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## INTRODUCTION

Amongst all the effluents generated in the hot dip galvanizing industries, the spent pickling baths (SPBs) appears as one of the most hazardous due to its high content of  $ZnCl_2$  and  $FeCl_2$  in HCl media. Consequently, they have to be treated previously to their disposal.

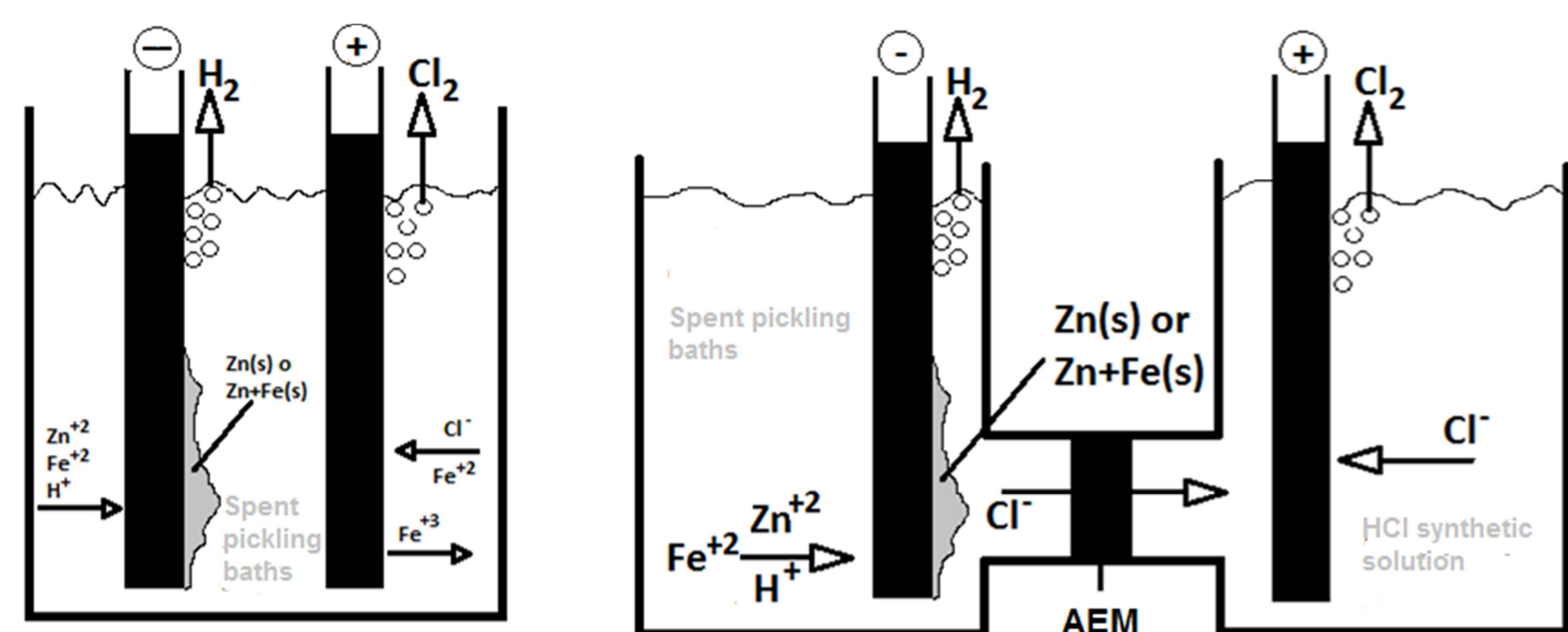
Although, some experimental procedures permit to recycle the HCl or to separate the components, none of them permit the recovery of the most valuable component (Zn) back to the process. Zn recovery by the use of an electrochemical reactor becomes an interesting alternative. This technology is able to recover Zn from the SPBs in an efficient way but the Zn re-dissolution and Fe co-deposition appeared as the main drawbacks.

## GOAL

This work aims to establish the main mechanisms equations that controls the electrochemical reactor in the zinc recovery from SPBs process

## METHODOLOGY

The process was studied under galvanostatic control using a stirred batch electrochemical reactor in the absence/presence of an anion-exchange membrane (AEM) (Fig. 1). The applied current ranged from 150-700 mA.



▲ Figure 1. Schematic representation of the electrochemical reactor and its main reactions in absence (left) and presence (right) of an AEM

### General equations

#### Zinc Mass balance

$$V \frac{d[Zn^{+2}]}{dt} = -\frac{i_{cat} \cdot \varphi_{Zn}}{n \cdot F} \cdot A_e \quad \text{Eq. 1}$$

#### Chlorine redissolution

$$V \frac{d[Zn^{+2}]}{dt} = -\frac{i_{cat} \cdot \varphi_{Zn}}{n \cdot F} \cdot A_e + k_2 \cdot [Cl_2]_{sat} \quad \text{Eq. 2}$$

#### Chlorine and $Fe^{+3}$ attack

$$V \frac{d[Zn^{+2}]}{dt} = -\frac{i_{cat} \cdot \varphi_{Zn}}{n \cdot F} \cdot A_e + k_2 \cdot [Cl_2]_{sat} + k_3 [Fe^{+3}] \quad \text{Eq. 3}$$

$$[Fe^{+3}] = [Fe^{+2}]_0 - [Fe^{+2}] \quad \text{Eq. 4}$$

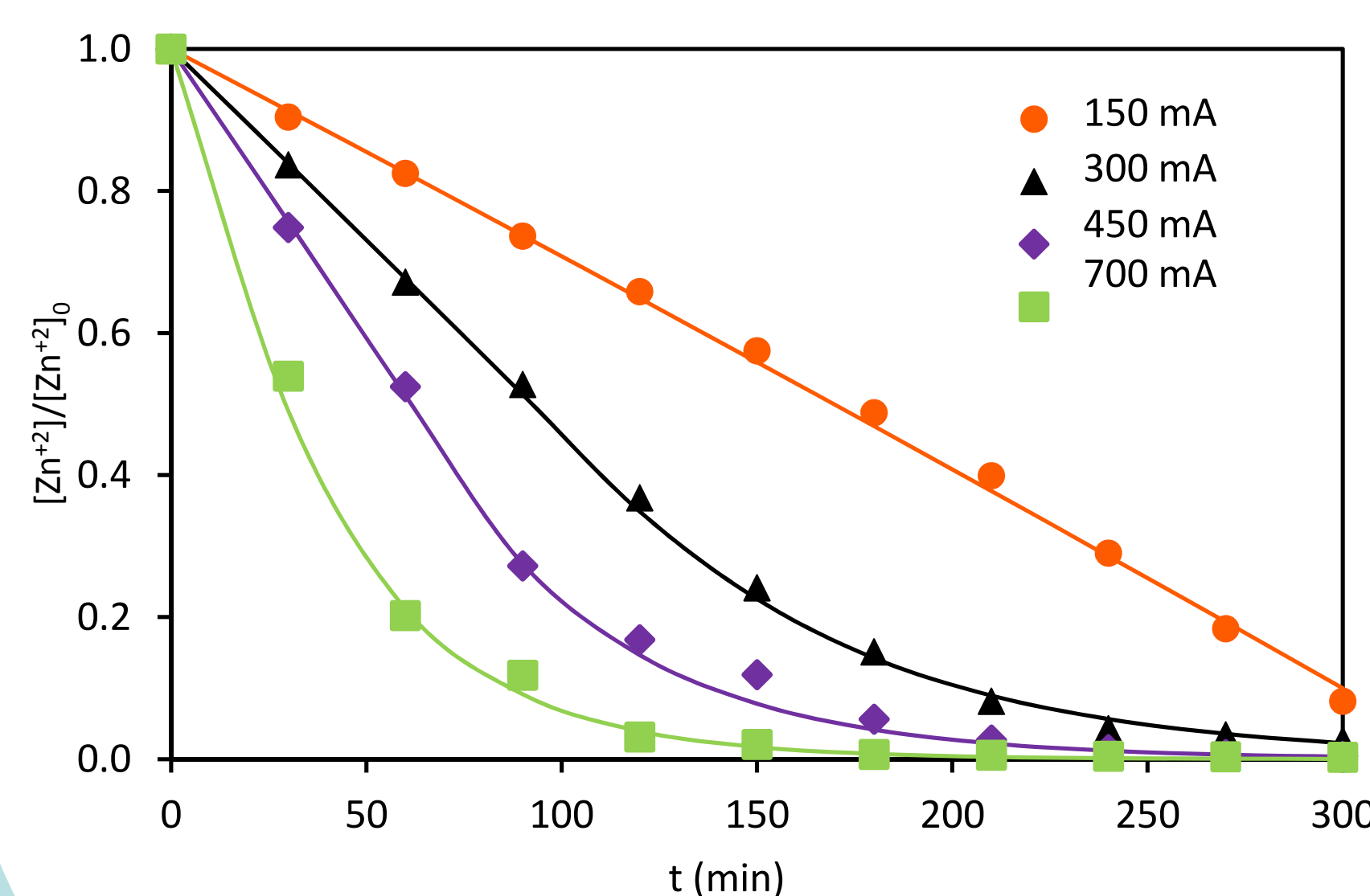
$$V \frac{d[Fe^{+2}]}{dt} = -\frac{i_a \cdot \varphi_{Fe}}{n \cdot F} \cdot A_e \quad \text{Eq. 5}$$

### Case 1:

#### Membrane reactor

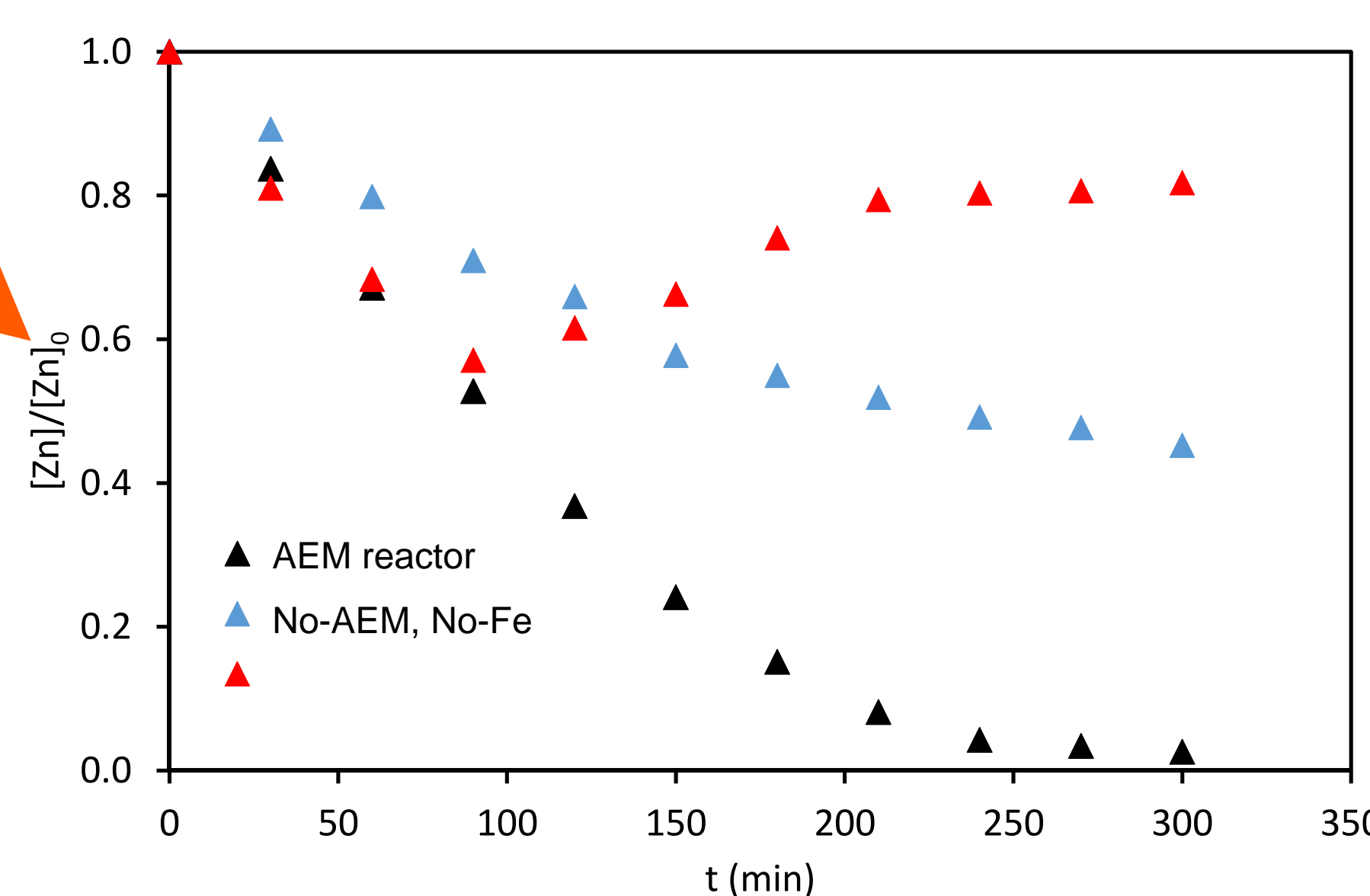
Model suggested Eqs. 1

Hypothesis The membrane avoids the redissolution phenomenon



▲ Figure 3.  $[Zn^{+2}]/[Zn^{+2}]_0$  as a function of t. Case 1

The different zinc profile obtained at each operating conditions indicates that zinc electrodeposition behaviour is strongly influenced by both chlorine and iron.



▲ Figure 2.  $[Zn]/[Zn]_0$  at 300mA for 1:50 diluted spent baths and 0.055M  $ZnCl_2$  (No-Fe)

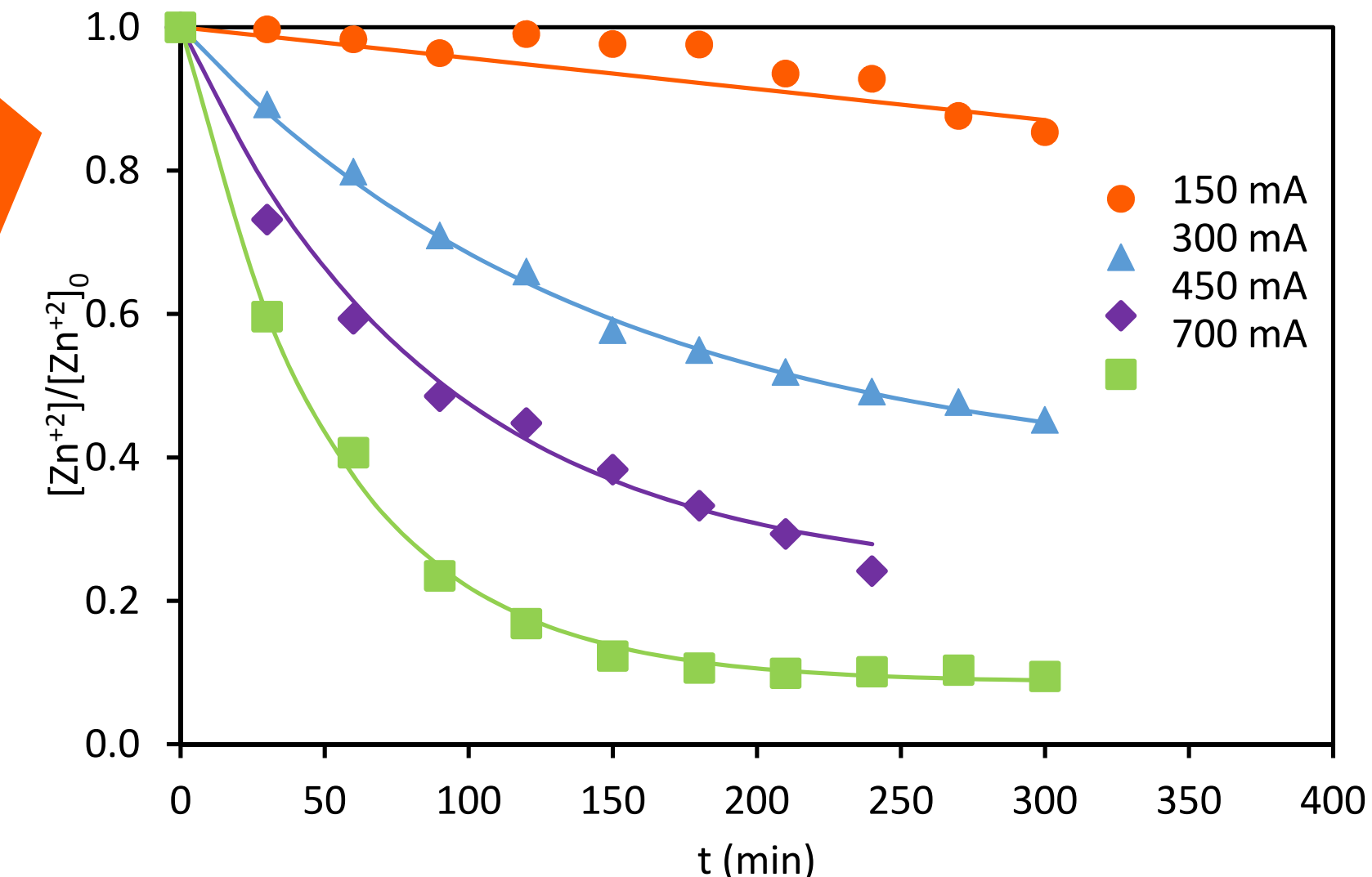
In each Figure, the symbols represent the experimental data while the lines show the simulated values of the corresponding model.

### Case 2:

#### No membrane, No $Fe^{+3}$

Model suggested Eqs. 1 to 2

Hypothesis The solution is saturated with chlorine



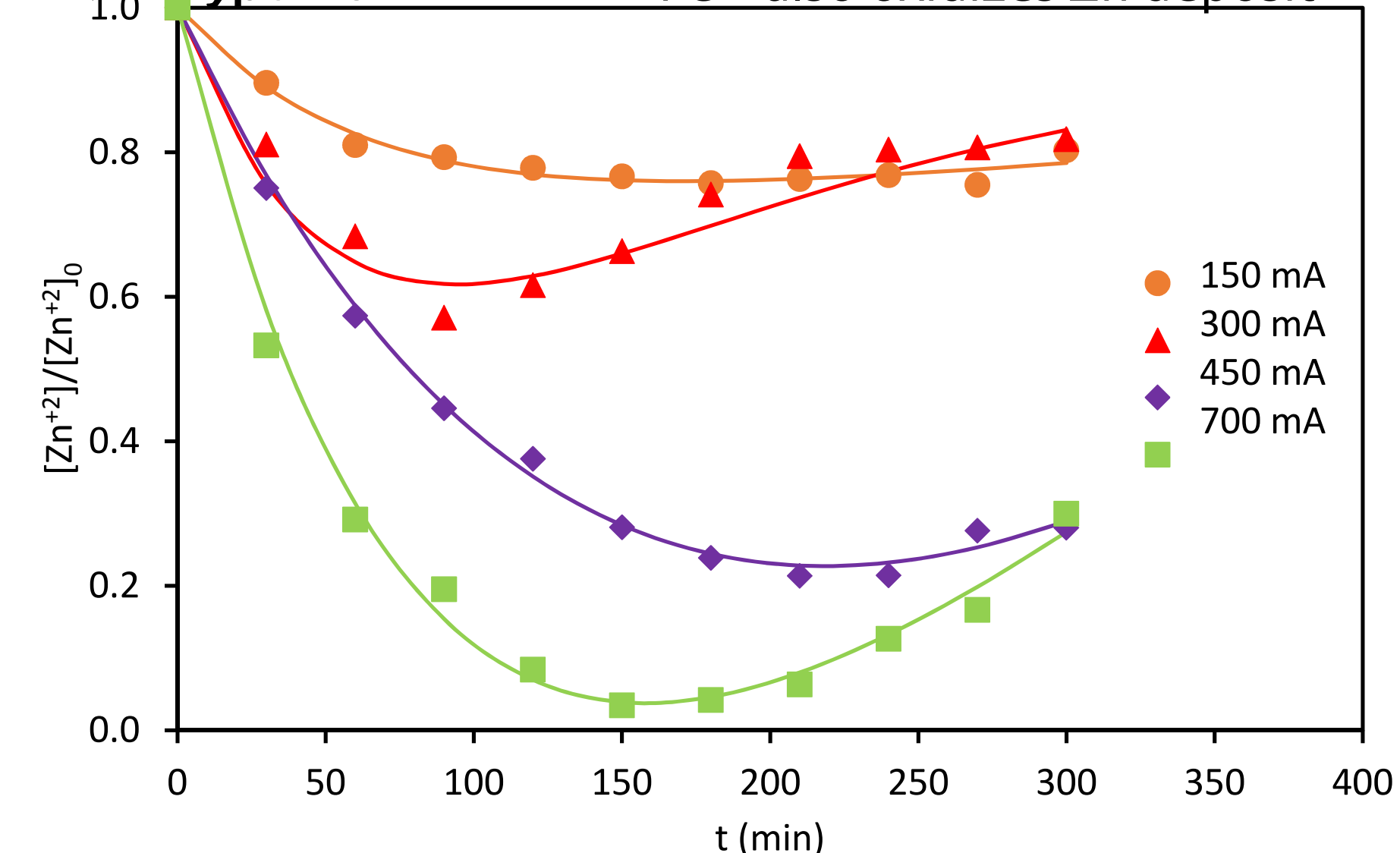
▲ Figure 4.  $[Zn^{+2}]/[Zn^{+2}]_0$  as I function. Case 2

### Case 3:

#### No membrane, $Fe^{+3}$ presence

Model suggested Eqs. 1 to 5

Hypothesis  $Fe^{+3}$  also oxidizes Zn deposit



▲ Figure 5.  $[Zn^{+2}]/[Zn^{+2}]_0$  as a function of t. Case 3

## CONCLUSIONS

The models purposed allow zinc recovery modelling from SPBs at each of the operating conditions. Zinc electrodeposition is strongly influenced by  $Fe^{+3}$  and  $Cl_2$ , both causing zinc redissolution.

## ACKNOWLEDGEMENTS

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