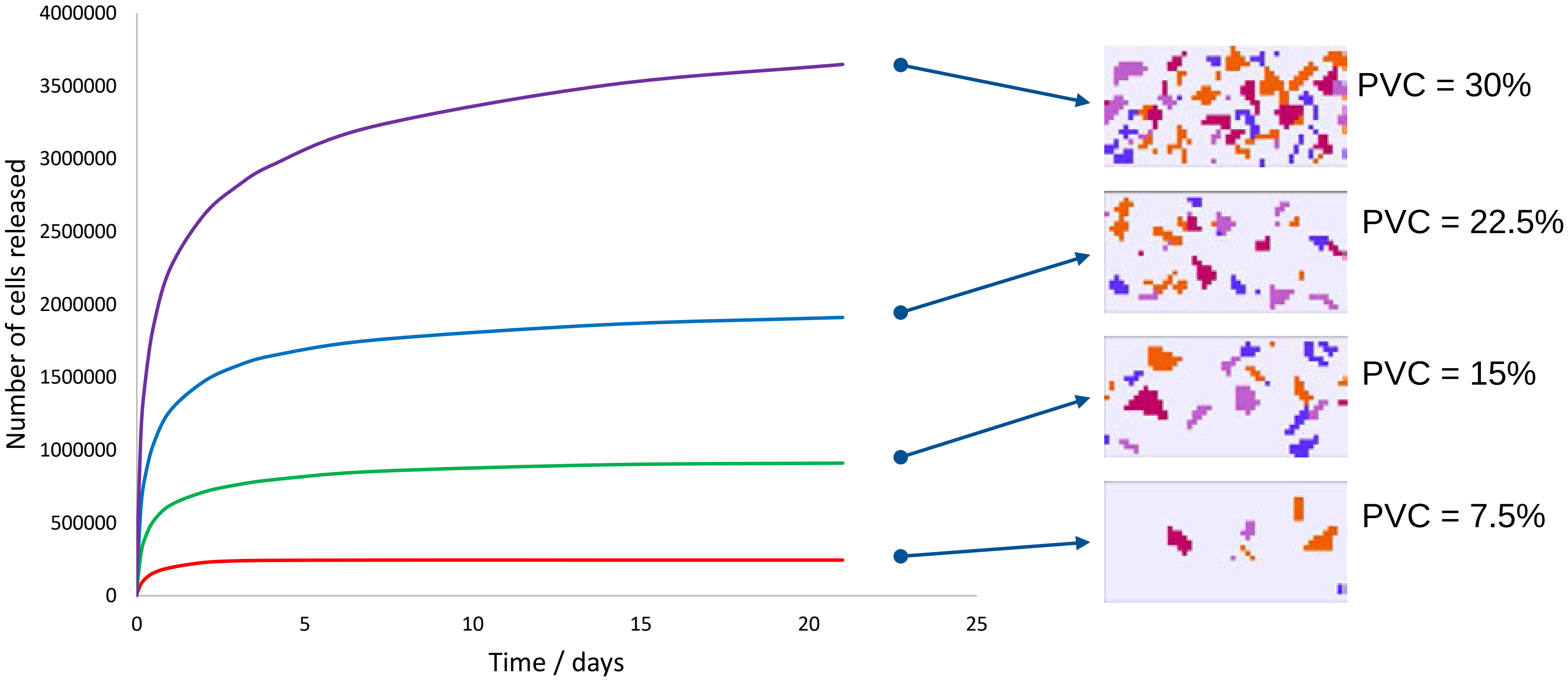



Random distribution of inhibitor particles results in unique connectivity profiles.
Averages are needed over multiple configurations to represent real systems



H2020-MSCA-ITN-2016/721451

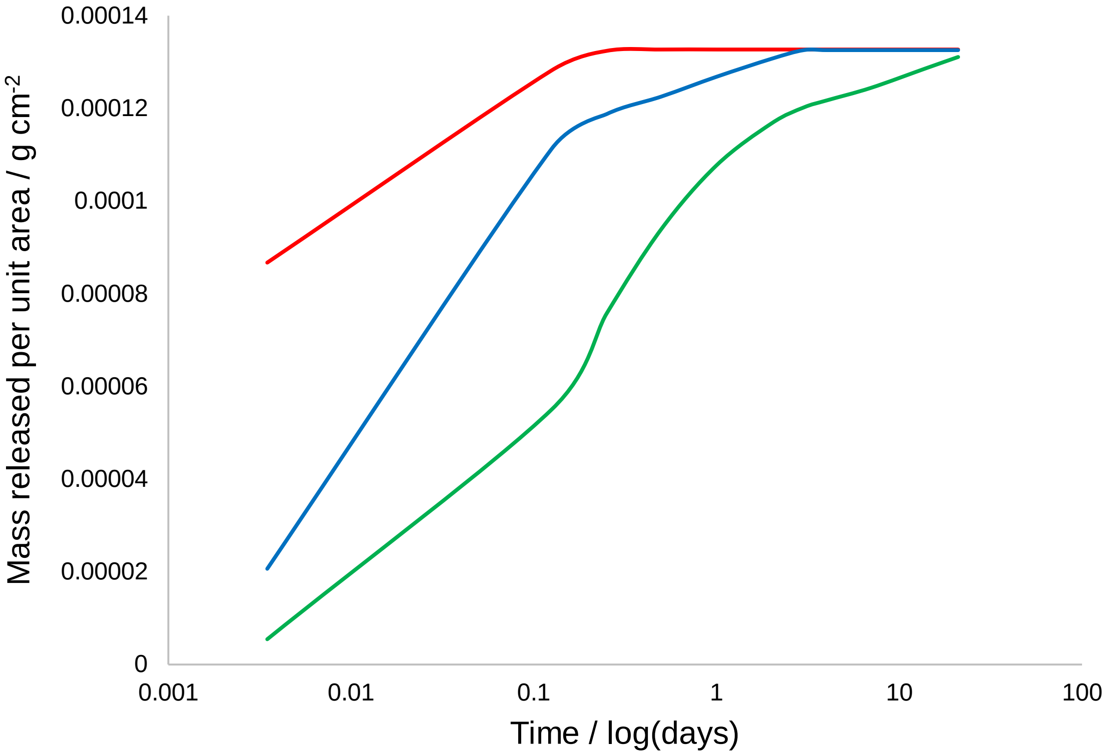
# Effect of PVC






H2020-MSCA-ITN-2016/721451

# Effect of solubility



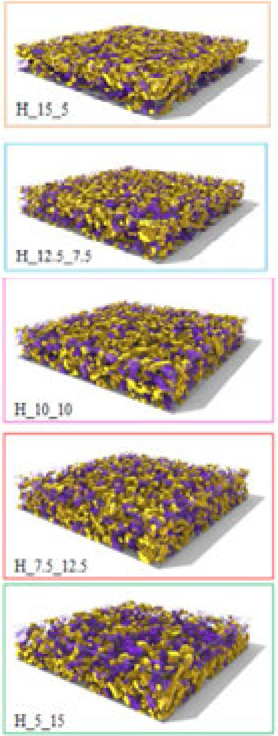

**Solubility**

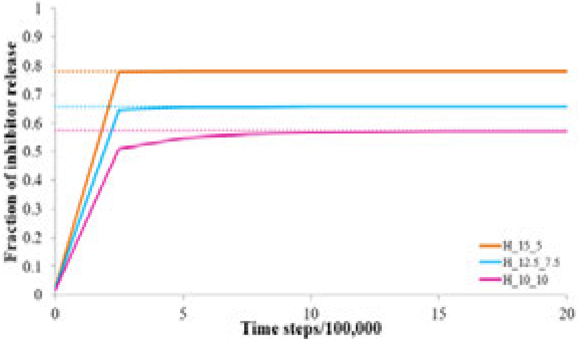
S = 0.13 g/cm$^3$

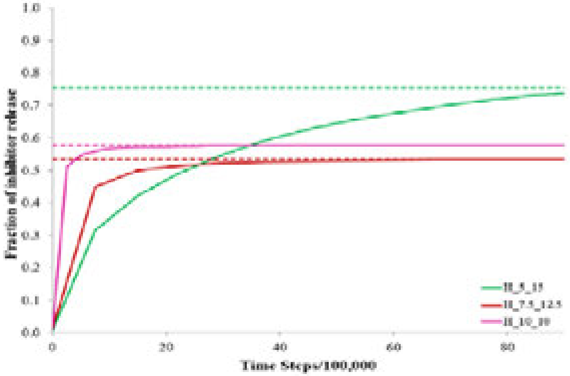
S = 0.013 g/cm$^3$

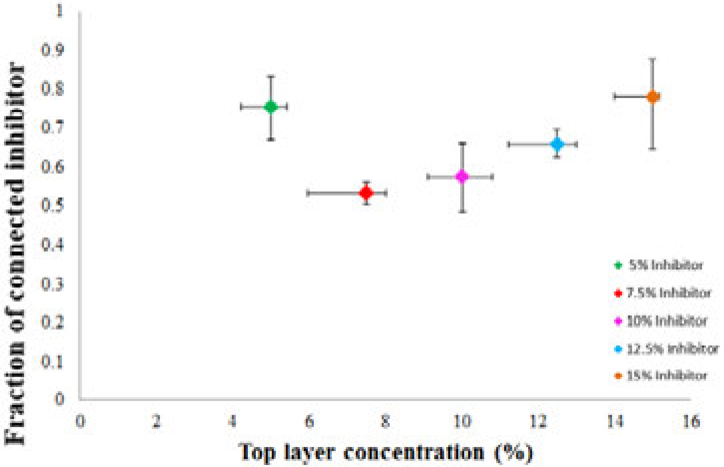
S = 0.0013 g/cm$^3$

# Effect of particle distribution



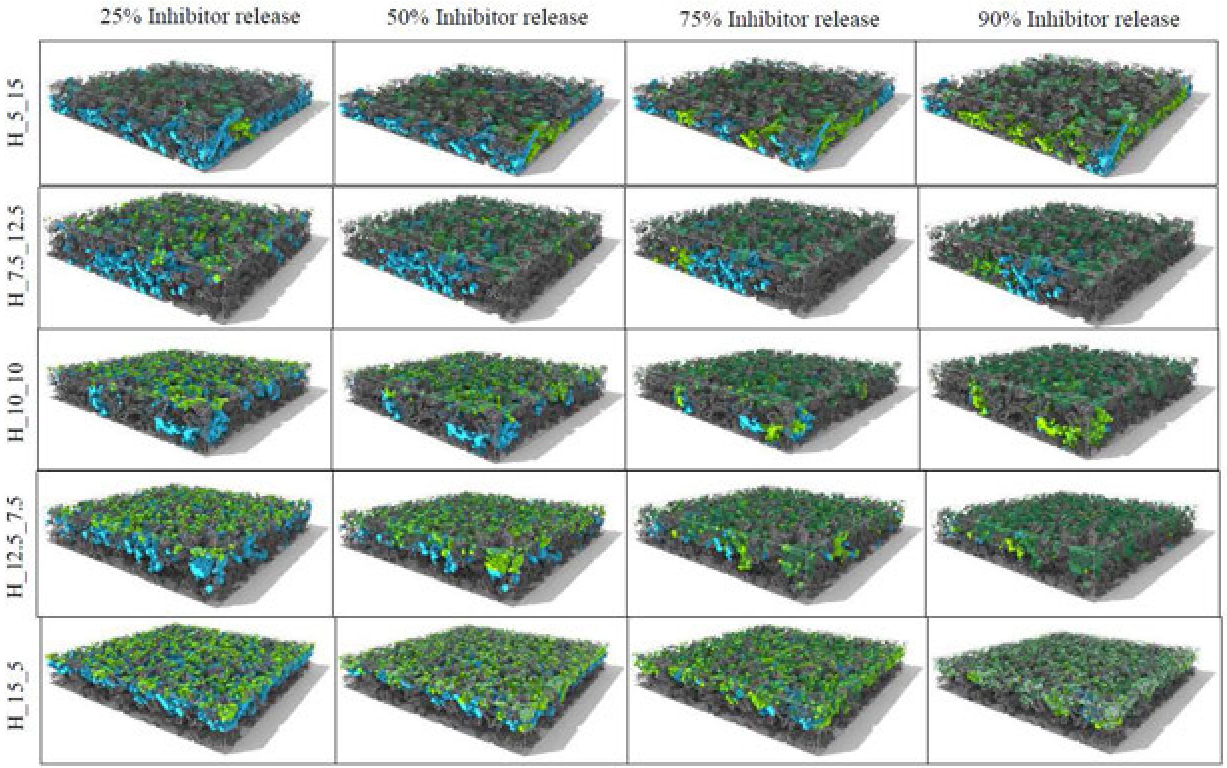

Spatial heterogeneity can affect the connectivity between inhibitor particles



H2020-MSCA-ITN-2016/721451

AkzoNobel MANCHESTER 1824 SUSTICOAT

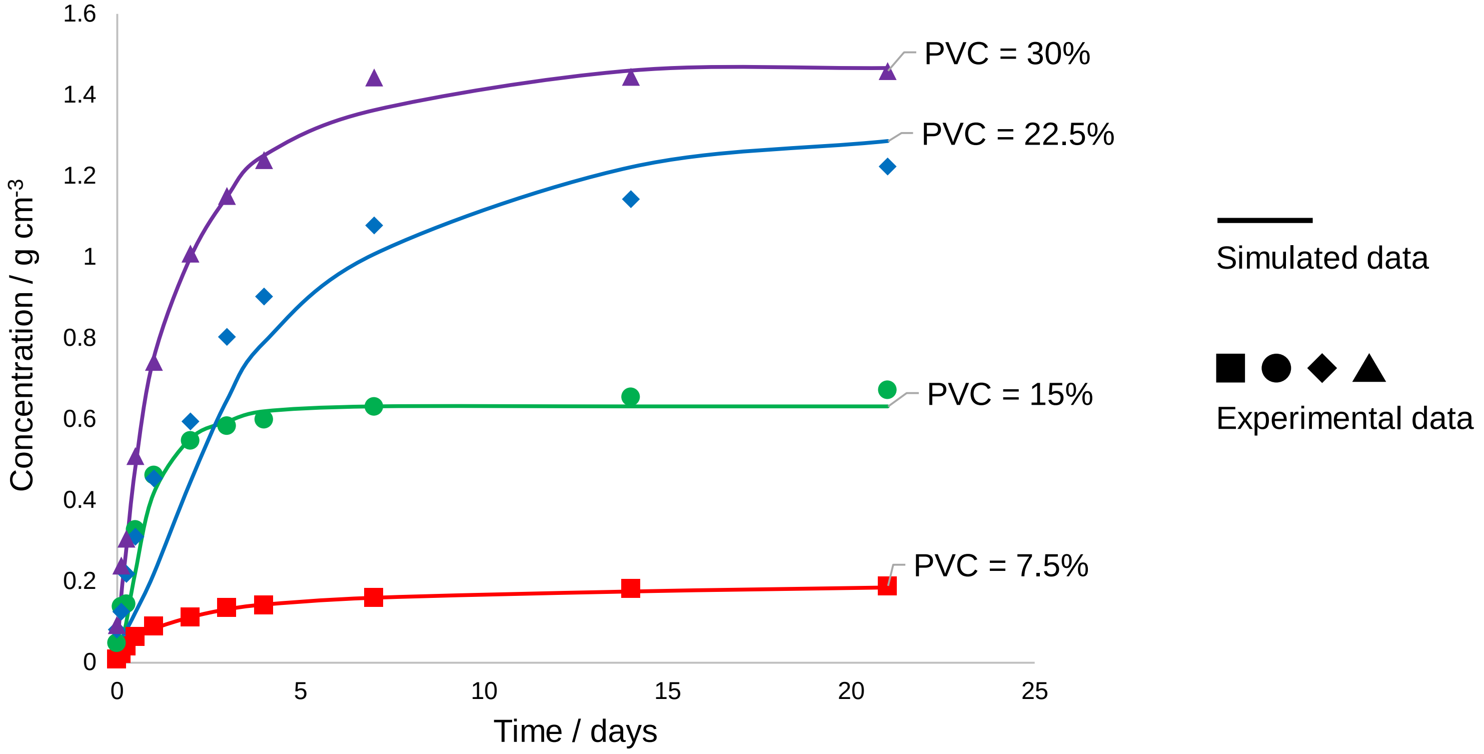
# Effect of particle distribution





H2020-MSCA-ITN-2016/721451

# Comparison with experimental data






H2020-MSCA-ITN-2016/721451

# Conclusions

- The release of corrosion inhibitors from primer coatings can be modelled using the **CA approach**
- Models can show the influence of **microstructure** and **pigment properties** on the release, enabling **control** on the factors that affect the process
- Simulations can provide important insight on the structure-property relationship in complex coatings to enable **optimal formulation design**


H2020-MSCA-ITN-2016/721451

# Acknowledgments

Dr. Yanwen  Liu

Ms Maria Georgiades

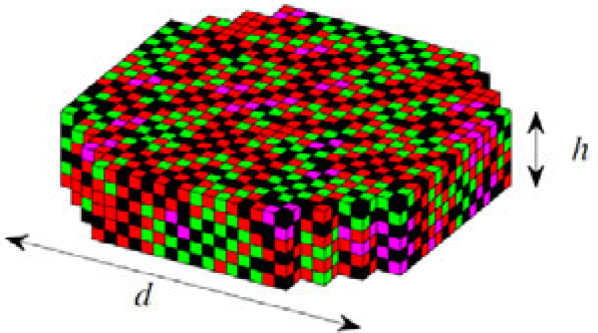
Assistance given by the IT Services and the use of the Computational Shared Facility at the University of Manchester.

University of Manchester – AkzoNobel Corrosion Protection Partnership

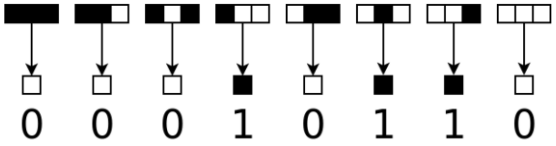
This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 721451

# Cellular Automata model

**Discrete approach**




**Transition rules**




**Locality**