# pH-Triggered Release of $NaNO_2$ from Novel Colophony Microcapsules in Simulated Concrete Pore Solution

**J. Ress, U. Martin, J. Bosch, *D.M. Bastidas**

**ACS Applied Material & Interfaces**

National Center for Education and Research on Corrosion and Materials Performance,
NCERCAMP-UA, Dept. Chemical, Biomolecular, and Corrosion Engineering,
The University of Akron, 302 E Buchtel Ave, Akron, OH 44325-3906, USA.

# Contents



# INTRODUCTION

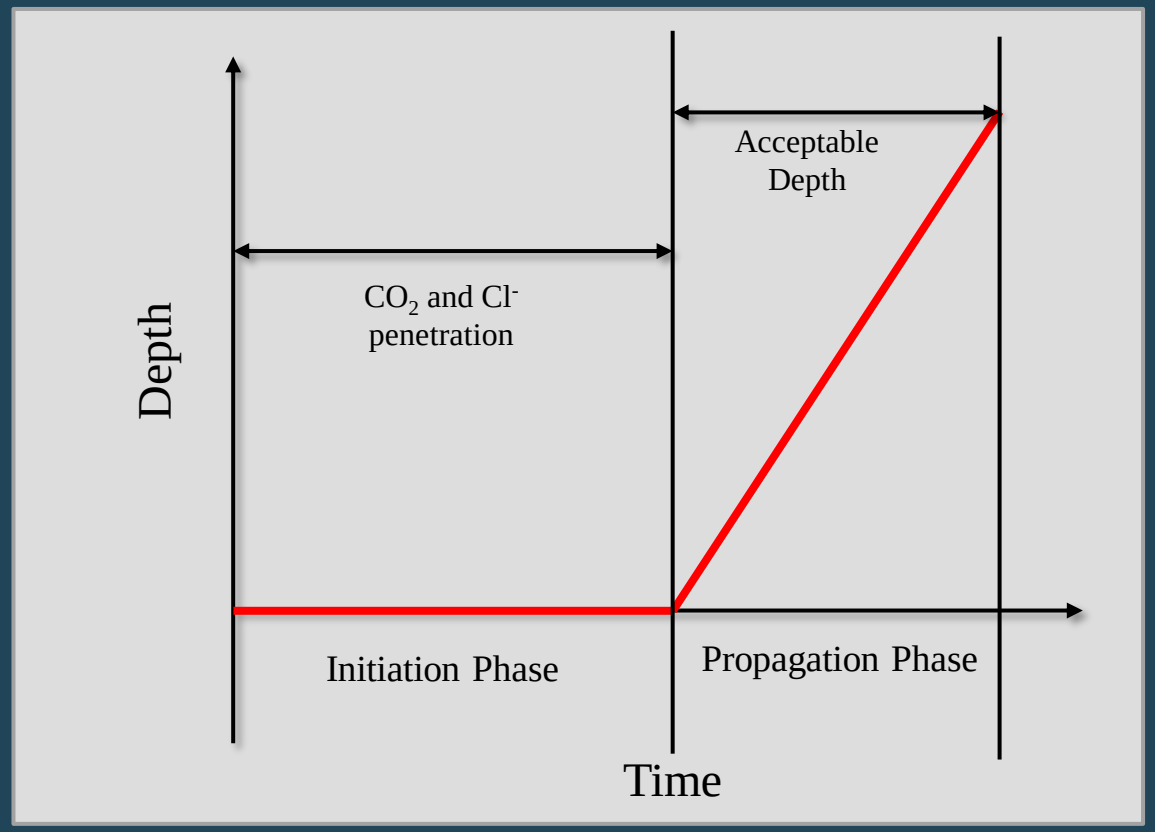
# Background

Photo credit: Charlotte Observer

- Corrosion of steel reinforced concrete presents a significant threat to the US and global economy
  - An estimated 4% of GDP over all industrialized countries in 2018,
    - Raoul François, Stéphane Laurens, Fabrice Deby, 1 - Steel Corrosion in Reinforced Concrete, Editor(s): Raoul François, Stéphane Laurens, Fabrice Deby, Corrosion and its Consequences for Reinforced Concrete Structures, Elsevier, (2018): 1-41
  - When steel corrodes, the volume expands and cracks the concrete, thus damaging the overall structure
- In 2000, Lowes Motor Speedway Bridge collapsed in Raleigh N.C. due to corrosion causing 100 injuries

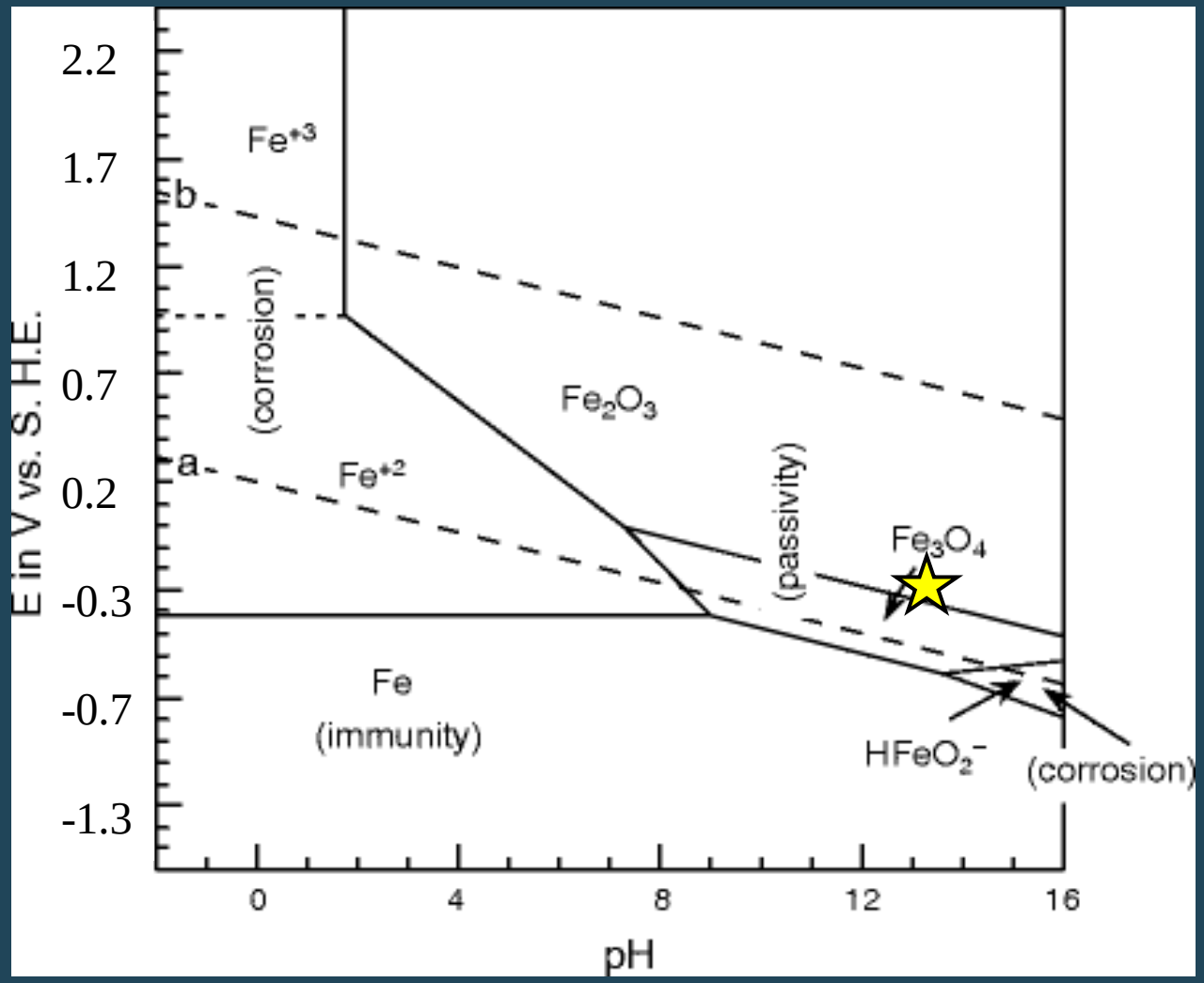
# Reinforcement Corrosion

Tutti Model for Corrosion of concrete reinforced steel




- Initiation
  - Aggressive agents penetrate
- Propagation
  - Corrosion begins until replacement or failure

# Corrosion of Steel Reinforced Concrete




- Initially concrete pH ≅ 12.6, thus no corrosion
- Passivity is broken by Carbonation and Chloride attack
  - Chloride attack causes local pH drop and pitting corrosion
  - Carbonation causes pore solution pH to drop, destroying passive layer and initiating uniform corrosion

# Corrosion Protection of Reinforced Concrete

The half-cell reactions that take place are:

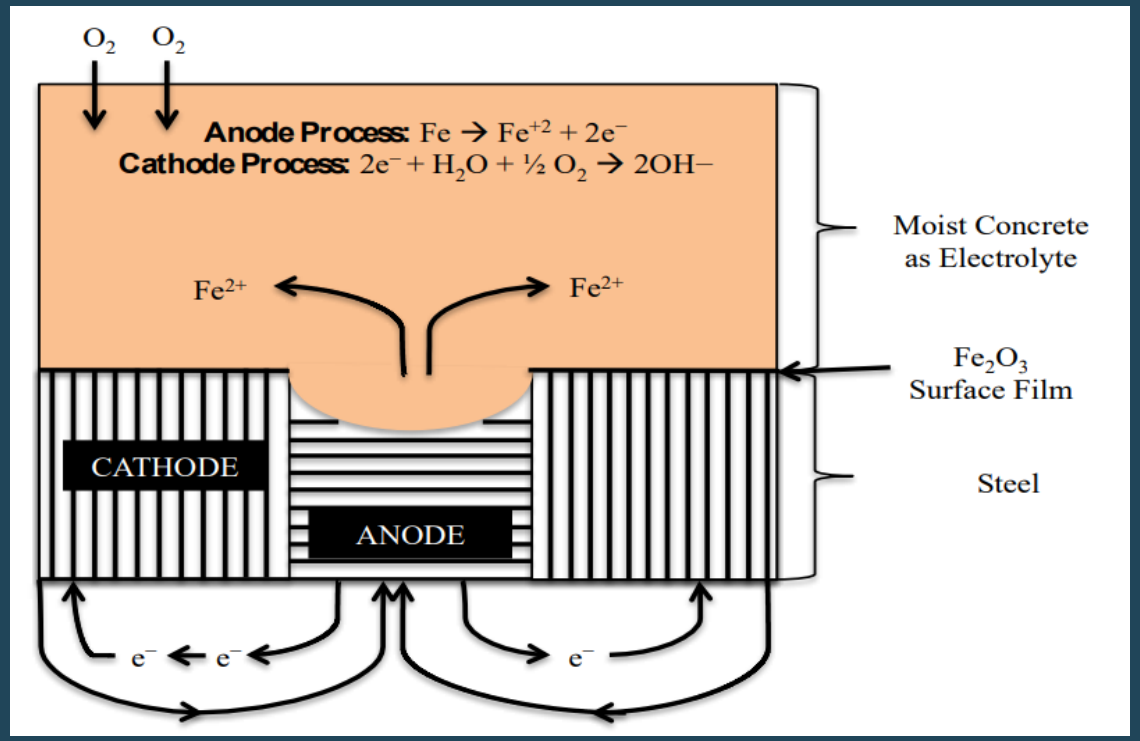
Anode Reaction:

Iron Acid hydrolysis:

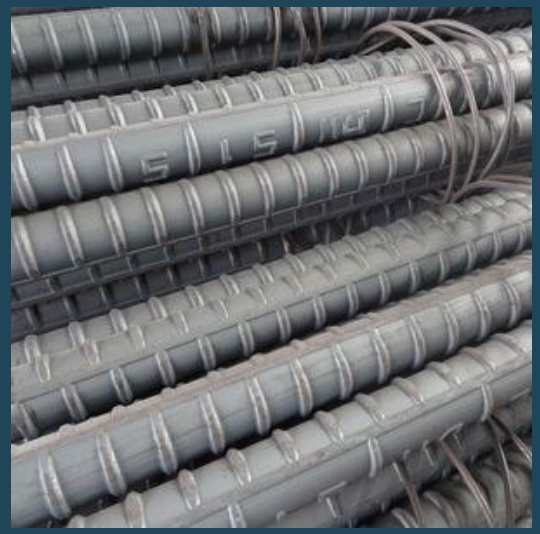
$$Fe + 2H^{+} + \tfrac{1}{2}O_2 + 2Cl^{-} \rightarrow FeCl_2 + H_2O \rightarrow Fe^{2+} + 2Cl^{-} + 2e^{-} + H_2O$$

Cathodic Reaction:

Oxygen reduction reaction: $2e^{-} + H_2O + \frac{1}{2}O_2 \rightarrow 2OH^{-}$




- Methods to prevent include:
  - Stainless steel reinforcements
  - Corrosion inhibitors
  - Cathodic protection
  - Coating application

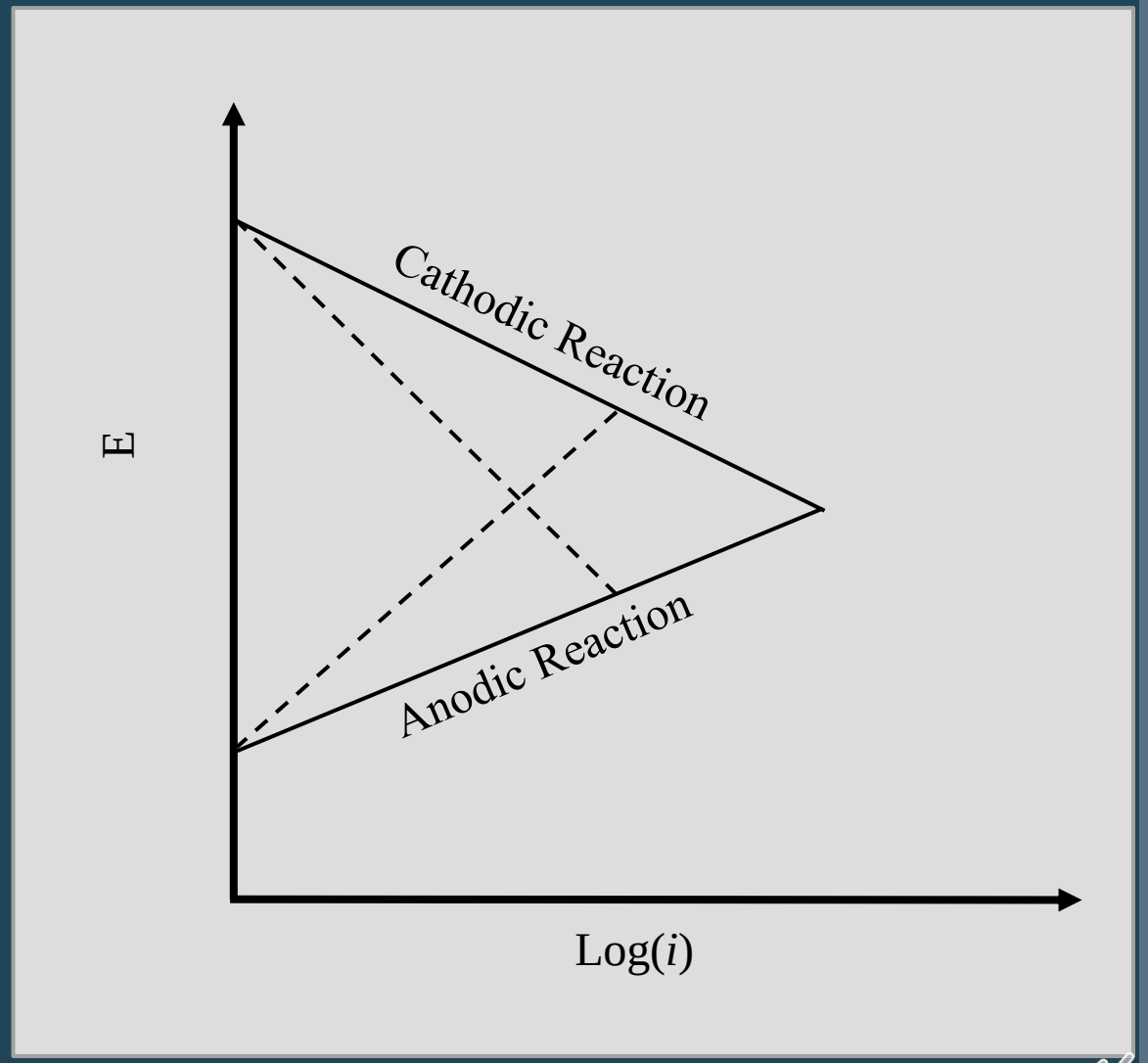


Valspar Greenbar epoxy Coating

Fiona Wang Liaocheng Tianrui Steel Pipe Co., Ltd

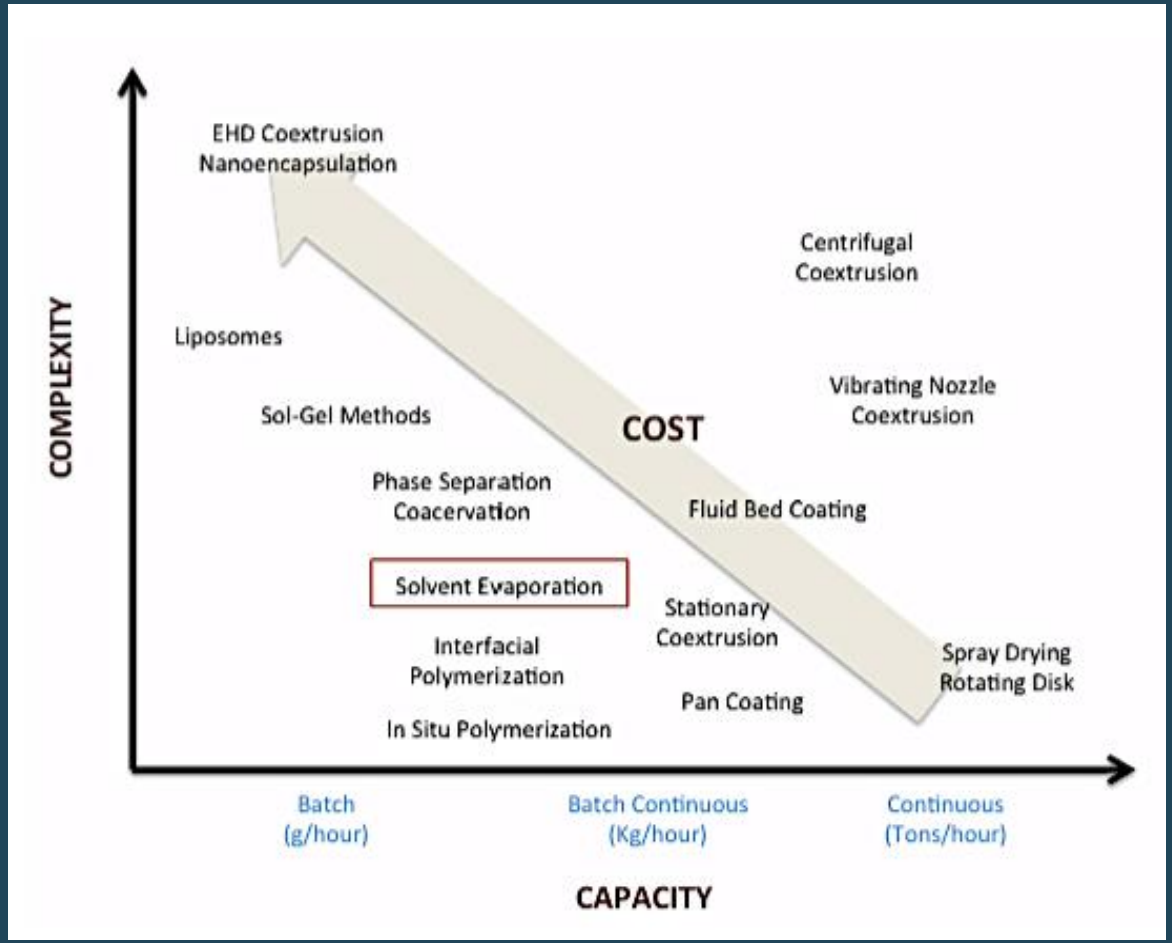
# Corrosion Inhibitors

- Application Types
  - Admixture inhibitors added to fresh concrete
  - Migrating inhibitors that diffuse in hardened concrete
- Inhibitor Types
  - Cathodic inhibitors – Acts upon the cathodic reaction, capturing the oxygen and preventing corrosion.
  - Anodic inhibitors – Act upon the anode to avoid steel dissolution. Forms an oxide film on the metallic surface and increases the corrosion potential.
  - Mixed inhibitors – Act on both anode and cathode sites on steel.



# Microencapsulation

- Prevents:
  - ✓ Leaching of inhibitors
  - ✓ Inhibitor binding to the matrix
  - ✓ Early reaction of inhibitors




Peteu, S.F.; Oancea, F.; Sicuia, O.A.; Constantinescu, F.; Dinu, S. Responsive Polymers for Crop Protection. Polymers 2010, 2, 229-251.

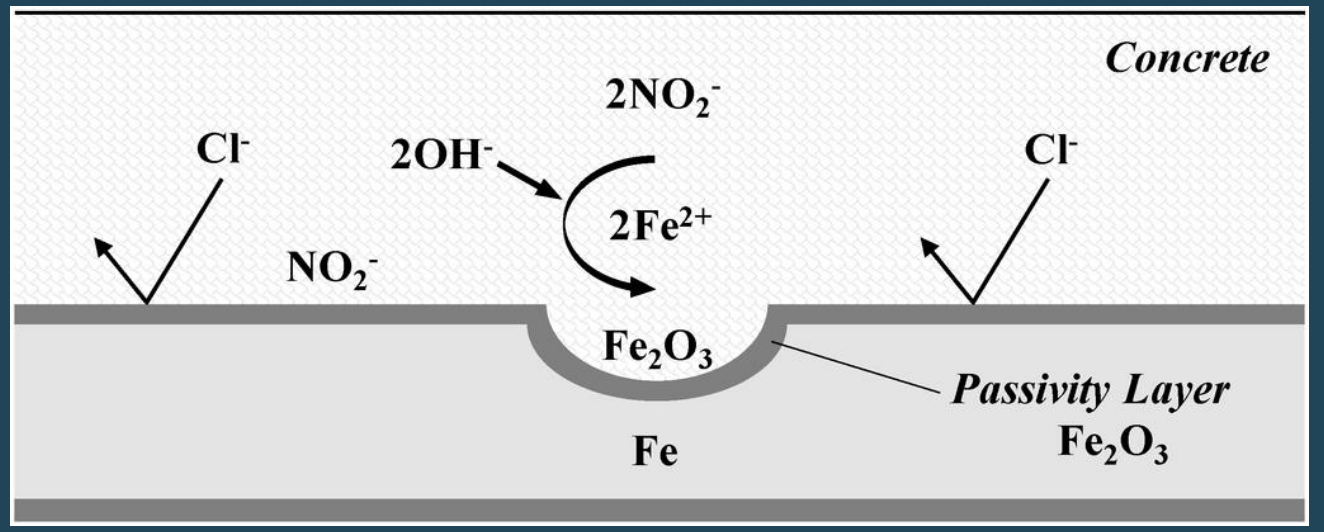
# Nitrite Corrosion inhibitors

- Nitrites function as anodic inhibitors facilitating the formation of a passive oxide film at the steel surface

- Nitrites are common and effective commercially available  inhibitors for concrete reinforced steel

Nitrite inhibitors compete with chloride ions to form ferric oxides and γ-FeOOH

$$2Fe^{2+} + 2OH^{-} + 2NO_2{}^{-} \rightarrow 2NO \uparrow + Fe_2O_3 + H_2O$$
$$Fe^{2+} + OH^{-} + 2NO_2{}^{-} \rightarrow 2NO \uparrow + \gamma - FeOOH$$



# Colophony

Sigma Aldrich




Colophony Chemical Structure
(Abietic acid [~90%])

~ $20 per kg

- Colophony has shown to improve concrete's physical, mechanical and chemical properties
  - Colophony reduces the amount of water absorbed by concrete
  - Reduces porosity
  - Increases resistance to compression and flexural forces
    - M.F. Cánovas, N.H. Selv, G.M. Kawiche, Influence on the physical-mechanical properties of portland-cement mortar, have admixtures of colophony and tannin Mater. Construcc. 216 (1989) 15–22.
- Colophony is a composite of resin acids that are organic and environmentally friendly and renewable and cost effective
- Used by S. Panda in 2013 for controlled delivery of drug into human body

# Goals and Motivation

- To develop a smart corrosion inhibitor delivery agent in the reinforced concrete environment and study its corrosion inhibitive performance

- Colophony microcapsules will be synthesized by water in oil emulsion containing sodium nitrite and characterized by FT IR and SEM. The release of the inhibitor will be studied, and the corrosion performance analyzed using polarization and impedance tests

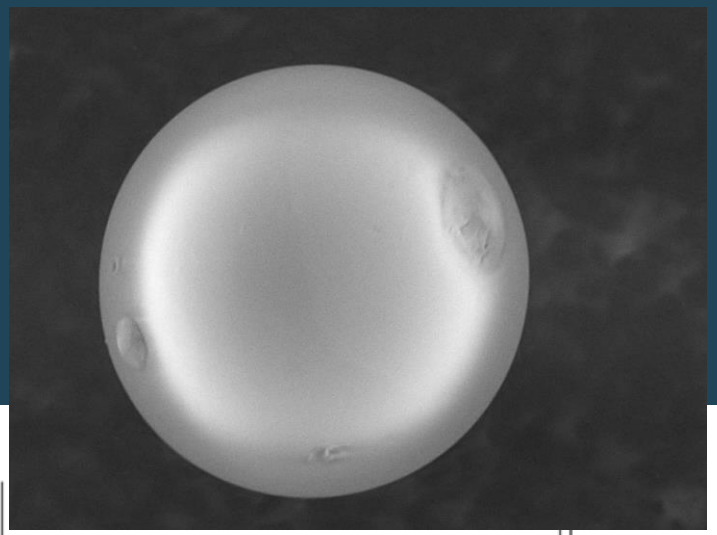
# EXPERIMENTAL

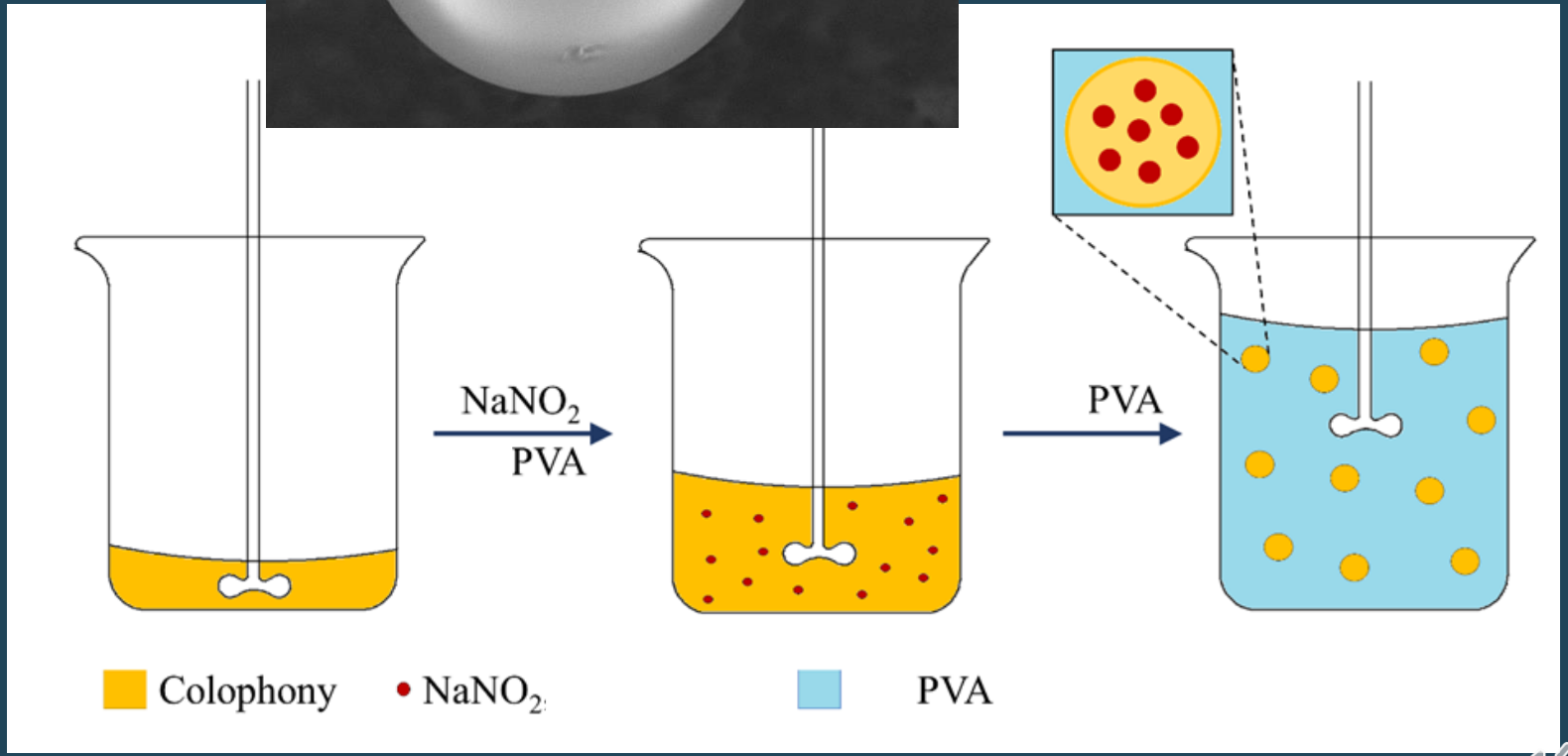
# Synthesis

Solvent for organic phase:
Diethyl Ether

Suspension was stirred using electric overhead mixer

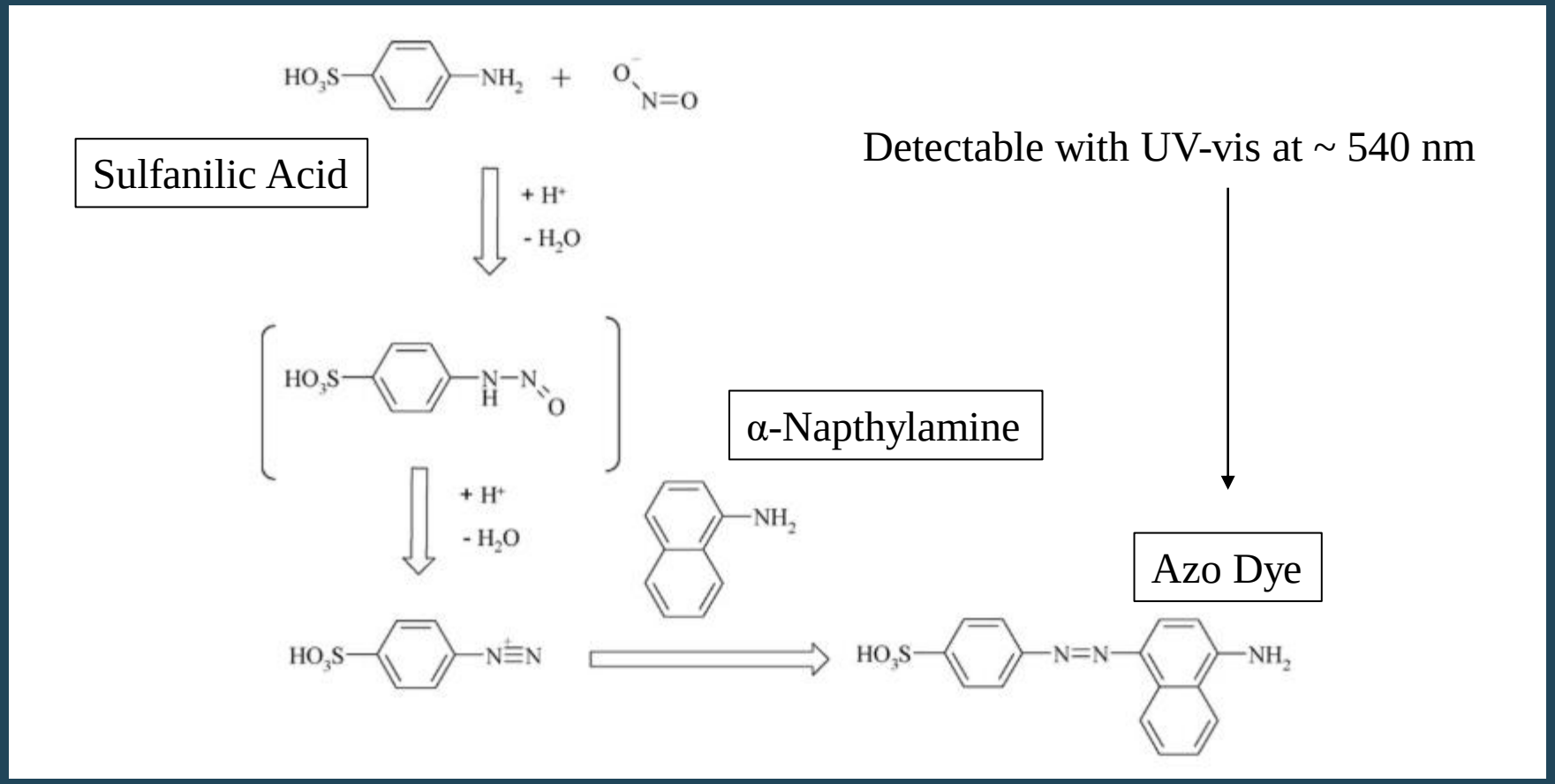
Ether was evaporated at 60ºC while stirring leaving solid colophony





# Inhibitor Release

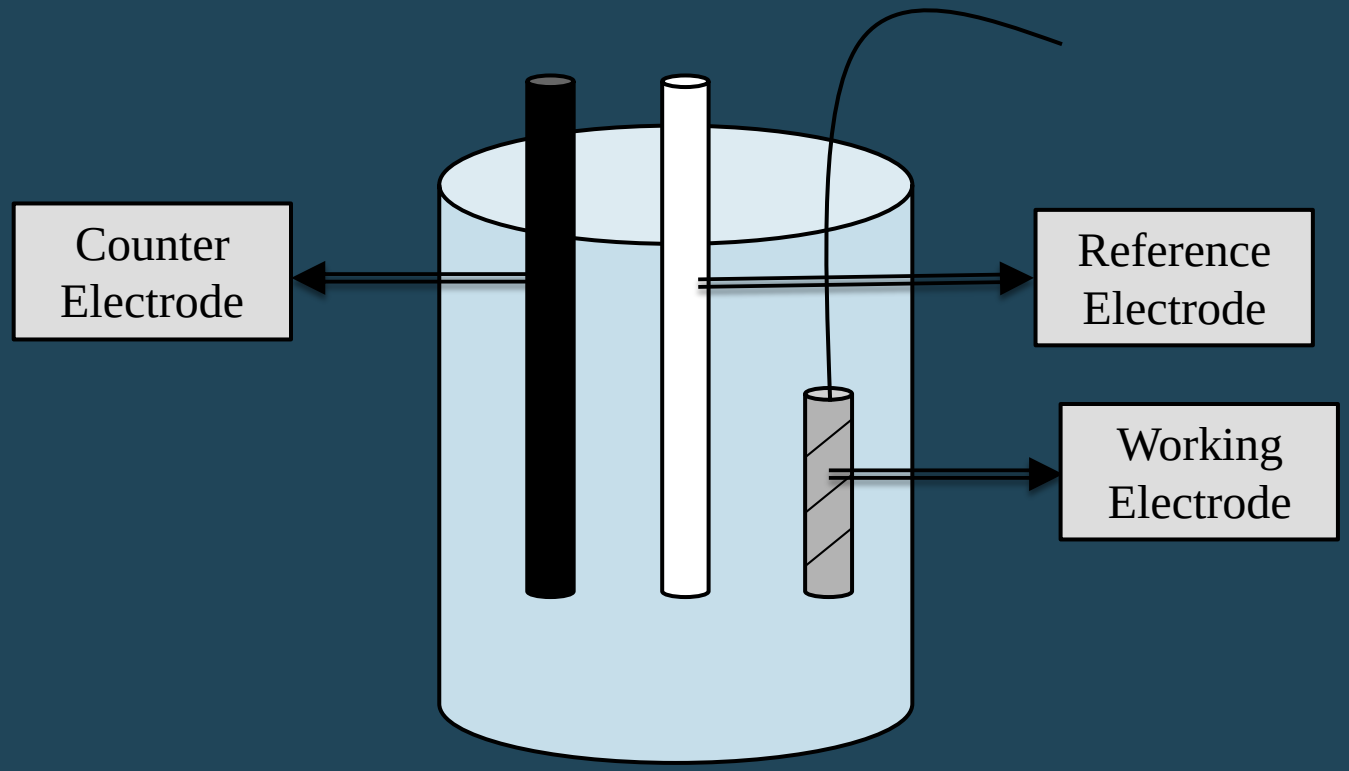
The release of the corrosion inhibitor was measured using the Griess Reagent method




J.P. Griess Ber Deutsch Chem Ges, 12 (1879), p. 426

# Electrochemical Measurements

- 3 Electrode set-up
  - Reference- Saturated Calomel Electrode
  - Counter Electrode – Graphite
  - Working electrode – Steel rebar
- Cyclic Potentiodynamic Polarization
  - $-200\ mV_{OCP}$ to $200mV_{OCP}$
  - Scan Rate of 0.1667 mV/s
- Electrochemical Impedance Spectroscopy
  - 10 mV r.m.s.
  - At OCP
  - 10 points per decade
  - Scan Range: 10 mHz – 100 kHz




| C | Mn | P | S | Si | Cu | Ni | Cr | Mo | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.38 | 1.08 | 0.019 | 0.043 | 0.2 | 0.37 | 0.16 | 0.16 | 0.05 | 0.0379 | Bal. |

*Table 1 Composition of Grade 75 carbon steel rebar in accordance to ASTM A615/A615M-16 measured by X ray Fluorescence. Values in % (w/w)*

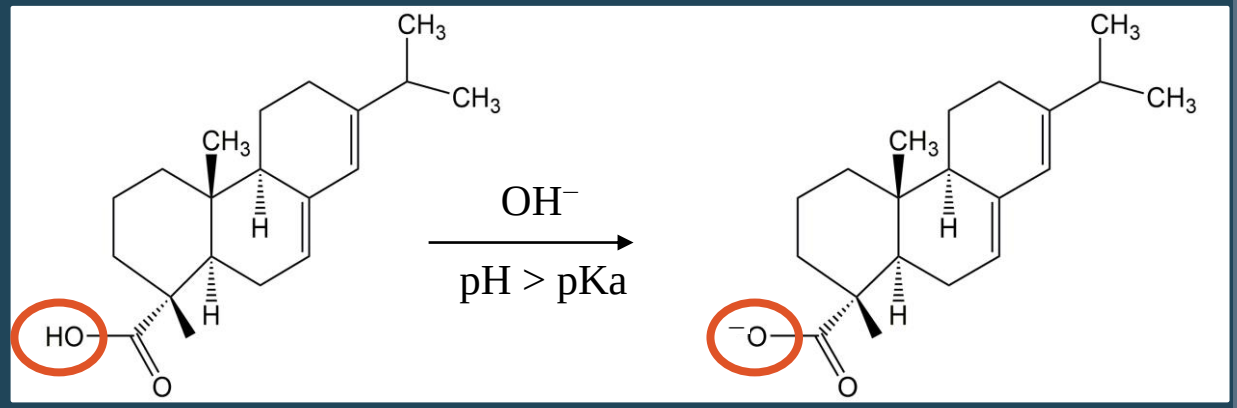
# Solutions Tested

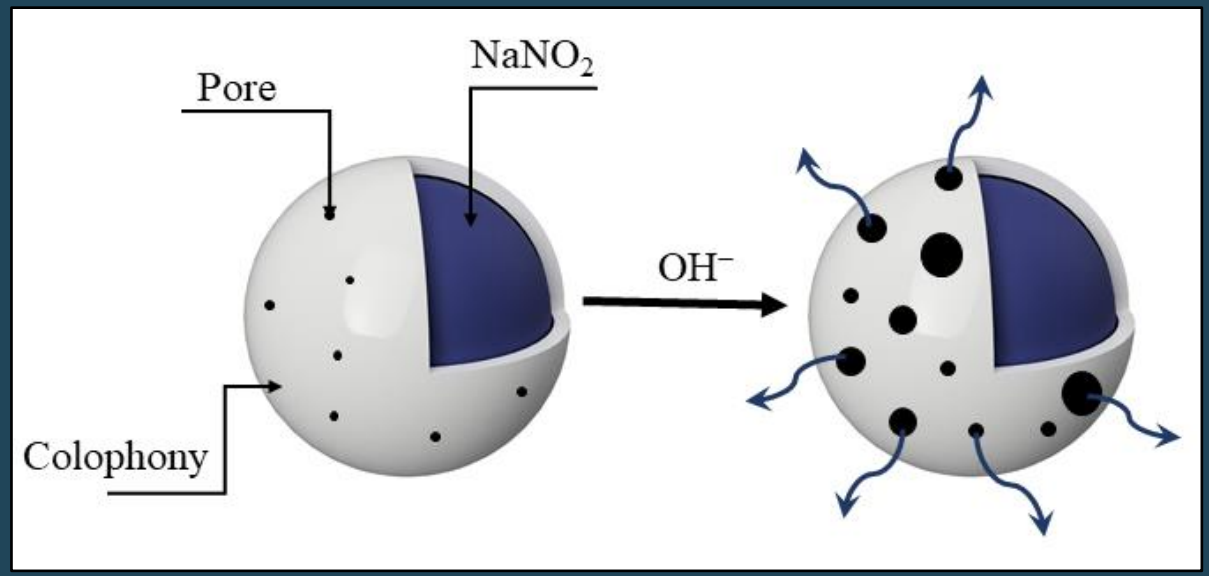
pKa of Colophony (abietic acid) = 7.2

Solutions were tested with pH:

DI water (6.8),
Carbonate/bicarbonate buffer (9.1), and
Simulated concrete pore solution (12.6)

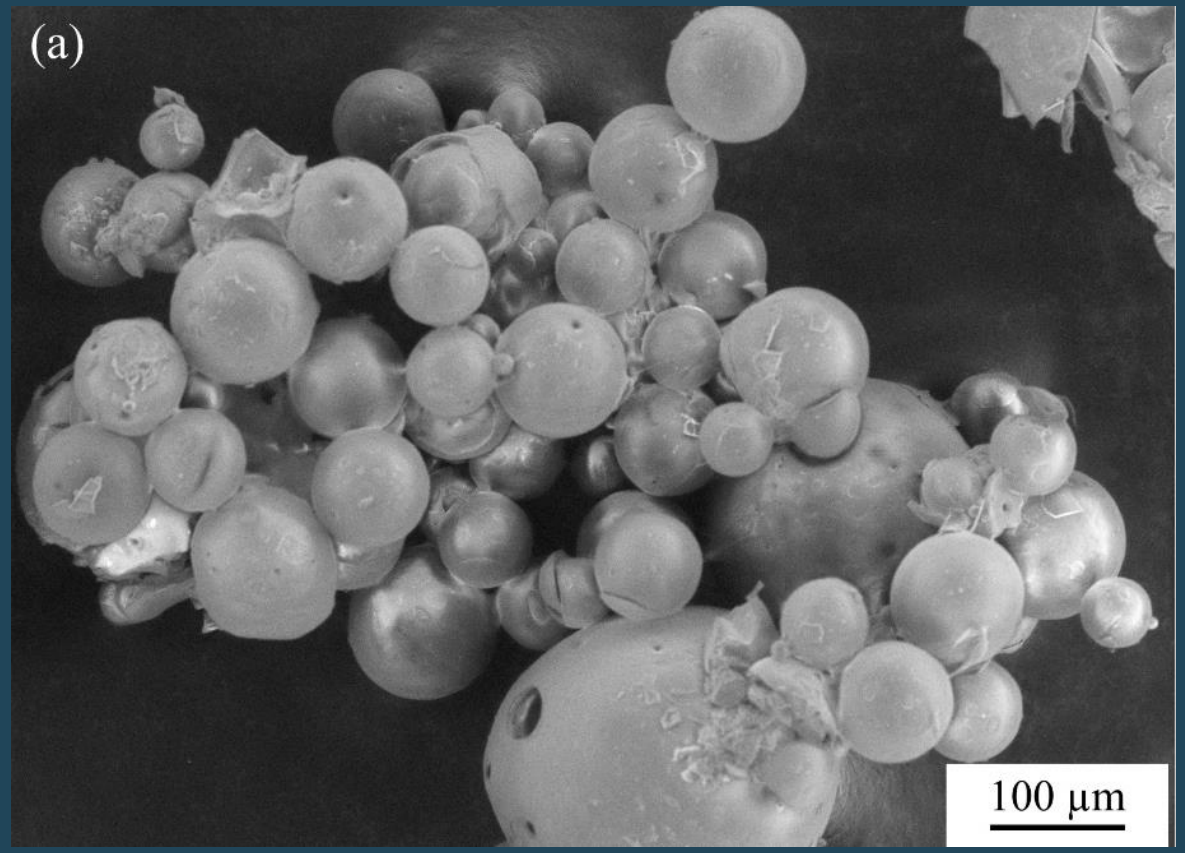
6.8 < pKa < 9.1 < 12.6



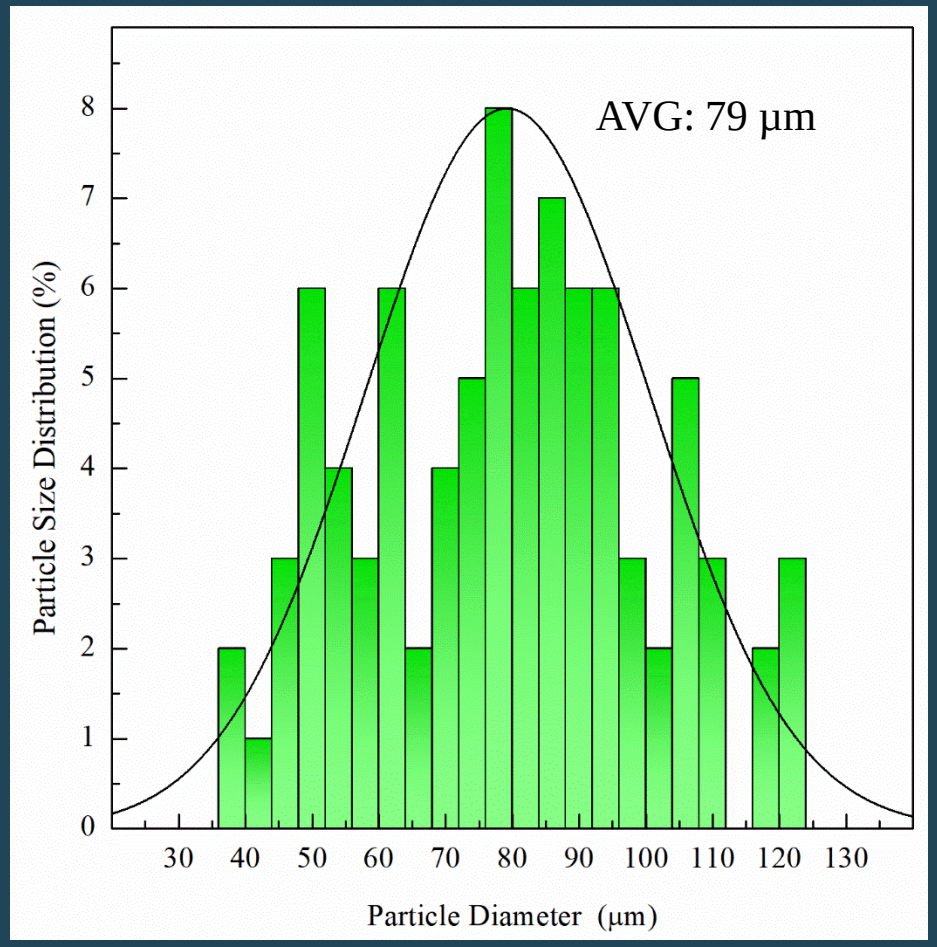



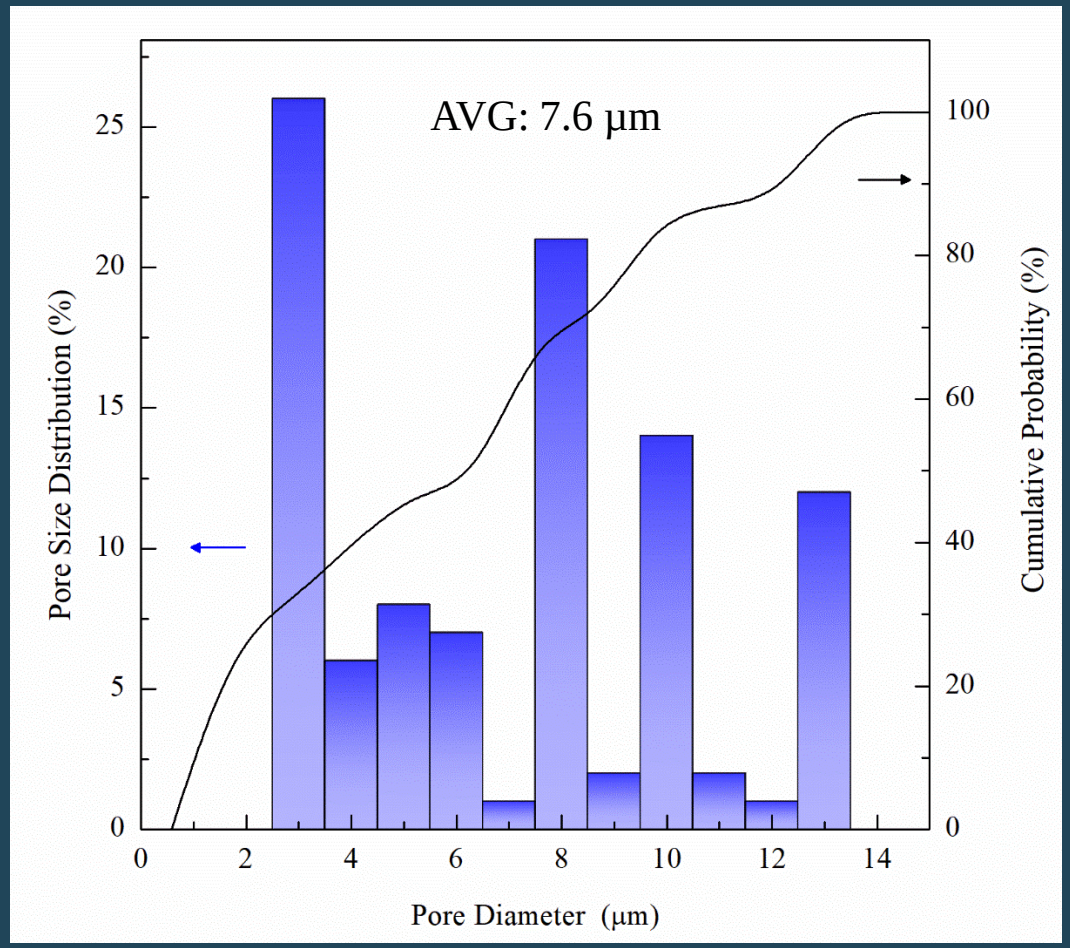
# RESULTS AND DISCUSSION

# SEM images of Colophony microcapsules




# Diameter and Pore Size Distribution

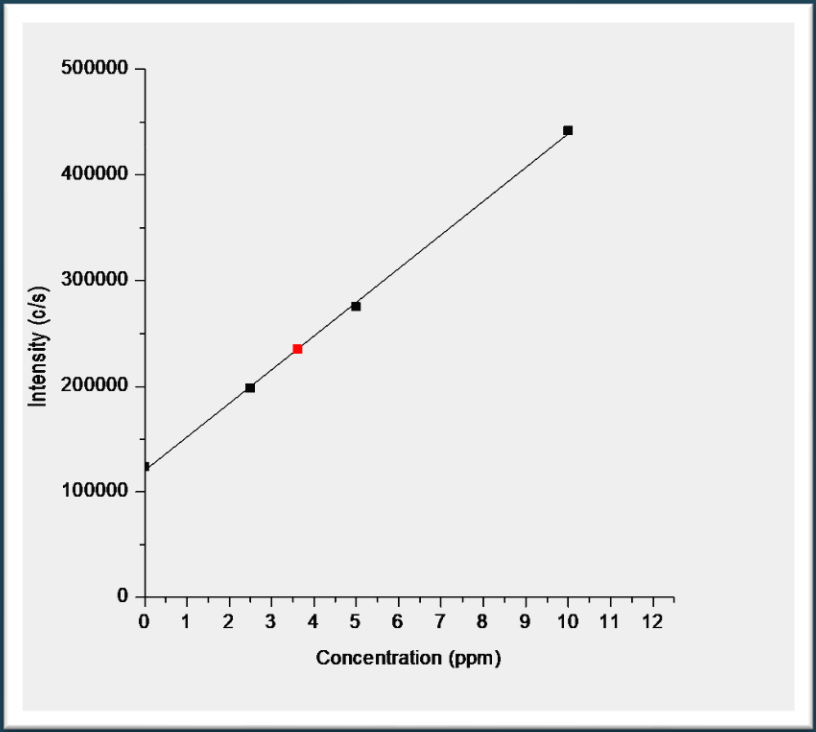


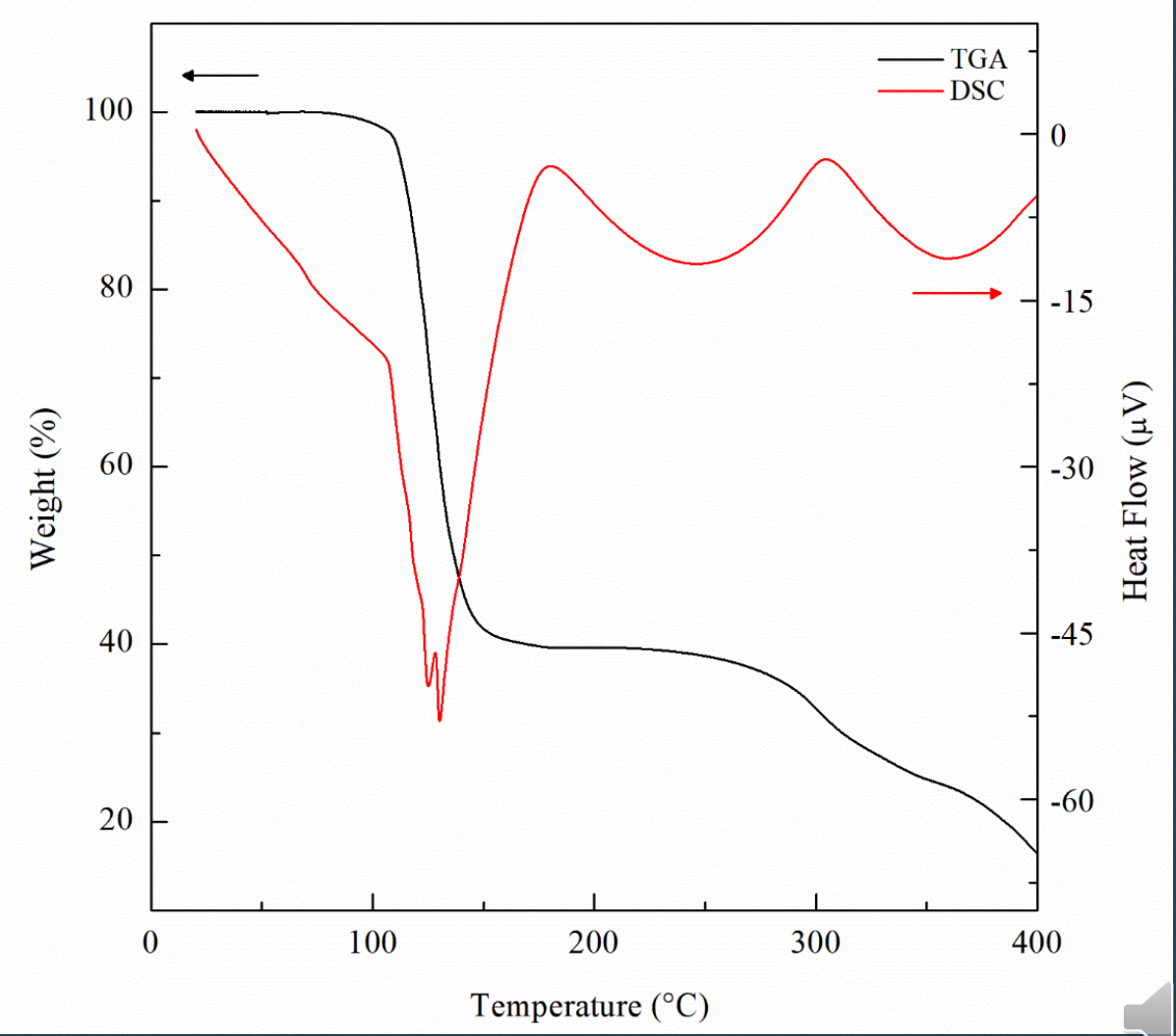



# Encapsulation Efficiency and Thermal Stability

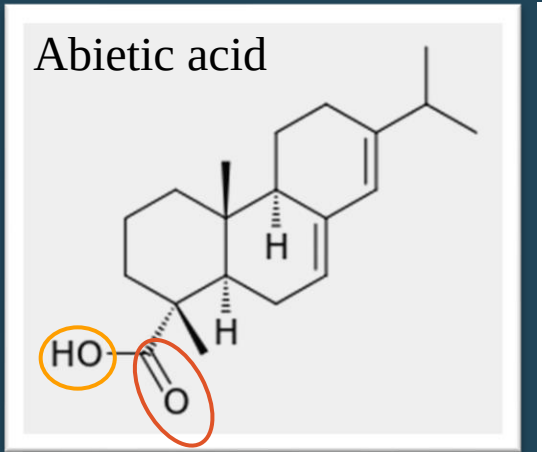
Theramal stability below 110 °C

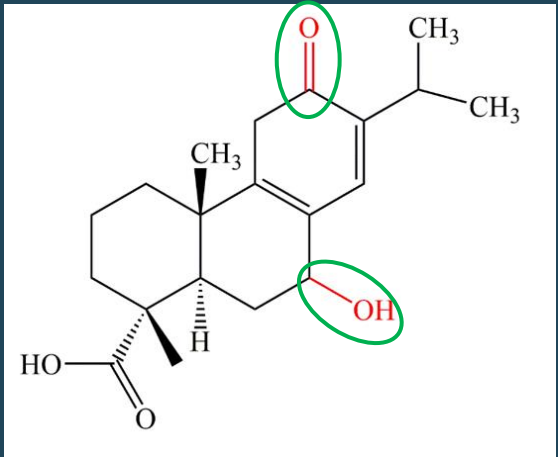
Encapsulation efficiency = 83.2%
measured by ICP-OES



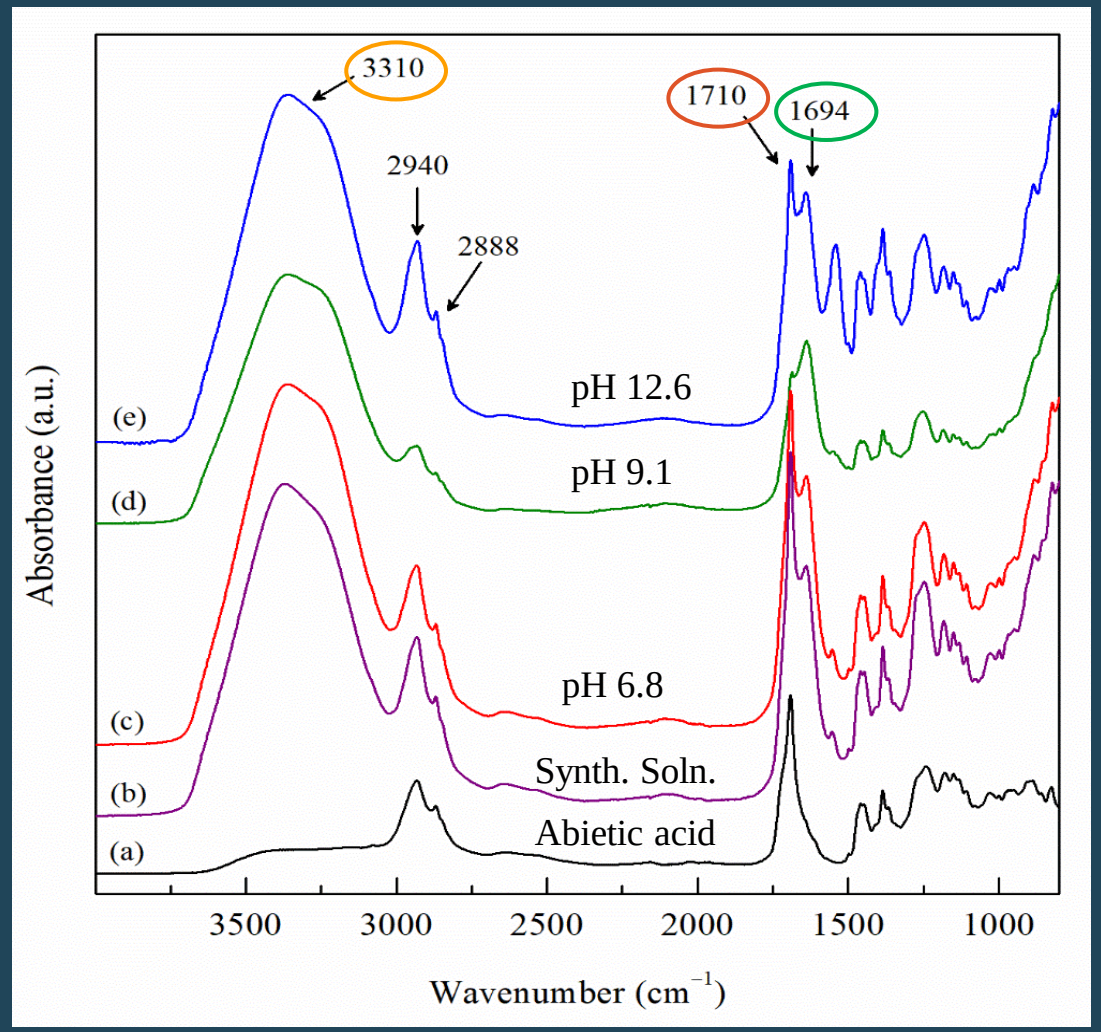



# FT-IR Spectra of Colophony Microcapsules



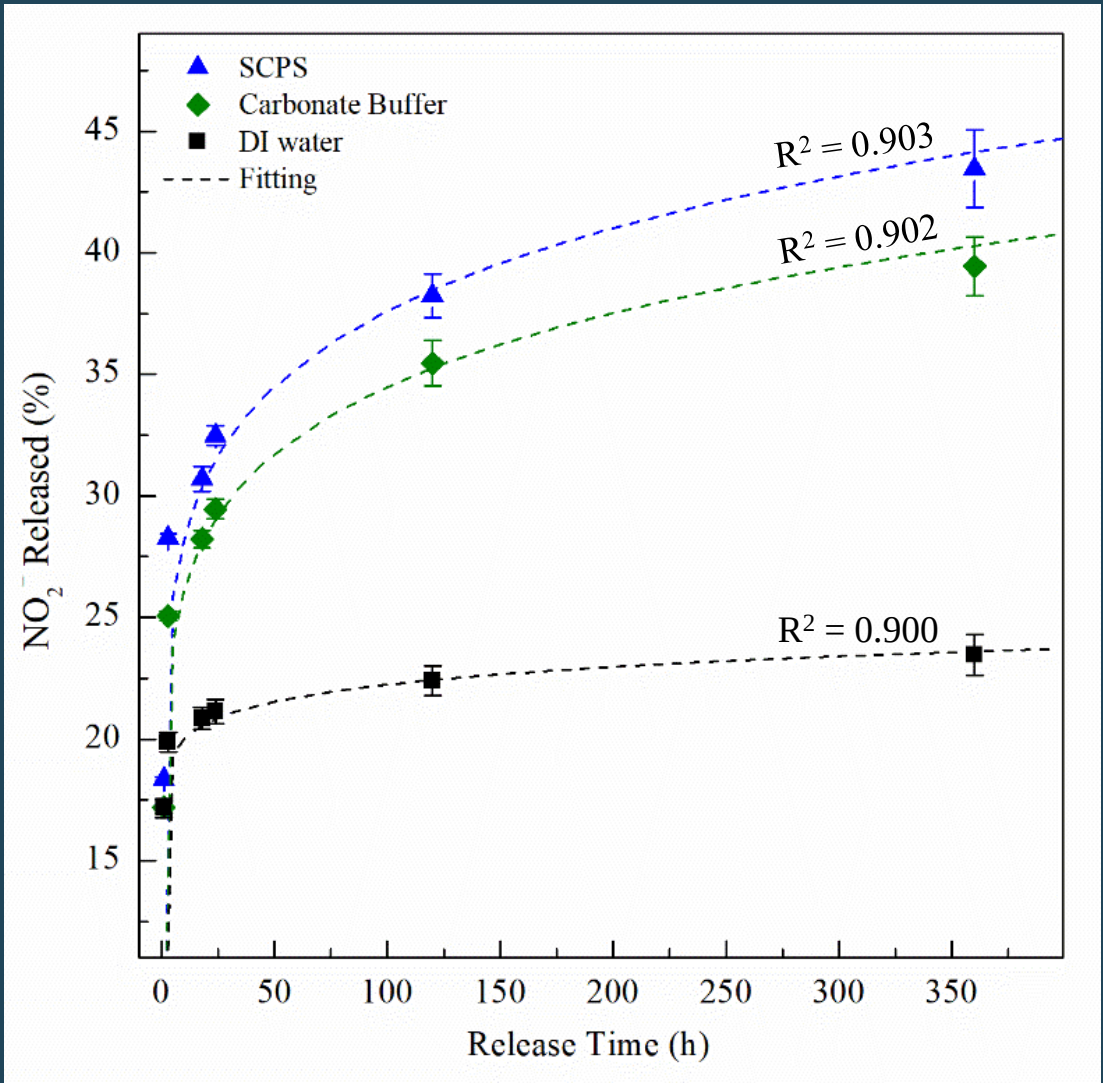




| Vibration Mode | Wavenumber ($cm^{-1}$) |
|---|---|
| O–H stretching | 3310 |
| $-CH_2-$ stretching | 2940 |
| C–H stretching | 2888 |
| C=O stretching (carboxylic acid) | 1710 |
| C=O stretching (aliphatic ketone) | 1694 |
| C=C stretching (cyclic alkene) | 1550 |
| C–H bending (alkane) | 1465 |
| C–H bending (aldehyde) | 1390 |
| C–O stretching (carboxyl group) | 1265 |




F. Ren, Y.-F. Zheng, X.-M. Liu, X.-Y. Yue, L. Ma, W.-G. Li, F. Lai, J.-L. Liu, W.-L. Guan, An investigation of the oxidation mechanism of abietic acid using two-dimensional infrared correlation spectroscopy, J. Mol. Struct. 1084 (2015) 236–243. https://doi.org/10.1016/j.molstruc.2014.12.055.

# Inhibitor Release




$$\frac{M_t}{M_\infty} = kt^n$$

Ritger and Peppas Power Law release model for spherical particles

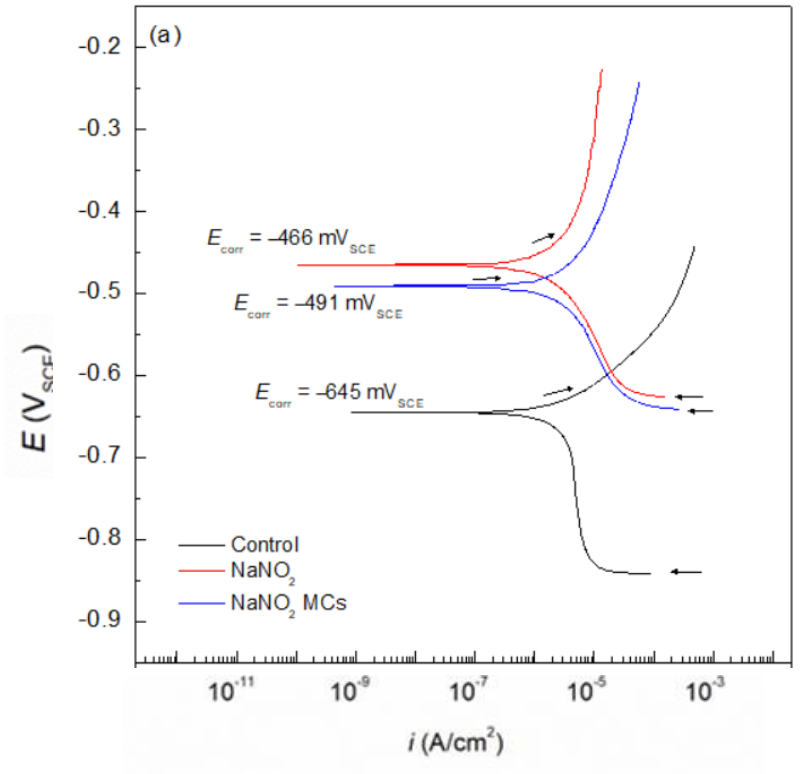
P.L. Ritger, N.A. Peppas, A simple equation for description of solute release I. Fickian and non-fickian release from non-swellable devices in the form of slabs, spheres, cylinders or discs, J. Control. Release 5 (1987) 23–36.

# ELECTROCHEMICAL MONITORING

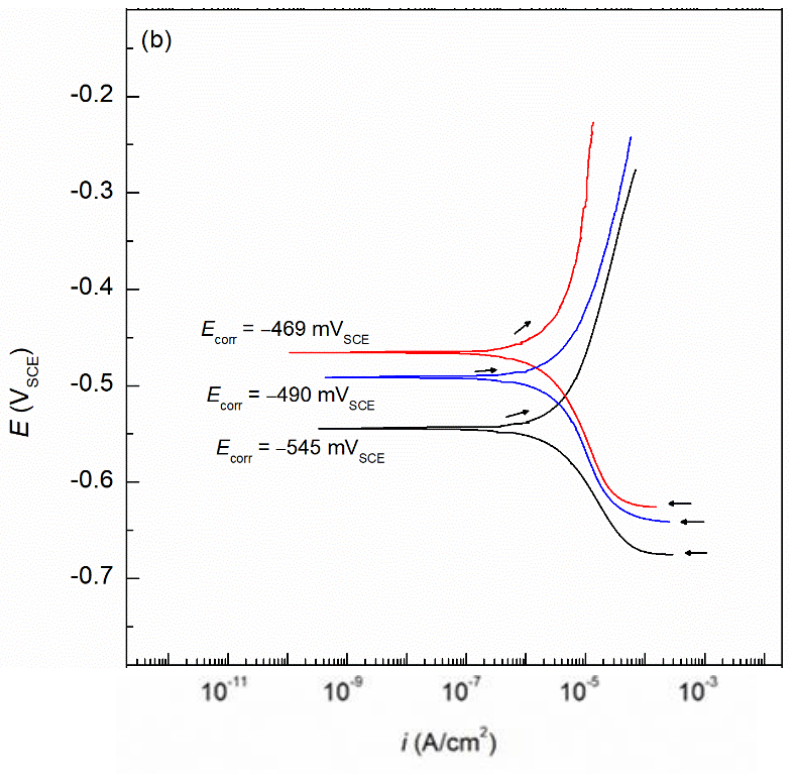
# Potentiodynamic Polarization

## 0.4 wt.% $Cl^-$

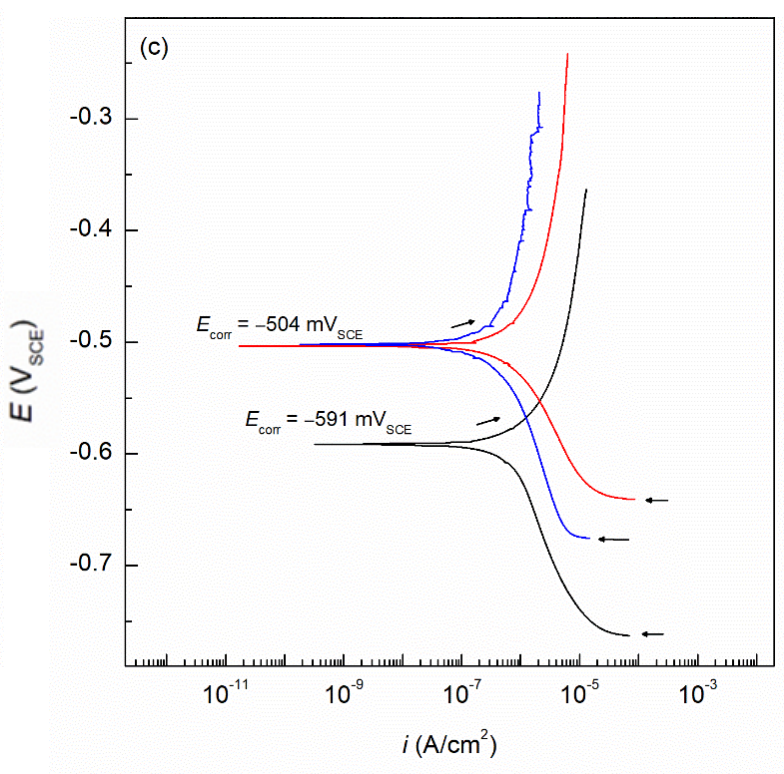
pH 6.8




pH 9.1

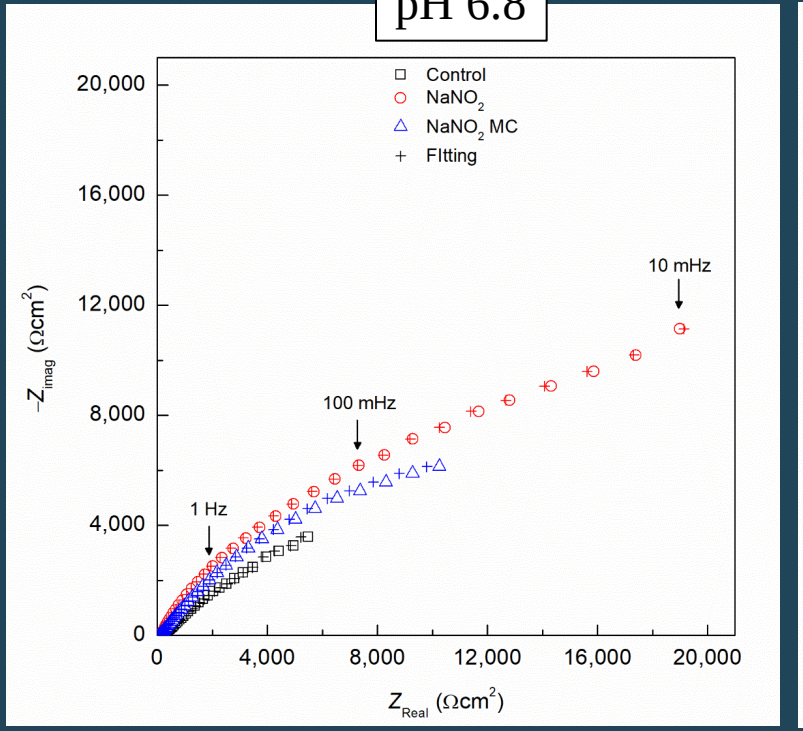



pH 12.6

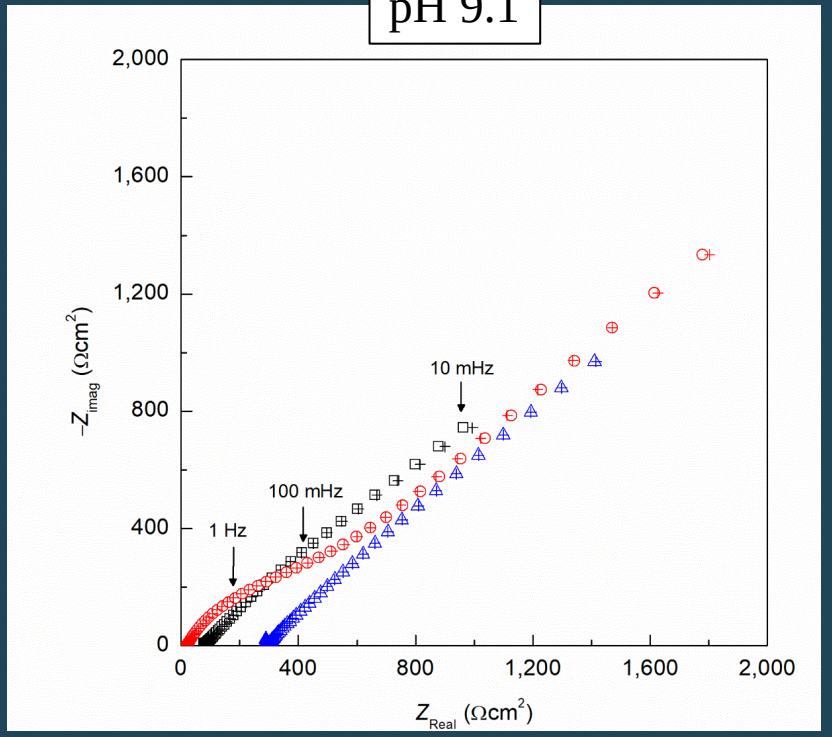


# Electrochemical Impedance Spectroscopy
# 7 Days exposure to 0.4 wt.% $Cl^-$ ions

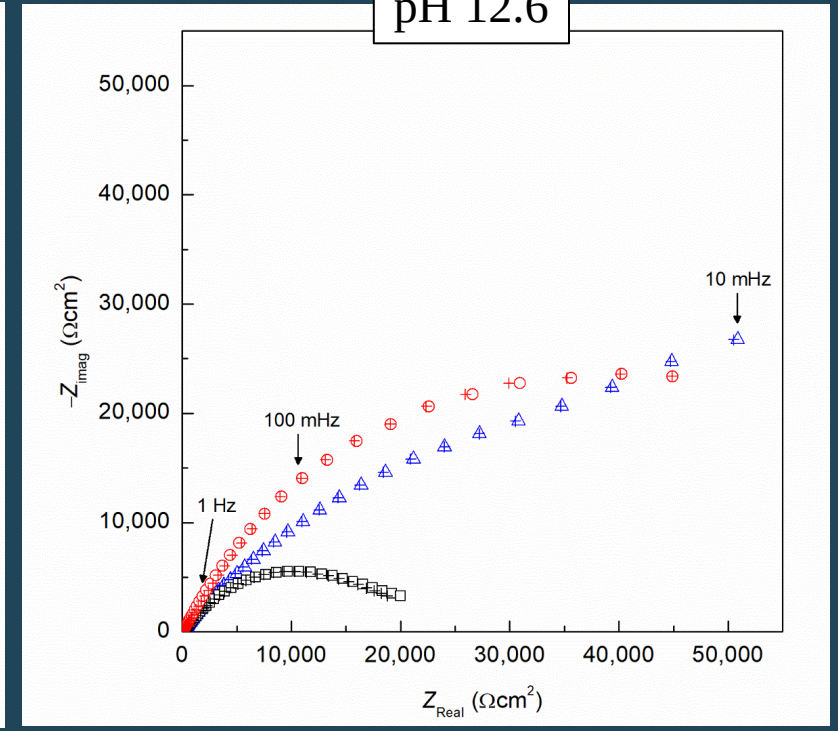
pH 6.8



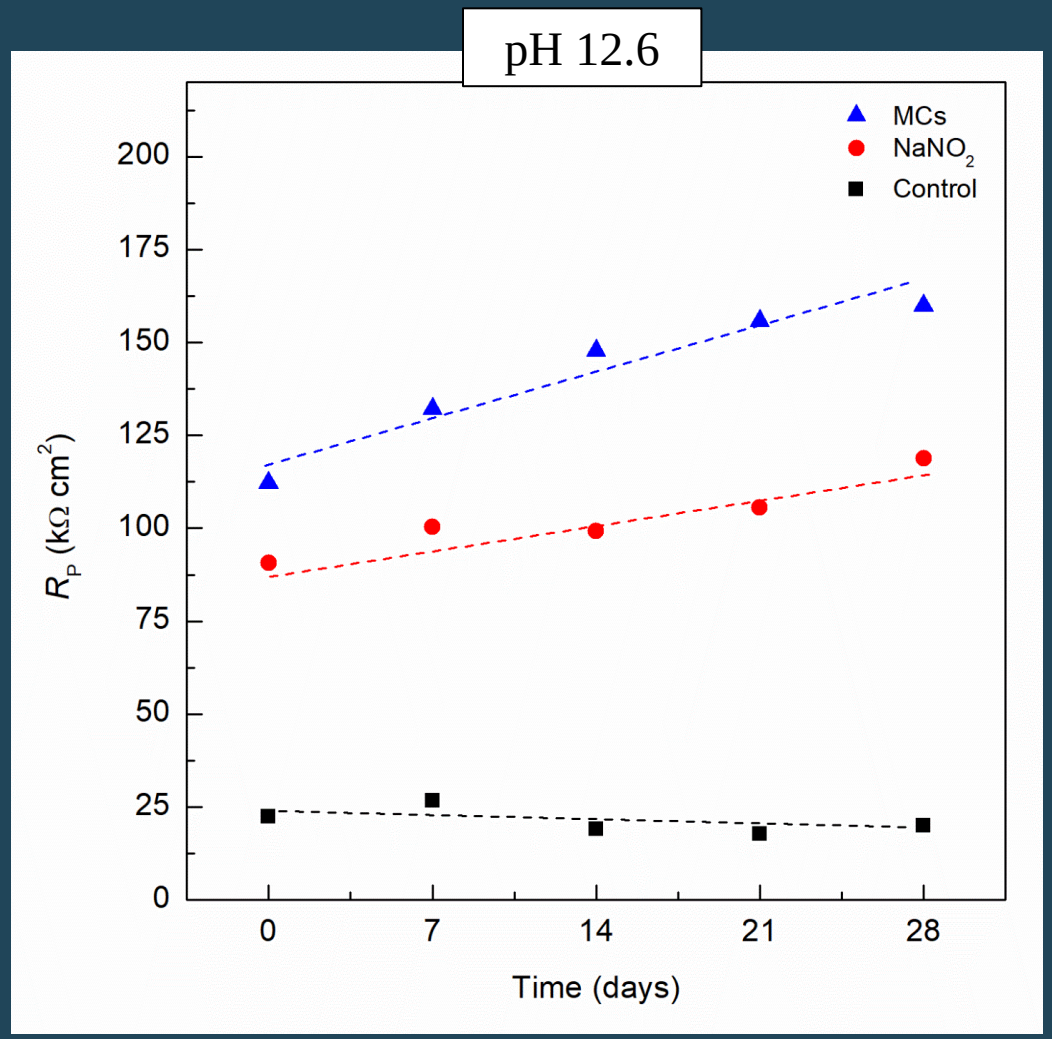

pH 9.1

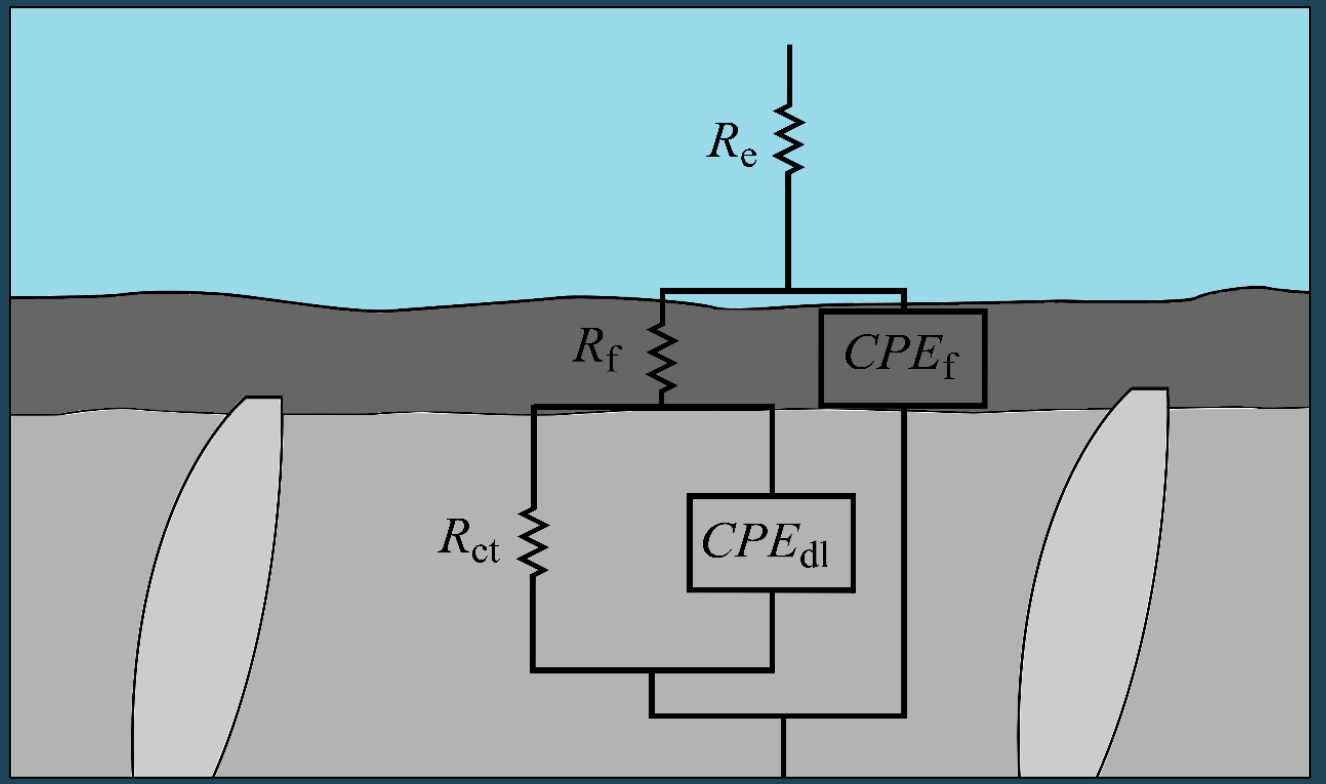



pH 12.6



# Electrical Equivalent Circuit Modeling



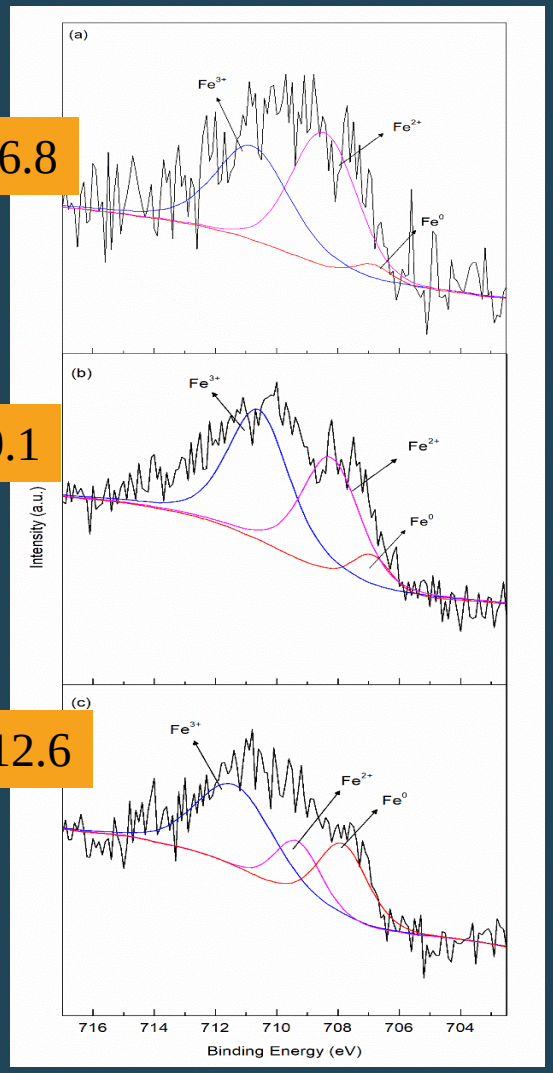



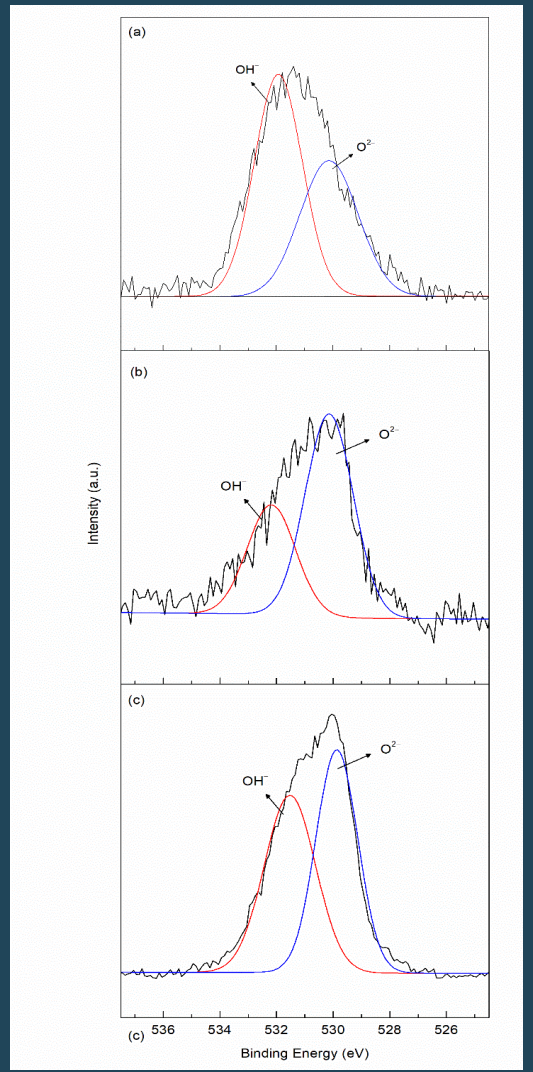
# Passive film development

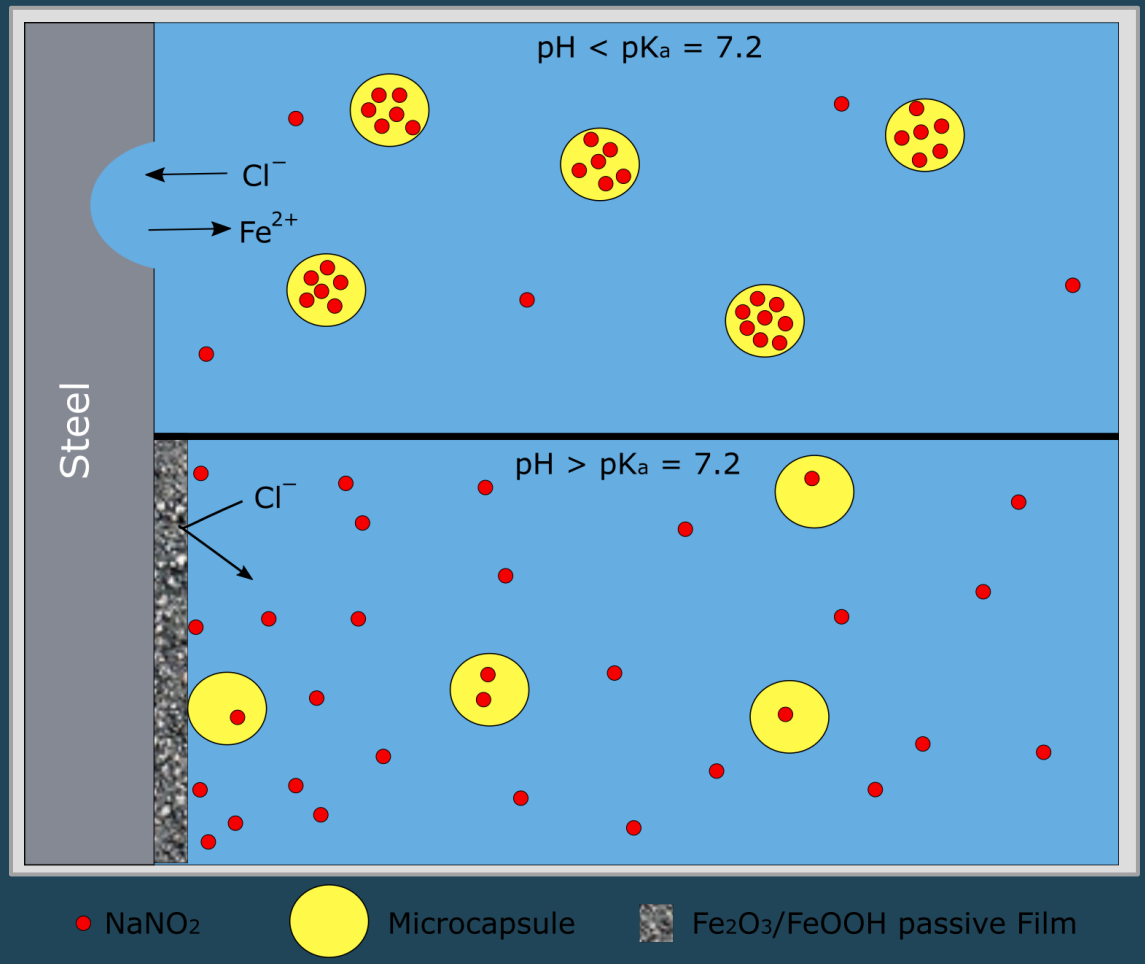
pH 6.8

pH 9.1

pH 12.6

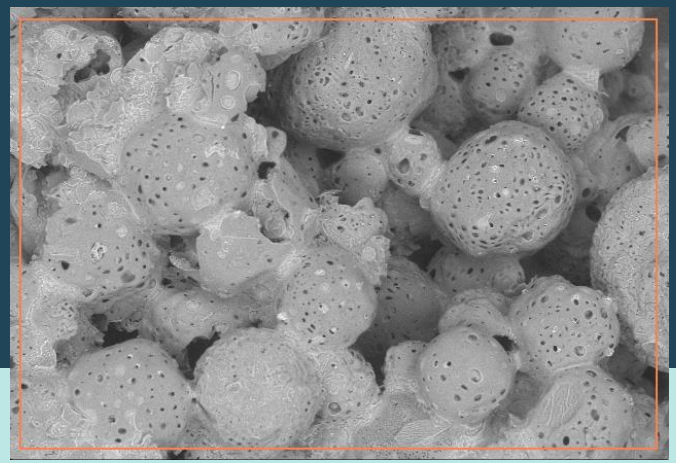


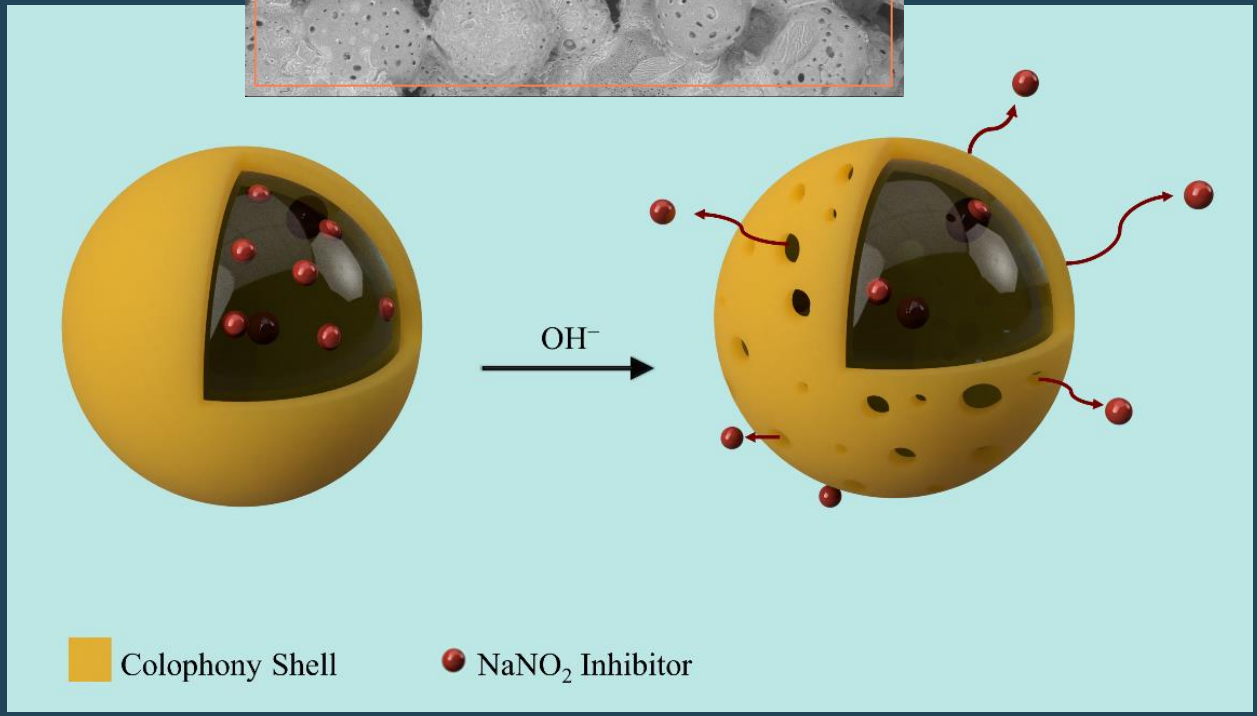



# Conclusions

- Environmentally-friendly colophony microcapsules can be successfully synthesized by emulsion method
- The colophony microcapsules show decreased corrosion current densities by polarization scans and a mixed inhibition mechanism through anodic inhibitors and $O_2$ scavenging. By EIS, the Rp was found to increase greatly for colophony microcapsules in simulated pore solution compared to the control and free inhibitor specimens.
- Colophony microcapsules can be a cost effective, and renewable strategy to prevent corrosion of steel reinforced concrete structures





# Acknowledgements


- The College of Engineering and Polymer Science
- The Department of Chemical, Biomolecular, and Corrosion Engineering
- The University of Akron
- NCERCAMP

# Questions?